

# Electronic Supplementary Information

for

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

In-Hyeok Park,<sup>a</sup> Anjana Chantapally,<sup>b</sup> Hyeong-Hwan Lee,<sup>a</sup> Hong Sheng Quah,<sup>b</sup>  
Shim Sung Lee,<sup>\*a</sup> and Jagadese J. Vittal<sup>\*ab</sup>

<sup>a</sup>Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea

<sup>b</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

## TABLE OF CONTENTS

### Experimental Section

General and synthetic methods for **1** and **2**

X-ray crystallographic analysis for **1** and **2**

<b>Table S1</b>	Crystallographic data and refinement parameters of <b>1</b> and <b>2</b>
<b>Fig. S1</b>	PXRD patterns for <b>1</b>
<b>Fig. S2</b>	PXRD patterns for <b>2</b>
<b>Fig. S3</b>	TGA curve of <b>1</b>
<b>Fig. S4</b>	TGA curve of <b>2</b>
<b>Fig. S5</b>	Solid-state photoluminescence spectra of <b>1</b> and <b>2</b>
<b>Fig. S6</b>	Photographs of crystals <b>1</b> and <b>2</b> at room light and under 365 nm
<b>Fig. S7</b>	The structures of [Zn(bdc)(fa) <sub>2</sub> ] layer in <b>2</b>
<b>Fig. S8</b>	The [Zn(fa)] chains showing different coordination modes in (a) <b>1</b> and (b) <b>2</b>
<b>Fig. S9</b>	A view showing two disordered fa ligands in <b>2</b>
<b>Fig. S10</b>	Views of the [Zn <sub>6</sub> (bdc) <sub>2</sub> (fa) <sub>4</sub> ] square rings in (a) <b>1</b> and (b) <b>2</b>
<b>Fig. S11</b>	A view showing the disordered water molecules along <i>c</i> -axis in <b>2</b>
<b>Fig. S12</b>	Topological representations of the 2-fold interpenetrated 3D structures of <b>1</b>
<b>Fig. S13</b>	Topological representations of the non-interpenetrated 3D structures of <b>2</b>

## EXPERIMENTAL SECTION

**General.** All chemicals were purchased of reagent grade and were used without further purification. The bpeb ligand was synthesized by the reported procedure.<sup>S1</sup> The elemental analyses were carried out a LECO CHNS-932 elemental analyser. The infrared spectra (IR) were recorded (4000 – 400 cm<sup>-1</sup>) on the Thermo Fisher Scientific Nicolet iS 10 FT-IR spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 5°C min<sup>-1</sup> using a TA Instruments TGA-Q50 thermogravimetric analyser. The solid state emission spectra were obtained from Shimadzu RF-5301PC. Powder X-ray diffraction (PXRD) patterns were recorded on a D8 DISCOVER with GADDS (Bruker AXS) with graphite monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature (23 °C).

**[Zn<sub>2</sub>(bpeb)(bdc)(fa)<sub>2</sub>] (1):** A mixture of bpeb (20.2 mg, 0.071 mmol), H<sub>2</sub>bdc (11.8 mg, 0.071 mmol), and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (18.7 mg, 0.071 mmol) dissolved in DMF (1 mL) and H<sub>2</sub>O (1.5 mL) were placed in a 10 mL glass tube, and then a drop of concentrated HNO<sub>3</sub> were added. The tube was sealed and kept at 100 °C for 48 h, followed by cooling to room temperature over 8 h. Orange block-shaped crystals **1** suitable for X-ray analysis were obtained (35.7 mg, Yield 76% based on Zn(II) salt). Due to the higher humidity in the non-airconditioned lab in Singapore, **1** adsorbed ~1.5H<sub>2</sub>O on the crystal surface. Anal. Calcd for [Zn<sub>2</sub>(bpeb)(bdc)(fa)<sub>2</sub>], [C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub>Zn<sub>2</sub>]: C, 53.84; H, 3.31; N, 4.19. Found C, 53.69; H, 3.34; N, 4.27%. IR (KBr pellet, cm<sup>-1</sup>) 3454, 2936, 2881, 1618, 1560, 1508, 1499, 1438, 1425, 1384, 1356, 1231, 1068, 1032, 958, 890, 832, 810, 751, 619 and 533.

