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**Application of Molecular Simulation Methods for Development
of Organic-Inorganic Hybrid Layered Materials**

Habilitation Thesis

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Introduction

Present work is a list of selected published articles which are targeted to complex structure analysis of disordered layered materials like phyllosilicates and layered double hydroxides intercalated with organic dyes and organic anions respectively by molecular mechanics and classical molecular dynamic methods. Results of theoretical methods are compared with experimental measurements (X-ray diffraction, infrared spectroscopy, chemical analysis, thermogravimetry, TEM, SEM, etc.), which allow us validation of the calculations. The knowledge of mutual interactions and structure-property relationship plays a crucial role in the preparation of new materials with desirable properties.

Presented publications are focused for intercalated organo-inorganic hybrid materials. Intercalation means exchange of original cations or anions in the interlayer space with other ones or insertion various kinds of guest organic molecules without chemical exchange of covalent bonded sheets in layers of the structure. I focused for intercalation of rhodamine B and methylene blue into the interlayer space of natural or modified montmorillonite [1, 2, 3, 4, 5] and various derivatives of benzoate and porphyrins anions into layered double hydroxides [5, 6, 7].

Molecular simulation methods were used for crystal structures optimization to obtain minimum energy of presented conformations. Experimental data and suitable force fields were used to obtain valuable results in case of disordered crystal structures. Selected optimized models with the best agreement with experimental data were used to describe mutual interactions between species, charge distribution, total sublimation energy, calculated X-ray patterns, concentration profiles, orientation functions etc.

The present results show usefulness of molecular simulations for structure analysis of disordered or partially disordered structures. We create simulation procedures of negative charged layers intercalated with various kinds of organic cations or neutral polar molecules and the different procedures for positive charge layers with anions. At the end we did not solve only intercalated materials but also adsorption of organic molecules on surface of layered materials was successfully calculated. Simulations results show importance of knowledge of mutual interactions and arrangements of individual species in the interlayer space and on the surface.

2. Molecular Mechanics

Molecular modeling methods search the best conformation of calculated model with thousand and more atoms to find its energy minimum. Energy is described by simple analytic potential terms and necessary parameters are saved in the force field. Parameters there are derived on the base of experimental data or on the base of ab initio calculations. We assume that motion of the nuclei is calculated and electrons are fixed with nuclei. Properties of electrons are covered and atoms are described as points connected by springs with different elasticity given by force field constants. Potential energy functions, which describe mutual atomic interactions, can be divided into bond and non-bond terms. The quality of results strongly depends on the corresponding force field parameters and on the choice of energy terms. In fact on the base of known previous structures, on which parameters were derived, we try to interpolate new unknown structure to describe its behavior, arrangement, interactions and properties. Correct using of force field is crucial for successful solving of model. Molecular mechanic and classical molecular dynamic calculations [8, 9] were carried out in the Material Studio 4.3 modelling environment and some data were collected in Cerius² modelling environment [10].

2.1 Bond Energy Terms

The terms consist of two-body interactions (bonding energy E_b), three body interactions (valence angle energy E_θ), four-body interactions (out of plane deformation – improper term and torsional angle energy E_ϕ) and other additional terms like Urey –Bradley potential (interaction of two atoms connected to third one) and cross terms which couple bond-bond bond-angle, angle-angle, torsion-angle, etc.

The simple approach of bond length deformation in the calculation programs is the approximation with the harmonic potential. Bonds are representing as a mechanical spring whose force constants are strong for small interatomic distances and weak for large ones.

$$E_b = \frac{1}{2} k_b (r_{ij} - r_0)^2 , \quad (1)$$

where E_b is the bonding energy, k_b is the force constant, r_0 is the ideal bond distance, r_{ij} is the instantaneous deviation from ideal bond distance. Anharmonicity can be included to calculation

by addition of higher-order terms of the corresponding expansion or by using function like Morse potential:

$$V(r) = D [1 - \exp(-\alpha (r - r_0))]^2, \quad (2)$$

where α describes the curvature, D is the depth of the potential function.

Valence angle deformation for organic molecules used in this work is described by harmonic potential:

$$E_\theta = \frac{1}{2} k_\theta (\theta_{ijk} - \theta_0)^2, \quad (3)$$

where E_θ is the angle energy, k_θ is the angle force constant, θ_0 is the ideal angle value, θ_{ijk} is the instantaneous deviation from ideal angle value. Anharmonicity can be described by the addition of higher-order terms of the corresponding Taylor expansion.

Torsional rotations around multiple and single bonds are different processes. In the case of multiple bonds a torsional rotation results in the transformation of one isomer into another. The single bond rotation leads to interconversion of conformers. The torsional rotations about single and multiple bonds are described with the same type of potential function but they have different force constant. For example, a Fourier expansion of the torsional angle ϕ with only cosine terms is generally used:

$$E_\phi = \sum_n \frac{1}{2} k_n (1 + \cos(m_n (\phi - \phi_{\text{offset}}))) , \quad (4)$$

where m is the multiplicity and ϕ_{offset} is the phase shift (offset angle).

The out of plane terms means deviation of atoms from the plane of three connected atoms, for example can be simply described:

$$E_{\text{inv}} = 1/2 k_\omega (\cos\omega - \cos\omega_0)^2, \quad (5)$$

where k_ω is force constant and ω is angle between bond of out of plane atom l and projection of the bond of atom l to the plane of the atoms i, j, k , which are connected together.

When the bond length, valence angles and torsional angle terms are weakly coupled, cross-terms may take care of exceptions to this approximation [11]. In many programs these terms are neglected.

2.2. Non-Bond Energy Terms

The Van der Waals energy is calculated using the Lennard-Jones potential:

$$E_{vdw}(R) = D_{ij0} \left[\left(\frac{R_{ij0}}{R} \right)^{12} - 2 \left(\frac{R_{ij0}}{R} \right)^6 \right], \quad (6)$$

where E_{vdw} is the Van der Waals interaction energy between atoms i and j ; R is the interatomic separation between atoms i and j ; D_{ij0} is the Lennard-Jones well-depth parameter for atoms i and j ; R_{ij0} is the Lennard-Jones radius parameter for atoms i and j .

D_{ij0} and R_{ij0} are calculated by combining values for the two elements involved in the interaction. The D_{ij0} is always combined geometrically:

$$D_{ij0} = \sqrt{D_{i0} D_{j0}}. \quad (7)$$

The R_{ij0} can be either arithmetic or geometric mean:

$$R_{ij0} = \frac{(R_{ii0} + R_{jj0})}{2} \quad (8)$$

$$R_{ij0} = \sqrt{R_{ii0} R_{jj0}}, \quad (9)$$

where D_{i0} is the Lennard-Jones well depth for element i , R_{ii0} is the Lennard-Jones well minimum for element i .

Coulomb term calculates electrostatic interaction between charged atoms. The charges in this work were calculated by the Charge equilibrium approach (QEq) [12] or charges were assigned by appropriate force field. The total charge in the crystal is zero. The electrostatic interactions are calculated between all charged atoms by the Ewald summation method [13, 14]. The slowly converging real-space Coulomb sum is divided into a quickly converging modified real-space sum and a summation in reciprocal-space. The division is specified by three parameters: (i) the Ewald sum constant, (ii) the real-space sum cutoff distance and (iii) the reciprocal-space sum cutoff distance. The Ewald sum constant controls the division of calculation between the real- and reciprocal-space sums. The larger Ewald sum constant, the faster is the convergence of the real-space sum, but slower is the convergence of the reciprocal-space sum.

2.3 Minimization Algorithms

The algorithm, which is used in most of the minimizers, is the so-called *line search* [10]. This part of minimizers changes the coordinates to a new lower-energy conformation of the structure. The derivative vector in the initial positions defines the *line search* direction on the energy surface but this vector does not generally lead directly to the minimum. This algorithm tries to find a minimum on this line and from this minimum point assigns the subsequent

derivative vector, which is orthogonal to the previous derivations. Direction vectors are determined for all iterations and each *line search* is orthogonal to the previous one. *Line searches* do not depend on the algorithm that determined the direction vector. This method provides an efficient path to the minimum, especially for approximately quadratic surfaces. Steepest descent and Conjugate gradients methods were used.

In Steepest descent method, the *line search* direction is defined along the direction of the local downhill gradient $\nabla E(x_i, y_i)$. Because *line search* produces a new direction that is perpendicular to the previous gradient the directions can oscillate along the way near the minimum. If the *line search* were eliminated and the position would simply be updated any time that the trial point along the gradient had a lower energy then the number of function evaluations performed per iteration would be dramatically decreased. Furthermore, by constantly changing the direction to match the current gradient, oscillations along the minimization path might be damped. If the trial point has a higher energy, the step size is adjusted downward and a new trial point is generated. The steps in this method are more erratic, but the number of iterations for finding minimum is nearly the same. The advantage of this method is that some calculation time for the function evaluation is saved.

The steepest descent method is often used when the gradients are large and the configurations are far from the minimum. It is an extremely robust method for beginning of optimization but the convergence is slow near the minimum, as the gradient approaches zero. The steepest descent method should be used generally for the first 10-100 steps of minimization, and then the Conjugate gradients method is used.

Conjugate gradient method cross the disadvantage of steepest descent near minima by producing a complete basis set of mutually conjugate directions such that each successive step continually refines the direction toward the minimum. If these conjugate directions really span the space of the energy surface, then minimization along each direction in turn must by definition end in arriving at a minimum.

In conjugate gradients, $\mathbf{h}_{i+1}$, the new direction vector leading from point $i+1$, is computed by adding the gradient at point $i+1$, $\mathbf{g}_{i+1}$, to the previous direction $\mathbf{h}_i$ scaled by a constant γ_i :

$$\mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma_i \mathbf{h}_i, \quad (10)$$

where γ_i is a scalar that can be defined in two ways. In the Polak-Ribiere method, γ_i is defined as:

$$\gamma_i = [(\mathbf{g}_{i+1} - \mathbf{g}_i) \cdot \mathbf{g}_{i+1}] / \mathbf{g}_i \cdot \mathbf{g}_i, \quad (11)$$

and in the Fletcher-Reeves method, γ_i is defined as:

$$\gamma_i = \mathbf{g}_{i+1} \cdot \mathbf{g}_{i+1} / \mathbf{g}_i \cdot \mathbf{g}_i \quad (12)$$

The direction determined by this method replaces the gradient in the steepest descent method near minima. This construction has the remarkable property that the algorithm produces a set of mutually orthogonal gradients and a set of mutually conjugate directions. This method converges in approximately N steps, where N is the number of degrees of freedom.

3. Molecular Dynamics

3.1 Integration Algorithm and Timestep

Molecular dynamics is based on solving Newton's equations of motion:

$$\mathbf{F}_i(t) = m_i \mathbf{a}_i(t), \quad (13)$$

where $\mathbf{F}_i$ is the force, m_i is the mass and $\mathbf{a}_i$ is the acceleration of atom i .

The force $\mathbf{F}_i$ can be computed directly from the derivative of the potential energy V with respect to the coordinates $\mathbf{r}_i$:

$$-\frac{dV}{d\mathbf{r}_i} = m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i(t), \quad (14)$$

These classical equations of motion are deterministic. That means, once the initial coordinates and velocities are known the coordinates and velocities at a later time can be determined. The initial coordinates are determined in the input file or from a previous operation but the initial velocities are randomly generated at the beginning of a dynamic run according to the desired temperature. Therefore, dynamic runs cannot be repeated exactly but average state values should correspond. To calculate forces in reasonable time the good integrator is necessary. Widely used integrator in molecular dynamics is Verlet leapfrog [15] which accomplishes following criteria: (i) require little computer memory, (ii) permit to use a relative long timestep, (iii) present good conservation of energy and (iv) is fast and require one energy evaluation per timestep. Disadvantage is that the calculated positions and velocities are half a timestep out of synchrony. The Verlet leapfrog algorithm is as follows:

$$\mathbf{v}(t + \frac{1}{2} \Delta t) = \mathbf{v}(t - \frac{1}{2} \Delta t) + \Delta t \mathbf{a}(t), \quad (15)$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \Delta t \mathbf{v}(t + \frac{1}{2} \Delta t), \quad (16)$$

$$\mathbf{a}(t + \Delta t) = \frac{\mathbf{f}(t + \Delta t)}{m}, \quad (17)$$

where $\mathbf{f}(t + \Delta t)$ is evaluated from $-\mathbf{d}V/\mathbf{d}\mathbf{r}$ at $\mathbf{r}(t + \Delta t)$, $\mathbf{r}(t)$ is the position, $\mathbf{v}(t - \Delta t/2)$ is the velocity, $\mathbf{a}(t)$ is the acceleration.

Δt is the integration timestep and it is a key parameter in the integration algorithms because large timestep causes instability and inaccuracy in the integration process, small timestep causes very time consuming calculations. Main limitation is the highest-frequency motion that must be considered. A vibrational period must be split into at least 8-10 segments for molecular systems to satisfy the Verlet assumption that the velocities and accelerations are constant over the timestep used. The highest vibrational frequency is usually given by frequency of C-H bond stretching, whose period is of the order of 10 fs. The integration timestep should therefore be about 0.5-1 fs for models presented here.

3.2 Statistical Ensembles

Depending on which state variables are kept fixed, different statistical ensembles can be generated. Structural, energetic and dynamic properties can be analyzed from the molecular dynamic trajectories. In the thermodynamic limit, the first-order properties obtained in one ensemble are equivalent to those obtained in other ones (differences are on the order of $1/N$). However, second-order properties such as specific heat, compressibility, and elastic constant differ between ensembles. Therefore, it is important to use the appropriate ensemble. The transformation and relation between different ensembles has been discussed in detail by [16].

NVE ensemble: The constant-energy, constant-volume, constant number of particles ensemble, also known as *the microcanonical ensemble*. It is obtained by solving the standard Newton equations without any temperature and pressure control with constant energy. Due to calculation errors from the rounding and truncation we obtain slight fluctuation of energy. This is an useful ensemble for exploring the constant energy surface of the conformational space.

NVT ensemble: The constant temperature, constant volume, constant number of particles ensemble also referred to the *canonical ensemble*. Direct temperature scaling can be used only

during the beginning of dynamics because it does not produce a true canonical ensemble. This is the appropriate ensemble when conformational changes of non-periodic models are investigated. We can use this ensemble when the pressure is not a significant factor.

NPT ensembles: The constant temperature, constant pressure, constant number of particles ensemble allows control over both the temperature and pressure. This method can be applied only to periodic models. The unit cell vectors can be variable and the pressure is adjusted by adjusting the volume of crystal. Pressure can be controlled by the Berendsen (only the size and not the shape of the unit cell can be changed) [17] or Parrinello-Rahman method (the cell volume and its shape can be change) [18]. Temperature should be controlled by any available method (Berendsen, Andersen) except the temperature – velocity scaling method. NPT ensemble is used when the correct pressure, volume, and densities of the models are important in simulation. It is suitable ensemble during equilibration stage to achieve valuable state variables for analysis.

3.3 Temperature

Temperature is a state variable that specifies the thermodynamic state of the system. Temperature is connected to the microscopic description of molecular simulations through the kinetic energy, which is calculated from the atomic velocities. The temperature and the distribution of atomic velocities are related through the Maxwell-Boltzmann equation:

$$f(v) dv = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} 4\pi v^2 dv, \quad (18)$$

where m is the mass of molecule, v is the velocity of molecule, T is the thermodynamic temperature, $f(v)$ is the probability that molecule of mass m has a velocity of v when it is a temperature T , k is Boltzmann constant.

The x , y , z components of the velocities fulfill Gaussian distributions:

$$g(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}} dv_x, \quad (19)$$

The initial velocities are generated from the Gaussian distribution of v_x , v_y , v_z randomly. The temperature has meaningful only at equilibrium. It is related to the average kinetic energy of the model through the equipartition principle. That means that every degree of freedom has an average energy of $kT/2$ associated with it. During dynamics the kinetic energy is changed to

potential energy as the minimized structure changes to the thermal equilibrium structure. We can use several methods to control temperature, for example Berendsen method of temperature bath coupling [17]. In this method all velocities are multiplied by a factor λ given by:

$$\lambda = \left(1 + \frac{\Delta t}{\tau} \left(\frac{T - T_0}{T} \right) \right)^{\frac{1}{2}}, \quad (20)$$

where Δt is the timestep, τ is the characteristic relaxation time, T_0 is the target temperature, T is the instantaneous temperature.

3.4 Types of Dynamics

Impulse dynamics allows assigning initial directional velocities to selected atoms or molecules before carrying out dynamics. This dynamics is usually connected with NVE ensemble. This type of dynamics is useful for pushing interacting molecules over energy barriers before allowing the structure to relax.

Quench dynamics allows structure optimization between defined period of dynamics. Dynamics run and set of optimized structures are saved in different files. This type of dynamics is useful for conformational search.

Simulated annealing dynamics allows repeated alteration of temperature from initial to final and back. This dynamics is useful for investigation of phase transition and for overcoming energy barriers when the structure is trapped in a conformation with local energy minimum.

Dynamics simulations are usually carried out in two stages, equilibration and data collection. The duration of these stages depends on the models as well as on the purpose of the run. The investigated model is in equilibrium when (i) the various thermodynamic quantities fluctuate around their averages, which remain constant over time or (ii) the series of initial models with different initial conformations and velocities are calculated and these models converge to similar conformations and properties. This is a good indicator that equilibrium was reached. The result from equilibrium dynamics are saved in trajectories files which allow subsequent analysis of temperature, energies, volume, pressure, cell parameters and thermodynamic properties, time dependent processes, diffusions etc. More information about molecular simulations can be found for example in *Cerius²* documentation [10] or in Comba P. and Hambley T.W. [8].

4. Inorganic Layered Host Structures

4.1 Montmorillonite

Montmorillonite (MMT), one type of phyllosilicates [19], was used for intercalation in this work. MMT was first described by Damour and Salvétat in 1847 [20] as nodules in a brownish shale from Montmorillon in France. Montmorillonite acquires charge mostly by the replacement of octahedral Al by Mg atoms. The idealized structural formula is $[Al_{4-x}Mg_x][Si_8]O_{20}(OH)_4$. The following crystallochemical formulas of MMT were used in presented articles [P4 – publication number 4]:

- Wyoming: $Na_{0.41}K_{0.14}Ca_{0.07}(Al_{3.01}Mg_{0.48}Fe^{3+}_{0.49})[Si_{7.81}Al_{0.17}Ti_{0.02}]O_{20}(OH)_4$,
- Cheto: $Na_{0.10}K_{0.04}Ca_{0.50}(Al_{2.80}Mg_{1.00}Fe^{3+}_{0.20})[Si_{7.86}Al_{0.14}]O_{20}(OH)_4$.

MMT is composed from one octahedral sheet (Mg, Al, Fe^{2+} , Fe^{3+}) and two adjacent tetrahedral sheets (Si, Al). This layer exhibit negative layer charge caused by substitutions predominantly in octahedral sheet. Whatever the original net negative charge, its magnitude must be compensated by a corresponding positive charge in the interlayer so that the crystal as a whole is electrostatically neutral. See figure 4.1.

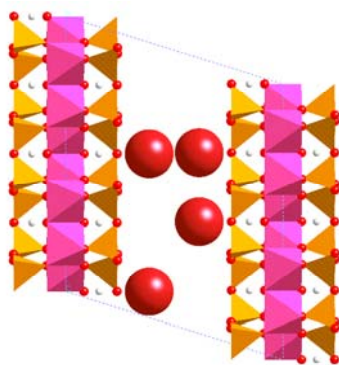


Figure 4.1: Natural montmorillonite, Na^+ cations in the interlayer - big red balls, Si - orange tetrahedral cations, Mg, Al - purple octahedral cations, O – small red balls, H – small dark white-grey balls. View along X-axis.

Montmorillonite with exchangeable metal cations in the interlayer space is strongly hydrophilic. This leads to swelling of MMT with creation of hydration sphere around exchangeable cations first and it continues with creation of one or more water layers in the interlayer space. This can be observed in changes of basal spacing $d(001)$ in dependence on the amount of interlayer water.

Phyllosilicates, on the base of octahedral sheet characteristics, can be divided into two subgroups: (i) di-octahedral and (ii) tri-octahedral. Octahedral sheets are called dioctahedral when only two of three octahedral sites are occupied by mainly trivalent cations and trioctahedral when all three octahedral sites are populated by predominantly divalent cations. In the presented

publications we used dioctahedral smectite montmorillonite. Smectite is a group of phyllosilicates with expandable structure. The interlayer space of smectites can be easily changed by various kinds of cations and intercalation plays a key role in using of this material for industrial applications [21, 22, 23, 24, 25]. Moreover, small monovalent cations like Li^+ can be immersed into hexagonal cavities and allow decreasing of layer charge. It can rule out intercalation of other cations to interlayer for high amount of Li^+ cations immersed in the layer [26].

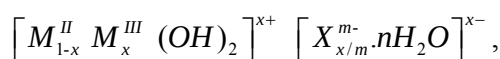
Another phenomenon of smectite behavior is the so-called a "turbostratic" layer stacking which cause the disorder of resultant structure and it is characterized by the shift and random azimuth rotation of two successive silicate layers [27, 28]. Generally, the mutual interactions between the two adjacent silicate layers are weak and it allows simple intercalation or ion exchange. The water content in the interlayer space of smectites depends on the character of exchangeable cations and on the relative humidity and hydrostatic pressure. General space group is C2/m and structural formula for dioctahedral smectites is $[\text{Al}_{4-y-z}\text{Fe}_y^{3+}\text{Mg}_z]_4^{\text{VI}} [\text{Si}_{8-x}\text{Al}_x]^{\text{IV}} \text{O}_{20} (\text{OH})_4 \text{Me}_{x+z}^+$, where x is the number of central Al atoms in tetrahedron; y is the number of central Fe^{3+} atoms in octahedron; z is the number of central Mg (res. Fe^{2+}) atoms in octahedron; Me^+ is the number of exchangeable positions. The smectites with $x > z$ are usually called beidellites and those with $z < x$ montmorillonites [19, 29, 30].

4.2 Layered double hydroxides

Layered double hydroxide (LDH) is general name for synthetic or natural lamellar hydroxides with two kinds of metallic cations in the main layers with positive charge and interlayer space containing charge compensating anionic species [5, 6, 31]. This wide family of compounds is also referred to as *anionic clays*, or LDHs are also reported as hydrotalcite-like compounds by reference to one of the polytypes of the corresponding Mg-Al based mineral. The first described natural mineral belonging to this family was discovered in Sweden in the 1842 and it was named as hydrotalcite. Its formula was $\text{Mg}_6\text{Al}_2 (\text{OH})_{16} \text{CO}_3 \cdot 4\text{H}_2\text{O}$ and the first work on the synthesis, stability, solubility and structure determination are dated in 1930s. The layer structure is based on $\text{M}(\text{OH})_6$ octahedral units sharing their oxygen edges in order to build $\text{M}(\text{OH})_2$ brucite-like layers. These octahedral units contain both divalent (M^{II}) and trivalent (M^{III}) metallic cations causing positive charge, which is proportional to the trivalent metal ratio:

$$x = \frac{M^{III}}{M^{II} + M^{III}}.$$

The crystal structure of LDH is composed of layer stacking with anionic species and water molecules in the interlayer [32] as it is shown in Figure 4.2. The general formula for LDH is



where X is an exchangeable anion, n represents number of water molecules and m is a valence of interlayer anion.

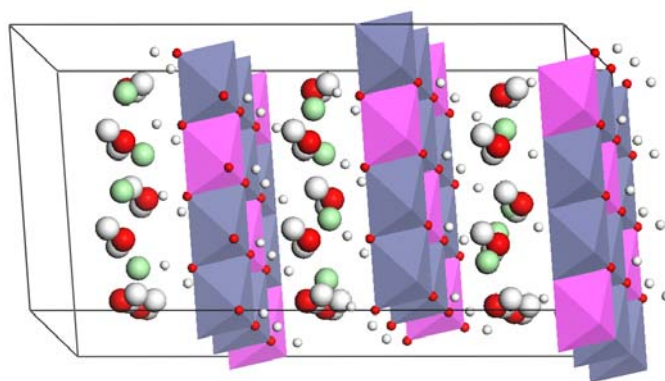


Figure 4.2. Natural ZnAl-Cl LDH. Zn cations in the layer - grey octahedron, Al cations - violet octahedron, O – small red balls, H – small dark white-grey balls, Water – big red and white-grey balls in the interlayer, Cl - green balls.

The divalent and trivalent metal cations appeared in LDHs belong generally to the third and the fourth period of the periodic table of the elements: (i) divalent cations: Mg, Mn, Co, Ni, Cu, Zn and (ii) trivalent cations: Al, Mn, Fe, Co, Ni, Cr, Ga. LDH accommodate a relative wide range of trivalent ratio, which lies between the x values of 0.2 and 0.4 [6]. The upper limit is connected with electrostatic repulsions between trivalent metals in the layers and anionic species in the interlayer. The lower limit is related to low electrostatic interactions between layer and anions to prevent collapse of interlayer. One major advantage of LDHs is a weak bound between the interlamellar ions and the layers. A large set of anions can therefore be placed between the layers during the creation of the lamellar structure or during intercalation. For example, anions can be (i) halides: fluoride, chloride; (ii) oxo-anions: carbonate, nitrate, sulphate, bromate; (iii)

organic anions: carboxylates, phosphonates, alkyl sulphates, etc. Moreover, interlayer space can contain water molecules and other neutral species. High variability of anions in the interlayer can cause difficult characterization of its arrangement. Small anions do not influence stacking of the layer, on opposite of this big anions can change layer stacking for long range ordering (turbostatic effect) [33]. This can be observed by X-ray diffraction patterns or calculated by molecular modelling methods. LDHs usually crystallize in two polytype structures, one with a two-layer hexagonal stacking sequence (polytype 2H, space group P63/mmc, or P63/mcm) and one with a three-layer rhombohedra sequence (polytype 3R) which is represented by space group R-3m.

LDH attract attention for industrial applications from the end of 1960s to obtain new materials in many branches like structural characterization [34], electrochemical and magnetic properties [35], catalysis [36], pharmaceutical applications [6, 37], etc. In the case of molecular modeling a several works focusing on theoretical aspects concerning new LDH force fields developing and studies of pure LDHs or intercalated mainly by small organic species have been published [38, 39]. In this work LDH with composition of Zn_2Al and Mg_2Al with the ideal formulas $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}][(\text{NO}_3)_2 \cdot 4.5 \text{ H}_2\text{O}]$ and $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{NO}_3)_2 \cdot 4 \text{ H}_2\text{O}]$ respectively were investigated as host layer materials for intercalation and as host inorganic host frameworks in our calculated models.

5. Published results

Intercalation of MMT and LDH in the presented publications is based on the ion-exchange reaction between the natural cations or anions and organic ions. Ion exchange reaction was used for intercalation of rhodamin B and methylene blue cations in case of MMT. LDH was intercalated by benzoate and porphyrin anions.

5.1 Strategy of Modeling

Experiment plays crucial role in molecular simulations for creation of modeling strategy and verification of results. The most of calculated samples are disordered structures where direct solving of crystals from X ray powder diffraction is not possible. Disorder in clay crystals can be caused by interlayer arrangement of organic species or by unregularly stack of layers. Calculations allow prediction of structure and comparison of its calculated and experimentally measured diffraction patterns. Experimental diffraction patterns are usually affected with preferred orientation of clay particles, show broaden lines of $00l$ peaks and turbostratic layer stacking and this caused difficulties during calculation and solving of structure. On the opposite side characteristic features of clays in diffraction patterns hk -bands allow keeping of layers rigid during calculation because there are no changes in intercalated structure with respect natural sample. This is very useful for the strategy of modeling to save calculation time. Other experimental techniques were used for calculated data verification, like infrared spectroscopy, chemical analysis, thermogravimetry, TEM, SEM, UV VIS spectroscopy etc.

The basic methods and strategies of molecular calculations were worked out primary on X – ray powder diffraction data to reveal the structures and structure-properties relationship of intercalates. Modeling procedure stated on experimental data includes the building of initial models, the setup of energy expression and the choice of an appropriate empirical force field. The first structure optimization runs under conditions characterizing the MMT or LDH structure (variable and fixed cell parameters, variable and fixed atomic positions for certain atoms, rigid units, etc.). Selected models from the optimization showing good agreement with experimental data are used as input models for molecular dynamics. In order to get the system into the global minimum, the detailed search of conformation space is carried out using molecular dynamic methods. Generally, constrain conditions of molecular dynamics for clay layers mean frozen layers and movable guest species. Dynamic simulations were carried out mainly under following

conditions: quench dynamics, NVT ensemble, dynamic timestep 1 fs, Berendsen thermostat etc. Dynamic trajectories were analyzed and promising models were optimized to obtain minimum of energy. The Ewald summation method [13, 14] was used to calculate the Coulomb and van der Waals energies. Charges were calculated using the QEq method (charge equilibrium approach) [12]. Detail description of calculation setup is in publications in chapter 9.

5.2 Montmorillonite Intercalated with Rhodamine B [P1 – P3]

The first series of publication is focused on intercalation of Rhodamin B (RB) cation, which exhibit photoluminescence properties (shown in figure 5.1) into Na-montmorillonite from Crook County. Intercalate was prepared by repeated saturation of MMT with solution of RB. After each step the sample was centrifuged and a new fresh portion of rhodamine B solution was added. Fully saturated intercalate was then washed out with deionized water and air-dried.

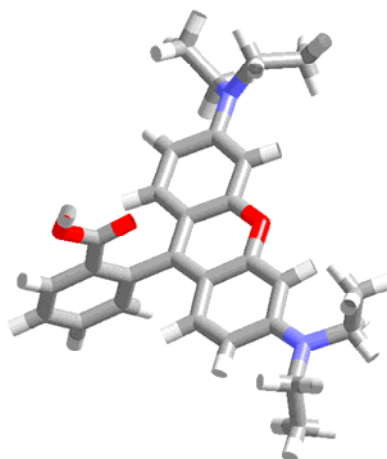


Figure 5.1 Rhodamine B cation.

Experimentally prepared samples were described by chemical analysis, X – ray diffraction, infrared spectroscopy, VIS absorption spectroscopy, adsorption isotherms, and fluorescence spectra. Structure and arrangement of RB in MMT was solved in the interlayer and on the surface by molecular modeling methods. It was shown that structure of the intercalated RB strongly depends on the concentration of RB in the intercalation solution. Diffraction patterns show possible presence of two independent phases in the sample. This was confirmed by simulations of fully exchanged interlayers by RB. One phase of 18 Å show bilayer arrangement of guest that means two successive layers of RB arranged as dimers or monomers and the second phase of 23 Å with monolayer tilted arrangement of guest. In both phases dimers and monomers can coexist. Three probably types of dimers were described by calculations (i) H- dimer (head to head) in phase 18 Å, (ii) Sandwich type (head to tail) in phase 23 Å, and (iii) J – dimer (head to tail) in phase 23 Å. H – dimer arrangements seems to be the most stable from point of view

mutual non bond interactions. Calculations of minimum energy of samples with water give prove that MMT with RB is very hydrophilic and samples must be dried before measurements to avoid misinterpretation.

Next investigation was focused to investigate the influence of various concentration of intercalation solutions resultant dimer/monomer ratio of RB in MMT. Absorption spectra confirm aggregation of RB for increasing concentration from $2.00 \times 10^{-6} \text{ mol dm}^{-3}$ to $3.75 \times 10^{-3} \text{ mol dm}^{-3}$. It was calculated that partially exchanged models with two or one Na cations can exist for low concentration of RB in the intercalation solutions. Models with 2 Na cations represents 18 Å phase, model with one Na cations is related to 23 Å phase. Intercalation of high concentrations of RB proves both phases for fully exchanged samples.

Knowledge of structural arrangement allows us study fluorescence behavior of fully exchanged RB in the interlayer and on the surface. Analysis shows that mutual positions and orientation of RB in the interlayer space and mostly on the surface of MMT strongly influence the resultant fluorescence spectrum and both arrangements are different for given sample. In the interlayer of fully exchanged samples, the most stable arrangement is bilayer with xanthene part of RB parallel with silicate layers. On the surface prevail tilted, like J-dimer, arrangement. Mutual combination of interlayer and surface arrangement influence resultant fluorescence spectrum.

5.3 Montmorillonite Intercalated with Methylene Blue [P4 – P6]

Methylene blue (MB) is a heterocyclic aromatic compound with molecular formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ (see Figure 5.2) which was used for intercalation into MMT with various layer charge. The characteristic color of MB is caused by the strong absorption band in the 550–700 nm area with the maximum molar absorptivity at 664 nm. MB absorption spectrum is concentration-dependent due to dimerization similarly like RB, which may change in the presence of charged layers. MB has been extensively used for photo oxidation of natural and synthetic molecules. These mechanisms are important in photo dynamical therapy for damaging biomolecules in treating a variety of cancerous and non-cancerous diseases.

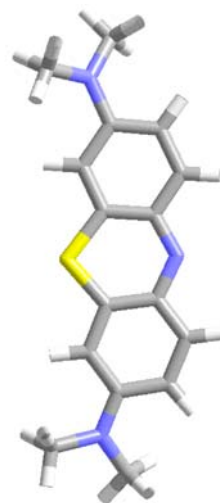


Figure 5.2: Methylene blue cation.

Methylene blue cations aggregate in dependence of concentration. Two montmorillonite layers with different layer charge were intercalated with different amount of MB. Increasing concentration of MB in solutions leads to fully exchanged original cations in the Wyoming type montmorillonite (Na-SWy) and Cheto montmorillonite (Ca-Cheto). Intercalation amount very well correlate with basal spacings d_{001} . Higher amount of intercalated MB leads to broadening of diffraction line which shows disorder in the structure. Low concentration of MB in solutions leads to monolayer parallel arrangement of MB in the interlayer space of Na-SWy and to the two parallel layers of MB in case of Ca-Cheto. Intercalated MB exhibits luminescence in MB-SWy and no luminescence in MB-Cheto samples with nearly twice higher layer charge.

On the previous experiences from RB intercalation we focused for surface arrangement of MB cations. Photoluminescence measurements can be strongly influenced by the surface arrangement of MB cations. Adsorption of MB on surface of Na-SWy and Ca-Cheto was calculated. Due to lower value of charge in case of Na-SWy, MB cations lie parallel, like monomers, to the silicate layers for all calculated models. In case Ca-Cheto, MB cations have tilted arrangement for higher adsorption leading to aggregation and resultant structure was less energy stable. Low adsorption and parallel arrangement of monomers contribute to higher photoluminescence. Similar for Ca-Cheto, low adsorption and parallel arrangement allow photoluminescence for sample with small concentration of MB in intercalation solution. Higher sorption quench photoluminescence and these conclusions are in a good agreement with experimental measurements.

The aim of another work was decrease the layer charge in Na-SWy and Ca-Cheto samples. The reduced charge MMT were prepared by Li^+ ions intercalation and heating up to temperature of 210°C . Li ions remain in the octahedral sheet and decrease the layer charge. Series of both MMT was prepared to decrease the MB aggregation. Reduction of charge tunes the aggregation of MB and it allows control intercalation of dimers or monomers. It was presented that intensity of fluorescence of low loaded MB to reduce MMT enhanced by several orders of magnitude in comparison with non-reduced charge MMT. Experimental measurements show that interlayer space of MMT collapsed for samples heated over 210°C and MB adsorbed on the surface. Lower layer charge suppress aggregation of MB and it imply huge fluorescence intensities which is emitted by MB monomers which are individually spread in parallel

arrangement at reduced charge surface of MMT. Simulations confirm weak interaction between MB and silicate layer and long distance (0.31 nm) among MB cations.

5.4 LDH Intercalated with Benzoate and Porphyrin Anions [P7 – P9]

Benzencarboxylate (benzoate) with the chemical formula $\text{C}_6\text{H}_5\text{COO}^-$

(Figure 5.3) was intercalated into Zn_4Al LDH. The intercalation of benzoate was done by equilibrating the nitrate form of LDH with an 0.5 mol/dm^3 aqueous solution of $\text{C}_6\text{H}_5\text{COONa}$ (molar ratio $\text{C}_6\text{H}_5\text{COO}^-_{\text{solution}} / \text{NO}_3^-_{\text{solid}} = 10$) for 24 hours. The recovered solid was three times washed with CO_2 free deionized water and dried over P_4O_{10} .

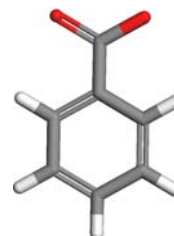


Figure 5.3 Molecular structure of benzoate

Optimized models show anchoring of COO^- groups to OH groups on the LDH layer via the hydrogen bond. The long axis is nearly perpendicular to the LDH layer with departure in the range ± 10 degrees. Benzene ring exhibit ordering like parquet arrangement with small deviations from ideal positions. Small shift around $0.3 \text{ \AA}$ along metal – oxygen bond in ordering of two successive layers was confirmed by calculations. Water content was compared with the data from thermogravimetry and found number of 24 water molecules in one guest layer given by calculation agrees with experiments. Water molecules are closed to the COO^- planes, as they are hydrogen bonded to the OH groups in host layers and to carboxyl groups and they create water planes which are adjacent to layers. It was shown that calculation can describe structure disorder and water concentration in the model.

The word porphyrin stems from the ancient Greek word porphura, which was used to describe the color purple. The basic structure of the parent porphyrin macrocycles consists of four pyrrole rings joined together by four methine bridges (see Figure 5.4). The planar porphyrin macrocycle is an $18\text{-}\pi$ electron aromatic system. The two inner NH groups lose protons under basic conditions in order to form a dianion species. Such a porphyrin dianion is able to coordinate almost every metal within its cavity to form a metalloporphyrin [40].

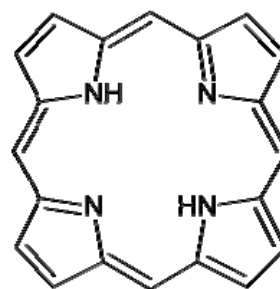


Figure 5.4. A scheme of planar porphyrin.

A typical porphyrin absorption spectrum consists of two regions, one at around 400 nm, which is referred to as the Soret or B-band region, and one at around 550 nm, which is called the Q-band region. The first corresponds to an allowed transition from the ground state to the second excited state. The latter corresponds to a transition from the ground to the first excited state [34, 41].

The calculation were performed for arrangement of [5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS)] intercalated in Mg₂Al LDH. Three types of structural models were created. The first one with complete saturated interlayer space by TPPS (Type 1), the second with one part consecutively saturated with TPPS and followed by second part of interlayers with NO₃⁻ (Type 2) and the third one with mixture of TPPS and NO₃⁻ anions in one interlayer (Type 3). TPPS were tilted in all models and horizontally shifted up to one-half of the TPPS diameters. The calculated diffraction patten for Type 1 and Type 3 are very similar. Type 2 exhibit splitting of the diffraction peaks in dependence on the level of saturation and can be explained by broadening of experimentally measured peaks. Simulations give decision that Type 3 model is energetically worse than Type 2 models, both with 75% TPPS saturation.

TPPS were intercalated into Mg_RAl LDH (R=2-4) and into the Zn_RAl LDH interlayer space (R = 2-4). The hydrothermal treatment increases crystallinity of Zn_RAl LDH and originally intercalated TPPS is metalated to ZnTPPS, while intercalated TPPS in Mg_RAl LDH remains unchanged. Mg_RAl-TPPS hybrids produce O₂(1Δg), while no measurable amount of this species was found for exchanged Zn_RAl LDH-based hybrids. Calculations show that the distance between two neighbouring central atoms varies from 6 to 9 Å that is much longer than that of about 3.5 Å typical in parallel stacking of aromatic compounds. The porphyrins molecules are parallel each other and their plane is partially inclined with respect to normal of LDH layers around 14° for both types.

6. Conclusions

Presented results and publications show that molecular calculations are very useful and complementary method for structural analysis in combination with experimental measurement like X ray diffraction, infrared spectroscopy, TEM, SEM, AFM, UV VIS spectroscopy, thermogravimetry, chemical analysis, etc. Results of calculation can give advice to preparation and measurements of samples or can support experimental results as we presented in case of rhodamine B and methylene blue intercalated into MMT and benzoate, porphyrin into LDH.

Analysis of results from molecular simulations allow us to compare experimental and calculated diffraction patterns, mutual interactions between host layer and guest species and their positions and orientations, characterize charge distributions and disorder in layer stacking, total sublimation energy and its components van der Waals and Coulomb contributions, etc. This detail knowledge allows us to give recommendation for measurement improving and for design materials with requested properties for industrial applications.

Molecular simulations allow calculating various kinds of materials. Selected presented papers are focused for similar type of layered materials like cationic and anionic clays intercalated with organic dyes. Our calculations show their important contribution for development and improvement of investigated materials. Presented structures were calculated in our lab and verified with accessible experimental results to confirm importance of the detail structure knowledge.

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9.1 Structure analysis of montmorillonite intercalated with rhodamine B; modelling and experiment – P1

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Structure analysis of montmorillonite intercalated with rhodamine B: modeling and experiment

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Abstract The intercalation process and the structure of montmorillonite intercalated with [rhodamine B]⁺ cations have been investigated using molecular modeling (molecular mechanics and molecular dynamics simulations), X-ray powder diffraction and IR spectroscopy. The structure of the intercalate depends strongly on the concentration of rhodamine B in the intercalation solution. The presence of two phases in the intercalated structure was revealed by modeling and X-ray powder diffraction: (i) phase with basal spacing 18 Å and with bilayer arrangement of guests and (ii) phase with average basal spacing 23 Å and with monolayer arrangement of guests. In both phases the monomeric and dimeric arrangement can coexist in the interlayer space. Three types of dimers in the interlayer structure have been found by modeling: (i) H-dimer (head-to-head arrangement) present in the 18 Å phase, (ii) sandwich type of the head-to-tail arrangement (present in the 23 Å phase) and (iii) J-dimer (head-to-tail arrangement) present in the 23 Å phase.

Keywords Montmorillonite · Intercalate · Rhodamine B · Molecular mechanics · Molecular dynamics

Introduction

Clay minerals represent very attractive matrices for the intercalation of dye molecules. When, for example, rhodamine is intercalated into the clay, which is transparent in the UV–visible region, it appears to be more thermally stable and to exhibit more efficient luminescence. [1]

The intercalation of xanthene dyes in smectite-type clays is followed by changes observed in the absorption spectrum (the so-called metachromatic effect), whereby the main absorption band is shifted to higher energies. [1, 2, 3] This effect is explained by: (i) the interaction between the aluminosilicate layers and the dye (i.e. the interaction between the electron lone pairs of clay surface oxygens and the dye π -system) and (ii) the interaction between the dye molecules in the interlayer space of the clay structure (i.e. dimerization and the π – π interaction between two monomers in the dimer). Rhodamine dyes are considered good probe molecules for studying the clay–dye complexes, as they can be intercalated into the clay structure easily via a cation-exchange mechanism and their photophysics depends on the environmental factors.

In recent years, the photophysics of clay-intercalated xanthene dyes has been studied intensively. [3, 4, 5, 6, 7, 8, 9] In previous studies of the clay–dye complexes, the arrangement of guest molecules in the interlayer space was suggested on the basis of steric considerations and X-ray diffraction measurements. [1, 5, 9, 10, 11, 12, 13] Our present work deals with a structure analysis of montmorillonite intercalated with rhodamine B. It is well known that structure analysis based on the diffraction method is extremely difficult in the case of intercalated clays, especially those of the smectite group, due to the turbostratic disorder of their structures. In such a case, molecular modeling using empirical force fields is a very powerful tool in the investigation of the interlamellar structure. An atomistic computer modeling study of the interlamellar structure in dye–clay complexes was carried out by Breu et al. in [14, 15]. In the present work, we use molecular mechanics and classical molecular dynamics in the *Cerius*² modeling environment [16] combined with X-ray powder diffraction and IR spectroscopy to investigate the arrangement and conformation of [rhodamine B]⁺ cations in the interlayer space of montmorillonite. The presence of water molecules in the interlayer structure was taken into account in the present calculations. As a result of modeling, we obtain a

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detailed structural model including characterization of the disorder and possible conformational changes. In addition to conventional diffraction analysis, we obtain energy characteristics such as the total sublimation energy and its components (van der Waals, electrostatic, H-bond).

Experiment

Sample preparation and chemical analysis

The montmorillonite samples fully intercalated with rhodamine B were prepared using SWy (montmorillonite, Crook County, Wyoming) and rhodamine B (Fluka Standard Chemika) that was recrystallized twice from deionized water. A saturated sodium form of SWy was prepared from the SWy fraction with grain size less than 5 μm by repeated saturation with 1 mol dm^{-3} NaCl solution. After each step, the sample was centrifuged and a fresh portion of NaCl solution was added. The fully saturated Na form of SWy was then washed out with deionized water and air dried. The montmorillonite samples fully intercalated with rhodamine B were prepared by a similar technique. For the preparation of individual fully saturated samples, rhodamine B solutions of concentration ranging from 1.1×10^{-4} to 4.00×10^{-3} mol dm^{-3} were used (see also Table 1). The saturation was repeated several times until the Na form of SWy was fully intercalated. In each saturation step, the amount of intercalated dyes was determined from the difference between the total rhodamine B concentration before and after saturation. In order to determine the total rhodamine B concentration (monomer and dimer), the solutions were diluted to an approximate concentration of 10^{-5} mol dm^{-3} so that only monomer forms of rhodamine B were present. The total concentrations of rhodamine B solutions were then determined by photometric methods at a wavelength of 552 nm. The correctness of the calculated total amount of intercalated rhodamine B (Table 1) was also checked through the content of C, H, N and O belonging to the rhodamine B cations present in intercalated Swy determined by elemental analysis.

X-ray diffraction measurements

The powder diffraction data for the series of rhodamine B–montmorillonite samples prepared using intercalation solutions with various guest concentrations were collected in the 2θ range $1\text{--}10^\circ$. An INEL X-ray powder diffractometer with a PSD 120 position sensitive detector was used and the measurements were carried out under the following conditions: the reflection mode, rotating sample holder (capillary) and Cu $K_{\alpha 1}$ radiation. A mixture of

silicon and Ag-behenate was used as a calibration standard for the PSD. The results of the powder diffraction analysis are summarized in Table 1, where one can see the effect of the rhodamine B concentration in the intercalation solution on the basal spacing d_{001} and on the interlayer structure of the intercalate. As one can see from Table 1, low concentrations of the intercalation solution lead to two broad diffraction maxima corresponding to basal spacings of about 23 Å and 18–19 Å. Two examples of the diffraction pattern are shown in Fig. 1a, b for samples 1 and 7 (see Table 1). This result suggests the existence of two phases of the intercalated structure for intercalation solutions with low guest concentration. On the other hand, intercalation solutions with a high guest concentration lead to a monophasic composition of intercalate with one d_{001} diffraction line at ~ 18.1 Å. These results support the hypothesis of monomeric and dimeric arrangements of the rhodamine B in the intercalated structure, depending on the concentration of the intercalation solution. [3] The large broadening and slight peak shift of the diffraction lines will be discussed later together with the modeling results.

IR spectroscopic measurements

The structural and optical properties of the samples were checked using Fourier transform infrared (FTIR) spectroscopy. Infrared spectroscopic measurements were performed on a Nicolet IM-PACT 400 FTIR spectrometer in an H_2O -purged environment. All spectra in the range $400\text{--}4000\text{ cm}^{-1}$ with 2-cm^{-1} spectral resolution were obtained from compressed KBr pellets in which the samples were evenly dispersed. Two hundred scans were used to record each FTIR spectrum. The spectra were corrected for the H_2O and CO_2 content in the optical path. The measured IR spectra for the host structure, guest compound and intercalate (sample 7) are shown in Fig. 2. The strategy of modeling and structure analysis is based on comparison of IR spectra for: (i) the host structure Na-montmorillonite, (ii) the guest compound rhodamine B chloride and (iii) the intercalate rhodamine B–montmorillonite. By comparing these three spectra, we obtain information about possible changes in conformation of the guest molecules and about the bonding geometry of the host layers during intercalation.

Modeling strategy

The initial model for the montmorillonite layer was built using structural data published by Tshipursky and Drits (1984): [17] space group, $C2/m$. The unit cell parameters according to Méring (1967) [18] were used to define the planar unit cell dimensions: $a=5.208$ Å and $b=9.020$ Å. The composition of montmorillonite layer according to chemical analysis was $(\text{Al}_{1.53}\text{Mg}_{0.23}\text{Fe}^{3+}_{0.25})(\text{Si}_{3.89}\text{Al}_{0.10}\text{Ti}_{0.01})\text{O}_{10}(\text{OH})_2$. To create a supercell of reasonable size for the calculations, the structure formula was modi-

Table 1 Concentration of the rhodamine B in the intercalation solution and corresponding values of the guest concentration in the montmorillonite with the basal spacing detected in the diffraction pattern

Sample No.	Concentration of rhodamine B in the intercalation solution (mol dm^{-3})	Amount of rhodamine B absorbed in montmorillonite (mmol g^{-1})	Basal spacings obtained from the X-ray diffraction pattern d_{001} (Å)	
			First maximum	Second maximum
1	0.00011	0.7060	23.2	18.8
2	0.00046	0.7790	22.9	18.7
3	0.00102	0.7910	21.5	18.7
4	0.00110	0.7960	21.0	18.3
5	0.00370	0.8939	19.7	
6	0.00400	0.8981	18.6	
7	0.00399	0.9045	18.1	

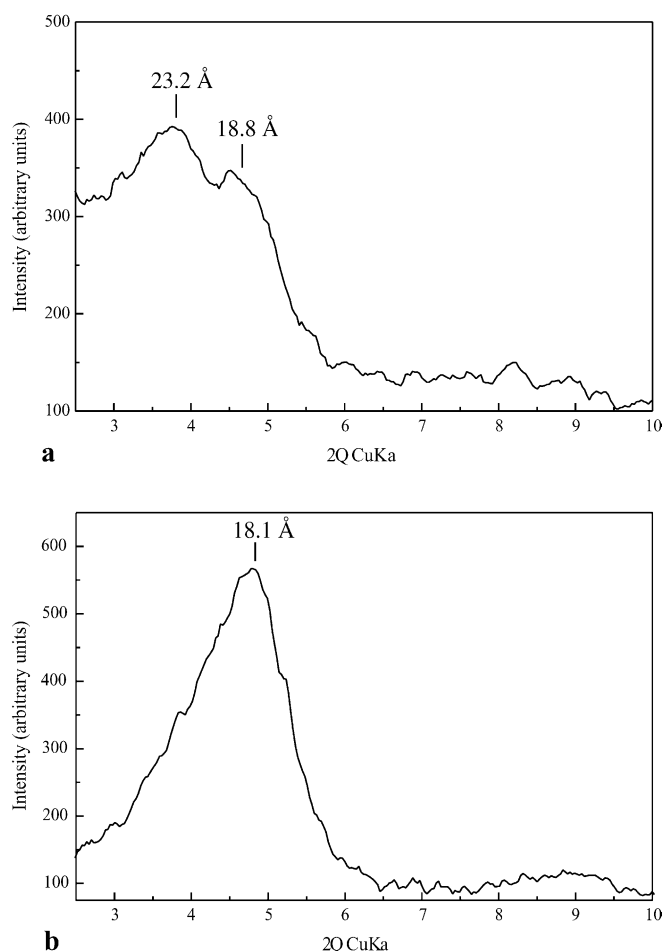


Fig. 1 **a** X-ray powder diffraction pattern of the sample 1, prepared in intercalation solution with the lowest guest concentration (see Table 1). **b** X-ray powder diffraction pattern of the sample 7, prepared in the intercalation solution with the highest guest concentration, according to Table 1

fied slightly. Consequently, the supercell $3a \times 2b \times 1c$ with layer composition $(\text{Al}_{18}\text{Mg}_3\text{Fe}^{3+}_3)(\text{Si}_{47}\text{Al}_1\text{O}_{120}(\text{OH})_{24})$ was built with a total negative layer charge of -4 . The c values in the initial model were set up according to the basal spacings obtained from X-ray powder diffraction for samples prepared under different conditions, allowing the replacement of the Na^+ cations by [rhodamine B] $^+$ cations in the interlayer space.

As the intercalation of [rhodamine B] $^+$ into montmorillonite is based on an ion exchange reaction, the host–guest interaction is of a non-bonded nature. This is an important assumption for the modeling strategy. Comparing the IR spectra for the host structure Na-montmorillonite and intercalate in Fig. 2, one can see that the main bands corresponding to the silicate layers are preserved in the spectrum of the intercalate and, consequently, the silicate layers can be treated as rigid bodies during energy minimization. Comparing the IR spectrum of the guest compound rhodamine B chloride with the spectrum of the intercalate, one can see the smoothing and broadening of the vibration bands of [rhodamine B] $^+$ in the intercalated structure. These changes are especially pronounced for bands corresponding to the carboxyl group, skeletal vibrations of the aromatic rings and bending of the ring C–H bonds. (For more details see the next paragraph.) Consequently, the coordinates of all atoms in the [rhodamine B] $^+$ cations were varied during energy minimization, which was performed under

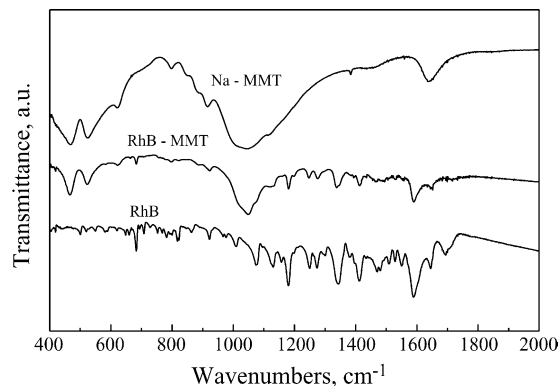


Fig. 2 IR spectra of the host structure Na-montmorillonite (*upper* spectrum), rhodamine B chloride (the *lowest* spectrum) and the intercalate RhB–montmorillonite (the *middle* spectrum)

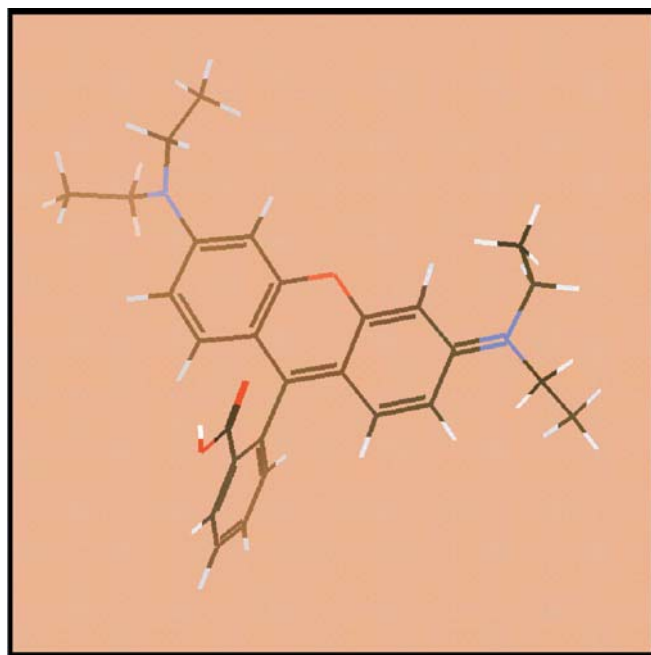


Fig. 3 The rhodamine B cation minimized in vacuum using the universal force field [21]

the following conditions: variable supercell parameters c , α , β and fixed a , b , γ and with variable bonding geometry and variable position of the [rhodamine B] $^+$ cations. The Ewald summation method was used to calculate the Coulomb energy in a crystal structure. [19] The Ewald sum constant was $0.5\text{ \AA}^{-1}$. The minimum charge taken into the Ewald sum was $0.00001e$. All atom pairs with separations less than $10\text{ \AA}$ were included in the real-space part of the Ewald sum and all reciprocal-lattice vectors with lengths less than $0.5\text{ \AA}^{-1}$ were included in the reciprocal part of the Ewald summation. Charges in the crystal are calculated in *Cerius²* using the QEq method (charge equilibrium approach [20]). For the van der Waals energy (VDW) we used the well-known Lennard-Jones functional form, with the arithmetical radius combination rule. The non-bond cut-off distance for the VDW interactions was $7.0\text{ \AA}$.

