# A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H_2O)_3]_n$

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Although zeolites and related materials combine nanoporosity with high thermal stability, they are difficult to modify or derivatize in a systematic way. A highly porous metal coordination polymer $[Cu_3(TMA)_2(H_2O)_3]_n$ (where TMA is benzene-1,3,5-tricarboxylate) was formed in 80 percent yield. It has interconnected $[Cu_2(O_2CR)_4]$ units (where R is an aromatic ring), which create a three-dimensional system of channels with a pore size of 1 nanometer and an accessible porosity of about 40 percent in the solid. Unlike zeolites, the channel linings can be chemically functionalized; for example, the aqua ligands can be replaced by pyridines. Thermal gravimetric analysis and high-temperature single-crystal diffractometry indicate that the framework is stable up to 240°C.

Nanoporous materials that are based on zeolites and metal phosphates have found a wide range of technological applications (for example, acting as molecular sieves, desiccants, ion exchangers, and catalysts). Although chemically and thermally stable, these materials create challenges to the engineering of specific pore sizes (*1*) or to the formation of chiral channels (*2*) and allow a rather limited variation of chemical formulation and functionality (*3*). The relatively new field of microporous metallo-organic polymers (*4–7*), although offering great potential for chemical and structural diversity and including the direct incorporation of catalytic sites, (*4*) suffers from general difficulties in the control of polymer dimensionality or framework stability. Low-dimensional coordination polymers can still show selective absorption based on guest-host shape recognition (*5*), but they lack framework integrity. Furthermore, although ligands can be designed to create large voids, the resulting coordination polymers are frequently plagued by lattice interpenetration (*6*) or a framework breakdown upon the removal of absorbates (*7*).

We report the synthesis, structure, and some preliminary findings on the physical and chemical properties of a highly porous open-framework metal coordination polymer $[Cu_3(TMA)_2(H_2O)_3]_n$ (referred to as HKUST-1). This polymer forms face-centered-cubic crystals that contain an intersecting three-dimensional (3D) system of large square-shaped pores (9 Å by 9 Å). The pores themselves contain up to 10 additional water molecules per formula unit. The material has a reasonable degree of thermal stability (up to 240°C) and a capacity for chemical functionalization of the channel linings.

The control of dimensionality is a major challenge within the metal coordination polymer field. Even when polyfunctional ligands are used, ancillary ligation by water or other solvent ligands may result in low dimensionality. In the case of Cu and trimesic acid [benzene-1,3,5-tricarboxylic acid ($TMA\text{-}H_3$)], one-dimensional chain polymers $[Cu(TMA\text{-}H)(H_2O)_3]_n$ (*8*) or $[NaCu(TMA)(H_2O)_5]$ (*9*) form from alcoholic solutions of cupric ions and trimesic acid at room temperature (RT). The low dimensionality is caused by the ligation of three aqua groups per square-pyramidal $Cu^{2+}$ ion.

For entropic reasons, synthesis at a higher temperature can promote the formation of polymer frameworks of higher dimensionality through the loss of terminal ancillary ligands. Thus, for example, Wood *et al.* (*10*) have found a condensed 3D structure for [Mn(TMA)], whereas a discrete molecular complex $[Mn(TMA\text{-}H_2)_2(H_2O)_4]$ is formed at RT (*11*). Our exploration of the solvothermal chemistry of the copper trimesate system has resulted in the discovery of HKUST-1 (*12*), in which the number of ancillary aqua ligands was reduced to just one per metal center.

Single-crystal structure analysis (*13*) revealed that the polymer framework of HKUST-1 is composed of dimeric cupric tetracarboxylate units (Fig. 1), with a short Cu-Cu internuclear separation of 2.628(2) Å (number in parentheses is the estimated standard deviation of the final significant digit). The framework is electrically neutral; the 12 carboxylate oxygens from the two TMA ligands bind to four coordination sites for each of the three $Cu^{2+}$ ions of the formula unit. Each metal completes its pseudooctahedral coordination sphere with an axial aqua ligand opposite to the Cu-Cu vector. Such bimetallic tetracarboxylate units are a common and often highly stable arrangement found not just for Cu but also for many other transition metal carboxylates. Examples include the quadruply-bonded Mo dimers such as $[Mo_2(O_2CCH_3)_4]$ (*14*) and its catalytically active Rh analog $[Rh_2(O_2CCH_3)_4]$ (*15*). Several hundred such complexes have been crystallographically characterized, with a wide variety of metals, carboxylate bridges, and axial ligands.

