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Supplementary Information

Phase Transition Triggered Aggregation-Induced Emission in a Luminescent Uranyl-Organic Framework

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Experimental section

***Caution!** All uranium compounds were investigated in an authorized laboratory designed for actinide element studies. Standard protections for radioactive materials should be followed.*

General

Reagents and solvents employed were commercially available and used as received. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) equipped with a Lynxeye one-dimensional detector. Thermal gravimetric analysis was carried out on a NETZSCH STA 449F3 instrument in the range of 30 – 900 °C under nitrogen flow at a heating rate of 10 °C / min. The UV-vis spectra were measured using a Craic Technologies microspectrophotometer. A Quantachrome Autosorb Gas Sorption analyzer IQ2 was used to perform water vapor adsorption measurements.

X-ray Crystallography

Data collection was performed on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector at room temperature. The data frames were collected using the program APEX2 and processed using the SAINT routine. The structures were solved by direct methods and refined by the full-matrix least squares on F2 using the SHELXTL-2014 program[1]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic and refinement details are summarized in **Table S1**.

Computational Methods

The absolute geometry configurations of two adjacent ligands before and after the phase transition were chosen as the computational models (**Fig 4c, e**). The COO^- terminals, which coordinate to U in the bulk phase, were replaced by single H atoms. Single-point energies were carried out at the M062x-D3/6-31+G(d) level.[2-5] The interaction energies [E(int)] between two ligands was calculated by:

$$E(int) = E(total) - E(ligand1) - E(ligand2),$$

where E(total) indicates the total energy of the two ligands, and E(ligand1) and E(ligand2) indicate the energy of each ligand. The basis set superposition error (BSSE) has been excluded in E(int). The E(int) was further decomposed into:

$$E(int) = E(steric) + E(orb) + E(disp),$$

where E(steric) indicates the steric interactions, including electrostatic and exchange repulsion interactions. E(orb) indicate the orbital interactions, which reflects the electron density polarization. E(disp) represents the dispersion interactions, which typically arise from weak van der Waals (VDW) interactions. All calculations were performed using the Gaussian 09 program.[6]

Synthesis of Compound 1

H_3BCPBA (39.4 mg, 0.1 mmol) and $UO_2(NO_3)_2 \cdot 6H_2O$ (50.2 mg, 0.1 mmol) were dissolved in a mixture of 4 mL DMF and 1 mL H_2O and three drops concentrated nitric acid. The mixture was sealed in a 20 mL glass vial and heated at 100 ^{o}C for four days. The reaction system was cooled gradually to ambient temperature. After filtration and subsequent washing three times with ethanol, light yellow block-shaped crystals suitable for X-ray structural analysis were collected. Yield: *ca*. 49% (based on U). Elemental analysis *ca*. (%) for $C_{29}H_{35}N_3O_{13}U$: C, 39.15; H, 4.162; N, 4.724. Found C, 39.95; H, 4.018; N, 4.822. CIF information for compound 1 can be found in the Cambridge Crystallographic Database (CCDC No. 1579368).

Synthesis of Compound 2

Soaking compound 1 in aqueous solutions for less than 10 minutes or exposed in air with *ca.* 45% relative humidity, it was found that compound 1 transitions completely into compound 2. Compound 2 is also characterized by forming yellow block-shaped crystals suitable for X-ray structural analysis. Yield: 100% (based on compound 1). Elemental analysis *ca.* (%) for $C_{23}H_{25.8}NO_{13.4}U$: C, 35.63; H, 3.612; N, 1.955. Found C, 35.93; H, 3.359; N, 1.822. CIF information for compound 2 can be found in the Cambridge Crystallographic Database (CCDC No. 1579369)

Table S1. Crystallographic parameters of **compound 1** and **2**.

