Porous Organic Crystals

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Molecular Organic Crystals: From Barely Porous to Really Porous**

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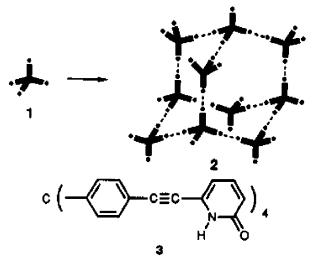
In 1991,[1] before the avalanche of interest in nanoporous hybrid crystals, such as metal–organic frameworks (MOFs),[2] Wuest and co-workers reported a diamondoid organic crystal based on the principal of molecular tectonics. The word "tecton" (from the Greek, tecton = builder) refers to a molecule whose interactions are dominated by particular associative forces that induce the self-assembly of an organized network with specific architectural or functional features. Specifically, a tetrahedral molecule, **3**, containing four pyridone "sticky sites" was found to assemble into a diamondoid crystal, **2**, with large internal chambers, broadly according to the authors' design scheme (Scheme 1). Likewise, a related



Scheme 1. Tectonic assembly of a three-dimensional hydrogen-bonded organic crystal.[1]

tetradiaminopyrine tecton formed a robust hydrogen-bonded network with exchangeable enclathrated guests[3] which was subsequently desolvated to generate permanent porosity.[4]

In his 1991 Communication, Wuest concluded that: "*We believe that this strategy can be used to build predictably ordered materials with useful properties, including selective enclathration, microporosity, high ratios of strength to density, and catalytic activity.*"[1]

As it turns out, extended frameworks, such as MOFs and covalent organic frameworks (COFs)[5] have since fulfilled this vision more thoroughly than molecular organic crystals. A primary reason is the directional intermolecular bonding that defines the crystalline structure of MOFs and COFs, making it possible to produce "isoreticular" series of materials.[2d] By contrast, molecular crystals comprise a more complex set of weak intermolecular interactions that often precludes de novo structural design. As Desiraju put it:[6] "*Predictability of crystal structure is the first step towards fine-tuning of properties. It is of little use if a given crystal structure is very sensitive to minor molecular changes because such changes would be required anyway in the optimization of the crystal properties.*"

Extended bonding in frameworks can also stabilize the framework toward guest removal, leading to materials with remarkably low framework densities.[7] In molecular crystals, incipient pore structures, for example in solvates, tend not to withstand guest removal.[8] Two broad strategies have been used to form porous molecular crystals: extrinsic porosity, which arises from inefficient molecular packing;[9] for example in the well-established tris-*o*-phenylenedioxycyclotriphosphazene (TPP) system,[10] and intrinsic porosity, in which porosity is covalently "prefabricated", for example in molecular cages[11] or calixarenes.[12] These two strategies are not mutually exclusive and can be combined.[13] Recently, a new generation of intrinsically porous molecules have exhibited promising pore volumes.[14] Using the convenient (if imperfect) measure of Brunauer–Emmett–Teller (BET) surface area (SA_{BET}), the state-of-the-art was set recently at 2071 $m^2 g^{-1}$ for a porous organic cage synthesized by Mastalerz and co-workers,[11c] building on cages (SA_{BET} $\approx 1400\ m^2 g^{-1}$) reported previously by the same group[11b] and by our own team.[15] These findings suggested that covalent-cage synthesis might be superior to "extrinsic" self-assembly strategies, at least for high pore volume materials.

A recent study,[16] again by Mastalerz and Oppel, challenges that conclusion. In a remarkable paper, a triptycene trisbenzimidazolone (TTBI; Scheme 2) is shown to self-assemble through programmed hydrogen-bonding to form an extrinsically porous solid (Figure 1) with a large pore volume and a surface area, SA_{BET}, of 2796 $m^2 g^{-1}$.

The density of the solvent-free crystal is 0.755 $g cm^{-3}$. In terms of apparent surface area, this is easily the most porous *molecular* crystal of any kind produced to date. By combining

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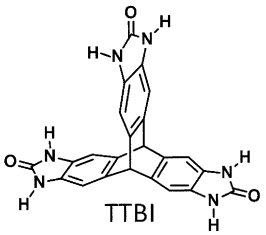

Scheme 2. Structure of a triptycene trisbenzimidazolone (TTBI) tecton.