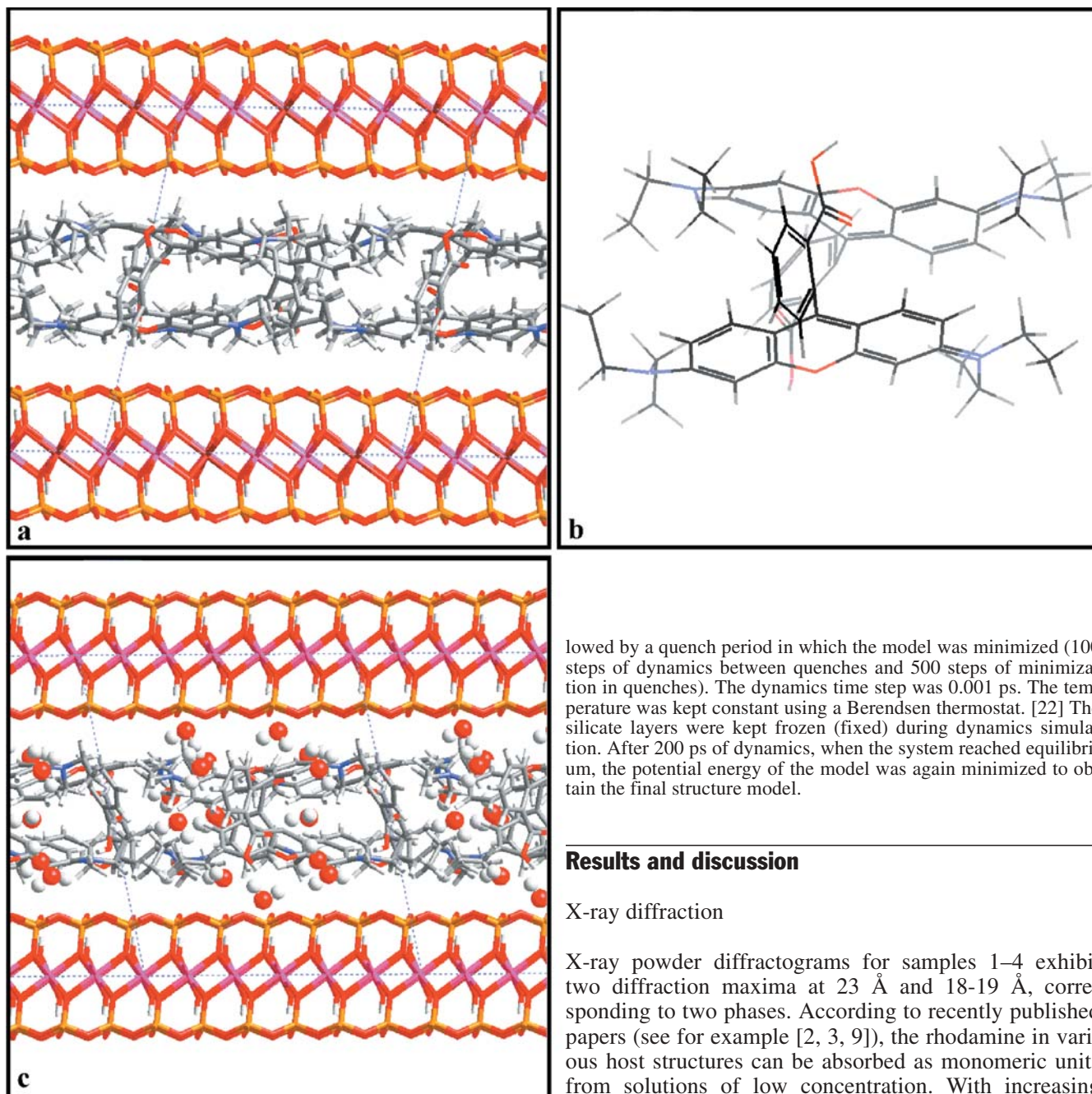


Fig. 4 **a** A side view of the intercalated structure of the phase 18 Å with H-dimeric arrangement, without interlayer water. **b** Detailed view of the H-dimer. **c** Side view of the H-dimeric structure of the phase 18 Å with interlayer water (model 4 in Table 2, with 16 water molecules per $3a \times 2b \times 1c$ supercell)

Molecular mechanics calculations and classical dynamic simulations were performed in the *Cerius²* modeling environment. The Universal force field [21] was used to describe the potential energy of initial models. After the first energy minimization in the *Minimizer* module in *Cerius²*, molecular dynamic simulations were started. Quench dynamics was used in an NVT ensemble (constant number of atoms, volume and temperature) at $T=300$ K. In the quench dynamics, periods of dynamic simulations were fol-

lowed by a quench period in which the model was minimized (100 steps of dynamics between quenches and 500 steps of minimization in quenches). The dynamics time step was 0.001 ps. The temperature was kept constant using a Berendsen thermostat. [22] The silicate layers were kept frozen (fixed) during dynamics simulation. After 200 ps of dynamics, when the system reached equilibrium, the potential energy of the model was again minimized to obtain the final structure model.

Results and discussion

X-ray diffraction

X-ray powder diffractograms for samples 1–4 exhibit two diffraction maxima at 23 Å and 18–19 Å, corresponding to two phases. According to recently published papers (see for example [2, 3, 9]), the rhodamine in various host structures can be absorbed as monomeric units from solutions of low concentration. With increasing concentration, aggregation of rhodamine B in the solution can be observed and consequently, monomeric and dimeric arrangements can coexist in the intercalated structure. According to this assumption, the dimeric arrangement exhibits the 18.1 Å basal spacing, while the dominant monomeric arrangement leads to the 22–23 Å basal spacing. The large broadening of the diffraction profile, especially for those peaks corresponding to the monomeric phase for the samples 1–4, indicates a high degree of disorder in the interlayer space accompanied by considerable mechanical strain. When discussing the diffraction line broadening, one must also take the Hendricks–Teller effect into account. [23] This is due to the irregular mixing of two interlamellar distances 18.1 Å and ~23 Å, which occurs at the phase boundaries. As a

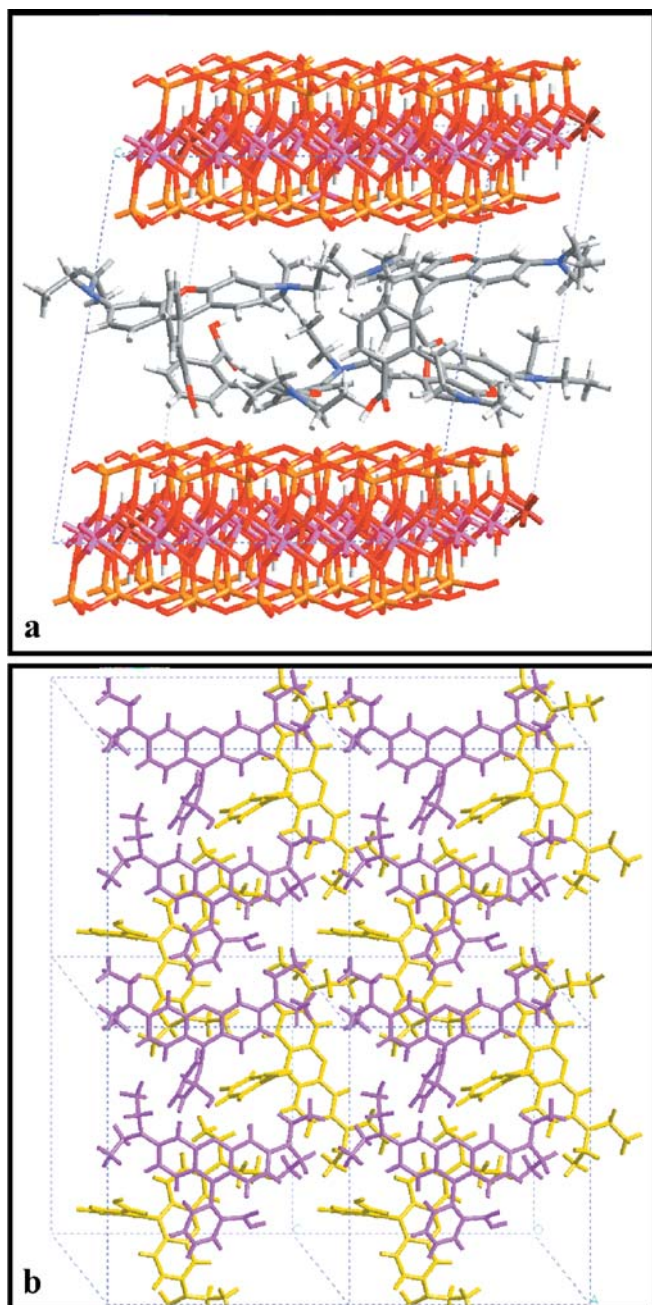


Fig. 5 **a** Side view of structure of the phase 18 Å, with bilayer arrangement of monomers (model 6 in Table 2). **b** Top view of structure of the phase 18 Å, with monomeric arrangement of [rhodamine B]⁺ cations in two layers (lower layer yellow, upper layer magenta, silicate layer removed for clarity)

result of the Hendricks–Teller effect, we observe a peak shift and broadening of the 00 l diffraction lines for the mixed phases. Another reason for the 00 l broadening of the diffraction lines is the adsorption of water into the interlayer space, which causes fluctuations of the interlayer distance.

IR spectroscopy

Detailed analysis of the IR spectra for the host structure Na-montmorillonite, guest compound rhodamine B chloride and intercalate rhodamine B–montmorillonite confirmed the rigidity of the silicate layers and showed the changes in the IR spectra of rhodamine B in the intercalated structure. (Spectrometric identification was performed using [24, 25]) First of all, comparing the spectrum of rhodamine B chloride and the intercalate in Fig. 2, one can observe the large broadening (smoothing) for the C=O stretching band in the carboxyl group at $\sim 1700\text{ cm}^{-1}$ in the spectrum of the intercalate. Internal H-bonding reduces the carbonyl stretching frequency from 1720 cm^{-1} to $1665\text{--}1680\text{ cm}^{-1}$ and the smoothing of this band indicates orientational disorder of the carboxyl groups. The same effect of carboxyl disorder can be observed in the case of the C–O–H in-plane bending at $\sim 1413\text{ cm}^{-1}$ and in case of C–O stretching at $\sim 1300\text{ cm}^{-1}$, this band almost disappears in the spectrum of intercalate.

The changes in the absorption bands corresponding to the aromatic rings are also evident in the spectrum of intercalate. As one can see in Fig. 2, there is a significant broadening (smoothing) of the bands corresponding to: (i) the in-plane bending of the ring C–H bonds in the region $1000\text{--}1300\text{ cm}^{-1}$, (ii) the out-of-plane bending of the ring C–H bonds at $\sim 675\text{--}900\text{ cm}^{-1}$ and (iii) the skeletal vibrations involving carbon–carbon stretching within the ring at $\sim 1585\text{--}1600\text{ cm}^{-1}$ and $1400\text{--}1500\text{ cm}^{-1}$. These changes in band profiles confirm the irregular positioning of the rhodamine B cations with respect to the silicate layers, the intramolecular rotations of the rhodamine B cations and a possible distortion of the xanthene part of the rhodamine B cation in the intercalate.

Results of modeling

A series of 80 initial models was investigated with various initial arrangements of monomers and dimers, with and without interlayer water. The molecular mechanics and dynamics simulations, carried out for the series of 80 initial models, result in two types of interlayer structure with the basal spacing 18.1 Å (phase 18 Å) and $\sim 23\text{ Å}$ (phase 23 Å). The two phases differ significantly in the interlayer structure, but they exhibit certain common features:

- No regularly ordered positions of the rhodamine B anchored to the silicate layers were found, either for phase 18 Å or for 23 Å.
- Intramolecular rotation about the xanthene–amine bonds was observed in both phases. However, the change from the planar to pyramidal arrangement of the xanthene–diethylamine double bond is stronger for the phase 18 Å. The average departure from planarity for the phase 18 Å is $\sim 29^\circ$ and for the phase 23 Å about 21° . The presence of interlayer water slightly

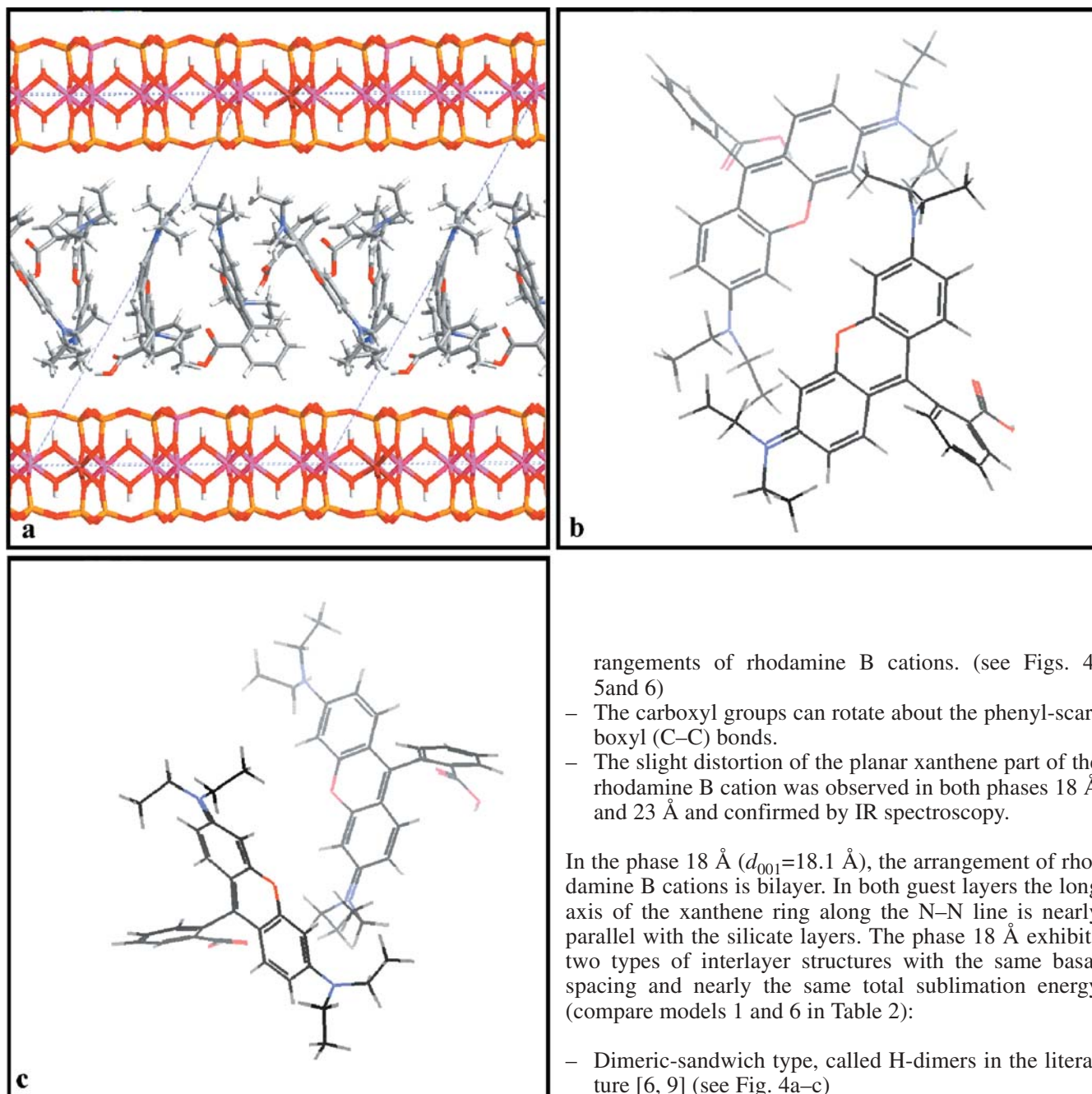


Fig. 6 **a** Side view of the phase 23 Å structure with monolayer arrangement of guests [rhodamine B]⁺ (model 8 in Table 2). **b** Detailed view of the head-to-tail sandwich type of dimer occurring in the phase 23 Å. **c** Detailed view of the head-to-tail J-dimer occurring in the phase 23 Å

increases the departure from planarity, depending on the water content.

- The carboxyphenyl rings are perpendicular to the xanthene plane in the rhodamine B cation minimized in vacuum (see Fig. 3). In the interlayer space of montmorillonite, the phenyl rings may rotate about the xanthene–phenyl bonds in both phases and in all ar-

rangements of rhodamine B cations. (see Figs. 4, 5 and 6)

- The carboxyl groups can rotate about the phenyl–carboxyl (C–C) bonds.
- The slight distortion of the planar xanthene part of the rhodamine B cation was observed in both phases 18 Å and 23 Å and confirmed by IR spectroscopy.

In the phase 18 Å ($d_{001}=18.1$ Å), the arrangement of rhodamine B cations is bilayer. In both guest layers the long axis of the xanthene ring along the N–N line is nearly parallel with the silicate layers. The phase 18 Å exhibits two types of interlayer structures with the same basal spacing and nearly the same total sublimation energy (compare models 1 and 6 in Table 2):

- Dimeric-sandwich type, called H-dimers in the literature [6, 9] (see Fig. 4a–c)
- Monomeric bilayer, see Fig. 5a, b

The H-dimeric arrangement is illustrated in Fig. 4a (a side view of the structure). In H-dimers, the rhodamine B cations interact with each other via the carboxyl groups. A detailed view of the H-dimer is shown in Fig. 4b. One can see the carboxyl groups pointing at the oxygen atom in the xanthene ring of the neighboring rhodamine B cation. It is also evident from Fig. 4b that the double xanthene=amine bonds of the two cations in the dimer are oriented in the same direction (head-to-head arrangement). Inclusion of water molecules into the interlayer space of the phase 18 Å leads to an increase of the total sublimation energy, as one can see in Table 2. That means the sorption of water is very probable. The

Table 2 Summary of the modeling results. Basal spacing and the total sublimation energy for the phases 18 Å and 23 Å with various arrangements of guests and with variable water content. Water

Phase	Model no.	Structure	Number of water molecules in one supercell	Basal spacing d_{001} (Å)	Total subl. energy per one supercell (kcal mol ⁻¹)
18 Å	1	H-dimer	No water	18.1	876
18 Å	2	H-dimer	4	18.1	1052
18 Å	3	H-dimer	8	18.1	1133
18 Å	4	H-dimer	16	18.1	1425
18 Å	5	H-dimer ^a	32 ^a	22.4 ^a	3003 ^a
18 Å	6	Monomers bilayer	No water	18.1	842
18 Å	7	Monomers bilayer	8	18.1	1030
23 Å	8	Monomers–dimers monolayer	No water	21–25	630–790
23 Å	9	Monomers–dimers monolayer	16	22.4	1491

^a Prevailing water positions between the silicate layer and guest layer

increasing water content up to 16 water molecules per supercell $3a \times 2b \times 1c$ with two H-dimers does not change the basal spacing 18.1 Å (see Table 2), as there is a lot of empty space between the rhodamine B cations. Model 4 with 16 water molecules per supercell $3a \times 2b \times 1c$ is shown in Fig. 4c. Model 5 with 32 water molecules per one supercell exhibits an increase of basal spacing up to 22.4 Å and a large increase of the total sublimation energy per supercell (see Table 2). In contrast to models 2, 3 and 4, water molecules in model 5 reside mostly between the silicate and the guest layer. This effect of hydration explains the asymmetric broadening of the 001 diffraction line of the phase 18 Å in Fig. 1b. This phase 18 Å with the H-dimeric arrangement arises for intercalation solutions with high guest concentrations (see Table 1), i.e. with a strong tendency to dimerization.

The monomeric arrangement of rhodamine B cations in the phase 18 Å obtained from the modeling is shown in Fig. 5a, b. Figure 5a shows a side view of the structure, and the structure of the guests layers is shown in Fig. 5b from above (silicate layers were removed in Fig. 5b for clarity; the lower guest layer *yellow* and the upper guest layer *magenta*). Models 6 and 7 in Table 2 represent this structure, where only small interactions between the monomers occur. As one can see, the basal spacing is the same as in case of the H-dimeric arrangement, 18.1 Å. The total sublimation energy is slightly lower in comparison with model 1. The effect of hydration for the bilayer monomeric structure is the same as in case of the H-dimeric structure described above. The existence of this monomeric arrangement is a very important result of the modeling, as it can explain the presence of the phase 18 Å in the samples prepared from intercalation solutions with very low guest concentrations, i.e. with monomeric guest species.

The phase 23 Å was observed using intercalation solutions with very low concentrations of guests with prevailing monomeric arrangements. Modeling of the monomeric arrangement in the interlayer space of montmorillonite led to: (i) the bilayer arrangement (phase 18 Å) described above and (ii) to the monolayer arrangement of tilted monomers with a basal spacing within

content and the values of the total sublimation energy are related to one supercell $3a \times 2b \times 1c$

Table 3 Comparison of the mutual intermolecular interaction energy between monomers in three types of dimers (interaction energy includes the non-bond, i.e. the van der Waals and electrostatic contributions)

Dimer type	H-dimer	Head-to-tail sandwich	J-dimer
Interaction energy (kcal)	23.5	9.3	5.1

21–25 Å, which we denoted as “phase 23 Å”. An example of this structure is shown in Fig. 6a. In this phase 23 Å, the rhodamine B cations are tilted to the silicate layers. The tilting angles are in the range 40–60°. This wide range of positions and orientations of the rhodamine B cations in the interlayer results in disorder and strain in the interlayer space, which is intensified by the presence of interlayer water and leads to large fluctuations of the basal spacing. In this structure, the interactions between the monomers are stronger than in the bilayer phase 18 Å. In the phase 23 Å, a mixture of monomers and dimers was found in the interlamellar space. The two types of head-to-tail dimer found in this structure are illustrated in Fig. 6b and c. The dimer in Fig. 6b is the head-to-tail sandwich type (note the position of the single and double xanthene–amine bonds). On the other hand, the head-to-tail dimer in Fig. 6c is the so-called J-dimer described in the literature. [6, 9] It is evident that the J-dimer allows a higher degree of aggregation in the interlamellar space of montmorillonite. Insertion of water molecules into the interlayer structure of the phase 23 Å leads to fluctuations of the basal spacing, within the range 21–25 Å.

Conclusions

The present results have revealed in detail the structure of montmorillonite intercalated with [rhodamine B]⁺ cations and the mechanism of the intercalation process.

Two structural phases were observed by X-ray diffraction and modeling: (i) phase 18 Å with a bilayer arrangement of guests and (ii) phase 23 Å with a monolayer arrangement of guests. In both phases, the coexistence of monomeric and dimeric arrangement is possible. Three types of dimer have been observed using molecular mechanics and molecular dynamics simulations: H-dimer (head-to-head), head-to-tail sandwich and head-to-tail J-dimer. Comparing their mutual non-bond interaction energy (see Table 3), one can see that the H-dimers are most stable.

The present modeling results agree with the X-ray diffraction measurements. Both methods revealed the existence of the two phases, where the basal spacing obtained from modeling agrees with the experimental value. The results of modeling also help to explain the structural disorder and its effect on the diffraction pattern (line shift and line broadening). IR spectroscopic measurements also corroborate the modeling results. The intramolecular rotational disorder obtained from modeling has a corresponding response in the IR spectra of the intercalate. As a result of this intramolecular rotation, we can observe the broadening of the C=O and C–O stretching and C–O–H in-plane bending bands. The broadening of bands corresponding to the in-plane and out-of-plane bending of the ring C–H bonds and of the skeletal vibrations involving carbon–carbon stretching within the ring indicates slight distortions of the xanthene ring, which have been obtained by modeling.

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9.2 The rhodamine B intercalation of montmorillonite – P2

The rhodamine B intercalation of montmorillonite

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Abstract

Using photometric methods the dissociation constants and weight fractions of rhodamine B dimer in water solutions at different concentrations were determined. The montmorillonite (SWy) samples were fully intercalated with rhodamine B (RhB) solutions at various monomer/dimer ratios. The amount of rhodamine B in fully intercalated montmorillonite (RhB–SWy) increases with increasing concentration of dye in water solutions, i.e., with increasing dimer/monomer ratio. The sum of exchangeable guest cations in RhB–SWy is approximately constant (0.900 meq g^{-1}) for all samples, because RhB–SWy samples with prevailing dye monomer also contain higher amounts of non-exchanged alkali elements. The experimental data are supported by calculated structure models that illustrate the changes in RhB–SWy structure depending on monomeric and/or dimeric arrangement of guests. The analysis of the calculated structure models confirmed the existence of two phases with different basal spacings, $d \sim 1.8$ and ~ 2.3 nm, revealed by X-ray diffraction.

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Keywords: Rhodamine B; Aggregation; Montmorillonite; Intercalation; Molecular simulation

1. Introduction

Due to the negative charge of their interlayer, the smectites have a suitable host structure for the intercalation of various guests (e.g., metals, inorganic complexes, and organic cations). Intercalated materials find a variety of applications (sorbents of some organic compounds, catalyst carriers, selective membranes, etc.). In recent years interest has focused on the utilization of intercalated smectites by organic dyes, e.g., methylene blue, proflavine, acridine, orange, thionine, pyronin Y, crystal violet, methylene green, rhodamine B, and rhodamine 6G. These materials are exploited in modern photochemistry and photophysics by reason of their transparency in the visible wavelength region and their optical activity [1–6].

In this paper we focus on montmorillonite intercalation by rhodamine B. This dye is utilized as a laser pigment, as a sensitizer in various photochemical reactions (e.g., [7–10]), or as a source for singlet oxygen formation [3,11,12]. In water solutions rhodamine B aggregates, forming dimers. The proportion of the dimers to the monomers increases

with increasing concentration of dye [13–16]. Except for interaction strengths between dye monomers, the formation of dimers is also influenced by the surrounding environment properties, e.g., dye concentration, pH, and ionic strength. The intercalation of dye (guest) into montmorillonite (host) runs on the principle of the ion-exchange reaction. This process is controlled by coulombic and van der Waals strengths, H-bonds, and also nonbond energy contributions between guest and host and between guest and guest [17–19].

The aim of this paper is to elucidate the influence of rhodamine B aggregation in water solution on the composition and structure of rhodamine B-montmorillonite.

2. Material and methods

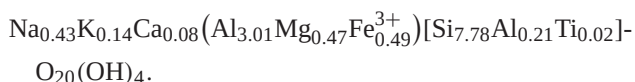
2.1. Samples and chemicals

Na-montmorillonite (Na–SWy) from Wyoming (USA) was used for the intercalation of rhodamine B. From the original sample a fraction below 0.045 mm was prepared and air-dried. The bulk chemical analysis of this sample was performed and recalculated on the following crystallochemical

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formula [20]:



This formula is very similar to the one that has already been given by Weaver and Pollard [21]. The specific surface area of this sample is $136 \text{ m}^2 \text{ g}^{-1}$ and cation exchange capacity (CEC) is 0.88 meq g^{-1} . Rhodamine B (RhB) produced by Fluka Standard Chemica was dissolved in distilled water, recrystallized, and then dried under vacuum to a constant mass. The basic water solution of rhodamine B ($5.00 \times 10^{-3} \text{ mol dm}^{-3}$) was prepared by dissolution of recrystallized dye in distilled water; solutions of lower molar concentrations were then prepared by its dilution with distilled water.

2.2. Methods and instruments

The chemical analysis of Na-SWy was determined by X-ray fluorescence (SpectroLab) and atomic absorption spectrometry was used for the determination of Na, K, Ca, and Mg (Unicam 969). X-ray patterns of Na-SWy with intercalated RhB were recorded by X-ray powder diffractometer (INEL X with PCD, Ge monocrystal, and Cu- K_α radiation). The absorption spectra of rhodamine B in the water solution were recorded by UV-vis spectrophotometry (Lambda 25, Perkin-Elmer) using glass cells of thickness 0.1–1 cm. The more concentrated solutions of rhodamine B (about $3.75 \times 10^{-3} \text{ mol dm}^{-3}$) were measured in cells with thickness below 0.1 cm prepared using spacers.

The contents of C, H, N, O in fully intercalated Na-SWy samples by RhB (RhB-SWy) were determined by the elemental analysis using a CHNS-O analyzer (fy FLASH). Moisture (W) and loss of ignition (LI) of samples were determined by drying at $105\text{--}110^\circ\text{C}$ and by ignition at 1000°C , respectively.

2.3. Adsorption isotherms

Adsorption isotherms were determined at $20 \pm 2^\circ\text{C}$ using 0.1 g of Na-SWy and series of 50 cm^3 water solutions of rhodamine B with various concentrations (c). The suspensions were shaken for 24 h at the laboratory temperature in tight glass vessels using batch equilibrium techniques. They were centrifuged for 40 min at a rotation speed of 5000 rpm. Supernatant and washings were collected. The concentration of rhodamine B solutions before and after adsorption was determined/checked by a photometric method.

2.4. Preparation of fully intercalated samples of Na-SWy by rhodamine B

The fully intercalated samples RhB-SWy (Nos. I–X) were prepared by repeated intercalation of Na-SWy with rhodamine B solutions. The amount of 0.1 g of Na-SWy

for samples I and II and the concentrations of dye 1.06×10^{-4} and $4.60 \times 10^{-4} \text{ mol dm}^{-3}$ were used, respectively. Samples III–X were prepared using 0.5 g of Na-SWy and 100 cm^3 of the rhodamine B solutions with concentrations ranging from 1.02×10^{-3} to $4.79 \times 10^{-3} \text{ mol dm}^{-3}$. For each sample the intercalation was repeated until the dye adsorption was measurable. Each intercalation step was performed for 24 h of sample shaking with rhodamine B solution. The suspensions were then centrifuged for 40 min at a rotation speed of 5000 rpm. After supernatant dilution to a dye concentration below $2 \times 10^{-6} \text{ mol dm}^{-3}$ the absorbance of solutions at 552 nm wavelength was determined and their concentration calculated. From these data the total intercalated amount of dye was evaluated. The samples (RhB-SWy) were dried in vacuum.

3. Results and discussion

3.1. Aggregation of rhodamine B in water solution

VIS absorption spectra of rhodamine B in water solutions at different concentrations are given in Fig. 1. They show two absorption maxima. The first is at 552 nm and relates to the monomeric form of rhodamine B, while at 520 nm a second maximum occurs, relating to the dimeric form of the dye [7,14,22,23].

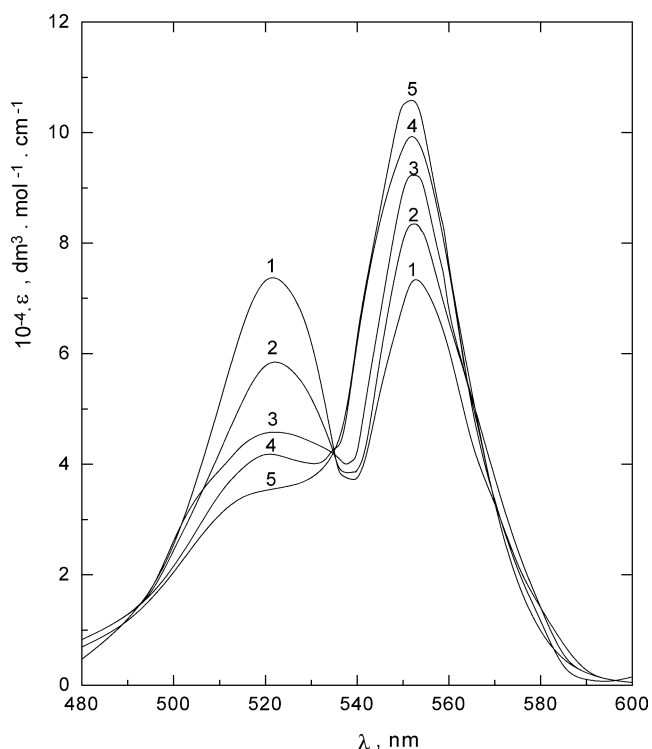
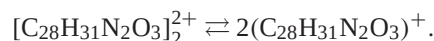


Fig. 1. Absorption spectra of rhodamine B water solutions. (1) $3.75 \times 10^{-3} \text{ mol dm}^{-3}$; (2) $1.50 \times 10^{-3} \text{ mol dm}^{-3}$; (3) $6.00 \times 10^{-4} \text{ mol dm}^{-3}$; (4) $6.00 \times 10^{-5} \text{ mol dm}^{-3}$; (5) $2.00 \times 10^{-6} \text{ mol dm}^{-3}$.

The dissociation of rhodamine B dimer in a water solution can be expressed by the following equation:



The dissociation constant of rhodamine B dimer (K) for this chemical reaction is defined as

$$K = \frac{c_M^2}{c_D} = \frac{2(cw_M)^2}{(1-w_M)c} = \frac{2w_M^2c}{1-w_M}, \quad (1)$$

where the concentration of dye c is expressed as $c = c_M + 2c_D$. c_M is the concentration of the monomeric and c_D the concentration of the dimeric form of the dye in water solution.

The weight fraction of the monomeric form of dye w_M is defined as follows:

$$w_M = \frac{c_M}{c} = \frac{(c - 2c_D)}{c}. \quad (2)$$

The value w_M ranges from 0 to 1, depending on the concentration of the dye in a water solution. From Eq. (2) the concentrations c_M and c_D can be expressed as a function of w_M and c .

For the calculation of the dissociation constant K the absorption spectra of rhodamine B (Fig. 1) and the method of Selwyn and Steinfeld [7] were used.

The best fit between experimental ε (Fig. 1) and calculated $\varepsilon_{\text{calc}}$ molar absorption coefficients was found for the dissociation constant $K = 7.0 \times 10^{-4} \text{ mol dm}^{-3}$ (correlation coefficients $r = 0.996$ and $r = 0.980$ for wavelengths 520 and 552 nm, respectively).

The dissociation constant K of the rhodamine B dimer dissociation in a water solution had already been determined before. Rohatgi and Singhal [24] calculated $K = 7.3 \times 10^{-4} \text{ mol dm}^{-3}$ and Selwyn and Steinfeld [7] $K = 6.8 \times 10^{-4} \text{ mol dm}^{-3}$. The agreement between the previously measured data and our result ($K = 7.0 \times 10^{-4} \text{ mol dm}^{-3}$) is very good.

3.2. Adsorption isotherm

The adsorption isotherm of the rhodamine B on Na-SWy was measured using the batch equilibrium technique. The adsorbed rhodamine B was recalculated to 1.0 g Na-SWy (a_{RhB}) and the data are plotted for the related equilibrium concentrations of rhodamine B in Fig. 2. The adsorption data were tested on the agreement with Langmuir and Freundlich isotherms. It was found that they fit better with the Langmuir isotherm (correlation coefficient 0.998) than with the Freundlich isotherm (correlation coefficient 0.950). The calculated Langmuir isotherm ($c/a = 992.8c + 0.06967$) is plotted in Fig. 2.

3.3. The influence of the rhodamine B aggregation on the composition of RhB-SWy

The influence of the rhodamine B aggregation in a water solution in relation to the composition of fully interca-

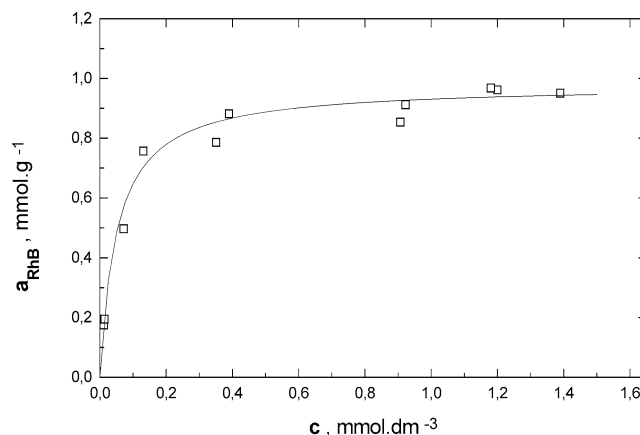


Fig. 2. Adsorption isotherm of rhodamine B on Na-SWy.

lated RhB-SWy was studied using 10 samples (Nos. I–X). Because every Na-SWy sample was repeatedly intercalated with the dye solution of the same concentration it can be assumed that this dye concentration relates to fully intercalated RhB-SWy. For these solutions the weight percentages of monomer ($10^2 w_M$) were calculated from Eq. (1) using the dissociation constant $K = 7.0 \times 10^{-4} \text{ mol dm}^{-3}$. The experimental and calculated data are given in Table 1. The intercalated rhodamine B in RhB-SWy samples (a_{RhB}) increases with the increasing concentration of the dye (c), i.e., with increasing portion of RhB dimers in water solution (from about 0.71 in sample I to 0.90 meq g^{-1} in sample X).

Among samples I–X two structural phases with basal spacing d_{001} 1.8 nm and 2.1 to 2.3 nm were determined by X-ray diffraction (Table 1). In both phases probably the coexistence of monomeric and dimeric arrangements is possible. X-ray diffraction profiles of basal spacing are shown for fully intercalated samples of RhB-SWy III and IX containing different portions of dye monomer 43.9% and 24.8%, respectively (Fig. 3).

3.4. Elemental composition of intercalated RhB-SWy samples

The amount of rhodamine B in the intercalated RhB-SWy samples was verified using elemental analyses (C, H, O, and N) and the following recalculations. For this three fully intercalated samples of RhB-SWy (Nos. I, VIII, and IX) were used. In Table 2 moisture (W), loss on ignition (LI), and results of elemental analyses are presented. Loss on ignition (LI) covers loss of mass due to the evaporation of moisture (W) and ignition of C, H, N, and O from RhB-SWy samples at 1000 °C in the oxygen atmosphere. Elements C and N are present only in the intercalated RhB part, while H and O are present also in –OH groups of the SWy part of RhB-SWy samples. During the elemental analyses the hydroxyl groups from the montmorillonite part of RhB-SWy are decomposed and the nascent water is determined, together with the water formed from H_{RhB} after the ignition of the sample in the oxygen-containing atmosphere.

Table 1

Experimentally determined intercalated amounts of rhodamine B (a_{RhB}) and alkaline cations a_{Alk} , X-ray diffraction pattern d_{001} , and calculated data (w_M , a_{sum}) of fully intercalated RhB–SWy samples

Sample	c (mol dm ^{−3})	$10^2 w_M$ (wt%)	a_{RhB} (meq g ^{−1})	a_{Alk} (meq g ^{−1})	a_{sum} (meq g ^{−1})	d_{001} (nm)	
						1. Maximum	2. Maximum
I	1.06×10^{-4}	80.4	0.706	0.224	0.930	2.07–2.32	1.87
II	4.60×10^{-4}	57.2	0.779	0.135	0.914	2.07–2.32	1.87
III	1.02×10^{-3}	43.9	0.791	0.125	0.916	2.07–2.32	1.87
IV	1.10×10^{-3}	43.0	0.796	0.140	0.936	2.07–2.32	1.87
V	2.40×10^{-3}	31.6	0.855	0.093	0.948	2.07–2.32	1.74
VI	3.70×10^{-3}	26.4	0.894	0.065	0.963		1.96
VII	4.00×10^{-3}	25.5	0.898	0.076	0.974		1.86
VIII	3.99×10^{-3}	25.6	0.905	0.051	0.956		1.83
IX	4.30×10^{-3}	24.8	0.900	0.045	0.945		1.84
X	4.79×10^{-3}	23.6	0.895	0.050	0.945		1.75

Note. c is concentration of rhodamine B in water solution, $10^2 w_M$ are calculated weight percentages of the rhodamine B monomer in water solution, a_{RhB} is intercalated rhodamine B (meq/1 g Na–SWy), a_{Alk} is sum of Na⁺, K⁺, and Ca²⁺ (Alk) in 1 g Na–SWy, a_{sum} is the sum of a_{RhB} and a_{Alk} , and d_{001} is interlayer distance.

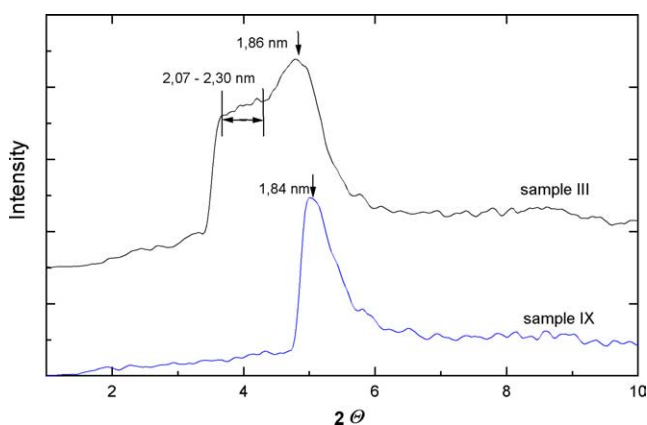


Fig. 3. X-ray diffraction profiles d_{001} : patterns of samples RhB–SWy Nos. III and IX.

Table 2

Moisture and elemental composition of RhB–SWy samples

	Sample I (wt%)	Sample VIII (wt%)	Sample IX (wt%)
W	2.14	1.84	1.99
C	17.59	21.45	22.70
H	2.19	2.60	2.88
N	1.55	1.73	1.87
O	5.91	7.48	8.02
$10^2 w_{\text{C,H,N,O}}$	27.24	33.26	35.47
LI	29.60	35.33	37.58

Notes. W is moisture—content of water in analytical sample, $10^2 w_{\text{C,H,N,O}}$ is sum of weight percentages of C, H, N, and O in analytical samples RhB–SWy, and LI is loss on ignition (related to analytical samples RhB–SWy).

For the recalculation of the elemental analyses (Table 2) the molar ratio $\text{O}_{\text{RhB}}:\text{H}_{\text{RhB}} = 3:31$ (i.e., the mass ratio $\text{O}_{\text{RhB}}:\text{H}_{\text{RhB}} = 1.535$) was established from the chemical formula of rhodamine B cation $[\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3]^+$. The contents of H_{RhB} and O_{RhB} present in RhB (guest) and the contents of H_{SWy} and O_{SWy} present in SWy (host) parts of the RhB–SWy samples were calculated. The weight fraction of RhB

in RhB–SWy (w_{RhB}) is then the sum of analyzed (C and N) and calculated (H_{RhB} and O_{RhB}) contents.

In Table 3 the data obtained from elemental and spectrometric analyses for three fully intercalated samples RhB–SWy are presented. For the recalculations of w_{RhB} from the ratio RhB:SWy and a_{RhB}^a , the following data were used: molecular weight of rhodamine B cation, $M(\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3^+) = 443.57 \text{ g mol}^{-1}$, molecular weight of Na montmorillonite $M(\text{Na–SWy}) = 751.69 \text{ g mol}^{-1}$ and $M(\text{SWy}) = 733.12 \text{ g mol}^{-1}$ (calculated from crystallochemical formula of Na–SWy minus ion-exchangeable cations Na⁺, K⁺, and Ca²⁺).

The comparison of the intercalated rhodamine B calculated from elemental analyses (a_{RhB}^a) and calculated from photometric measurements (a_{RhB}^b) shows good agreement between both independently obtained results (see Table 3).

3.5. Cations in interlayer of RB–SWy

Except for fully intercalated samples of RhB–SWy, alkaline cations from the original Na–SWy sample remained in their interlayer space. Values a_{RhB} and a_{Alk} are given in meq g^{−1} (Table 1). It was assumed that the intercalated monomer of rhodamine B cation in the interlayer space has a +1 charge $[\text{RhB}^+]$ and the dimer has +2 charges $[\text{RhB}]_2^{2+}$. The value a_{Alk} was calculated as a sum of meq of Na⁺, K⁺, and Ca²⁺ from the analyses of Na, K, and Ca leached out by HCl solution (1:4) from the interlayer of RhB–SWy samples. The sum of meq of both types of guest cations ($a_{\text{sum}} = a_{\text{RhB}} + a_{\text{Alk}}$) is approximately constant. In the samples RhB–SWy intercalated with dye solutions in which monomer prevailed, a higher content of alkali elements was present, and vice versa. The presence of chlorine anions in the interlayer space of RhB–SWy was not detected (LOD 0.010 meq/g).

Table 3
Evaluation of intercalated amount of rhodamine B determined by different methods

	Sample I	Sample VIII	Sample IX
w_{RhB}^a	0.238	0.286	0.304
RhB:SWy	0.516	0.662	0.722
a_{RhB}^a	0.688	0.880	0.960
mmol sorb. RhB/1 g Na–SWy ^a			
a_{RhB}^b	0.706	0.905	0.900
mmol sorb. RhB/1 g Na–SWy ^b			
Calculated formulae of RhB (guest) cation ^b	$[\text{C}_{26.6}\text{H}_{32.5}\text{N}_2\text{O}_{3.2}]^+$	$[\text{C}_{28.9}\text{H}_{32.9}\text{N}_2\text{O}_{3.4}]^+$	$[\text{C}_{28.3}\text{H}_{34.4}\text{N}_2\text{O}_{3.3}]^+$

Note. w_{RhB} is weight fraction of rhodamine B in RhB–SWy (g RhB/g RhB–SWy); RhB/SWy is molar ratio between RhB and SWy (mol/mol); a_{RhB} is intercalated rhodamine B (meq/1 g Na–SWy).

^a Calculated from elemental analysis data (see Table 3).

^b Data from spectrophotometric measurements (Table 1).

3.6. Structure analysis using molecular modeling

Molecular mechanics and classical molecular dynamics have been used to investigate the structure of montmorillonite intercalated with rhodamine B cations with various concentrations of guests and with different degrees of their dimerization in the interlayer space. For this purpose a series of 120 initial models of Na–montmorillonite completely or partially exchanged with rhodamine B cations in a monomeric or dimeric arrangement have been built.

3.6.1. Strategy of modeling

The strategy of modeling using an empirical force field was based on the experimental data (chemical analysis, IR spectroscopy, and X-ray powder diffraction [25]). The initial model for montmorillonite layer was built using structure data published by Tshipursky and Drits [26]: space group, $C2/m$. The unit cell parameters according to Méring and Oberlin [27] have been used to define the planar unit cell dimensions: $a = 5.208$ nm and $b = 9.020$ nm. The composition of the montmorillonite layer calculated on the base of chemical analysis was $(\text{Al}_{3.01}\text{Mg}_{0.47}\text{Fe}_{0.49}^{3+})(\text{Si}_{7.78}\text{Al}_{0.21}\text{Ti}_{0.02})\text{O}_{20}(\text{OH})_4$. For calculations in the *Cerius*² [28] modeling environment the structure formula of the layer was slightly modified to create a supercell of a reasonable size. The $3a \times 2b \times 1c$ supercell was built with the layer composition $(\text{Al}_{18}\text{Mg}_3\text{Fe}_3^{3+})(\text{Si}_{47}\text{Al}_1)\text{O}_{120}(\text{OH})_{24}$. The total negative layer charge per $3a \times 2b \times 1c$ supercell was (-4) . The c values in the initial models were taken from X-ray powder diffraction for samples prepared under different conditions, allowing the full or partial replacement of the Na^+ cations by [rhodamine B]⁺ cations in the interlayer space of montmorillonite. The host–guest interactions in RhB–SWy are of a nonbonded nature. This is a very important assumption for the modeling strategy.

A recent comparison of IR spectra for the host structure Na–montmorillonite and for montmorillonite intercalated with rhodamine B cations showed that the bands corresponding to the silicate layer remained unchanged after intercalation [25]. That means that the silicate layers can be treated as rigid bodies during energy minimization. On the other hand, the bonding geometry and positions of all

atoms in the $[\text{RhB}]^+$ cations and Na^+ cations in the interlayer space were variable during energy minimization and dynamics simulations. Molecular mechanics and classical molecular dynamics simulations have been performed in the *Cerius*² modeling environment. The universal force field [29] has been used to describe the potential energy of initial models. Charges in the structure have been calculated using the *QEq*-method (charge equilibrium approach [30]). After the first energy minimization in the *Minimizer* module the molecular dynamic simulations were started. Calculations in the *Minimizer* module were performed under the following conditions: rigid silicate layers, variable supercell parameters c , α , β , and fixed a , b , γ . The Ewald summation method is used to calculate the Coulomb energy in a crystal structure [31]. The well-known Lennard–Jones functional form is used for the van der Waals energy (VDW), with the arithmetical radius combination rule. Quench dynamics has been used in an NVT ensemble (constant number of atoms, volume, and temperature) at $T = 300$ K. A dynamics time step was set up at 0.001 ps, the temperature was kept constant using a Berendsen thermostat [32]. The silicate layers were kept frozen (fixed) during dynamics simulation. After 200 ps of dynamics, when the system reached equilibrium, the potential energy of selected models was again minimized under the conditions described above to get the final structure model.

3.6.2. Results of modeling

Analysis of the calculated structure models confirmed the existence of two phases with different basal spacings $d \sim 1.8$ and ~ 2.3 nm revealed by X-ray diffraction [25] (see also Table 1). Four calculated models have been chosen to illustrate the intercalated structures of RhB–SWy with partially and completely exchanged RhB–SWy and with monomeric and dimeric arrangement of guests:

- Model 1 represents partially exchanged RhB–SWy with two Na^+ cations and two $[\text{RhB}]^+$ monomers per one $3a \times 2b \times 1c$ supercell. (See Figs. 4 and 5—top and side view.)

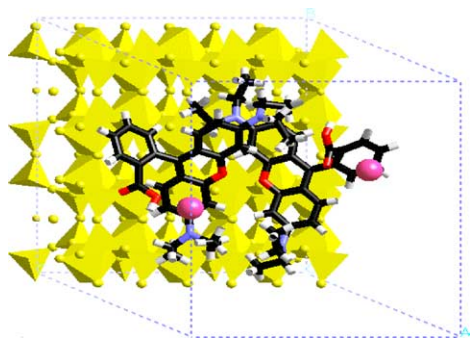


Fig. 4. The top view of one $3a \times 2b \times 1c$ supercell in Model 1, illustrating phase 18-M.

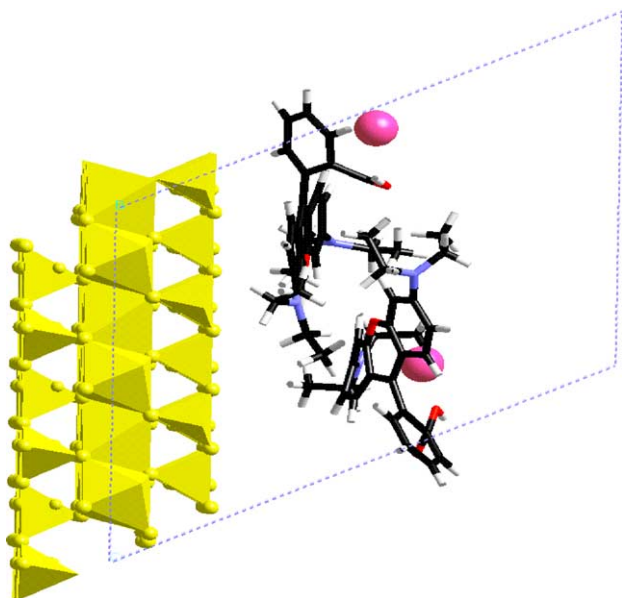


Fig. 5. The side view of one $3a \times 2b \times 1c$ supercell in Model 1, with two rhodamine B monomers and two Na cations, illustrating phase 18-M.

- Model 2 represents partially exchanged RhB–SWy with one Na^+ cation and three $[\text{RhB}]^+$ monomers per one $3a \times 2b \times 1c$ supercell. (See Fig. 6—side view.)
- Model 3 illustrates fully exchanged RhB–SWy with four $[\text{RhB}]^+$ monomers per one $3a \times 2b \times 1c$ supercell. (See Fig. 7—side view.)
- Model 4 illustrates fully exchanged RhB–SWy with two $[\text{RhB}]_2^{2+}$ H-dimers [25] per one $3a \times 2b \times 1c$ supercell. (See Fig. 8—side view.)

Table 4 shows a summary of the results calculated for Models 1–4, i.e., the basal spacing, the total sublimation energy, and the van der Waals and electrostatic contributions related to one $3a \times 2b \times 1c$ supercell. As can be seen in Fig. 5, Model 1 exhibits a disordered monolayer arrangement of rhodamine B monomers with two Na^+ -cations marked as small balls. In this model the xanthene rings are nearly parallel with the silicate layers. This model with calculated basal spacing 1.81 nm corresponds to the experimentally observed phase with $d \sim 1.74$ –1.87 nm in partially ex-

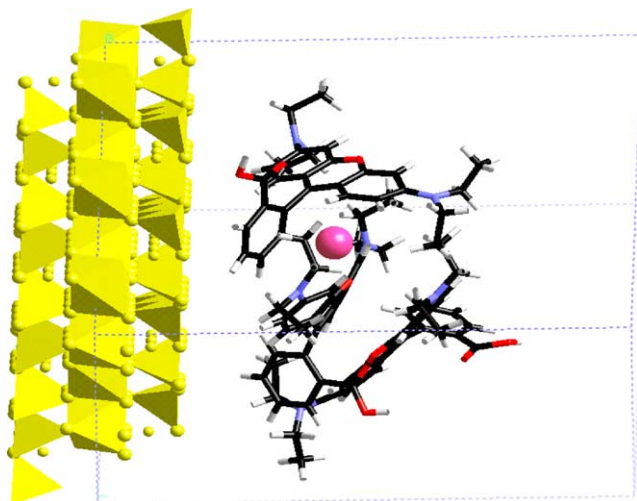


Fig. 6. The side view of one $3a \times 2b \times 1c$ supercell in Model 2, with three rhodamine B monomers and one Na cation, illustrating phase 2.3.

