VIEWPOINT

Topology, chirality and interpenetration in coordination polymers

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This Viewpoint turns back the clock to 1998 when a contribution by Carlucci, Ciani, Macchi and Proserpio (*Chem. Commun.,* 1998, 1837–1838) addressed the existence of multiple properties in coordination polymer networks and the use of topology for classifying network connectivity, thereby serving as a presage of the exponential growth in the field of coordination polymers that continues unabated to this day.

Introduction

The early 1990's was a time when advances in technology related to X-ray crystallography such as faster and better data collection methods and crystallographic databases profoundly impacted our ability to systematically study and better understand crystalline solids. The seeds planted by Desiraju,[1] Etter[2] and Robson[3] rapidly led to the realisation that the crystal structures of certain classes of molecular and coordination compounds are inherently amenable to self-assembly in a predictable manner. This enabled the design of new classes of compounds with desired structure and, ultimately, properties, as outlined in two recent Viewpoint articles.[4,5] Crystal engineering thereby evolved from a dream (and a not particularly well respected dream) to where today it offers a paradigm shift from the more random, high-throughput approach that has traditionally been used in materials discovery and development. In 1998 there was growing activity and considerable promise for coordination polymers, CPs, but in hindsight this was the proverbial "quiet before the storm". Interest in CPs exploded in 1999 following reports concerning HKUST-1[6] and MOF-5,[7] the prototypal extra-large surface area porous CPs, PCPs,[8] or metal–organic frameworks, MOFs.[7] Bibliometrics makes it possible to quantify the dramatic growth in activity (>4000 papers per year) and impact (>130 000 citations per year) of this subject (Fig. 1, data obtained with Web of Science®). The inflection point after 1999 is undoubtedly linked to interest generated by HKUST-1 and MOF-5 but is also a result of the influence of China, which today contributes *ca.* 50% of articles and, if anything, is increasing its share of publications (Fig. 2).

Form before function

Crystal structure prediction[9] has advanced in parallel to crystal engineering but it is not synonymous with crystal engineering.[10]

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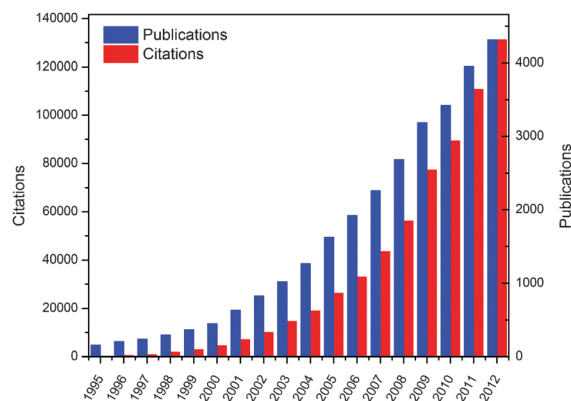
Fig. 1 Number of publications and citations per year from 1995–2012 for articles on the topics of ''coordination polymers'' or ''metal–organic frameworks''.
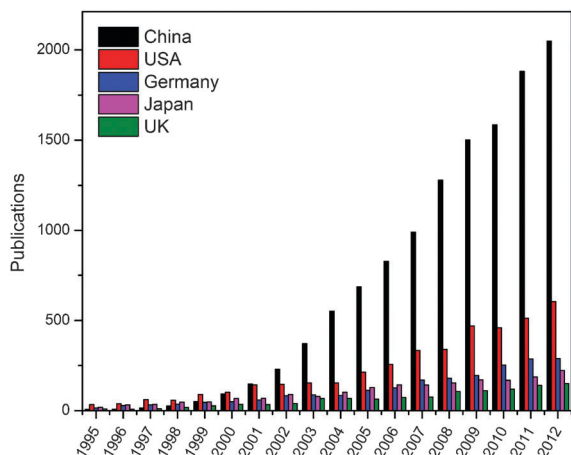

Fig. 2 China's impact upon CPs is revealed by a country breakdown of articles per year from 1995–2012 on the topics of ''coordination polymers'' or ''metal–organic frameworks''.