**[Zn<sub>2</sub>(poly-bppcb)(bdc)(fa)<sub>2</sub>]·H<sub>2</sub>O (2):** The pale yellow needle-shaped crystals of **2** were obtained by UV irradiation of single crystals of **1** for 2 h. Anal. Calcd for [Zn<sub>2</sub>(poly-bppcb)(bdc)(fa)<sub>2</sub>], [C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub>Zn<sub>2</sub>] for the dried sample: C, 53.84; H, 3.31; N, 4.19. Found: C, 54.22; H, 3.24; N, 4.31%. IR IR (KBr pellet, cm<sup>-1</sup>) 3448, 2934, 2881, 1647, 1425, 1350, 1220, 1122, 1066, 1034, 924, 892, 834, 808, 752, 630, 573 and 520.

**X-ray crystallographic analysis.** Crystal data for **1** and **2** at 173 K were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) generated by a rotating anode. The preliminary cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected

frames). Data collection, data reduction, and absorption correction were carried out using the software package of APEX2.<sup>S2</sup> All of the calculations for the structure determination were carried out using the SHELXTL package.<sup>S3</sup> Relevant crystal data collection and refinement data for the crystal structures of **1** and **2** are summarized in Table S1.

CCDC 955835 (**1**) and 955836 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

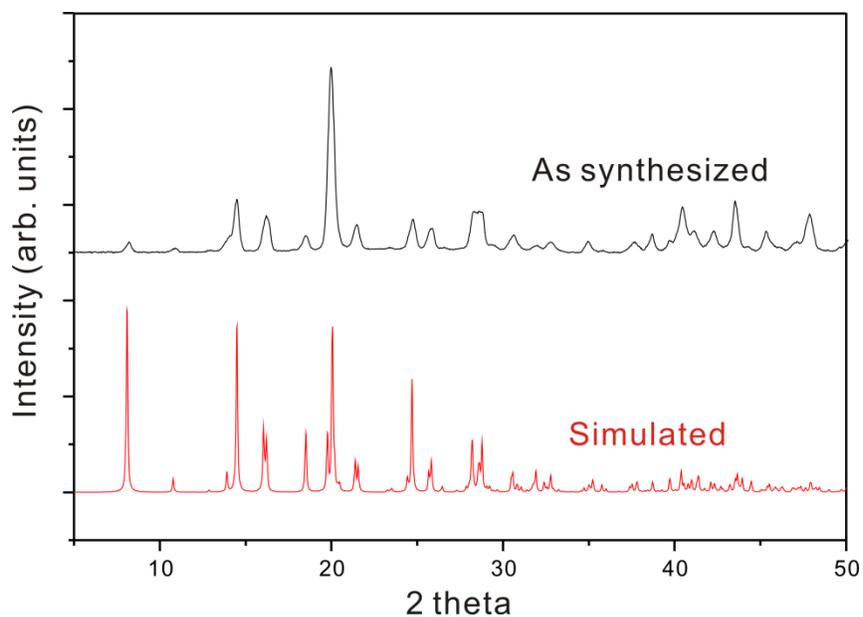
### References:

- S1. A. V. Gutov, E. B. Rusanov, L. V. Chepeleva, S. G. Garasevich, A. B. Ryabitskii, A. N. Chernega, *Russ. J. Gen. Chem.* 2009, **79**, 1513–1518.
- S2. Bruker, *APEX2 Version 2009.1-0 Data Collection and Processing Software*; Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.
- S3. Bruker, *SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2001.

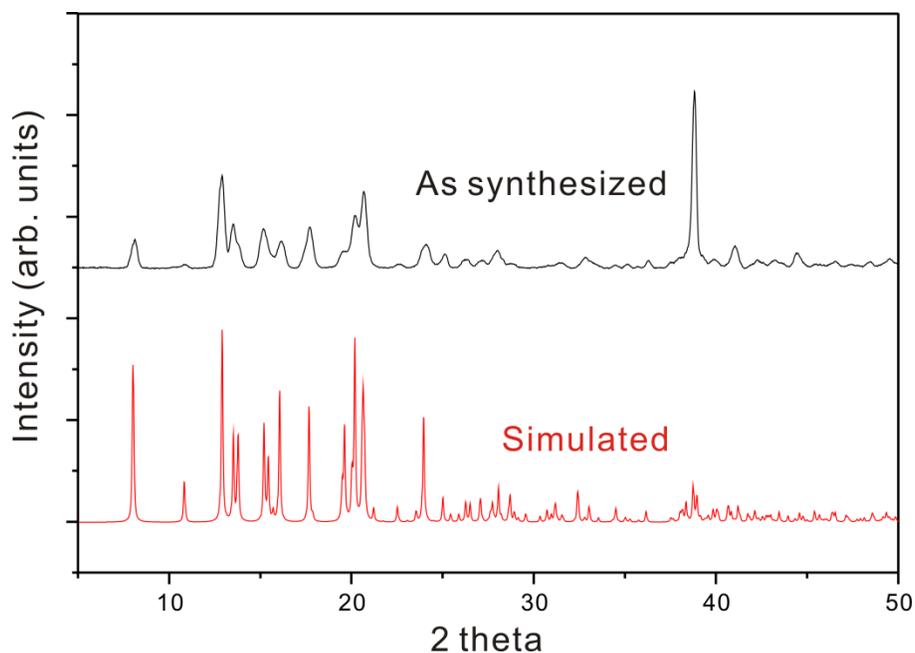
**Table S1** Crystallographic data and refinement parameters of **1** and **2**

