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Excavations in molecular crystals†

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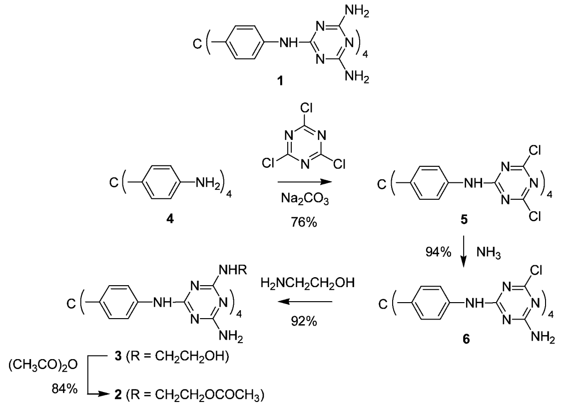
Single crystals built from porous molecular networks can react with agents that penetrate the crystals, cleave fragments from the network, and thereby increase the volume available for guests, all without loss of crystallinity.

Ordered microporous materials are indispensable in modern technology, particularly in catalysis and separation.[1,2] The resulting need to control and enhance porosity has driven research in the field of zeolites and related inorganic materials for decades. More recently, impressive molecular analogues have been devised, using compounds joined by coordination to metals, hydrogen bonds, or other interactions to form open networks.[1–3] In both zeolites and their molecular analogues, the well-defined volume of the ordered host network normally sets a fixed upper limit on the volume available for accommodating guests. Here we describe a strategy for increasing the useable volume in porous molecular networks by excavating the interiors of single crystals.

Molecular crystals with accessible interiors can be made conveniently by an approach that has been called molecular tectonics.[4] This approach is based on the programmed association of special sticky compounds, called tectons from the Greek word for builder, that form directional interactions with their neighbors according to reliable motifs. The crystallization of such molecules tends to produce open networks filled with potentially mobile guests. Porous networks joined by multiple hydrogen bonds are normally robust enough to allow guests in single crystals to be exchanged or even partially removed without loss of crystallinity, thereby making the interiors accessible to various agents.[5] In principle, this allows the porosity to be increased rationally by introducing agents that 1) react with the constituent tectons at predetermined sites and 2) liberate small molecular fragments that can escape the network by diffusion, all without loss of crystallinity.

Initial work showed that tecton **1** (Scheme 1) crystallizes to form an open network held together by hydrogen bonding of triaminotriazine groups. In this network, –NH_2 groups not used in intertectonic hydrogen bonding lie in guest-filled channels. We expected –NHR groups in substituted derivatives to be located similarly, making them accessible to external agents. To test this hypothesis, we made tetraacetate **2** by the route shown in Scheme 1. X-ray diffraction established that tecton **2** crystallizes from DMSO–acetone–H_2O in the tetragonal space group $I4_1/a$ to give the network represented by Figs. 1–2.‡ The 4 triaminotriazine groups of each tecton form a total of 16 hydrogen bonds with 4 neighboring tectons (Fig. 1), resulting in a robust non-interpenetrated network with diamondoid connectivity.[6] In addition, the 4 –$NH(CH_2)_2OCOCH_3$ groups of each tecton are involved in a total of 8 hydrogen bonds with 4



Scheme 1 Tecton **1** and the synthesis of tecton **2**.

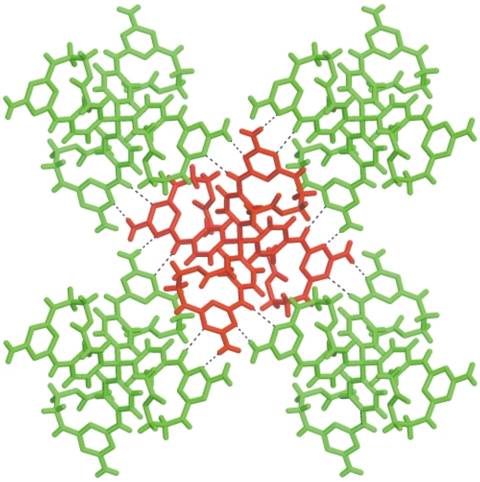


Fig. 1 View along the *c* axis of the crystal structure of tecton **2** showing a central tecton (red) and the 4 neighbors (green) with which it interacts by hydrogen bonds (blue) involving triaminotriazine groups.

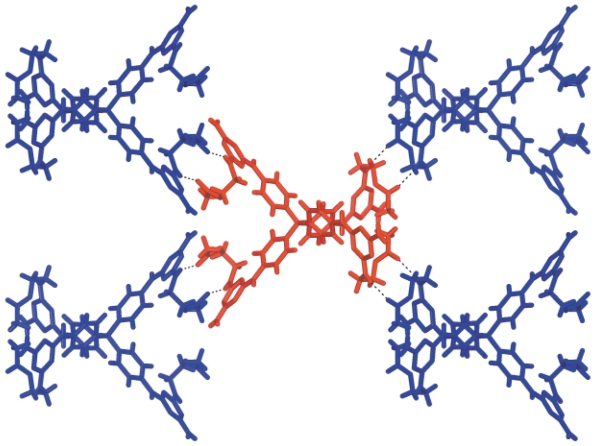


Fig. 2 View along the *a* axis of the crystal structure of tecton **2** showing a central tecton (red) and the 4 neighbors (blue) with which it interacts by hydrogen bonds (blue) involving –$NH(CH_2)_2OCOCH_3$ groups.

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† Electronic supplementary information (ESI) available: experimental details for syntheses and crystallographic analyses. See http://www.rsc.org/suppdata/cc/b3/b308355a/

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additional neighbors (Fig. 2). This yields a structure in which each tecton forms a total of 24 hydrogen bonds with 8 neighbors.

