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An extremely stable open-framework metal–organic polymer with expandable structure and selective adsorption capability†

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A novel porous framework polymer with expandable structure, over 8% volume expansion upon inclusion, has been characterized.

Crystal engineering of metal–organic polymers with functional building blocks may produce structures with tunable properties.[1–9] Mimicking zeolite structures, coordination polymers can be deliberately designed to have micropores and large open channels. These zeolite-like materials have potential applications in catalysis and molecular separations.[5] The key factors contributing to these applications are the highly stable porous open-frameworks, active transition metal centers and molecular selectivity with regard to size, shape, hydrophilic or hydrophobic properties. Up to now, only a few porous metal–organic polymers have been reported to have cell volume changes, ranging from ~2.5%,[10] ~3%,[7b] to 5% upon inclusion,[11] respectively. Here we present a novel material, with over 8% volume expansion upon inclusion, and highly stable framework, thermally stable up to 300 °C. The structure is so stable that the expanded crystal structures are reversible upon removal and binding of guests and the expanded structures were characterized by single crystal X-ray diffraction technique. Due to the presence of functional carboxylate groups in the framework, only the hydrophilic molecules entered into the channels when both alkane and alcohol molecules were present.

Our research in crystal engineering of new metal–organic polymers has been focusing on the selection of transition metal centers as well as organic building blocks. Metal–organic networks have shown intriguing architectures due to the coordination preferences of different metal centers and their interactions with organic ligands. The metal centers play a key role in molecular recognition processes. Our recent studies[12–14] along with other reports[3,15,16] have shown that pyridylcarboxylate ligands such as isonicotinate (IN) tend to bind metal centers with both pyridyl and carboxylate groups to form extended networks, where carboxylate groups balance the metal charges. The copper(II) atoms display square pyramidal geometry in these copper(II) nicotinato complexes.[12–14] Althouth the formation of a solely square pyramidal geometry single-network structure can not be precisely controlled by self-assembly reactions, we have synthesized compound $\{[Cu(IN)_2]2H_2O\}$ **1** with a single-net three-dimensional spiral open-framework by combining the square pyramidal Cu(II) and IN ligand.

The structure of **1**‡ consists of square pyramidal copper atoms (Fig. 1) coordinated by two pyridyl groups and two carboxylate groups of four IN units in a monodentate fashion at the equatorial positions. Another IN moiety occupies the remaining apical site of the square pyramidal geometry by using carboxylate monodentate coordination. The square pyramidal copper atoms are linked by five two-connected tridentate IN units in such a way that a novel five-connected three-dimensional network is formed with spiral open-framework channels running along the *a* axis (Fig. 2). Five-connected polygonal superamolecular polymers represent an area that remains undeveloped.[17] The channels in the spiral structure of **1** display Cu–Cu separations of 0.8918 × 0.8910 × 0.7903 × 0.8918 nm and are occupied by water molecules (Fig. 3). A

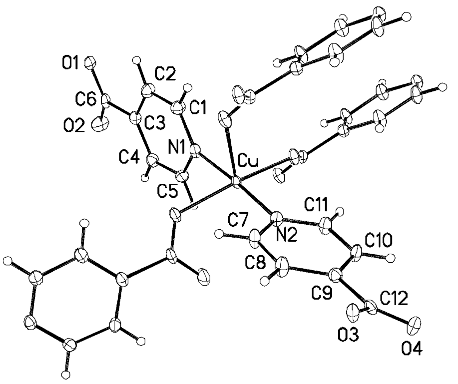

Fig. 1 View of the coordination about Cu showing the atom numbering scheme.

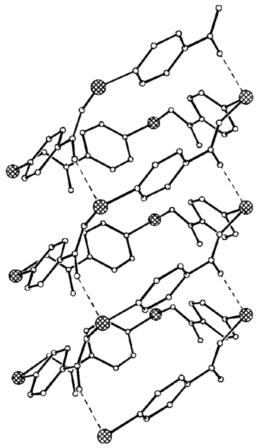

Fig. 2 Side view of the spiral framework, with axial Cu–O bonds shown as dashed lines.

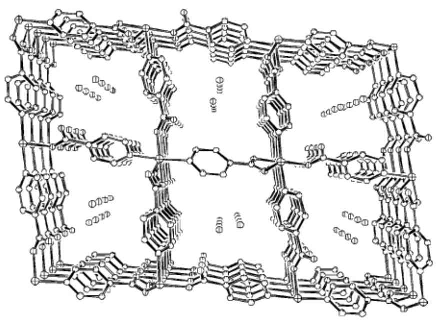

Fig. 3 View down the *a* axis showing the open-framework with inclusion water molecules (hydrogen atoms are not shown).