	<b>1</b>	<b>2</b>
formula	C <sub>30</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> Zn <sub>2</sub>	C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> O <sub>9</sub> Zn <sub>2</sub>
formula weight	669.24	687.26
crystal system	monoclinic	monoclinic
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	6.8414(1)	7.3685(18)
<i>b</i> (Å)	21.8416(4)	22.092(4)
<i>c</i> (Å)	9.4560(2)	9.448(2)
$\alpha$ (°)	90	90
$\beta$ (°)	110.684(1)	111.283(10)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	1321.91(4)	1433.1(5)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.681	1.593
$\mu$ (mm <sup>-1</sup> )	1.873	1.732
2 $\theta$ <sub>max</sub> (°)	51.98	52.00
reflections collected	21774	12614
independent reflections	2607 ( <i>R</i> <sub>int</sub> = 0.0311)	2810 ( <i>R</i> <sub>int</sub> = 0.1037)
goodness-of-fit on <i>F</i> <sup>2</sup>	1.097	1.047
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0316, 0.0342	0.0672, 0.0996
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0781, 0.0794	0.1487, 0.1631

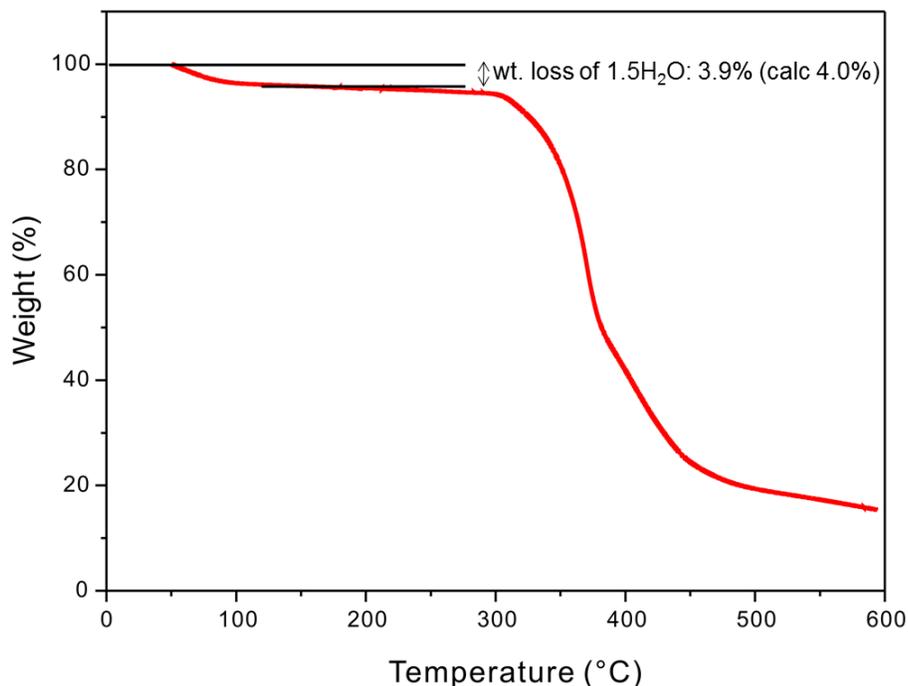
These are original (un-squeezed) data.



