Crystal Engineering

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# Nanoporous Organic Alloys**

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The crystalline state presents many advantages for the design of functional materials. Components in crystals are ordered and oriented (usually anisotropically), crystals are generally more robust than amorphous solids, and the crystal packing can be arranged to leave gaps to allow absorption of and interaction with guest species. However crystals are not so easily tuned as amorphous materials, because compositions cannot in general be varied freely. Crystal packing generates an array with symmetry and dimensions which are specific to the system. An altered component which might moderate a property (for example, optical extinction or refractive index) may not fit into the array, and will often be rejected.

Adjustable stoichiometries are fairly common for inorganic materials such as metal alloys, minerals and coordination polymers, where similarly sized components (e.g. metal ions) and/or strong directional bonding allows substitutions within crystal frameworks.[1,2] However for organic molecular crystals, with diverse structures governed by weak intermolecular forces, such exchanges are more problematic. There are some examples where solid solutions ("organic alloys")[3] are formed from molecules which can be mixed in any ratio within the same crystal structure. However, this has only been possible where the molecules concerned are very similar in size, shape, and nature.[1,3,4] Herein we report a new approach to the preparation of crystals from continuously variable mixtures of organic molecules. The strategy allows the incorporation of multiple and diverse units, including molecules which may not crystallize by themselves. Moreover these organic alloys can accept guests which are not part of the crystal array, increasing the prospects for useful functionality.

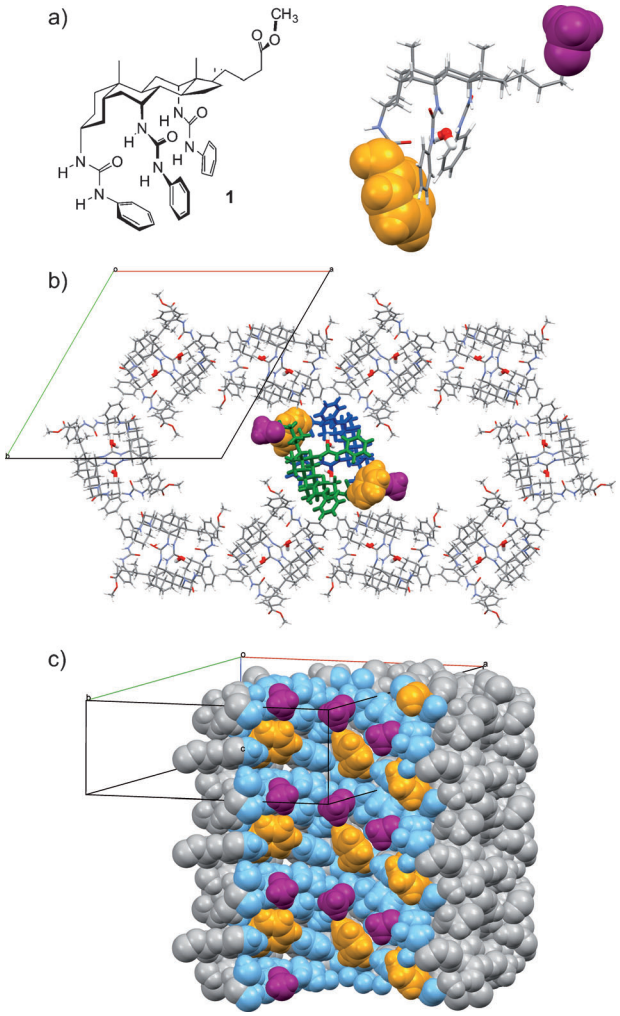


***Figure 1.*** The crystal structure of archetypal channel-forming steroidal urea **1**. a) Formula of **1** and the structure of a single molecule. The terminal $OCH_3$ and NHPh groups are shown in space-filling mode, colored magenta and orange, respectively. The steroid is solvated by a molecule of water (shown with thick bonds) which forms hydrogen bonds to all three ureas. b) Packing of **1** viewed down the crystallographic *c* axis (along the line of the channels). All the molecules are in the same environment, but two are highlighted (one blue, one green, except that $OCH_3$ and NHPh groups are space-filling and retain their coloring). The channels are of average diameter 1.6 nm with walls 1.3 nm thick and a helix repeat distance of 1.15 nm along the *c* axis. c) A single channel sliced in half along the *c* axis, viewed in space-filling mode. Terminal $OCH_3$ and NHPh groups retain their coloring, other atoms near or at the internal surface are shown as light blue. The channel surface is formed by two parallel helices of steroids with alternating alignments. Six steroids are required for each turn of each helix.

