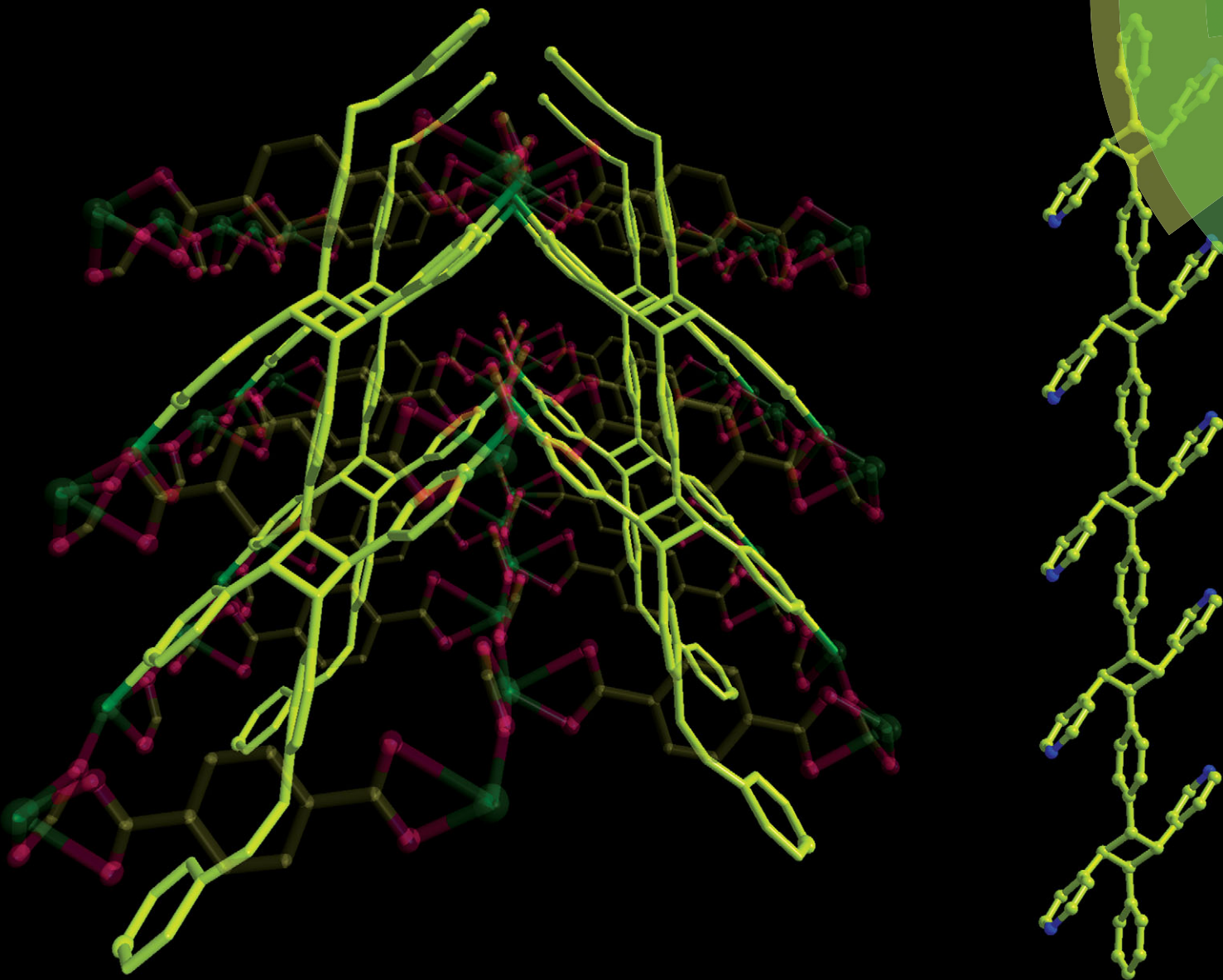


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Shim Sung Lee, Jagadese J. Vittal *et al.*