The crystal engineer has the distinct advantage of being able to preselect starting materials or molecular building blocks, MBBs,

in a manner that resembles an architect designing a building and choosing the components for its construction. CPs are exceptional because their modular nature can afford control over structure while enabling diversity of composition. Families of related compounds can thereby be studied in systematic fashion. This is especially the case for CPs based upon well-defined metal coordination spheres or high symmetry cluster MBBs that are assembled with rigid organic MBBs according to the "node-and-linker" principle.[3] By 1998 it had become evident that control over structure could be exerted with uninodal CPs based upon tetrahedral or octahedral metals, which, when linked by rigid linear organic linkers, afford diamondoid[5,11] or primitive cubic[12] nets, respectively. However, the study of properties, with one or two very notable exceptions,[13] and cataloguing of topology, had not yet advanced to the same level. This is where the contribution of Carlucci, Ciani, Macchi and Proserpio made a difference. They reported[14] the reaction of an extended variant of 4,4-bipyridine, 1,2-bis(4-pyridyl)ethyne (bpethy), with $Cu(NO_3)_2$. [{$Cu(bpethy)_2(H_2O)_2$}{$Cu(bpethy)_2(NO_3)(H_2O)$}$_2$][NO_3]$_4$·bpethy· 1.33H_2O, **2**, one the products thereby obtained, is noteworthy because it exhibits three seemingly unrelated features that remain at the forefront of CP research because of their continuing relevance to design and properties: chirality, interpenetration and novel topology.

Chirality, interpenetration and topology in 2

2 exhibits $7^5 9$ topology (a uninodal net from 4-connected nodes requires that the connectivity of the shortest six circuits be defined) that the authors termed a '**dense net**' (it can also be labelled a **quartz dual** net). This **dense net** is a chiral net built by linking 4-connected square planar Cu^{2+} MBBs (Fig. 3). Whereas nets built through linking of 4-connected nodes (*e.g.* tetrahedral or equatorially substituted octahedral metal cations) were ubiquitous in CPs even before 1998, the **dense net** of **2** was unprecedented at the time of publication. Perhaps more importantly, that the net is chiral is an inherent property of the structure and means that **2** represents a prototypal example of a chiral crystal structure that can be generated from achiral MBBs. This matter remains of topical interest as discussed later.

It is also of note that **2** crystallizes such that three networks interpenetrate, *i.e.* there are no covalent or coordination bonds between the networks but they cannot be separated without breaking bonds (Fig. 4). Whereas interpenetration was well documented in CPs by 1998,[11,15] **2** is unusual in that its interpenetrated nets exhibit differences in the axial coordination of
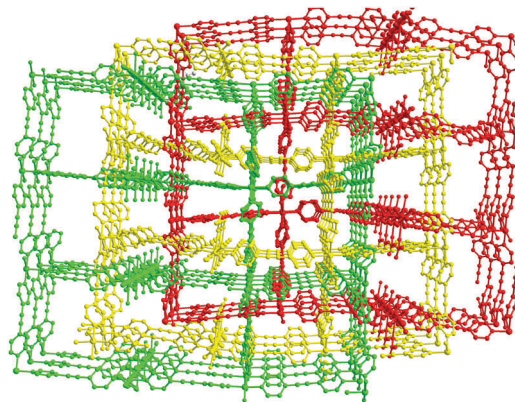

Fig. 4 An illustration of the 3-fold interpenetration of two chemically different nets in **2**.

the Cu^{2+} ions: axial ligands on the Cu^{2+} ions are two aqua ligands in one net whereas a nitrate and aqua ligand are the axial ligands in the other two nets. To summarize, **2** represents a microcosm of several aspects of CP chemistry. The balance of this Viewpoint addresses why **2** attracted so much attention in terms of citations and why it remains of interest even 15 years later.

