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Fundamentals and applications of functional framework materials: a themed collection

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Over the past few decades, the field of nanotechnology has undergone exponential expansion, showcasing remarkable progress in technological capabilities and methodologies for the development of novel framework materials. While the early emphasis predominantly centred on metal–organic frameworks (MOFs), the trajectory of recent years has seen efforts progress towards the creation of cutting-edge systems including covalent organic frameworks (COFs), hydrogen-bonded organic frameworks (HOFs), porous organic cages (POCs), and porous (coordination) polymers (PCPs). These advancements have been driven by a growing comprehension of their unique properties, and the field has matured to strive beyond basic science, towards the development of new applications and technologies.

Now there exists concurrent desires, in part to understand the fundamental chemistry of porous materials, while also pushing the boundaries towards their utility in diverse applications. In this themed collection, "Fundamentals and Applications of Functional Framework Materials", we seek to showcase some of the latest reports dedicated to this topic and encourage additional investigation into this dynamic and complex area of materials chemistry.

Pristine framework materials often lack favourable interactions with their surrounding environment, such as solvents or polymeric matrices, due to disparities in chemical and physical properties. This mismatch often leads to suboptimal interfaces and compromised overall performance. To address these challenges, the grafting of polymers onto framework surfaces has emerged as a widely employed strategy, leveraging the diverse chemical moieties and properties inherent to polymers. This is highlighted in the review article by Morris *et al.*, which offers an in-depth examination of the design and synthesis of polymer-grafted MOF particles, elucidating various polymerization techniques and grafting reactions that have proven successful on MOF surfaces (**https://doi.org/10.1039/D3TC03373B**).

This themed collection self-selected for 5 general themes: studies concerning dynamic bonding, small molecule–material

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interactions, harnessing the chemistry of the $[ZrO_4(OH)_4]^{12+}$ cluster, materials composed of elements heavier than Zr, and charge transport pathways in porous networks.

Novel insights into dynamic bonding of materials

Stimuli responsive materials are useful for a wealth of applications, but the challenge remains being able to read, write, and modify the response. Three of this issues papers address this: https://doi.org/10.1039/D3TC03693F where spin-crossover properties of the framework depend on crystallite morphology; https://doi.org/10.1039/D4TC00360H, where the authors demonstrate that spin-crossover also depends on the microscopic organic functionalization; and https://doi.org/10.1039/D3TC01732J that highlights that Cd-based coordination polymers can interconvert upon application of pressure.

Interfacial chemistry with water, other small molecules and ions

Although molecule–material interfaces have been of interest since the conception of porous materials themselves, ongoing efforts continue to develop materials with unprecedented selectivity and stability. Milner and colleagues remind us that we still can learn more and develop applications for MOF-74, and report that the material has a unique ability to selectively uptake N_2O https://doi.org/10.1039/D3TC04492K. Sun and Su *et al.* (https://doi.org/10.1039/D3TC02493H) harness the water stability of ZIF-8 to perform photocatalytic degradation of antibiotics in waste water. In a complementary study to the work on MOFs, Taylor and colleagues present a unique porous organic polymer capable of selectively capturing Co from waste water streams https://doi.org/10.1039/D3TC03320A. Another study by Dhakate *et al.* sheds light on the conductive pathways in COFs, making them potentially useful for aqueous electrocatalysis https://doi.org/10.1039/D3TC03648K.

A continued interest in materials made from the $[ZrO_4(OH)_4]^{12+}$ cluster

Another prevalent theme in this issue centres on harnessing the stability and structure directing properties of the $[ZrO_4(OH)_4]^{12+}$ clusters. https://doi.org/10.1039/D3TC01313H revisits the water–cluster interface, while https://doi.org/10.1039/D3TC03606E shows that such MOFs do provide access to novel material phases, including the evasive *sqc* topology. Two further studies examine the use of the linker as an antenna to capture light and transfer the exciton to perform CO_2 reduction https://doi.org/10.1039/D3TC04175A, or act as a sensor for acids and bases https://doi.org/10.1039/D3TC03120A.

Materials made from elements heavier than Zr

The pursuit for new materials with emergent properties remains strong. One reason for this is that Tb, Gd, Eu, Ce, and other heavy elements tend to form predictable clusters, mimicking that of the aforementioned Zr cluster. However, the inclusion of these heavier elements can enable access to valuable photophysical properties. In https://doi.org/10.1039/D3TC01199B, Howarth and colleagues modify the Tb : Gd : Eu ratio to obtain white light emission in a UiO-66 analogue. In https://doi.org/10.1039/D3TC04365G Pang, Zhang and Zhang *et al.* pursue a similar mission of controlling photophysical properties with a stepwise post-synthetic installation of secondary linkers with targeted properties. In the related chemistry in https://doi.org/10.1039/D3TC04154A, Wang and Wang and colleagues show that Ce Eu substitutions in a Gd framework for D_2O detection at 0.001%, are sensitive to concentrations of D_2O existing in natural water sources.

In a remarkable study by Pedersen and coworkers (https://doi.org/10.1039/D3TC02088F) the authors form frameworks from low valent heavy elements, namely Mo(0) and W(0) using direct vapor-phase substitution of CO by ditopic 4,4′-bipyridine. This report shows that crystals can be isolated with inner sphere metal carbonyls, and result in a novel route to install multi-electron redox active metal-sites with implicitly labile CO ligands. This study could potentially prove useful for heterogeneous catalysis.

Charge transport

Finally, one of the grand challenges in framework chemistry has been the ability to separate excited state holes and electrons, to form conductive pathways. Such advances are important for developing novel sensors and energy storage devices. In https://doi.org/10.1039/D3TC04362B, Akiyoshi, Tanaka, and colleagues present a series of new reduced dimensional Pb-based semiconductors with elegant structure–function relationships. https://doi.org/10.1039/D3TC02379F demonstrates that a reduced dimensional Cu–S based coordination polymer has well-defined inorganic conductive pathways and is a potentially useful thermoelectric.

In two final studies, https://doi.org/10.1039/D3TC04155G and https://doi.org/10.1039/D3TC03237J, the authors lean on the electron accepting character of tetracyanoquinodimethane (TCNQ) to try and develop novel electrical conductors. In the former, the same MOF invoked by Milner and colleagues (https://doi.org/10.1039/D3TC04492K) was impregnated with TCNQ, and the resultant materials become moderately conductive. In the latter, Abrahams and colleagues develop a Cu-TCNQ 2D network, a solid-state metal–organic analogue to the charge transfer material tetrathiafulvalene (TTF)-TCNQ, and show its electrical properties stem from a similar mechanism.

In https://doi.org/10.1039/D3TC02276E by Gutiérrez, Díaz, Cohen and Douhal present a review on functional MOFs that arise from the utilization of low-dimensional building blocks. This review aligns with one of the most promising features of framework materials: strategic bottom-up control of structure–property relationships within materials

through judicious selection of molecular building blocks.

Despite the tremendous progress in the field of MOFs, further research is needed to unravel the full extent of the capabilities of these materials and optimize their performance across diverse applications. Through further research centred on bridging the fundamental understanding of MOF materials with their functional utility, we have the opportunity to unlock the full potential of these extraordinary materials and realize their promise for the betterment of society.