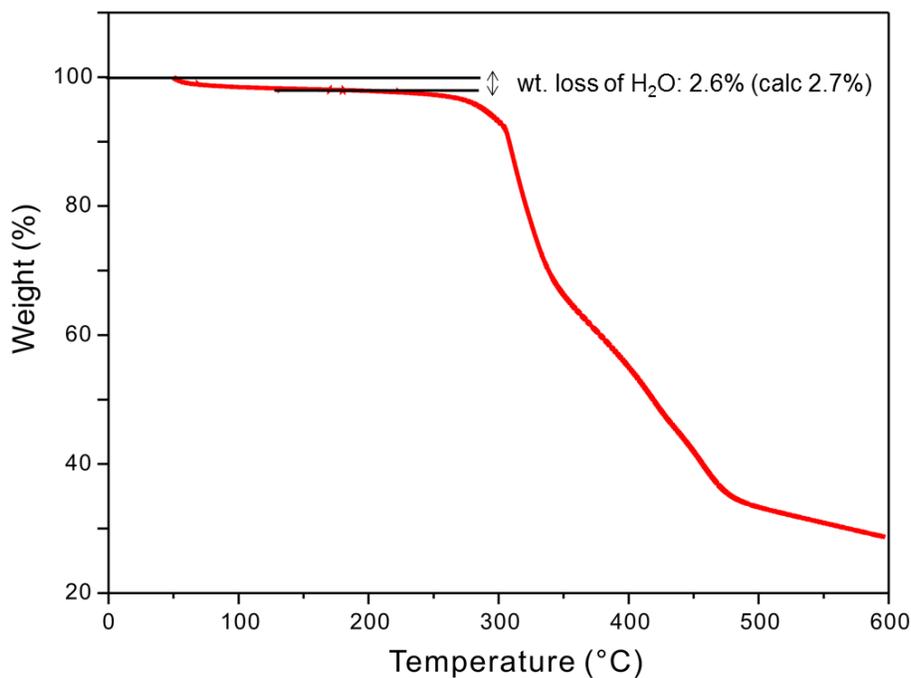
**Fig. S1** PXRD patterns for **1**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The intensity variations in these patterns may be due to the preferred orientations of the powder form.



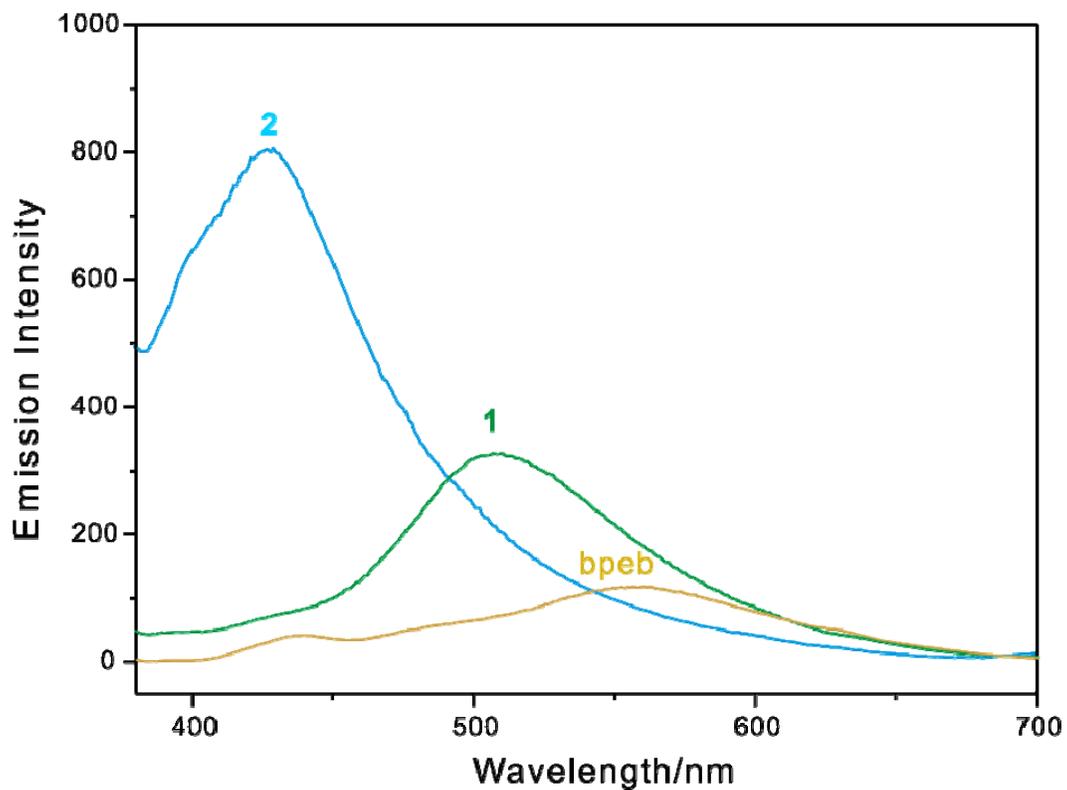
**Fig. S2** PXRD patterns of **2**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The intensity variations in these patterns appear to be due to the preferred orientations of the powder form.