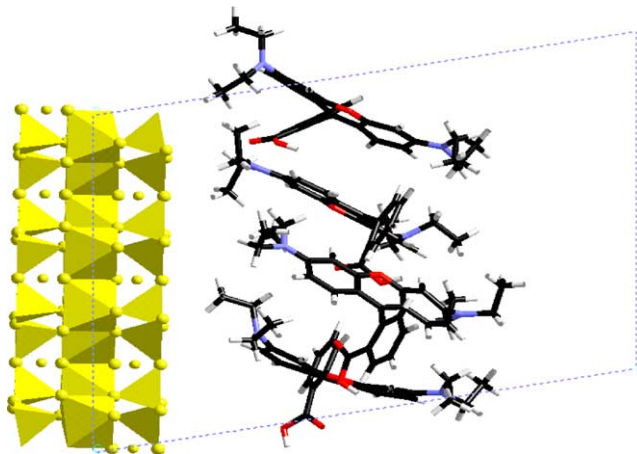


Fig. 7. The side view of one $3a \times 2b \times 1c$ supercell in Model 3, illustrating the fully exchanged rhodamine B–montmorillonite, phase 2.3.

changed samples I–V (see Table 1). This phase occurs in the samples intercalated in solutions with a low concentration of rhodamine B and consequently with a prevailing monomeric arrangement of guests in the interlayer space and for further discussion will be denoted as phase 1.8-M.

The analysis of the calculated models showed that higher ratios of rhodamine B monomers lead to a disordered monolayer arrangement, where the xanthene rings are more tilted to the silicate layers (i.e., out of parallel), resulting in higher basal spacing ~ 2.23 nm for Model 2 and 2.52 nm for Model 3. This range of basal spacings obtained by modeling was confirmed by the X-ray powder diffraction, as can be seen in Table 1 and Fig. 7. This structure with tilted monomers with the average basal spacing ~ 2.3 nm was described in [25] and denoted as phase 2.3 nm. Calculated Models 2 and 3 are two examples of this phase. In our recent work [25] it was found that phase 2.3 nm may contain a dimeric arrangement as well as various types of dimers, where all the xanthene parts are tilted to the silicate lay-

Table 4

Summary of the modeling results for models with different amounts of Na^+ and RhB cations in the interlayer space of montmorillonite, basal spacing (d_{calc}), total sublimation energy, and van der Waals and Coulomb contributions

Model	Number of RhB ⁺	Number of Na ⁺	d_{calc}	E_{total}	E_{VDW}	E_{coul}
MODEL 1	2	2	18.1	739	100	639
MODEL 2	3	1	22.3	714	114	600
MODEL 3	4	0	25.2	681	139	542
MODEL 4	4	0	18.1	876	244	632

Note. Values are related to one supercell $3a \times 2b \times 1c$.

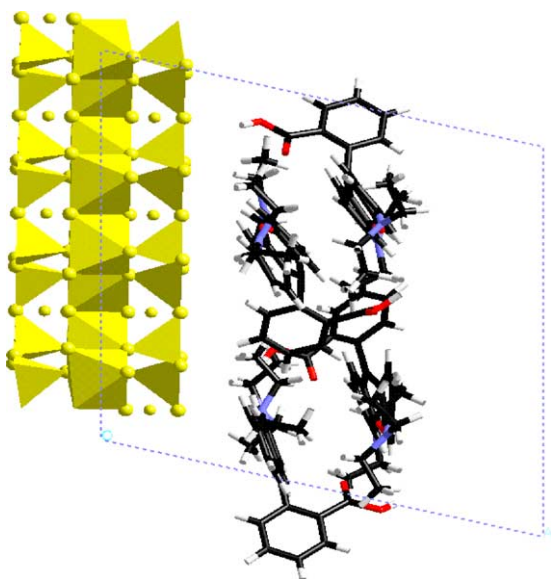


Fig. 8. The side view of one $3a \times 2b \times 1c$ supercell in Model 4, illustrating the fully exchanged rhodamine B–montmorillonite, H-dimeric arrangement of rhodamine B cations in phase 18-D.

ers. The diffraction profiles of basal reflections in Fig. 3 show that in sample III both phases are present: 1.8-M and phase 2.3. Phase 2.3, in addition, exhibits large profile broadening, which indicates large concentration inhomogeneity and disorder in the interlayer arrangement of monomers and dimers.

Model 4 (see Fig. 8) describes the dimeric arrangement in the fully exchanged RhB–SWy when the intercalation solution contains a large concentration of RhB dimers. Rhodamine B cations are arranged in the so-called H-dimers [14,33,34] interacting with each other via the carboxyl groups [25]. Xanthene parts are parallel with the silicate layers and the calculated basal spacing for this arrangement is 1.81 nm. This model corresponds to the samples VII–X in Table 1, which has been prepared using an intercalation solution with a higher concentration of rhodamine B dimers. This phase should be denoted as 1.8-D to distinguish it from the phase 1.8-M present in the samples I–V and containing mainly the rhodamine B monomers. Sample VI in Table 4 represents an interstratified phase with irregular mixing of basal spacings 1.8 and 2.3 nm.

The calculated Models 1–4 differ significantly in the arrangement of rhodamine B cations, but they exhibit some common features [25]:

- No regular ordered positions and orientation of the rhodamine B cations with respect to the silicate layers have been found.
- The carboxyphenyl rings are perpendicular to the xanthene plane in the rhodamine B cation minimized under universal force field in vacuum. In the interlayer space of the intercalated samples the phenyl rings may rotate about the xanthene–phenyl bonds.
- The carboxyl groups can rotate about the phenyl–carboxyl (C–C) bonds.
- The slight distortion of the planar xanthene part of rhodamine B cation has been observed and confirmed by IR spectroscopy [25].

Acknowledgments

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9.3 Effect of surface and interlayer structure on the fluorescence of rhodamine B-montmorillonite: modeling and experiment – P3

Effect of surface and interlayer structure on the fluorescence of rhodamine B–montmorillonite: modeling and experiment

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Abstract

The surface and interlayer structure of rhodamine B (RhB)–montmorillonite for various guest concentrations has been studied using a combination of X-ray powder diffraction and molecular modeling (molecular mechanics and molecular dynamics) in the *Cerius*² modeling environment. The joint effect of surface and interlayer structure on the fluorescence spectrum has been observed and discussed in relation to the position and orientation of RhB⁺ cations with respect to the silicate layer. Structural analysis showed that the surface and interlayer structures are different as to the arrangement of RhB⁺ cations, and both of them strongly depend on the guest concentration in the intercalation solution and on the method of preparation. The repeated intercalation of montmorillonite by rhodamine B used in the present work allowed obtaining RhB–montmorillonite in the maximum degree of ion exchange for every sample.

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Keywords: Surface structure; Interlayer structure; Rhodamine B–montmorillonite; Molecular modeling; Fluorescence of rhodamine B

1. Introduction

The increasing interest in dye/inorganic nanocomposites is focused on changes in optical properties during adsorption and/or intercalation of the dye in an inorganic matrix. Intercalation of organic dyes into layered silicates is one method of producing ordered organic–inorganic hybrid materials with interesting photofunctions [1–11]. Especially, the smectite group is used as a very convenient host structure for the intercalation of organic dyes for two reasons. (i) First of all, smectites are transparent in the visible wavelength region, and (ii) in addition, smectites as host structures provide features attractive for intercalation (swelling behavior, ion-exchange properties). Various dye–clay systems offer an interesting area of material research targeted on the development of new photofunction units [11–18]. The organization of the photoactive species within the microstructure is entirely dependent upon the host–guest and guest–guest interactions within the microstructure.

Rhodamines, which have a high absorption coefficient and fluorescent yield, are convenient dyes for collecting and utilizing photoenergy. Rhodamines are often used as an active medium of dye lasers. They also represent an ideal probe for studying heterogeneous systems because of their strong dependence of the absorption and fluorescence capacity on the matrix of the solvent. The optical properties of these dyes are environmentally sensitive and depend on the arrangement and configuration of the dye molecules (i.e., as monomers or various types of dimers). Rhodamine B (RhB) has a strong tendency to aggregation, depending on the concentration in the intercalation solution and on the charge distribution in the solvent or a matrix. According to the theory of exciton splitting, the sandwich-type H-dimers are nonfluorescent, while the monomers and oblique or coplanar J-dimers with an inclined transition dipole moment are fluorescent. (For the review of theoretical papers see, for example, Kemnitz et al. [17].)

The adsorption of rhodamine onto clays leads to the metachromatic effect [16] in the absorption spectra, whereby the main absorption band is shifted to higher energies. The fluorescence band of the rhodamine–clay system is shifted to

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Table 1

Concentration of rhodamine B in the intercalation solution c_{RhB} , fraction of monomers in the intercalation solution w_{mono} , amount of rhodamine B adsorbed in montmorillonite a_{RhB} , and 001 basal spacing d_{001} observed in the powder diffraction pattern

Sample No.	Concentration of RhB in the intercalation solution c_{RhB} [mol dm ⁻³]	Fraction of monomers in the intercalation solution w_{mono}	Amount of RhB adsorbed in montmorillonite a_{RhB} [mmol g ⁻¹]	Basal spacings d_{001} [Å]	
1	1.06×10^{-4}	0.891	0.706	22.90	18.70
2	1.10×10^{-3}	0.250	0.796	20.67	18.30
3	4.30×10^{-3}	0.058	0.900	18.40	

higher wavelength compared with that of the rhodamine in aqueous solution [12,13,16]. In addition, the emission band becomes broader as a consequence of the structural inhomogeneity of the rhodamine–clay system, where the surface structure may differ significantly from that in the interlayer space. To generate monochromatic laser light and to control the fluorescent properties, the structure of the dye–matrix system should be homogeneous, with controlled positions and aggregation of the dye molecules. The host–guest chemical and geometrical complementarity plays a key role in the design of these hybrid dye–host matrix systems.

The aim of this work is to find a correlation of the spectroscopic properties with the specific allocation of the dye molecules intercalated in montmorillonite. Special attention will be paid to the comparison of the interlayer and surface guest structure of RhB^+ cations as a function of their concentration, following our recent study of the interlayer structure of RhB–montmorillonite [19]. Molecular mechanics and classical molecular dynamics in the *Cerius²/Materials Studio* modeling environment [20] were combined with X-ray powder diffraction to investigate the interlayer and surface structure of RhB–montmorillonite. The fluorescence spectra were measured for three intercalated RhB–montmorillonite samples with different guest concentration and different structure. The changes in fluorescence spectra in dependence on the guest concentration are discussed, taking into account the surface and interlayer structure of RhB–montmorillonite. This paper is a continuation of our recent work [19] dealing with the interlayer structure of RhB–montmorillonite with various guest concentrations.

2. Sample preparation and characterization

The montmorillonite samples fully intercalated with rhodamine B were prepared using SWy (montmorillonite, Crook County, Wyoming) and rhodamine B (Fluka Standard Chemika). The composition of montmorillonite layer according to the chemical analysis was $(\text{Al}_{1.53}\text{Mg}_{0.23}\text{Fe}^{3+}_{0.25})(\text{Si}_{3.89}\text{Al}_{0.10}\text{Ti}_{0.01})\text{O}_{10}(\text{OH})_2$. A sodium form of SWy was prepared from an SWy fraction with grain size less than 5 μm by repeated ion exchange with a 1 mol dm⁻³ NaCl solution. After each step the sample was centrifuged and a new fresh portion of NaCl solution was added. Na-form of SWy was then washed out with deionized water and air-dried. The specific surface area of this sample is 136 m² g⁻¹ and

cation exchange capacity (CEC) is 0.89 meq g⁻¹. The montmorillonite samples fully intercalated with rhodamine B cations (RhB^+) were prepared by similar technique, i.e., by repeated intercalation. For the preparation of fully intercalated samples, rhodamine B solutions of concentration 1.06×10^{-4} (sample 1), 1.10×10^{-3} (sample 2), and 4.30×10^{-3} (sample 3), were used (see Table 1). The intercalation was repeated several times until the Na-form of SWy was fully intercalated. After the last intercalation, RhB–montmorillonite samples were washed out with deionized water and air-dried. In each step the amount of intercalated dyes was determined from the difference between the total rhodamine B concentration before and after intercalation. In order to determine the total rhodamine B concentration in the intercalation solution, the solutions were diluted to an approximate concentration of 10^{-5} mol dm⁻³ so that only monomer forms of rhodamine B were present. Then the total concentrations of rhodamine B solutions were determined by photometric methods at a wavelength of 552 nm. The correctness of the calculated total amount of intercalated rhodamine B (Table 1) was also checked through the content of C, H, N, and O belonging to rhodamine B cations present in intercalated SWy. The content of C, H, N, and O was determined by elemental analysis. In fully intercalated RhB–montmorillonite samples 1, 2, and 3 the percentages of ion-exchanged RhB were 80%, 89%, and 100%, respectively (calculated as percentages from the CEC). The sample characteristics are summarized in the Table 1.

The powder diffraction data for the RhB–montmorillonite samples were collected in the 2θ range 1° – 10° . The INEL X-ray powder diffractometer with the PSD 120 position-sensitive detector was used and the measurements were carried out under the following conditions: reflection mode, rotating sample holder (capillary), and $\text{CuK}\alpha_1$ radiation. The mixture of silicon and Ag-behenate was used as a calibration standard for PSD. Fig. 1 shows a comparison of the X-ray diffraction patterns for sample 1 and 3 (the diffraction profile of sample 2 was just between those for 1 and 3 and was omitted for clarity). The results of the powder diffraction analysis are summarized in Table 1 illustrating the effect of the RhB^+ concentration on the basal spacing d_{001} . As one can see from Table 1 and Fig. 1, the lower concentration of RhB in the intercalation solution leads to the two broad partially overlapping diffraction maxima corresponding to basal spacings of ~ 20 – 23 Å and ~ 18 – 19 Å. This result suggests the existence of two phases in the intercalated structure with

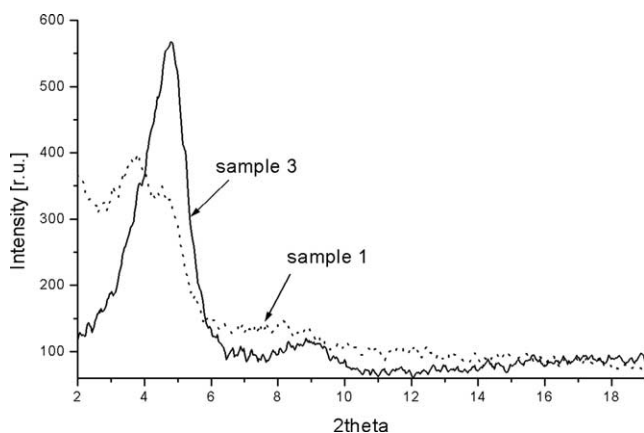


Fig. 1. Diffraction pattern of sample 1 (dotted line) with two overlapping maxima for $d_{001} \sim 22.90$ and 18.70 Å corresponding to two phases with different interlayer arrangements of RhB^+ cations. The diffraction pattern of sample 3 (solid line) exhibits sharper maxima for the first and second orders of basal reflection, $d_{001} \sim 18.40$ Å, indicating a homogeneous monophase composition with a bilayer arrangement of flat-lying RhB^+ cations.

two basal spacings: phase I (basal spacing ~ 18 – 19 Å) and phase II (basal spacing ~ 20 – 23 Å).

For, sample 3, with the highest RhB^+ content, the diffraction pattern exhibits only one relatively sharp 001 peak with the corresponding second-order 002 reflection, indicating the monophase composition (see solid line in Fig. 1). The results of chemical and diffraction analysis showed two important facts:

- The structure and phase composition of the intercalate depends on the guest concentration in the intercalation solution.
- The fully intercalated RhB -montmorillonite need not be fully ion-exchanged. Disordered monomers adsorbed at the edges of clay particles may create a steric barrier to further intercalation, and consequently the repeated intercalation does not lead to fully ion-exchanged samples.

3. Fluorescence of RhB -montmorillonite

The samples were placed in quartz cuvettes for fluorescence measurement. The fluorescence was excited using a cw He–Ne laser at 543 nm. The laser beam (power of about 1 mW) was focused by a 10-cm lens onto the front side of the sample; the fluorescent light was collected under about a 45° geometry and focused on the entrance slit of the grating spectrograph (Multispec, Oriel) with a diode array. The spectral resolution of the apparatus was about 0.5 nm. Measurements were done at room temperature.

The fluorescent spectra for samples 1–3 are in Fig. 2, where one can see that the increasing amount of RhB^+ content in the montmorillonite leads to a shift of the fluorescence band toward higher wavelengths and to a significant

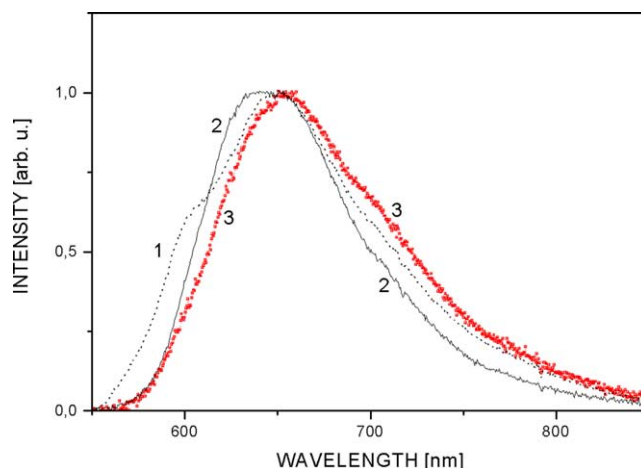


Fig. 2. Fluorescence spectra for sample 1 (dotted line), sample 2 (solid line), and sample 3 (little squares).

Table 2

Results of the fluorescence measurements for samples 1–3: a_{RhB} is the amount of RhB absorbed in montmorillonite, λ_{max} is the band maximum, λ_c is the wavelength corresponding to the peak centroid, and HW is the halfwidth of the fluorescence band

Sample No.	a_{RhB} [mmol g ⁻¹]	λ_{max} [nm]	λ_c [nm]	HW [nm]
1	0.706	650	653	120
2	0.796	644	653	95
3	0.900	655	667	109

change in band profile. The changes of band profile result in the irregular shift of the band maximum λ_m with increasing RhB^+ concentration in montmorillonite. Anyway, the centroid λ_c of the fluorescent bands 1–3 moves toward higher wavelength with increasing RhB^+ content in montmorillonite (see Table 2, where the centroid of band λ_c is the wavelength corresponding to the centroid of the fluorescent band, which is defined as the center of the band halfwidth).

Similar behavior of the fluorescent band was observed for Rh590 in saponite [13], Rh3B and Rh6G in hectorite [12,16], and RhB incorporated into silica gel glasses [11] and RhB adsorbed on quartz surface [14,17]. However, according to our previous results of interlayer structure analysis [19], the RhB -montmorillonite with the high guest concentration exists in monophase composition with basal spacing ~ 18 Å, where the interlayer structure prefers bilayer flat-lying RhB^+ in the H-dimeric arrangement. According to the theory of exciton splitting, the sandwich-type H-dimers are nonfluorescent. The strong fluorescence observed in sample 3, with the highest RhB^+ content and with basal spacing 18.4 Å, stimulated molecular modeling in order to investigate the surface structure contributing to the measured intensity.

The changes in fluorescence band profile with increasing RhB^+ concentration reflect the changes in relative proportions of monomers, dimers, and higher aggregates adsorbed on the external surface and intercalated into the interlayer space. Changes in the interlayer structure can be observed in

the X-ray diffraction pattern. To investigate the surface structure and to correlate the structure and fluorescence changes, we used molecular mechanics and molecular dynamics simulations.

4. Strategy of modeling

4.1. Modeling of interlayer structure

The initial model of the montmorillonite layer was built in *Cerius*² (*Crystal builder* module) using structure data published by Tsipursky and Drits [21]: space group *C2/m*. The unit cell parameters according to Méring and Oberlin [22] have been used to define the planar unit cell dimensions: $a = 5.208 \text{ \AA}$ and $b = 9.020 \text{ \AA}$. The composition of the montmorillonite layer, according to the chemical analysis, was $(\text{Al}_{3.06}\text{Mg}_{0.46}\text{Fe}_{0.50}^{3+})(\text{Si}_{7.78}\text{Al}_{0.20}\text{Ti}_{0.02})\text{O}_{20}(\text{OH})_4$. To create a supercell of reasonable size for calculations, the structural formula was slightly modified. Consequently the supercell $3a \times 2b \times 1c$ with layer composition $(\text{Al}_{18}\text{Mg}_3\text{Fe}_3^{3+})(\text{Si}_{47}\text{Al}_1)\text{O}_{120}(\text{OH})_{24}$ was built with the total negative layer charge -4 . The c values in the initial model were set up according to the basal spacings obtained from X-ray powder diffraction for samples prepared under different conditions, allowing the replacement of the Na^+ cations by rhodamine B^+ cations in the interlayer space.

The Ewald summation method was used to calculate the Coulomb energy in a crystal structure [23]. The Ewald sum constant was $0.5 \text{ \AA}^{-1}$. The minimum charge taken into the Ewald sum was $0.00001e$. All atom pairs with separations less than $10 \text{ \AA}$ were included in the real-space part of the Ewald sum and all reciprocal-lattice vectors with lengths less than $0.5 \text{ \AA}^{-1}$ were included in the reciprocal part of the Ewald summation. Atomic charges in the silicate layer were calculated in *Cerius*² (Qeq method [24]); atomic charges on RhB^+ were calculated using Gaussian 98 [25]. For the van der Waals energy (VdW) we used a Lennard–Jones functional form, with the arithmetical radius combination rule. A nonbond cutoff distance for the VdW interactions was $7.0 \text{ \AA}$.

Molecular mechanics calculations and classical dynamic simulations have been performed in the *Cerius*² modeling environment. The universal force field [26] has been used to describe the potential energy of the initial models. After the first energy minimization in the *Minimizer* module in *Cerius*², the molecular dynamic simulations have been started. Quench dynamics has been used in an NVT ensemble (constant number of atoms, volume, and temperature) at $T = 300 \text{ K}$. In quench dynamics, periods of dynamic simulations are followed by a quench period, in which the model is minimized (100 steps of dynamics between quenches and 500 steps of minimization in quenches). The dynamics time step was set up at 0.001 ps . The temperature was kept constant using a Berendsen thermostat [27]. The silicate layers were kept frozen (fixed) during dynamics simulation. The

total length of the dynamics trajectory was 200 ps . The initial models for the final energy minimization were extracted from the equilibrium part of the dynamics trajectory.

As the intercalation of RhB^+ into montmorillonite is based on the ion exchange reaction, the host–guest interaction is of a nonbonded nature. This is an important assumption for the modeling strategy. Comparison of the IR spectra for the host structure, Na–montmorillonite, and the intercalate showed that the main bands corresponding to the silicate layers remain preserved in the spectrum of the intercalate and consequently the silicate layers can be treated as rigid bodies during energy minimization. Comparing the IR spectrum of the guest compound rhodamine B chloride with the spectrum of the intercalate, one can see the smoothing and broadening of the rhodamine B^+ vibration bands in the intercalated structure. These changes are especially pronounced for bands corresponding to the carboxyl group, skeletal vibrations of aromatic rings, and bending of the ring C–H bonds. (For more details see [19].) Consequently, the coordinates of all atoms in the RhB^+ cations were variable during energy minimization, which was performed under the following conditions:

- fixed supercell parameters a , b , γ and rigid silicate layers;
- variable supercell parameters c , α , β , bonding geometry, and position of RhB^+ cations.

Series of initial models was created to describe the interlayer structure of RhB –montmorillonite. The results of modeling were described in details in our previous paper [19]. To describe the interlayer structure of the present samples 1–3 (see Table 1) we have chosen the following models:

1. Model *Int-2Na2RhB-18* (Fig. 3), which has to describe phase I ($d \sim 18\text{--}19 \text{ \AA}$) in samples 1 and 2 with the lowest amount of RhB absorbed in montmorillonite, $a_{\text{RhB}} = 0.706 \text{ mmol g}^{-1}$. Sample 1 was prepared using the intercalation solution with the lowest concentration of RhB , $c_{\text{RhB}} = 1.06 \times 10^{-4} \text{ mol dm}^{-3}$, and with the highest fraction of monomers in the intercalation solution, $w_{\text{mono}} = 0.891$. According to the chemical analysis this sample was not fully exchanged; consequently the supercell $3a \times 2b \times 1c$ in this model contains two Na^+ and two RhB^+ cations compensating for the layer charge -4 . The xanthene planes of RhB^+ monomers in this starting model were parallel to the silicate layers to set up the initial basal spacing $18 \text{ \AA}$.
2. Model *Int-1Na3RhB-23* (Fig. 4), describing the phase II ($d \sim 23 \text{ \AA}$) in samples 1 and 2. These samples are not fully exchanged; they differ slightly in the RhB^+ content, but they differ significantly in the fraction of monomers in the intercalation solution (see Table 1). In the model *Int-1Na3RhB-23* the supercell $3a \times 2b \times 1c$ contains one Na^+ and three RhB^+ cations. In this model

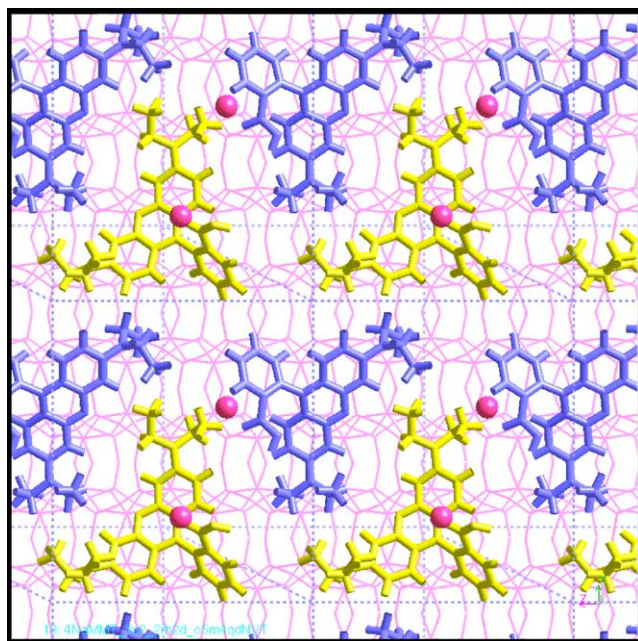


Fig. 3. Top view of the calculated model *Int-2Na2RhB-18* of the interlayer structure of sample 1 (not fully exchanged, basal spacing 18.1 Å) with two Na^+ and two RhB^+ cations per $3a \times 2b \times 1c$ supercell with flat-lying RhB^+ cations in bilayer. (Lower RhB^+ layer—dark, upper RhB^+ layer—light, Na^+ —small balls.)

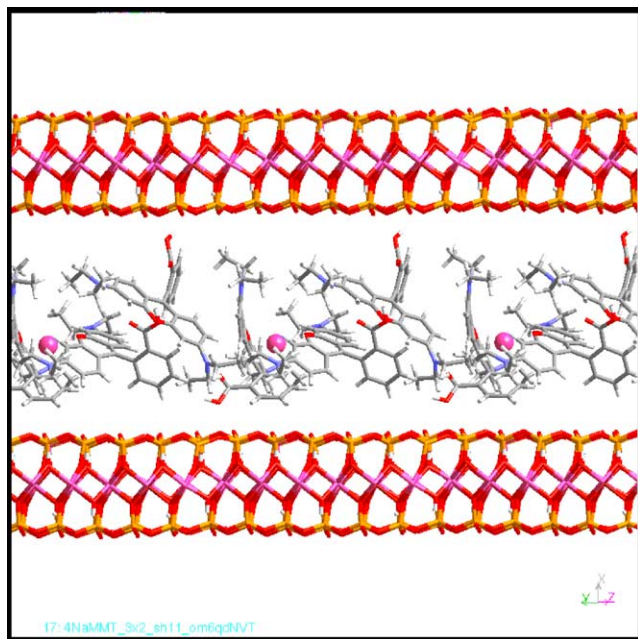


Fig. 4. Calculated model *Int-1Na3RhB-23* of the interlayer structure of samples 1 and 2 (not fully exchanged, basal spacing 22.3 Å) with one Na^+ and three RhB^+ cations per $3a \times 2b \times 1c$ supercell with tilted RhB^+ cations (Na^+ —small balls.)

xanthene planes were tilted to the silicate layers to set up the basal spacing 23 Å.

3. Model *Int-4RhBJDIM-23* (Fig. 5) for the phase II ($d \sim 23$ Å) in samples 1 and 2, where the supercell $3a \times 2b \times 1c$ with basal spacing 23 Å contains four

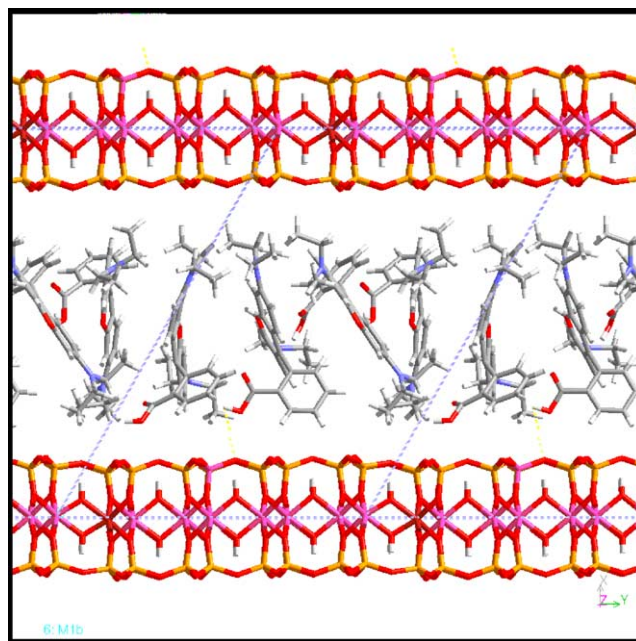


Fig. 5. Calculated model *Int-4RhBJDIM-23* of the interlayer structure for the fully exchanged sample, with four RhB^+ cations per $3a \times 2b \times 1c$ supercell. Tilted RhB^+ cations in J-dimeric arrangement led to the average basal spacing 23 Å.

RhB^+ cations in a J-dimeric arrangement with xanthene planes tilted to the silicate layer (i.e., fully exchanged phase).

4. Model *Int-4RhBHDIM-18* (Fig. 6) for sample 3 ($d \sim 18$ Å). This sample was prepared using the intercalation solution with the highest concentration of RhB, $c_{\text{RhB}} = 4.30 \times 10^{-3} \text{ mol dm}^{-3}$, with a very low fraction of monomers, $w_{\text{mono}} = 0.058$. The RhB content absorbed in montmorillonite, $a_{\text{RhB}} = 0.900 \text{ mmol g}^{-1}$, indicates that sample 3 was fully exchanged. That means that four RhB^+ cations in H-dimeric arrangement were placed into the $3a \times 2b \times 1c$ supercell, compensating for the layer charge -4 , with the initial basal spacing 18 Å and with xanthene planes parallel to silicate layers.
5. Model *Int-4RhBJDIM-18* (Fig. 7) for the fully exchanged sample 3 ($d \sim 18$ Å) with bilayer arrangement of J-dimers.

4.2. Modeling of surface structure

A initial model of the surface structure was built using the *Surface builder* module in *Cerius*². A two-dimensional supercell, $6a \times 2b$, was built, consisting of one silicate layer with one adjacent surface guest layer and one adjacent Na^+ layer on the opposite side. The structure formula of the montmorillonite layer in the $6a \times 2b$ supercell was $(\text{Al}_{36}\text{Mg}_6\text{Fe}_6^{3+})(\text{Si}_{94}\text{Al}_2)\text{O}_{240}(\text{OH})_{48}$, carrying the layer charge -8 . For modeling of fully exchanged montmorillonite (corresponding to sample 3), the surface guest layer contained four RhB^+ cations, compensating for the layer

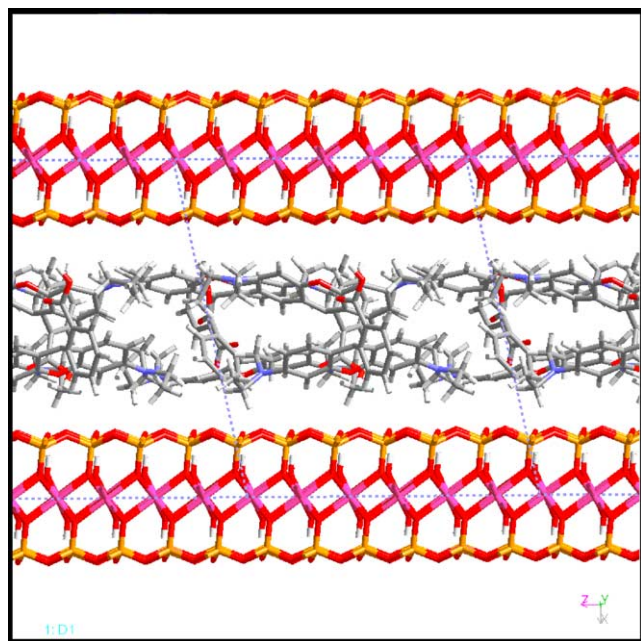


Fig. 6. Calculated model *Int-4RhBHDIM-18* of the interlayer structure for the fully exchanged sample, with four RhB^+ cations per $3a \times 2b \times 1c$ supercell. H-dimeric arrangement of RhB^+ cations led to the average basal spacing 18.1 Å. High value of the total sublimation energy confirmed the result of X-ray diffraction, where for the fully exchanged sample the observed basal spacing was 18.4 Å.

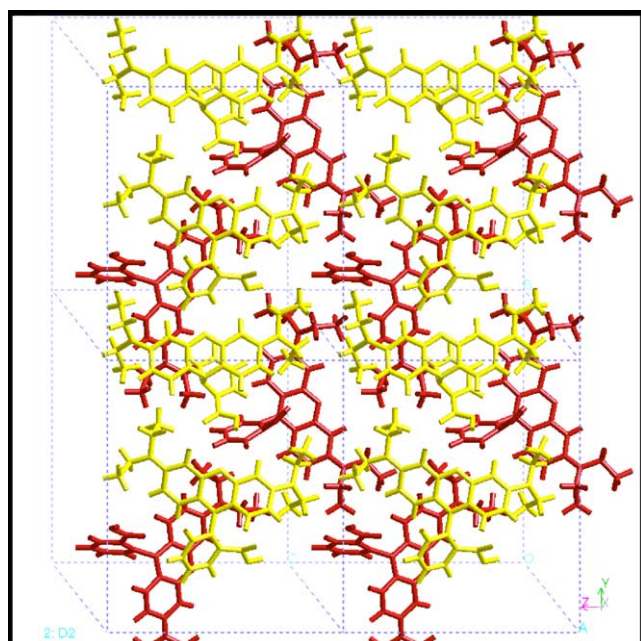


Fig. 7. Top view of the calculated model *Int-4RhBJDIM-18* of the interlayer structure for the fully exchanged sample, with four RhB^+ cations per $3a \times 2b \times 1c$ supercell. Bilayer arrangement of RhB^+ cations (out of plane J-dimers) led to the average basal spacing 18.1 Å. Relatively high value of the total sublimation energy and calculated basal spacing close to the observed value show that this model could also be a good candidate for the description of real structures. (Lower RhB^+ layer—dark, upper RhB^+ layer—light, silicate layer hidden for clarity.)

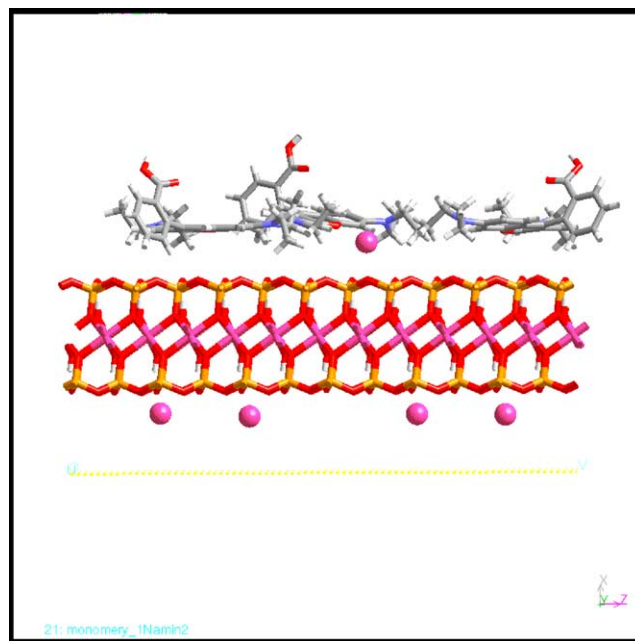


Fig. 8. Calculated model *Ext-1Na3RhBmono* describing partially exchanged montmorillonite surface with one Na^+ and three flat-lying RhB^+ cations on the upper side of the silicate layer in the $6a \times 2b$ surface supercell.

charge on the upper side of the $6a \times 2b$ supercell. In the case of partially exchanged montmorillonite (samples 1 and 2), three RhB^+ and one Na^+ cation were placed on the upper side of the $6a \times 2b$ supercell. An additional four Na^+ cations were placed in the bottom of the $6a \times 2b$ supercell under the silicate layer to compensate for the total silicate layer charge and the effect of the bulk structure (see Figs. 8–11).

The variety of monomeric and dimeric arrangements of RhB^+ cations on the silicate layer surface was tested using a combination of energy minimization and dynamics simulations. For the description of the real samples 1–3 we have chosen the following models:

1. Model *Ext-1Na3RhBmono* (Fig. 8) to describe the partially exchanged montmorillonite surface prepared using the intercalation solution with low RhB^+ concentration and with prevailing monomers. In this model one Na^+ and three flat-lying RhB^+ cations reside on the upper side of the silicate layer in the two-dimensional $6a \times 2b$ supercell.
2. Model *Ext-4RhBinplane* (Fig. 9) to describe the fully exchanged montmorillonite surface (sample 3) with four RhB^+ cations per $6a \times 2b$ supercell and with xanthene planes parallel with the silicate layer.
3. Model *Ext-4RhBHDIM* (Fig. 10) to describe the fully exchanged montmorillonite surface (sample 3) with two RhB^+ H-dimers per $6a \times 2b$ supercell and with xanthene planes parallel with the silicate layer.
4. Model *Ext-4RhBJDIM* (Fig. 11) to describe the fully exchanged montmorillonite surface with two RhB^+ J-dimers per $6a \times 2b$ supercell (sample 3).

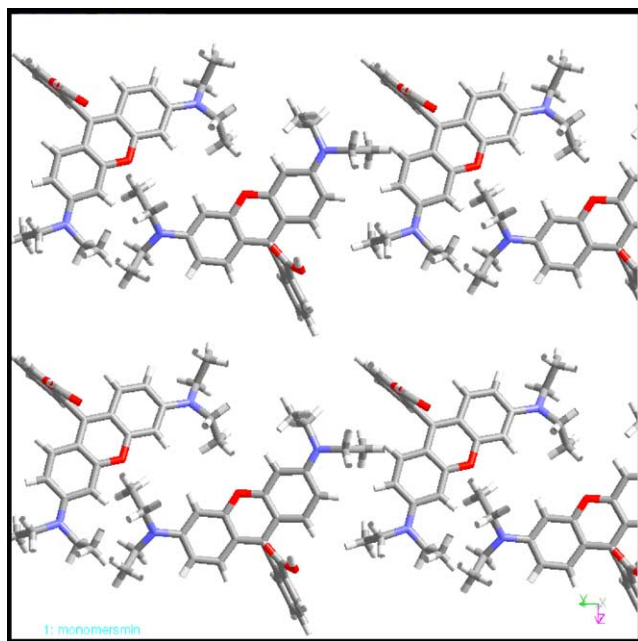


Fig. 9. Top view of the surface structure in calculated model *Ext-4RhBinplane* describing the fully exchanged montmorillonite surface with flat-lying RhB^+ cations in monolayer. (Four RhB^+ cations per $6a \times 2b$ surface supercell; silicate layer hidden for clarity.) The low value of the sublimation energy for this model shows that in the case of fully exchanged samples the surface structure prefers xanthene planes tilted to the silicate layer.

The strategy of modeling in the case of surface structure was the same as for the bulk structure, i.e., based on the combination of molecular mechanics and molecular dynamics. The effect of water was investigated by insertion of 42 water molecules into the surface structure in one $6a \times 2b$ supercell.

5. Results of modeling

5.1. Interlayer structure

Results of modeling are summarized in Table 3. The sublimation energy used for characterization of the various structure models was calculated as the nonbond intermolecular interaction energy (i.e., van der Waals and electrostatic) for guest–guest and host–guest interactions, related to one supercell (intramolecular interactions not included). Modeling revealed the interlayer structure of two phases in not fully exchanged samples 1 and 2. The phase I in sample 1 with $d \sim 18\text{--}19 \text{ \AA}$ is represented by the model *Int-2Na2RhB-18* (see Table 3 and Fig. 3). In this model the interlayer structure contains two Na^+ cations and two RhB^+ monomers per one $3a \times 2b \times 1c$ supercell. RhB^+ monomers in the bilayer arrangement have their xanthene planes nearly parallel or slightly tilted to the silicate layers (see Fig. 3). In this model the calculated basal spacing, $18.1 \text{ \AA}$, agrees with the experimental values, $18\text{--}19 \text{ \AA}$.

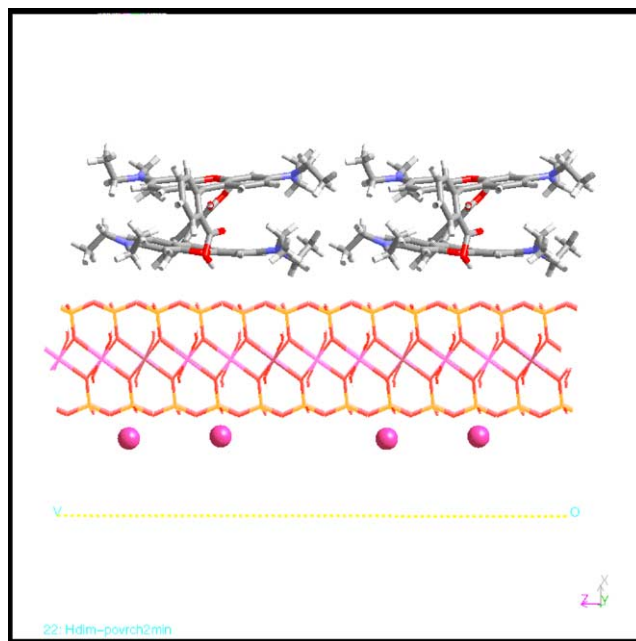


Fig. 10. Calculated model *Ext-4RhBHDIM* describing the fully exchanged montmorillonite surface with two H-dimers per $6a \times 2b$ surface supercell and with xanthene planes parallel with the silicate layer. The low value of the sublimation energy excludes this model from the description of a real surface structure.

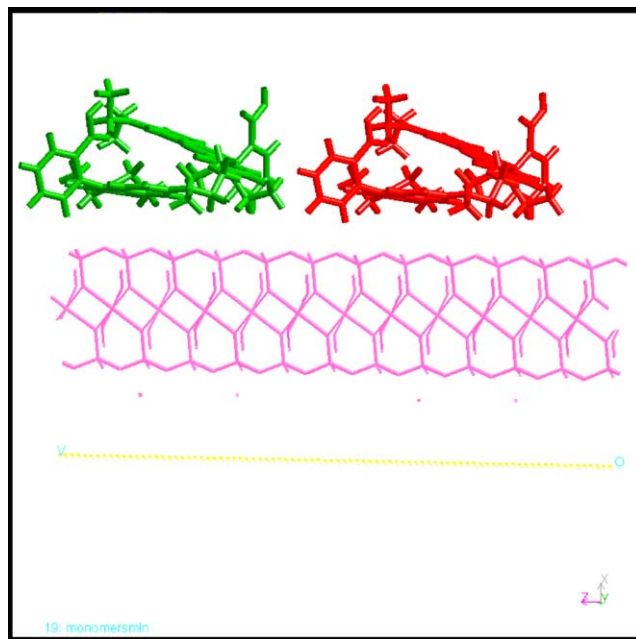


Fig. 11. Calculated model *Ext-4RhBJDIM* describing the fully exchanged montmorillonite surface with two J-dimers per $6a \times 2b$ surface supercell. This model was found to be the most probable one for the real surface structure.

Phase II in samples 1 and 2 with $d \sim 20\text{--}23 \text{ \AA}$ can be described with the model *Int-1Na3RhB-23* (see Fig. 4). In this model the interlayer structure contains one Na^+ and three RhB^+ cations in one $3a \times 2b \times 1c$ supercell. A mixture of monomers and J-dimers in the interlayer space (xanthene

Table 3

Results of modeling for the interlayer structure: calculated basal spacing d_{calc} and sublimation energy E_S per $3a \times 2b \times 1c$ supercell

Model	d_{calc} [Å]	E_S [kcal/mol]	Arrangement of RhB^+ in the interlayer
<i>Int-2Na2RhB-18</i>	18.1	739	Monomers in bilayer, xanthenes parallel or slightly tilted to the silicate layer (Fig. 3)
<i>Int-1Na3RhB-23</i>	22.3	713	Monomers and J-dimers, xanthenes strongly tilted to the silicate layer (Fig. 4)
<i>Int-4RhBJDIM-23</i>	23.0	710	J-dimers, xanthenes strongly tilted to the silicate layer (Fig. 5)
<i>Int-4RhBHDIM-18</i>	18.1	876	H-dimers, xanthenes parallel to the silicate layer (Fig. 6)
<i>Int-4RhBJDIM-18</i>	18.1	842	Monomers and J-dimers in bilayer, xanthenes parallel to the silicate layer (Fig. 7)

Table 4

Results of modeling for the surface structure: the total sublimation energy E_S per $6a \times 2b$ surface supercell before and after insertion of 42 water molecules per one supercell

Model	E_S [kcal/mol] without water	Arrangement of RhB^+ on the surface	E_S [kcal/mol] with water
<i>Ext-1Na3RhBmono</i>	571	Monomers, xanthene planes parallel to the silicate layer (Fig. 8)	786
<i>Ext-4RhBinplane</i>	520	J-dimers with in-plane xanthenes (Fig. 9)	840
<i>Ext-4RhBHdim</i>	445	H-dimers with xanthene planes parallel to the silicate layer (Fig. 10)	758
<i>Ext-4RhBJdim</i>	577	J-dimers with xanthenes out of plane (Fig. 11)	771

planes strongly tilted to the silicate layer) leads to the calculated basal spacing 22.3 Å, which is in agreement with the measured value of 23 Å. Model *Int-4RhBJDIM-23* describes the fully exchanged RhB^+ –montmorillonite with four RhB^+ cations in the $3a \times 2b \times 1c$ supercell. Strongly tilted RhB^+ cations in the J-dimeric arrangement led to the calculated basal spacing 23 Å, which corresponds to the measured values for phase II. Anyway, this model has low sublimation energy, which means that the interlayer structure with $d \sim 23$ Å is not very stable and can occur only under specific conditions as an intermediate stage by partial intercalation with the low guest concentration in the intercalation solution. Broadening of the diffraction pattern and shift of peak maxima, observed in a series of these not fully exchanged samples is a result of the Hendricks–Teller effect [28], means that there is an irregular mixture of different basal spacings in the crystal structure.

Model *Int-4RhBHDIM-18* represents the fully exchanged RhB^+ –montmorillonite with four RhB^+ cations in the $3a \times 2b \times 1c$ supercell in H-dimeric arrangement with xanthene planes parallel with the silicate layer. In this model the calculated basal spacing, 18.1 Å, agrees with the experimental value, 18.4 Å, for the fully exchanged sample 3, prepared using highly concentrated intercalation solution with the highest fraction of dimers. The highest value of the sublimation energy for this model leads to the conclusion that the H-dimeric arrangement of RhB^+ cations is the most probable and most stable one in the fully exchanged sample. This result explains the fact that in sample 3, which was prepared using the intercalation solution with the highest guest concentration, only one phase with $d \sim 18.4$ Å has been observed in the diffraction pattern. This is in agreement with our previous result [19]. However, according to the theory of exciton splitting, the sandwich-type H-dimers are nonfluorescent, which means that this model of interlayer structure cannot explain the strong fluorescence observed in sample 3. Fluorescence measurement refers to a large contribu-

tion of surface structure to the fluorescence intensity and/or to another arrangement of RhB^+ cations with $d \sim 18$ Å. Such an arrangement could be represented by the model *Int-4RhBJDIM-18*, with the basal spacing $d \sim 18.1$ Å and with bilayer stacking of RhB^+ . In this model the xanthene planes are parallel with the silicate layers and the interlayer structure can be characterized as a bilayer arrangement of J-dimers (see Fig. 7). The sublimation energy for this model, 840 kcal/mol, differs by less than 5% from that for the H-dimeric bilayer, and hence this model *Int-4RhBJDIM-18* cannot be excluded as describing the real interlayer structure of sample 3. In addition, this J-dimeric arrangement of RhB^+ cations would explain the high fluorescent intensity observed for sample 3.

5.2. Surface structure

Results of surface structure modeling are summarized in Table 4 for four models: *Ext-1Na3RhBmono*, *Ext-4RhBinplane*, *Ext-4RhBHdim*, and *Ext-4RhBJdim*. Model *Ext-1Na3RhBmono* describes a partially exchanged RhB –montmorillonite surface with one Na^+ and three RhB^+ cations in a $6a \times 2b$ surface supercell. It is evident that in the case of a low guest concentration with prevailing monomeric form in the intercalation solution the RhB^+ cations have xanthene planes parallel with the silicate layer (see Fig. 8, model *Ext-1Na3RhBmono*). For the fully exchanged RhB –montmorillonite the surface structure with flat-lying RhB^+ cations is less favorable, as is evident from the value of sublimation energy E_S for the model *Ext-4RhBinplane* (see Fig. 9, Table 4). Insertion of 42 water molecules into the surface structure led to the tilting of xanthene planes and consequently to a change of the energy value E_S from 520 to 840 kcal/mol for the fully exchanged surface model *Ext-4RhBinplane*.

The sandwich-type H-dimers (xanthenes parallel to the silicate layer) represents the least-favorable surface structure

for the fully exchanged RhB–montmorillonite (see model *Ext-4RhBHdim* in Fig. 10). This model exhibits the lowest sublimation energy E_S even after the insertion of water. On the other hand, the most stable surface structure without water has been found in the model *Ext-4RhBJdim*, with out-of-plane J-dimers, shown in Fig. 11.

The effect of water on the surface structure is similar to that in the interlayer structure, as described in our recent work [19]. Water stabilizes the structure, enhancing the sublimation energy. In both cases (interlayer and surface structure), water molecules can be adjacent to the silicate layers and fill the empty space between the rhodamine cations. There are no preferential positions for the water molecules, neither in the interlayer, nor in the surface structure. The presence of water does not change the structure type for a given concentration of guests and a given method of sample preparation.

6. Discussion and conclusions

The present structural analysis of RhB–montmorillonite led to three main conclusions:

1. The surface and interlayer structure strongly depend on the method of preparation.
2. The surface and interlayer structure for a given sample are different.
3. The concentration dependence of the RhB⁺ arrangement is different for the surface and interlayer structure.

While for low loading the surface structure prefers a flat-lying RhB⁺ cations, the interlayer structure is more complex, containing the phase 23 Å with tilted xanthenes as well as the phase 18 Å with flat-lying RhB⁺ cations in the interlayer. Both phases have nearly the same sublimation energy, as one can see by comparing models *Int-1Na3RhB-23* and *Int-2Na2RhB-18*.

The most important difference between surface and interlayer structure occurs in the case of fully exchanged samples, i.e., between the models with four RhB⁺ cations per one $3a \times 2b \times 1c$ supercell in the interlayer space and four RhB⁺ cations per one $6a \times 2b$ surface supercell. In the interlayer space the most stable structure with the highest sublimation energy is the bilayer arrangement of RhB⁺ with xanthenes parallel with the silicate layers (models *Int-4RhBHDIM-18* and *Int-4RhBJDIM-18*; see Fig. 6 and 7). However, on the fully exchanged sample surface, the most stable structure is the J-dimeric arrangement with xanthene planes tilted to the silicate layer surface (model *Ext-4RhBJdim*, Fig. 11).

Modeling also showed that the phase 18 Å in the fully exchanged samples could be formed by two ways:

- with H-dimers (see model *Int-4RhBHDIM-18* in Fig. 6) and/or

- with J-dimers in bilayer arrangement, where xanthene planes are parallel to the silicate layers (see model *Int-4RhBHDIM-18* in Fig. 7).

From the relatively small difference in the sublimation energy between the two models one can conclude that both structures may be present in real samples. The insertion of 42 water molecules into $6a \times 2b$ surface supercell caused the tilting of flat-lying RhB⁺ cations in the models *Ext-4RhBinplane* and *Ext-4RhBHdim* with the consequent rearrangement of the energy values in Table 4.

Fluorescence measurements of samples 1–3 show that increasing loading of RhB⁺ leads to a red shift of the fluorescence band. This result is not surprising and is in agreement with previous similar studies carried out for Rh6G–hectorite [16], RhB–silica surface [11], and other dye–inorganic systems [14,15,17,29]. However, the fluorescence band shape exhibits more complicated behavior with increasing RhB⁺ concentration, going from sample 1 to sample 3. This is illustrated in Table 2, where one can see the concentration dependence of the wavelengths corresponding to the fluorescence band maximum ($\lambda_{\max}$) and to the band centroid (λ_c) and concentration dependence of the fluorescence band-width (HW).

The irregularity in the concentration dependence of these spectral characteristics is a result of joint effects of the surface and interlayer structure of RhB–montmorillonite, where the concentration dependence of RhB⁺ arrangement is different for external and internal cations. Sample 2 exhibits a relatively narrow fluorescence band and it seems to be more homogeneous as to spectroscopic properties than samples 1 and 3. This effect could be explained by structural homogeneity. Tilted RhB⁺ cations prevail in the surface structure (model *Ext-4RhBJdim*) as well as in the interlayer structure (model *Int-1Na3RhB-23*); this means that in sample 2 the surface and interlayer structure are nearly the same as to the anchoring of RhB⁺ cations to the silicate layer. On the other hand, in the case of sample 1 with low loading, the surface structure consists of flat-lying RhB⁺ cations (model *Ext-1Na3RhBmono*), but the interlayer structure contains flat-lying as well as tilted cations (models *Int-2Na2RhB-18* and *Int-1Na3RhB-23*). A similar situation occurs in sample 3, where the surface structure for the fully exchanged montmorillonite prefers the J-dimers with tilted xanthenes, while the interlayer structure has homogeneous one-phase composition with a bilayer arrangement of flat-lying RhB⁺ cations.

Acknowledgments

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**9.4 Composition, structure, and luminescence of montmorillonites
saturated with different aggregates of methylene blue – P4**

Composition, structure, and luminescence of montmorillonites saturated with different aggregates of methylene blue

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Abstract

The distribution of various aggregates (dimers, trimers, and tetramers) of methylene blue (MB) formed in aqueous solution at various concentrations of dye has been calculated using the equilibrium aggregation constants β_q . Two montmorillonite samples with different cation exchange capacities, surface areas, and interlayer distances d_{001} , Na-SWy, and Ca-Cheto, were saturated with methylene blue (MB) solutions with various ratios between monomers and higher aggregates of dye. The total amount of MB in the intercalated montmorillonite samples (MB-SWy and MB-Cheto) increases with increasing concentration of dye in water solutions, i.e., with increasing aggregates/monomers ratio of MB in water solution. In all intercalated montmorillonite samples with methylene blue except guest q th aggregate cations $[\text{MB}_q^{q+}]$ low contents of Na^+ (in MB-SWy) and Ca^{2+} (in MB-Cheto) cations were also determined. A very good positive correlation between the basal spacing d_{001} and the MB/montmorillonite molar ratio was revealed for saturated MB-montmorillonite samples. Structural analysis using a combination of diffraction data with molecular modeling revealed the differences in the interlayer arrangement of MB guests in MB-SWy and MB-Cheto intercalates. Also, fluorescence measurements showed the strong effect of the silicate layer charge on the spectroscopic behavior of MB guests intercalated in montmorillonite. Methylene blue exhibits a certain luminescence in MB-SWy samples with cation exchange capacity 0.80 meq g^{-1} and almost no luminescence in MB-Cheto samples with higher cation exchange capacity 1.50 meq g^{-1} .