Chirality in CPs today

Chirality is an essential feature of the everyday world and plays a vital role in various biological functions. Further, there are numerous potential applications in chemistry that relate to chirality as exemplified by the demand for enantioselective catalysis and separations. It should therefore be unsurprising that chiral PCPs have been targeted for study since they can combine chirality and porosity in a single material. There are two distinct approaches to design of chiral PCPs: pre-synthesis and post-synthetic modification, PSM. Pre-synthesis exploits homochiral MBBs or achiral MBBs to build chiral nets. PSM is facilitated by the porosity of PCPs and can be accomplished through attachment of chiral moieties at the organic linker[16] or at unsaturated metal centres.[17] **2** demonstrated that generation of chiral nets from achiral building blocks can be accomplished but there is a drawback: such PCPs tend to crystallise as racemic conglomerates. Such was the case when Zaworotko *et al.*[18] reported CPs based on helical chains formed by Ni^{2+} cations and achiral 4,4′-bipyridine linkers that generate large cavities which incorporate organic guest molecules. However, the issue of racemic conglomerates was subsequently addressed through chiral induction, *e.g.* the use of chiral solvent or chiral additives that serve as templates. Chiral induction was demonstrated by Morris and co-workers[19] when 1-butyl-3-methyimidazolium L-aspartate, an ionic liquid, facilitated spontaneous resolution *via* crystallization of a homochiral CP. The corresponding D-aspartate ionic liquid afforded a CP with the opposite chirality. Bu *et al.*[20] also demonstrated chiral induction from achiral MBBs by employing chiral additives such as D- or L-camphoric acid.

Interpenetration in CPs today

Interpenetration has traditionally been thought of as a handicap to application of PCPs because it necessarily reduces pore

Fig. 3 A schematic view of the $7^5 9$ or '**dense net**' network topology exhibited by compound **2**.

size, free volume and surface area. As such, various approaches to prevent interpenetration have been developed: bulky groups on the organic linkers; large molecules as template or solvent; lowering the concentration of reactants; controlling temperatures; liquid phase epitaxy. However, interpenetration can also enhance properties, especially in the context of small molecule separations and gas storage where tight confinement might be advantageous (*e.g.* H_2 and CO_2). Zhou *et al.* reported that 2-fold interpenetration in PCN-6 (PCN-6′) increases Langmuir surface area and affords a 133% increase in volumetric hydrogen uptake in comparison with its non-interpenetrated variant, PCN-6.[21] In similar fashion, Eddaoudi, Zaworotko *et al.* recently reported a study of the non-interpenetrated and 2-fold interpenetrated variants of $[Cu(bpethy)_2(SiF_6)]$, SIFSIX-2-Cu and SIFSIX-2-Cu-i, respectively.[22] SIFSIX-2-Cu-i was found to exhibit significant enhancement of CO_2 uptake when compared with its non-interpenetrated, less dense counterpart, SIFSIX-2-Cu. In addition, SIFSIX-2-Cu-i also demonstrated exceptional CO_2 *vs.* CH_4 and CO_2 *vs.* N_2 selectivity that exceeds that of any other PCPs with coordinatively saturated metal centres. This observation was attributed to the enhanced heat of adsorption (Q_{st}) of SIFSIX-2-Cu-i *vs.* SIFSIX-2-Cu, a feature that can in turn be ascribed to the better overlap of attractive electrostatic potential fields of opposite walls in the relatively narrow pores in SIFSIX-2-Cu-i. Thus, the large pores that can be generated in non-interpenetrated CPs are perhaps undesirable for small molecule separations and interpenetration can result in optimal pore size and distribution.