A view down the [100] direction of the cubic cell of HKUST-1 reveals ~1-nm-size channels with fourfold symmetry (Fig. 2). Using the atomic centers of carboxylate oxygens as the points of a square, we measured the edge of the "square" as 9.5 or 13.3 Å across its diagonal. The nanochannels intersect to provide a 3D connected network of pores. A view through the cell body diagonal [111] reveals a honeycomb arrangement of large hexagonal-shaped windows (Fig. 3), each composed of a ring of six metal dimers and six trimesate groups, which measure 18.6 Å between opposite vertices. These windows are cross sections of the "cavities" formed at the intersection of the three orthogonal sets of channels.

The experimentally determined absorption properties of HKUST-1 that was pretreated by heating in a vacuum are consistent with the high porosity indicated by its crystal structure. A $N_2$ adsorption/desorption isotherm study gave the following values: Brunauer-Emmett-Teller (BET) surface area = 692.2 $m^2\ g^{-1}$, Langmuir surface area = 917.6 $m^2\ g^{-1}$, and single-point total pore volume = 0.333 $cm^3\ g^{-1}$. Using a calculated density of 1.22 $g\ cm^{-3}$, we found that the accessible porosity is 40.7% (that is, the void fraction is 0.41). This value compares favorably with the void fractions (0.47 to 0.50) of the most open zeolites, such as the faujasite, paulingite, and zeolite A families (*16*).

The tetracarboxylate unit provides a structural motif with potential fourfold symmetry, and the trimesic acid provides a threefold symmetry element. However, it is not the direct combination of these two that creates the cubic symmetry of the crystal, because the Cu-Cu axis is not coincident with [100] and has only a twofold crystallographic symmetry. Instead, the origin of the nanometer-sized channels can be considered as arising from the formation of larger secondary building units (SBUs). The key SBU in HKUST-1 is an octahedral unit (Fig. 4) with $Cu_2$ dimers at its six vertices and four trimesate ions tetrahedrally disposed as "panels" for four of the eight triangular faces of the octahedron.

The framework was then achieved by connecting the SBU with other units through

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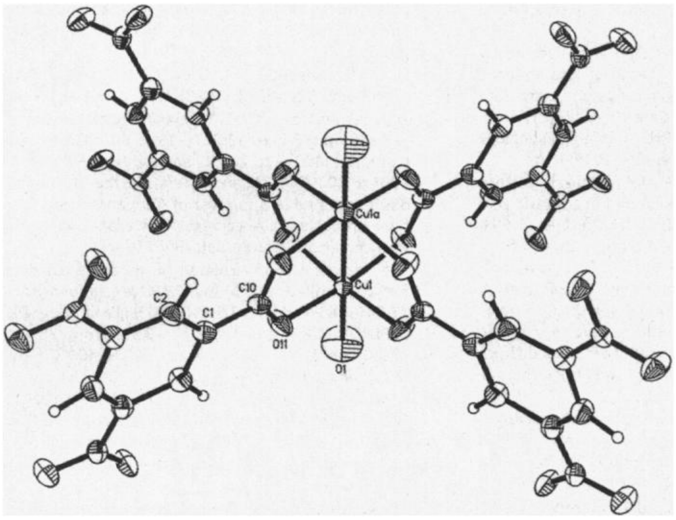