	Compound 1	**Compound 2**
Formula	$[(CH_3)_2NH_2][(UO_2)(BCPBA)]\cdot 2$ DMF$\cdot H_2O$	$[(CH_3)_2NH_2][(UO_2)(BCPBA)]\cdot 3.4H_2O$
Formula weight (mol g^{-1})	871.63	768.67
Crystal system	Monoclinic	Monoclinic
a (Å)	11.217(2)	11.4098(16)
b (Å)	10.2614(18)	9.3291(13)
c (Å)	14.346(3)	14.383(2)
α (°)	90	90
β (°)	97.541 (6)	96.391(4)
γ (°)	90	90
V (Å^3)	1637.0(5)	1521.5(4)
Z	2	2
D_c (g cm^{-3})	1.768	1.678
μ (mm^{-1})	5.026	5.394
F (000)	852	740
T (K)	168(2)	168(2)
GOF on F^2	1.021	1.106
R1,[a] *w*R2[b] ($I > 2\sigma(I)$)	0.0506, 0.1108	0.0533, 0.1480
R1,[a] *w*R2[b] (all data)	0.0772, 0.1207	0.0674, 0.1554

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

NOTE: Since there are highly disordered solvent molecules in the free space, the SQUEEZE[7] routine in PLATON was applied to remove the diffraction peaks contributed from those highly disordered guest molecules. The chemical formula of compound 2 was determined by the combination of the crystal data (SQUEEZE result), TGA, and elemental analysis. Based on the SQUEEZE result, the solvent molecules was identified as one $[(CH_3)_2NH_2]^+$ cation and 3.4 water molecules. All disordered molecules have been included in the .ins file, and all parameters of compound 2 reported in the CIF were changed subsequently, although it was different from the calculated data.

The SQUEEZE results are as follows:

```
# SQUEEZE RESULTS
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
```

```
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
     1 -0.029 -0.061    0.545              659              120 ' '
_platon_squeeze_void_probe_radius                                    1.20
_platon_squeeze_details
```

As noted above, 120 electrons were removed from the unit cell by the SQUEEZE process. This could correspond with some 120 / 2 = 60 electrons being removed from the asymmetric unit. According to elemental analysis and TGA, we confirm ultimately the removed 60 electrons are from one $[NH2(CH3)2]^{+}$ (26 electrons) and 3.4 water molecules (34 electrons).

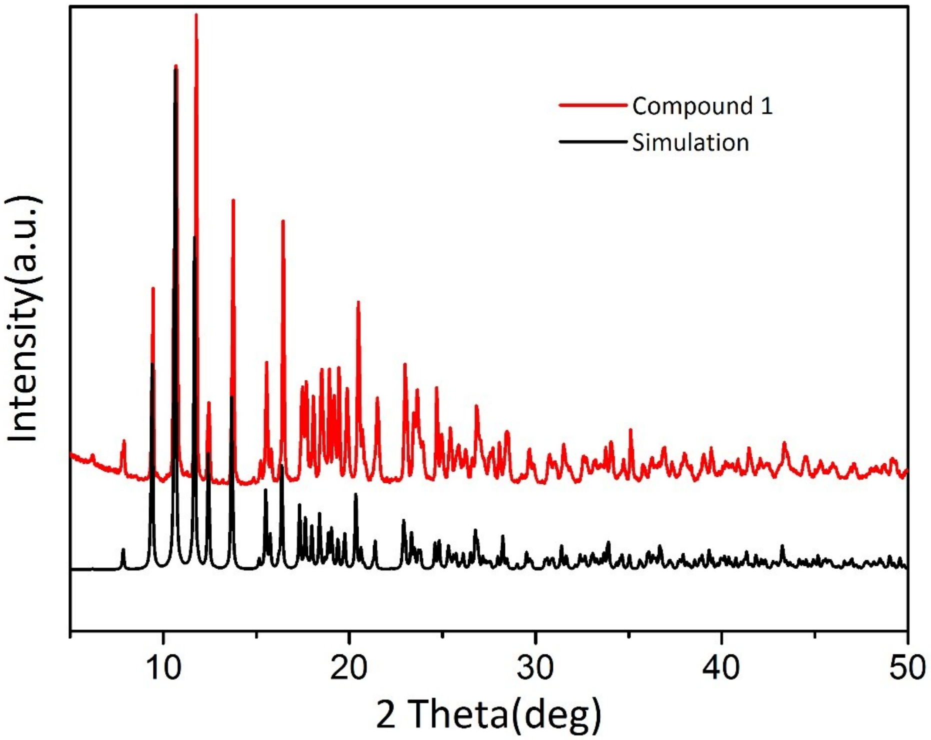

Fig. S1 PXRD of compound **1**.