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Keywords: Methylene blue; Aggregation; Montmorillonite; Intercalation; Molecular simulation

1. Introduction

Adsorption of cations of some dyes onto the surfaces of colloidal particles often results in changes of dye color. This metachromatic effect relates to the formation of molecular aggregates; i.e., the content of dye monomers decreases in favor of dimers and higher aggregates [1–3]. The first information about the metachromatic effect that accompanied adsorption of dye cations onto clays was published almost 40 years ago by Bergmann and O’Konski [4]. For very intensive characteristic adsorption bands of monomers and higher aggregates and for simple and quick processes of intercalation based on ion exchange, methylene blue (MB) is very often used for the study

of montmorillonite intercalation with cationic dyes [5], because it can be followed easily by vis spectroscopy [1,6,7].

In the visible part of the absorption spectra, four different absorption bands of methylene blue in clay suspensions were observed. The monomer of this dye absorbs at 650–675 nm, the dimer at 605 nm, and trimers, tetramers, and still higher aggregates at 570–590 nm [7,8]. Bujdák et al. [2] also mention absorption of H-aggregates (the face-to-face cations) of MB at wavelength 570 nm and Bujdák et al. [3] for high-order H-aggregates mention an absorption band at 525 nm. Moreover, protonated cations of methylene blue (MBH^{2+}) and/or J-aggregates (the head-to-tail cations) at about 770 nm have also been described [9].

Yariv and Lurie [10] (1971) affiliated the spectral changes at shorter wavelengths to the π interactions of dye electrons with the free electron pairs of oxygen from the inner surface

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of the clay. The position and shape of the absorption bands of dye aggregates noticeably depend on various structural parameters such as number of chromophore pairs and distance between neighboring interacting molecules [3]. Adsorption of dyes onto the clay surface is a quick process, often followed by slow changes between nonaggregated and aggregated forms of dye adsorbed onto the clay surface [9]. Optical behavior of dyes in clay suspensions is then related to the type and amount of dye forms (monomer and higher agglomerates) in the reaction environment.

After the adsorption of MB onto the solid surface of a clay mineral, the orientation of the molecular axis of the dye, which is characterized by different surface contact, may vary [11]. It is influenced not only by interactions between the guest (e.g., MB) and host (e.g., montmorillonite), but also by accessible interlayer space. Probably Hang and Brindley [12] were the first authors to study the orientation of MB in MB-montmorillonite complexes. Using X-ray diffraction data and the rectangular dimensions of the MB molecule with approximate dimensions $1.70 \times 0.76 \times 0.325$ nm, they suggested four possible orientations of MB in the interlayers of Na- and/or Ca-montmorillonites for various conditions. They are:

- For small amounts of adsorbed MB under vacuum, a 1.26-nm spacing was determined, which relates to the thickness of MB molecules (0.32 nm) lying flat in the interlayer of Ca-montmorillonite. The presence of Ca^{2+} ions in the interlayer is also assumed.
- For greater amounts of adsorbed MB under vacuum, about 1.48-nm spacing could relate to an ordering in which the molecules are partly overlapped and are tilted to the inner plane of the Ca-montmorillonite interlayer. The presence of Ca^{2+} ions in the interlayer is also assumed here.
- With greater adsorption of MB under wet conditions, a 1.58-nm spacing can be interpreted by the presence of a double layer of MB molecules (2×0.325 nm) lying flat together with water molecules coordinated octahedrally around the Ca^{2+} ions. The presence of Ca^{2+} ions in the interlayer decreases as the space between the double layers of flat-lying MB molecules decreases.
- For full saturation of Na-montmorillonite by MB, characterized by 1.71-nm spacing, Hang and Brindley [12] suggested one layer of MB molecules (1×0.76 nm) without the presence of Na^+ cations.

Recently the tilted orientation of MB^+ cations to the surface of layered silicates with different layer-charge densities was studied using polarized UV–vis transmission spectroscopy [3]. The results showed that MB adsorbed on the clay need not be of parallel orientation (see (a), (c), and (d) above), but rather it is tilted to the clay surface. The angle of the adsorbed dye to the silicate surface is considerably influenced by the charge density of the surface. Kaneko et al. [13], who studied H-agglomerates of oxazine 4 (Ox4), came to a similar conclusion concerning the orientation of dye cations adsorbed in the clay interlayer. Moreover, Kaneko et al. [13] revealed that the basal spacing of thermally treated Ox4-montmorillonite samples mostly de-

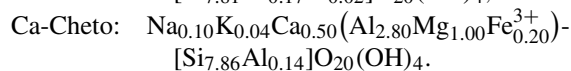
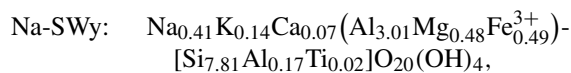
creases with decreased layer-charge densities of their surfaces. The formation of H-aggregates of the dye was observed only on surfaces with very high charge densities, and these aggregates also exhibited the most tilted orientation to the layered surface.

For the acquisition of a perspective on the ordering of molecules in interlayers, the method of molecular modeling is an invaluable tool [14–16]. The results obtained by this method show that intercalated molecules (guests) deposited in the interlayers of, e.g., smectites (host) are bonded to basal tetrahedral nets of clay minerals by weak interactions (van der Waals, Coulomb, and H-bonds). The objective of this paper was to investigate the influence of methylene blue aggregation in water solution on the composition, structure, and fluorescence of intercalated MB-montmorillonites.

2. Materials and methods

2.1. Samples and chemicals

Na-montmorillonite SWy-2 (Na-SWy) and Ca-montmorillonite SAz-2 (Ca-Cheto) samples were used as hosts for the intercalation with methylene blue (MB). Both samples come from the Source Clays Repository (USA). The first one is from Wyoming, the second one from Arizona. Fractions with grain size below $45 \mu\text{m}$ were prepared from the original samples by sedimentation in distilled water and then were air-dried. The bulk chemical analyses of these samples were performed and recalculated on the following crystallochemical formulae [17]:



The specific surface areas are 136 and $93 \text{ m}^2 \text{ g}^{-1}$ and the cation exchange capacities (CEC) are 0.80 and 1.50 meq g^{-1} for Na-SWy and Ca-Cheto, respectively. Methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$), produced by Fluka Standard Chemica, was dissolved in distilled water, recrystallized, and then dried under vacuum to a constant mass. The basic water solution of methylene blue of concentration $1 \times 10^{-2} \text{ mol dm}^{-3}$ was prepared by dissolution of recrystallized dye in distilled water; solutions of lower molar concentrations were prepared by dilution of the above basic solution with distilled water.

The saturated samples of Na-SWy and Ca-Cheto with MB were prepared by repeated saturation of both montmorillonites by methylene blue solutions. The samples of montmorillonite (0.5 g) and 100 cm^3 of MB solution were shaken at $20 \pm 2^\circ\text{C}$. The concentrations of dye solutions used were (II) 5.00×10^{-5} , (III) 2.00×10^{-4} , (IV) 5.00×10^{-4} , (V) 2.00×10^{-3} , and (VI) $5.00 \times 10^{-3} \text{ mol/L}$. For each sample, the saturation was repeated until the dye adsorption was measurable. Each intercalation step was performed for 3 h by shaking with related methylene blue solution. The separation of solid/liquid phases was performed by centrifugation (40 min

at 5000 rpm). The dye concentration in the fugate was determined by the method described below. The prepared fully saturated samples MB-SWy(II), MB-SWy(III), MB-SWy(IV), MB-SWy(V), MB-SWy(VI), MB-Cheto(II), and MB-Cheto(VI) were washed three times with distilled water and then dried in vacuum.

2.2. Methods and instruments

The chemical analyses of major elements of Na-SWy and Ca-Cheto samples were determined by X-ray fluorescence (SpectroLab); the determination of Na, K, Ca, and Mg was done by atomic absorption spectrometry (Unicam 969) after 1 h leaching of samples in 2 M HNO₃ at 90 °C.

The contents of C, H, N, and O in saturated MB-SWy and MB-Cheto samples were determined by elemental analysis using a CHNS-O (FLASH) analyzer. Loss on ignition (LOI) of dried (at 105–110 °C) MB-SWy and MB-Cheto samples was determined by ignition at 1000 °C.

The specific surface areas were determined by BET method with N₂ using Sorptomatic 1900 (TermoFinnigan).

The absorption spectra of MB in the water solution were recorded by UV–vis spectrophotometry (Lambda 25, Perkin–Elmer) using glass cells of thickness 0.10–5.0 cm. The most concentrated solution of methylene blue (1.0×10^{-2} mol dm⁻³) was measured in a cell with thickness 0.002 cm prepared with spacers.

The check analytical concentration of MB in water solutions was determined after supernatant dilution to a MB concentration below about 3×10^{-6} mol dm⁻³; absorbance was then measured at 660 nm in 5-cm cells.

The procedure for the calculation of adsorbed dye on montmorillonite samples is given in Section 3.3, together with determined and calculated data.

For the fluorescence measurement the powder samples were placed in quartz cells. The fluorescence was excited using a cw He–Cd laser at 325 nm. The laser beam (power about 1 mW) was focused by a 10-cm lens onto the front side of the sample. The fluorescent light was collected under about 45° geometry and focused on the entrance slit of the grating spectrograph (Multispec, Oriel) with a diode array. The spectral resolution of the apparatus was about 0.5 nm. Measurements were done at room temperature.

X-ray powder diffraction measurements were carried out to characterize the structure of intercalated samples, i.e., the basal spacing and degree of disorder in the interlayer structure. Using the INEL X-ray powder diffractometer with the PSD 120 position-sensitive detector, the measurements were carried out under the following conditions: the reflection mode, rotating sample holder (capillary), and CuK α_1 radiation. The mixture of silicon and Ag-behenate was used as a calibration standard for PSD.

Molecular modeling using an empirical force field (the Universal force field [18]) in the *Cerius*² modeling environment [19] was carried out to complete the structural characterization obtained from X-ray powder diffraction. The initial model of the montmorillonite layer was built using structural data

published by Tsipursky and Drits [20]: space group *C2/m*. The unit cell parameters according to Méring and Oberlin [21] have been used to define the planar unit cell dimensions: $a = 0.5208$ nm and $b = 0.9020$ nm. To create a supercell of reasonable size for calculations, the structural formula determined by chemical analysis had to be slightly modified. Consequently the supercell $3a \times 2b \times 1c$ with the layer composition (Al₁₈Mg₃Fe₃³⁺)(Si₄₇Al₁)O₁₂₀(OH)₂₄ was built for SWy-montmorillonite with total negative layer charge -4 and the supercell $3a \times 2b \times 1c$ with the layer composition (Al₁₇Mg₆Fe₁³⁺)(Si₄₇Al₁)O₁₂₀(OH)₂₄ was built for Cheto montmorillonite with total negative layer charge -7 . This means that modeling of fully exchanged montmorillonite requires four MB⁺ cations in the interlayer space of the $3a \times 2b \times 1c$ supercell for SWy and seven MB⁺ cations for Cheto montmorillonites.

Molecular mechanics calculations and classical dynamic simulations have been performed in the *Cerius*² modeling environment. The Universal force field [21] has been used to describe the potential energy of initial models. Charges were calculated by the charge equilibration method (Qeq) [22]. Molecular mechanics in the *Minimizer* module in *Cerius*² was combined with quench-type molecular dynamic simulations in the NVT ensemble at $T = 300$ K. The temperature was kept constant using a Berendsen thermostat [23]. The silicate layers were kept frozen (fixed) during dynamic simulation. The total length of the dynamics trajectory was 200 ps. The set of initial models for the final energy minimization were extracted from the equilibrium part of the dynamics trajectory.

3. Results and discussion

3.1. Aggregation of methylene blue in water solution

In contrast with, e.g., rhodamine B, which aggregates in water solutions, forming dimers, and whose isosbestic point is characteristic for this aggregation [16,24], methylene blue cations also form trimers, tetramers, and probably even higher aggregates. For higher dye aggregation, absence of an isosbestic point is typical in the visible part of the spectrum, and moreover, for increasing concentration of MB in aqueous solution, the wavelength of the absorption maximum of higher aggregates (about 600 nm) is continuously moving.

Absorption spectra of methylene blue at different concentrations in water solutions are given in Fig. 1. The first absorption maximum is at 660 nm and relates to the monomer of methylene blue, while the second maximum varies from about 605 nm (related to the dimer) to about 585 nm (which can be probably attributed to the prevailing tetramer or even higher aggregates of the dye) [25]. With increasing concentration of dye, a decrease of dye monomer (660 nm) in favor of higher aggregates (~ 605 – 585 nm) is observable, as well as a continual decrease of the maximum absorption wavelength from 605 to 585 nm.

The aggregation of the cations of methylene blue MB⁺ in water solution can be expressed by the following equation:



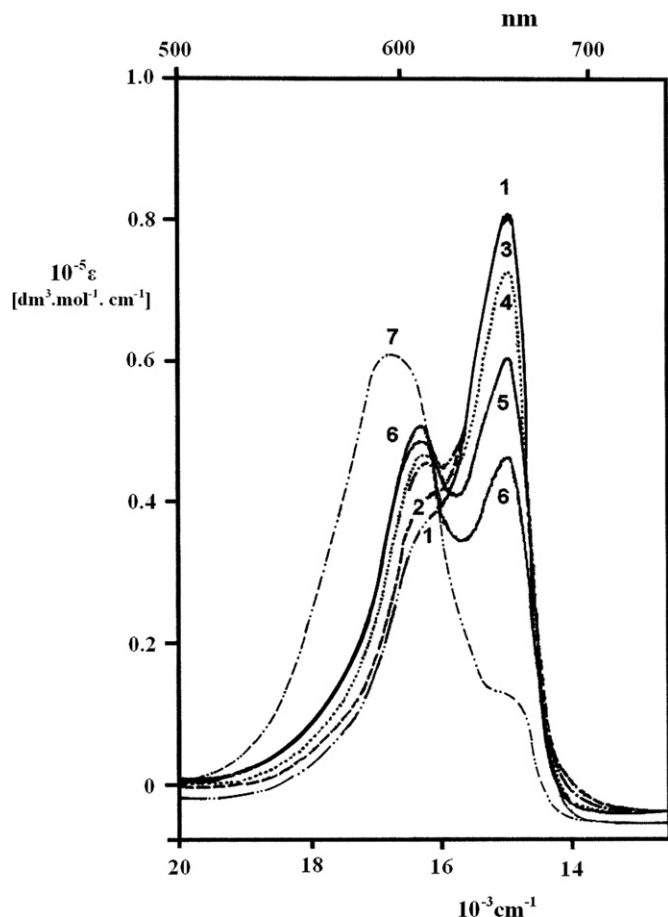


Fig. 1. Absorption spectra of methylene blue in aqueous solutions. ϵ , molar absorption coefficient; 1, 3.0×10^{-6} mol/L, thickness of cell 5.0 cm; 2, 7.5×10^{-6} mol/L, thickness of cell 2.0 cm; 3, 1.5×10^{-5} mol/L, thickness of cell 1.0 cm; 4, 3.0×10^{-5} mol/L, thickness of cell 0.5 cm; 5, 7.5×10^{-5} mol/L, thickness of cell 0.2 cm; 6, 1.5×10^{-4} mol/L, thickness of cell 0.1 cm; 7, 1.0×10^{-2} mol/L, thickness of cell 0.002 cm.

For simplicity it is assumed that the number of MB^+ cations (q) varies from 2 to 4; i.e., dimers, trimers, and tetramers are formed. According to Eq. (1), the formation of the q th polymer $[\text{MB}_q^{q+}]$ can be characterized by the equilibrium aggregation constant β_q ,

$$\beta_q = \frac{[\text{MB}_q^{q+}]}{[\text{MB}^+]^q}, \quad (2)$$

and/or by the stepped aggregation constant K_q of the reaction



which is defined by the formula:

$$K_q = \frac{[\text{MB}_q^{q+}]}{[\text{MB}_{q-1}^{(q-1)+}][\text{MB}^+]}, \quad (4)$$

where $\beta_2 = K_2$, $\beta_3 = K_2 K_3$, $\beta_4 = K_2 K_3 K_4$.

The analytical concentration of methylene blue (c_{MB}) equals the sum of nonaggregated and all aggregated equilibrium forms of methylene blue:

$$c_{\text{MB}} = \sum_{q=1}^4 q [\text{M}_q^{q+}]. \quad (5)$$

The aggregation constants for methylene blue in water solution have been calculated by many authors. For example, Ghosh and Mukerjee [25] and Klika [26] utilized data from visible spectrometric measurements and for calculation they used a two-parameter model IV suggested by Rossotti and Rossotti [27]. The calculated stepped aggregation constants of Ghosh and Mukerjee [25] and Klika [26] are: $K_2 = 2.1 \times 10^3$, $K_3 = 4.0 \times 10^3$, and $K_4 = 3.0 \times 10^3$ and $K_2 = 2.54 \times 10^3$, $K_3 = 1.35 \times 10^3$, and $K_4 = 2.06 \times 10^2$, respectively. Using these constants and the above equations, the percentages of various MB aggregate forms in relation to analytical concentration of methylene blue (c_{MB}) in aqueous solutions were calculated. The results are plotted in Fig. 2.

The results show that in diluted MB solutions (up to $c_{\text{MB}} \leq 2 \times 10^{-5}$ mol/L), monomers of MB prevail, forming mixtures only with dye dimers. The dye dimers appear at $c_{\text{MB}} \doteq 3 \times 10^{-6}$ mol/L and their percentages increase with increasing concentration of MB up to about $c_{\text{MB}} \doteq 3 \times 10^{-4}$ mol/L; at higher concentrations of MB percentages of dimers again decrease. Trimers appear at $c_{\text{MB}} \doteq 3 \times 10^{-5}$ mol/L and tetramers at about 7×10^{-5} mol/L; percentages of both polymers then increase and at about $c_{\text{MB}} \geq 1 \times 10^{-3}$ mol/L they prevail. At concentration $c_{\text{MB}} = 10^{-2}$ mol/L, content of monomers is less than 10%; tetramers, trimers, and dimers of MB absolutely prevail, notwithstanding the difference between the data (Figs. 2a and 2b).

3.2. Montmorillonites saturated with different aggregates of methylene blue

The Na-SWy and Ca-Cheto samples were fully saturated with methylene blue solutions at different concentrations; five samples of MB-SWy(II, III, IV, V, and VI) and two samples of MB-Cheto(II and VI) were prepared in order to study the influence of methylene blue aggregation on the composition, structure, and fluorescence of fully saturated MB-montmorillonites. In Table 1, the analytical concentration of MB (c_{MB}) and the percentages of individual methylene blue aggregates in their saturation solutions are stated. The percentages of dye polymers presented in Table 1 were calculated as arithmetic means from both calculated data [25,26]. Because every montmorillonite sample was repeatedly saturated with the dye solution at the same concentration, we can assume equilibrium between the analytical concentration of methylene blue (and its calculated agglomerates) and prepared fully saturated montmorillonites [16]. In the same Table 1, the values of basal spacing d_{001} of saturated MB-montmorillonites are given. The changes of basal spacing d_{001} for MB-SWy samples from 1.51 up to 1.58 nm and for MB-Cheto samples from 1.71 up to 1.86 nm relate to the different concentrations of saturated MB solutions (see Table 1). The results convincingly show that with increasing concentration of methylene blue in saturated water solution, i.e., with increasing ratio of higher agglomerates to the monomer of dye, the basal spacing d_{001} of saturated montmorillonites increases.

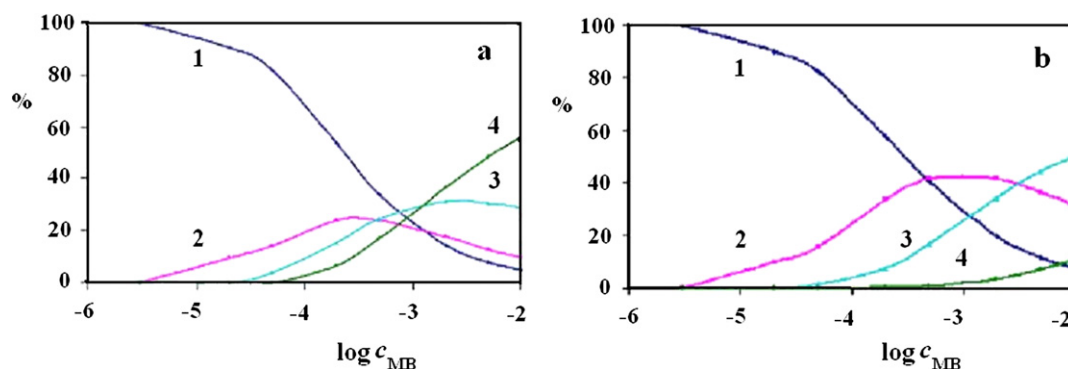


Fig. 2. The calculated percentages of monomer (1), dimer (2), trimer (3), and tetramer (4) aggregates of methylene blue in aqueous solutions of different analytical concentration c_{MB} (mol/L). Calculated according to data of (a) Ghosh and Mukerjee [25], (b) Klika [26].

Table 1

Mean calculated percentages of dye aggregates in methylene blue water solutions and X-ray diffraction pattern d_{001} of saturated MB-montmorillonite samples

Sample		c_{MB} (mol/L)	$10^2 q[\text{M}_q^{q+}]/c_{\text{MB}}$ (%)				$\bar{q}$	d_{001} (nm)
			Monomer	Dimer	Trimer	Tetramer		
MB-SWy	MB-SWy(II)	$5.00. \times 10^{-5}$	82	15	3	0	1.10	1.51
	MB-SWy(III)	2.00×10^{-4}	55	29	12	4	1.34	1.53
	MB-SWy(IV)	5.00×10^{-4}	37	33	21	9	1.59	1.54
	MB-SWy(V)	2.00×10^{-3}	18	30	32	20	2.05	1.55
	MB-SWy(VI)	5.00×10^{-3}	10	25	38	27	2.39	1.58
MB-Cheto	MB-Cheto(II)	5.00×10^{-5}	82	15	3	0	1.10	1.71
	MB-Cheto(VI)	5.00×10^{-3}	10	25	38	27	2.39	1.86

Note. c_{MB} is the analytical concentration of MB solution; $[M_q^{q+}]$ is the calculated concentration of the q th aggregate of MB in the related MB solution; $\bar{q}$ is a mean q th MB aggregate, defined as: $\bar{q} = \sum_1^q q[M_q^{q+}]/\sum_1^q [M_q^{q+}]$; d_{001} is the interlayer distance of MB-montmorillonites (calculated from broadened X-ray diffraction profiles using centre center of gravity position).

Table 2

Analyses of elemental composition of MB-SWy and MB-Cheto samples

Sample	(wt%)						
	C	H	N	S	O	$10^2 \times w_{C,H,N,O,S}$	LOI
MB-SWy(II)	11.81	1.65	2.30	1.75	2.66	20.17	21.10
MB-SWy(III)	11.79	1.59	2.25	1.72	2.66	20.01	20.93
MB-SWy(IV)	12.97	1.59	2.40	1.83	2.75	21.54	21.53
MB-SWy(V)	13.24	1.45	2.38	1.82	3.40	22.29	22.54
MB-SWy(VI)	14.46	2.07	2.71	2.07	2.72	24.03	23.72
MB-Cheto(II)	17.90	2.60	3.32	2.53	3.21	29.56	30.06
MB-Cheto(VI)	20.90	3.26	3.91	2.98	2.67	33.72	34.13

Note. $10^2 \times w_{C,H,N,O,S}$: sum of weight percentages of C, H, N, O, and S in MB-montmorillonite samples; L.O.I.: loss on ignition.

3.3. Elemental composition of saturated MB-montmorillonites

The elemental analyses (C, H, N, O, and S) of dried saturated samples of MB-SWy (Nos. II–VI) and MB-Cheto (Nos. II and VI) are given in Table 2. Elements C, N, and S are present only in the MB part of MB-montmorillonite, O only in the OH groups of montmorillonite, and H is present both in the MB and the montmorillonite parts of the MB-montmorillonite samples. During elemental analyses in air-containing atmosphere (at 1000 °C), the elements C, H, N, and S are burned, forming volatile oxides, and O present in OH groups of montmorillonite is removed in the form of water vapor. Loss on ignition (LOI) then approximately equals the sum of C, H, N, S, and O

($10^2 w_{C,H,N,O,S}$) determined in the MB-montmorillonite samples.

The hydroxyl groups of the montmorillonite part of MB-montmorillonite are decomposed and the nascent water is determined, together with the water formed from hydrogen present in the MB part $[C_{16}H_{18}N_3S]^+$ of MB-montmorillonite. The hydrogen related to the OH groups in montmorillonite (H_{MMT}) can be calculated using the formula: $H_{MMT} = \frac{2.016}{16.000}O$, where oxygen (O) is given in Table 2 and was removed from the MB-montmorillonite samples in the form of H_2O vapor. After subtraction of H_{MMT} from total hydrogen (H), given in Table 2, we obtain hydrogen in the MB part of MB-montmorillonite (H_{MB}). The weight fraction of MB (w_{MB}) in MB-montmorillonite is then the sum of analyzed C, N, and S and calculated H_{MB} content. The recalculated data on elemental composition of MB-montmorillonite samples are given in Table 3.

Using the weight fractions of methylene blue (w_{MB}) and montmorillonite (w_{MMT}) from Table 3 and the related molecular weights, the molar ratios x between methylene blue and the related negatively charged montmorillonite part of intercalated MB-MMT samples were calculated from the formula $x = n_{MB}/n_{MMT}$, where $n_{MB} = w_{MB}/MW(MB^+)$ and $n_{MMT} = (1 - w_{MB})/MW(MMT)$. The used molecular weights were, for the cation of MB^+ , $MW(MB^+) = 284.23 \text{ g mol}^{-1}$, for the negatively charged montmorillonite part of SWy, $MW(SWy) = 733.12 \text{ g mol}^{-1}$, and for the negatively charged montmorillonite part of Cheto, $MW(Cheto) = 725.08 \text{ g mol}^{-1}$. The molecular

Table 3

Recalculated percentages of C, H, N, S, and O on methylene blue (MB) and montmorillonite (MMT) parts of the intercalated MB-montmorillonite samples

Sample		(wt%)						
		C	H _{MB} ; H _{MMT}	N	S	O = O _{MMT}	10 ² × w _{MB} ; 10 ² × w _{MMT}	10 ² × w _{C, H, N, O, S}
MB-SWy(II)	MB	11.81	1.31	2.30	1.75	–	17.17	20.17
	SWy	–	0.34	–	–	2.66	3.00	
MB-SWy(III)	MB	11.79	1.25	2.25	1.72	–	17.01	20.01
	SWy	–	0.34	–	–	2.66	3.00	
MB-SWy(IV)	MB	12.97	1.24	2.40	1.83	–	18.44	21.54
	SWy	–	0.35	–	–	2.75	3.10	
MB-SWy(V)	MB	13.24	1.03	2.38	1.82	–	18.47	22.29
	SWy	–	0.42	–	–	3.40	3.82	
MB-SWy(VI)	MB	14.46	1.73	2.71	2.07	–	20.97	24.03
	SWy	–	0.34	–	–	2.72	3.06	
MB-Cheto(II)	MB	17.90	2.20	3.32	2.53	–	25.95	29.56
	Cheto	–	0.40	–	–	3.21	3.61	
MB-Cheto(VI)	MB	20.90	2.92	3.91	2.98	–	30.71	33.72
	Cheto	–	0.34	–	–	2.67	3.01	

Note. 10² × w_{MB}: sum of weight percentages of C, H, N, and S in methylene blue (MB) part of MB-montmorillonite samples; 10² × w_{MMT}: sum of weight percentages of H and O in montmorillonite (MMT) part of MB-montmorillonite samples; 10² × w_{C, H, N, O, S} = 10²(w_{MB} + w_{MMT}): sum of weight percentages of C, H, N, S, and O in MB-montmorillonite samples.

weights of negatively charged MW(SWy) and MW(Cheto) do not include the ion-exchangeable cations Na⁺, K⁺, and Ca²⁺ and they are calculated from the crystallochemical formula with the O₂₀(OH)₄ unit given above.

The molecular weights (MW) of MB-SWy and MB-Cheto with the symbolic formula (MB)_xMMT were calculated from the equation

$$\text{MW}(\text{MB-MMT}) = x\text{MW}(\text{MB}^+) + \text{MW}(\text{MMT}), \quad (6)$$

the intercalated amount of methylene blue (q_{MB}) in Na-SWy (meq MB/g Na-SWy) was calculated from the equation

$$q_{\text{MB}} = 10^3 \frac{w_{\text{MB}} \cdot \text{MW}(\text{MB-SWy})}{\text{MW}(\text{MB}^+) \text{MW}(\text{Na-SWy})}, \quad (7.1)$$

and the same parameter (q_{MB}) for Ca-Cheto (meq MB/g Ca-Cheto) was calculated from the equation

$$q_{\text{MB}} = 10^3 \frac{w_{\text{MB}} \cdot \text{MW}(\text{MB-Cheto})}{\text{MW}(\text{MB}^+) \text{MW}(\text{Ca-Cheto})}. \quad (7.2)$$

The molecular weights $\text{MW}(\text{Na-SWy}) = 751.69 \text{ g mol}^{-1}$ and $\text{MW}(\text{Ca-Cheto}) = 743.36 \text{ g mol}^{-1}$ were calculated from the crystallochemical formula given above. Recalculation similar to that for q_{MB} was also used for the sum of Na, K, and Ca (q_{Alk}). These cations remained not exchanged in the interlayer of the MB-montmorillonite samples and were determined after leaching of samples in HNO₃ solution. All calculated data are presented in Table 4.

In saturated MB-montmorillonite samples, except MB residual content of Na, K, and Ca was also determined after their leaching out by 2 M HNO₃ at 90 °C. From these data, q_{Alk} values were calculated. In the MB-montmorillonite samples saturated with dye solutions in which monomer prevailed, a higher content of alkali elements was present and vice versa. The presence of chlorine anions in the interlayer space of RhB-SWy was not detected (LOD 0.010 meq/g).

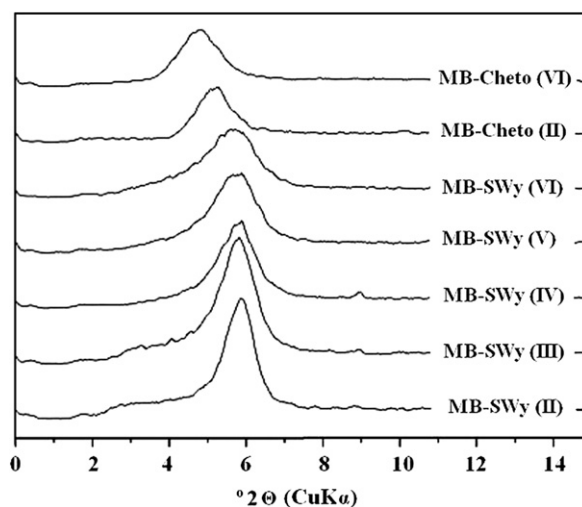


Fig. 3. X-ray diffraction patterns with 001 profiles for samples MB-SWy and MB-Cheto.

3.4. X-ray diffraction patterns and fluorescence of intercalated MB-montmorillonites

By comparing the X-ray diffraction line profiles for montmorillonite samples, a slight shift of peak maximum and increasing line broadening can be observed going from MB-SWy(II) to MB-SWy(VI) and/or from MB-Cheto(II) to MB-Cheto(VI). The interlayer distances (d_{001}) of MB-montmorillonite samples were given in Table 1 and the X-ray diffraction profiles of the d_{001} patterns are plotted in Fig. 3. In more concentrated intercalation solutions, the aggregation of the methylene blue is higher, so that higher methylene blue aggregates in the interlayer of saturated MB-montmorillonite samples can be also expected. The MB-SWy samples saturated by more concentrated methylene blue solutions with a high fraction of M_q^{q+} aggregates are of higher structural inhomogeneity,

Table 4
Intercalated amounts of methylene blue and interlayer elements in saturated MB-montmorillonite samples

Sample	w_{MB}^{a} (g g ⁻¹)	x^{b} (mol/mol)	MW(MB-MMT) ^c (g/mol)	q_{MB}^{d} (meq g ⁻¹)	$q_{\text{Alk}}^{\text{e}}$ (meq g ⁻¹)	$q_{\text{sum}}^{\text{f}}$ (meq g ⁻¹)
MB-SWy(II)	0.172	0.536	885.5	0.71	0.26	0.97
MB-SWy(III)	0.170	0.528	883.2	0.70	0.22	0.92
MB-SWy(IV)	0.184	0.581	898.3	0.77	0.13	0.90
MB-SWy(V)	0.185	0.585	899.5	0.78	0.19	0.97
MB-SWy(VI)	0.210	0.685	927.8	0.85	0.15	1.00
MB-Cheto(II)	0.260	0.896	979.8	1.21	0.32	1.53
MB-Cheto(VI)	0.307	1.124	1044.5	1.52	0.22	1.74

^a w_{MB} is the weight fraction of MB in MB-montmorillonite (g MB/g MB-montmorillonite; see Table 3).

^b $x = n_{\text{MB}}/n_{\text{MMT}}$ is the calculated molar ratio between MB and SWy and/or MB and Cheto (mol/mol).

^c MW(MB-MMT) is the molecular weight (g/mol) of the methylene blue intercalated montmorillonite with symbolic formula (MB)_xMMT.

^d q_{MB} is the intercalated amount of MB (meq MB/g Na-SWy or meq MB/g Ca-Cheto).

^e q_{Alk} is a the sum of Na, K, and Ca (meq Alk/g Na-SWy or meq Alk/g Ca-Cheto).

^f $q_{\text{sum}} = q_{\text{MB}} + q_{\text{Alk}}$.

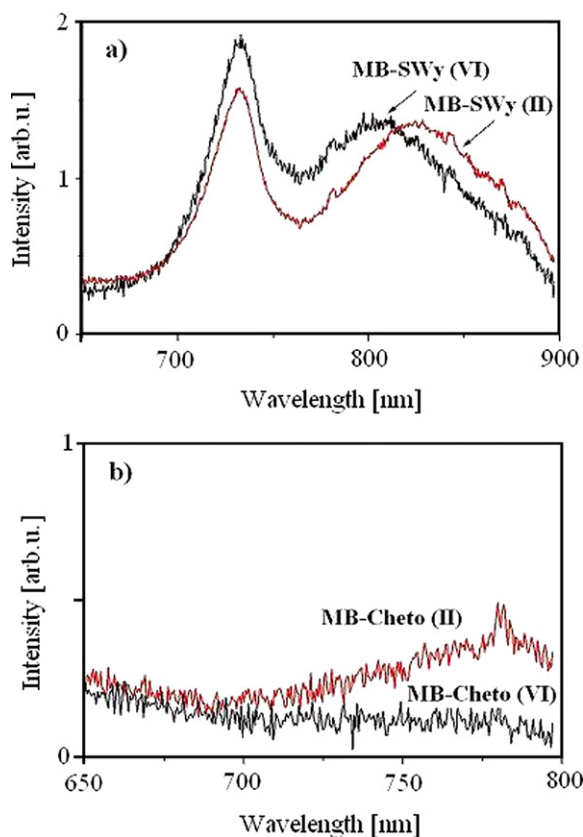


Fig. 4. Fluorescence bands of selected MB-SWy (a) and MB-Cheto (b) samples.

and therefore the diffraction line profiles exhibit broadening, observable especially for samples MB-SWy(IV, V, and/or VI). The broadening of the interlayer distance (d_{001}) is not seen between the samples MB-Cheto(II) and MB-Cheto(VI). This can probably be explained by a significant difference in basal spacing of MB-SWy and MB-Cheto samples arising from the different layer charge and consequently the different cation exchange capacity of both montmorillonites.

Fluorescence measurements of MB-SWy samples show similar band profiles covering a wide wavelength range for the samples SWy(II) and SWy(VI) (Fig. 4a). The difference between the two spectra can probably be attributed to different

concentrations of MB in the interlayer space and consequently also different concentrations of interlayer cations q_{Alk} (see Table 4). Anyway, the silicate layer charge, which plays the key role in the fluorescence properties of MB-silicate intercalates, is the same for MB-SWy(II) and MB-SWy(VI). In contradiction to the MB-SWy, the fluorescence intensity of the MB-Cheto(II) sample is very low and for the MB-Cheto(VI) sample (see Fig. 4b) even almost negligible. The higher interlayer charge of Cheto montmorillonite results in a higher concentration of methylene blue in the interlayer space. Fluorescence quenching due to the increasing dye concentration has been also reported by Endo et al. [28].

3.5. Structure of intercalated MB-montmorillonites

Molecular modeling was used to elucidate the interlayer structure of MB-montmorillonites. A series (more than 100) of initial models have been built for MB-SWy and MB-Cheto montmorillonites with various starting arrangements of guest molecules in the interlayer space. To fit all the real guest concentrations into the intercalated samples (see Table 1), we would need to build too large a supercell with variable size and charge and consequently with too large a demand of computational (CPU) time. Real samples in fact exhibit large structural and also compositional inhomogeneity (see the X-ray diffraction patterns with 001 profiles in Fig. 3). That means that calculated models can never completely describe real samples. A series of models for partially and fully exchanged montmorillonite have been built with various starting interlayer structures, simulating well-ordered dimers (MB_2^{2+}) with various orientations with respect to silicate layers, disordered monomers (MB^+), and disordered higher aggregates of (MB_q^{q+}) guests. Cavities in the interlayer intercalated structure were gradually filled with water to show the possible effect of water content on the basal spacing of intercalates.

Calculated models of partially exchanged SWy-montmorillonite with three cations of MB^+ and one cation of Na^+ per $3a \times 2b \times 1c$ supercell without water in the interlayer space exhibit basal spacing about 1.37 nm. Water content increases the basal spacing up to 1.46 nm for 12 water molecules in

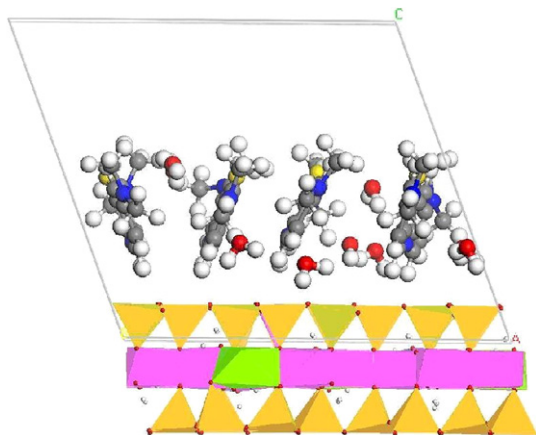


Fig. 5. Calculated structure of the fully exchanged MB-SWy montmorillonite with 8 water molecules per $3a \times 2b \times 1c$ supercell. (N, blue; S, yellow; O, red.) For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.

the $3a \times 2b \times 1c$ supercell with 3MB^+ and 1Na^+ . Calculated models of fully exchanged MB-SWy without water in the interlayer space (i.e., 4MB^+ per $3a \times 2b \times 1c$ supercell) exhibit the same crystal energy for the large range of basal spacing $d \sim 1.40\text{--}1.58$ nm for different arrangements of methylene blue cations in the interlayer space. The basal spacing strongly depends on the degree of MB^+ aggregation and the equal energy means equal probability of all the structural arrangements. The presence of water molecules in the interlayer space stabilizes the structure by increasing the total crystal energy and the non-bond energy and increases the basal spacing up to 1.62 nm for the interlayer content of: 4MB^+ and $12\text{H}_2\text{O}$ per $3a \times 2b \times 1c$ supercell. One example of the interlayer structure of fully exchanged SWy-montmorillonite with eight water molecules per $3a \times 2b \times 1c$ supercell is shown in Fig. 5. Guest cations of methylene blue prefer the orientation of the long axis tilted to silicate layers. Results of modeling are consistent with the X-ray powder diffraction results. The structural disorder, which has been obtained by modeling (i.e., the same crystal energy corresponding to a large variety of structural arrangements with large range of basal spacing), was confirmed by X-ray diffraction profiles.

Modeling of MB-Cheto montmorillonite structure led to similar conclusions as to the structural disorder. The higher layer charge and consequently higher MB^+ content in the interlayer space leads to a higher basal spacing than in the case of MB-SWy montmorillonite. Models of partially exchanged MB-Cheto montmorillonite with five cations of MB^+ and one cation of Ca^{2+} per $3a \times 2b \times 1c$ supercell have basal spacing about 1.53 nm, where the guest cations have a monolayer arrangement similar to that in the case of MB-SWy montmorillonite (see Fig. 5). Adding 12 water molecules into the interlayer space of the $3a \times 2b \times 1c$ supercell with 5MB^+ and 1Ca^{2+} increased the basal spacing from 1.53 to 1.61 nm and stabilized the structure by increasing the total crystal energy. Calculated basal spacing for the fully exchanged MB-Cheto montmorillonite (i.e., for 7MB^+ in a $3a \times 2b \times 1c$ supercell) is in the range 1.84–1.90 nm. Adding 8 water molecules in the

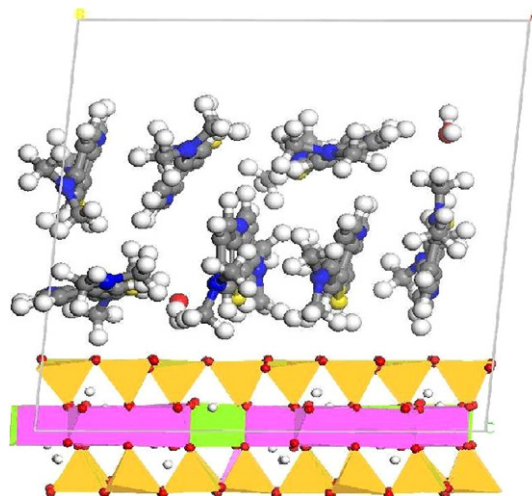


Fig. 6. Calculated structure of the fully exchanged MB-Cheto montmorillonite with 2 water molecules per $3a \times 2b \times 1c$ supercell. (N, blue; S, yellow; O, red.) For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.

$3a \times 2b \times 1c$ supercell led to the value 1.94 nm. The model of fully exchanged Cheto montmorillonite with bilayer arrangement of MB^+ guests and two water molecules in the supercell is shown in Fig. 6.

3.6. Discussion

Recently Bujdák et al. [3] and Kaneko et al. [13] came to the conclusion that with increasing layer charge of montmorillonites, the orientation of intercalated dye molecules in the montmorillonite interlayer become more tilted, and at high layer charge of montmorillonite, this orientation becomes almost perpendicular. This conclusion obtained on the base of polarized UV–vis spectrometry measurements by Kaneko et al. [13] is in agreement with our results of X-ray diffraction and modeling. Among our data obtained for fully saturated MB-montmorillonites, a good relationship between the basal spacing d_{001} (Table 1) and the molar ratio x ($n_{\text{MB}}/n_{\text{MMT}}$) (Table 4) was revealed. The ratio MB/montmorillonite (x) relates to the mean crystallochemical coefficient of symbolic MB^+ cations bonded with one negative charged part of montmorillonite molecule ($\text{MB}_x\text{-montmorillonite}$). The relation plotted in Fig. 7 validates on the quantitative level the recent work of Kaneko et al. [13], because it shows a relation between molar ratios x and basal spacing d_{001} of X-ray diffraction patterns of fully saturated $\text{MB}_x\text{-montmorillonites}$.

All our calculated simple models of molecular modeling also confirmed that the long axis of guest cations of methylene blue is tilted to the silicate layers. On the other hand, the configuration of large methylene blue aggregates in the interlayer of the montmorillonite is more complicated. Molecular modeling shows that the presence of water molecules and/or alkali cations in the interlayer space can stabilize the structure by increasing the total crystal energy and the nonbond energy. The presence of some amount of alkali cations in all saturated MB-montmorillonite samples was really verified by chemical analyses (Table 4). Moreover, among the MB-SWy

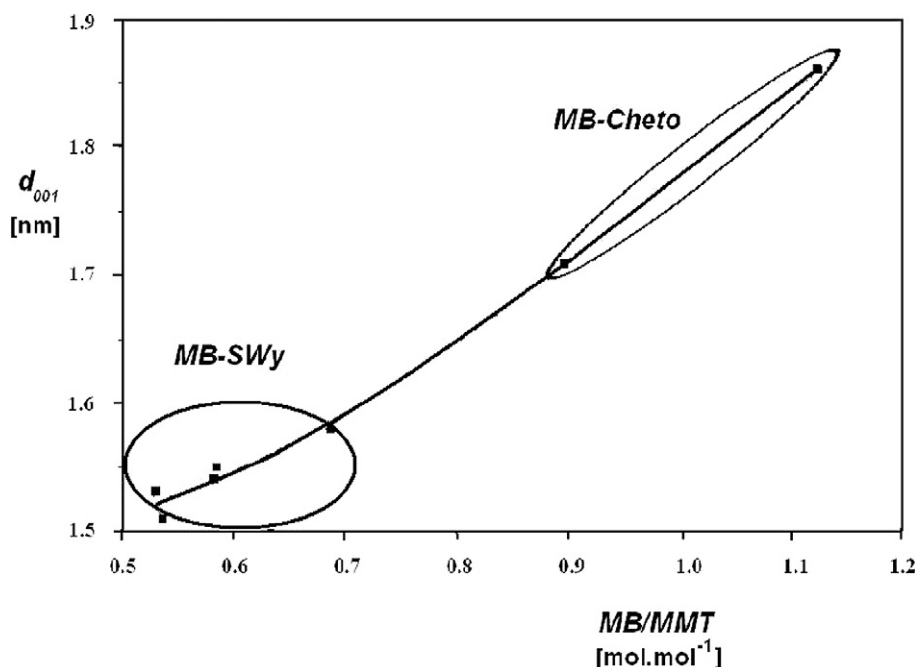


Fig. 7. Plot of basal spacing d_{001} versus molar ratio MB/montmorillonite (x) of intercalated MB-montmorillonites.

data, the higher d_{001} and x values are observed for those MB-montmorillonites that were fully saturated with higher concentrations of MB, i.e., with higher (MB_q^{q+}) agglomerates of methylene blue (Fig. 7). The same is valid for MB-Cheto data. Both for MB-SWy and MB-Cheto samples, the charge of the interlayer space is somewhat compensated for by the rest of alkali cations that have not been ion-exchanged by methylene blue (Table 4).

4. Conclusion

The self-association of MB in water solution increases with increasing concentration of dye, and MB aggregates tend to be more disordered in the interlayer space than monomers intercalated from low-concentration solutions. The interlayer structure has only a small effect on the fluorescence of MB in montmorillonite, as one can see in Fig. 4. It was shown that the layer charge is the most significant factor affecting the fluorescence. The X-ray interlayer distance (d_{001}), as well as the (MB/MMT) molar ratio in the MB-MMT intercalates, increases with increasing MB concentration in the intercalation solution. MB-SWy samples intercalated by more concentrated MB aqueous solutions also show greater basal diffraction line broadening. This line broadening can be the result of inhomogeneity in the interlayer structure, as well as the result of stacking disorder in interstratified layered structures, where two successive silicate layers exhibit different interlayer distances as a result of concentration inhomogeneity in the direction perpendicular to silicate layers (Hendricks–Teller effect; for more details, see for example, [29]). This effect is not observable for MB-Cheto samples with bigger interlayer distances (d_{001}). For MB-SWy and MB-Cheto samples, the residue content of Na, K, and Ca in the interlayer of montmorillonites decreases with increasing concentration of methylene blue. It has been found that

after the montmorillonite saturation with very dilute MB solutions in which dye monomers prevail, MB is deposited in one layer in Na-SWy (with lower interlayer charge), while in MB-Cheto, with higher interlayer charge, MB is deposited in two layers.

Acknowledgments

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9.5 Molecular modeling of surface modification of Wyoming and Cheto montmorillonite by methylene blue – P5

Molecular modeling of surface modification of Wyoming and Cheto montmorillonite by methylene blue

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Abstract The surface area of various types of montmorillonites (MMT) with different values of layer charge plays a very important role in surface arrangement of methylene blue cations (MB). Photoluminescence measurements can be strongly or partially influenced by this surface arrangement of cations. For these reasons and on the basis of our previous results, molecular simulations were performed for various types of montmorillonites covered with methylene blue cations. Adsorption of methylene blue cations on Na-Wyoming MMT surface is different from Ca-Cheto MMT. In the case of Wyoming with a lower layer charge, MB cations lie parallel to the silicate layer for all investigated samples. On the other hand, Cheto surface is covered with a higher amount of MB cations. The results obtained from molecular modeling indicate that MB lies parallel to low loading case and become tilted with respect to layer for a higher loading. Moreover, a higher amount of MB cations covering the silicate layer are much less energy-stable. A higher loading of MB cations leads to aggregates but at low loading MB cations degrade to monomers.

Keywords Intercalation · Methylene blue · Surface · Molecular simulations · Montmorillonite · Sorption

Introduction

The techniques of molecular mechanics and classical molecular dynamics have been intensely used to study the interlayer arrangement of species in layer silicates, both cations (Keggin, ammonium, dyes) and neutral molecules (different types of amine). A review about this type of structure analysis using molecular simulations was given by Čapková *et al.* [1]. This technique is very useful for studying the arrangement of organic molecules on the surface of layer silicates because different arrangements with respect to the minimum energy can be studied. The disadvantages of molecular simulations are usually the simplification of the modeled structure, difficulty in obtaining correct description of energy potential, and difficulty in finding an adequate method for validation of calculated and experimental results. On the other hand, the advantages include: (i) detailed description of the probable structural arrangement, (ii) understanding of mutual interactions, (iii) better and more precise explanation of experimental results.

Klika *et al.* [2] gave a detailed description of preparation and many related experimental results of methylene blue cations intercalated into two different types of montmorillonites (Na-Wyoming and Ca-Cheto) together with molecular modeling of interlayer space of these intercalates. A lot of works focused on studying the arrangement and position of methylene blue cations [3] and other organic dyes [4, 5] with respect to various silicate layers [6] in the interlayer and on the surface. We focused directly on studying MB interactions within the interlayer or surface for different types of silicates in solid, colloid or liquid

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states. Various influences impacting MB arrangements were studied like the effect of various exchangeable cations [7], layer charge density of smectites [8, 9] or ageing [10] mentioned in previous work [6].

Let's investigate the influence of the layer charge on MB arrangement. It has been confirmed by experimental measurements that MB cations form aggregates in case of higher layer charge and mutual distances between MB are short. On the other hand, layers with low layer charge with active sites far between each other result in longer distances between MB cations, which suppress the aggregation. The position of layer charge in octahedral or in tetrahedral sheets plays an important role in MB arrangement. Tetrahedral charge is not able to aggregate MB cations due to repulsions in contrast to octahedral charge, which allows the agglomeration of MB on the silicate surface [9].

In the present work we calculated the arrangement of different amounts of methylene blue cations on the surface of Wyoming and Cheto MMT reported earlier by Klika *et al.* [2]. Various types of structural arrangement could better explain the influence on photoluminescence properties of intercalates. We also compare our results with previous predictions concerning MB positions on MMT surface derived from experimental results and stoichiometry presumptions. There is a number of publications describing measurements of methylene blue cations on silicate surfaces in colloid liquids and predicting the existence of a silicate monolayer with adsorbed methylene blue cations. On their basis we calculate models with a specific amount of water molecules to compare them with the ones without presence of water molecules.

Experimental

Na-montmorillonite SWy-2 (Na-SWy) and Ca-montmorillonite SAz-2 (Ca-Cheto) samples were used as the hosts for the intercalation and sorption with methylene blue cations (MB). The first sample is from Wyoming, USA, the second one from Arizona, USA. The preparation and measurement of samples is described in detail in our previous work [2]. For this reason we focus directly on the description of the molecular modeling strategy used.

Table 1 Energy characteristics of SWy montmorillonite at various loading of MB cations

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
25	-209	-34	-175
50	-236	-86	-150
75	-263	-122	-141
100	-288	-175	-113

Table 2 Effect of water at different loading of MB cations on the surface of SWy montmorillonite

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
25	-460	-124	-335
50	-507	-173	-334
75	-495	-224	-270
100	-304	-182	-121

Modeling strategy

The initial model of the surface structure was built in Surface builder in *Cerius²* modeling environment [11]. The constructing of the host framework was done according to the following structure data published in [12, 13]: $a=5.208 \text{ \AA}$, $b=9.020 \text{ \AA}$. We created a $3a \times 4b$ two-dimensional supercell with the following dimensions: $A=15.624 \text{ \AA}$, $B=36.080 \text{ \AA}$. The composition of the layer was: $(\text{Al}_{36} \text{Mg}_6 \text{Fe}_6^{3+})(\text{Si}_{94} \text{Al}_2)\text{O}_{240}(\text{OH})_{48}$ with the layer charge of -8 el for Swy montmorillonite and $(\text{Al}_{34} \text{Mg}_{12} \text{Fe}_2^{3+})(\text{Si}_{94} \text{Al}_2)\text{O}_{240}(\text{OH})_{48}$ with the layer charge of -14 el for Cheto montmorillonite, respectively. Methylene blue (MB) as a cation with the charge of +1 was placed on the host surface. The model consisted of the host layer, one adjacent surface guest layer, and of the sheet layer of charge balancing cations on the opposite site of the surface. In the case of modeling of fully exchanged montmorillonite, the surface guest layer contained four MB cations for Wyoming and 7 MB cations for Cheto. In the case of partially exchanged montmorillonite the charge compensating cations (Na^+ or Ca^{2+}) were placed on the upper side of the host supercell between MB cations. We built a set of initial models with various loadings of methylene blue cations on the surface and with various positions of methylene blue cations with respect to the host surface layer and with respect to each other. The effect of water on the arrangement of the guests and on the energy was simulated by adding 42 water molecules above the guest layer.

