[10] FTIR difference spectroscopy showed asymmetric and symmetric methylene stretching vibrations characteristic for the G4–CD assemblies at 2852 and 2916 cm^{-1}, respectively, as well as a broad band centered around 3250 cm^{-1} for the vibrations of ammonium, urea, and hydroxyl protons of the dendrimer and CD.

[11] XPS analysis confirmed the adsorption of the G4–CD$_{32}$ assemblies by an increase in N$_{1s}$ and a decrease in S$_{2p}$ signals, which are most indicative of adsorption. Moreover, the C$_{1s}$ and O$_{1s}$ signals increased and decreased, respectively.

[12] Advancing contact angles are $68\pm2°$ and approximately 20° before and after adsorption of G4 assemblies onto the CD SAMs, respectively.

[13] EIS was performed with an external redox couple at the open cell potential. From the Nyquist plot, the charge-transfer resistance was determined by using an equivalent Randles circuit. When the negatively charged $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4-}$ couple was used, the charge-transfer resistance decreased from 38 to 3 kΩ, because the electrostatic attraction by the dendritic core facilitates the oxidation/reduction at the electrode surface.

[14] The apparently slow adsorption as shown in the first parts of Figure 2a upon increase of the G4 concentration can be attributed to diffusion of G4 in solution, since the adsorption in the SPR setup leads to a depletion of the liquid above the surface of >100 μm, while diffusion in solution over such distances probably takes more than 1 s.

QMOF-1 and QMOF-2: Three-Dimensional Metal–Organic Open Frameworks with a Quartzlike Topology[**]

Jinyu Sun, Linhong Weng, Yaming Zhou, Jinxi Chen, Zhenxia Chen, Zhicheng Liu, and Dongyuan Zhao[*]

The construction of metal–organic framework (MOF) coordination polymers is currently receiving considerable attention owing to their potential properties as functional solid materials, as well as their fascinating framework structures.[1–3] Particularly widely explored have been MOFs with porous chiral structures in which chiral ligands, chiral templates, or chiral functionalization of achiral zeolites are used to perform enantioselective separations and syntheses.[4–7] It is challenging to prepare chiral MOF materials with known chiral topology from an achiral building unit.

Learning from nature's minerals, and utilizing the well-defined coordination geometries of metal centers, some structures of minerals with specific functionality, such as perovsktie,[8] rutile,[9] PtS,[10] and feldspar[11] have been artificially produced by replacing monoatomic anions (O^{2-}, S^{2-}) with polyatomic organic μ ligands. The quartz phase, which is chiral, has unique piezoelectricity and thermally sensitive properties and is widely used in resonators and sensors.[12] Although the SiO_2 phase with quartz topology is thermodynamically more stable than cristobalite which has diamond topology, in nature or in artificial materials, known phases which have quartz topology are rare with only one example, a cyano-bridged coordination polymer, reported by Robson and co-workers.[13] Generally, most materials comprising four-connected tetrahedral (T) units, including MOFs, exist in the diamond topology,[1c,d,14] rather than the quartz topology, while SiO_2 and GeO_2 are minerals that have both a quartz polymorph and cristobalite with diamond topology. Interestingly, when cristobalite is quenched to room temperature,[15] it is transformed reconstructively to the quartz polymorph.

Herein we report the preparation of two quartzlike, chiral, open MOFs, $Zn(ISN)_2\cdot 2H_2O$ (ISN = isonicotinate), assigned QMOF-1, with the low symmetry of α-quartz and $InH(BDC)_2$ (BDC = terephthalate), QMOF-2, with the high symmetry of β-quartz. QMOF-1 with a large (~8.6 Å) left-handed channel was successfully synthesized with an asymmetric ISN ligand by using a low-temperature diffusion method (room temperature) similar to the preparation of metal carboxylate[17]. On using a highly distorted complex anion $[In(O_2CR)_4]^-$ as the T block,[16] and terephthalate as a linear rod, we could assemble the anion-type β-quartzlike network QMOF-2 with a right-handed channel (~7.8 Å).