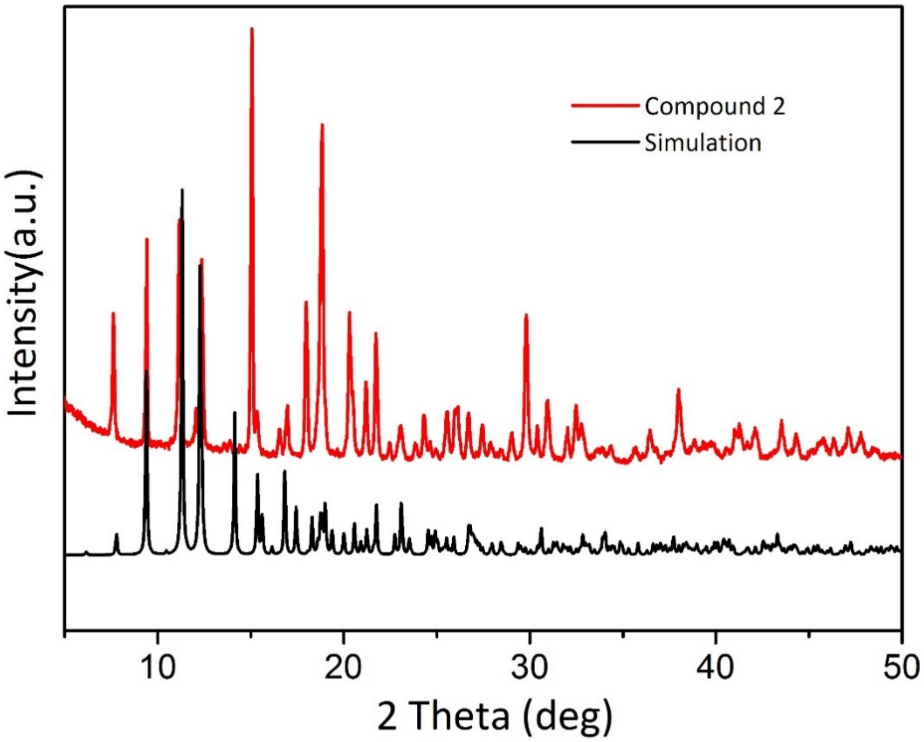

Fig. S2 PXRD of compound **2**.

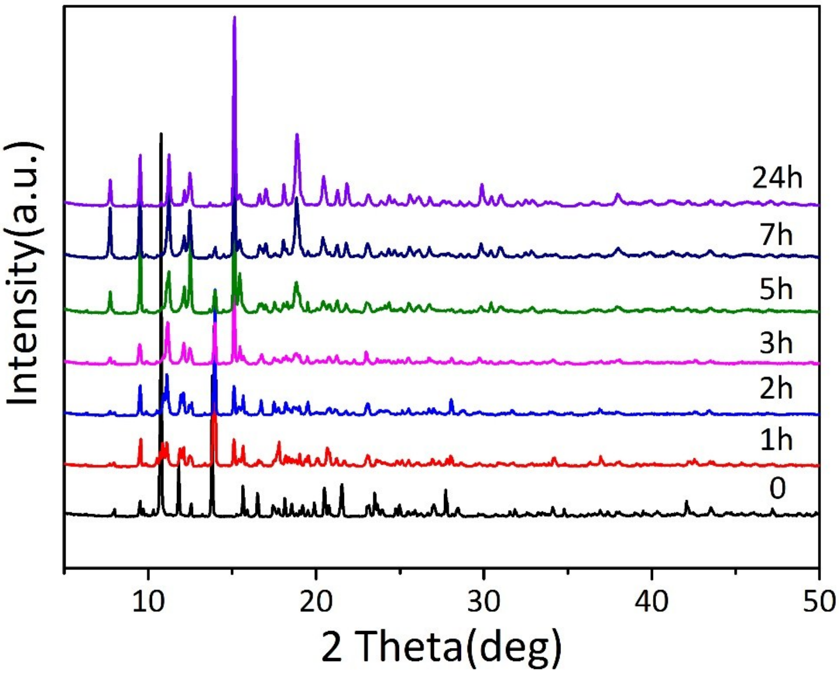

Fig. S3 Changes in the PXRD of compound **1** under air with moderate moisture.