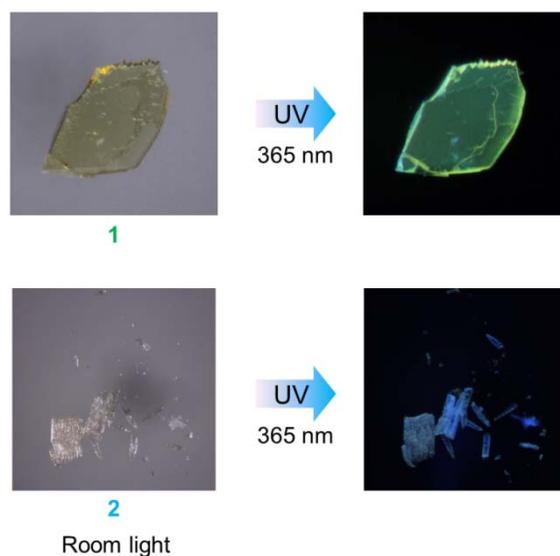
**Fig. S3** TGA curve of **1** with heating rate of 5 °C·min<sup>-1</sup> under N<sub>2</sub> flow. The desolvated **1** is stable up to 300 °C. The water seems to be adsorbed on the surface.



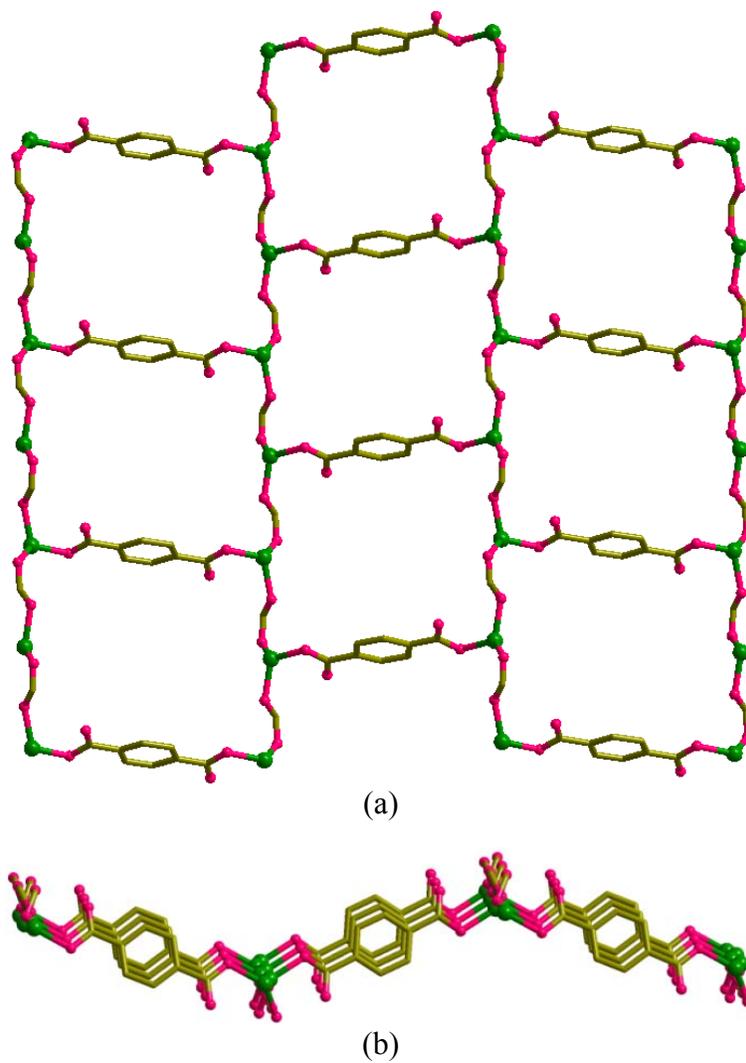
**Fig. S4** TGA curve of **2** with heating rate of 5 °C·min<sup>-1</sup> under N<sub>2</sub> flow. The desolvated **2** is stable up to 270 °C.