The modeling of the molecular mechanics and of the classical molecular dynamics was performed in *Cerius²* and *Materials Studio* modeling environment [11, 14]. Universal

Table 3 Energy characteristics of Cheto montmorillonite at various loading of MB cations

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
14	-658	-29	-629
43	-660	-96	-564
71	-640	-191	-449
100	-570	-271	-299

Table 4 Effect of water at different loading of MB cations on the surface of Cheto montmorillonite

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
14	-1021	-112	-909
43	-955	-207	-748
71	-769	-277	-492
100	-733	-364	-369

field of force was used to describe the potential energy of the models [15]. During energy minimization the host layers and the sheet layer of charge-balancing cations were kept fixed. Charges were calculated by Gasteiger method [16]. All atoms of the surface guest layer with cations were variable. After energy minimization, molecular dynamics simulations were carried out. The quench dynamics was simulated using the NVT statistical ensemble (constant number of atoms, volume and temperature) at 300 K. In quench dynamics, periods of dynamics simulations are followed by a quench period, in which the model is minimized (in our case 100 steps of dynamics between quenches and 500 steps of minimization in quenches). The dynamics time step was set up to 0.001 ps. The silicate layers were kept frozen (fixed) during the dynamics simulations and the total length of the dynamics trajectory was 50 ps.

Results and discussion

The results of molecular simulations are summarized in Tables 1, 2, 3, 4. Tables 1 and 3 describe energy characteristics of the models with varying loading of MB cations on the host surfaces. The tables show total sublimation energy (E_{total}) and its components - electrostatic energy ($elst$) and van der Waals energy contributions (vdW). The effect of water on the surface is summarized in Tables 2 and 4.

Wyoming Montmorillonite covered with different amounts of methylene blue cations

Table 1 shows the energy characteristics for 25%, 50%, 75%, and 100% loading of MB cations on the host surface of SWy-montmorillonite. We can see that the total sublimation energy decreases with the increasing loading of MB cations. The increasing loading of the guests leads to a rapid decrease of the values of van der Waals energy contributions; on the other hand the increasing guest loading leads to the slow increase of the value of electrostatic energy contributions and in the case of the full cation exchange the value of van der Waals contribution is a dominant component in the total sublimation energy. As shown in Table 1, the total sublimation energy has no local minimum with respect to the guest loading, so the charge balancing cations on the host surface of Wyoming montmorillonite can be exchanged for MB cations up to 100%. Figure 1 shows the top view of the arrangement of

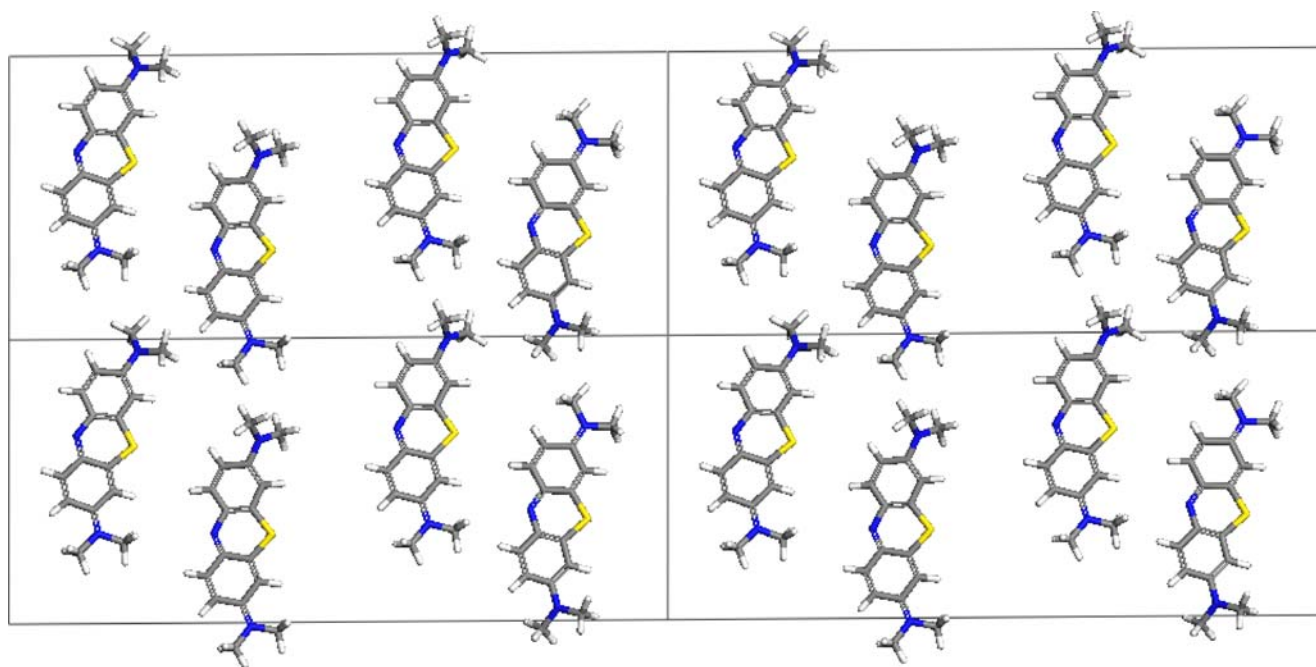
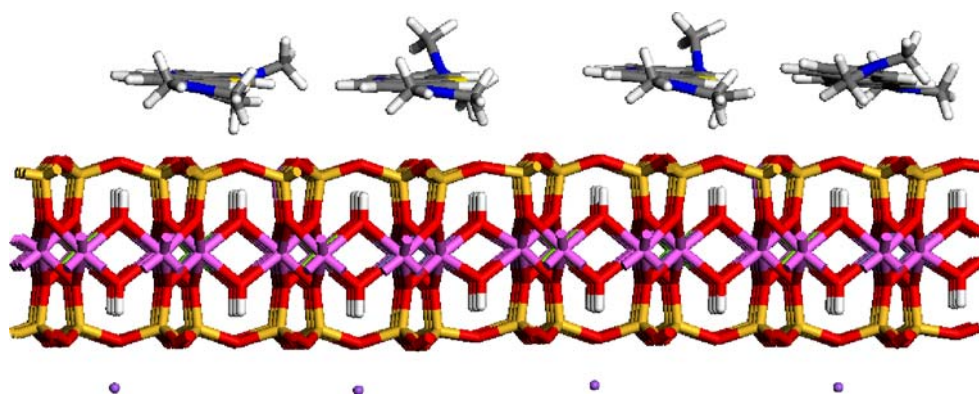
**Fig. 1** Top view on the arrangement at 100% loading of MB cations on the host surface of SWy montmorillonite

Fig. 2 Side view on the arrangement at 100% loading of MB cations on the surface of SWy montmorillonite



MB cations on the fully exchanged surface. In this case, MB cations form a dimeric-like arrangement as the one with the lowest total sublimation energy. The calculations showed a very similar value for the monomer arrangement of the guests; therefore both of these arrangements can be expected in the real sample.

Figure 2 shows a side view of the fully exchanged sample. Since the charge of the surface layer of Wyoming montmorillonite is much lower (-8 el) than in the case of Cheto montmorillonite (-14 el) the guests are able to adopt a parallel arrangement with respect to the host surface even in the case of full exchange, which can be important for the observed photoluminescence properties.

The simulations showed a significant influence of water in the sample. The results are summarized in Table 2. It can be seen that in all cases water stabilizes the structure that is accompanied by a significant decrease of the total sublimation energy with respect to the values of the total sublimation energy presented in Table 1. The highest decrease of the energy occurs in the case of 25% and 50% exchange and, due to relatively low loading of MB cations, most of the water molecules tend to form a monolayer arrangement with respect to the host surface as can be seen in Fig. 3. In the case of 75% and 100% exchange the decrease of the total sublimation energy is lower than in the previous cases

because the hydrophobic guest layer covers the majority of the host surface. In general, surface water has no influence on mutual orientation of the guests or on their orientation with respect to the host surface.

Cheto Montmorillonite covered with different amounts of methylene blue cations

The results for Cheto montmorillonite are summarized in Table 3. It shows energy characteristics for 14%, 43%, 71%, and 100% loading of MB cations. In comparison to Table 1 we can see that Cheto montmorillonite shows the following differences:

- 1/ The total sublimation energy reaches its lowest value in the case of 14% and 42% cationic exchange and both these models also show very similar sublimation energies. Higher loading of the guests leads to an increase of the total sublimation energy indicating that in comparison to Wyoming the guest anions prefer to be accommodated on the host surface in a lower loading. On the other hand, the increasing loading of the guests leads to their tilted orientation with respect to the host surface. In the case when 5 MB cations are accommodated on the host surface we still obtain their

Fig. 3 Side view on the model with 25% loading of MB cations and water molecules on the host surface of SWy montmorillonite

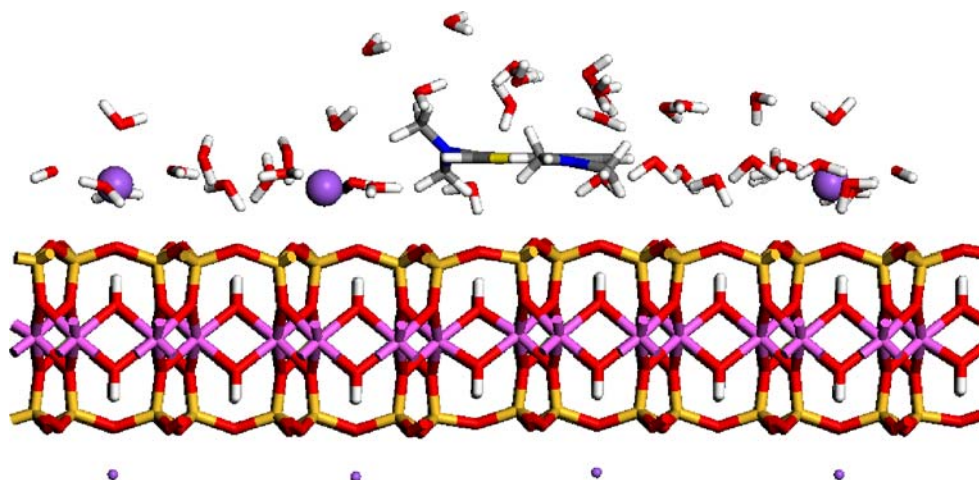
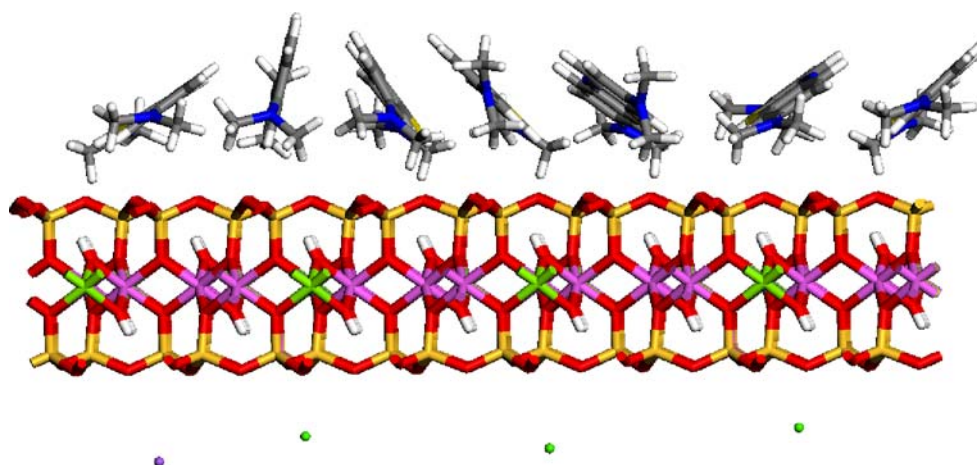


Fig. 4 Side view of the tilted orientation of 100% loading of MB cations on the surface of SAz montmorillonite



parallel arrangement, but in the case of a higher loading the orientation of the guests becomes tilted as can be seen in Fig. 4.

- 2/ Due to a higher layer charge in the case of Cheto montmorillonite electrostatic contributions are dominant in comparison to Wyoming where in the case of full cationic exchange the electrostatic contribution is lower in comparison to the van der Waals contribution. The effect of high loading accompanied by the tilted orientation and stronger electrostatic interactions in comparison to SWy montmorillonite results in differences between the optical properties of these two samples and causes quenching of photoluminescence.

Moreover, the models of Cheto montmorillonite exhibit very different repulsive interactions between the species in the guest layer (interactions between MB cations and the charge-balancing cations). Repulsive interactions in the guest layer for Cheto are 457 ± 30 kcal mol⁻¹, whereas for Wyoming montmorillonite the value is 138 ± 5 kcal mol⁻¹. The big difference between the interactions is due to the

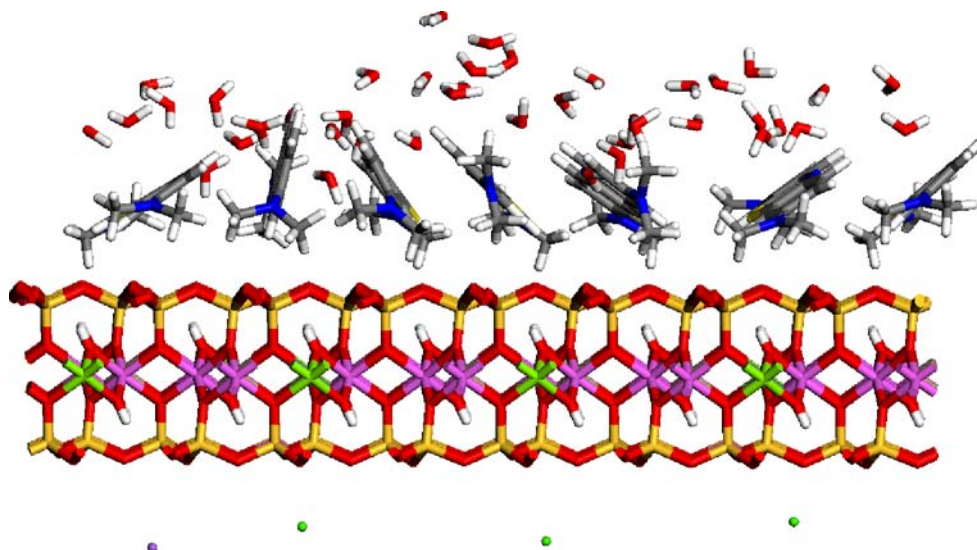
existence of different charge-balancing cations in the guest layer (Ca^{2+} in case of Cheto and Na^+ for Wyoming) and in the case of fully exchanged models due to the high loading of guests in Cheto. This difference between the interactions can also contribute to the explanation of the observed difference in photoluminescence properties [2].

The effect of water is similar as in the case of Wyoming, i.e., the decreasing of the absolute value of energy contributions with increasing intensity of the guests. The effects of surface water on the energy characteristics are summarized in Table 4. Figure 5 shows a side view of a fully exchanged sample where the majority of water molecules are located above the hydrophobic guest layer.

Conclusions

Two different types of MMT were investigated with respect to MB sorption. A different behavior depending on the layer charge of MMT was observed. In the case of lower

Fig. 5 Side view of the tilted orientation of 100% loading of MB cations on the surface of SAz montmorillonite and water molecules



amounts of adsorbed MB cations, the cations lie parallel with respect to the silicate layer for both types of MMT. In the case of Wyoming the charge value is not sufficient to obtain a tilted arrangement of the guests. We can conclude that due to lower value of charge the MB arrangement is always parallel and this investigated type of Wyoming MMT surface is covered just by a monolayer of guests with are oriented parallel to the surface. The parallel orientation of MB noticeably contributes to the photoluminescence of the samples. On the other hand, we obtained models of Cheto montmorillonite with parallel arrangement for a low loading of MB and a tilted irregular arrangement for a high sorption of MB on the silicate layer. A low photoluminescence value was detected for low MB sorption and it can be partially compared to MB arrangement in the case of Wyoming MMT. High sorption of MB cations and mutual interactions between the species strongly influences the photoluminescence and leads to its complete quenching. In this case MB has longitudinal axes parallel to the silicate layer but the transverse axis is tilted. This irregular arrangement completely quenches photoluminescence and strongly confirms the experimental measured values. It can be concluded that not only the interlayer space is important for increasing and quenching of the photoluminescence but also the surface arrangement can influence the photoluminescence results [2].

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9.6 Fluorescence of reduced charge montmorillonite complexes with methylene blue: Experiments and molecular modeling – P6



Fluorescence of reduced charge montmorillonite complexes with methylene blue: Experiments and molecular modeling

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ABSTRACT

The intensity of fluorescence of montmorillonites fully saturated by methylene blue (MB) is very poor due to energy dissipation in MB aggregates. A series of reduced charge montmorillonites (RCM) were prepared from Na-homoionic SWy and Ca homoionic SAz with the aim to decrease the MB aggregation. Fine tuning MB adsorption degree by charge reduction and MB concentration enabled controlled production of different dye species from aggregates via dimers to monomers. It was shown that the intensity of the fluorescence of low-loaded MB-RCM complexes is enhanced by several orders of magnitude with respect to dye-saturated original montmorillonites. XRD analyses, molecular modeling, and diffuse reflectance spectroscopy revealed that low MB-loaded RCMs are very probably adsorbed mainly on the external montmorillonite surface as isolated dye molecules. Such a state cannot be achieved in the solid state without very careful tailoring of the host–guest interaction.

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1. Introduction

The first study on the metachromatic behavior of methylene blue (MB) in clays was reported by Bergmann and O'Konski [1]. Since that time, interactions between clays and cationic dyes have been intensively studied but there are still a lot of uncertainties. In clay suspensions with methylene blue different absorption bands of the dye are observed. The dye monomer absorbs at 650–675 nm, the dimer and higher polymers absorb at 590–610 and/or 570 nm, and protonated cations of methylene blue (MBH^{2+}) absorb at about 760 nm [2–4]. Protonated cations MBH^{2+} exist only in very acid aqueous solutions and they are supposed also on the acid sites of clays. In the most recent works the absorption at about 770 nm is attributed to J-aggregates (head-to-tail cations) of methylene blue rather than to MBH^{2+} cations adsorbed on acid sites of clays [5]. Bujdák et al. [6] also noted the presence of H-aggregates (face-to-face orientation) of MB absorbing at 570 nm and even absorption of the high-ordered H-aggregates at 525 nm. It was pointed out that position and shape of individual MB species significantly depend on various structure parameters, e.g., number of chromophores and distance between neighboring interacting MB molecules [6].

The permanent charge in clay minerals originates from isomorphous substitutions, e.g., Si(IV) by Al(III) in tetrahedrons and Al(III)

by Mg(II) in octahedrons in structural sheets. This charge relates to the structure and composition of the clay minerals and it is relatively stable in a wide pH range of aqueous solutions [7]. Additionally, to this “stable charge”, a variable charge is a result of the reactions of specific functional groups located on clay edges with polar solvents. They can react as Brønsted acids or bases [8]. Anyway, in smectites the variable charge is much lower than the permanent charge. The charge imbalance is usually offset by exchangeable and/or adsorbed cations, such as Na^+ and Ca^{2+} . After intercalation of dioctahedral smectites by a cation with small ionic radii (e.g., Li^+) and the following heating at temperatures of 200–300 °C, the small cation is dehydrated, migrates into pseudo-hexagonal holes in the tetrahedral layers and vacant octahedral positions, and hence reduces the “stable charge” of the aluminosilicate skeleton [9,10]. For deep penetration of the small cation into the silicate layers the upper limit radius of the cations about 0.085 nm is supposed. This process is also accompanied by complete dehydration of the interlayer space and by reduction of the negative charge of the dioctahedral smectites [11]. This phenomenon is also known as the Hofmann–Klemen effect [12]. Reduction of the layer charge after the small cation fixation can easily be tailored by the actual ion radius and temperature and time of the smectite heating. However except decreasing of the layer charge also surface acidification was reported [5] as well as the reaction of Li^+ with OH^- groups in the octahedral layers [13].

The visible spectrum of MB with the reduced charge smectites provides very good information about the density of the layer

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charge. Distribution of the layer charge controls a distance between MB cations adsorbed on the smectite surface and thereby the type of MB aggregation. High density of the smectite charge results in shorter distance between the neighboring adsorbed MB cations and therefore their aggregation is promoted as indicated by the absorption bands at 570–590 nm. Vice versa, low density of the smectite charge results in longer distances between the adsorbed MB cations and therefore the aggregation is prevented (the absorption bands at 650–675 nm) [6,11,14]. The behavior and properties of reduced charge smectites have been summarized in a work of Komadel et al. [15].

Adsorption of the dyes on clays is very quick and therefore their distribution on the surface can be heterogeneous. There are positions where the dye is fully adsorbed and less attractive positions where the density of the dye is very low. This redistribution of the dye on the clay surface is usually accompanied by the changes of the absorption bands in the visible spectra. MB-smectite spectra also vary with varying layer charge. Suspensions of MB with the higher charge smectites are of violet–blue color while the suspensions with small charge smectites are of green–blue color [3,7].

Fluorescence of fully saturated montmorillonites with MB shows similar band profiles covering a wide wavelength range and has low intensity. The higher interlayer montmorillonite charge results in the higher adsorbed amount of MB in the interlayer space and the smaller fluorescence intensity [16]. Fluorescence quenching due to the increasing dye concentration has been reported by Endo et al. [17].

In this paper fluorescence of MB complexes with reduced charge montmorillonites (RCMs) is reported. The principal goal of this paper was to find conditions for the preparation of MB/RCM complexes with high fluorescence intensity.

2. Materials and methods

2.1. Samples and chemicals

Na-montmorillonite SWy-2 (Na/SWy) and Ca-montmorillonite SAz-1 (Ca/SAz) with varying charges were used as hosts for the intercalation with methylene blue. The first one comes from Wyoming (USA) and the second one from Arizona (USA); both were supplied by Source Clays (The Clay Minerals Society, Purdue University, IN, USA). The air-dried fractions with grain size below 0.045 mm were prepared by sedimentation from the original montmorillonite samples. The cation-exchange capacities (CEC) of Na/SWy and Ca/SAz are 0.75 and 1.40 meq g⁻¹ and specific surface areas of 136 and 93 m² g⁻¹, respectively.

Methylene blue (Fluka) was dissolved in distilled water, recrystallized, and dried under vacuum to constant mass. The diluted solutions of MB were prepared by dilution of the basic MB solution (1×10^{-2} mol dm⁻³) with distilled water. Precise concentrations of the dye solutions were determined spectroscopically.

2.2. Instruments and methods

Absorption spectra of MB in the aqueous solutions were recorded by UV–Vis spectrophotometer (Lambda 25, Perkin Elmer) using glass cells of 1.0 and 5.0 cm thickness. The spectra of MB/RCM complexes in solid state were recorded by diffuse reflectance spectra (DRS) methods using a Perkin Elmer Lambda 35 spectrometer equipped with an integrating sphere (Labsphere). The spectra of the montmorillonite powders were measured in circular cells with quartz windows between 250 and 1100 nm (40,000–9090 cm⁻¹) with a 0.5-nm step.

For the fluorescence measurements the powder samples were placed on the quartz substrates. The fluorescence was excited

using a cw He–Cd laser at 325 nm. The laser beam (power of about 1 mW) was focused by a 10 cm lens onto the front side of the sample; the fluorescence light was collected under 45° geometry and focused on the entrance slit of the grating spectrograph with a CCD. The spectral resolution of the apparatus was about 0.5 nm. The measurements were done at room temperatures (20 ± 2 °C).

X-ray powder diffraction measurements were carried out and the basal spacings d_{001} of the interlayer distances were determined for the structure characterization of the intercalated montmorillonites. The measurements were carried out using INEL X-ray powder diffractometer with PSD 120 position-sensitive detector under the following conditions: the reflection mode, rotating sample holder (capillary), and CuK α_1 radiation. The mixture of silicon and Ag-behenate was used as a calibration standard for PSD.

BET surface area measurements were carried out on the Sorptomatic 1990 (Termo-Finnigan) using adsorption of nitrogen at 77 K.

Cation-exchange capacity of the samples was determined using the ion-exchange reaction with barium chloride solutions [7]. Concentrations of not ion-exchanged barium cations after reaching equilibrium were determined by atomic absorption spectrometry.

2.2.1. Preparation of reduced charge montmorillonites

For the preparation of montmorillonites saturated with Li⁺ cations (Li/SWy and Li/SAz) 2.5 g portions of Na/SWy and Ca/SAz were used. They were shaken in the polypropylene vessels of an ultrasonic bath with 100 cm³ of 1 mol dm⁻³ LiNO₃ solution at 20 ± 2 °C for 2 h at 200 oscillations per minute. Then the clay suspensions were centrifuged at 4500 rpm for 40 min. After the supernatants were removed shaking of the solid samples with fresh 1 mol dm⁻³ LiNO₃ solution was repeated several times in order to obtain the fully saturated Li/montmorillonite samples. They were washed out with distilled water to remove nitrate ions and dried in vacuum. The reduced charge montmorillonites (RC-SWy and RC-SAaz) were then prepared by heating Li/SWy and Li/SAz at 40, 130, and 210 °C for an hour [14].

2.2.2. Preparation of MB complexes with M and RCM

Montmorillonites (M) and/or RCM with different interlayer charges were used for the preparation of the solid state complexes with methylene blue. About 0.4 g of solid state sample was added to 100 cm³ of 5×10^{-4} and/or 5×10^{-3} mol dm⁻³ methylene blue solution in the polypropylene vessel. Then the suspensions were shaken in an ultrasonic bath at 200 oscillations per minute for 20 min. After the separation of solid/liquid phases by centrifugation at 4500 rpm for 20 min the samples were rinsed out with distilled water and MB/M and MB/RCM samples were dried in vacuum. Basic montmorillonite samples are summarized in Table 1.

2.2.3. Molecular modeling conditions

Molecular modeling using an empirical force field in Cerius² and Materials Studio modeling environments [18,19] was used to investigate the montmorillonite surface and interlayer arrangement of methylene blue cations. The constructing of the montmorillonite layer was done using structure data published by Méring and Oberlin [20]: $a = 5.208$ Å, $b = 9.020$ Å. We created a supercell $6a \times 2b \times 1c$ with the following layer composition: (Al₃₆Mg₆Fe₆³⁺)(Si₉₄Al₂)O₂₄₀(OH)₄₈ for SWy with a layer charge of –8 electrons and a supercell ($5a \times 2b \times 1c$) with the following layer composition: (Al₃₀Mg₅Fe₅³⁺)(Si₇₈Al₂)O₂₀₀(OH)₄₀ with a layer charge of –7 electrons. The supercell with the same dimensions ($6a \times 2b \times 1c$) and a layer charge of –14 electrons was built for SAz with the following composition (Al₃₄Mg₁₂Fe₂³⁺)(Si₉₄Al₂)O₂₄₀(OH)₄₈ and a supercell ($4a \times 2b \times 1c$) with the following composition: (Al₂₂Mg₈Fe₂³⁺)(Si₆₃Al₁)O₁₆₀(OH)₄₈ with a layer charge –9 electrons [21]. The surface layers of both SWy and SAz were built in Surface Builder module in Cerius². We created a 2D supercell ($12a \times 4b$) with the same

Table 1
Basic montmorillonite samples.

Sample	Treatment of montmorillonite	Labeling
1	Montmorillonite	M
2	Montmorillonite fully saturated with MB (5×10^{-4} mol dm $^{-3}$)	MB/M
3	Montmorillonite fully saturated with MB (5×10^{-3} mol dm $^{-3}$)	MB/M
4	RCM prepared from Li/M at 40 °C	RCM(40)
5	RCM prepared from Li/M at 130 °C	RCM(130)
6	RCM prepared from Li/M at 210 °C	RCM(210)
7	RCM(40) fully saturated with MB	MB/RCM(40)
8	RCM(130) fully saturated with MB	MB/RCM(130)
9	RCM(210) fully saturated with MB	MB/RCM(210)
10	RCM(210) with 100% MB-loading	MB/RCM(210)
11	RCM(210) with 50% MB-loading	MB/RCM(210)
12	RCM(210) with 10% MB-loading	MB/RCM(210)

Note: M represents Na/SWy and/or Ca/SAz; e.g., RCM is RC-SWy and/or RC-SAaz; MB/RCM(40) is complex of RC-SWy(40) and/or RC-SAaz (40) prepared at 40 °C, etc. Samples 7–9 were saturated either with 5×10^{-4} or 5×10^{-3} mol dm $^{-3}$ MB; samples 10–12 only with 5×10^{-4} mol dm $^{-3}$ methylene blue. Percentages of MB-loading are based to CEC of related samples 10, 11, or 12 (100% MB-loading relates to CEC of sample 6, see Table 2).

dimensions and compositions of the layers as in the case of 3D models.

Lithium cations were placed into the previously vacant octahedra in the models representing RCM(210). In the models prepared at temperature of 40 and 130 °C some Li $^{+}$ cations were placed into the hexagonal cavities and some into vacant octahedral in different proportions. Li $^{+}$ cations in the hexagonal cavities moved mostly to vacant octahedra or in rare cases above the silicate layer during minimization. From this reason, Li $^{+}$ cations reducing MMT charge in minimized models were placed in the vacant octahedra. The layer charge was compensated by the lithium and methylene blue cations so that the total charge of the supercell was zero.

Molecular mechanics and molecular dynamics simulations were performed in Cerius 2 and Materials Studio modeling environments. The potential energy was described by Universal force field [22]. Charges were calculated by the charge equilibration method (Q_{eq}) [16] in the case of the 3D interlayer arrangement and the Gasteiger method [23] was used to calculate the charges in the case of 2D models. During the energy minimization of 3D models the layers were kept as rigid units and cell parameters c , α , and β were variable to optimize the d_{001} basal spacing. In the case of 2D models the layers were kept frozen (fixed) with respect to x , y , z coordinates. In all cases positions of Li $^{+}$ cations in the host layers were variable as well as MB cations. After the first energy minimization the models with the lowest total sublimation energy were chosen and quench dynamics simulations were carried out. In the quench dynamics, periods of dynamics simulations are followed by a quench period, in which the model is minimized (in our case, 100 steps of dynamics between quenches and 500 steps of minimization in quenches). The dynamics time step was set up to 0.001 ps. The silicate layers were kept frozen (fixed) during the dynamics simulations and the total length of the dynamics trajectory was 50 ps. An NVT statistical ensemble (constant number of particles, volume, and temperature) at a temperature of 300 K was used. After the quench dynamics the models with the lowest energy were minimized to obtain final structure models.

3. Results and discussion

3.1. Montmorillonites with reduced charge

The interlayer charges of Li/SWy, and Li/SAz samples were reduced by their heating at temperatures of 40, 130, or 210 °C. The

Table 2
Principal characteristics of RCM samples.

Samples	T (°C)	d_{001} (nm)	S (m 2 g $^{-1}$)	CEC $_{RCM}$ (meq g $^{-1}$)		Q_{Li} (%)	
RC-SWy	4	40	1.16	0.66	0.80	12	0
	5	130	1.05	0.44	0.56	41	25
	6	210	0.95	0.12	0.25	84	67
RC-SAaz	4	40	1.16	1.14	1.11	19	21
	5	130	1.00	0.58	0.46	59	67
	6	210	0.93	0.10	0.19	93	86

Note: CEC $_{RCM}$ and Q_{Li} were determined in duplicate.

interlayer spacing (d_{001}), cation-exchange capacity, and specific surface area (S) of RCMs were determined for these calcines (Table 2). There are no significant differences between interlayer spacing d_{001} of RC-SWy and RC-SAaz prepared at the same temperature. In agreement with previous works [3,5] this parameter decreases with increasing temperature of RCM preparation. More significant differences are observed in their cation-exchange capacities (CEC $_{RCM}$), which essentially decrease with increasing temperature of the RCM preparation (from 0.73 mmol g $^{-1}$ (40 °C) to 0.18 mmol g $^{-1}$ (210 °C) and from 1.13 mmol g $^{-1}$ (40 °C) to 0.14 mmol g $^{-1}$ (210 °C) for RC-SWy and RC-SAaz, respectively). These data are in a good agreement with previously presented data of Bujdák and Iyi [24]. Increase of the specific surface area of RC-SWy and RC-SAaz samples with decreasing CEC $_{RCM}$ can be explained by dehydration of the interlayer space because of Li $^{+}$ transport from the interlayer into the tetrahedral layers and vacancy octahedral positions at the higher temperatures [9–11]. The amount (meq g $^{-1}$) or percentages of captured Li $^{+}$ (Q_{Li}) was calculated using the following formula

$$Q_{Li} = \text{CEC} - \text{CEC}_{RCM} \quad \text{and} \quad \%Q_{Li} = 10^2 \cdot \frac{Q_{Li}}{\text{CEC}} \quad (1)$$

where CECs for Na/SWy and Ca/SAz are 0.75 and 1.40 meq g $^{-1}$, respectively. The calculated values of Q_{Li} were plotted versus temperature of the RCM preparation (Fig. 1).

3.2. Fluorescence spectra of RCM and MB complexes

Recently it was shown that fluorescence spectra of MB/SWy and MB/SAz fully saturated with MB (samples 2 and 3) show very similar band profiles covering a wide wavelength range regardless of degree of methylene blue aggregation. Their fluorescence intensities were also very low [16]. For better understanding the influence of some parameters (e.g., montmorillonite charge, concentration of MB, and dye loading) on the fluorescence intensity new experiments with MB/RCM complexes were performed.

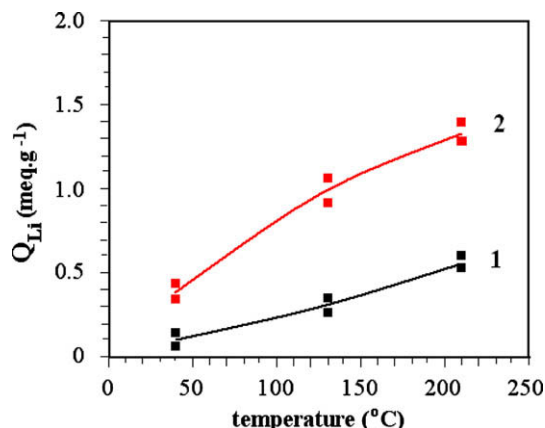


Fig. 1. The plot between Q_{Li} (meq g $^{-1}$) and temperature (°C) of the RCM preparation. 1, RC-SWy; 2, RC-SAaz.

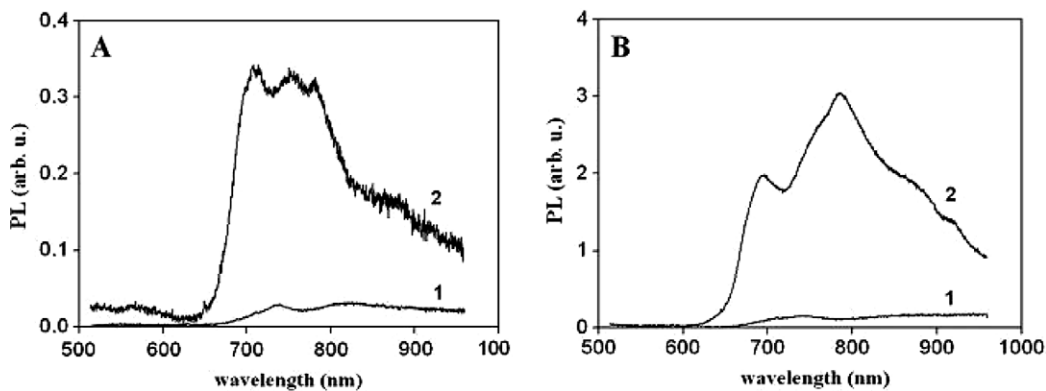


Fig. 2. Fluorescence spectra of MB/RC-SWY (A) and MB/RC-SAz (B) prepared from RCM(130) (spectrum 1) and RCM(210) (spectrum 2) by their full saturation with 5×10^{-3} mol dm $^{-3}$ MB aqueous solution.

The fluorescence spectra of MB/RCM (samples 8 and 9) prepared by saturation of RCM with 5×10^{-3} mol dm $^{-3}$ methylene blue solution are plotted in Fig. 2. The fluorescence intensity increases very sharply with the increasing temperature of the preparation, i.e., with the decreasing RCM charge. The intensities of MB/RCM(40) spectra (sample 7) are even below those of MB/RCM(130).

The influence of MB concentrations on the fluorescence intensity of MB/RCM(210) complexes (sample 9) is shown in Fig. 3. These complexes were prepared by the full saturation with 5×10^{-4} and 5×10^{-3} mol dm $^{-3}$ aqueous MB solutions. The complexes fully saturated with diluted MB solution (5×10^{-4} mol dm $^{-3}$) have higher fluorescence intensities than those related to the complexes prepared by the saturation with MB of 5×10^{-3} mol dm $^{-3}$. We suppose that the higher fluorescence is caused by lower aggregation of dye in more diluted aqueous suspensions [16].

In the experiments demonstrated in Figs. 2 and 3 MB/RCM(210) complexes were prepared by the repeated full saturation of RCM(210) with MB. Next MB/RCM(210) complexes were prepared using dye loadings of 100% (sample 10), 50% (sample 11), and 10% (sample 12) of CEC_{RCM} related to the RCM(210) samples (see Table 2, sample 6). The fluorescence spectra of these samples are given in Fig. 4. Decrease of the dye loadings in MB/RCM(210) resulted in the huge (by more than four orders of magnitude higher) fluorescence intensity. The reason is likely the decreasing amount of adsorbed MB as discussed above. Moreover, very broad fluorescence bands ranging from about 700 to 800 nm (Figs. 2 and 3) changed to narrower ones (700 nm) after dye loading less than 100% on RCM(210) samples (Fig. 4). These changes also show much higher ordering of

MB species on the RCM(210) samples. Lower fluorescence of MB/RC-SWY(210) in contrast with MB/RC-SAz(210) complexes (Fig. 4) can be explained by higher content of Fe in the SWY layer (see crystallochemical formulas under *Molecular modeling conditions*). The quenching of fluorescence due to presence of iron in clays intercalated by dyes has been reported, e.g., by Villemure et al. [25].

3.3. XRD data of RCM and MB complexes

The interlayer spacings d_{001} of MB/SWY and MB/SAz depend on the concentration of MB used for the saturation. Using more concentrated MB aqueous solutions, higher MB aggregates (dimers, trimers, and tetramers) with higher d_{001} values are formed (Fig. 5A and B, samples 2 and 3). The changes in the interlayer spacings d_{001} were also recorded in the MB complexes with RCMs. Sample 4 heated on 40 °C show only negligible (Fig. 5A) or small (Fig. 5B) decrease of d_{001} while sample 5 (130 °C) and sample 6 (210 °C) show a lucid d_{001} decrease. The decreased interlayer spacings of those samples are in an agreement with their lower CEC values (Table 2).

Fully saturated MB/RCM prepared at 130 °C (sample 8) and 210 °C (sample 9) cannot reach the d_{001} values of samples 2 and/or 3 because Li $^{+}$ ions are already fixed in the pseudohexagonal holes and vacant octahedral positions and therefore the ion-exchanged amount of MB is smaller in consistency with their lower CECs (Table 2). Sample 9 could be partially intercalated by MB due to the high amount of MB during saturation because the silicate layers could probably be fractionally reopened.

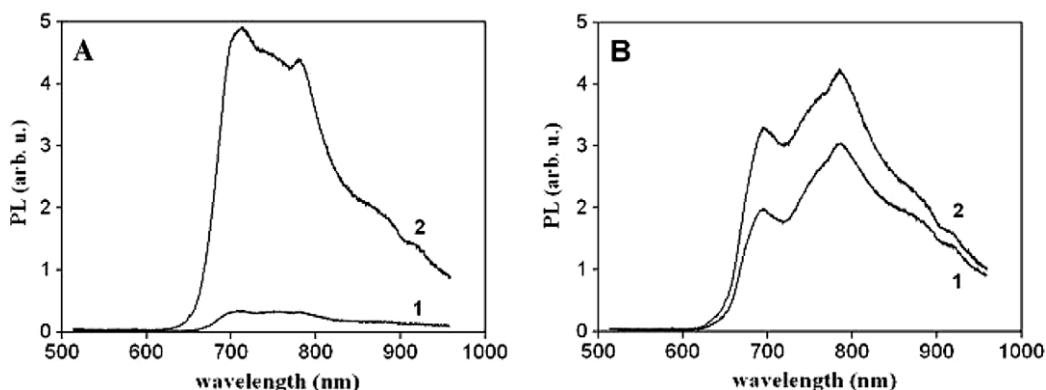


Fig. 3. Fluorescence spectra (A) of MB/RC-SWY(210) and spectra (B) of MB/RC-SAz(210) prepared by full saturation with the 5×10^{-3} mol dm $^{-3}$ (spectrum 1) and 5×10^{-4} mol dm $^{-3}$ (spectrum 2) aqueous solutions of MB.

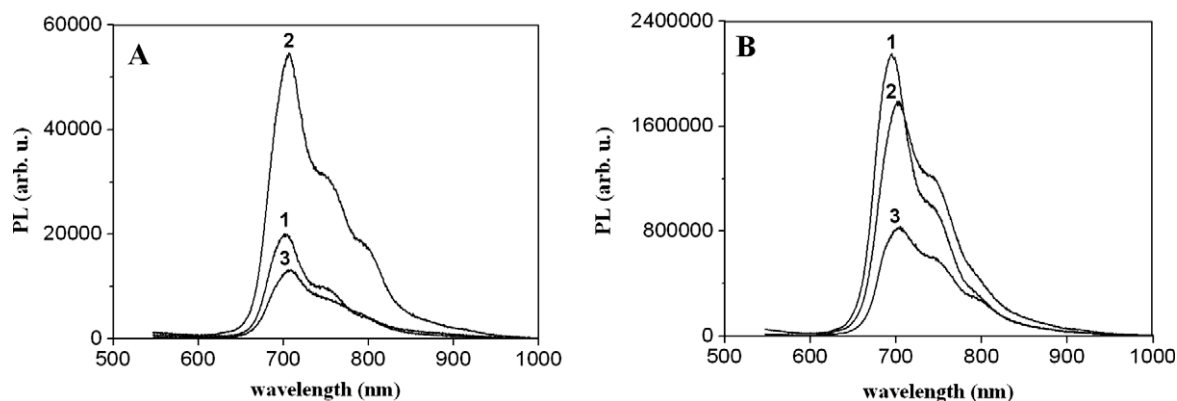


Fig. 4. Fluorescence spectra (A) of MB/RC-SWy(210) and spectra (B) of MB/RC-SAz(210) prepared by different dye loadings: 10% (spectrum 1), 50% (spectrum 2), and 100% of CEC of RCM(210) (spectrum 3).

In contrast to samples 7, 8, and 9, which were prepared by the full MB saturation of RCM samples 10, 11, and 12 were prepared at dye loadings 100% (sample 10), 50% (sample 11), and 10% (sample 12) of the CEC_{RCM} (Fig. 5). The interlayer spacings of those samples (10, 11, and 12) are very similar and close to d_{001} of sample 6. As CECs of sample 6 were significantly decreased it can be supposed that MB in samples 10, 11, and 12 is predominantly adsorbed on the external montmorillonite surfaces. Findings following from the fluorescence spectra and XRD patterns were confirmed by molecular modeling.

3.4. Molecular modeling of RCM and MB interactions

The results of modeling for the interlayer arrangement of MB in SWy and SAz are summarized in Table 3. It shows characteristics of samples 7–9, such as the actual reduced charge in the calculated models, i.e., percentages of captured Li cations located in the host layer (Q_{Li}), the calculated basal spacing d_{001} , and tilted angle of MB cations with respect to the host layer. In the case of sample 7, where the amount of the charge reduction is low ($Q_{Li} = 0\%$ or $Q_{Li} = 12\%$), we obtained results similar to those published by Klika et al. [16]. In fully intercalated SWy, MB cations adopt a tilted orientation (tilted angle is about 70°) with respect to the host layer and the reduction of charge (12% reduction corresponds to 1 Li cation in the host layer of our models) leads to a lower tilted angle of MB cations that is 50° . In the case of SAz the trend of lowering tilted angle is similar.

Sample 8 for SWy exhibits a higher variability of the amount of reduced charge for SWy ($Q_{Li} = 25\%$ and $Q_{Li} = 41\%$ corresponds to 2 and 3.28 Li cations in the layer). Fig. 6 shows a side view on the structure model of SWy containing 6 MB cations (2 Li cations in the layer) in the interlayer space. The tilted angle of MB cations in this case is of 40° and basal spacing corresponding to this arrangement is of 1.44 nm. The model with 3 Li cations in the layer and 4 MB in the interlayer is shown in Fig. 7. In this case the charge reduction of the host layer leads to significant changes of the guests' orientation in the interlayer space. The guests tend to adopt a parallel arrangement with respect to the layer with departures of about $10\text{--}20^\circ$ at maximum. In the case of SAz we used a model with 5 MB cations in the interlayer; i.e., 9 Li cations were located in the layers, which corresponds to the $Q_{Li} = 64\%$. The obtained basal spacing was in agreement with experimental basal spacing of 1.30 nm, which corresponds to the nearly parallel arrangement of the guests in the interlayer as was found for SWy.

The experimental basal spacings of sample 9 were 1×15 and 1.05 nm for SWy and SAz, respectively. We modeled the lowest concentration of the guests in the interlayer by the presence of 1 MB cation. This low concentration corresponds to the calculated basal spacings of 1.26 and 1.20 nm, which is the lowest d_{001} value of montmorillonite to be able to accommodate some MB cations in the interlayer. A nonintercalated model of SWy and SAz without interlayer water molecules exhibits a basal spacing of 0.95 nm, which indicates that sample 9 (both SWy and SAz) were not intercalated and in the interlayer space only charge compensating Li

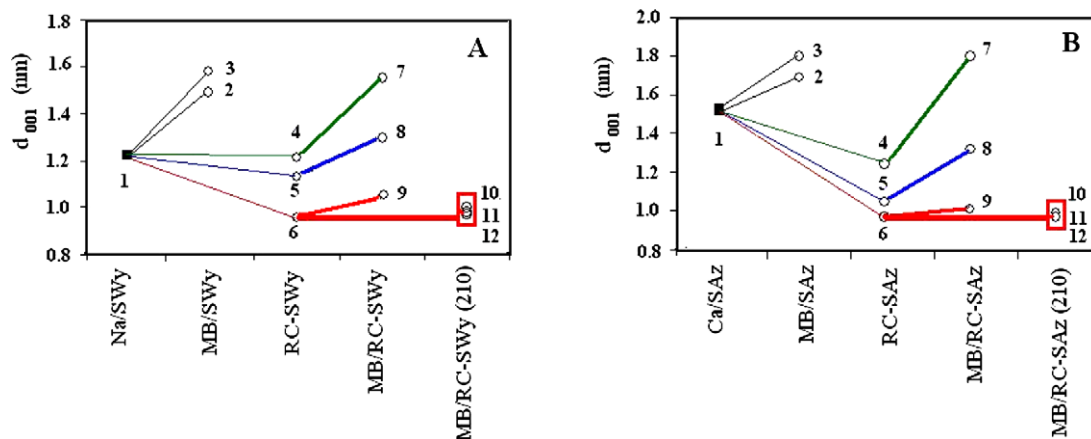


Fig. 5. Interlayer spacings d_{001} of SWy (A) and SAz (B) samples (1–12). The samples are simply described and labeled in Table 1 in detail.

Table 3

Modeling results of SWy and SAz intercalated with MB cations.

Montmorillonite (supercell)	Sample	Q_{Li} (%)	Li/MB	d_{001} (nm)	Tilted angle (°)
SWy (6a × 2b × 1c)	7	13	1/7	1.51	50
	8	25; 38	2/6; 3/5	1.44; 1.30	40; 10
	9	87	7/1	1.26	0
SWy (5a × 2b × 1c)	7	0	0/7	1.51	60
	8	29; 43	2/5; 3/4	1.36; 1.23	40; 10
	9	85	6/1	1.20	0
SAz (6a × 2b × 1c)	7	21	3/11	1.80	70
	8	64	9/5	1.30	10
	9	93	13/1	1.26	0
SAz (4a × 2b × 1c)	7	11	1/8	1.82	70
	8	56	5/4	1.35	40
	9	89	8/1	1.20	0

cations and probably some water molecules are present. These samples contain MB exclusively on their external surface.

Fig. 8 shows a mutual arrangement of MB cations (50% amount) above the surface of (12a × 4b) 2D supercell of SAz with Q_{Li} = 86%. The distance between the host surface and the guests is about 0.31 nm. We observed big differences in energy characteristics between reduced and nonreduced charge montmorillonites. Table 4 shows the energy characteristics (total sublimation energy E_{total} , components—electrostatic interactions E_{lst} , and van der Waals energy vdW) of RC–SAz (Fig. 8) and SAz and describes samples with 43% amount of MB on the surface. We can see that the value of electrostatic energy is the dominant term in the total sublimation energy [23], while in the case of charge reduction the value of electrostatic interactions is very low because of the presence of a high amount of Li cations in the layer. These fundamental differences in the energy characteristics are important for a better insight into fluorescence properties found for these samples: the measured fluorescence intensity of MB/SAz is very low, while the fluorescence of MB/RC–SAz(210) is significantly amplified.

We explain this phenomenon by a different charge distribution in the system. The high electrostatic interaction energy of SAz leads to overflow of charge from MB cations to the silicate layers. On the other hand, in the case of a low layer charge of RC–SAz the higher electron density remains on MB cations and thus their huge fluorescence.

The molecular simulations gave a better insight into the arrangement of MB cations in the interlayer space and on the silicate surface. It was found out the increasing charge reduction caused by the presence of Li cations in the layer leads to much

weaker electrostatic interactions between the MB and the surface, which is demonstrated by the lower tilted angle of MB cations. Moreover a gradual increase of charge reduction does not lead directly to a gradual decrease of the tilted angle of the guests with respect to the layer. Using Q_{Li} = 25% and Q_{Li} = 29% for SWy and Q_{Li} = 56% and Q_{Li} = 57% for SAz MB molecules adopt a tilted orientation with an angle of about 40°. A slightly higher charge reduction (Q_{Li} = 38% for SWy and Q_{Li} = 64% for SAz) leads to a parallel arrangement of the guests with maximal departure of about 10°.

3.5. Vis electronic spectra of RCM and MB complexes

In contrast with, e.g., rhodamine B, which also forms dimers beside monomers in aqueous solutions [10], MB monomer also forms H and J-aggregates and protonized species. The very similar spectra of MB complexes with SWy and SAz samples (2–12) were recorded by DRS (Fig. 9). Similar absorption spectra of MB in SWy and SAz indicate similar MB adsorbed species.

The large absorption bands occurring in high MB-load montmorillonites at 520–530 nm and prevailing in samples 2–3 and 7–8 can be assigned to major H-aggregates [24]. All these samples were prepared from M (samples 2 and 3) or from RCM heated at 40 and 130 °C (samples 7 and 8) by full saturation by the dye. In absorption spectra of these samples the absorption band at about 765 nm related to the presence of J-aggregates (or MBH^{2+} cations) can be observed. The similarity and high aggregation of MB in these samples is given by little differences of the interlayer charge, CEC, and the interlayer spacings d_{001} among MB/SWy, MB/RC–SWy(40) and MB/RC–SWy(130) samples. It well agrees with the findings reported by Bujdák et al. [14] that higher MB aggregates are formed on the smectite surface with its higher charge.

For sample 9 the most intensive absorption band is shifted to lower wavelengths (about 570 nm) shoving the first step of the decrease of MB aggregation. In these samples also the dye dimers (600 nm) and monomers (660 nm) occur. The decrease of the dye aggregation in sample 9 can be explain by substantially decreased charges of RCM(210) samples (Table 2).

The dye aggregation is almost suppressed in MB/RCM(210) samples that were prepared by 100% (sample 10), 50% (sample 11), and 10% (sample 12) dye loadings. For these samples the absorption band at 660 nm is the most characteristic, indicating the presence of MB monomer.

The Vis electronic spectra indicate that the huge fluorescence intensities of MB/RCM(210) are observed in montmorillonites with strongly reduced charges in which the dye loading is less than 100% and MB is present in the form of the monomer.

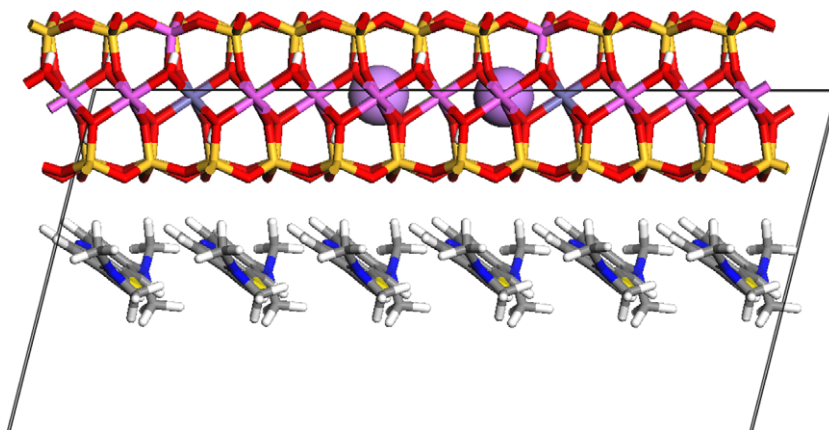


Fig. 6. A side view on the structure model of SWy montmorillonite containing 6 MB cations in the interlayer space. Violet balls represent Li cations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

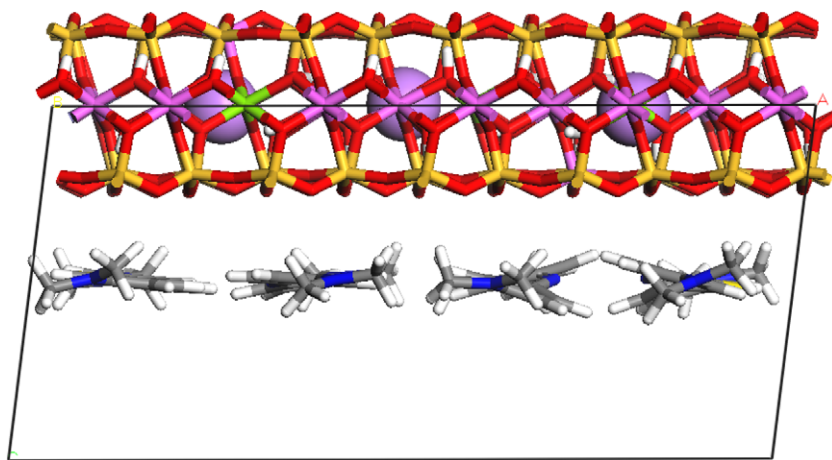


Fig. 7. A side view on the structure model of SWy montmorillonite containing 4 MB cations in the interlayer space. Violet balls represent Li cations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

The reduced charge monmorillonites were prepared by their intercalation with lithium ions and heating at temperatures up to 210 °C. It was found that with increasing heating temperature the d_{001} values and silicate layer charges expressed by CECs decreased substantially. Consequently original and reduced charge montmorillonites were intercalated with methylene blue at various concentrations, degree of aggregation, and geometry of MB/clay mineral associate. From the d_{001} interlayer spacings obtained from XRD patterns it was deduced that MB adsorbed on RC-SWy/SAz heated at 210 °C was located on the external montmorillonite surface and not in the interlayers as in the original montmorillonites. The fluorescence spectra indicated that a low layer charge and low adsorbed MB amount induce huge fluorescence intensities of MB after laser excitation. Additionally, from the Vis electronic spectra of the solid complexes it followed that when the layer charge is low the formation of methylene blue aggregates and MBH^{2+} cations are suppressed. The huge fluorescence was emitted by MB monomers (individual molecules), which predominate at the reduced charge layers.