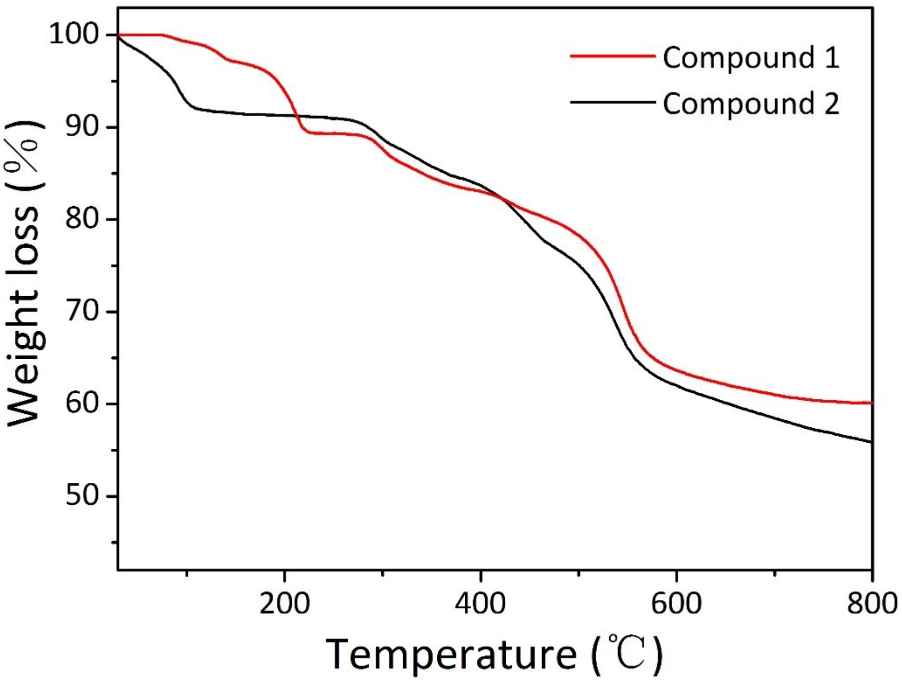

Fig. S4 TGA of compound **1** and compound **2**.

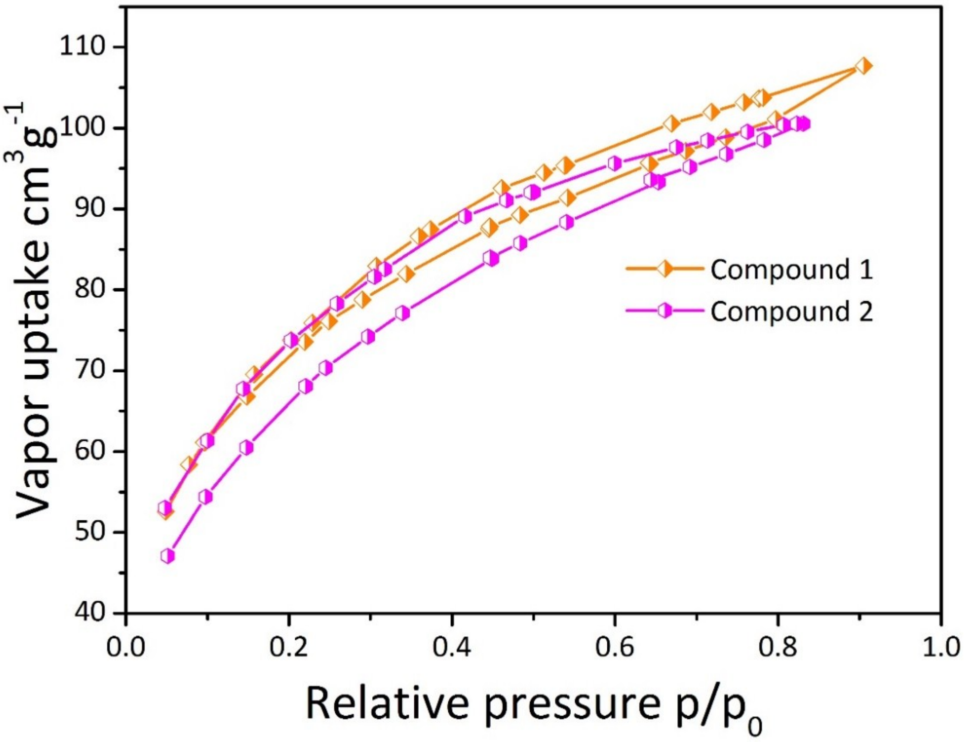

Fig. S5 Water vapor uptake of compound **1** and compound **2**.