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To obtain an organic alloy, it is generally necessary that the crystals of the individual molecules should possess almost identical structures with the same space group and closely similar unit cell parameters. Usually, this implies that the molecular structures are almost identical, perhaps differing by a few atoms. However, in principle this need not be true if the crystal contains substantial open space. Effectively, the molecule can expand into the voids without interfering with the crystal packing. A variety of compounds can therefore crystallize in the same format, part of the structure remaining constant and controlling the packing while the remainder contains the variability. If the spaces are sufficiently large, and the canonical structure robust, it should be possible to form a wide range of continuously tunable materials. Organic crystals with large voids are quite rare,[5] but we have recently discovered a family of compounds which allow the realization of this concept. Exemplified by **1**, these nanoporous steroidal ureas (NPSUs) form crystals with hexagonal $P6_1$ symmetry in which the molecules form helices surrounding broad channels (up to 1.6 nm average diameter, 30% of crystal by volume).[6]

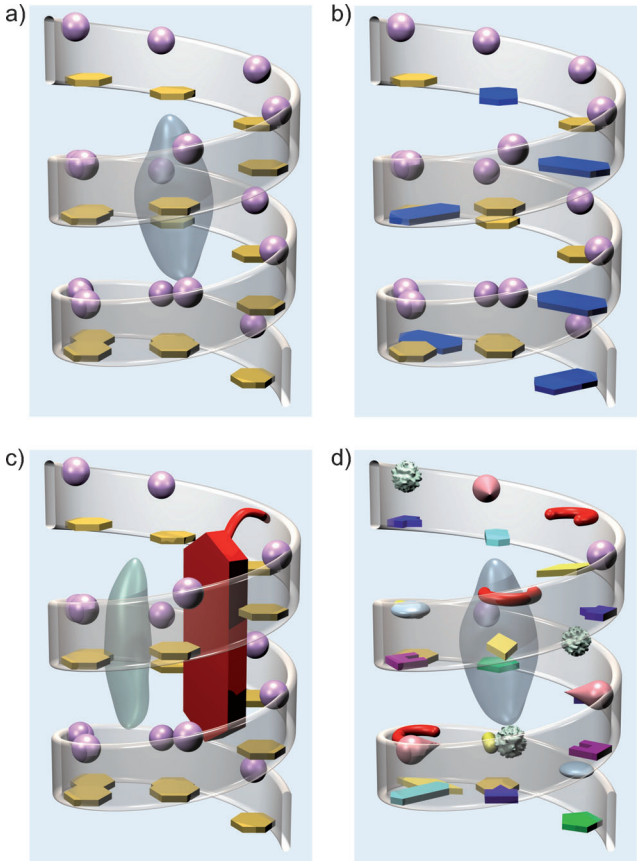
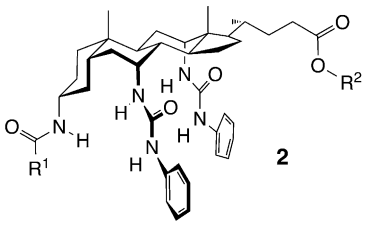


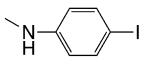

***Figure 2.*** Schematic depictions of NPSUs. a) Crystal formed from a single component, with spheres and hexagonal prisms representing the terminal groups (OMe and NHPh for **1**; cf. Figure 1c). Guest molecules may enter the channels. b) Alloy formation with a second component (blue) allows tuning of macroscopic properties. c) Larger groups can be positioned in the channel if incorporated in low ratios. Depending on the size of the group and the level of doping, guest molecules may also be accommodated. d) Multicomponent alloy with diverse terminal groups acting in concert on absorbed guest molecules.

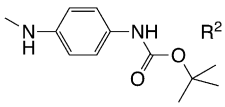
As illustrated in Figure 1, the central core of the steroid provides the scaffolding for the material while groups at either end point into the channels. The channels are chiral and can accept guest molecules, but can also accommodate a variety of end groups. Indeed, we have found that a number of molecules of general structure **2** crystallize in the same manner as **1** with almost identical unit cell parameters.[6,7] Groups $R^1$ and $R^2$ form part of the channel surface, and may be used to control the internal diameter, optical properties, and chemical nature of the pores.