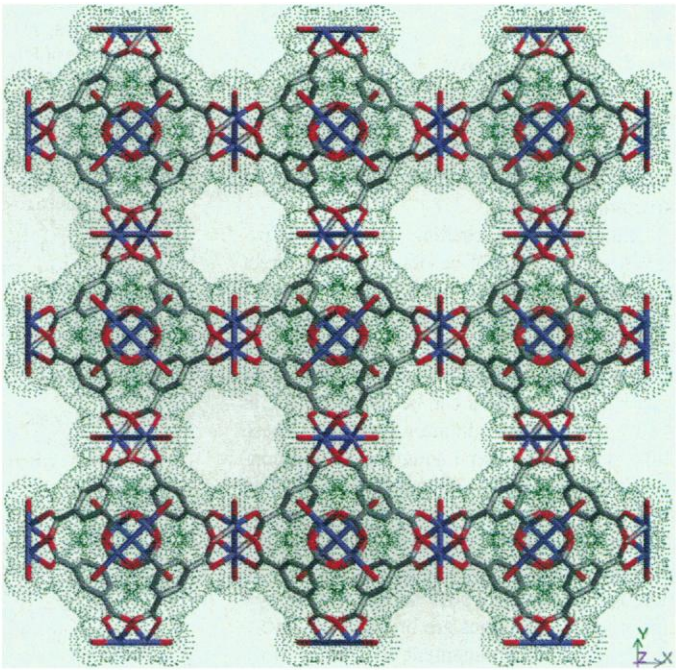

**Fig. 1 (left).** Dicopper(II) tetracarboxylate building block for HKUST-1. Key distances are Cu–Cu = 2.628(2) Å, Cu–OCO = 1.952(3) Å, and Cu–$OH_2$ = 2.165(8) Å. **Fig. 2 (right).** $[Cu_3(TMA)_2(H_2O)_3]_n$ polymer framework viewed down the [100] direction, showing nanochannels with fourfold symmetry.

corner sharing of the octahedra. The self-assembly of these SBUs bears a strong resemblance to the formation of the molecular "coordination aggregate" $[\{Pd(en)\}_6(tpt)_4]$ (where en is ethylenediamine and tpt is tripyridyl-triazine) found by Fujita and coworkers (*17*), which contains 10 molecular fragments. Furthermore, such building blocks were also found by Robson and coworkers (*18*) in the cubic interpenetrated network polymer $[Cu_3(tpt)_4][ClO_4]_3$. In this case, individual Cu atoms form the octahedron vertices and create the corner sharing.

Many open zeolite structures also possess large SBU fragments, such as double six-membered rings, or sodalite cages, which are then connected to create large pore sizes. However, there are only a few zeolite structures, such as faujasite, in which large pores intersect in a multidimensional sense, although Stucky and coworkers (*1*) recently synthesized a variety of metal phosphates with three-dimensional intersecting 12-ring channels. In the case of HKUST-1, the relatively large SBU allows for similarly large-sized cavity formation. The structure is analogous to the [NaCl] rock-salt structure, with the octahedral building blocks centered on one sublattice of sites and the water-filled cavities centered on the other. Although the analogy to zeolite SBUs may be useful in further assisting the design of other open-framework coordination-based solids, one direct advantage of organic-based molecular building blocks is that facile pore-size engineering can be envisaged through the use of extended ligands (*19*). Expanded ligands with enforced trigonality, such as a carboxylate analog of tpt, thus offer the prospect of pore-size expansion in the HKUST-1 system.

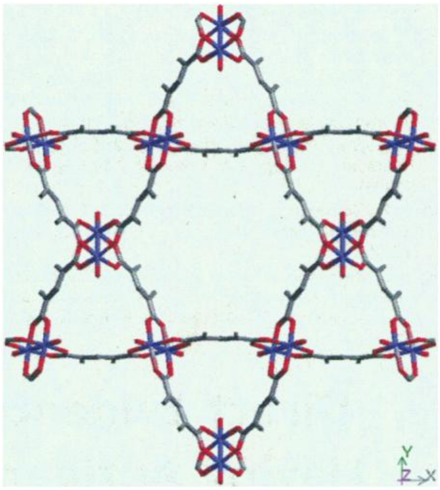

**Fig. 3.** $[Cu_3(TMA)_2(H_2O)_3]_n$ viewed along the cell body diagonal [111], showing a hexagonal-shaped 18 Å window at the intersection of the nanopores.

Architectural modification should also be possible with different polyfunctional carboxylates as network bridges. Recently, a 2D network polymer $[Zn\{C_6H_4(COO)_2\}(H_2O)]_n$ possessing a dizinc tetracarboxylate core was formed by RT synthesis from dimethylformamide (DMF). It was proposed that this subsequently formed a 3D network with 5 Å 1D pore channels upon condensative loss of $H_2O$ (*20*).