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

In-Hyeok Park,^a Anjana Chanthapally,^b Hyeong-Hwan Lee,^a Hong Sheng Quah,^b Shim Sung Lee*^a and Jagadese J. Vittal*^{ab}

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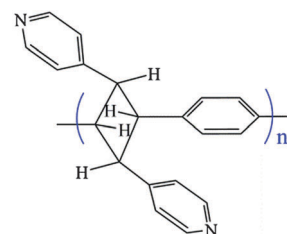
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The bpeb ligands aligned in a slip-stacked manner in a two-fold interpenetrated non-porous metal-organic framework (MOF) [Zn₂(bpeb)-(bdc)(fa)₂] undergo [2+2] cycloaddition reaction in a single-crystal to single-crystal manner to a non-interpenetrated 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-stacked 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.

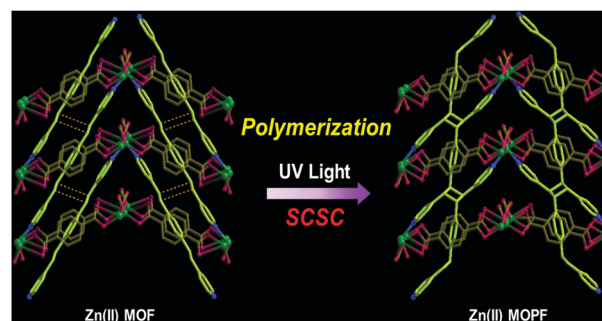
The product contains a 1D organo polymeric chain and a 1D coordination polymer fused together as metal-organo polymeric frameworks (MOPFs). The generality of the strategy for using [2+2]



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

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 2 The SCSC transformation from MOF to MOPF by polymerization via [2+2] photo-cycloaddition reaction.

^a Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea. E-mail: ssllee@gnu.ac.kr; Fax: +82 55-753-7614; Tel: +82 55-772-1483

^b Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: chmjv@nus.edu.sg; Fax: +65 6779 1691; Tel: +65 6516 2975

† Electronic supplementary information (ESI) available: XRPD patterns, TGA curves, solid-state photographs and crystal structures. CCDC 955835 (1) and 955836 (2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00228h



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 $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1,4-benzenedicarboxylic acid (H_2bdc) and bpeb in a mixture of DMF (dimethylformamide) and water at 100°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°C revealed that the asymmetric unit contains only half of the atoms in the formula unit of **1**.[‡] 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 [$99.76(8)$ – $124.65(8)^\circ$] is coordinated to one N atom of the bpeb spacer ligand, one O atom of the bdc ligand and O atoms of two formate ligands (Fig. 1a). The $\text{Zn1} \cdots \text{O2}$ and $\text{Zn1} \cdots \text{O4}$ distances, 2.77 and 2.90 Å, respectively, are considered very weak.

In **1**, the Zn(II) atoms are bridged by the formate ligands forming a chain along the $[\bar{1}01]$ 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 **cds** topology in **1** (Fig. 1d) with Schlafli symbol $\{6^5 \cdot 8\}$. The large