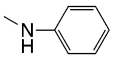
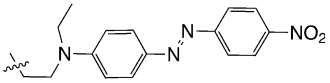
Given the isostructural nature of NPSUs, there seemed no reason why two or more should not crystallize together in any ratio, to form continuously variable nanoporous materials. As illustrated in Figure 2, the phenomenon could be exploited in various ways. Firstly, binary mixtures could be formed in any ratio to achieve desired macroscopic physical properties such as density, dielectric constant, refractive index, etc. (Figure 2b). Secondly, steroids with exceptionally large and complex termini could be included in the mixture (Figure 2c). Such molecules could not form the nanoporous structure by themselves, because the channels could not accommodate such large units attached to every molecule (6 for each turn of the helix). However, if they are mixed in low ratio with smaller host steroids, the problem disappears. Thirdly, any

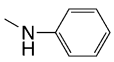
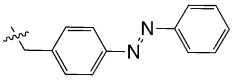


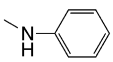
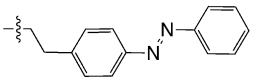
**2**

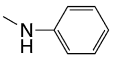
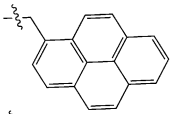
**2a** $R^1$ =  $R^2$ = $CH_3$

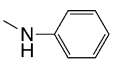
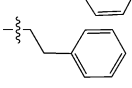
**2b** $R^1$ =  $R^2$ = $CH_3$

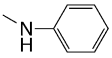
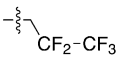
**2c** $R^1$ =  $R^2$ = 

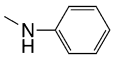
**2d** $R^1$ =  $R^2$ = 

**2e** $R^1$ =  $R^2$ = 

**2f** $R^1$ =  $R^2$ = 

**2g** $R^1$ =  $R^2$ = 

**2h** $R^1$ =  $R^2$ = 

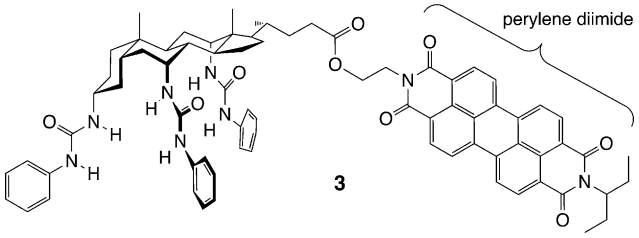
**2i** $R^1$ =  $R^2$ = 

number of steroids could be mixed together in principle, giving chiral crystalline nanoporous materials with highly diverse interior microenvironments (Figure 2d). These materials could be capable of sophisticated functions such as enzyme-like catalytic activity on bound guests, especially if a way could be found to organize the different components.

To explore these possibilities, we first employed prototype NPSU **1** and the closely similar analogue **2a**, bearing an iodine atom as a crystallographic probe. **2a** was prepared from the inexpensive steroid cholic acid, by a procedure analogous to that used for **1**.[6,8] As expected, **2a** crystallized from methyl acetate to give needles similar in appearance to those formed by **1**. Single crystal X-ray diffraction (SCXRD) confirmed that **2a** was isostructural with **1**, with slightly smaller cell dimensions (ca. 0.6%). A 1:1 mixture of **1** and **2a** was then crystallized under similar conditions. The resulting needles were collected and analyzed by $^1$H NMR spectroscopy to reveal a 65:35 ratio of **1** to **2a**.[8] To establish whether both molecules occurred in the same crystal, one of the needles was subjected to SCXRD.[8] Iodine atoms were detected in the appropriate position at roughly 30% occupancy, consistent with formation of an organic alloy.

The study was then expanded to involve NPSUs **2b–i**,[9] with further variations in both $R^1$ and $R^2$. Systems bearing azobenzene chromophores (**2c–e**) were included to facilitate analysis by optical microscopy. The synthesis of **2e** was reported previously,[7] while the remainder were prepared by analogy with established procedures.[8] A range of binary, tertiary and quaternary mixtures were co-crystallized as exemplified in Table 1.[8] In all but a very few cases, the mixtures gave needles with similar appearance to those formed by **1**. Crystallographic analyses confirmed the retention of the $P6_1$ nanoporous structure, with minor variations in cell parameters (see Table 1). Ratios of components in the bulk crystalline samples were determined by $^1$H NMR integration, while individual crystals were analyzed by SCXRD or electrospray mass spectrometry (ESMS) to confirm the presence of all components. For mixtures with colored components, optical microscopy provided further evidence that the chromophores were distributed throughout the sample. Overall the results suggested that, in a given mixture, some components were more readily included than others. Thus the compositions of the crystals deviated somewhat from the initial ratios, while some micrographs revealed variations in color intensity. The latter may be explained by unequal rates of incorporation—towards the end of a crystallization, the composition in solution could differ markedly from the initial ratio, leading to inhomogeneity. However, differences seem relatively small, and no evidence was obtained for the segregation of pure components, either in different crystals or in domains within individual crystals.