Topology in CPs today

Topology can play a critical role in advancing CP chemistry because it can offer blueprints for the design of families of related compounds. The program TOPOS has been developed for general use and it allows for the simplification and classification of the topologies of CPs.[23] Along with TOPOS, electronic resources such as the RCSR, which has introduced 3-letter codes to classify topology, and the EPINET project have also been developed.[24,25] Whereas it has become evident that there exists an effectively infinite number of possible topologies that can be generated by linking vertices and edges of MBBs, there are only a few network topologies that are accessible and robust enough to be easily fine-tuned and thereby regarded as "platforms". These are exemplified by uninodal nets with primitive cubic (**pcu**, 6-connected octahedral nodes), diamondoid (**dia**, 4-connected tetrahedral nodes) or niobium oxide (**nbo**, 4-connected square nodes) topology and binodal platforms such as 24-connected rhombicuboctahedra linked by triangles (**rht**) and twisted boracite (**tbo**, squares and triangles) nets. Proserpio *et al.* recently analysed 6620 3D CPs and determined that **dia**, **pcu**, **srs**, **cds**, **pts** and **nbo** are the most frequent nets if one focuses upon the underlying (simplified) topology.[26] Indeed, **dia** and **pcu** together represent around 50% of all CPs that have thus far been studied. This should be unsurprising for two reasons: tetrahedral or octahedral coordination spheres are the most commonly encountered geometries for transition metals; linear linking of tetrahedral or octahedral nodes affords **dia** nets or **pcu** nets, respectively, by default. Such default nets are ideal platforms for the design of families of PCPs in which both the size and the chemistry of pores can be controlled in a rational fashion.[22]

Conclusions

Crystal engineering and CPs have reached a level of maturity with respect to design principles that are effective across a diverse range of MBBs. These design principles include the use of topology to classify and generate specific structures, generation of chirality from achiral MBBs and control of pore size through interpenetration. In effect, this means that we are now at the "end of the beginning" and crystal engineers are well positioned to systematically examine a broad range of structure–function relationships. One might even assert that custom design of CPs to fit a specific task is now a realistic goal and issues like chemical stability, hydrophobicity and cost can be addressed as part of the design process. Nevertheless, it should be stressed that, with the exception of carboxylate MBBs, which have dominated the past decade of CP research but are not yet suitable for applications because of cost or chemical stability issues, many classes of CPs remain understudied. This partially explains why benchmark properties with respect to selectivity, chirality, magnetism, conductivity and catalysis are only now emerging. In this context, **2** remains noteworthy because chirality from achiral MBBs and interpenetration are highly desirable and relevant features when coupled with porosity. Indeed, if anything, there is even greater interest and potential today than in 1998.

Notes and references

1 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
2 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
3 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **122**, 1546.
4 C. Janiak, *Chem. Commun.*, 2013, **49**, 6933.
5 N. R. Champness, *Chem. Commun.*, 2013, **49**, 331.
6 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
7 O. M. Yaghi, H. Li, M. Eddaoudi and M. O'Keeffe, *Nature*, 1999, **402**, 276.
8 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
9 G. M. Day, *Crystallogr. Rev.*, 2011, **17**, 3–52.
10 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
11 M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283.
12 S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2561.
13 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
14 L. Carlucci, G. Ciani, P. Macchi and D. M. Proserpio, *Chem. Commun.*, 1998, 1837.
15 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
16 L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248.
17 M. Banerjee, S. Das, M. Yoon, H. Choi, M. Hyun, S. Park, G. Seo and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 7524.
18 K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1999, **38**, 492.

19 Z. Lin, A. Slawin and R. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880.
20 J. Zhang, S. Chen, R. Nieto, T. Wu, P. Feng and X. Bu, *Angew. Chem., Int. Ed.*, 2010, **49**, 1267.
21 S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858.
22 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.

23 V. A. Blatov, *Int. Union Crystallogr. Comm. Crystallogr. Comput. Newsl.*, 2006, **7**, 4, http://www.topos.ssu.samara.ru.
24 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782, http://rcsr.anu.edu.au/.
25 S. J. Ramsden, V. Robins and S. T. Hyde, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2009, **65**, 81, http://epinet.anu.edu.au/.
26 E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm*, 2011, **13**, 3947.