Covalent organic frameworks and organic cage structures

Rahul Banerjee*[a] and Neil R. Champness*[b]

a Physical/Materials Chemistry Division, CSIRNational Chemical Laboratory, Dr Homi Bhabha Road, Pune-411008, India. E-mail: r.banerjee@ncl.res.in
b School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK.
E-mail: neil.champness@nottingham.ac.uk

The last 20 years have seen an enormous interest in research on the topic of crystalline porous framework materials, especially metal–organic frameworks (MOFs). MOFs exploit reversible metal–coordination chemistry to create extended, crystalline solids.[1] However, a similar set of porous ordered covalent networks based on the reversible and modular connection of a vast array of rigid and symmetrical building blocks through covalent bonds has also emerged during this time. These materials, coined as "Covalent Organic Frameworks (COFs)", have summoned considerable attention in the last decade, starting with a significant contribution from the Yaghi group,[2] owing to their unique designing features as well as enormous potential.[3] Like COFs, porous molecular crystals that are not interconnected by covalent bonding have also picked up significant research interest. Although these materials do resemble COFs, unlike COFs, they can be solution processable.[4] For any structural chemists, these materials are excellent tools that can lead to more informed design processes and create a deeper understanding of how targeted porous extended structures should be made.

The rapid growth of interest in this field has inspired this *CrystEngComm* themed issue on "Covalent organic frameworks and organic cage structures". As exemplified by the articles, this themed issue focuses on the design strategies for the construction of porous organic materials, including covalent organic frameworks and organic cage structures with new physicochemical properties. Associated challenges regarding synthesis, crystallization, and structure–property relationships of covalent organic frameworks and organic cage structures are also covered.

An earlier themed issue on this topic edited by Andrew Cooper showcased the versatility of the COFs synthesized by reversible boronate ester bonds.[2] This current themed issue, however, showcases a diverse number of synthetic procedures, other than the reversible boronate ester bonds, to produce ordered crystalline porous solids with physical properties, such as sensing, separation, and conductivity, rather than focusing only on porosity. A collection of twelve research articles on covalent organic frameworks and organic cage structures is presented, which showcase the very significant fact that the COFs are not limited to boronate ester chemistry, nor are porous organic solids restricted to extended networks. The article by Andrew Cooper and co-workers (DOI: 10.1039/C7CE00783C) showcases the strategy towards modulating the assembly of porous organic cage crystals, whereas the article by Antonio Frontera and co-workers (DOI: 10.1039/C6CE02341J) describes the solid-state inclusion phenomena within a Zn-Porphyrin Cage.

Many of the articles have exploited the imine bond formation reaction, which has proved to be effective for generating highly porous materials and are represented by a number of articles in this issue. Felix Zamora and coworkers, along these lines, have showcased the self-assembly of an imine-based covalent organic framework into nanospheres. The articles by Yushan Yan and co-workers (DOI: 10.1039/C7CE00042A), Qingyuan Yang and co-workers and Dan Zhao and co-workers (DOI: 10.1039/C7CE00344G) on the topic of anion conduction, capture of radioactive iodine and hydrocarbon uptake and separation by COFs, confirm that the properties of porous organic materials are not restricted to porosity alone.

The other articles in this issue by Hong-Cai Zhou and co-workers on the topic of flexible covalent organic frameworks (DOI: 10.1039/C7CE00593H); Ronald Smaldone and coworkers on the effect of fluorine substituents on the properties of covalent organic frameworks (DOI: 10.1039/C7CE00598A); Xin Zhao and coworkers on hetero-pore covalent organic frameworks (DOI: 10.1039/C7CE00590C) and by Dana Medina and co-workers on fluorescence labeling of covalent organic frameworks (DOI: 10.1039/C7CE00684E) indicate the diverse opportunities for generating and understanding the structure–property relationships among these porous organic materials.

The articles included in this issue contribute to a growing argument that porous crystalline organic solids do present an exciting alternative compared to their metal–organic [MOFs] or inorganic [Zeolites] equivalents for certain applications, and opens up new possibilities, such as membrane separation and solution processability.

We would like to extend our thanks to all the authors who have contributed articles to this themed issue, as well as to the editorial staff of CrystEngComm who have worked hard to put this issue together.

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