

Abstract

Since 2016 there are world-wide more mobile phone contracts than people on the planet, and in all these devices critical raw materials (CRMs) are incorporated.^[1] For instance, commonly used silicon-based transistors are limited in their chemical modularity. Inorganic materials for solar cells and photocatalysis suffer from critical raw elements content, low apparent quantum efficiencies and photodegradation. Hence, considerable research interest in recent years is focused on development of new high-performance devices for optical and electronic applications that avoid CRMs entirely. To address all these problems materials chemists are exploring for new pathways towards making more sustainable and reliable materials. In that respect, porous organic π -conjugated polymers (POPs) are among the most promising candidates and have gained tremendous attention in materials research over the last decade, especially in the fields of photocatalysis, opto- and electrochemical sensorics, and microelectronics. Synthetic diversity, chemical and physical stability, as well as comparatively low production costs and scalability enable POPs to overcome the drawbacks of inorganic materials. Moreover, the absence of rare earth elements in the purely organic structure of POPs makes these materials more environmentally friendly. Recently, we introduced a sub-class of polymeric organic frameworks – sulphur and nitrogen containing porous polymers (SNPs). SNPs have all the above-mentioned benefits of POPs due to modular fully organic and micro- and mesoporous molecular backbone. In addition, we incorporate donor-acceptor (D-A) domains into the framework of our materials which creates intrinsic push-pull effects and enables enhanced charge separation in the excited state, i.e. prevents fast recombination of photogenerated electrons and holes. Assembling in one structure aromatic π -conjugated tectons with different electron affinity enables fine tuning of the optical bandgap, which together with increased charge carriers lifetime enables hitherto unmatched efficiency in photocatalysis.

We developed a library of sixteen new polymers along with full structure and morphology resolution. The materials design principle leads to organic frameworks with remarkable optical and electrochemical properties. Obtained SNPs are highly fluorescent which makes them capable for fluorescence on-off sensing of organic volatile compounds. Moreover, sulphur and nitrogen heteroatoms can act as electron-donating centres for p-type reversible doping with HCl/NH₃

vapours. This effect can be used to manufacture naked-eye acid-based sensors due to rapid colour change of SNPs. We also show that electronic and magnetic properties of the resulting materials can be tuned depending on the combination of molecular building blocks. Some of the obtained SNPs effectively act as photocatalysts in visible light induced water splitting with hydrogen evolution rate (HER) up to $3158 \mu\text{mol h}^{-1} \text{g}^{-1}$ – one of the highest reported value for as-received conjugated microporous polymers to date.

We believe that the polymers design aspects as well as theoretical investigations described in this work will widen the understanding of the nature of charge-transfer and charge-separation in porous donor-acceptor networks and will enable truly rational design of such systems. Finally, first proof-of-concept tests show that these materials show promise not only in heterogeneous (photo-)catalysis but also as opto-electronic devices such as gas sensors and photo-luminescent dyes. In Figure 1 we highlight the step-by-step pathway of this work, starting from rational design and screening of different materials types and going towards their suitability in aforementioned practical applications.

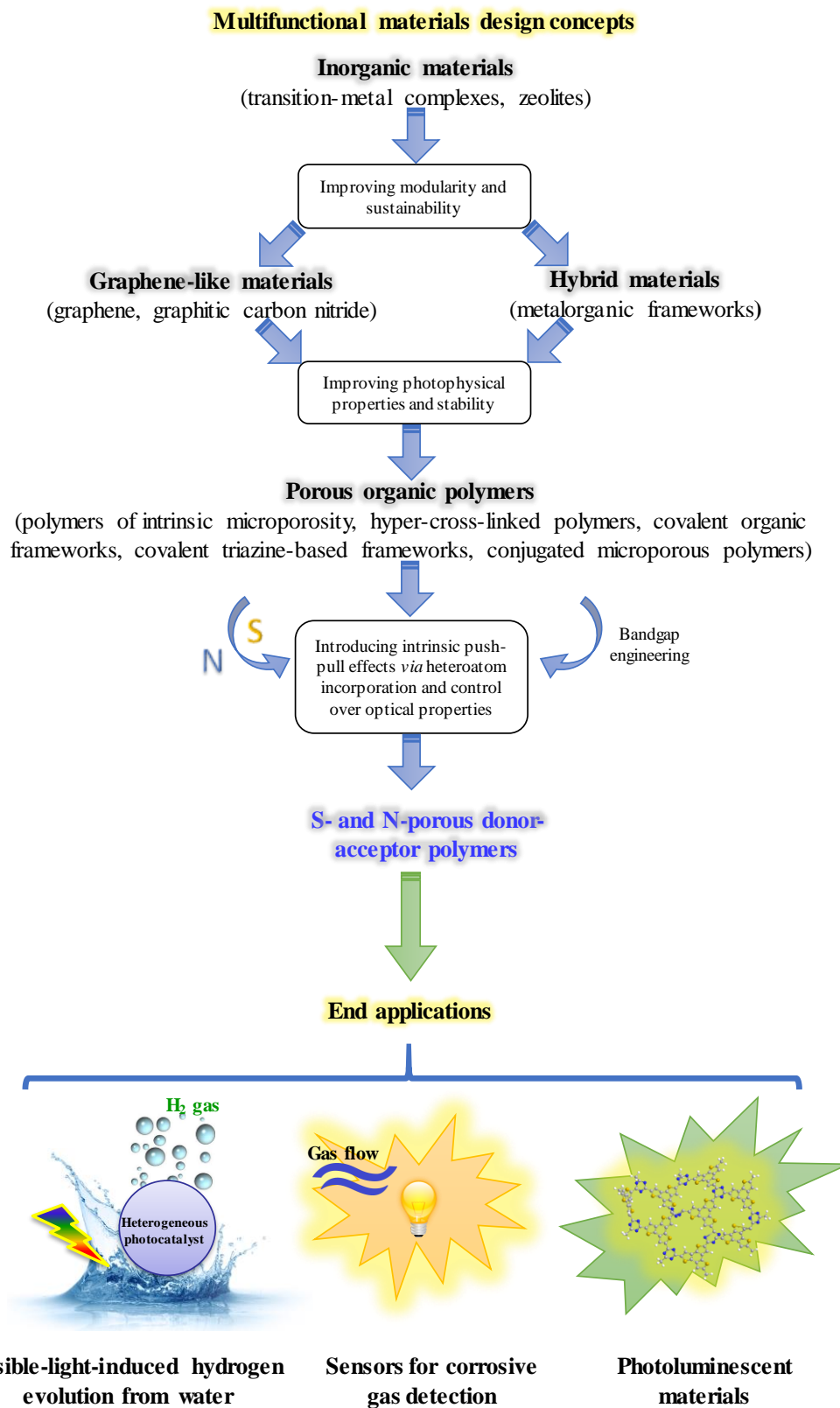


Figure 1. Graphical abstract of the current work.