Having demonstrated the formation of binary (Figure 2b) and multicomponent (Figure 2d) alloys, we investigated the possibility of incorporating steroids with large terminal units as dopants in a matrix of simpler hosts (Figure 2c). Perylenediimide (PDI, see **3**) is a widely used chromophore which is valued for its high fluorescence quantum yield, thermal and photochemical stability, and ability to act as an n-type semiconductor.[10] Modeling suggested that, as present in **3**, it is also sufficiently bulky to exhaust the free space in the $P6_1$ nanoporous structure.[8] Steroid **3** was synthesized from **1** by ester hydrolysis followed by coupling to the appropriate *N*-hydroxyethyl perylenediimide.[8] As expected, **3** failed to crystallize by itself, despite extensive efforts. However, when mixed in 1:1 ratio with **1** it yielded red needles of composition **3**:**1** = 40:60 ($^1$H NMR spectroscopy) (Figure 3a). SCXRD confirmed the $P6_1$ structure but could not locate the perylene units, which were presumably disordered within the channels.




With PDI derivative **3** in hand, we were positioned to illustrate the potential of NPSUs for crystal tuning. The optical properties of PDI-based materials are strongly affected by the relationship between individual chromophores. If the PDI units are spread throughout the material at low density they will behave independently, as if in dilute solution. However, if they are closer together, they can interfere with each other resulting in quenching and other phenomena.[11] In particular, anisotropic arrays of PDI systems can serve as optical waveguides in which light-energy is absorbed, re-emitted at longer wavelengths and transmitted over long distances.[12] Much effort has been devoted to controlling the arrangement of PDI units, but

***Table 1:*** Organic alloys formed from steroidal ureas **1** and **2**.

| Components | Initial ratio | Ratio in crystals (bulk)[a] | Homogeneity[b] | Crystallographic unit cell parameters [Å][c] | |
|---|---|---|---|---|---|
| | | | | *a*,*b* | *c* |
| **1**, **2a** | 50:50 | 65:35 | SCXRD | 29.0453(4) | 11.4639(2) |
| **1**, **2b** | 50:50 | 50:50 | ESMS | 28.986(1) | 11.456(5) |
| **1**, **2c** | 50:50 | 65:35 | ESMS[d] | 28.800(3) | 11.470(14) |
| **1**, **2d** | 50:50 | 55:45 | ESMS[d] | 28.918(6) | 11.429(3) |
| **1**, **2e** | 50:50 | 55:45 | ESMS[d] | 28.911(8) | 11.425(5) |
| **1**, **2f** | 50:50 | 45:55 | ESMS | 28.834(9) | 11.426(5) |
| **1**, **2g** | 50:50 | 50:50 | ESMS | 28.91(4) | 11.450(14) |
| **1**, **2h** | 50:50 | 50:50 | ESMS | 28.85(3) | 11.409(11) |
| **2a**, **2e** | 50:50 | 45:55 | SCXRD | 29.1427(19) | 11.4342(15) |
| **1**, **2b**, **2e** | 33:33:33 | 35:35:30 | ESMS[d] | 28.880(8) | 11.425(3) |
| **1**, **2c**, **2g** | 33:33:33 | 35:35:30 | ESMS[d] | 28.984(8) | 11.462(3) |
| **1**, **2d**, **2i** | 33:33:33 | 40:25:35 | ESMS[d] | 28.942(5) | 11.448(2) |
| **1**, **2b**, **2c**, **2h** | 25:25:25:25 | 25:25:30:20 | ESMS[d] | 28.899(11) | 11.439(5) |

[a] Determined by $^1$H NMR integration. [b] Method used to show that all components were present in a single crystal. [c] Standard deviations are given in parentheses, and are smaller for those cases where a full structural determination was performed. [d] Supported by optical microscopy.