Table 4

Comparison of energy characteristics of reduced charge and natural SAz with MB cations on the surface.

Samples	E_{total} (kcal mol ⁻¹)	vdW (kcal mol ⁻¹)	E_{lst} (kcal mol ⁻¹)
RC-SAaz	-186	-151	-35
SAz	-955	-207	-748

Note: 43% amount of MB on the montmorillonite surface was used for calculation.

By the molecular simulations of MB interactions with montmorillonites it was found that the increasing charge reduction leads to weaker electrostatic interactions between the single MB molecules and the surface, which is demonstrated by lowering their tilting angles. For instance, For RC-SWy/SAz(210) MB molecules were placed on the surface in a parallel arrangement within the distance of 0.31 nm.

Both experiments and molecular modeling revealed that the tilted angles between MB molecules and montmorillonite surfaces are finely tuned by a surface charge of the clay mineral host. The low montmorillonite layer charge causes the nearly parallel orientation of adsorbed MB monomers. Similar conclusions for oxazine 4/ montmorillonite complexes were published by Kaneko et al. [26].

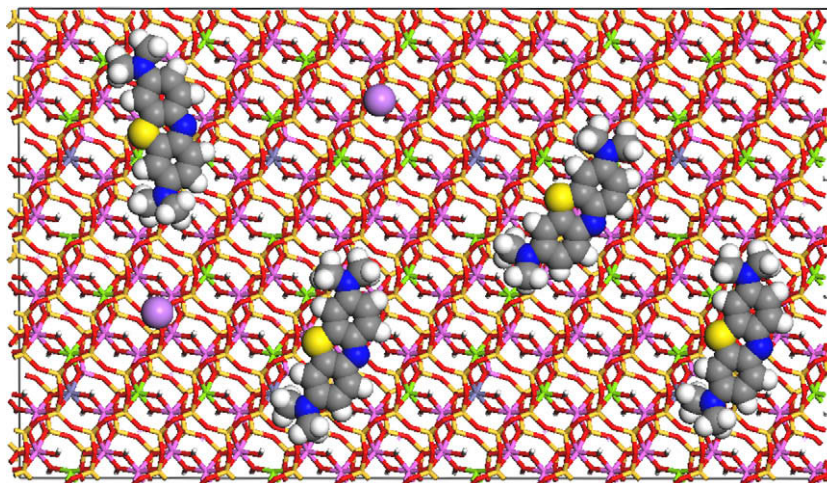


Fig. 8. A top view of surface arrangement of MB cations on the surface of SAz montmorillonite. Violet balls represent nonexchanged Li cations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

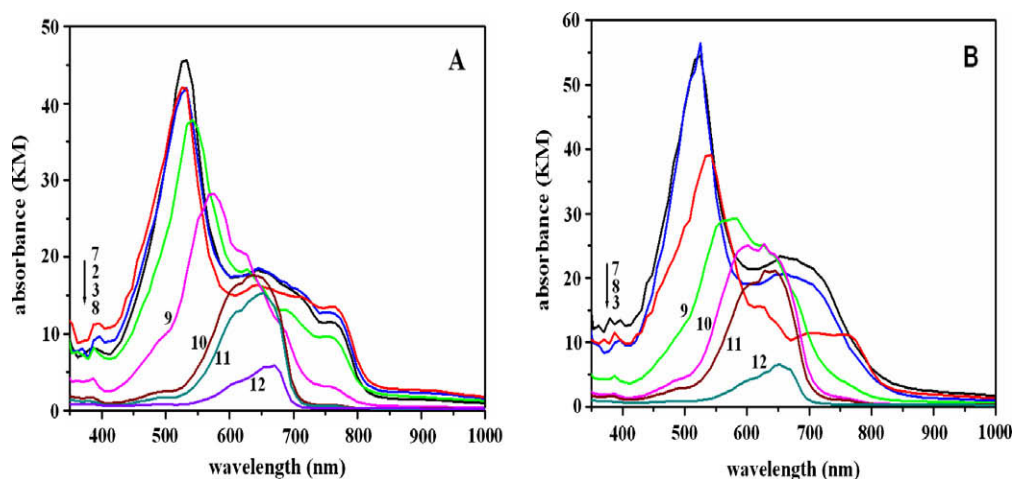


Fig. 9. Vis electronic spectra of solid state complexes of montmorillonites with methylene blue. (A) MB complexes with SWy and RC-SWy; (B) MB complexes with SAz and RC-SAz. The samples are numbered as in Table 1.

Acknowledgments

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**9.7 Molecular modeling of layered double hydroxide intercalated
with benzoate, modeling and experiment – P7**

Molecular modeling of layered double hydroxide intercalated with benzoate, modeling and experiment

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Abstract The structure of Zn_4Al_2 Layered Double Hydroxide intercalated with benzenecarboxylate ($\text{C}_6\text{H}_5\text{COO}^-$) was solved using molecular modeling combined with experiment (X-ray powder diffraction, IR spectroscopy, TG measurements). Molecular modeling revealed the arrangement of guest molecules, layer stacking, water content and water location in the interlayer space of the host structure. Molecular modeling using empirical force field was carried out in Cerius² modeling environment. Results of modeling were confronted with experiment that means comparing the calculated and measured diffraction pattern and comparing the calculated water content with the thermogravimetric value. Good agreement has been achieved between calculated and measured basal spacing: $d_{\text{calc}}=15.3 \text{ \AA}$ and $d_{\text{exp}}=15.5 \text{ \AA}$. The number of water

molecules per formula unit ($6\text{H}_2\text{O}$ per $\text{Zn}_4\text{Al}_2(\text{OH})_{12}$) obtained by modeling (i.e., corresponding to the energy minimum) agrees with the water content estimated by thermogravimetry. The long axis of guest molecules are almost perpendicular to the LDH layers, anchored to the host layers via COO^- groups. Mutual orientation of benzoate ring planes in the interlayer space keeps the parquet arrangement. Water molecules are roughly arranged in planes adjacent to host layers together with COO^- groups.

Keywords Benzoate · Layered double hydroxide · Molecular modeling · X-ray diffraction

Introduction

Layered double hydroxides (LDHs), sometimes called hydrotalcites, belong to a wide family of lamellar compounds called anionic clays. They are characterized by regular stacking of layers that bear a positive charge. The layers are formed of octahedral units $\text{M}(\text{OH})_2$ where M is mostly a divalent or a trivalent cation. The interlayer space contains water molecules and anions that compensate the positive charge of the layers. Hydrotalcites can be represented by a general formula:

$$[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+} [\text{A}_{x/n}^{n-}]^{x-} \cdot m \text{H}_2\text{O},$$

where M^{2+} and M^{3+} are bi- and trivalent metal cations. A is the interlayer anion with the charge of n^- [1].

The charge balancing anions can be exchanged by a wide amount of anions of inorganic or organic molecules [1–4]. The anion exchange is a widely used intercalation method [5, 6].

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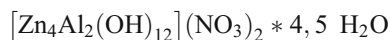
LDH offer a wide scale of practical application like catalysts (e.g., precursors for preparation of other catalysts [7], synthesis of organic molecules [8], chemical reactions [9]), polymer stabilizers [10, 11], drug carriers [12] and drug improvers [13], sorbents [14, 15], etc. Intercalation of guest species possessing chromophoric groups into LDH gives rise to hybrid organo - inorganic nanostructure materials for various photofunction [16, 17].

In the present work we investigated the structure of LDH intercalated with benzoate anions. Many papers dealing with LDH intercalated with benzoic acid and its derivatives such as salts of benzoic acid, terephthalate have been published [18–25] mostly with only on a rough assessment of structure model based on the measured basal spacing. In this paper we investigated the structure and guest arrangement in benzoate - LDH intercalate using combination of molecular modeling with experiment (X-ray powder diffraction, IR spectroscopy and thermogravimetry).

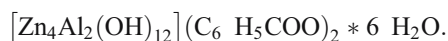
Experiment

Samples preparation and chemical analysis

Well crystallized hydrotalcite - like compound (HTlc) of formula $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}](\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, was obtained with a procedure accomplished by the thermal hydrolysis of urea [26]. The corresponding chloride form was obtained by titrating the carbonate form, dispersed in a 0.1 mol/dm^3 NaCl solution, with a 0.1 mol/dm^3 HCl by means of Radiometer automatic titrator operating at pH stat mode, and pH value of 5. Finally, the hydrotalcite in nitrate form was obtained by equilibrating the chloride form with an aqueous solution of NaNO_3 0.5 mol/dm^3 (molar ratio $\text{NO}_3^-/\text{Cl}^- = 10$). The composition of host structure was the following:



The intercalation of benzoate anions was achieved by equilibrating the nitrate form of hydrotalcite with an aqueous solution of $\text{C}_6\text{H}_5\text{COONa}$ 0.5 mol/dm^3 (molar ratio $\text{C}_6\text{H}_5\text{COO}^-_{(\text{solution})}/\text{NO}_3^-_{(\text{solid})} = 10$) for 24 hours. The recovered solid was three times washed with CO_2 -free deionized water and dried over P_4O_{10} . The composition of the intercalated structure was:



The Zn and Al content of the HTlc, was obtained with standard EDTA titration after having dissolved a weighed amount of the sample (~100 mg) in a few drops of concentrated HCl and diluted with water to 50 ml. The

Cl^- , NO_3^- and $\text{C}_6\text{H}_5\text{COO}^-$ counterions in solution, before and after equilibration, were determined by ion chromatography. Water and $\text{C}_6\text{H}_5\text{COO}^-$ content of the solids were obtained by thermogravimetry.

TG/DTA analysis were performed in air by a Stanton 781 Thermoanalyser at the heating rate of $5^\circ\text{C}/\text{min}$.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) showed two endothermic peaks related to loss of co-intercalated water and to dehydroxylation of the inorganic layers between 80° and 300°C . Furthermore, the main weight loss between 300°C and 600°C may be ascribed to decomposition of organic parts. ZnO and ZnAl_2O_4 , starts to be formed at temperatures higher than 600°C as confirmed by the XRPD patterns of the sample heated at 900°C .

X-ray diffraction

The measurement conditions: X-ray powder diffraction (XRPD) patterns were taken with a computer-controlled PW 1710 Philips diffractometer operating at 40 kV, 30 mA, using a PW 1820 goniometer, supplied with a bent graphite monochromator in the diffracted beam, and Cu-K α radiation. XRPD patterns were taken with the step-scanning technique. The samples were prepared using the side-loading procedure in order to minimize preferred orientations. Diffractograms were collected from $2\theta^\circ = 2$ to 120° using steps of 0.01° and a counting time of 20 s per step.

The diffraction pattern of the intercalated structure measured at temperature of 30°C is shown in Fig. 1. It exhibits characteristic features of a layered structure, that means very strong basal reflections due to the strong preferred orientation and weak broaden non-basal reflections indicating a slight stacking disorder. Nevertheless the crystal structure of the intercalate exhibits a high degree of three-dimensional ordering (non-basal reflections quite pronounced). Anyway due to the slight structural disorder

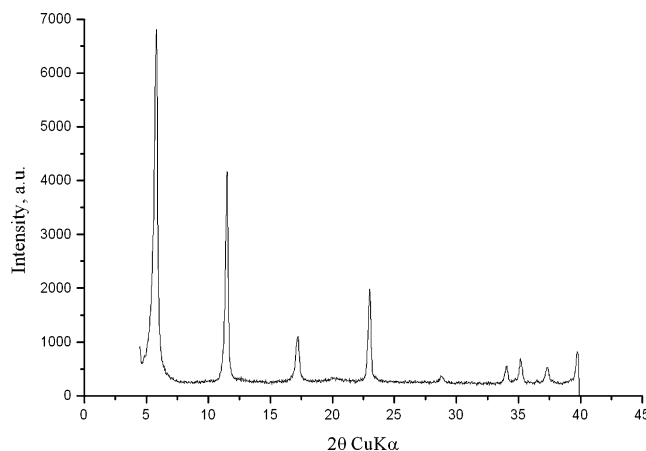


Fig. 1 Powder diffraction pattern of the intercalated structure

the structure of the intercalate cannot be solved by diffraction method only and it is suitable to use molecular modeling.

IR spectroscopy

FT-IR spectra of the solid samples were recorded under vacuum with a Bruker IFS 113V spectrometer by the KBr pellet technique.

The FT-IR spectrum (see Fig. 2) shows a strong broad band in the 3000–3750 cm^{-1} range due to the lamellae OH stretching which are involved in H- bonds. The sharp and intense bands at 1537 cm^{-1} and 1397 cm^{-1} are ascribable to the asymmetric and symmetric stretching vibrations of the equivalent carbon-oxygen bonds of COO^- group. Moreover, are visible the typical signals of monosubstituted aromatic ring: the in-plane skeletal vibration at 1595 cm^{-1} and the two adsorption bands at 719 cm^{-1} and 689 cm^{-1} due to the bending of the five adjacent hydrogen atoms of the ring.

Molecular modeling

Molecular modeling using an empirical force field was carried out in *Cerius*² modeling environment [27]. Initial model of the host structure was built according the crystallographic structure data obtained from refinement by means of Rietveld procedure. Unit cell of the host structure is trilayer, the space group is *R*-3*m* with triclinic cell and lattice parameters $a=3.07598$ Å, $c=23.2048$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$.

The Al and Zn atoms in the host layers were randomly distributed so that the composition of the host structure corresponded to the experimental one. The measured value of basal spacing, was $d_{\text{exp}}=15.5$ Å, thus the interlayer

distance in the initial model was set to this value. To investigate the arrangement of guest molecules in the interlayer space we built the supercell $4a \times 6a \times 1c$ with the lattice parameters: $4a=12.3039$ Å, $6a=18.4559$ Å, where the $c=3d_{\text{exp}}=46.5$ Å. The charge of this trilayer supercell is + 24 *el.*, that means 24 benzoate anions were placed into the interlayer space of the supercell, consisting of 3 host layers and 3 guest layers (i.e., 8 benzoates per one guest layer in the supercell).

A series of initial models have been built with various positions and orientations of guests and with variable water content:

- (1) Benzoate ring planes parallel to the host layers in bilayer or trilayer guest arrangement in the interlayer space.
- (2) Benzoate ring planes tilted to the host layers in bilayer guest arrangement in the interlayer space.
- (3) Benzoate ring planes perpendicular to the host layers and with various mutual orientations and various positions of COO^- groups with respect to OH groups on the host structure.

Energy minimization was carried out in *Universal force field* [28]. The electrostatic energy was calculated by Ewald summation method [29], van der Waals energy was expressed by Lennard-Jones potential [30]. The minimization of the total crystal energy was carried out in the *Minimizer* module according to the following strategy:

All the host layers in the supercell were kept as rigid units during energy minimization. Variable parameters were: c , α , β (this enables to optimize the mutual positions of the layers) and all atomic positions in guest layers. The minimization was carried out by modified Newton procedure.

The calculated structure models obtained from various starting geometries were sorted using two criteria:

- The value of crystal energy minimum.
- The similarity of calculated and measured diffraction pattern.

After reaching the optimum positions and orientation of guest molecules we tried to find the optimum water content and water location. As the water content has the significant influence on the total energy we could find the optimum water content. The following strategy was used: We compared the total nonbonded energy (i.e., sum of electrostatic and van der Waals interactions) of the optimized structure models containing various water content in the interlayer space. By using this procedure we can find out the affinity rate of water molecules to the interlayer space. On the other hand position of water molecules in the interlayer space affects strongly the intensity profiles in the diffraction pattern. This effect enables us to refine the water location.

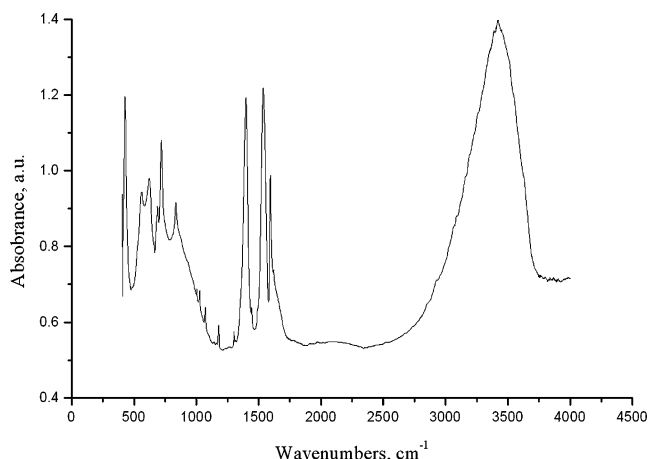


Fig. 2 IR spectra of the intercalated structure

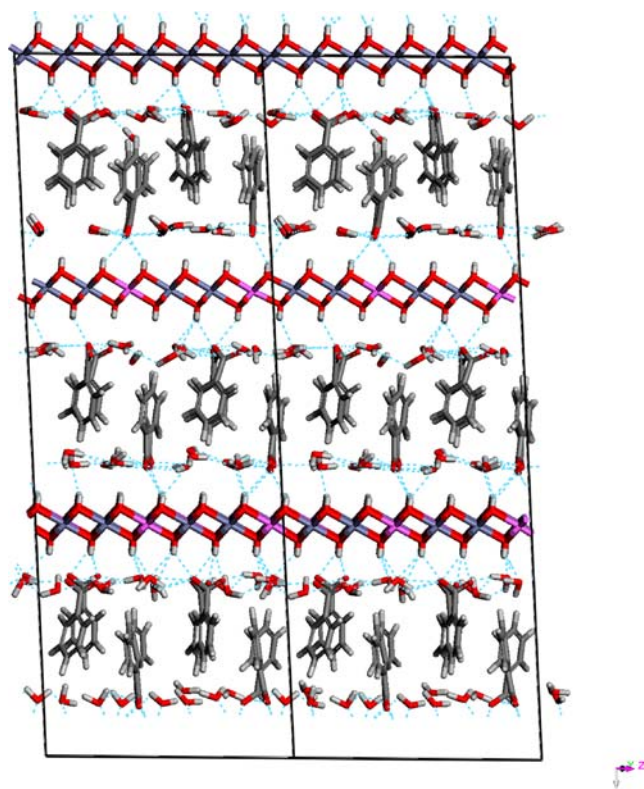


Fig. 3 Side view of the optimized structure with the hydrogen-bond interactions (broken line)

Results

Results of modeling led to the conclusions concerning the orientation and position of the benzoate anions in the interlayer space. The optimized structure model is shown in Fig. 3. The long axis of benzoate is oriented perpendicular to the hydrotalcite layers with small departure within the range of ± 10 degrees. COO^- groups are anchored to OH groups of the LDH layer via the hydrogen bond. The detailed view of orientation of COO^- groups with respect to OH groups is shown in Fig. 4. Carboxyl group can rotate freely along the C-C bond in long benzoate axis that means while the ring planes exhibit ordering, the orientation of carboxyl groups is disordered. Mutual orientation of the ring planes keeps parquet arrangement with a small departure within the range of ± 10 degrees (see Fig. 5a,b).

Mutual positions of two successive host layers in the intercalated structure exhibit a slight shift from their starting

Fig. 4 Detailed top view of the orientation of COO^- groups with respect to the OH groups (gray balls represent hydrogen atoms of OH groups of the layer)

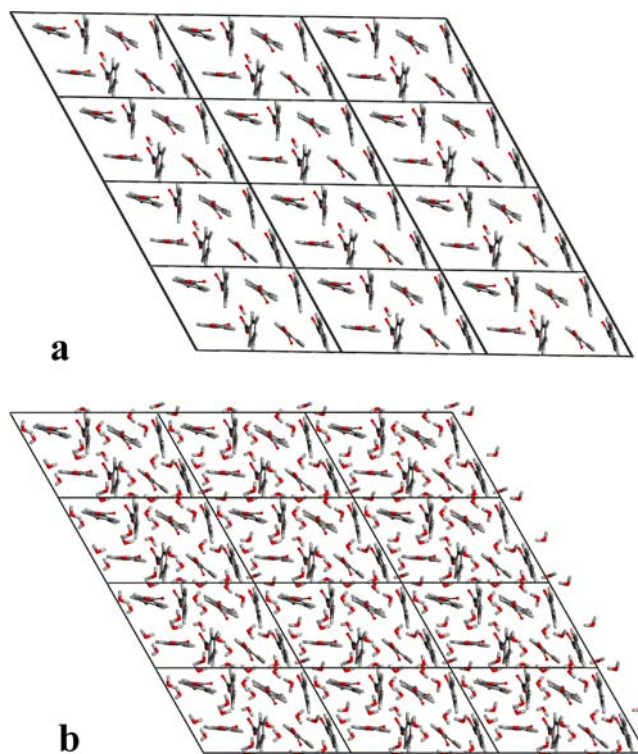
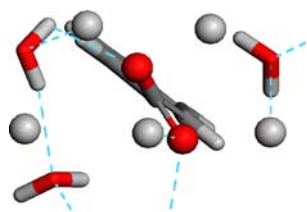


Fig. 5 **a)** Top view of parquet arrangement of the ring planes **b)** Top view of parquet arrangement of the ring planes and arrangement of water molecules

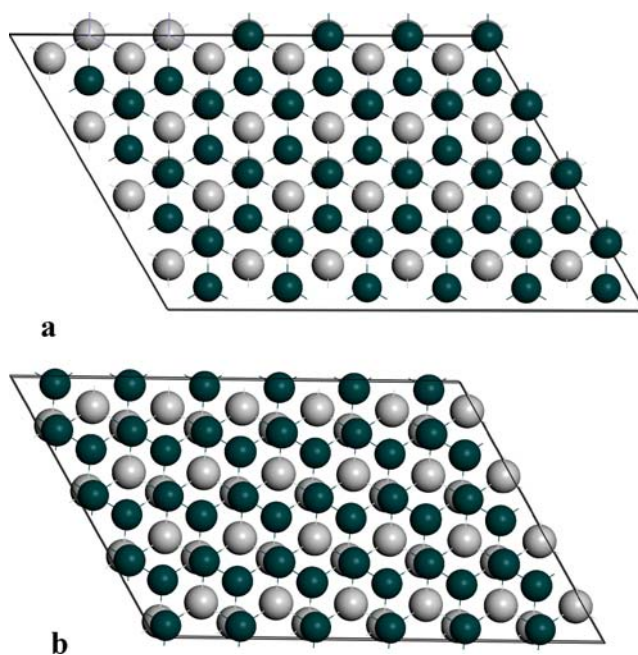
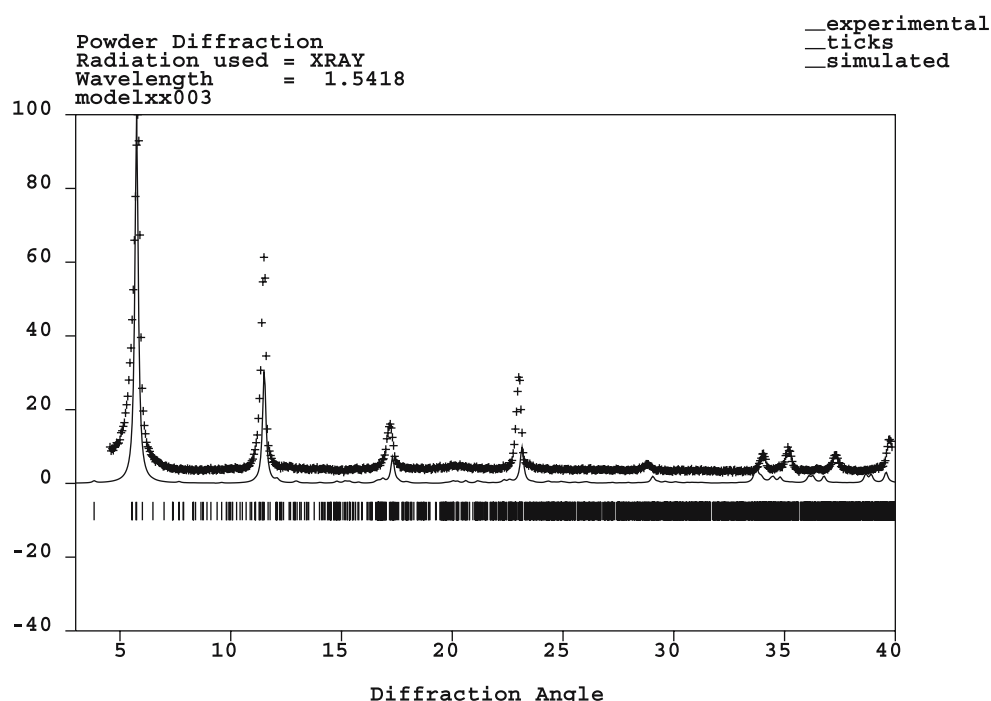


Fig. 6 **a)** Top view of stacking of two successive layers in the starting model (metal atoms represented by bright balls, oxygen atoms represented by dark balls) **b)** Top view of stacking of two successive layers in the optimized model (metal atoms represented by bright balls, oxygen atoms represented by dark balls)

Fig. 7 Calculated powder diffraction pattern

positions in the host structure. This shift in direction along metal - oxygen bonds is about 0.3 Å at maximum (see Fig. 6a,b).

The calculated diffraction pattern of the optimized structure is shown in Fig. 7. The higher intensity of basal reflection with respect to the others in comparison to the experimental diffraction pattern is due to the roughness of the surface of the experimental sample which is not taken into account in the calculating software. The roughness of the surface takes effect just at low values of diffraction angle and results in a decline of the intensity of basal reflection in the experimental diffraction pattern. Optimum water content found using energy minimization is 72 water molecules per unit cell, that means 24 H₂O in one guest layer, see Table 1. This water content is in good agreement with that estimated by thermogravimetric measurement. The location of water molecules refined using comparison of calculated and measured intensity ratio in the diffraction pattern is illustrated in Figs. 3 and 5b. Water molecules are not regularly distributed in the interlayer space, but concentrated in the two planes adjacent to the host layers

coinciding with the COO[−] planes, as they are hydrogen bonded to the OH groups in host layers and to carboxyl groups.

Discussion and conclusions

Molecular modeling enabled us to solve the crystal structure of benzencarboxylate-LDH intercalate, where the conventional diffraction analysis failed due to the slight structural disorder, caused by the slight disorientation of guests.

Molecular modeling provides not only the detailed structure model but in addition revealed the character of this disorder. There is a slight disorder arising from mutual slight shift of two successive host layers. This disorder in the host layers is a consequence of slight disorder in the orientation of guests (rotation about long guest axis), disorder in orientation of carboxyl groups and in position of guests on the host layers. Results of the present work show that molecular modeling is useful not only in

Table 1 Comparing the total nonbonded energy of models containing various number *n* of water molecules per one inter-layer space

<i>n</i>	<i>E</i> _{total} /kcal	<i>E</i> _{elst.} /kcal	<i>E</i> _{vdw} /kcal	<i>d</i> _{calc} /Å
20	−15051	−14830	−221	15,2
22	−15165	−14977	−188	15,2
24	−15363	−15167	−196	15,3
26	−15200	−15110	−90	15,3
28	−15110	−15050	−60	15,4

structure analysis but also in estimation of water content and guest concentration. The close cooperation of modeling and experiment is a necessary requirement for successful structure solution.

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**9.8 Mg-Al layered double hydroxides intercalated with porphyrin
anions: molecular simulations and experiments – P8**

Mg–Al layered double hydroxide intercalated with porphyrin anions: molecular simulations and experiments

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Abstract Molecular modeling in combination with powder X-ray diffraction (XRD) provided new information on the organization of the interlayer space of Mg–Al layered double hydroxide (LDH) containing intercalated porphyrin anions [5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS)]. Anion-exchange and rehydration procedures were used for the preparation of TPPS-containing LDH with an Mg/Al molar ratio of 2. Molecular modeling was carried out in the Cerius² and Materials Studio modeling environment. Three types of models were created in order to simulate the experimental XRD patterns of LDH intercalates with a TPPS loading of 70–80% with respect to the theoretical anion exchange capacity (AEC). The models represent single-phase systems with a 100% TPPS

loading in the interlayer space (Type 1) and models represent the coexistence of two phases corresponding to the total exchange from 75 to 92% (Type 2). To cover other possible arrangements, models with the coexistence of both TPPS and NO₃[−] anions in the same interlayer space were calculated (Type 3). The models are described and compared with experimental data. In all cases, guest TPPS anions are tilted with respect to the hydroxide layers, and are horizontally shifted to each other by up to one-half of the TPPS diameter. According to the energy characteristics and simulated XRD, the most probable arrangement is of Type 2, where some layers are saturated with TPPS anions and others are filled with original NO₃[−] anions.

Keyword Layered double hydroxide · Porphyrin · Molecular simulations · Intercalation · X-ray diffraction

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Introduction

Layered double hydroxides (LDHs), known also as hydrotalcite-like compounds or anionic clays, are layered materials with a chemical composition represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} [A^{n-}_{x/n} \cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n−} is *n*-valent anion, *y* is the number of water molecules, and *x* ranges usually between 0.20 and 0.33. The crystal structure is similar to that of brucite, Mg(OH)₂, where each Mg²⁺ cation is octahedrally surrounded by six hydroxyl groups and the adjacent octahedra share edges to form infinite sheets. The sheets are stacked and held together by non-bonded interactions. In the LDHs, the M^{II}/M^{III} isomorphous substitution in the octahedral sites of hydroxide

sheets results in a net positive charge that is compensated by anionic species localized together with water molecules in the interlayers.

A great number of LDHs with a variety of M^{II} and M^{III} cations in hydroxide layers and various interlayer anions have been reported. These materials have a wide range of applications, e.g., in polymer processing, heterogeneous catalysis, adsorption and decontamination processes, or pharmacy [1–4]. LDHs are often used as host structures for the loading of various organic anions. New applications of organic/inorganic hybrid materials based on intercalated LDHs have been proposed during the last decade, including analytical chemistry, electrochemistry, photochemistry (modified electrodes, sensors, etc.) [1, 5], pharmaceutical and biomedical applications (drug carriers, gene therapy) [2, 6, 7], or preparation of novel LDH/polymer nanocomposites [2, 8, 9]. In research and development of these hybrid materials, computer simulations represent a useful tool for obtaining an insight into the arrangement, properties, and dynamic behavior of interlayer organic species [10].

Molecular simulations allow information to be obtained about the structure and mutual interactions among constituents, including energy characteristics. Detailed descriptions of the interlayer structure, orientation and arrangement of interlayer species with respect to inorganic layers, and the influence of interlayer water molecules have been reported, e.g., citrate in LDH [11] or amino acids, phenylalanine, and tyrosine in LDH and montmorillonite [12]. Such simulations result in a more precise description of intercalated products compared to models based on stereochemistry and experimental data [13], allowing better understanding of individual interactions [14]. As the distribution and orientation of water molecules in the interlayer space are important factors for the resulting properties and arrangement of interlayer anionic species, the presence of water molecules cannot be neglected [10, 15, 16].

LDHs are characterized by relatively weak bonding between interlayer anions and hydroxide sheets, and these anions can be exchanged under suitable conditions. As carbonate anions show high affinity to hydroxide sheets, their replacement by anion exchange is very difficult. Therefore, the synthesis of LDHs containing specific interlayer anions requires carbonate- and CO_2 -free conditions. By contrast, interlayer Cl^- and NO_3^- anions can be exchanged easily, and the chloride and nitrate forms of LDHs are often used as precursors in anion-exchange reactions. An alternative procedure is the rehydration of mixed oxides obtained by thermal decomposition of LDHs containing volatile interlayer anions (e.g., CO_3^{2-} or NO_3^-). During heating of Mg–Al– CO_3 LDHs, interlayer water is released below 200 °C [1]. The dehydroxylation of

hydroxide layers and the loss of interlayer carbonate take place at higher temperatures (350–450 °C) followed by the collapse of the layered crystal structure to Mg–Al mixed oxides. These mixed oxides prepared at moderate calcination temperatures of 400–600 °C can be rehydrated in water. The rehydration process results in the reconstruction of the original layered structure, where compensating anions are anions dissolved in solution. Both anion-exchange and rehydration procedures can be used for intercalation of the desired anionic species into the LDH hosts.

The intercalation of intercalated porphyrin anions has practical consequences as [5,10,15,20-tetrakis (4-sulfonatophenyl)porphyrin (TPPS)] can be excited by visible light, and the formed porphyrin triplet states interact rapidly with oxygen molecules by energy transfer leading to the formation of singlet oxygen 1O_2 . Singlet oxygen is a highly reactive oxidation agent and it is generally accepted that 1O_2 [mostly $O_2(^1\Delta_g)$] is the main cytotoxic species in photodynamic therapy of cancer [17]. In our previous work, we described the structural and photophysical properties of LDH powders and oriented films with intercalated porphyrin sensitizers [5, 18]. We have shown that the behavior of the porphyrin triplet state in LDHs is similar to that in solution. The possibility of fabricating LDH-based films, the reactivity, and short lifetime of 1O_2 suggest that these hybrids are suitable for the construction of photoreactive surfaces, especially those with bactericidal properties.

The present work focuses on Mg–Al LDH intercalated with TPPS. The arrangement of similar structures was studied using various experimental and calculation techniques. For example, the basal spacing and the size of guest dianions were compared using semi-empirical molecular orbital calculations. The results revealed the fact that guest anions act as a bridge between two adjacent LDH layers, and the relationship between the anion size (terephthalate, 2,6-naphthalenedisulfonate, 1,5-naphthalenedisulfonate, and 2,7-naphthalenedisulfonate) and interplanar spacing [19, 20]. In the case of tetrasulfonated porphyrin intercalates, their perpendicular orientation with respect to the LDH layers was suggested [13, 21]. The shape of the porphyrin molecule is crucial because static and dynamic optical properties change consistently with the increase in the nonplanarity of the porphyrin macrocycle. This nonplanarity can give rise to polar excited states, affecting charge transfer processes. It is noteworthy that a macroscopic dipole moment may occur even when a distorted macrocycle is highly symmetric, and even in the absence of central metal effects [22]. All the above mentioned influences were taken into consideration for TPPS characterization and calculations.

Experimental methods

Preparation of samples

The tetrasodium salts of TPPS (Aldrich, St. Louis, MO), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaOH (all Penta, Prague, Czech Republic) were used as purchased.

Synthesis of Mg–Al LDH hosts

The hydrotalcite-like host in the nitrate form was prepared by coprecipitation. Aqueous solution (450 ml) of Mg and Al nitrates with an Mg/Al molar ratio of two and a total metal ion concentration of 1.0 mol l^{-1} was added at a flow rate of 7.5 ml min^{-1} to a 1,000 ml reactor containing 200 ml distilled water. The flow rate of simultaneously added 3 M NaOH was controlled to maintain a pH value of 10.0 ± 0.1 . Carbonate-free distilled water was used for dissolution of components and the reaction was carried out under nitrogen to avoid any contamination of the product with carbonate anions. Coprecipitation proceeded under vigorous stirring at 75°C and the resulting suspension was stirred for 1 h at 75°C . The product was filtered off, washed several times with carbonate-free distilled water, and dried at 60°C . The obtained product was denoted as $\text{Mg}_2\text{Al-NO}_3$ based on the Mg/Al molar ratio of Mg and Al nitrates in the solutions used.

Anion exchange

The LDH precursor $\text{Mg}_2\text{Al-NO}_3$ was dispersed in a carbonate-free aqueous solution (400 ml) of TPPS (0.001 M, pH 9 adjusted by 3 M NaOH). After mixing the components, the suspension was sealed in a 500 ml glass bottle under nitrogen and stirred for 6 days at 30°C . The intercalated product was filtered off, washed with carbonate-free distilled water, and dried at 60°C . The LDH host/porphyrin molar ratio was adjusted to achieve 100% loading with respect to the theoretical anion-exchange capacity (AEC) using a 10% molar excess of porphyrin. The product was denoted as $\text{Mg}_2\text{Al/TPPS-AE}$.

Rehydration procedure

The LDH precursor $\text{Mg}_2\text{Al-NO}_3$ was heated for 4 h at 450°C in air and then cooled in a desiccator to room temperature. The Mg–Al mixed oxide obtained was dispersed under nitrogen in 75 ml of a carbonate-free aqueous solution of TPPS (0.001 M, pH 9 adjusted by 3 M NaOH) and placed in a 100 ml Teflon-lined stainless steel bomb. The rehydration reaction was carried out under hydrothermal conditions at 120°C and autogenous

pressure for 20 h. The rehydrated product was filtered off, washed with carbonate-free distilled water, and dried at 60°C . The Mg–Al mixed oxide/porphyrin molar ratio was adjusted to achieve 100% loading with respect to the theoretical AEC of the resulting LDH, using a 10% molar excess of TPPS. The sample obtained was labeled by $\text{Mg}_2\text{Al/TPPS-R}$.

Characterization of the products

The phase composition of the prepared products was determined by powder X-ray diffraction (XRD) using a Siemens D5005 diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K_α radiation ($\lambda = 0.1542 \text{ nm}$, 40 kV, 30 mA, diffracted beam monochromator) in the 2θ range ($2\text{--}80^\circ$, step size 0.02° , 10s/point). The qualitative analysis was performed with the HighScore software package (PANalytical, Almelo, the Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, version 8.0), and JCPDS PDF-2 database. The magnesium and aluminum content was determined by volumetric analysis after dissolution of the samples in concentrated sulfuric acid. The content of intercalated porphyrin was estimated using UV-vis spectroscopy by measurement the absorption spectra of solutions before and after the intercalation process on a PerkinElmer Lambda 35 spectrometer. The content of interlayer water was estimated using the thermal analysis (simultaneous TGA/DSC/DTA QMS) on a NETZSCH apparatus STA 409 coupled with a quadrupole mass spectrometer Balzers QMG 420 (air atmosphere with a flow rate of 75 ml/min, heating rate of 10 K/min, gaseous products, i.e., $18\text{-H}_2\text{O}^+$, 44-CO_2^+ , and 46-NO_2^+ were continually monitored).

Molecular modeling

Molecular mechanics and classical molecular dynamics [23] were carried out in the Cerius² and Materials Studio modeling environment [24]. The host framework of $\text{Mg}_2\text{Al-NO}_3$ is a trilayered structure with a trigonal cell in hexagonal axes. The space group is R-3m. The cell parameters $a=b=3.046 \text{ \AA}$ were determined from experimental XRD patterns. The layer of the composition $[\text{Mg}_{32}\text{Al}_{16}(\text{OH})_{96}]^{16+}$ with a total charge of +16 is composed of 48 linked individual cells (lattice parameters: $A=18.276 \text{ \AA}$ and $B=24.368 \text{ \AA}$) with Al cations distributed regularly on condition that the location of Al cations in neighboring octahedra is excluded [25].

The basal spacing of the initial models was set to the mean value obtained from the experimental XRD data ($d_{003}=22.1 \text{ \AA}$, see below). Porphyrin TPPS was built in the 3D-Sketcher module [24]. Sazanovich et al. [22] reported a geometry of porphyrin derivatives from a semiempirical

point of view; the geometry and optical properties were investigated by successive addition of ethyl substituents at beta-pyrrole positions of free-base 5,10,15,20-tetraphenyl porphyrin (TPP). Semiempirical calculations indicated that the TPP molecule has a planar geometry. We started calculations using various force fields (Universal, Dreiding, Cff, Pcff) [26–30]. Porphyrin TPPS was built by the adding of SO_3^- groups at the *p*-positions of the phenyl rings, and the optimized planar geometry of TPPS used for subsequent calculations was obtained in the Dreiding force field parameters, which were able to maintain the planar geometry. The distance between two neighboring sulfur atoms of SO_3^- groups in TPPS is of 13.4 Å and the diagonal distance between two sulfur atoms is 19.0 Å.

The number of water molecules and TPPS tetraanions intercalated into the interlayers was determined by experimental measurements. Based on thermogravimetry, we estimated the water content to be 3.6–4.5 water molecules per $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]^{2+}$ unit. Therefore, our models contained four water molecules per $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]^{2+}$, which corresponds to the reported amount of interlayer water in the LDH precursor [3]. The analysis of TPPS solutions before and after intercalation procedures indicated that the achieved TPPS loading with respect to the theoretical AEC was approximately 70–80% [5].

Costantino et al. [31] and Miyata [32] reported the preparation and properties of LDHs containing various loadings of organic anions in the interlayer space. They showed that increasing the loading of organic anions in the interlayer results in changes in the positions and intensities of diffraction lines in powder XRD patterns. Since the TPPS loading in investigated samples was up to about 80% of AEC, we built three types of structure models. The aim was to obtain the optimized geometries and, by comparing the experimental and calculated X-ray diffraction patterns of the models, to address the most probable porphyrin orientations in real samples.

Type 1: The structure models have 100% TPPS loading in the interlayer space. A set of models with various orientations of guest porphyrin anions with respect to each other and to the LDH layers was created containing water molecules localized near the LDH layers. The total composition of the supercell was $\text{Mg}_{96}\text{Al}_{48}(\text{OH})_{288}(\text{TPPS})_{12} \cdot 96\text{H}_2\text{O}$.

Type 2: These models represent a coexistence of two phases, with an overall TPPS loading of 75, 83, and 92%. For this purpose, we created a supercell consisting of 12 hydroxide layers with 9, 10, or 11 interlayers completely exchanged for TPPS anions respectively, while the remaining interlayers contained original NO_3^- anions. The d_{003} basal spacing of the nitrate LDH precursor was

set to the value of 8.77 Å. The cell parameters of the investigated supercells were: $A=18.276$ Å, $B=24.368$ Å; the C parameter depended on the total TPPS loading. The total compositions and C values of the supercells were as follows: $[\text{Mg}_{384}\text{Al}_{192}(\text{OH})_{1152}][(\text{TPPS})_{36}(\text{NO}_3)_{48} \cdot 384\text{H}_2\text{O}]$ and $C = (9 \times 22.1 + 3 \times 8.77) = 225.21$ Å, $[\text{Mg}_{384}\text{Al}_{192}(\text{OH})_{1152}][(\text{TPPS})_{40}(\text{NO}_3)_{32} \cdot 384\text{H}_2\text{O}]$ and $C = (10 \times 22.1 + 2 \times 8.77) = 238.54$ Å, and $[\text{Mg}_{384}\text{Al}_{192}(\text{OH})_{1152}][(\text{TPPS})_{44}(\text{NO}_3)_{16} \cdot 384\text{H}_2\text{O}]$ and $C = (11 \times 22.1 + 8.77) = 251.87$ Å for supercells with a TPPS loading of 75, 83, and 92 %, respectively. We created models with various interlayer sequences, e.g., TPPS, NO_3^- , TPPS, TPPS, NO_3^- , etc., and models representing two segregated phases loaded with TPPS and NO_3^- (i.e., the sequences TPPS, TPPS,..., NO_3^- , NO_3^- ,...). In the latter case, the models consisted of 9 and 10 successive interlayer regions with TPPS and the remaining successive interlayers were saturated by NO_3^- . This corresponds to a total TPPS loading of 75 and 83 %, respectively.

Type 3: The models suggest the coexistence of both TPPS and NO_3^- anions in each interlayer space. Thus, the models corresponding to the total 75% TPPS loading contained three TPPS tetraanions, and the remaining positive layer charge was compensated by four NO_3^- anions. Models with various orientations of TPPS anions with respect to each other and to the hydroxide layers were created and NO_3^- anions were distributed randomly. The composition of the final supercell was $\text{Mg}_{96}\text{Al}_{48}(\text{OH})_{288}(\text{TPPS})_9(\text{NO}_3)_{12} \cdot 96\text{H}_2\text{O}$ with the lattice supercell parameters $A=18.276$ Å, $B=24.368$ Å, and $C = 3 \times d_{003} = 66.3$ Å.

To be able to describe all the atoms in the models and the energy characteristics, the initial models were minimized in the Universal force field. Charges were calculated using the Qeq method (charge equilibrium approach) [33], the electrostatic energy was calculated using the Ewald summation method [34], and the van der Waals energy was calculated using the Lennard-Jones potential [35].

Minimization was carried out in the Minimizer module according to the following strategy: first, the minimization of the models with 100% loading of TPPS in the interlayer was carried out (Type 1) to obtain the optimized positions of the guests with respect to the host layers. These arrangements were later used in the models of Type 2. LDH layers were kept as rigid units during the energy minimization. The cell parameters c , α , and β were variable, which allowed the mutual position of individual

layers to be refined, and the calculations to be accelerated. In the case of the Type 2 models, the cell parameters and the atoms of the host layers, except for hydrogen atoms of the OH groups were kept fixed during energy minimization. All positions of atoms in the interlayer were variable. The minimization strategy in the Type 3 models was the same as in the case of Type 1. The geometry of the minimized models was then refined by quench dynamics, a type of dynamics simulation where new arrangements of the interlayer space are generated. After a given number of dynamics steps the structure model is minimized, allowing elucidation of the dependence of the total crystal energy on the arrangement of the species in the interlayer space and their geometry. It helps to determine the most probable interlayer arrangement. The dynamics simulations were carried out in an NVT statistical ensemble (N = constant number of atoms, V = constant volume, T = constant temperature) at 300 K. One dynamic step was 0.001 ps and 70–100 ps of dynamics were carried out. During quench dynamics, all positions of atoms in the interlayer space and hydrogen atoms of the hydroxide OH groups were variable, while the positions of the remaining atoms in the layers were kept fixed. After that, the selected partially minimized structures were minimized to obtain the final structure models.

Results and discussion

Characterization of the prepared samples

Chemical analysis of the $\text{Mg}_2\text{Al-NO}_3$ precursor showed that the Mg/Al molar ratio corresponds to that adjusted in nitrate solutions used for coprecipitation. The chemical formula $\text{Mg}_{2.03}\text{Al}_{1.00}(\text{OH})_{6.06}(\text{NO}_3) \cdot 1.2\text{H}_2\text{O}$ was determined from the results of chemical and thermal analysis. In the powder XRD patterns of the coprecipitated $\text{Mg}_2\text{Al-NO}_3$ sample, only a well-crystallized hydrotalcite-like phase, as indicated by the hexagonal lattice of the rhombohedral symmetry, was found (Fig. 1). The successful intercalation of bulky porphyrin anions into the LDH interlayer space was confirmed by a marked shift of the basal (003) diffraction line towards lower diffraction angles, i.e., the d_{003} value increased from 8.77 to 22.1 Å for $\text{Mg}_2\text{Al-NO}_3$ and $\text{Mg}_2\text{Al/TPPS-AE}$, respectively (Fig. 1). Similarly, the other basal diffraction lines, e.g., (006), were shifted.

Rehydration of the calcined $\text{Mg}_2\text{Al-NO}_3$ precursor resulted in the formation of the corresponding hydroxide form ($\text{Mg}_2\text{Al-OH}$). This phase of the chemical composition $\text{Mg}_{1.98}\text{Al}_{1.00}(\text{OH})_{5.96}(\text{OH}) \cdot m\text{H}_2\text{O}$ is characterized by a d_{003} basal spacing of 7.63 Å. The intercalated phase with d_{003} of 21.4 Å together with the admixture of the $\text{Mg}_2\text{Al-OH}$ phase

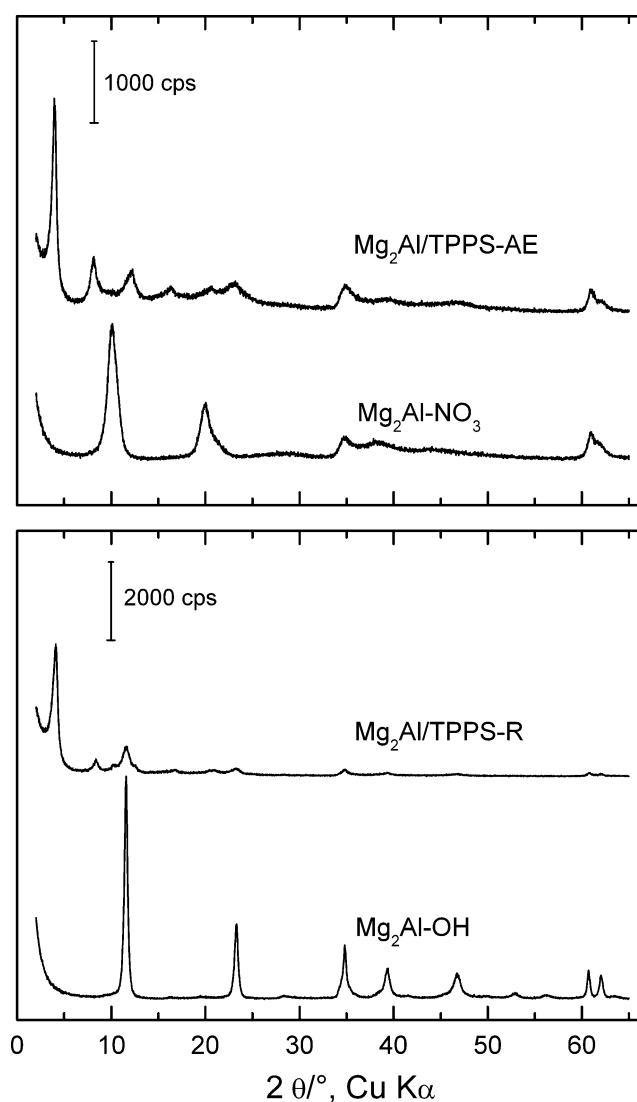


Fig. 1 Powder X-ray diffraction (XRD) patterns of Mg-Al layered double hydroxide (LDHs) intercalated with 5,10,15,20-tetrakis (4-sulfonatophenyl)porphyrin (TPPS) by anion exchange (AE) and rehydration (R) procedures: $\text{Mg}_2\text{Al-NO}_3$ coprecipitated sample for anion exchange, $\text{Mg}_2\text{Al-OH}$ product obtained by rehydration of calcined $\text{Mg}_2\text{Al-NO}_3$ sample in distilled water, $\text{Mg}_2\text{Al/TPPS}$ intercalated products obtained using concentration conditions for 100% porphyrin loading with respect to the theoretical anion exchange capacity (AEC)

were found in the samples rehydrated in porphyrin-containing solutions (Fig. 1). The d_{003} value of the intercalated phase was close to that determined for the sample prepared by anion exchange. Evidently, during the rehydration process hydroxide anions in the interlayer space of the rehydrated product are substituted by porphyrin anions. The rehydrated samples exhibited slightly lower TPPS loading (about 70%). The presence of the parent nitrate LDH phase in $\text{Mg}_2\text{Al/TPPS-R}$ is in accordance with the measured TPPS loading of 70 % with respect to AEC.

The orientation of porphyrin anions within the interlayer space can be roughly estimated by comparing the interlayer distance with the size of porphyrin molecules. Taking into account the thickness of the hydroxide sheet (~ 4.8 Å), the interlayer distance corresponds to about 17 Å. The adjacent sulfur atoms of TPPS are separated by about 13.4 Å and the most remote oxygen atoms of the adjacent SO_3^- groups are about 16.3 Å away. In addition, water molecules forming organized sheets close to the polar hydroxide surfaces contribute to the measured basal spacing [36]. The proportions indicate that two adjacent sulfonate groups of porphyrin anions interact with a hydroxide sheet via the hydroxyl groups of the positively charged sites. The opposite hydroxide sheet compensates for two remaining sulfonate groups. We have carried out the molecular modeling calculations using the parameters of the prepared LDH phases. The agreement between measured and calculated XRD diffraction lines of simulated systems allows for obtaining detailed information on the orientation of porphyrin moieties with respect to the hydroxide sheets, on the structure of porphyrin anions upon interaction with hydroxide sheets, and on the relative stability of the phase with mixed intercalated anions (i.e., Type 3). The results obtained are discussed below in more detail.

Molecular modeling

Molecular simulations combined with XRD resulted in a potential arrangement of the guest anions in the interlayer space and provided insights into the energy characteristics and location of water molecules. The calculated powder XRD patterns of the models representing one phase and the models representing the coexistence of two phases are described and compared with the experimental measurements in Fig. 2. The LDH basal diffraction lines were present at intervals of 2θ from 3 to 25° . Because the XRD module used does not take into account the roughness and bending of the hydroxide layers (the LDH layers were kept as rigid bodies), the calculated XRD patterns exhibit lower relative intensities of diffraction lines in comparison with the measured lines.

Single-phase models (Type 1 and Type 3)

Before discussing the XRD diffraction patterns, we will address possible horizontal arrangements of TPPS anions in the interlayer space. Calculations were performed for both Type 1 and Type 3 models. We present the three most different arrangements. The top views of the linked cells of Type 3 are presented in Figs. 3, 4, and 5. The arrangement A in Fig. 3 is characterized by the following features: (1) the porphyrin moieties tend to be parallel to each other with approximately $\pm 10^\circ$ variability; (2) the porphyrin moieties

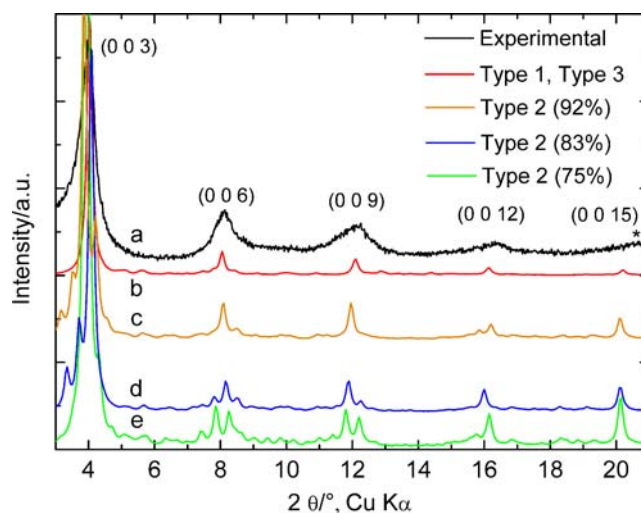
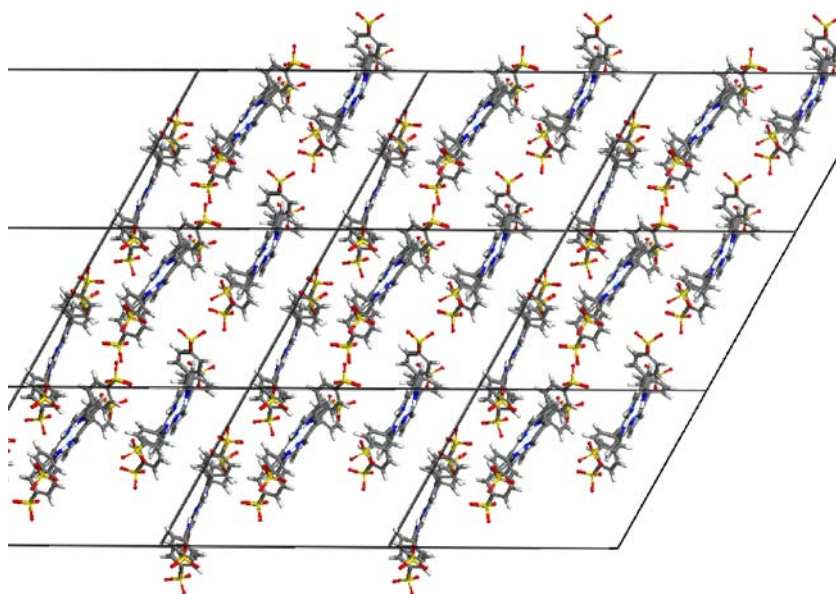


Fig. 2 Powder XRD patterns of $\text{Mg}_2\text{Al/TPPS-AE}$: comparison of experimental (a, impurity is labeled by *) and calculated XRD for single-phase (Type 1 and Type 3; b) and two-phase models (Type 2) with 92 (c), 83 (d) and 75% (e) exchange

are horizontally shifted by about 6 Å, i.e., approximately one-half of the TPPS anion size; and (3) the arrangement of TPPS anions in the interlayer space is disordered. The alternative arrangement B (Fig. 4) shows that (1) guest TPPS anions are more ordered than in A, (2) TPPS are arranged in rows following the $[110]$ crystallographic direction, and (3) the guest anions are parallel and horizontally shifted similar to arrangement A (about 6 Å). Arrangement C (Fig. 5) has disordered rows of guest anions with variations in the mutual horizontal shift equal to about one-fourth of the TPPS anion size (4 Å). In all cases the remaining positive charges are compensated by NO_3^- located near the hydroxide layers. The sublimation energies per single interlayer are given in Table 1. The energy characteristics, i.e., electrostatic and van der Waals interactions, and the total energies differ only slightly ($<1\%$). Therefore, all three arrangements can be adopted with the same probability, and a combination in which each interlayer was filled with the different arrangement in the sequence A, B and C was used for subsequent calculations. In the case of Type 1 models, the sublimation energy values per one interlayer differ in the range of 9% and therefore the arrangement A in Fig. 3 is more probable than those in Figs. 4 and 5. The powder XRD patterns of the Type 3 model are similar to experimental data (Fig. 2, traces a and b).