Disordered guests occupy nearly 40% of the volume of the crystals,[7,8] which have the approximate composition **2**·3 DMSO·1 acetone·n H_2O as estimated by ^1H NMR spectroscopy of dissolved samples.[9] The guests occupy interconnected helical channels into which the acetate groups extend, as anticipated. In principle, guests diffusing inside crystals of tecton **2** can reach any point within the channels by multiple redundant pathways.

When single crystals of dimensions 0.8 mm × 0.5 mm × 0.3 mm were treated with acetone–H_2O at 25 °C for 24 h, they remained transparent and morphologically unchanged, continued to exhibit uniform extinction between crossed polarizers, and showed closely similar unit cell parameters when studied by single-crystal X-ray diffraction. However, analysis of dissolved samples by ^1H NMR spectroscopy established that the initial guest, DMSO, had been replaced completely. Similar exchanges in single crystals could be effected with CH_3OH, CH_3CN, THF, and dioxane. As a result, crystals of tecton **2** appear well designed to allow suitable reagents to enter by diffusion and cleave the exposed acetyl groups without necessarily changing the basic architecture of the network. In principle, such processes should yield isostructural single crystals of higher porosity, now built from tetrol **3** (Scheme 1).

This concept was tested by growing single crystals of tecton **2** from DMSO–acetone–H_2O, replacing included solvent with CH_3CN–H_2O, and then exposing the exchanged crystals to aqueous $N(CH_3)_4^+$ OH^- at 25 °C for 2 weeks. Under these conditions, hydrolysis occurred within the crystal to give tetrol **3** in which 40–60% of the original acetate groups had been cleaved, as measured by ^1H NMR spectroscopy of dissolved samples. The resulting solid appeared morphologically identical to the original crystals, remained transparent, exhibited uniform extinction between crossed polarizers, and continued to diffract.

Single-crystal X-ray diffraction of the product confirmed the results of NMR spectroscopy and established that hydrolysis occurs isostructurally to give crystals belonging to the tetragonal space group $I4_1/a$, with unit cell parameters similar (±2%) to those of tetraacetate **2**.‡ The resulting structure was solved and shown to be similar to that of precursor **2**, but refinement of the acetyl group with full occupancy led to thermal displacement parameters that converged at unreasonable values. Refinement with a variable occupancy factor yielded acceptable values for the thermal parameters and suggested that at least 30% of the acetyl groups had been cleaved, in agreement with measurements based directly on NMR spectroscopy of dissolved samples. Other nucleophiles with dimensions allowing access to the interior of crystals of tetraacetate **2**, such as NH_3 and N_2H_4, proved to be less effective than $N(CH_3)_4^+$ OH^- for cleaving the acetyl groups with retention of crystallinity.

Longer contact of crystals of tetraacetate **2** with aqueous $N(CH_3)_4^+$ OH^- increased the extent of hydrolysis, but the product was no longer crystalline.[10] The acetyl groups are involved in one-third of the hydrogen bonds in the crystal structure of tecton **2**, so it is not surprising that extensive hydrolysis decreases the robustness of the network markedly. Quantitative formation of tetrol **3** from tetraacetate **2** in the solid state without changing the unit cell parameters or the geometry of the conserved molecular core would create a structure in which the volume available for including guests is increased from 40% to more than 50%.[7,8] Most of this theoretical increase can be achieved in practice without loss of crystallinity, so our experiments establish that excavating permeable molecular crystals is an effective new strategy for increasing porosity.

It is instructive to compare this strategy with other procedures that increase the porosity of materials by post-synthetic modifications. For example, 1) templates can be removed from inside zeolites and their analogues by calcination; 2) imprinted polymers can be created by removing specific substituents;[11] and 3) dendrimers can be cored by similar procedures.[12] Our strategy for excavation is distinctly different because it produces crystalline products under mild conditions. Simple increases in porosity are an obvious application of this strategy, but more ambitious post-crystallization modifications could excavate covalently attached transition-state analogues or structural mimics from the interior of permeable molecular crystals, leading to effective new ordered materials for selective catalysis and separation.

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Notes and references

‡ Crystallographic data were collected using a Bruker SMART 2000 CCD diffractometer with Cu Kα radiation (λ = 1.54178 Å). Intensities were integrated using the SAINT program[13] and corrected for absorption and other effects using the SADABS program.[14] Structures were solved and refined using the SHELX suite of programs.[15]

Crystal data for tecton **2**·3 DMSO·1 acetone·n H_2O: T = 293 K, crystal size 0.41 × 0.14 × 0.14 mm, tetragonal, space group $I4_1/a$, a = b = 25.6644(3) Å, c = 12.2028(3) Å, V = 8037.5(2) Å^3, Z = 4, θ_{max} = 72.95°, 32725 reflections measured, 3976 unique (R_{int} = 0.055). Final residual for 193 parameters and 2230 reflections with $I > 2\sigma(I)$: R_1 = 0.0824, wR_2 = 0.1885 and GoF = 1.097.

Crystal data for tetrol **3** produced by solid-state hydrolysis: T = 223 K, crystal size 0.30 × 0.20 × 0.15 mm, tetragonal, space group $I4_1/a$, a = b = 25.6490(6) Å, c = 11.9240(4) Å, V = 7856.3(4) Å^3, Z = 4, θ_{max} = 59.19°, 18629 reflections measured, 2675 unique (R_{int} = 0.046). Final residual for 210 parameters, 75 restraints and 559 reflections with $I > 2\sigma(I)$: R_1 = 0.1196, wR_2 = 0.3102 and GoF = 1.094.

CCDC 222274–222275. See http://www.rsc.org/suppdata/cc/b3/b308355a/ for crystallographic data in .cif or other electronic format.

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