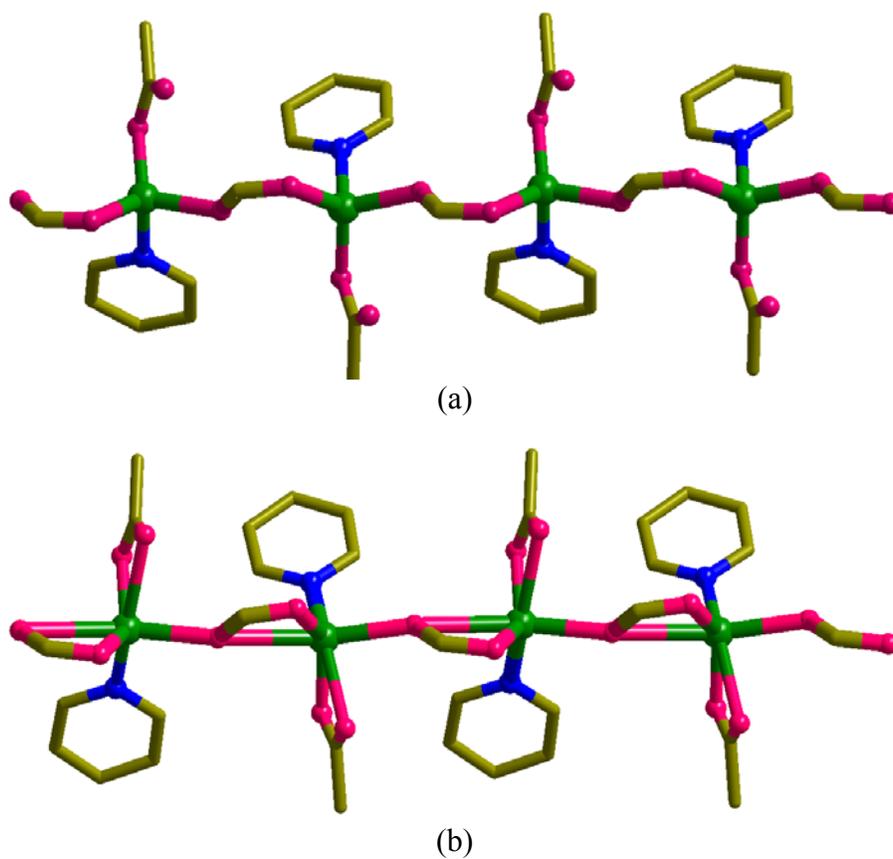
**Fig. S5** Solid-state photoluminescence spectra of **1** and **2** at room temperature (excitation at 360 nm).



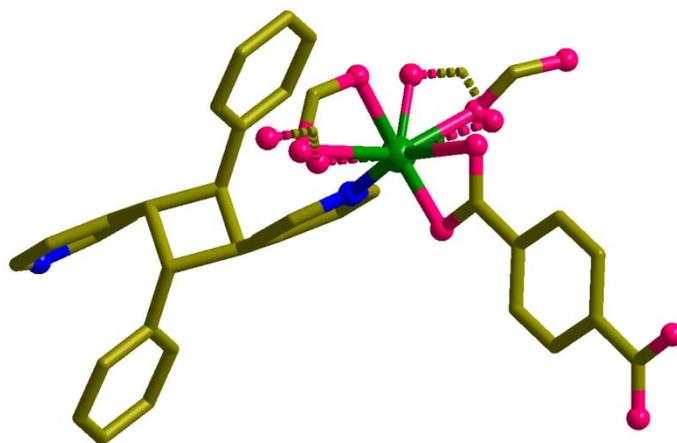
**Fig. S6** Photographs of crystals **1** and **2** under (left) room light and (right) 365 nm. The plate-shaped crystals **1** were broken to the smaller pieces (crystals **2**) by the [2+2] cycloaddition reaction accompanying the SCSC transformation.



