COMMUNICATION
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Solid-state conversion of a MOF to a metal-organo polymeric framework (MOPF) via [2+2] cycloaddition reaction†

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The bpeb ligands aligned in a slip-stacked manner in a two-fold interpenetrated non-porous metal–organic framework (MOF) [Zn₂(bpeb)-(bdc)(fa)₂] undergo [2+2] cycloaddition reaction in a single-crystal to single-crystal manner to a non-interpenetrated 3D structure with a new topology comprising an organic polymer ligand and a 2D coordination polymer.

A number of highly crystalline organic polymers can be made in the solid state from a variety of monomers.1 In contrast, although organic polymers containing pendant metal complexes are known,2 their solid state structures could not be determined due to their very low crystallinity. The reason being, the traditional crystallization method may not be applicable to synthesize single crystals of metal complexes containing organo polymeric ligands. Recently we have observed that such a metal complex of an organic polymer ligand can be obtained indirectly by the [2+2] cycloaddition reaction in the solid state.3 The organic polymer containing cyclobutane rings has been incorporated into a metal–organic framework (MOF) using 1,4-bis[2-(4’-pyridyl)ethenyl]benzene (bpeb). This is possible because of the infinitely slip-staked conjugated C=C bonds of the bpeb ligands forming a plane in the MOF. The photo-dimerization of these C=C bond pairs in the solid state under UV light polymerized these diolefins to furnish the desired metal-complex of the organic polymer ligand 1,3-(4,4’-bipyridyl)-2,4-phenylene-cyclobutane (poly-bppcb) as shown in Scheme 1.

The product contains a 1D organo polymeric chain and a 1D coordination polymer fused together as metal-organo polymeric frameworks (MOPFs). The generality of the strategy for using [2+2] cycloaddition photo-polymerization reaction to make MOPF compounds should be established before MOPF compounds could be designed with desired properties for various applications. In addition, the success of this method will provide a better understanding for extending this strategy to make MOF–COF (covalent–organic framework) hybrid compounds which may have better properties of MOFs and COFs.

We have tested the hypothesis that an infinite head-to-tail arrangement of the bpeb ligands in a plane is required such that each C=C bond in the bpeb ligand is aligned to different adjacent spacer ligands to generate poly-bppcb using a new photoreactive MOF with cds topology. Interestingly, a doubly interpenetrated structure undergoes single-crystal to single-crystal (SCSC) transformation yielding the desired MOPF containing the organic polymer as depicted in Scheme 2. The details are given in this communication.

Scheme 1 Diagram of a poly-bppcb ligand showing the stereochemistry.

Scheme 2 The SCSC transformation from MOF to MOPF by polymerization via [2+2] photo-cycloaddition reaction.
Orange block crystals of \([\text{Zn}_2(\text{bpeb})(\text{bdc})(\text{fa})_2]\) (1) suitable for single crystal X-ray data collection were obtained under solvothermal conditions from \(\text{Zn(NO}_3)_2\cdot 4\text{H}_2\text{O}, 1,4\)-benzenedicarboxylic acid (\(\text{H}_2\text{bdc}\)) and bpeb in a mixture of DMF (dimethylformamide) and water at \(100\, ^\circ\text{C}\), followed by slow cooling. The origin of a formate ligand in the structure is due to the partial hydrolysis of DMF solvent under the experimental conditions.\(^4\) Interestingly, intentional use of formic acid or sodium formate in the synthesis did not yield 1. The purity of the bulk product was however confirmed by comparing the simulated powder X-ray diffraction (PXRD) pattern of the single crystal with that of the bulk sample (Fig. S1, ESI†). X-ray crystallographic experiments carried out at \(-100\, ^\circ\text{C}\) revealed that the asymmetric unit contains only half of the atoms in the formula unit of 1.\(^5\) The crystallographic inversion centre is present in the middle of bpeb and bdc ligands. Further the second formate ligand is related by the \(n\)-glide through the O3 atom (Fig. 1a). The distorted tetrahedral Zn1 [99.76(8)–124.65(8) %] is coordinated to one N atom of the bpeb spacer ligand, one O atom of the bdc ligand and O groups (centroid to centroid distance of 3.616 Å) showing face-to-face \(\pi-\pi\) interactions. This makes only each C–C bond in a given spacer ligand is aligned to two different neighbouring ligands and the distance between the centres of C–C bonds is 3.559 Å. The \([2+2]\) cycloaddition reaction of 1 under UV light is expected to generate an organic polymer based on cyclobutane rings fused with the \([\text{Zn}_2(\text{bdc})(\text{fa})_2]\) layers forming an interesting MOPF structure.

