Porous Organic Crystals

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Rational Design of Multifunctional Nanopores by Mixing Matching Molecules**

Michael Mastalerz*

co-crystals · crystal engineering ·
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The interest in porous materials derived from discrete organic molecules has increased noticeably in recent years,[1] mainly because it was demonstrated that these materials can be freed from the solvent molecules trapped in their pores without collapse of the pore structure, and thus be made permanently porous.[2] Such porous organic crystals are novel alternative materials to established polymeric porous systems, such as metal–organic frameworks (MOFs),[3] covalent organic frameworks (COFs),[4] and similar porous organic polymers.[5] After initial contributions of Sozzani and Hulliger, demonstrating that molecular crystals show permanent porosities with Brunauer–Emmett–Teller (BET) surface areas of 240 m^2g^{-1},[6] significant improvements have been made by using shape-persistent cage compounds, resulting in materials with surface areas of up to 624 m^2g^{-1}.[7] In just two years the values of specific surface areas were approximately doubled for such systems.[8] Today, the highest value for BET surface areas for an organic crystalline system, consisting exclusively of discrete organic compounds, is 2071 m^2g^{-1},[9] and further improvements can be expected.

But surface area alone is just one parameter of porous compounds and not the only feature that makes porous systems interesting for several applications, such as gas storage/separation, or catalysis.[10] There are only a few examples in which various functional groups are incorporated inside the pores of organic crystals.[1] The introduction of such groups inside the pores opens the opportunity to create systems with new properties and functionalities. From a crystal-engineering point of view it is still challenging to rationally construct such nanoporous functional compounds for several reasons: 1) The prediction of a crystal structure by the knowledge of the structure of the molecular precursor is still very difficult, although a lot of progress has been made in the calculation of porous crystal structures.[11,7a] 2) It has been widely established that a small change of the molecular precursor can lead to a completely different molecular assembling in the crystalline state which does not necessarily form the desired pores. Therefore, systems have to be found where functional groups, directing into the pores of nanoporous crystals, interact mainly with the bulk solvent inside the pores rather than contributing to the formation of the assembling of the molecules in the solid state. Thus, the functional groups directing into the pores should be "bad" or orthogonal synthons in terms of crystal engineering and ideally should not interact with the functional groups (or synthons) that are responsible for the self-assembling of the molecules.

Such properties can be assigned to a number of hydrophobic dipeptides, which are known to crystallize into microporous structures which have adjustable channel diameters.[12,13] The channel diameters strongly depending on the hydrophobic side-chains of the crystallized dipeptides. In 2005 the Davis group showed that steroidal bisphenyl ureas **1a–c** (Figure 1) behave in a similar fashion, forming one-dimensional hydrophilic channels with average diameters between 11.6 Å and 14.3 Å in the crystalline state.[14] They recognized that the groups R^1 and R^2 are directed into the formed channels and did not seem to contribute to the self-assembling process. Regardless of the bulkiness of R^1, (nearly) the same molecular arrangement, accompanied by the formation of nanoporous channels occurred (Figure 2).

Later on, Davis and co-workers demonstrated that the molecular scaffold could be derivatized to adjust the pore dimensions of the crystals.[14] Therefore the aromatic group R^2 was varied in size, whereas R^1 was kept unchanged for all structures (-NHPh, see **2a–c** in Figure 1). The aromatic moieties R^2 cover the pore walls forming a hydrophobic environment with defined channel diameters of 5.5 to 7.6 Å. Although the pore walls are hydrophobic, water was trapped in 1D wire-like arrangement within the pore.[15] As already mentioned, the groups R^1 and R^2 seem not to influence the packing of the molecules in their crystalline states, which is also reflected by the same hexagonal space group $P6_1$ for all the crystals **1a** to **2b**. Furthermore, the unit-cell parameters are very similar for all three crystalline compounds ($a = b \approx 29$ Å, $c \approx 11.4$ Å). Those facts are the ideal basics for the formation of co-crystalline systems and offered Davis and co-workers the chance to mix the molecules however they liked, to create nanoporous "organic alloys"[16] with adjustable pore functionalities.[17] And indeed, it turned out that these

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[*] Dr. M. Mastalerz
Institute of Organic Chemistry II & Advanced Materials
Ulm University, Albert-Einstein-Allee 11, 89081 Ulm (Germany)
E-mail: michael.mastalerz@uni-ulm.de

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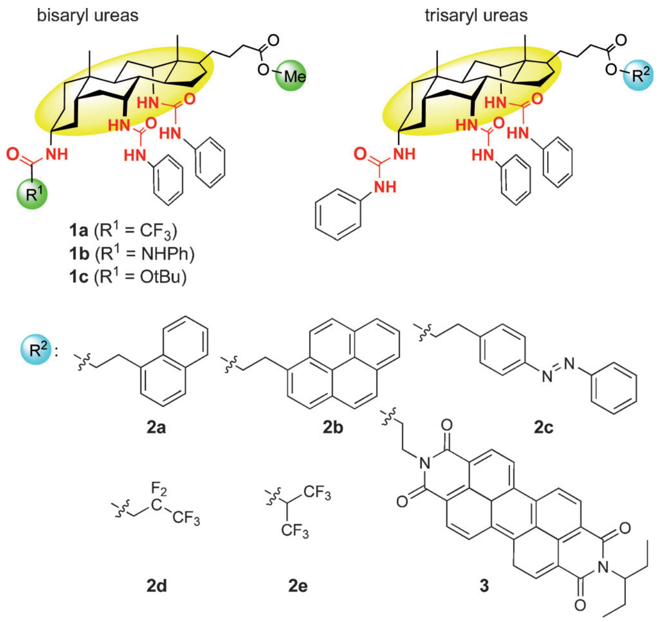

Figure 1. Selected bisaryl ureas (**1a**, **1c**) and trisaryl ureas (**1b**, **2a**–**e**, **3**) that form hexagonal nanoporous channels in the crystalline state. The rigid steroidal framework is highlighted in yellow; the urea moieties, mainly responsible for the self-assembling motifs are highlighted in red. The substituents highlighted in green (R^1 and Me) as well as in light blue (R^2) are pointing into the channels of the nanoporous crystals.