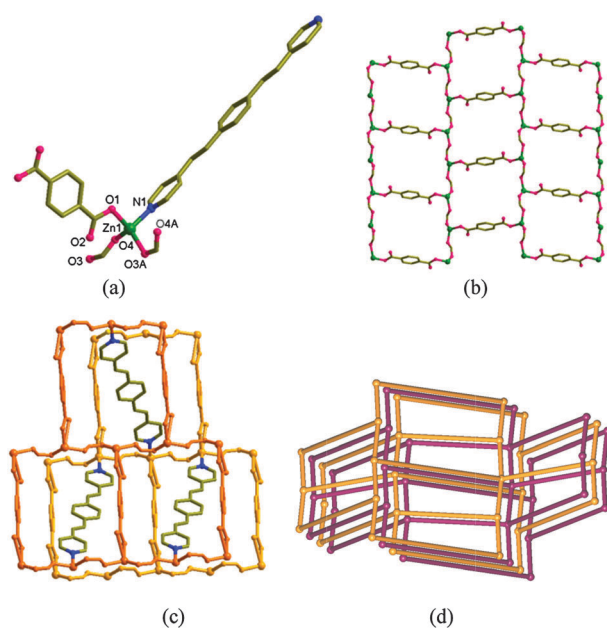


Fig. 1 Crystal structure of $[\text{Zn}_2(\text{bpeb})(\text{bdc})(\text{fa})_2]$ (**1**): (a) the coordination sphere of Zn1, symmetry operators for (A) $0.5 + x, 0.5 - y, 0.5 + z$, (b) brick-wall type $[\text{Zn}_2(\text{bdc})(\text{fa})_2]$ layer, (c) a view showing bpeb ligands connecting the brick-wall layers and (d) topology of the two-fold interpenetration viewed from the a -axis.

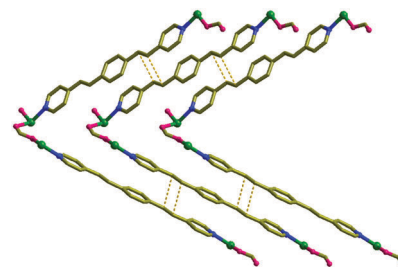


Fig. 2 A slip-stacked alignment of the neighbouring bpeb ligands in **1** showing only the relevant atoms.

void produced in this connectivity is filled by two-fold interpenetration (Fig. 1d) with little solvent accessible void.

The relative orientations of the bpeb ligands in the interpenetrated structures make **1** photoreactive. The C=C bonds in the neighbouring bpeb ligands are infinitely arranged closely in a slip-stacked manner as shown in Fig. 2. The phenylene rings are closer to the adjacent pyridyl groups (centroid to centroid distance of 3.616 Å) showing face-to-face π - π 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.[‡] Further characterisation by routine solution $^1\text{H-NMR}$ 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

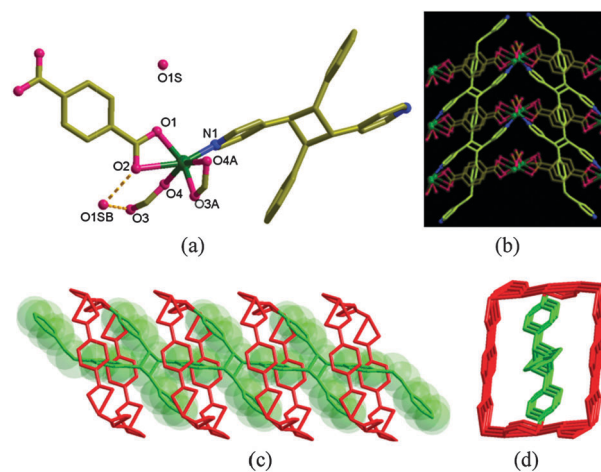


Fig. 3 Crystal structure of $[\text{Zn}_2(\text{poly-bppcb})(\text{bdc})(\text{fa})_2] \cdot \text{H}_2\text{O}$ (**2**): (a) the coordination sphere of Zn1, symmetry operator for (A) $x, 0.5 - y, 0.5 + z$; (B) $x + 1, y, z$, (b) poly-bppcb chain highlighted in **2** and (c) and (d) two views of the poly-bppcb (green) inside a $[\text{Zn}_2(\text{bdc})(\text{fa})_2]$ channel (red).



different space group setting is used ($P2_1/n$ in **1** and to $P2_1/c$ 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)₂] 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 enclosed inside the channels formed by the [Zn(bdc)(fa)₂] brick-wall layers along the *a*-axis and is cross-linked with the Zn^{II} atoms through pyridyl N atoms.