The calculated XRD patterns of Type 1 are characterized by five sharp basal diffraction lines (003), (006), (009), (0012) and (0015) in the 2θ interval from 3 to 25° (Fig. 2b) and match the measured patterns. The corresponding side view of the interlayer arrangement of porphyrin anions in the Mg_2Al -lattice with a d_{003} basal spacing of 22.2 Å is shown in Fig. 6a. The guest anions are not arranged perpendicularly with respect to the hydroxide sheets. The

Fig. 3 Top view of linked cells describing a disordered arrangement of TPPS anions (Arrangement A)



tilted angle measured between the host layer and tangent of the pyrrole units ranges from 53 to 63°. For comparison, Fig. 6b shows an example of the arrangement of the Type 3 model containing the single phase with 75% TPPS loading. Here, the porphyrin units are tilted less from the layer normal due to a lower concentration of TPPS, and the angle between the host layer and porphyrin planes ranges from 68 to 71°.

The relative energy of repulsive interactions between TPPS anions is of 343 ± 13 kcal mol⁻¹ per TPPS, and between TPPS and NO₃⁻ is of 347 ± 17 kcal mol⁻¹ per TPPS (Type 3). In addition, the attractive interactions between TPPS anions and the layers are $1,844 \pm 63$ kcal mol⁻¹ per TPPS. The attractive interactions between TPPS anions and the layers in Type 1 models are $1,842 \pm 63$ kcal mol⁻¹ per TPPS. However, the models differ

in the repulsive energy between the guest anions as this energy is about two times higher than in the case of Type 3. Evidently, this is because of the closer distance between TPPS moieties (ca. 5 Å) than in the Type 3 model (i.e., 6–8 Å). The higher repulsive interactions of the guests explain the differences between the tilted angles of the TPPS planes. The powder XRD patterns of the two models are very similar; therefore, only one XRD is shown in Fig. 2.

Two-phase models (Type 2)

The powder XRD patterns of the Type 2 model containing the interlayers saturated either with NO₃⁻ (L-NO3) or with TPPS (L-TPPS) anions are compared with those of the single-phase models in Fig. 2. The effect of the increasing total loading with TPPS anions on the XRD profiles is

Fig. 4 Top view of an ordered arrangement of TPPS anions into the rows that follow the [1 1 0] direction (Arrangement B)

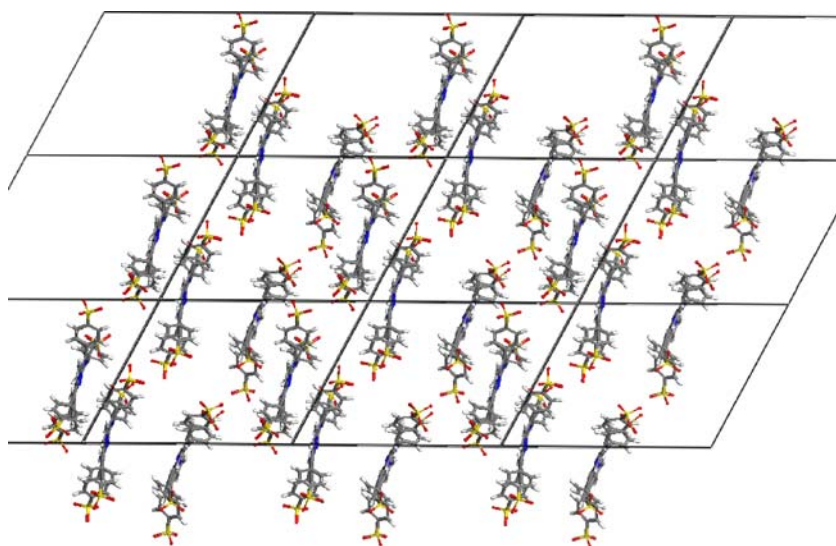
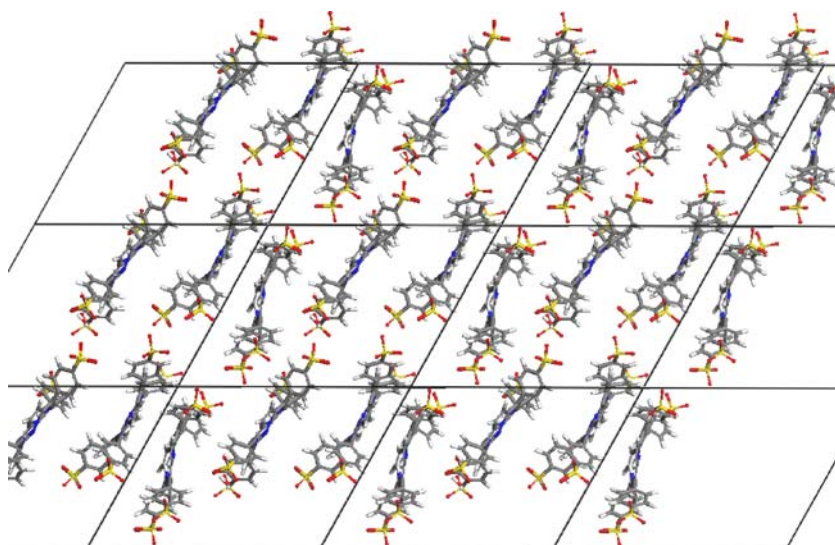


Fig. 5 Top view of an arrangement of TPPS anions into the rows that follow the [1 0 0] direction (Arrangement C)



evident. The calculated XRD patterns belong to the models containing a fully saturated part, with TPPS segregated from the non-exchanged part containing NO_3^- . The sequences with random alternation of individual interlayers (e.g.,...,TPPS, NO_3^- , TPPS, TPPS, NO_3^- ,...) exhibit considerable differences from the measured XRD patterns. Therefore, we have focused predominantly on consecutive sequences with a various number of individual interlayers (e.g.,...,TPPS, TPPS, NO_3^- , NO_3^- ,...).

In all cases, the powder XRD patterns are characterized by a sharp and intensive (003) diffraction line at 2θ ranging from 3.9 to 4.1° depending on the calculated model. These 2θ values correspond to the basal spacing values ranging from 21.7 to 22.8 Å, and are quite similar to the experimental value of 22.1 Å. The presence of non-exchanged LDH interlayers causes a splitting of the diffraction lines due to a mixing of the interlayers (L-TPPS, L- NO_3) on the nanometer scale. This is especially obvious for the diffraction lines around 8° and 12° , which are labeled as (0 0 6) and (0 0 9) in the single-phase models, respectively. In the case of Type 2 (75%), the supercell with 12 interlayers containing 9 L-TPPS and 3 L- NO_3 interlayers leads to the splitting of the diffraction line (0 0 6) into two at 2θ of 7.9 and 8.3° . Similarly, the line

(0 0 9) splits into two at 11.8 and 12.2° . The splitting of (0 0 3) line ($2\theta=4.3^\circ$) also occurs. The model Type 2 (83%) (10 L-TPPS+2 L- NO_3) is characterized by the central line with 2θ of 8.2° that is close to the (0 0 6) line of the single-phase models and by two symmetrically localized peaks. The line at $2\theta=11.9^\circ$ is surrounded by a weak line at 12.2° . The line with 2θ of 4.1° exhibits the additional contribution of lines at 3.3 and 3.7° . On the contrary, there is no influence of the non-exchanged layer in the Type 2 (92%) composed of 11 L-TPPS and 1 L- NO_3^- on the positions of the lines at 2θ of 8.1 and 12.0° . These are very similar to the (0 0 6) and (0 0 9) lines of the single-phase models. The intensive diffraction line at 3.9 is accompanied by the low intensity peaks at 3.2 and 3.5° similarly to Type 2 (83%).

Summing up, the presence of two phases can contribute to the broadening of the diffraction lines. If we compare the calculated XRD patterns, it is clear that both single-phase (i.e., Type 1 and Type 3) and two-phase (i.e., Type 2) models are possible. The observed broadening in the experimental XRD lines is determined by the low crystallinity of the samples that is a typical feature of coprecipitated LDHs composed of Mg and Al, thus overlapping the possible split of the diffraction lines. Since the structural calculated models are perfectly periodic, the broadening of the peaks is not observed in the calculated patterns.

While the comparison of calculated and experimental XRD patterns cannot give an explicit distinction between single- and two-phase models, the values of sublimation energy offer solid arguments. We compared the total sublimation energy of the single-phase model [12-layered supercell with a mixture of 3 TPPS and 4 NO_3^- anions in each interlayer space (Type 3) with that of the two-phase model having the same TPPS loading (Type 2; 75%). The total sublimation energies for the Type 3 and Type 2 (75%) models are $-46,780$ kcal mol $^{-1}$ and $-116,960$ kcal mol $^{-1}$,

Table 1 Sublimation energy characteristics (van der Waals (vdW) and electrostatic interactions and their sum per TPPS) of three arrangements of the guests for the Type 3 model

Arrangement	E_{total} / kcal/mol	vdW/ kcal/mol	Electrostatic/ kcal/mol
A	-1,258	-38	-1,220
B	-1,232	-37	-1,195
C	-1,209	-39	-1,170

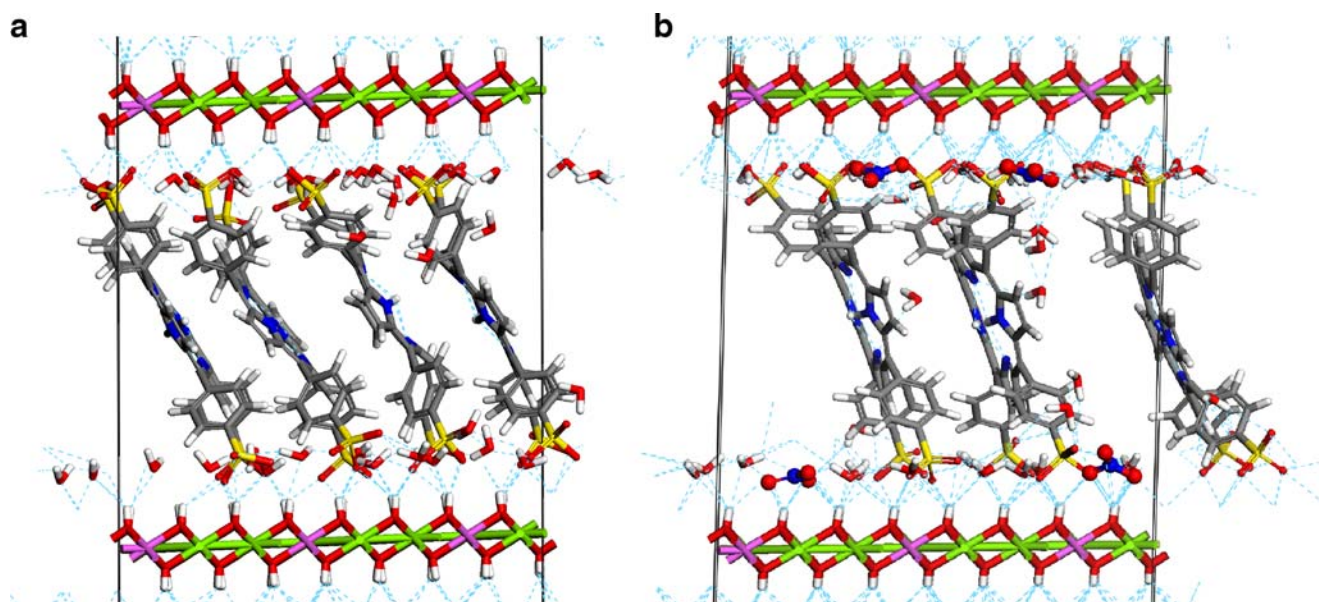


Fig. 6 Side view of the interlayer space in the Mg_2Al -lattice of Type 1 (**a**) and of Type 3 with NO_3^- anions located near LDH layers (**b**). Blue lines Hydrogen bonds

respectively. This indicates that the Type 2 model is more favorable than mixed anions in interlayers. Based on these arguments we suggest that the partial exchange of original anions in real samples leads to consecutively arranged interlayers filled with TPPS anions followed by others containing only original NO_3^- anions.

Geometry of TPPS anions

In general, the original flat moiety of TPPS anions (Fig. 7a) changes during dynamics simulations depending on the mutual arrangement of the guest anions, their location in the interlayer space, and the angle of tilt with respect to the host layers. There is continuous variation between two limited cases: the porphyrin moieties remain nearly planar, with small deviations from the original planar geometry (Fig. 7b), or are settled into the saddle conformation (Fig. 7c). In both cases, the phenyl rings with SO_3^- groups do not exhibit any significant bending or twisting with respect to the original porphyrin geometry. The models containing deviated guest anions in the interlayer space exhibit slightly different total energy when compared with the models based on nearly planar TPPS structure. Thus, from an energy point of view, the original planar geometry of TPPS anions might deviate after porphyrin interactions with the hydroxide sheets within the interlayer space. The water molecules are located near the hydroxide layers. In the presence of a lower concentration of TPPS (Type 3), a small amount of water (five molecules per supercell) can be located between the porphyrin cores and can interact with the pyrroles via hydrogen bonds. In the case of full saturation

with TPPS anions, water molecules are located near the hydroxide layers.

Conclusions

Molecular simulations were used to describe the arrangement of the interlayer space of Mg-Al LDH intercalated

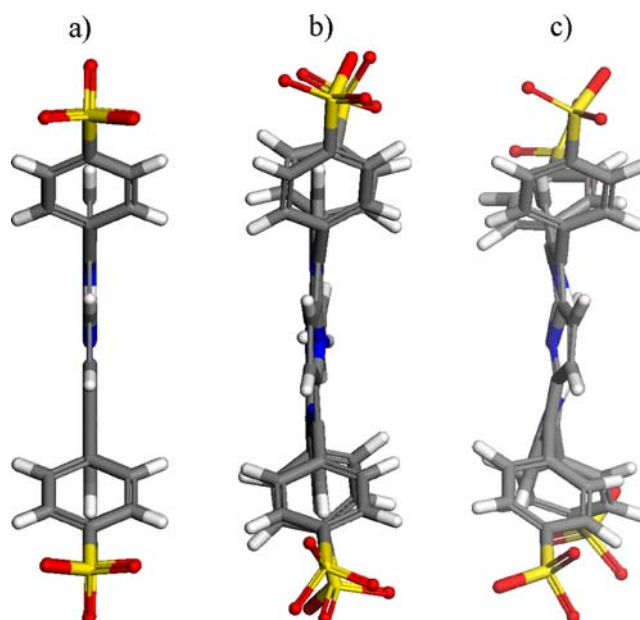


Fig 7a–c Geometry of TPPS. Original flat moiety (**a**) and two limited cases in the interlayer space obtained by molecular simulations—nearly planar geometry (**b**) and TPPS in the saddle conformation (**c**)

with TPPS anions. The calculations were performed for three types of structure models: (1) the complete saturation of the interlayer space by TPPS (Type 1), (2) two-phase models where a part of the interlayers was consecutively saturated with TPPS anions followed by the interlayers containing NO_3^- anions (Type 2), and finally (3) mixed TPPS and non-exchanged NO_3^- anions in the same interlayer space (Type 3). The tilted angle of TPPS anions was slightly affected by the TPPS concentration in the interlayer. In the Type 1 and Type 3 models, the tilted angle ranged from 53 to 63° and from 67 to 71° , respectively. In all cases, TPPS anions were horizontally shifted by up to one-half of the TPPS diameter. The powder XRD patterns are very similar for Type 1 and Type 3 and are characterized by sharp basal diffraction lines, while Type 2 exhibits splitting of the diffraction lines depending on the saturation of the supercell by TPPS anions. This splitting can cause broadening of the diffraction lines. The comparison of sublimation energy characteristics of Type 2 and Type 3 models with 75% saturation by TPPS (i.e., the value close to the experimental loading) revealed that the Type 3 model is energetically less favorable. Hence, we suggest that the most probable arrangement of interlayers in partially exchanged samples is of Type 2, with consecutive interlayers saturated by TPPS anions and the remaining interlayers containing NO_3^- anions.

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9.9 Porphyrins Intercalated in Zn/Al and Mg/Al Layered Double

Hydroxides: Properties and Structural Arrangement – P9

Porphyrins Intercalated in Zn/Al and Mg/Al Layered Double Hydroxides: Properties and Structural Arrangement

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The arrangement of porphyrin molecules in the interlayer space of layered double hydroxides (LDH) has been studied by a combination of experimental techniques and molecular dynamics simulations. Intercalation of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrins (TPPS) into Zn_RAl and Mg_RAl LDH hosts led to a gallery height of about 15.5 Å that is comparable with the size of the porphyrin molecules. The porphyrin sulfonate groups are located at about 4 Å from the center of the hydroxide layers that is consistent with hydrogen bonding interactions between the sulfonate groups and OH groups of the layers. The aromatic ring system in the middle of the gallery is rather disordered. A large number of in-plane diffraction lines suggests that the rigidity of the porphyrin framework has a beneficial effect on the layer ordering. Molecular dynamics simulations are in agreement with the experimental results showing that the interlayer space is filled with nearly parallel porphyrin units with a slightly inclined orientation of the porphyrin planes with respect to the normal of the hydroxide layers. The photophysical experiments proved that TPPS in Mg₂Al LDH hosts produce O₂(¹Δ_g) with long effective lifetimes. The LDH hybrids based on intercalated porphyrin sensitizers are suggested as new photofunctional materials.

Introduction

The prospect of obtaining novel materials gave impetus to studies of molecules immobilized in clays, layered double hydroxides (LDH), zeolites, or sol–gel derived matrices.^{1–7} Layered solids are materials that can be functionalized by intercalation of active molecules with specific properties. In this case, layered structures act as hosts with a two-dimensional expandable interlayer space for the placement and organization of guest molecules. The intercalated solids not only provide an easy-to-apply transport material, but mostly increase chemical, photochemical, and thermal stability of guests including the

control of their release during applications.^{8,9} The constrained geometry, enforced by host–guest noncovalent interactions, is reflected in physicochemical and photophysical properties of guest molecules.¹⁰

LDH are nanostructured materials of the general formula [M_{1-x}²⁺M_x³⁺(OH)₂]_{A_{x/m}^{m-} · nH₂O, abbreviated hereafter as M_R²⁺M³⁺–A, where M²⁺ and M³⁺ are divalent and trivalent cations, respectively, A is an anion of valence *m* and *R* = (1 – *x*)/*x* is the M²⁺/M³⁺ molar ratio. Their lamellar structure consists of brucite-like layers of positive charge counterbalanced by anionic species in the interlayer space together with water molecules.^{11,12} LDH have attracted much attention owing to their ability to intercalate a wide variety of anions, either organic or inorganic. As a consequence, LDH have found potential applications in catalysis,¹³ wastewater treatment,^{14–16} electrochemical sensors,¹⁷ or as fillers in polymers.¹⁸ Furthermore, LDH are environmentally friendly, biocompatible}

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materials with possible use as drug stabilizers and carriers.^{19,20} The important features are the flexibility of the two-dimensional interlayer space and the variable charge density of the hydroxide layers (x usually lies between 0.20 and 0.35) allowing the incorporation of variable amounts of bulky guest molecules^{21,22} including porphyrins and phthalocyanines.^{1,23–27}

Porphyrins and related macrocycles are photosensitizers with rich fluorescence properties and the ability to produce singlet oxygen, $O_2(^1\Delta_g)$.¹⁰ The photosensitized production of $O_2(^1\Delta_g)$ is based on excitation of a photosensitizer to the triplet states and energy transfer of this energy to the ground electronic state of oxygen that is excited to the lowest singlet state, $O_2(^1\Delta_g)$. The oxidative potential of $O_2(^1\Delta_g)$ can be exploited in chemical syntheses, photodynamic treatment of cancer, and disinfection. Planar porphyrin molecules tend to form stacked aggregates, in which absorbed excitation energy is dissipated through decay channels competing with desired photoinitiated reactions.^{10,28} The aggregation can be eliminated by the immobilization of the individual molecules in inorganic hosts of ordered structures such as LDH or layered silicates.^{3,6,11,24} In addition, the advantages are well-defined microscopic structures of the host matrices, specific organization, variability, and enhanced stability of the photoactive molecules. Recently, we have described the structural and photophysical properties of porphyrin–LDH hybrids prepared by ion exchange and shown that the porphyrin triplet states interact with oxygen molecules in the LDH interlayer to form $O_2(^1\Delta_g)$.²⁹ These hybrids can serve as handy sources of $O_2(^1\Delta_g)$ and in the form of films they are suitable, e.g., for the construction of bactericidal surfaces.³⁰

Molecular dynamics simulations in combination with powder X-ray diffraction (XRD) provide new information on the structural features, dynamics, and arrangement of the interlayer water and anions, the properties mostly not available by direct measurements.^{12,31,32} We recently modeled Mg_2Al LDH with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) in the interlayer and compared the measured XRD patterns of the sample prepared by anion exchange with simulated patterns.³³ The porphyrin units are horizontally shifted to each other, disordered, and inclined with respect to the hydroxide layers.

In the present work, we have investigated the intercalation of anionic TPPS and $Zn(II)$ -5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($ZnTPPS$) into Zn_RAl and Mg_RAl LDH by the coprecipitation method. In general, Zn_RAl LDH hybrids exhibit higher crystallinity than corresponding hybrids based on Mg_RAl LDH. The gain in crystallinity was accompanied with the stabilization of a Zn^{2+}/Al^{3+} ratio equal to 2, and with the appearance of many in-plane diffraction lines in XRD that allowed us to propose, for the first time, a structural model of the interlayer space of Zn_RAl LDH hosts. Molecular dynamics simulations and XRD refinements indicate an inclined orientation of the porphyrin planes with respect to the hydroxide layers. The formation of $O_2(^1\Delta_g)$ by porphyrin–LDH hybrids is also presented.

Materials and Methods

Preparation. The tetrasodium salt of TPPS (Aldrich, Germany), $Al(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $ZnCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, and NaOH (all by Acros Organics, France) were used as purchased. Deionized and decarbonated water was used throughout all experiments.

The LDH samples were prepared at constant pH using a coprecipitation technique adjusted to small quantities.^{24,34} A solution of Zn^{2+} and Al^{3+} (3 mL, 0.2 M) in a variable molar ratio ($R = Zn^{2+}/Al^{3+} = 2–4$) was slowly added at a rate of 0.01 mL/min to 10 mL of an aqueous TPPS solution. TPPS was in a 2-fold molar excess over the stoichiometry. In some experiments, $ZnTPPS$ obtained by stirring TPPS with an equimolar amount of Zn^{2+} for 1 h, was used instead of pure TPPS. The pH value was maintained constant at pH 7.5 for $R = 2$ and 3 and at pH 8.0 for $R = 4$ by the simultaneous addition of 0.4 M NaOH. Coprecipitation was carried out under vigorous stirring in a nitrogen atmosphere at room temperature in order to avoid dissolution of atmospheric CO_2 and subsequent contamination by carbonate anions. The addition of NaOH was completed after 5 h, and the resulting violet precipitate was aged for 24 h under stirring. The product was centrifuged, washed three times with water, and finally dried in air at room temperature. All

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samples were then submitted to a hydrothermal treatment. Typically, about 20 mg of the solids was suspended in 25 mL of water in a 30 mL Teflon inner vessel in a stainless autoclave and treated at 120 °C for 72 h under autogenous pressure. Mg_RAl LDH hybrids were synthesized similarly.

The samples were labeled, e.g., as Zn_2Al -TPPS, Zn_2Al -(Zn)TPPS^H, and Zn_2Al -ZnTPPS where the molar ratio $\text{M}^{2+}/\text{Al}^{3+}$ (R) used in the synthesis is given by subscript, the superscript H stands for hydrothermally treated samples, and the porphyrin used for the synthesis is expressed by TPPS or ZnTPPS. The fact that originally used TPPS was metalated to ZnTPPS during the hydrothermal treatment is indicated by (Zn). Zn_RAl -Cl LDH intercalated with chloride anions is used here as a reference.

Characterization Techniques. Powder X-ray diffraction (XRD) (see the Supporting Information) was performed on a PANalytical X'Pert PRO X-ray diffractometer in the Bragg–Brentano geometry. The sample Zn_2Al -ZnTPPS^H of high crystallinity was also analyzed in the Debye–Scherrer geometry equipped with a capillary sample holder and a hybrid mirror monochromator ($\text{CuK}\alpha_1$, $\lambda = 1.540598$ Å). In-situ high-temperature measurements were performed using a high-temperature Anton PAAR HTK-16 chamber.

The diffuse reflectance UV–visible spectra were acquired on a Perkin-Elmer Lambda 35 spectrometer equipped with a Lab-sphere RSA-PE-20 integration sphere. Thermogravimetric analyses (TG-DTA) were carried out on a Setaram SETSYS Evolution instrument in air. The gas emission analysis was performed using a Setaram SETSYS Evolution-16-MS coupled with a mass spectroscopy system. High-resolution transmission electron microscopy (HRTEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB₆ cathode, point resolution 1.7 Å). The time-resolved near-infrared luminescence of $\text{O}_2(^1\Delta_g)$ at 1270 nm was monitored using a Ge diode detector upon laser excitation by a Lambda Physik FL 3002 dye laser ($\lambda_{\text{exc}} = 425$ nm, incident energy ~ 1 mJ/pulse). The detailed description of all methods is given in the Supporting Information.

Molecular Modeling. Molecular mechanics and classical molecular dynamics³⁵ were carried out in the Cerius and Materials Studio modeling environment (see the Supporting Information).³⁶ The structure of ZnTPPS was optimized by the quantum-chemistry computational program Turbomole v5.9.³⁷ Zn_2Al -LDH is created as a trilayered structure with a trigonal cell in hexagonal axes.³³ The space group is $R\bar{3}m$, and the initial experimental cell parameters used were $a = b = 3.064$ Å. The basal spacing d_{003} was 23.05 Å. A layer $[\text{Zn}_{64}\text{Al}_{32}(\text{OH})_{192}]^{32+}$ was created by the linking of 96 individual cells to give the lattice parameters of $A = 49.024$ Å and $B = 18.384$ Å, with Al^{3+} cations distributed in the layers on the condition that the location of Al^{3+} in neighboring octahedra is excluded.³⁸ The total composition was $[\text{Zn}_{192}\text{Al}_{96}(\text{OH})_{576}](\text{ZnTPPS})_{24} \cdot 192 \text{H}_2\text{O}$ with the space group set to P1. Charges were calculated by the Qeq method.³⁹ The initial models were minimized in the Universal force field, the electrostatic energy was calculated by

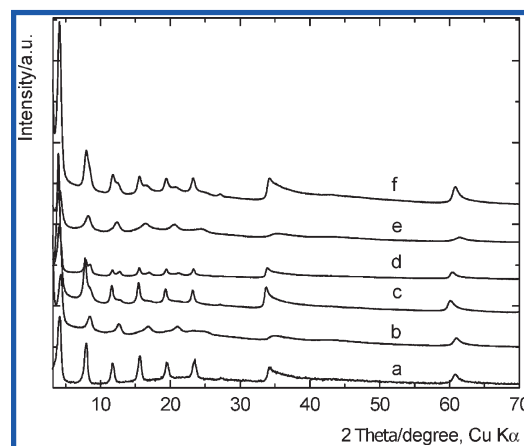


Figure 1. Powder XRD patterns of samples before hydrothermal treatment: Zn_2Al -ZnTPPS (a), Mg_4Al -TPPS (b), Zn_4Al -TPPS (c), Zn_3Al -TPPS (d), Mg_2Al -TPPS (e), and Zn_2Al -TPPS (f).

the Ewald summation method,⁴⁰ and the van der Waals energy was calculated by the Lennard-Jones potential.⁴¹ The dynamics simulations were carried out in an NVT statistical ensemble at 300 K. One dynamic step was 0.001 ps, and dynamics of 200 ps were carried out.

Results and Discussion

Characterization of LDH Intercalated with Porphyrins.

The coprecipitation method facilitates the effective intercalation of bulky porphyrin anions to compensate for the positive charge of the layers. Furthermore, this method often viewed as a self-assembly process should permit an adjustment of the $\text{M}^{2+}/\text{M}^{3+}$ ratio, i.e., to control the layer charge density and make it coincide with the charge *per* unit area for the intercalated anion. The composition based on Zn^{2+} and Al^{3+} is advantageous because Zn_RAl LDH hosts usually have higher crystallinity than Mg_RAl LDH. Here, we present the properties of both Zn_RAl and Mg_RAl LDH hybrids.

The XRD patterns of as-prepared samples were recorded in the Bragg–Brentano geometry and were all indexed in the rhombohedral space group $R\bar{3}m$, typical for LDH-based systems (Figure 1). A splitting of 003n basal lines of Zn_RAl LDH indicates two phases with close interlayer distances that are both consistent with the intercalation of the porphyrin molecules. The cell parameters, shown in Table 1, were obtained from the peak profile analysis, and it should be noted that the spherical harmonics correction for an anisotropic peak broadening⁴² due to size effects was essential to reach a good fit. The molar ratios R_{calc} were derived from a relationship between the cell parameter a and the $\text{M}^{2+}/\text{M}^{3+}$ molar ratio established for the Zn_RAl and Mg_RAl LDH series.⁴³ Both calculated, R_{calc} , and experimental, R_{exp} , values are comparable and in agreement with the initial molar ratios used for the synthesis (Table 1). The molar ratio

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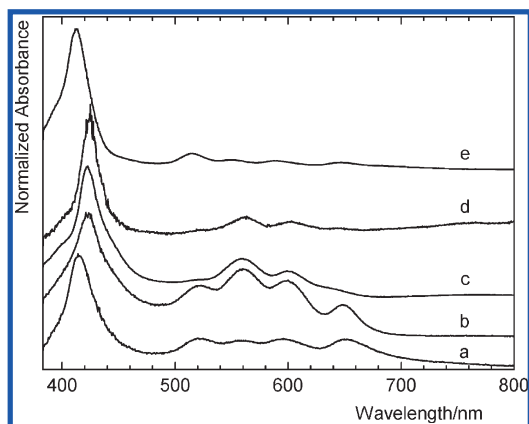
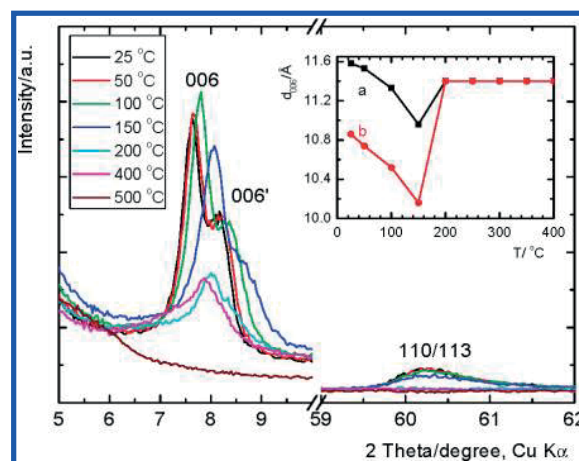
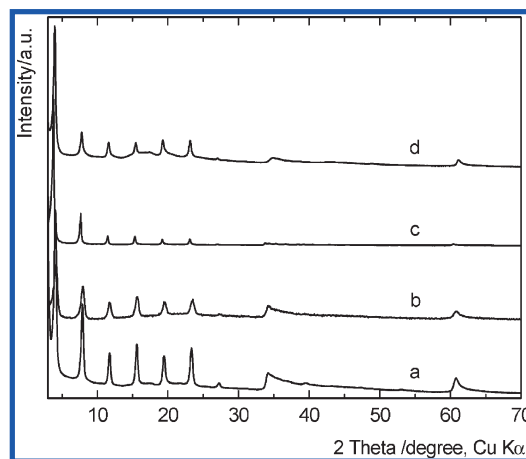
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Table 1. Refined Cell Parameters of Porphyrin–LDH Hybrids and the Molar M^{2+}/M^{3+} Ratios Obtained from XRD (R_{calc}) and Elemental Analysis (R_{exp})

samples	$a/\text{\AA}$	$c/\text{\AA}$	$d_{003}/\text{\AA}$	R_{calc}	R_{exp}
Mg ₂ Al–TPPS	3.0300(3)	65.093(9)	21.70	1.5	
Mg ₂ Al–TPPS ^H	3.0351(2)	69.105(5)	23.03	1.8	1.73
Zn ₂ Al–TPPS	3.0548(2)	68.856(3)	22.95	1.8	1.94
	3.0548(2)	64.332(9)	21.44		
Zn ₂ Al–(Zn)TPPS ^H	3.0568(4)	68.702(9)	22.90	1.7	1.90
Zn ₂ Al–ZnTPPS	3.0621(2)	69.215(7)	23.07	1.8	
Zn ₂ Al–ZnTPPS ^H	3.0625(3)	69.090(1)	23.03	1.8	1.91
Zn ₄ Al–TPPS	3.0859(3)	68.909(9)	22.97	4.1	3.60
	3.0859(3)	63.740(3)	21.25		
Zn ₄ Al–(Zn)TPPS ^H	3.0667(2)	69.047(4)	23.01	2.1	3.05

sulfur/Al³⁺ suggests that over 80% of hydroxide positive charges were compensated by the sulfonated groups of the porphyrin molecule. An explanation for the origin of the two interlayer distances can be deduced from the absorption spectra and thermal behavior. The absorption spectrum of pure TPPS displays the Soret band at 412 nm and four Q bands at 516, 550, 590, and 647 nm, while ZnTPPS shows the intensive Soret band at 424 nm and only two Q bands peaking at 561 and 603 nm due to the increase of the porphyrin symmetry (Figure 2). The spectra of Zn_RAl–TPPS differ from those of pure TPPS showing a red-shifted Soret band of 423 nm and more intensive absorptions at 560 and 600 nm, while the spectra of Mg_RAl–TPPS and TPPS have the same features. This documents a partial metalation of TPPS by Zn²⁺ during the Zn_RAl LDH synthesis. This is further corroborated by Zn₂Al–ZnTPPS, prepared using ZnTPPS, whose spectrum equals that of pure ZnTPPS (Figure 2) and the XRD patterns are not split as in the case of Zn₂Al–TPPS (Figure 1). Evidently, Mg₂Al–TPPS is characterized by a single basal spacing of 21.70 Å, while two phases containing either TPPS or ZnTPPS within the Zn₂Al LDH interlayer space result in two different basal spacings of 21.44 and 22.95 Å, respectively.

Although the absorption spectra clearly show the presence of both TPPS and ZnTPPS in Zn_RAl–TPPS, one must check whether the variations of the interlayer water content might also contribute to the two distances observed by XRD. Hence, the thermal behavior of Zn₄Al–TPPS

**Figure 2.** Normalized diffuse reflectance spectra before hydrothermal treatment: Mg₂Al–TPPS (a), Zn₂Al–TPPS (b), and Zn₂Al–ZnTPPS (c) compared with ZnTPPS (d) and TPPS (e).**Figure 3.** In-situ high-temperature XRD patterns of Zn₄Al–TPPS. The inset shows the relationship between the d_{006} (a) and $d_{006'}$ (b) basal spacings and temperature.**Figure 4.** Powder XRD patterns of Zn₂Al–(Zn)TPPS^H (a), Zn₂Al–ZnTPPS (b), Zn₂Al–ZnTPPS^H (c), and Mg₂Al–TPPS^H (d).

was examined by *in situ* high-temperature XRD (Figure 3). A gradual shift of the 006 double line toward higher 2θ values after increasing temperature from 50 to 150 °C indicates a decrease of the interlayer distance due to the removal of interlayer water. This was also confirmed by mass spectroscopy during thermogravimetric analysis (see below). The intensity of the 006 lines reaches a maximum at 100 °C suggesting a maximal ordering of the interlayer at this temperature. At 200 °C, dehydroxylation of the hydroxide layers is evidenced by the collapse and disappearance of the 006 and 110/113 lines, respectively. The fact that the 006 double line does not merge into a single line, even at 150 °C, supports the existence of two distinct phases that differ in the nature of intercalated porphyrin. Indeed, if these two basal lines were due to the different interlayer water content, we would have expected the two peaks to fuse into a single peak during interlayer dehydration.

The hydrothermal treatment causes a net increase of crystallinity of all samples (Table 1, Figure 4). The disappearance of the two-phase XRD patterns (Figures 1 and 4) and corresponding absorption spectra document that originally intercalated TPPS in Zn_RAl

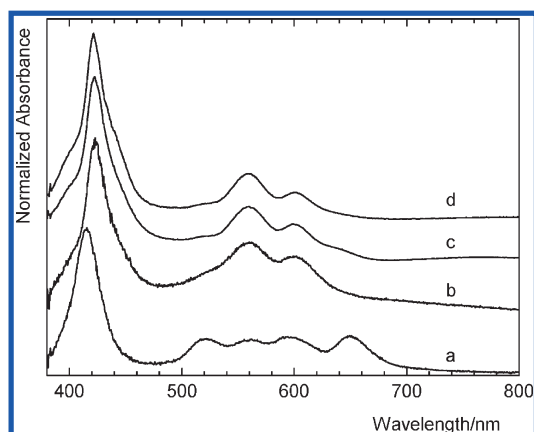


Figure 5. Normalized diffuse reflectance spectra of $\text{Mg}_2\text{Al-TPPS}^{\text{H}}$ (a), $\text{Zn}_2\text{Al-(Zn)TPPS}^{\text{H}}$ (b), and $\text{Zn}_2\text{Al-ZnTPPS}$ (c) compared with $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ (d).

LDH is completely metalated to ZnTPPS , while intercalated TPPS in Mg_2Al LDH remains unchanged (Figure 5). It is worth noting that TPPS metalation is not unexpected due to the high affinity of TPPS toward free Zn^{2+} in solution. The XRD patterns of $\text{Zn}_3\text{Al-(Zn)TPPS}^{\text{H}}$ and $\text{Zn}_4\text{Al-(Zn)TPPS}^{\text{H}}$ newly show the diffraction lines of ZnO that is accompanied by a decrease of the $\text{Zn}^{2+}/\text{Al}^{3+}$ ratio (R_{calc}) within the hydroxide layers to 2 as deduced from the decrease of the cell parameter a (Table 1). It can be attributed to a dissolution/decomposition of Zn -based LDH during the hydrothermal treatment in conjunction with the low octahedral crystal field stabilization energy of Zn^{2+} ions.⁴⁴ In contrast, the metal ratio in Zn_2Al LDH host remains unchanged with no signs of the ZnO presence. The stability of Zn_2Al LDH under specific hydrothermal conditions indicates that the most energetically favorable host–guest charge and structure alignment are reached at this molar ratio.

The absorption spectra (Figure 5) and XRD patterns of $\text{Zn}_2\text{Al-ZnTPPS}$ and $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ (Figures 4 and 6) document the stability of ZnTPPS in the interlayer space and very high crystallinity after the hydrothermal treatment. This is indicated by not only the very narrow 003n basal lines, but also by the appearance of many 10n and 01n in-plane lines at high 2θ angle values. One must say that the observation of the in-plane reflections is quite rare in LDH. The high crystallinity of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ allowed us to extract additional information on the intercalate structure (see below).

Thermal Behavior. The amount of physisorbed and interlayer/structural water molecules can be determined using thermogravimetric analyses (Table 2). The TG-DTA curves, describing the general thermal behavior of hybrids, have similar features (Supporting Information Figure S1). The amount of physisorbed water was determined by evacuating the samples at 50 °C for 5 h. The thermal processes are characterized by three weight loss steps. Depending on sample crystallinity, all these thermal events are either well-separated or superimposed

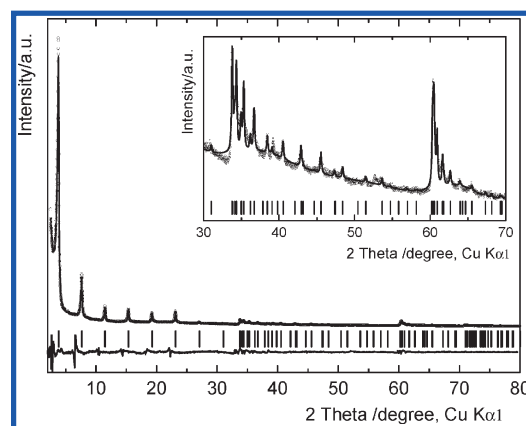


Figure 6. Profile analysis of the XRD pattern of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ recorded in the Debye–Scherrer geometry: experimental X-ray diffraction (circles), calculated (line), Bragg reflections (ticks), and difference profiles. Refined unit cell parameters: $a = 3.0604(6)$ Å and $c = 69.01(1)$ Å. $R_{\text{Bragg}} = 0.08\%$. (inset) Extended region 30–70°/ 2θ .

phenomena. The loss between 50 and 150 °C, accompanied by a decrease of the interlayer spacing (Figure 3), is attributed to the removal of interlayer water molecules. The results show that 40–75% of total water belongs to physisorbed water molecules. The number of intercalated water molecules is close to that reported for LDH, i.e., about two water molecules per Zn_2Al formula unit. In the case of Mg_2Al LDH, the obtained number is less accurate because of less defined weight losses related to their lower crystallinity. The second step (150–400 °C) involves two simultaneous processes, dehydroxylation of the brucite-like layers, and decomposition of interlayer anions, while the third step above 400 °C is a consequence of decomposition and combustion of intercalated anions.

The thermal stability of the porphyrin molecules intercalated between the hydroxide layers was investigated by TG-DTA in conjunction with mass spectroscopy. Pure porphyrins and their intercalated phases exhibit complex thermal behavior (Supporting Information Figures S2–S5); therefore, the most sensitive measure of thermal behavior appears to be the evolution of gases due to porphyrin decomposition, namely SO_2 and NO_2 . While the onset of the evolution of NO_2 is not affected by intercalation, the evolution of SO_2 starts at lower temperature for both pure porphyrins. Thus, ZnTPPS starts to decompose at ca. 340 °C and the onset is shifted to nearly 465 °C after intercalation. In the case of the Mg_2Al LDH hybrid, the onset is shifted from ca. 310 to 480 °C. These results indicate that host–guest interactions thermally stabilize the porphyrin molecules similarly to other intercalated molecules.^{45–47}

XRD Analysis. $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ displays very narrow 003n diffraction lines which are characteristic of high coherency materials and a large number of the 10n and 01n in-plane diffraction lines. The latter observation is

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Table 2. Thermogravimetric Data of Porphyrin–LDH Hybrids

samples	weight loss/%			$n\text{H}_2\text{O}$ physisorbed	$n\text{H}_2\text{O}$ interlayer
	< 150 °C	150–400 °C	400–800 °C		
$\text{Mg}_2\text{Al}-\text{TPPS}$	2.6	8	19.1	1.89	0.61
$\text{Mg}_2\text{Al}-\text{TPPS}^{\text{H}}$	6.1	11.3	26.5	2.32	1.48
$\text{Zn}_2\text{Al}-\text{TPPS}$	5.6	10.2	27	1.33	1.67
$\text{Zn}_2\text{Al}-(\text{Zn})\text{TPPS}^{\text{H}}$	6.2	10.2	22.7	1.13	1.87
$\text{Zn}_4\text{Al}-\text{TPPS}$	5.7	10.6	22.4	^a	^a
$\text{Zn}_4\text{Al}-(\text{Zn})\text{TPPS}^{\text{H}}$	6.1	10.3	23.1	^a	^a

^a Not determined because of the formation of ZnO .

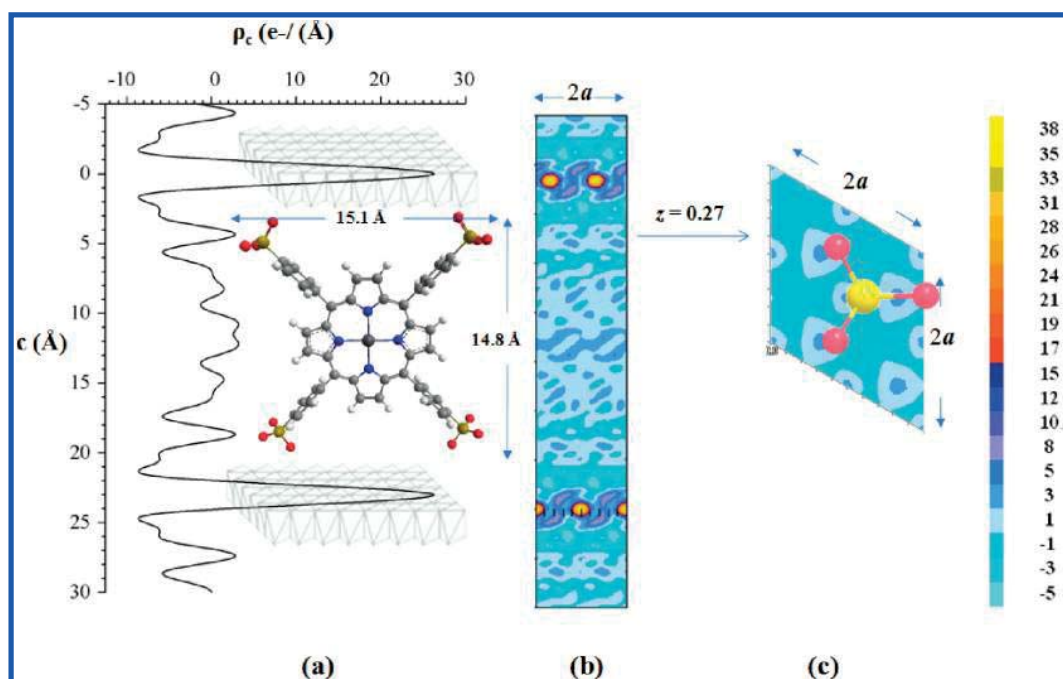


Figure 7. Structure model of $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$: (a) one-dimensional electron density determined from the Debye–Scherrer data projected along the c -stacking axis; (b) contoured Fourier map of the $(x0z)$ plane (summed from 0 to 1 along the b -axis); (c) contoured Fourier map of the $(xy0)$ plane ($z = 0.27$). The sulfonate group is overlaid on the $(xy0)$ plane to show the matching with the density spots observed at $z = 0.27$ (and $z = 0.07$). The electron density scale ($\text{e}^-/\text{\AA}$) is given on the right.

quite rare in LDH-based materials because these materials are known to be low crystalline, especially hybrid LDH, due to anisotropic size effects (i.e., platelet morphology), microstrains, and stacking faults. Besides, owing to the small difference between the Zn^{2+} and Al^{3+} X-ray atomic scattering factors and the low contribution expected from light atoms such as C, O, N, S, and H forming the skeleton of the porphyrin guest molecule, it would be too tentative to attribute the in-plane diffraction lines to either a cation ordering of Zn^{2+} and Al^{3+} within the hydroxide layer or to an ordering of the porphyrin molecules in the interlayer space. As the in-plane diffraction lines are expected for a 3R polytype without stacking faults, we can reasonably assume a nearly perfect 3R stacking of the hydroxide layers. It may be attributed to the rigidity of the porphyrin framework.

The large number of 003n diffraction lines (up to seven harmonics) related to the large size of the intercalated porphyrin molecule allows probing the structure of the

interlayer space projected on the c -axis via the Fourier transformation.⁴⁸ The one-dimensional (1D) electron density map for $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$, determined from Debye–Scherrer data, can be calculated using the known structure of a hydroxide layer, assuming a weak contribution from the interlayer part to total scattering (Figure 7a). The corresponding plots for $\text{Mg}_2\text{Al}-\text{TPPS}^{\text{H}}$ and $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$ determined using the Bragg–Brentano XRD data are compared in Supporting Information Figure S6A. The difference between the 1D plots for $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$ displayed in Figures 7a and S6A is due to resolution differences between the two XRD data sets; the high-resolution data obtained in the Debye–Scherrer mode gives the 1D plot with a better resolution.

The 1D electron density map of $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$ (Figure 7a) displays two strong maxima at 0 and 23 Å corresponding to the metal containing hydroxide layers. The five additional peaks of lower electron densities located in between can be attributed to the intercalated porphyrin and water molecules. Upon comparison with the dimensions of the porphyrin molecule ($\sim 15/4.3$ Å), a

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perpendicular arrangement of the porphyrin plane against the hydroxide layer can be proposed in agreement with previous study.²⁴ The sulfonate groups cause maxima at the outer parts of the interlayer space at about 4 Å from the center of the hydroxide layers that is consistent with hydrogen bonding interactions between the sulfonate groups and OH groups of the layers. These interactions along with Coulombic interactions dictate the orientation of the anions with respect to the LDH surface.⁴⁹ The central maxima and the two peaks on each side arise from the porphyrin ring. The splitting of the central maxima indicates an orientation disorder of the porphyrin molecules around a given central site (see below). If we assumed a perpendicular orientation, the porphyrin molecule would fill a surface area of $16.2 \text{ Å}^2/\text{e}^-$ that is largely compensated with the surface area of $23.5 \text{ Å}^2/\text{e}^-$ of the hydroxide layer. A far better accordance could certainly be obtained by slightly inclined molecular planes resulting in an increase of the surface required by the porphyrin molecule. Yet, the present data do not allow distinguishing between a perpendicular and inclined orientation. On the other hand, this result can be compared with the calculation of the interlayer space available for intercalated anions that is often applied in hybrid LDH:⁵⁰ $23.03 \text{ Å} (d_{003}) - 2.10 \text{ Å}$ (i.e., hydroxide layer thickness) $- 2 \times 2.70 \text{ Å}$ (i.e., hydrogen bonding) $= 15.5 \text{ Å}$. The gallery height thus obtained is comparable with the size of the porphyrin molecule and again indicates a perpendicular or nearly perpendicular orientation of the porphyrin units between the hydroxide layers.

The electron-density distributions on the ($x0z$) and ($xy0$) planes, plotted with the GFourier program,⁵¹ are presented in the form of contour plots in Figure 7b and c. In the same way as for the 1D projection, the phases and structure factors were computed from the known configuration of the hydroxide layer part of the structure. Note that the differences in the electron density between spots in the interlayer space are quite small, preventing us from a detailed description of the interlayer structure. Nevertheless, four important points can be drawn. (i) The highest density peaks observed at $z \sim 0.27$ and 0.07 , i.e., 4 Å from the center of the hydroxide layers, are localized vertically to metal cations and can be reasonably assigned to the sulfonate groups. This does not mean that the distance between sulfonate groups is equal to the distance between metal cations within the hydroxide layer, i.e., $\sim 3 \text{ Å}$. Indeed, one must keep in mind that equivalent positions that are too close to one another are only partially occupied by the sulfonate groups, in agreement with the $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$ chemical formula. The distances around 1.6 Å between density peaks observed at $z \sim$

0.27 (and ~ 0.07) are consistent with an S—O bond length. (ii) The aromatic ring system gives rise to a rather disordered electron density in the middle of the gallery. Such disorder suggests a low contribution, if any, of a superstructure based on regularly aligned porphyrin units. (iii) Assuming the $R\bar{3}m$ space group, metal ions of two successive hydroxide layers are shifted by $1/3$ in the $[110]$ direction, then the sulfonate groups located at the outer parts of the interlayer space exhibit the same shift, leading to a slightly inclined orientation of the porphyrin plane with an angle of ca. 8° with respect to the normal of the hydroxide layer. (iv) The decrease of the electron densities attributed to the sulfonate groups, after a thermal treatment at 100°C under vacuum, is indicative of the presence of water molecules located nearby the sulfonate groups (Supporting Information Figure S6B).

Comparison of the less resolved one-dimensional plots of $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$ and $\text{Mg}_2\text{Al}-\text{TPPS}^{\text{H}}$ calculated from the Bragg–Brentano XRD data is valuable since these two samples display the same $\text{M}^{2+}/\text{M}^{3+}$ molar ratio according to the chemical analysis; hence, they are intercalated with the same amount of porphyrin (Supporting Information Figure S6). The 1D plots show differences in the electron densities at the hydroxide layers and porphyrin ring positions. The lower electron density observed for the Mg_2Al hydroxide layers is due to the difference between Zn ($Z = 30$) and Mg ($Z = 12$) atomic numbers. In addition, the presence of Zn^{2+} in the middle of the porphyrin unit explains the higher electron density in the interlayer central plane of $\text{Zn}_2\text{Al}-\text{ZnTPPS}^{\text{H}}$.