The preparation of QMOF-1 was carried out in a wide range of conditions: $Zn(NO_3)_2\cdot 6H_2O$: 1.5–3.0 ISN: 1–10 triethylamine (TEA): 5–10000 dimethylsulfoxide (DMSO): 0–20000 ethanol. After one week, large colorless needlelike single crystals with dimensions up to $0.200\times0.200\times3$ mm were obtained quantitatively (relative to Zn). QMOF-2 was solvothermally obtained from $InCl_3$:terephthalate (1:2) at 160 °C for 3 days, yield 60% (relative to In). The IR spectra showed that the carboxylate group in QMOF-1 has monodentate coordination to the metal center, while that in QMOF-2 is bidentate.[18]

The single-crystal X-ray diffraction studies reveal that all the zinc ions in QMOF-1 are four-coordinate (Figure 1a).[19] Each Zn atom is coordinated by two nitrogen atoms of two ISN ligands and two oxygen atoms of two carboxylate groups from two other ISN ligands. All of the T units are slightly distorted, the Zn–O and Zn–N bonds are 1.95 and 2.02 Å, respectively, and the angles of N(1)-Zn(1)-N(2), N(1)-Zn(1)-O(2), N(1)-Zn(1)-O(1), O(1)-Zn(1)-O(2) are 113.5, 117.5, 104.9, 100.4°, respectively. The 3D twofold interpenetrated network with T blocks is characteristic of a 6^48^2-b net, similar to that of α-quartz (Figure 2, Figure S1 in the supporting information).[1c] In the QMOF-1 structure, large Zn cations replace the Si atoms in quartz structure, and the long ISN anions replace the O atoms, so that the separation between two T units can be expanded to 8.813 Å, only slightly different from the Zn–Zn separations in the diamondoid network

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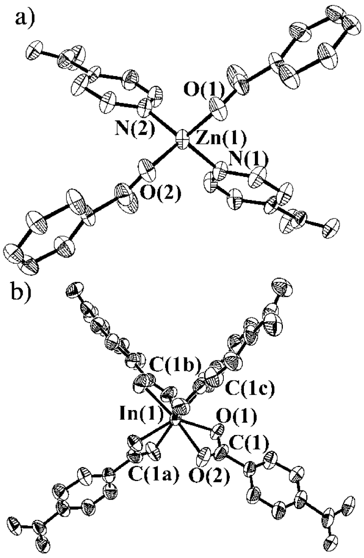

Figure 1. ORTEP drawings (thermal ellipsoids set at 50 % probability, all H atoms omitted for clarity) showing the. a) coordination of zinc ion in QMOF-1, b) coordination of the indium ion in QMOF-2.

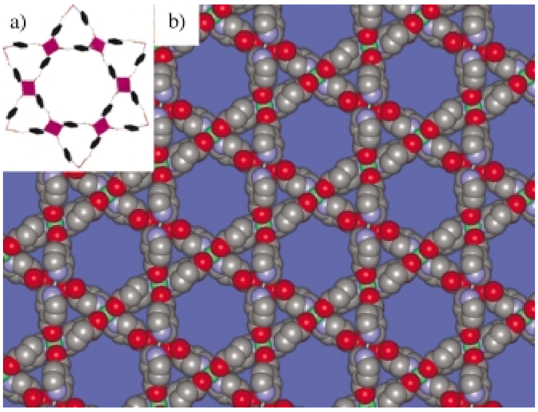

Figure 2. The crystal structure projection of QMOF-1 in the *c* direction, a) a single quartzlike net, ◆ = Zn atom, ⬬ = pyridine ring, b) CPK diagram of extended structure. The atoms are: ● = oxygen, ● = nitrogen, ● = zinc, ● = carbon.

recently reported (8.74 and 8.81 Å).[14] In contrast to the silica prototype, the $Zn(ISN)_2{\cdot}2H_2O$ open framework of QMOF-1 also contains a 3-fold screw axis in the *c* direction (Figure S2), and Zn tetrahedra along the 3-fold axis produce a left-handed channel (Figure 2b), which when the van der vaals radii are considered, is about 8.6 Å in diameter. Two disordered water molecules are observed in the pseudo-hexagonal channels, which are composed of 8-membered rings (eight Zn tetrahedrons). The asymmetry of the ISN anion results in a lower symmetry (from D_3 to C_3) than that of silica α-quartz. In contrast to the preparation of the diamondoid $Zn(ISN)_2$ which is produced by the solvothermal method at 130 °C,[14] the lower temperature used in the preparation of QMOF-1 might play a key role in the formation of the quartz structure, similar to the reconstructive transformation of cristobalite into quartz in silica polymorphs.[15]