Irradiation of the orange single crystals of 1 under a Xe-lamp of wavelength 365 nm for 2 h resulted in pale yellow broken crystals, but a single crystal suitable for the single crystal X-ray analysis was found.\(^6\) Further characterisation by routine solution \(^1\)H-NMR spectroscopy was not possible due to its insolubility even in strong acids, indirectly inferring that the expected organic polymer has formed. This behaviour is very similar to that reported recently.\(^3\) Moreover, the single crystals of 1 are also insoluble even when trying to digest using strong acids.

The X-ray crystallographic analysis of \([\text{Zn}_2(\text{poly-bppcb})(\text{bdc})(\text{fa})_2]\cdot \text{H}_2\text{O}\) (2) revealed that the quantitative photo-cyclization accompanied by structural transformation has occurred (Fig. 3). Although a void produced in this connectivity is filled by two-fold interpenetration (Fig. 1d) with little solvent accessible void.

In 1, the \(\text{Zn}(n)\) atoms are bridged by the formate ligands forming a chain along the [101] direction and further cross-linked by a bdc spacer giving a highly corrugated brick-wall type \([6,3]\) grid made from \([\text{Zn}_2(\text{bdc})(\text{fa})_2]\) (Fig. 1b). The 3D coordination polymer is produced by the connectivity of the spacer ligand bpeb. Dictated by the tetrahedral geometry at Zn1 in the \([\text{Zn}(\text{fa})_2]\) chain, only the alternate bpeb ligands point in the same direction as shown in Fig. 1c. Viewed along the \(a\)-axis, all these layers are well aligned leaving the bpeb ligands to occupy the channels. The resultant connectivity generated the \(\text{cds}\) topology in 1 (Fig. 1d) with Schlaflí symbol \([6^5\cdot 8]\). The large
different space group setting is used (P2₁/n in 1 and to P2₁/c in 2), 2 is essentially isomorphous to 1. Due to an increase in the volume of the unit cell (1321.91(4) Å³ in 1 to 1433.1(5) Å³ in 2), the crystals take up a water molecule from air during the experiment as revealed in the crystal structure (Fig. S11, ESI†). As might be expected, the water molecule (O1Sb) is stabilised by the H-bonds bound to the oxygen donors (O2 and O3) from bdc and fa (dashed lines in Fig. 3a).

The same crystallographic symmetries are present in 2 except that the c-glide is present along the [Zn(fa)]₃ chain. Due to the poly-bppcb ligand in 2, the coordination environment at Zn1 is perturbed from a highly distorted tetrahedral geometry in 1 to a highly distorted octahedral geometry with both carboxylates chelating the Zn₁ atom.

Due to the formation of cyclobutane rings between the cds structures that resulted in the new polymer ligand, poly-bppcb (Fig. 3b), the original two-fold interpenetrated net in 1 is now fused into a single net in 2 (Fig. 3c and d). The organic ligand, poly-bppcb, is encased inside the channels formed by the [Zn(bdc)(fa)]₉ brick-wall layers along the a-axis and is cross-linked with the Zn₁ atoms through pyridyl N atoms.

This SCSC photo-polymerization of the bpb ligands by [2+2] cycloaddition reactions causes the structural transformation of a doubly-interpenetrated non-porous MOF with cds topology to a non-interpenetrating network with a new topology. This unusual binodal net is built from the tetrahedral nodes of Zn(n) atoms and square planar nodes created by the cyclobutane rings of the poly-bppcb ligand. It is this infinite extension of the ligand which results in a planar nodes created by the cyclobutane rings of the poly-bppcb ligand. It is this infinite extension of the ligand which results in a planar MOFs where the Cd–O distances are equal (1.98 Å) and the Zn–O–Zn angles are close to 180° (Fig. 3a) and (Fig. 3c).

Notes and references

† Crystal data for C₃₀H₂₂N₂O₈Zn₂, fₐ = 669.24, monoclinic, P2₁/a, a = 6.8416(4) Å, b = 21.8416(4) Å, c = 9.4560(2) Å, β = 110.684(1)°, V = 1321.91(4) Å³, Z = 2, D₁₅ = 1.618 g cm⁻³, μ = 1.873 mm⁻¹, R₁ = 0.0311, GOF = 1.097, R₂ = 0.0316, wR₂ = 0.0781 for 2424 data I > 2σ(I); Crystal data for 2: C₃₀H₂₄N₂O₉Zn₂, fₐ = 687.26, monoclinic, P2₁/c, a = 7.3685(18) Å, b = 22.092(4) Å, c = 9.448(4) Å, β = 111.283(10)°, V = 1433.1(5) Å³, Z = 2, D₁₅ = 1.953 g cm⁻³, μ = 1.732 mm⁻¹, R₁ = 0.1037, GOF = 1.047, R₂ = 0.0672, wR₂ = 0.1487 for 1895 data I > 2σ(I).