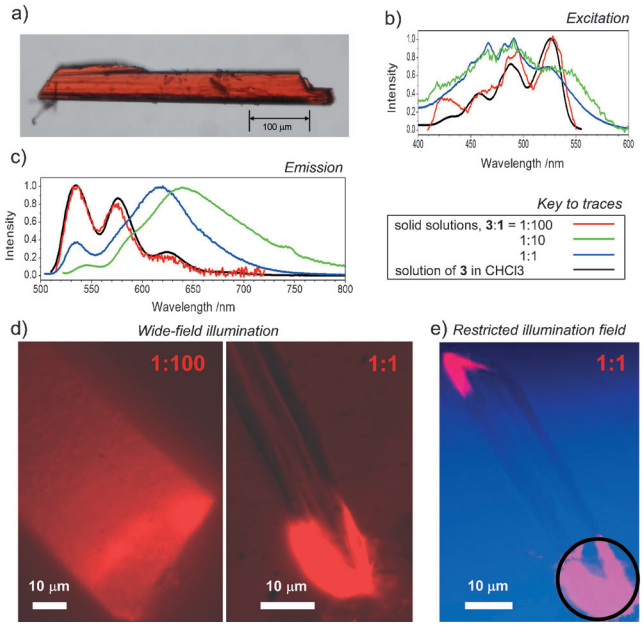



***Figure 3.*** a) Color bright-field image of a single needle obtained from crystallization of **3**:**1** = 1:1. b) Fluorescence excitation spectra, recorded at a fixed emission wavelength of 620 ± 5 nm, for **3** dissolved in chloroform (black) and for solid solution single needles crystallized from **3**:**1** = 1:1, (blue), 1:10 (green), and 1:100 (red). c) Fluorescence emission spectra recorded with excitation at 487 nm. Color coding as for (b). d) Fragments from single needles of solid solutions crystallized from **3**:**1** = 1:100 and 1:1, visualized by total internal reflection fluorescence (TIRF) microscopy using a laser wavelength of 488 nm. e) The crystal from **3**:**1** = 1:1 visualized by TIRF using an illumination field restricted to the marked circular region. The TIRF image was merged with a separate bright-field image to illustrate the location of the sample.

tuning by continuous variation within a crystalline environment has not previously been possible.

We therefore prepared crystals from a range of mixtures of **3** + **1**, and studied their optical behavior using fluorescence spectroscopy.[8] Figure 3b and c show selected results from three samples, obtained by crystallization of **3**:**1** in the ratio A) 1:1 (as discussed above), B) 1:10, and C) 1:100. The excitation (Figure 3b) and emission spectra (Figure 3c) show clearly the effect of chromophore proximity within the crystal. For the most dilute sample (C), the spectra are similar to those of **3** dissolved in chloroform, showing that there is little interaction between the chromophores (and also implying that the PDI units are evenly distributed within the solid). In contrast, the spectra for crystals (A) and (B) are very different to that of **3** in solution. The excitation spectra (Figure 3b) show substantial blue-shifts, consistent with interacting PDI chromophores. The emission spectra are red-shifted, implying the involvement of excimers (also supported by fluorescence lifetime measurements, see Supporting Information). The excitation and emission spectra from sample (A) are closely similar to literature absorption and emission data for a helical polyisocyanide polymer densely substituted with PDI units.[13]

Major differences were also revealed through fluorescence microscopy.[8] When PDI chromophores were spread thinly throughout the crystal [sample (C)], emitted light was observed from all regions as expected. However, for sample (A), with the highest density of PDI units, light was observed only from the ends (Figure 3d). When illumination was restricted to a small region in the middle of the crystal no emission was observed (Supporting Information, Figure S63b), but when one end was illuminated both ends emitted brightly (Figure 3e). It is known that the long axis of the needles coincides with the channel axis.[6] The results therefore imply that fluorescence is strongly quenched in the bulk of the material, or at surfaces parallel to the channels, but that emission occurs readily at (or near) surfaces which cross channels. Moreover, this emission is waveguided along the line of the channels with remarkable efficiency, with almost no loss of light from internal scattering in the bulk of the crystal (Figure S63c). The properties of the crystal are clearly anisotropic, highlighting the contrast between this organic alloy and a simple, amorphous mixture of compounds.

The distribution of the components in NPSU-based organic alloys remains an open question. The evidence thus far is consistent with random dispersions, but small-scale segregation or ordering may occur in some cases. The ability to control organization would further increase the potential utility, and it is interesting to speculate whether a guest molecule might serve as a template to impose order during crystallization. Alternatively, specific non-covalent interactions could be used to induce pairing, or steroidal components could be linked covalently before crystallization. Even with random ordering, there is broad scope for the development of applications through tuning of physical properties (by choice of components and adjustment of ratios), and/or the doping of effector units (e.g. for sensing, catalysis or flow control) within the channels.

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**Keywords:** crystal engineering · doping · fluorescence microscopy · microporous materials · supramolecular chemistry

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[8] For details, see the Supporting Information.

[9] Compounds **2b–i** crystallized individually to give $P6_1$ nanoporous structures. The structure of **2e** is reported in Ref. [7]. For the remainder, details will be given in a separate publication.

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