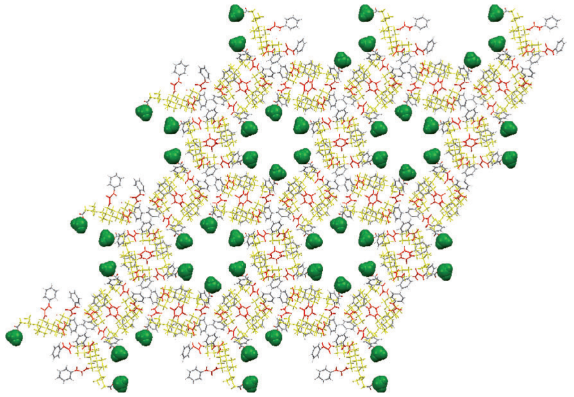

Figure 2. Crystal structure of bisaryl urea **1b**. Shown is a $3\times3\times1$ plot of the unit cell, viewed along the crystallographic *c* axis. The steroidal backbone is in yellow, the urea functional groups in red; the R^2 group (in this case methyl) is shown as a space-filling model to emphasize its placement inside the channels. Other groups (phenyl and carboxy) are in gray (carbon) and white (hydrogen).

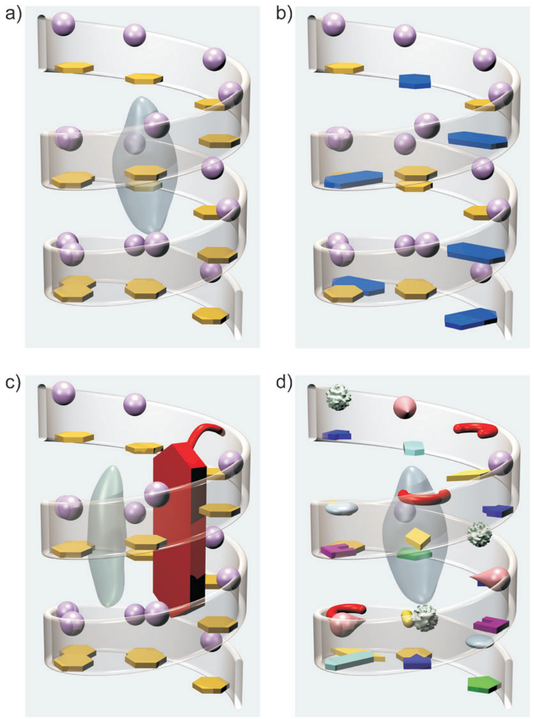

Figure 3. The development of nanoporous organic crystals to nanoporous organic alloys. a) Crystal formed from a single component (e.g. **1b**). Spheres represent R^2 = OMe and hexagonal prisms R^1 = NHPh. The amorphous gray shapes indicate the inner pore volumes. b) Cocrystal of two components (e.g. **1b** and **2b**) with random distribution of the R^2 groups. c) Formation of binary co-crystals of component **3** with bulky PDI substituents (red) with **1b**. d) Hypothetical multifunctional nanoporous organic alloy from precursors with different groups R^2. Graphics taken from Ref. [17].

molecules (**1b**, **2a**–**e**) can be mixed together to generate binary, ternary, and even quaternary porous co-crystals, with two, three, or four different functional groups dangling into the one-dimensional pores (Figure 3).[17] All mixtures formed needle-like crystals with the same crystallographic space group $P6_1$ and similar unit cell parameters. In the co-crystals the occupancy of functional groups (present only in one of the precursors) roughly matched the ratio of the precursor molecules, which was further confirmed by ^{1}H NMR spectroscopy and electrospray mass spectrometry.

A trisaryl urea (**3**) with perylenediimide (PDI) as group R^2 does not crystallize by itself, because R^2 is too large to fit into the channel, but **3** can be crystallized in various ratios (1:1, 1:10, 1:100) with **1b** forming brightly colored crystals with different fluorescence behavior when excited at 488 nm. The more "dilute" the PDI units are, the more comparable the fluorescence is with PDI in solution. Most interestingly, the sample with the highest PDI content, when illuminated only in a small region in the middle of the crystal, emitted brightly exclusively at the end of the crystal.

To date the distribution of the components in the crystal is still an open question and the precursors might be incorporated into the crystal randomly and/or statistically. Nevertheless it has been demonstrated that the pores can be decorated with various functional groups, generating new materials. Furthermore, the constructional need for orthogonality of the functional groups (those dangling into the pores of the crystals and those, which are mainly responsible for the crystalline packing) has restricted the variety of R^2 groups to aryl groups of various bulkiness, alkyl, as well as fluorinated alky chains. However, this still leaves a lot of room for improvement of such multifunctional porous systems towards even more functional materials.

This work of Davis and co-workers is a masterpiece in crystal engineering and creates the opportunity to tailor porous systems with desired functionalities. We can optimistically look forward to the next step of development for multifunctional pores in an even more sophisticated fashion on the basis of the contribution of Davis et al.[17]

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