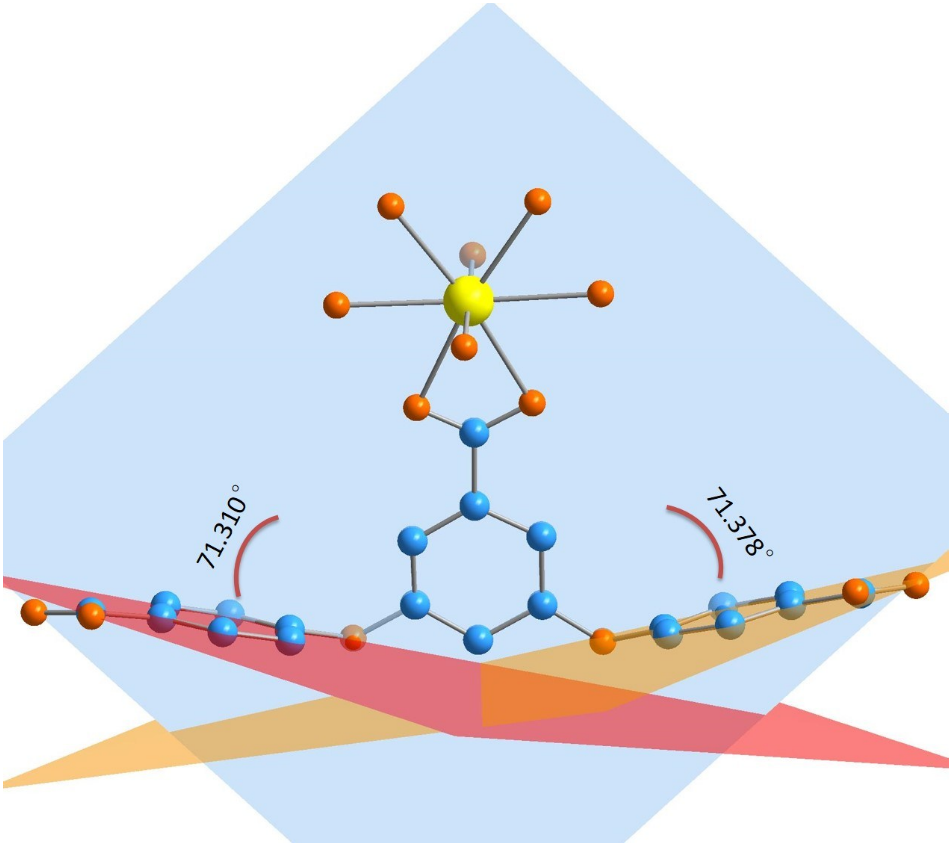

Fig. S6 Two dihedral angels between the different benzene rings of BCPBA in compound **1**.