In HKUST-1, the terminal axial water ligands are directed from the Cu atoms to the interior of the nanopores. Because of disorder, the additional water in the pore channels could not be directly located in the crystal structure analysis, but it was accounted for with a diffuse scattering model in its refinement. Thermal gravimetric analysis (TGA) indicated that there are up to 10 additional channel water molecules per $[Cu_3(TMA)_2(H_2O)_3]$ unit (*21*), a number that is also consistent with the packing of water molecules into the accessible pore volume with the density of ice. This water capacity (28.3 weight %) is similar to that of Linde 13× molecular sieves (*16*). Dehydration of the compound can be achieved by heating to 100°C in air, with a color change from turquoise to dark blue. Whereas the anhydrate is stable under nitrogen, the sample rehydrates on exposure to air.

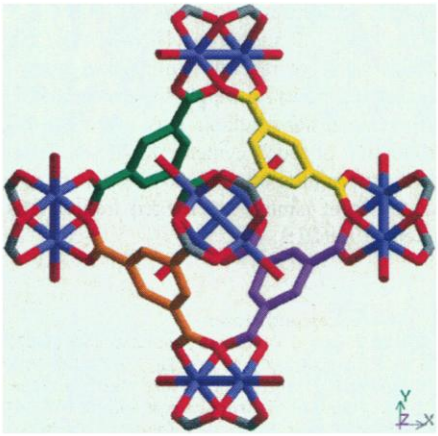

**Fig. 4.** Secondary building unit for $[Cu_3(TMA)_2(H_2O)_3]_n$, viewed along the [100] direction. The $Cu_2$ dimers bridge to other such SBUs.

The lability of the aqua ligands also allows their replacement by other groups. For example, treatment of the anhydrate $[Cu_3(TMA)_2]_n$

with dry pyridine (py), followed by washing with dichloromethane, gave a quantitative yield of a green derivative $[Cu_3(TMA)_2(py)_3]_n \cdot 0.5py \cdot 2H_2O$ (*22*). Its x-ray diffraction pattern is similar to that of HKUST-1 in *d*-spacing and line shape, demonstrating that chemical functionalization can be achieved without a loss of structural integrity.

Although the resulting polymer $[Cu_3(TMA)_2(py)_3]_n$ cannot be obtained by a direct treatment of Cu(II) salts with TMA in pyridine solution (*23*), the use of either DMF or dimethylsulfoxide (DMSO) as the crystallizing solvent affords phase-pure solids that are isostructural with HKUST-1. These can be formed at RT in >80% yield and in multigram quantities. These solids still possess axial aqua ligands but contain channel DMF/DMSO and water (*24*). How such polar organic solvents play a structure-directing role in the formation of the tetracarboxylate moieties remains to be established, although changes in both solution speciation and product solubilities are probably involved.

Finally, the replacement of Cu by more oxophilic metals ($Os_2$ and others) in the framework of HKUST-1 should help achieve thermal stabilities in excess of 300°C. A TGA study of anhydrous [Er(TMA)] (*25*), which we have recently synthesized hydrothermally, shows no weight loss up to 500°C. Other metal substitutions may allow the introduction of redox centers {Ru(II)-Ru(III)}, the incorporation of catalytic sites ($Rh_2$), or a switch from neutral to charged frameworks {Re(III)-Re(III)}.