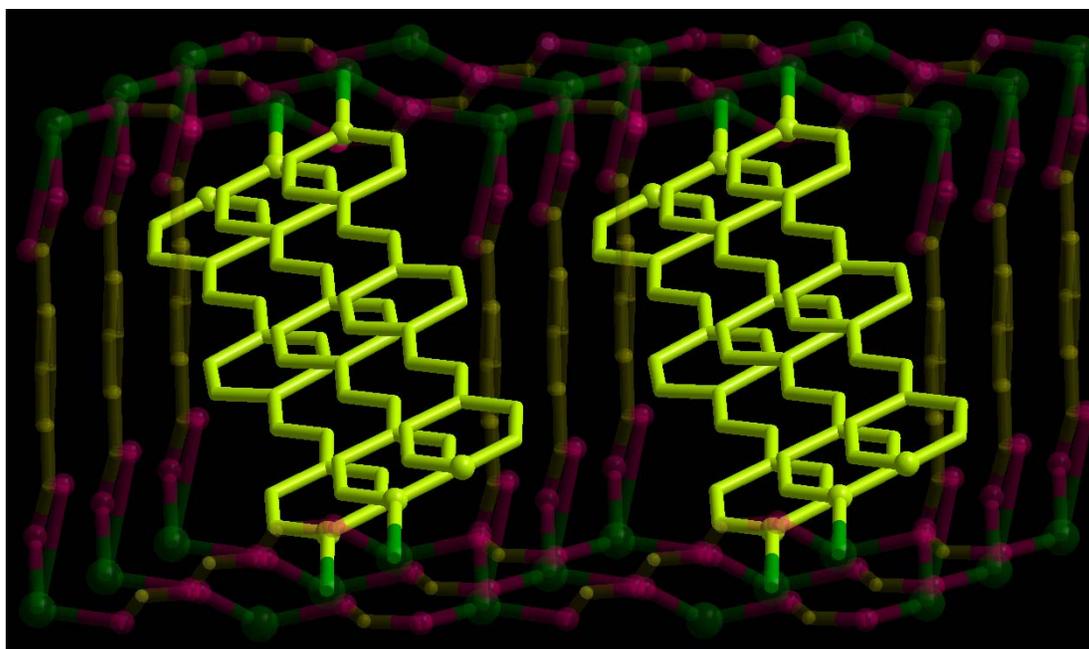
**Fig. S7** The structures of [Zn(bdc)(fa)<sub>2</sub>] layer in **2**: (a) a top view showing the [6,3] grid and (b) a wavy side view.



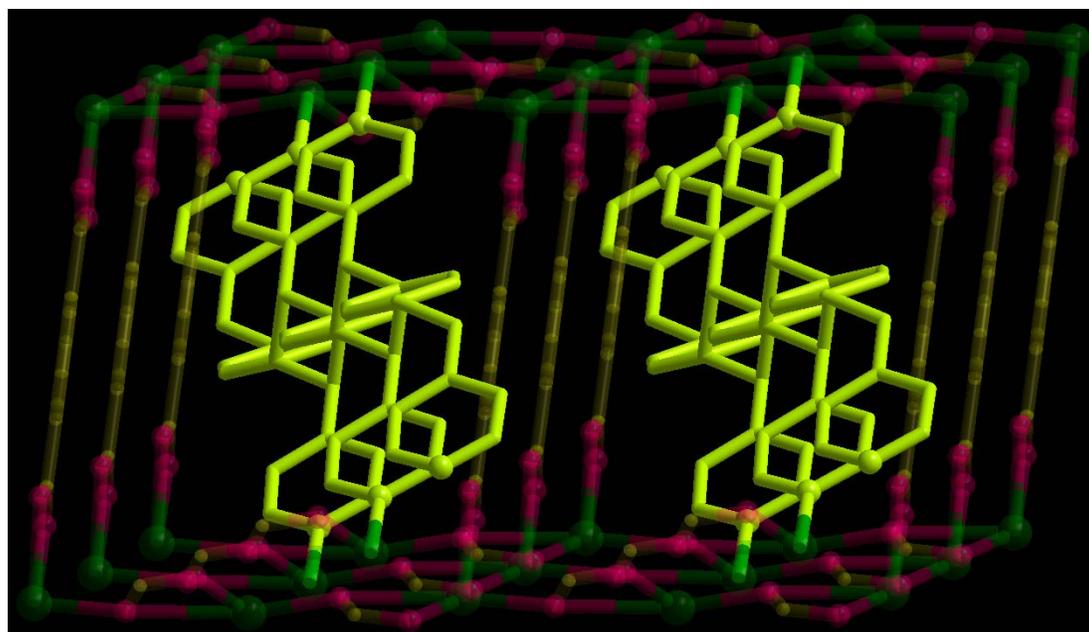
**Fig. S8** The  $[\text{Zn}(\text{fa})]$  chains showing different coordination modes in (a) **1** and (b) **2**.