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† Electronic supplementary information (ESI) available: Figs. S1 and S2: views of propanol inclusion structure. See http://www.rsc.org/suppdata/cc/b2/b200213b/

number of hydrogen bonds between the guest water molecules and the carboxylate group in the spiral open-framework have been formed (O(5)–H(5A)···O(2) 2.820(4) Å, O(5)–H(5B)···O(6) 2.819(5) Å, O(6)–H(6A)···O(5) 2.784(6) Å). Thermal analysis indicates that **1** is stable up to 300 °C. The open-framework is highly stable after water molecules were removed and the open-channel structure of {[Cu(IN)$_2$] **2** was characterized by single-crystal X-ray diffraction.‡ By soaking the crystals of **2**[18] in methanol and 1-propanol, respectively, methanol- and 1-propanol-inclusion complexes were obtained, while in the mixed-solvents ethanol–pentane and ethanol–1-propanol, the adsorption processes are very selective with only ethanol molecules included in the structure. The three new inclusion polymers {[Cu(IN)$_2$]·CH_3OH} **3**, {[Cu(IN)$_2$]·CH_3CH_2OH} **4** and {[Cu(IN)$_2$]·0.75$CH_3(CH_2)_2OH$} **5** were characterized by single crystal X-ray diffraction.‡ Surprisingly, these inclusion polymers revealed that the spiral open-framework is not only highly stable in its original dimensions, capable of selective adsorption but also expandable. The symmetry of the original spiral open-framework structure was maintained in the expanded structures. The volume of the unit cells of **1–5** varies from 1326.7(2) to 1434.5(2) Å^3. The β angles vary from 96.920(1) to 101.559(1)°. The expandability along the spiral open channel direction is quite like a tension spring. Note that in the mixtures of alkane and alcohol, only hydrophilic alcohol molecules were found in the channels. The alkane molecules are hydrophobic and cannot enter into the structure, even when crystals of **2** were placed in a pentane solution for 48 h. Aromatic molecules are excluded from entering into the channels. In the case of mixed ethanol–1-propanol, ethanol molecules took the positions in the channels, which revealed that the adsorption property of **2** is size-selective.

In summary, we have demonstrated an unusually stable spiral open-framework metal–organic polymer. In addition to the zeolite-like structural features such as a sturdy framework and porous channels with high stability, this novel spiral open-framework structure is expandable when linear molecules enter into the open channels while the original framework and symmetry is still maintained. The expanded structures, up to over 8% volume expansion, are so stable that the structures have been characterized by single crystal X-ray diffraction technique.

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Notes and references

‡ *Crystal data*: for **1** at 223(2) K: space group *Cc*, cell dimensions a = 4.958(1), b = 25.079(2), c = 10.988(1) Å, β = 98.068(1)°, V = 1352.7(2) Å^3, Z = 4, R = 0.0200, R_w = 0.0524. Elemental analysis: Calc. Cu, 18.49; C, 41.91; H, 3.49; N, 8.15%. Found: Cu, 18.23; C, 42.41; H, 3.49; N, 8.31%. For **2** at 223(2) K: space group *Cc*, cell dimensions a = 4.958(1), b = 24.631(2), c = 11.232(1) Å, β = 98.325(1)°, V = 1357.2(1) Å^3, Z = 4, R = 0.0203, R_w = 0.0555. Elemental analysis: Calc. C, 46.79; H, 2.60; N, 9.10%. Found: C, 46.85; H, 2.61; N, 9.08%. For **3** at 223(2) K: space group *Cc*, cell dimensions a = 4.921(1), b = 25.142(2), c = 10.801(1) Å, β = 96.920(1)°, V = 1326.7(2) Å^3, Z = 4, R = 0.0193, R_w = 0.0501. Elemental analysis: Calc. C, 45.91; H, 3.56; N, 8.24%. Found: C, 45.89; H, 3.57; N, 8.23%. For **4** at 223(2) K: space group *Cc*, cell dimensions a = 5.119(1), b = 24.627(1), c = 11.325(1) Å, β = 100.021(1)°, V = 1405.8(1) Å^3, Z = 4, R = 0.0201, R_w = 0.0530. Elemental analysis: Calc. C, 47.49; H, 3.96; N, 7.91%. Found: C, 47.44; H, 3.87; N, 8.00%. For **5** at 223(2) K: space group *Cc*, cell dimensions a = 5.165(1), b = 24.466(2), c = 11.585(1) Å, β = 101.559(1)°, V = 1434.5(2) Å^3, Z = 4, R = 0.0257, R_w = 0.0659. Elemental analysis: Calc. C, 48.47; H, 4.18; N, 7.94%. Found: C, 48.72; H, 4.01; N, 8.01%.

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18 The compound **1** is insoluble in most common solvents such as water, DMF, DMSO, acetone, CH_3CN, benzene, toluene, methanol, ethanol, propanol and pentane. Compound **2** was obtained by removing inclusion water molecules (a vial with transparent blue crystals was heated for 3 h at 170 °C, and the crystals maintained the transparent blue color, crystallinity and original shapes). The water molecules were completely removed below 140 °C based on the TGA data.