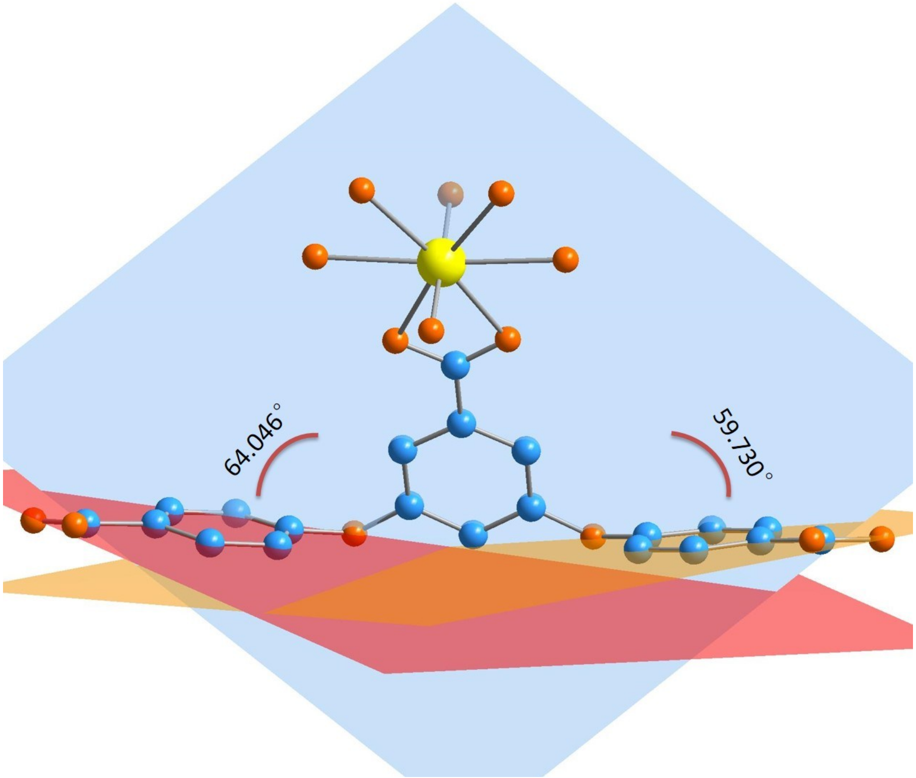

Fig. S7 Two dihedral angels between the different benzene rings of BCPBA in compound **2**.

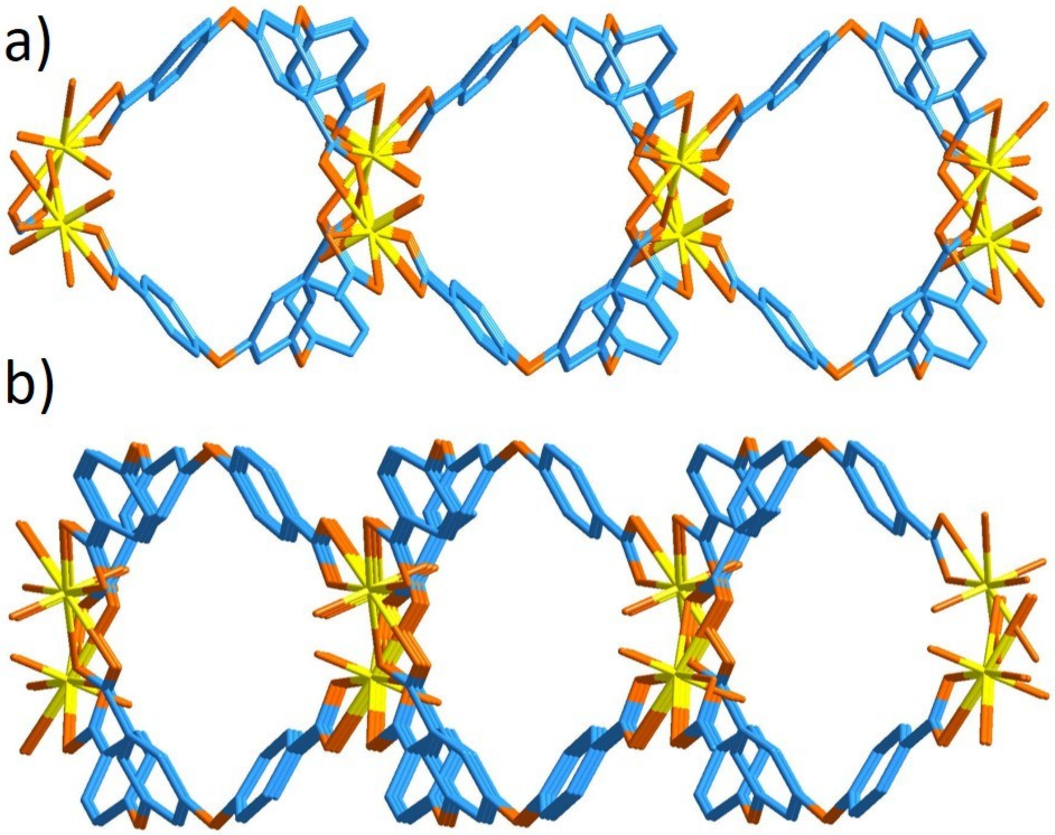

Fig. S8 a) The one-dimensional square channels in compound **1**; b) The similar one-dimensional square channels in compound **2**.

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