**Fig. S9** A view showing two disordered fa ligands with occupancy ratio of 57:43 in **2**.

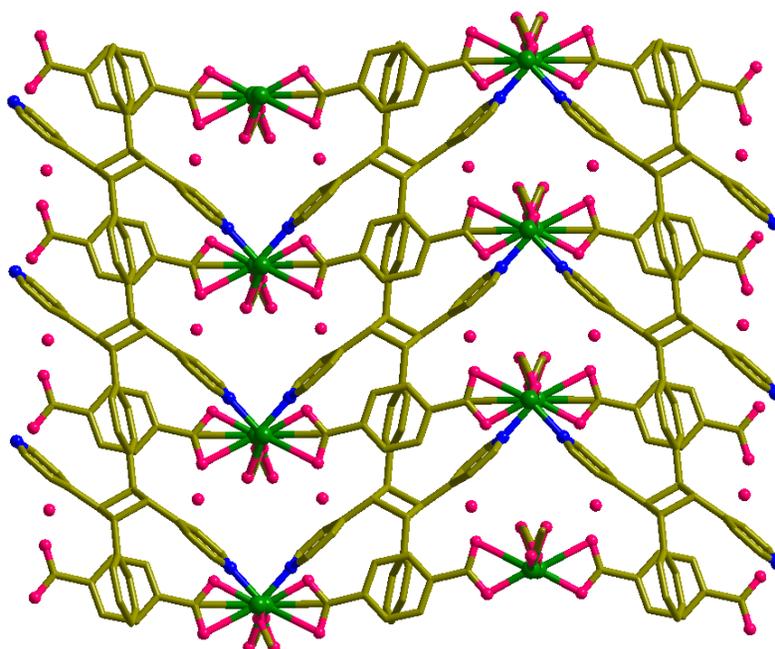


(a)

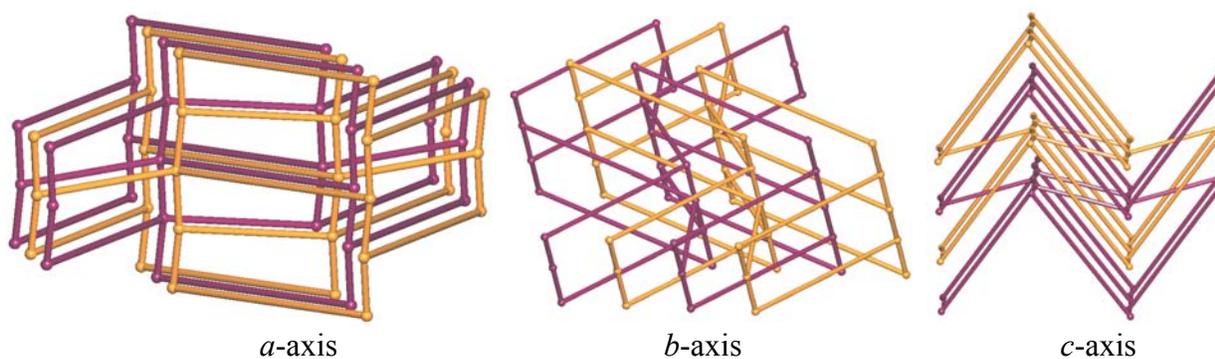


(b)

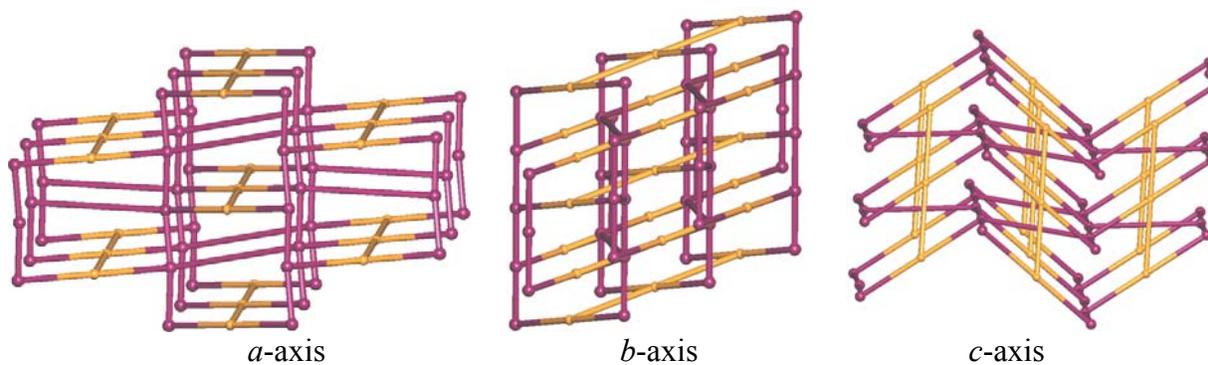
**Fig. S10** Views of the [Zn<sub>6</sub>(bdc)<sub>2</sub>(fa)<sub>4</sub>] square rings in (a) **1** and (b) **2**.



**Fig. S11** A view showing the disordered water molecules along *c*-axis in **2**.



**Fig. S12** Topological representations of the 2-fold interpenetrated 3D structures of **1**.



**Fig. S13** Topological representations of the non-interpenetrated 3D structures of **2**. Color code: Zn node (violet) and *poly*-bppcb node (yellow).