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11. Crystals of $[Mn(TMA\text{-}H_2)_2(H_2O)_4]$ were formed by layer diffusion of ethanolic $[TMA\text{-}H_3]$ into aqueous $Mn(OAc)_2$ at RT. The monoclinic crystal system data are as follows: unit cell edges are $a$ = 5.178(2) Å, $b$ = 13.127(3) Å, and $c$ = 15.142(3) Å; interaxial angle $\beta$ = 97.74(2)°; and cell volume $V$ = 1019(1) $Å^3$.
12. In a typical synthesis, 1.8 mM of cupric nitrate trihydrate was heated with 1.0 mM of trimesic acid ($TMA\text{-}H_3$) in 12 ml of 50:50 $H_2O$:EtOH (EtOH, ethyl alcohol) at 180°C for 12 hours in a Teflon-lined 23-ml Parr pressure vessel. This gave turquoise crystals up to dimensions of 80 μm in ~60% yield along with Cu metal and $Cu_2O$. Single-crystal x-ray analysis of the turquoise crystals (HKUST-1) was carried out with a Siemens diffractometer that was equipped with a SMART charge-coupled device.
13. Crystal data for HKUST-1 were measured as follows: $C_{18}H_{12}O_{15}Cu_3$, relative molecular mass $M_r$ = 658.9, cubic crystal system, space group *Fm-3m*, $a$ = 26.343(5) Å, $V$ = 18,280(7) $Å^3$, formula units per cell $Z$ = 16, density $D_x$ = 0.96 g $cm^{-3}$, conventional discrepancy index $R$ = 5.99, and weighted $wR2$ = 16.78; for 43 least-squares parameters and 853 reflections, diffraction angle $2\Theta$max = 50°. The structure was refined with SHELXL. A full description of the x-ray analysis is available at www.sciencemag.org/feature/data/986116.shl. The coordinates are on deposit with the Cambridge Structural Database, deposit number 112954.
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19. Lattice expansion occurred in a family of Cu polymers containing N,N′ donor bridges [S. Katawa *et al.*, *Inorg. Chem.* **35**, 4449 (1996); S. Kitagawa, paper presented at the 1st International Conference on Inorganic Materials, Versailles, 16 to 19 September 1998].
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21. TGA results for HKUST-1 gave weight loss $\Delta w$ = –28.2% from 25° to 120°C (–13 $H_2O$), thermal stability from 120°C to 250°C, and $\Delta w$ = –25.4% from 250° to 400°C (–$CO_2$ and others). Further heating to 800°C resulted in a mixture of CuO and glassy C as final products. TGA curves are available at www.sciencemag.org/feature/data/986116.shl.
22. The analytical and calculated (in parentheses) data for $[Cu_3(TMA)_2(py)_3] \cdot 0.5(py) \cdot 2H_2O$ are as follows: C, 43.54% (46.48%); H, 3.54% (3.01%); and N, 5.52% (5.30%). TGA showed $\Delta w$ = –3.9% from 25° to 120°C and $\Delta w$ = –54.2% from 120° to 400°C (–py, –$CO_2$, and others).
23. A 2D network polymer $[Cu_3(TMA)_2(py)_9] \cdot 3(py) \cdot 3H_2O$ (space group *R-3c*, $a$ = 19.142(5) Å, $c$ = 42.64(1) Å, and $V$ = 13,532 $Å^3$) was formed with large 48-membered rings of six individual Cu atoms and six TMA groups.
24. Analysis for the DMF product gave the best formulation as $[Cu_3(TMA)_2(H_2O)_3] \cdot 2.5(DMF) \cdot 2.5(H_2O)$, on the basis of combined chemical and thermal gravimetric analyses. The analytical and calculated (in parentheses) data are as follows: C, 34.6% (34.5%); H, 3.42% (3.89%); N, 4.01% (3.95%); $\Delta w$ = –11.4% from 25° to 120°C ($H_2O$ loss); and $\Delta w$ = –48.6% from 150° to 400°C (DMF and $CO_2$ loss). Variable-temperature single-crystal studies of the DMSO derivative showed no bound DMSO at RT; heating up to 200°C produced intensity changes due to solvent loss (reflection 222 increases in intensity and reflection 400 decreases). Cooling to RT resulted in a general reversal of these trends.
25. Anhydrous [Er(TMA)] was synthesized hydrothermally at 180°C in a manner similar to the synthesis of HKUST-1; TGA under $N_2$ produced $\Delta w$ = $<-1\%$ from 25° to 500°C and $\Delta w$ = –45.7% from 500° to 650°C, corresponding to decarboxylation.

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# Direct Evidence for $R^-$ Rotons Having Antiparallel Momentum and Velocity

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**Experimental evidence is presented that shows that the momentum of a $R^-$ roton (a particle-like excitation in liquid helium-4) is antiparallel to its velocity. Although this is anticipated from the negative slope of the dispersion curve for these excitations, it has only been possible to test since the development of a source of ballistic $R^-$ rotons. The backward refraction of the quantum evaporation process, which is the signature of antiparallel momentum and velocity, is observed.**

Particles in free space obey Newtonian laws of motion at low speeds and relativistic laws at high speeds. The momentum $\mathbf{p}$ and velocity $\mathbf{v}$ of such a particle are connected by an equation of the form $\mathbf{p} = m\mathbf{v}$, and because mass ($m$) is always a positive quantity, $\mathbf{p}$ and $\mathbf{v}$ are parallel. Particles that move in a medium do not necessarily have $\mathbf{p}$ parallel to $\mathbf{v}$ because the momentum is a composite quantity involving both the particle and the reaction of the medium to its motion. Liquid $^4He$ at temperatures $T < 2.1$ K has particle-like

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