In contrast to the tetrahedral zinc centers in QMOF-1, all the indium centers in QMOF-2 adopt triangulated dodecahedral geometries by the chelation of four carboxylate groups from four terephthalate anions (Figure 1b, 3a). The molecular structure shows that QMOF-2 is a complex anion with a proton to balance the charge.[16] If the carboxylate groups are considered as connecting points,[20] T blocks comprising carbon atoms around the indium centers in QMOF-2 show a highly distorted pseudo-tetrahedral geometry (Figure 3a), the angles of C-In-C are 91.5, 143.1, 100.0°. Each indium center in QMOF-2 connects to the other indium centers by linear terephthalate bridges to produce a quartz network (Figure 3b,c), the linear organic rods result in the high symmetry of β-quartz, $P6_422$. QMOF-2 is characteristic of twofold interpenetrated 6^48^2-b nets (Figure 3b) in which the pseudo-tetrahedron centers in one net occupy on the center of the 6-ring in another network, and the four "arms" of tetrahedron are interpenetrated through 6-ring each other in the up-down-up-down form (Figure 3b,d). Similar to β-quartz silica, the structure of QMOF-2 has not only a six-fold screw axis, but also a right-handed channel along this axis which runs in the *c* direction (Figure S3). The diameter of channel calculated from the distance between diagonally opposite In atoms is 15.0 Å. If van der waals radii are considered, the diameter of the channel is about 7.8 Å.

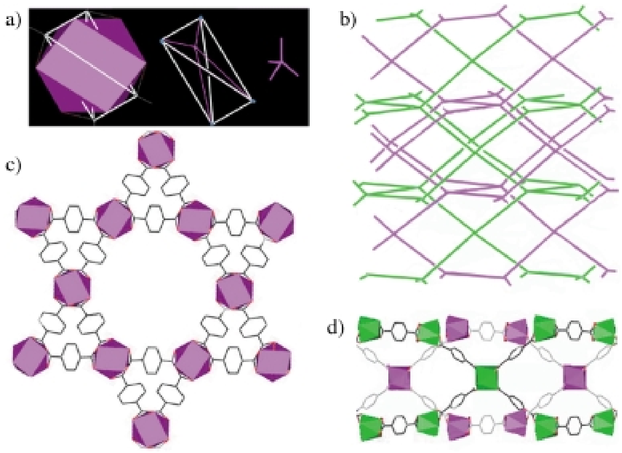

Figure 3. a) the T blocks model, showing that an 8-coordinated indium center acts as a 4-connected node b) the extended twofold interpenetrated networks with the simplified tetrahedron knot, c) the single quartz net in the *c* direction; d) showing the interpenetrated catenane structure.

Thermal analysis for QMOF-1 shows a shoulder peak at 100–140 °C with the weight loss of approximately 13 wt %, and an intense peak at 350–430 °C with the weight loss of approximately 58 wt %. The former is attributed to the desorption of two water molecules (calcd, 10.4 wt %); and the later corresponds to the collapse of the framework. Variable temperature XRD experiments reveal that the $Zn(ISN)_2{\cdot}2H_2O$ product is thermally stable up to 200 °C in air.

The results of thermal analysis of QMOF-2 in air show two endothermal peaks at around 100 and 270 °C, with about 25 wt % and 27.5 wt % weight loss respectively. The former is attributed to the desorption of the solvents adsorbed, which include 1.5 equivalents of dimethylformide and 4 equivalents of water (calcd, 27.5 wt %), the latter is related to the complete decarboxylization process (calcd, 27.5 wt %), so the framework of QMOF-2 collapses at 270 °C. These results suggest that two structures are thermally stable. N_2-adsorption/desorption measurements performed according to the normal method for microporous zeolite materials show that QMOF-1 and QMOF-2 products (Figure S9, S10) have type I isotherms, which suggests that the products have uniformed microporsity with large surface areas ($150\,m^2\,g^{-1}$ for QMOF-1 and $190\,m^2\,g^{-1}$ for OMOF-2).