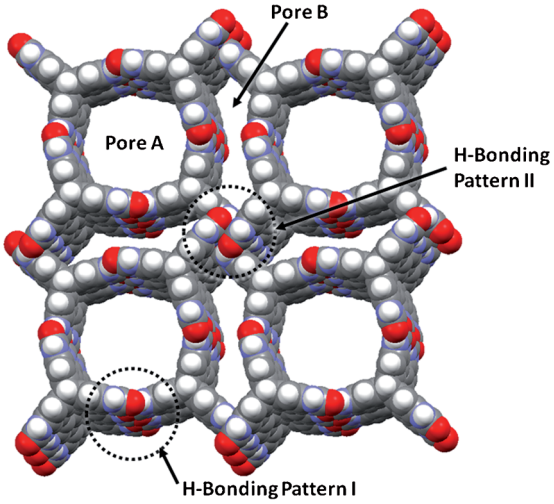

Figure 1. Single-crystal X-ray structure of TTBI, an extrinsically porous organic crystal with a surface area, SA_{BET}, of 2796 $m^2 g^{-1}$. Red O, blue N, gray C, white H.

a hydrogen-bonding mode exploited in non-porous assemblies[17] with the versatile triptycene moiety,[18] Mastalerz has pulled off an elegant coup in terms of the rational construction of extrinsic pore volume.

The crystal structure of TTBI is defined by one-dimensional pore channels that are generated by the ribbon-like self-assembly of hydrogen-bonded benzimidazolone tapes (Figure 1). This arrangement generates two kinds of pores: roughly cylindrical channels, each enclosed by a columnar stack of four TTBI molecules (Pore A; $d \approx 14.5$ Å; Figure 1) and smaller, slit-like pores (Pore B) between these cylindrical channels. Interestingly, the porous solid is not formed by straight thermal desolvation, but rather by multiple solvent exchanges to avoid stress on the hydrogen-bonding pattern. This approach, which is reminiscent of supercritical drying strategies for MOFs[19] might be important in producing other "ultraporous" organic crystals.

The exceptional surface area in this material was ascribed by Mastalerz and Oppel to the fact that no accessible molecular surface is lost, for example by π–π stacking. This situation can be contrasted with our own porous organic cages: these also tend not to exhibit π–π stacking but, nevertheless, only one face of each constituent benzene rings is accessible to guest sorption in most of the crystal packings observed to date.[11a,15]

This new result, along with other recent studies, changes the perception of what might be possible in terms of porous molecular solids (Figure 2), which have properties, such as solution processability, that are distinct from extended networks. While surface area is already well catered for by solids, such as carbons, polymers, MOFs, and COFs, the development of strategies to produce solids with larger pores and pore volumes is important if molecular crystals are to find applications beyond the sorption of very small molecules. As such, the recent study by Mastalerz and Oppel[16] is (another!)[11b,c,14] important milestone in the rational construction of porosity in organic molecular crystals.

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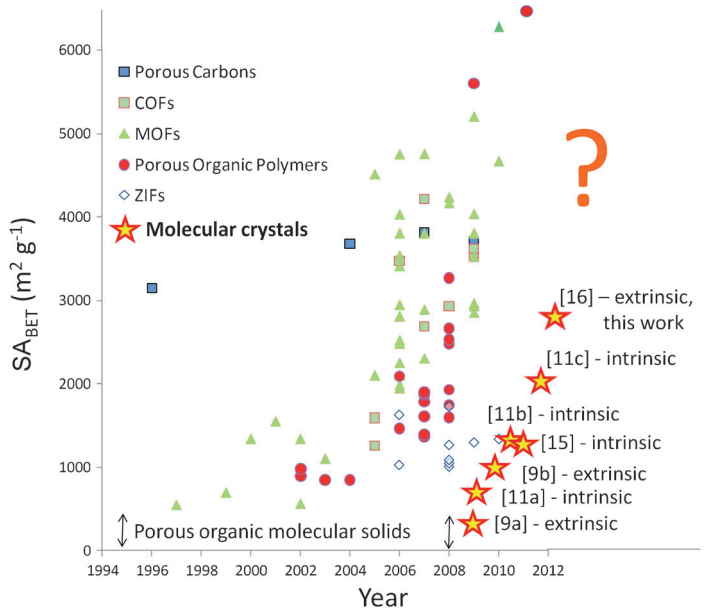

Figure 2. Graph showing the rapid evolution in porosity in molecular crystals since around 2009, illustrated with respect to the equivalent trend in extended networks and frameworks (adapted from Ref. [7]). Numbers in square brackets refer to references in this Highlight. ZIFs = zeolitic imidazolate frameworks.

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