The studies show that ordering of some organic anions within the interlayer galleries is relatively common, in contrast to the generally disordered interlayers filled with inorganic anions.¹² In this respect, we might speculate on the ordering of the porphyrin units. They are bulky and rigid, and the final arrangement is governed by the interplay of the Coulombic interactions of porphyrin anions with the positively charged layers, interactions between neighboring anions, and the hydrogen bonding interactions among the hydroxyl groups, porphyrin sulfonate groups, and water. The indexing calculations either using DiffracPlus Topas (v. 4.1) or Dicvol 2006 give a trigonal cell well-described by $a = 3.0625(3) \text{ Å}$, $c = 69.090(1) \text{ Å}$, and $\gamma = 120^\circ$. If one assumes that intercalated porphyrin units are ordered and create a superstructure, such an a parameter would not allow accommodating the porphyrin molecule with a size of ca. 15 Å . The simplest model that would permit the ordering of ZnTPPS anions within the $R\bar{3}m$ unit cell is the multiple application of the unit cell transformation ($\text{IIc}, a' = -2a, b' = -2b$)⁵² yielding a new a parameter of 24.5 Å . This parameter is comparable with the size of the porphyrin molecule; however, no additional diffraction lines allow this indexing of the XRD patterns. In fact, these additional lines are expected to be very weak, if any, because experimental electron density maps indicate some disorder in the middle of the

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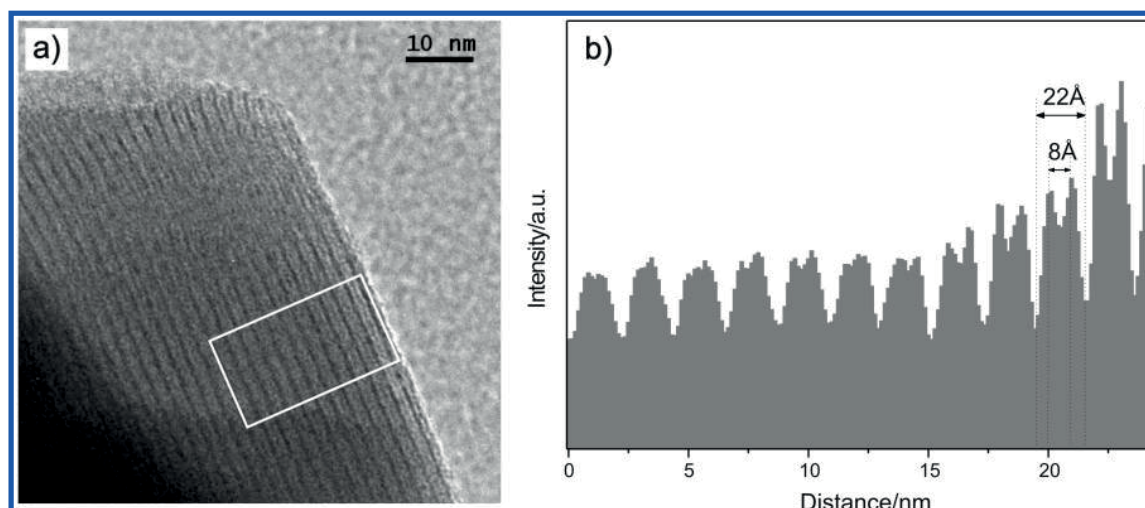


Figure 8. HRTEM observation of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$: (a) high-resolution micrograph, (b) intensity histogram of the area marked in part a.

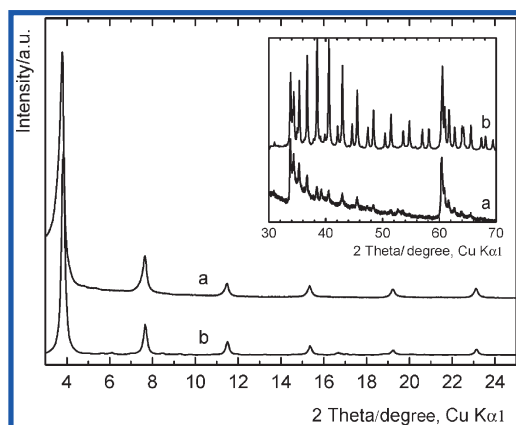


Figure 9. Experimental (a) and calculated (b) XRD basal diffraction lines of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ hybrid. (inset) Corresponding experimental (a) and calculated (b) XRD nonbasal diffraction lines.

interlayer and because of small differences between the atomic scattering factors of hydroxide metals.

Transmission Electron Microscopy. The HRTEM micrographs of original and porphyrin-intercalated LDH were recorded to observe the changes of the layered structure upon intercalation. The particles of original LDH, $\text{Zn}_2\text{Al-Cl}^{\text{H}}$, have a typical hexagonal shape; sometimes slightly irregular with the unequal length of sides (Supporting Information Figure S7). The size of the crystals is below $1\ \mu\text{m}$. The basal spacing of $\text{Zn}_2\text{Al-Cl}^{\text{H}}$, measured as a distance between the intensity minima, is about $8\ \text{\AA}$ (Supporting Information Figure S8), which corresponds to $7.75\ \text{\AA}$ obtained from the XRD patterns. The distance between the parallel fringes in $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ is about $22\ \text{\AA}$ (Figure 8), which is in good agreement with the d_{003} value of $23.03\ \text{\AA}$ determined by XRD. Moreover, the HRTEM micrographs reveal additional lattice fringes with a fringe separation of about $8\ \text{\AA}$ indicating an increase of electron density in the middle of the interlayer space (Figure 8b). In agreement with information obtained from XRD, this suggests that the metal centra of the porphyrin units are aligned in the middle of the interlayer space.

Molecular Modeling. The experimentally accessible XRD patterns bear important structural information. We constructed a structural model using the molecular simulations approach taking the van der Waals dimension of the porphyrin guest and by assuming that the intercalation process does not change measurably the structure of the hydroxide layers. The calculated XRD patterns of the optimized $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ structure and the experimental XRD are compared in the 2θ scale in Figure 9. The patterns exhibit typical features of a layered structure, i.e., basal lines $003n$. The measured basal spacing (Table 1), line positions, and intensities of diffraction lines are very similar. Some intensity differences might be due to the crystallite morphology and roughness of the sample surface.⁵³ The calculated XRD has additional very low intensity lines between 5 and 6° and 16 and 18° of the 2θ scale, which appear due to the forced periodicity of the model. In the calculation, the supercell is treated as a structural element, which is infinitely repeated in all directions forming an infinite and perfectly periodic 3D crystal. The forced repeating of the structural elements imposes the periodicity of central zinc atoms of ZnTPPS leading to the appearance of these lines. Indeed, once Zn atoms are removed from the model, the low intensity lines disappear. However, intensities of these diffraction lines are very low and it is difficult to differentiate them from possible imperfections and small amounts of impurities in the real sample.

The observation of the nonbasal lines and their comparison with calculated XRD bring additional information on the layer ordering (Figure 9). The experimental line positions are best reproduced by a model with $a = 3.063$ and $d_{003} = 23.05\ \text{\AA}$, the values that correspond well to the experimental ones (Table 1). The higher intensities of some calculated lines are imposed by the perfect layer periodicity of the model. The host layers were kept in the same layer stacking order as in the original nitrate form

(53) Kovář, P.; Pospíšil, M.; Nocchetti, M.; Čapková, P.; Melánová, K. *J. Mol. Model.* **2007**, *13*, 937.

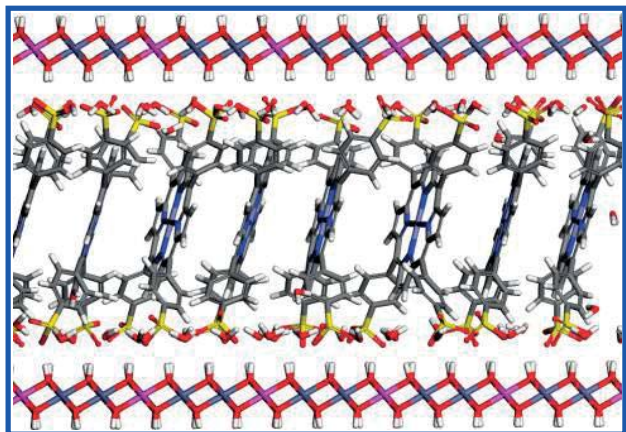


Figure 10. Interlayer space of the Zn_2Al LDH lattice filled with ZnTPPS.

(polytype 3R), therefore, the consistence between the calculated and experimental patterns indicates that the original symmetry is a good approximation for the layer stacking of the investigated intercalate. This is also corroborated by the fact that a horizontal shift of the layers violating the $R\bar{3}m$ symmetry induces many additional diffraction lines in the calculated XRD in disagreement with the experimental diffraction data. Because exchanging the Zn and Al atomic positions within the hydroxide layers does not affect the calculated diffraction patterns, an order/disorder arrangement of Al/Zn atoms is not distinguishable, and the nonbasal diffraction lines are governed only by a translation of atomic positions. Some layer nonperiodicity can be reproduced by the reoptimization of the final model with variable cell parameters (c , α , and β) used in step 2 (see the Supporting Information). It slightly changes the cell angles (0.3° at maximum) with only minor deviations of the layer stacking order, and as a result, the intensities of the calculated and experimental nonbasal diffraction lines are more similar.

The interlayer space in the minimized model (Figure 10) is filled with nearly parallel porphyrin units with a dihedral angle varying between 0 and 10° . The porphyrin planes are not perpendicular to the hydroxide layers. Instead, angle variations between the porphyrin plane and the layer normal satisfy the Gaussian distribution with the average angle of ca. 14° (Supporting Information Figure S9). In agreement with the HRTEM micrographs (Figure 8), porphyrin zinc atoms of ZnTPPS are in the middle of the interlayer space, i.e., $11.525 \pm 0.300 \text{ \AA}$ with respect to the neighboring (003) basal plane (basal spacing is $23.05 \text{ \AA}$). Due to a horizontal shift of the porphyrin units, their central Zn atoms are horizontally disordered (Figure 11). The distance between two neighboring porphyrin centra defined as a line connecting Zn atoms varies from 6 to $9 \text{ \AA}$. The top view shows that the porphyrin molecules are horizontally shifted by a distance varying from one-third to one-half of the porphyrin size, thus homogeneously occupying the interlayer space (Figure 11). The pyrrole rings of the porphyrin molecule impose a hydrophobic region in the midplane of the interlayer causing that the most of interlayer water molecules are located close to the hydrophilic hydroxide

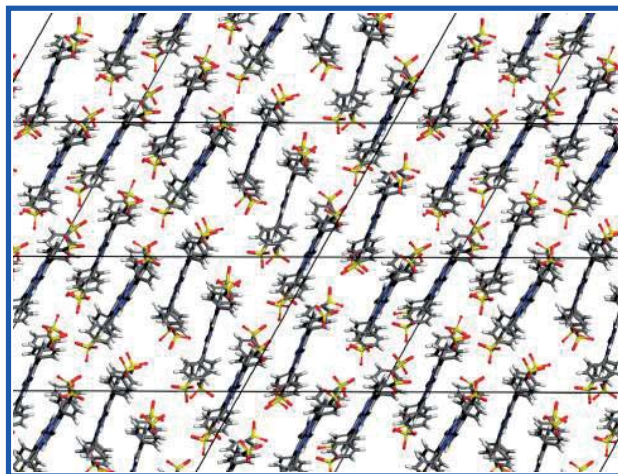


Figure 11. Top view of linked supercells containing ZnTPPS anions in the interlayer space.

layers together with the sulfonate groups of ZnTPPS (Figure 10) as documented by the XRD analysis. In this region, water molecules, oxygen atoms of the sulfonate groups, and the hydroxide surface are in close contacts indicating hydrogen bonding interactions. The hydrogen-bond donor is a surface OH group and the acceptors are oxygen atoms of a water molecule or sulfonate group. Only several water molecules ($1\text{--}2$ molecules per interlayer) are close to porphyrin zinc atoms among the porphyrin units (Figure 10). The modeled structural arrangement documents disorder of the central part of the interlayer that is in agreement with the XRD analysis. The TPPS molecules in the Mg_2Al LDH hosts are aligned similarly; however, the TPPS units can slightly deviate from the planarity.³³

To complement the model description, the atom concentration profile of the optimized interlayer was compared with the experimental electron density map (Supporting Information Figure S10). The concentration profile is derived from the atomic densities assuming the equivalence of all atoms. While the electron density peaks of the hydroxide layers ($d = 0$ and $23 \text{ \AA}$) and water molecules together with the sulfonate groups ($d \sim 4$ and $19 \text{ \AA}$) are well-reproduced by the concentration profile, the concentration of porphyrin zinc atoms in the middle of the interspace is expectantly of very low intensity. The electron density peaks of pyrrole atoms located near 8 and $15 \text{ \AA}$ are shifted by about $0.8 \text{ \AA}$ to the middle of the interspace. It might indicate that central zinc atom attracts nitrogen and carbon electrons toward the porphyrin center.

Photophysical Properties. The results document that LDH hosts are well suited for accommodating the porphyrin molecules. The absorption spectra enable the characterization of the molecular state of porphyrins because their aggregation is accompanied by considerable spectral changes. Comparing the absorption spectra of monomeric porphyrin solutions with those of TPPS and ZnTPPS intercalated in LDH, it is evident that the intercalation does not significantly alter the shape of the Soret band but only broadens it, an effect that we assign

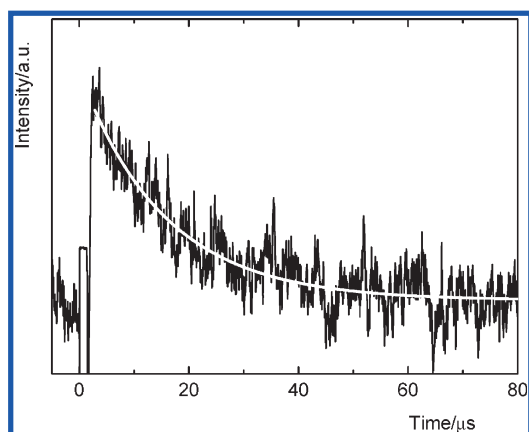


Figure 12. Time dependence of the $^1\text{O}_2$ luminescence signal of $\text{Mg}_2\text{Al-TPPS}$ ($\lambda_{\text{exc}} = 425$ nm, ~ 1 mJ, oxygen atmosphere, recorded at 1270 nm). The smoothed line is a least-squares monoexponential fit.

to a range of binding sites of the porphyrin molecules. Thus, extensive porphyrin aggregation, a process that often occurs in solutions and on solid templates, is ruled out.^{10,54} This is consistent with the molecular modeling results showing that the distance between two neighboring central atoms varies between 6 and 9 Å. The distance is considerably larger than the typical van der Waals separation of about 3.5 Å observed in π stacking of aromatic compounds.

Recently, we have described the photophysical properties of Mg_RAl hybrids containing intercalated porphyrin molecules.^{29,30} The production of $\text{O}_2(^1\Delta_g)$ was predicted on the basis of quenching of the porphyrins triplet states by molecular oxygen and directly evidenced using time-dependent luminescence spectroscopy at 1270 nm. The same approach was applied here on Zn_RAl and Mg_RAl LDH hybrids prepared by the coprecipitation method. Figure 12 depicts the $\text{O}_2(^1\Delta_g)$ luminescence intensity recorded after excitation of $\text{Mg}_2\text{Al-TPPS}$ hybrid. The effective lifetime of $\text{O}_2(^1\Delta_g)$ recovered from the monoexponential fits is 16 μs . Since pure LDH hosts do not exhibit any $\text{O}_2(^1\Delta_g)$ luminescence, it is evident that $\text{O}_2(^1\Delta_g)$ is generated solely by the porphyrin photosensitized reaction. Surprisingly, the formation of $\text{O}_2(^1\Delta_g)$ was observed only for the hybrids based on Mg_RAl LDH hosts practically not depending on the sample crystallinity, while Zn_RAl LDH-based hybrids do not produce any measurable amount of this species. The explanation is not clear because both TPPS and ZnTPPS are effective sensitizers with high quantum yields of $\text{O}_2(^1\Delta_g)$ in aqueous solutions.⁵⁵ We suppose that the lifetimes of the porphyrin triplet states and $\text{O}_2(^1\Delta_g)$ are considerably affected by Zn- and Al-coordinated OH groups oriented toward the interlayer space. Evidently, the best

photosensitizing LDH materials studied in this paper are based on the Mg_RAl LDH hosts.

Conclusions

LDH are suitable hosts of porphyrin sensitizers. Porphyrin TPPS is intercalated in Mg_RAl LDH ($R = 2-4$) to give the hybrids with a characteristic basal spacing of about 23 Å. Similar results are obtained for ZnTPPS within the Zn_RAl LDH interlayer space ($R = 2-4$). The hydrothermal treatment increases crystallinity of the hybrids and originally intercalated TPPS in Zn_RAl LDH is metalated to ZnTPPS, while intercalated TPPS in Mg_RAl LDH remains unchanged.

The presented results can be summarized as follows. (i) The rigid framework of ZnTPPS has a beneficial effect on the ordering of the hydroxide layers. (ii) The diffraction patterns are well characterized by the $R\bar{3}m$ rhombohedral space group, typical of LDH-based systems. (iii) Intercalated porphyrins do not aggregate, which is a prerequisite of effective photosensitization of $\text{O}_2(^1\Delta_g)$. The distance between two neighboring central atoms varies from 6 to 9 Å that is much longer than that of about 3.5 Å typical in parallel stacking of aromatic compounds. (iv) The gallery height of 15.5 Å is filled with nearly parallel porphyrin units. The porphyrin units are inclined with respect to the hydroxide layers with the average angle between the porphyrin plane and the layer normal of about 14°. Central zinc atoms of ZnTPPS are in the middle of the interlayer space. (v) The sulfonate groups are about 4 Å from the center of the hydroxide layers indicating the hydrogen bonding interactions between the sulfonate groups and OH groups of the layers with the contribution of water molecules. (vi) The disorder in the middle of the gallery suggests a low contribution, if any, of a superstructure based on regularly aligned porphyrin units. (vii) $\text{Mg}_R\text{Al-TPPS}$ hybrids produce $\text{O}_2(^1\Delta_g)$, while no measurable amount of this species was found for Zn_RAl LDH-based hybrids.

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Supporting Information Available: Details of characterization techniques and molecular modeling; TG-DTA curves, one-dimensional electron densities; HRTEM micrographs; angle distributions; experimental electron density vs atom concentration profiles. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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PORPHYRINS INTERCALATED Zn/Al and Mg/Al LAYERED DOUBLE HYDROXIDES: PROPERTIES AND STRUCTURAL ARRANGEMENT

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Characterization Techniques

Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert PRO X-ray diffractometer. In the Bragg-Brentano geometry, incident X-ray radiation produced from a line-focused PW3373/10 Cu X-ray tube operating at 40 kV and 30 mA beam ($\text{CuK}\alpha_1/\text{K}\alpha_2$, $\lambda = 1.540598/1.544426 \text{ \AA}$) passed through a 0.04 rad Soller slit, a $1/2^\circ$ divergence slit, a 10 mm fixed mask, and a 1° fixed antiscatter slit. The diffracted beam was detected by an X'Celerator RTMS detector. In front of the detector a β filter, a 0.04 rad Soller slit and an antiscatter slit of 5.5 mm were used. The detector was set in the scanning mode with an active length of 2.122° (2θ). In order to minimize preferred orientation effects, the powders were lightly pressed in a back loaded sample holder and were rotated with a spinning rate of 1 rotation/second. The acquisitions were performed at room temperature over a range of $2\text{--}90^\circ$ (2θ) with a step size of 0.0167° (2θ) and counting time 100 s/step.

The sample $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ of high crystallinity was also analyzed in the Debye-Scherrer geometry equipped with a capillary sample holder and a hybrid mirror monochromator ($\text{CuK}\alpha_1$, $\lambda = 1.540598 \text{ \AA}$), which gives the monochromatic parallel beam geometry. The diffracted beam with the X'Celerator configuration had an antiscatter shield and a Soller slit (0.04 rad). The powder was introduced in a glass capillary (outside diameter 0.3 mm, Hilgenberg GmbH) mounted on a goniometric head, which is screwed on a rotary sample stage with the spinning rate of 4 rotations/s. The high-resolution powder X-ray diffraction patterns were collected in the range $2\text{--}110^\circ$ (2θ) with a step size of 0.0167° (2θ) and counting time 7300 s/step at room temperature.

In-situ high-temperature measurements were performed using a high-temperature Anton PAAR HTK-16 chamber installed on a PANalytical X'Pert PRO X-ray diffractometer, in the Bragg-Brentano geometry. The powders were spread on a 10-mm heating platinum ribbon and the powder patterns were collected at different temperatures between 25 and 700°C in air; in the range $2\text{--}70^\circ$ (2θ) with a step size of 0.0167° (2θ) and 100 s/step. The heating rate was $5^\circ\text{C}/\text{min}$, which was identical to that applied in the thermogravimetric measurements.

All samples were analyzed using a sample holder exactly in the reference plane. For some of the samples, the powders were mixed with silicon in order to check the cell parameters and there was no difference between the cell parameters obtained with and without silicon.

The lattice parameters were determined by the full pattern matching analysis of the XRD diagrams obtained in the Bragg-Brentano geometry using the Fullprof suite.¹ The pseudo-Voigt profile function of Thompson, Cox and Hastings was used to generate the peak shapes of the simulated diffraction lines. To treat anisotropic size effects, the Lorentzian part of the peak broadening was modeled with linear combinations of spherical harmonics. In a second step, the integrated intensities of the 003n diffraction lines were used to calculate one-dimensional profiles along the c-stacking axis *via* the Fourier transformation.² The phases and structure factors were computed from the known configuration of the hydroxide layers³ assuming a weak contribution from the interlayer part to the total scattering. For the analysis of Zn₂Al-ZnTPPS^H recorded in the Debye-Scherrer geometry, the Rietveld refinement of the partial structure by considering only the hydroxide layers, was performed followed by the Fourier map calculation and visualization using the Gfourier software.⁴

Diffuse reflectance spectra were acquired on a Perkin Elmer Lambda 35 spectrometer equipped with a Labsphere RSA-PE-20 integration sphere. A sample holder with a fused silica window was filled with hybrid powder or BaSO₄ (Merck), which was used as a white standard. LDH powders were diluted with BaSO₄ prior to the measurements. The spectra were converted from reflection to absorbance by the Kubelka–Munk method and processed using the OriginPro7.5 software (OriginLab Co., USA).

Thermogravimetric analyses (TG-DTA) were carried out on a Setaram TGA 92 instrument in air. The measurements were conducted in three steps: (i) evacuation at 50°C during 5 hours in order to remove physisorbed water, (ii) temperature increase up to 200°C with a heating rate of 1°C/min, and (iii) temperature increase up to 800°C with a heating rate of 5°C/min. The gas emission analysis was performed using a Setaram SETSYS Evolution-16-MS coupled with a mass spectroscopy system.

Chemical analysis (H, Mg, Al, S and Zn) was performed by inductively coupled plasma atomic emission spectroscopy at the Vernaison Analysis Center of CNRS (France).

High-resolution transmission electron microscopy (HRTEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB₆ cathode, point resolution 1.7Å). Images were recorded on a CCD camera (1024x1024 pixels resolution) using the Digital Micrograph software package. Powder samples were dispersed in hexane and the suspension was treated in ultrasound for 10 minutes. A drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry in air at ambient temperature.

Time-resolved near-infrared luminescence of O₂(¹Δ_g) at 1270 nm was monitored using a Ge detector (1270 nm interference filter, Judson J16-8SP-R05M-HS Ge diode) upon

laser excitation by a Lambda Physik FL 3002 dye laser ($\lambda_{\text{exc}} = 425 \text{ nm}$, incident energy $\sim 1 \text{ mJ/pulse}$). The signal-to-noise ratio of the signals was improved by averaging of 100 to 500 individual traces. The short-lived signal produced by the scattering of excitation laser pulse and/or by red fluorescence was eliminated by exciting the sample in argon atmosphere, and subtracting the obtained signal from the signal recorded in oxygen atmosphere. The solid samples were equilibrated in a selected atmosphere by evacuating the cell and filling it with Ar or O₂. The treatment was repeated three times to ensure the desired atmosphere.

Molecular modeling

Porphyrin ZnTPPS was built in the 3D - Sketcher module.⁵ The structure was further optimized by the quantum-chemistry computational program Turbomole v5.9 using the RI-DFT method with B-P86 functional.⁶ A small def-SV(P) basis set and ECP on zinc (28 core electrons) and sulfur (10 core electrons) atoms were used because of the large size of the molecule (89 atoms). Several initial structures were optimized in order to find the global minimum with no symmetry restrictions. The optimized molecule was used in the following calculations.

Molecular mechanics and classical molecular dynamics⁷ were carried out in the Cerius and Materials Studio modeling environment. The Zn₂Al LDH host with a Zn²⁺/Al³⁺ molar ratio of 2 is a trilayered structure with a trigonal cell in hexagonal axes.⁸ The space group is $R\bar{3}m$, initial experimental cell parameters were $a = b = 3.064 \text{ \AA}$, and the basal spacing d_{003} was $23.05 \text{ \AA}$. A layer $[\text{Zn}_{64}\text{Al}_{32}(\text{OH})_{192}]^{32+}$ was created by the linking of 96 individual cells to give the following lattice parameters: $A = 49.024 \text{ \AA}$ and $B = 18.384 \text{ \AA}$, with Al³⁺ cations distributed in the layers on condition that the location of Al³⁺ in neighboring octahedra is excluded.⁹ Based on experimental results, ZnTPPS anions saturate over 80% of anion exchange capacity (AEC). The model structure was approximated by 100% AEC saturation assuming various orientations of guest anions with respect to the hydroxide layers and with respect to each other. The number of intercalated water molecules was estimated using thermal analysis giving the total composition of $[\text{Zn}_{192}\text{Al}_{96}(\text{OH})_{576}][(\text{ZnTPPS})_{24} \cdot 192 \text{ H}_2\text{O}]$ with the space group set to P1. Charges were calculated by the Qeq method (charge equilibrium approach).¹⁰ The initial models were minimized in the Universal force field, the electrostatic energy was calculated by the Ewald summation method,¹¹ and the van der Waals energy was calculated by the Lennard-Jones potential.¹²

The best agreement between the experimental and calculated XRD was achieved by the following strategy. After varying the d_{003} basal spacing to obtain agreement within $3 - 25^\circ$ (2θ), the positions of the diffraction lines ranging from 30 to 70° were optimized by varying the a cell parameter. After obtaining the initial a and d_{003} values, minimization in the Minimizer module was carried out iteratively in two steps. Step 1: The positions of Zn, Al and O atoms in the hydroxide layers were kept fixed. The porphyrin pyrrole units were kept rigid in their planar geometry, while all phenyl and SO_3^- atoms were variable together with the positions of water molecules and hydrogen atoms of the hydroxide layers. Step 2: The hydroxide layers were kept as rigid units, the pyrrole units were constrained as in Step 1, and the cell parameters c , α and β were variable. This procedure enabled to estimate the angle between the guest molecular planes and the host layers. Thus, a new value of the angle was estimated and the Step 1 and Step 2 were repeated until the calculated d_{003} value was in good agreement with the experimental one.

The geometry of the minimized models was further refined by quench dynamics. After a given number of dynamics steps, elucidation of the total crystal energy in dependence on the geometry and arrangement of the guest helps to determine the most probable interlayer arrangement. The dynamics simulations were carried out in an NVT statistical ensemble (N - constant number of atoms, V - constant volume, T - constant temperature) at 300 K. One dynamic step was 0.001 ps and dynamics of 200 ps were carried out. During quench dynamics, porphyrin pyrroles were kept fixed, while the other atomic positions in the interlayer space together with hydrogen atoms of the LDH hydroxide groups were variable. After quench dynamics, the partially minimized structures were again minimized by Step 1 and Step 2 to obtain the final structure models.

Figure S1. Thermogravimetric curves of $\text{Mg}_2\text{Al-TPPS}$, $\text{Mg}_2\text{Al-TPPS}^{\text{H}}$, $\text{Zn}_2\text{Al-TPPS}$, $\text{Zn}_2\text{Al-(Zn)TPPS}^{\text{H}}$, $\text{Zn}_4\text{Al-TPPS}$, $\text{Zn}_4\text{Al-(Zn)TPPS}^{\text{H}}$.

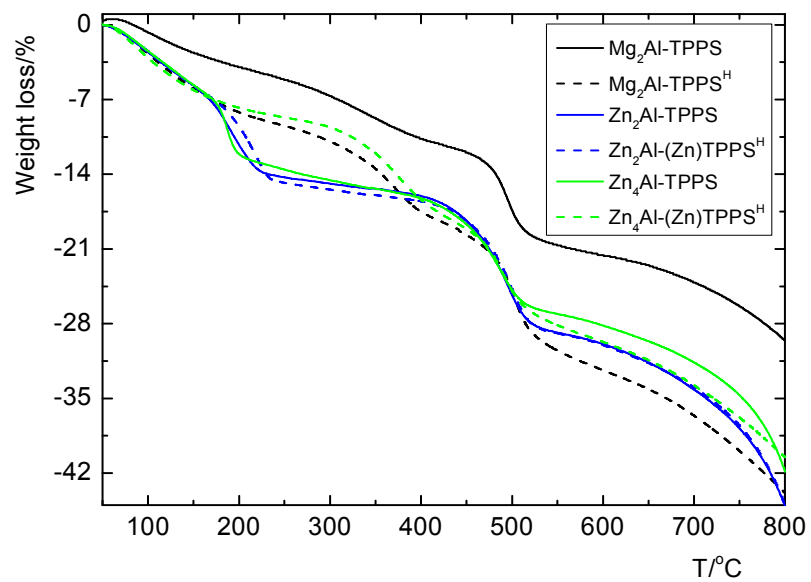
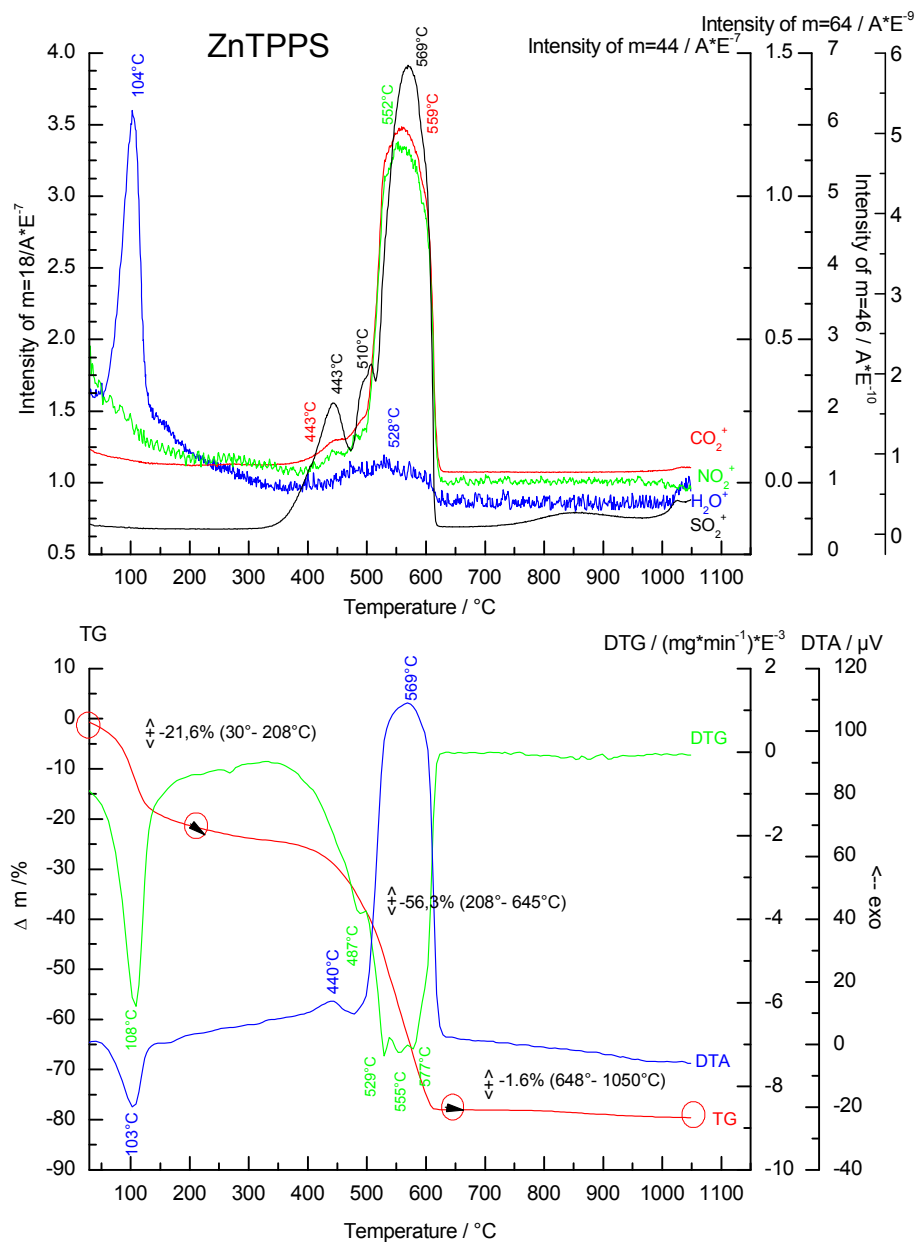
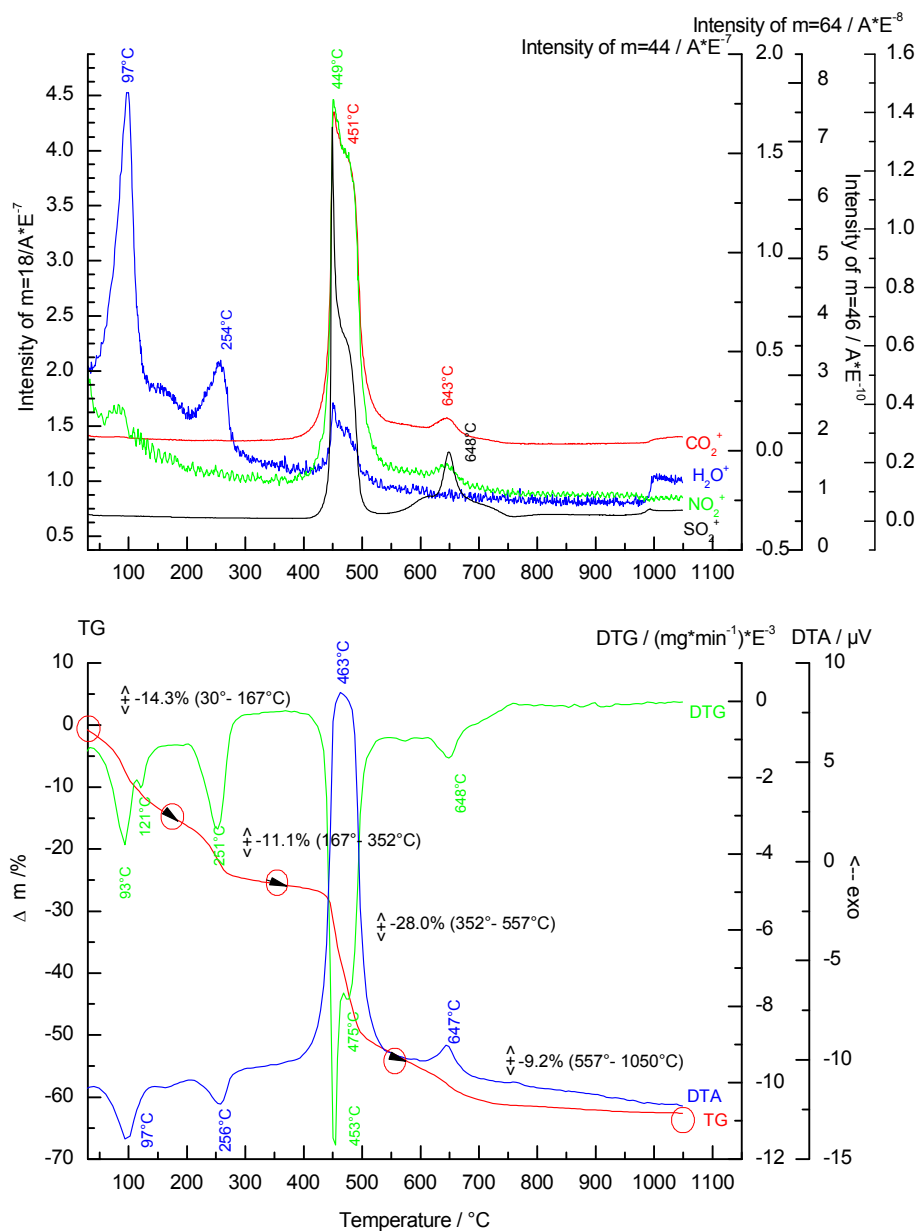


Figure S2. TG-DTA curves and the evolution of gases for ZnTPPS.



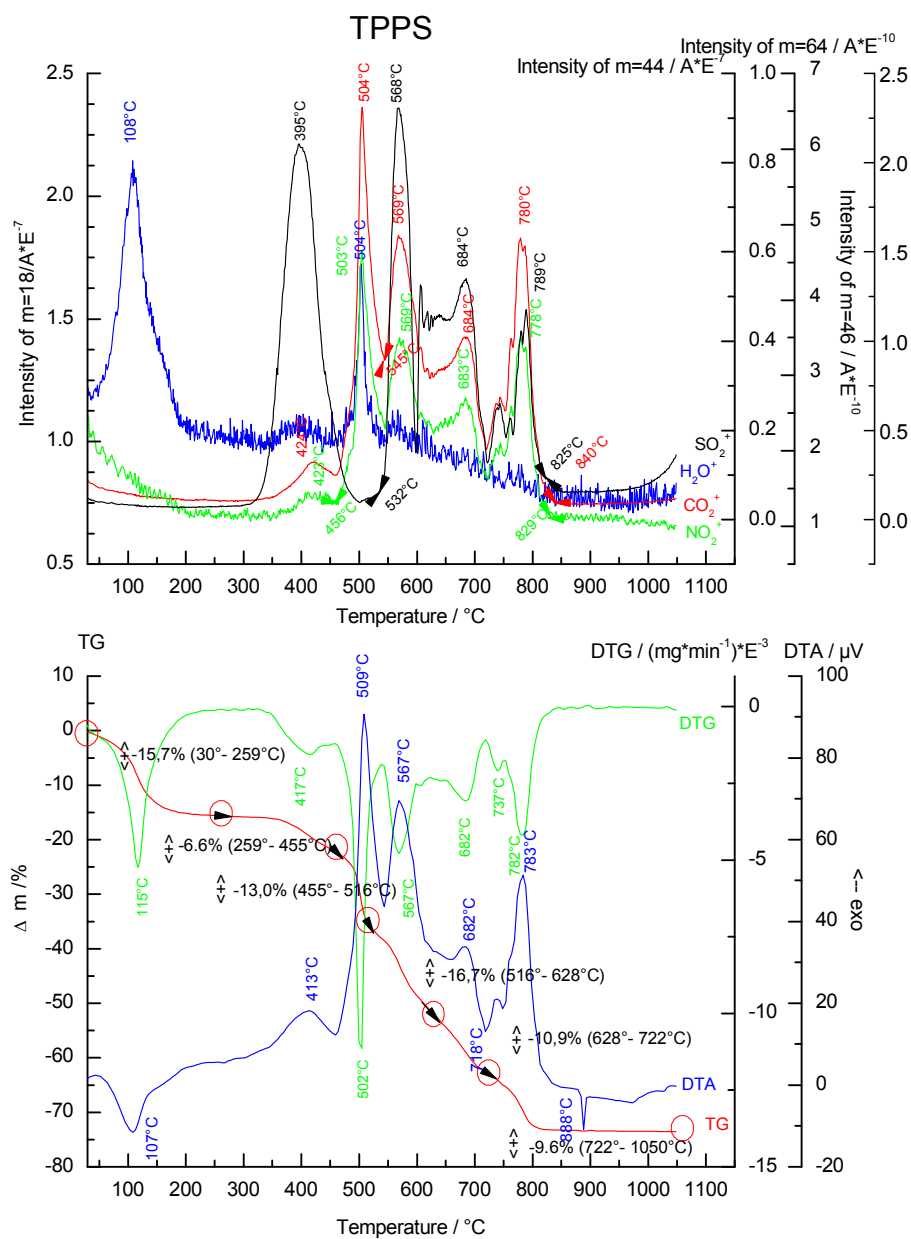
SETARAM Instrumentation		ZnTPPS	17.81mg
		Carrier gas	Air Synthetic 30ml/min.
		Crucible	Al ₂ O ₃ 100μl
SETSYS EVOLUTION-1750			Zone : 1 : 1050°C/5°C

Figure S3. TG-DTA curves and the evolution of gases for Zn₂Al-ZnTPPS^H.



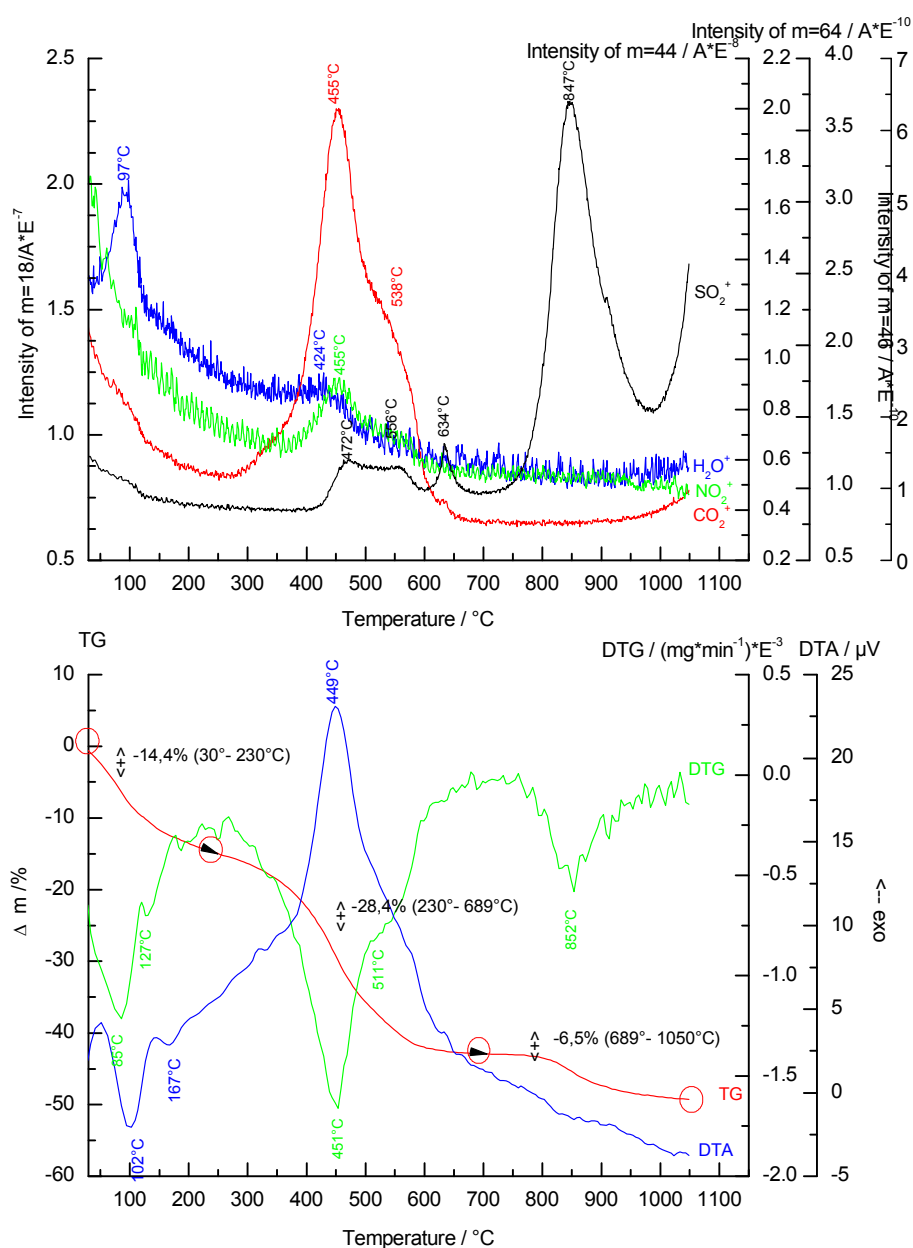
SETARAM Instrumentation		Zn ₂ Al-ZnTPPS ^H	19.91mg
		Carrier gas	Air Synthetic 30ml/min.
		Crucible	Al ₂ O ₃ 100μl
SETSYS EVOLUTION-1750			Zone : 1 : 1050°C/5°C

Figure S4. TG-DTA curves and the evolution of gases for TPPS.



SETARAM Instrumentation		TPPS	20.64mg
		Carrier gas	Air Synthetic 30ml/min.
		Crucible	Al ₂ O ₃ 100μl
SETSYS EVOLUTION-1750			Zone : 1 : 1050°C/5°C

Figure S5. TG-DTA curves and the evolution of gases for Mg₂Al-TPPS^H.



SETARAM Instrumentation	Experiment	Mg ₂ Al-TPPS ^H	9.91mg
		Carrier gas	Air Synthetic 30ml/min.
		Crucible	Al ₂ O ₃ 100μl
SETSIS EVOLUTION-1750			Zone : 1 : 1050°C/5°C

Figure S6A. One-dimensional electron density of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ (a, black line) and $\text{Mg}_2\text{Al-TPPS}^{\text{H}}$ (b, red line) projected along the c -stacking axis. The densities were calculated from the Bragg-Brentano XRD data recorded at room temperature.

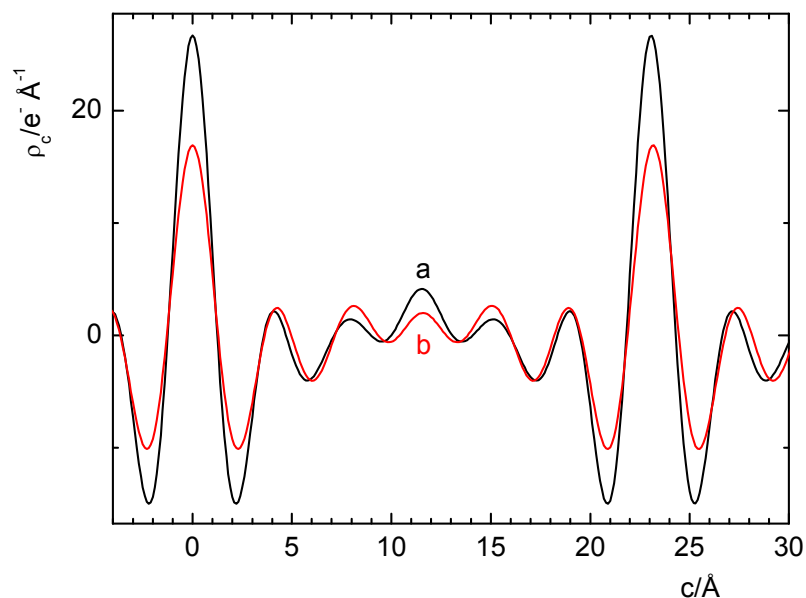


Figure S6B. One-dimensional electron density for $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$ projected along the c -stacking axis and determined from the Bragg-Brentano data recorded at room temperature (black line) and at 100°C under vacuum (grey line).

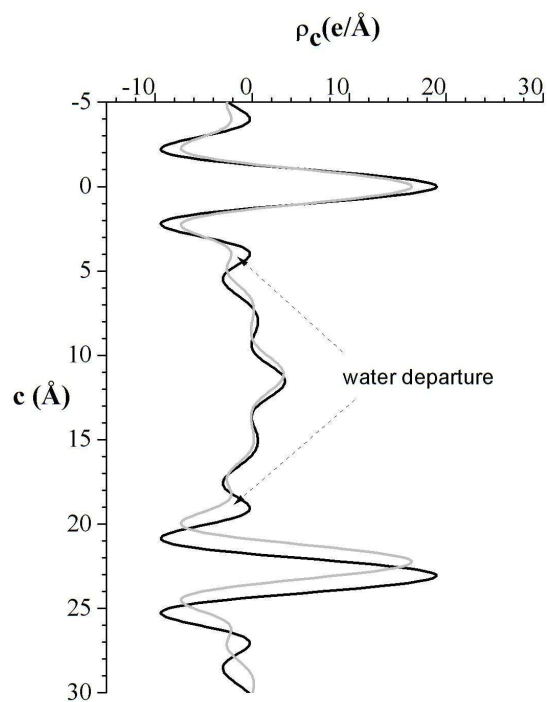


Figure S7. HRTEM observations of $\text{Zn}_2\text{Al-Cl}^{\text{H}}$: a) bright-field image of typical hexagonal crystals, b) electron diffraction along $[001]$.

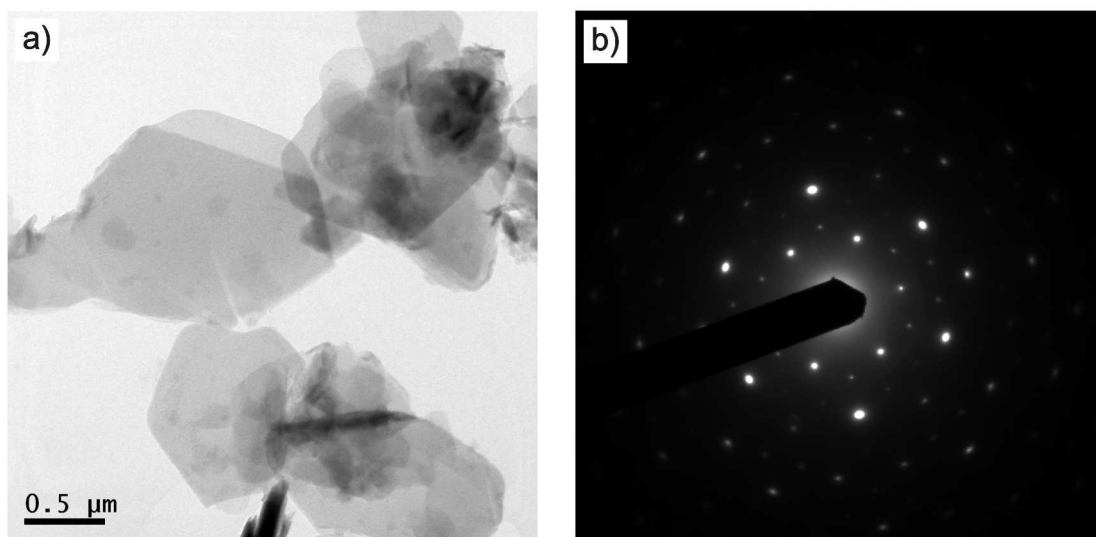


Figure S8. HRTEM observation of $\text{Zn}_2\text{Al-Cl}^{\text{H}}$: a) high-resolution micrograph, b) intensity histogram of the area marked in a).

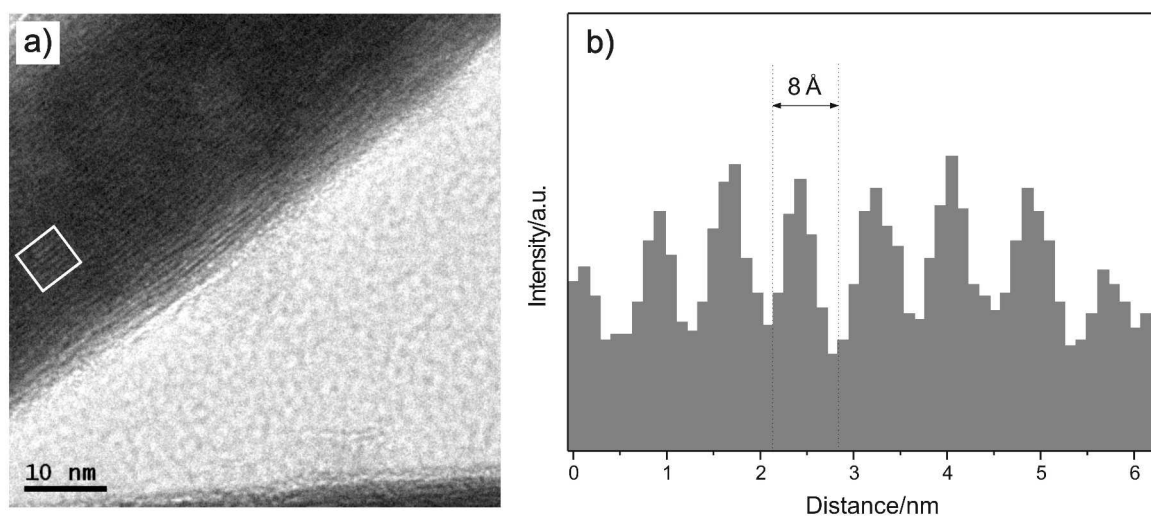


Figure S9. Distribution of angles between the porphyrin plane and hydroxide layer normal.

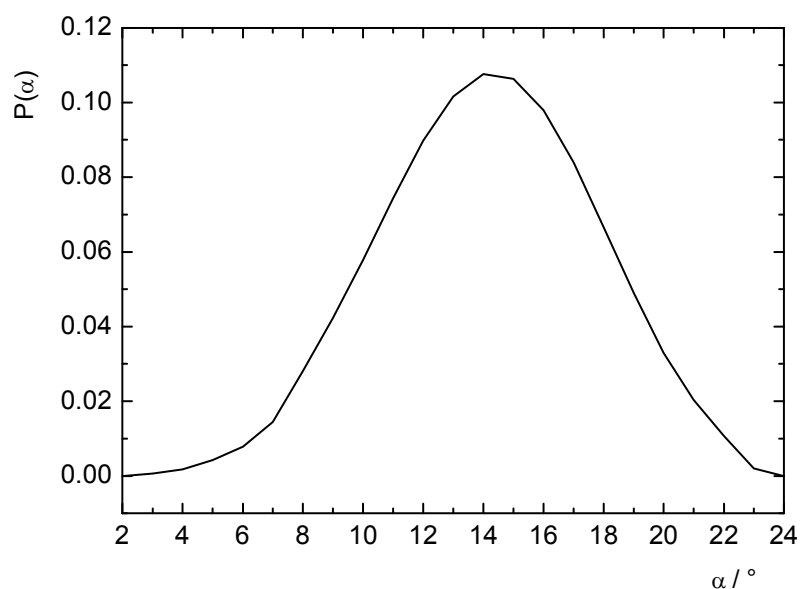
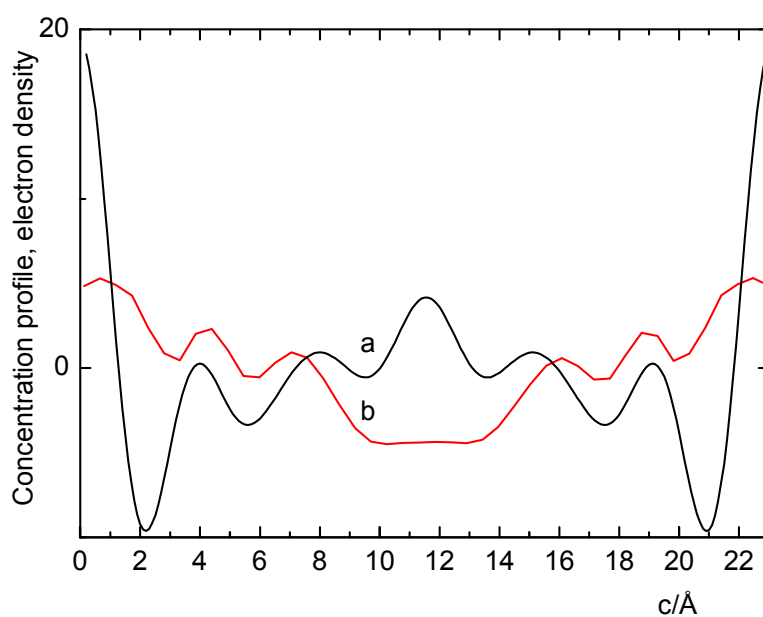


Figure S10. Comparison of the experimental electron density (a) with calculated atom concentration (b) profiles of $\text{Zn}_2\text{Al-ZnTPPS}^{\text{H}}$. The electron density was calculated from the Bragg-Brentano XRD data.



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- P19. Kalendová, A., Pospíšil, M., Kovářová, L., Měřínská, D., Valášková, M., Vlková, H., Šimoník, J., Čapková, P. "Influence of chain length on intercalation process of

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