This SCSC photo-polymerization of the bpeb 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(II) 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 new (4, 4) connected net which we call **jjv2** with point symbol {6².8³.10}{6⁵.8}₂ and vertex symbol [6⁶.6².6.8⁴][6².6².8⁵.8⁵.8⁶.10¹⁸] as shown in Fig. 4. Such a polyfused [4+4] grid in coordination polymers can result in new or rare topologies.³

Solid state photoluminescence spectra were recorded for **1** and **2** and were compared with that of the bpeb ligand. The free ligand is weakly emissive in the yellow region, λ_{max} = 558 nm when excited at λ_{ex} = 360 nm. Compound **1** shows a strong green emission with a λ_{max} at 507 nm while **2** has a weaker emission which is blue shifted to more strong blue emission at λ_{max} = 429 nm which might be due to the loss of extended conjugation upon polymerization (Fig. S7 and S8, ESI†).

In this work an interesting photoreactive non-porous MOF containing two different carboxylate spacer ligands was synthesized. The formate anion could only be incorporated into this MOF indirectly by the partial hydrolysis of the DMF. The bpeb ligands have been aligned in a slip-stacked manner in a plane such that each C=C bond in the

bpeb ligand is aligned to different adjacent spacer ligands. Hence photochemical [2+2] cycloaddition reaction leads to the polymerization of the conjugated dienes in the bpeb ligands via [2+2] cycloaddition reaction. The infinite slip-stacked alignment has been achieved by the tetrahedral Zn(II) atoms in the **cds** topology instead of a diamondoid network as reported earlier.³ The original two-fold interpenetrated **cds** structure is transformed under UV light to a non-interpenetrated structure **jjv2**, with a new topology, in a SCSC manner due to the formation of cyclobutane rings between the adjacent C=C bonds. This 3D structure has a 2D coordination polymer [Zn₂(bdc)(fa)₂] fused together with an organic polymer, poly-bppcb, to give a new MOPF compound which is unlikely to be synthesized by any other means. We are currently exploring the possibility of extending this strategy to synthesize MOF-COF hybrid structures which are expected to exhibit interesting sorption properties.

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Notes and references

‡ Crystal data for **1**: C₃₀H₂₂N₂O₈Zn₂, *f*_w = 669.24, monoclinic, $P2_1/n$, *a* = 6.8414(1) Å, *b* = 21.8416(4) Å, *c* = 9.4560(2) Å, β = 110.684(1)°, *V* = 1321.91(4) Å³, *Z* = 2, *D*_x = 1.681 g cm⁻³, μ = 1.873 mm⁻¹, *R*_{int} = 0.0311, GOF = 1.097, *R*₁ = 0.0316, *wR*₂ = 0.0781 for 2424 data *I* > 2σ(*I*). Crystal data for **2**: C₃₀H₂₄N₂O₉Zn₂, *f*_w = 687.26, monoclinic, $P2_1/c$, *a* = 7.3685(18) Å, *b* = 22.092(4) Å, *c* = 9.448(2) Å, β = 111.283(10)°, *V* = 1433.1(5) Å³, *Z* = 2, *D*_x = 1.593 g cm⁻³, μ = 1.732 mm⁻¹, *R*_{int} = 0.1037, GOF = 1.047, *R*₁ = 0.0672, *wR*₂ = 0.1487 for 1895 data *I* > 2σ(*I*).

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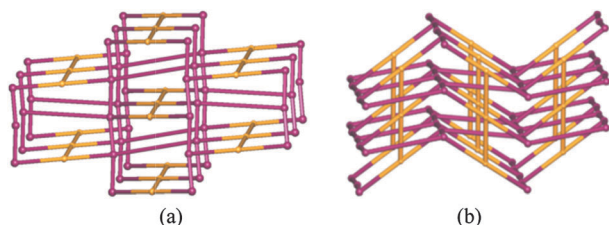


Fig. 4 (a) The topological representation of the 3D framework created from the corrugated [Zn(bdc)(fa)₂] sheets (purple) and a poly-bppcb node (yellow) along the *a*-axis. (b) Another view of the non-interpenetrated net **jjv2** along the *c*-axis.