In summary, two novel chiral open MOFs with rare α and β-quartz structures have been successfully synthesized. QMOF-1, prepared by using a simple diffusion method at room temperature has a neutral open framework with the low symmetry of α-quartz and a large (~8.6 Å) left-handed channel. QMOF-2, prepared by solvothermal method at 160 °C is the first anion β-quartz-like network with uniform T units.

Experimental Section

QMOF-1 was synthesized by liquid–liquid diffusion at room temperature. Typical procedure: A colorless solution of $Zn(NO_3)_2{\cdot}6\,H_2O$ (0.301 g, 1 mmol) in DMSO (10 mL) was mixed with isonicotinic acid (0.224 g, 2 mmol) in DMSO (5 mL) and stirred for 30 min. A solution of triethylamine (1–10 mmol) in ethanol was slowly diffused into the colorless solution, and large single needles were obtained quantitatively. A suitable crystal was selected for single crystal X-ray diffraction studies. Elemental analysis calcd (%) for QMOF-1 ($Zn(ISN)_2{\cdot}2\,H_2O$): C 41.74, H 3.48, N 8.12, Zn 18.84; found: C 42.78, H 2.71, N 8.54, Zn 18.90; IR spectra (KBr): $\tilde{\nu} = 3437\,cm^{-1}$ (br, OH of water), ν_{as} and ν_s, 1633, 1365 cm^{-1} (C=O, mondentate carboxylate group).

QMOF-2 was solvothermally prepared. Typical procedure: $InCl_3$ (0.301 g, 1 mmol) and terephthalic acid (0.332 g, 2 mmol) were dissolved in DMF (8 mL) with stirring to form a gel solution. The solution was left for 8 h at room temperature, then sealed in a 25-mL teflon-lined bomb and placed in an oven at 160 °C for 3 days. The resulting large colorless needles (ca. 0.100 × 0.100 × 1.00 mm) were collected and washed with DMF, yield 60%. Elemental analysis calcd (%) for QMOF-2 ($[InH(BDC)_2]$): C 43.26, H 2.03, In 25.87, found after vacuum desiccation: C 42.78, H 2.71, In 26.01; IR spectra (KBr): $\tilde{\nu} = \nu_{as}$ and ν_s, 1575, 1401 cm^{-1} (C=O for chelated carboxylate group).

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[19] The full hemisphere of data was collected on a Brucker SMART Apex CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The frames were integrated with the Saint Software Package. The structure was solved by direct method and the subsequent difference Fourier synthesis and refined with the SHELXTL (Version 5.10) software package. X-ray data for QMOF-1 ($Zn(ISN)_2{\cdot}2\,H_2O$), crystal size, 0.080 × 0.080 × 1.000 mm, hexagonal, space group, $P3_1$ (No. 144), $a = 15.526(5)$, $c = 6.258(3)$ Å, $\gamma = 120°$, $Z = 3$, $V = 1306.4(8)$ Å^3, $\rho_{calcd} = 1.250\,mg\,m^{-3}$, $\mu = 1.424\,mm^{-1}$, $1.57 < \theta < 27.08°$, $T = 293$ K, $R_1 = 0.0636$, $wR_2 = 0.1707$ for 3663 ($I > 2\sigma(I)$) of 3664 [$R_{int} = 0.0364$] unique reflections and 180 parameters. GOF = 1.142, refinement method was full-matrix least-squares on F^2; X-ray data for QMOF-2 ($H[In(BDC)_2]$), crystal size, 0.100 × 0.100 × 1.000 mm, hexagonal, space group $P6_422$ (No. 181), $a = 15.087(4)$, $c = 12.032(5)$ Å, $\gamma = 120°$; $Z = 3$, $V = 2371.7(13)$ Å^3, $\rho_{calcd} = 1.827\,mg\,m^{-3}$, $\mu = 1.537\,mm^{-1}$, $1.56 < \theta < 25.0°$, $T = 293$ K, $R_1 = 0.0669$, $wR_2 = 0.2182$ ($I > 2\sigma(I)$) of 1400 [$R_{int} = 0.0697$] unique reflections and 58 parameters. GOF = 1.339, Refinement method was full-matrix least-squares on F^2. CCDC-188415 (QMOF-1), CCDC-187976 (QMOF-2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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