

Electronic Supplementary Information

**Gas Sorption of Nano-Porous Supramolecule Formed by Multi-Hydrogen Bonding  
Coordination Capsules**

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## Preparations

[ $\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\text{Cl}$ ](**2**): The solution suspended [ $\text{Re}^{\text{I}}(\text{CO})_5\text{Cl}$ ] (0.50 g, 1.39 mmol) and  $\text{H}_2\text{bim}$  (0.16 g 1.39 mmol) in THF (200  $\text{cm}^3$ ) was refluxed for 6 hours, and the obtained clear solution was evaporated in dryness to give a yellow solid. Then it was dissolved in a hot acetone, and the acetone solution was slowly evaporated at room temperature to be recrystallized as yellow plate crystals. Yield, 0.48 g (79.4%). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3178(*br*), 2021, 1927, 1899, 1878, 1633, 1529, 1427, 1319, 1186, 1137, 1088, 858, 761, 687, 649, 632; Anal. Calcd for  $\text{ReC}_9\text{H}_6\text{N}_4\text{O}_3\text{Cl}$ : C, 24.58%, H, 1.37%, N, 12.74%, Re, 42.34%, Found: C, 24.90%, H, 1.10%, N, 12.34%, Re, 42.43%, FAB-mass (NBA):  $m/z = 442$  ( $[\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\text{Cl}]^+$ )

$[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})](\text{CF}_3\text{SO}_3)_3$  (**3**)

The solution added [ $\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\text{Cl}$ ](**2**) (0.33 g, 0.76 mmol) and  $\text{AgCF}_3\text{SO}_3$  (0.19 g, 0.76 mmol) to acetone (200  $\text{cm}^3$ ) was refluxed for 4 hours under Ar after that the produced white solid was filtered, and the filtrate was evaporated in dryness. Subsequently, the obtained solid and tpta (0.079 g, 0.25 mmol) was added to MeOH (200  $\text{cm}^3$ ) and refluxed for 3 days under Ar. The evaporated yellow solid was recrystallized from MeOH/hexane to give yellow crystals. Yield, 0.38 g (76.0%). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 2026, 1897, 1574, 1516, 1373, 1290, 1223, 1163, 1092, 1024, 802, 756, 635; Anal. Calcd for  $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})](\text{CF}_3\text{SO}_3)_3 \cdot 2\text{MeOH}$  ( $\text{Re}_3\text{C}_{50}\text{H}_{38}\text{N}_{18}\text{O}_{20}\text{F}_9\text{S}_3$ ): C, 29.49%, H, 1.53%, N, 12.78%, Found: C, 29.90%, H, 1.88%, N, 12.38%, FAB-mass (NBA):  $m/z = 1523$  ( $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})]^+$ )

$[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim})\}_3(\text{tpta})]_2$  (**1**)

$[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})](\text{CF}_3\text{SO}_3)_3$  (**3**) (0.010 g, 0.005 mmol) was dissolved in the mixed solvent of MeCN/ $(\text{CH}_2\text{Cl})_2 = 1/1$  (*v/v*) (0.3  $\text{cm}^3$ ). The solution was deprotonated by a little bit of MeOH solution with a  $t\text{BuOK}$  base to obtain yellow plate crystals. Yield, 0.05g (48.0%). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 2971, 2015, 1880, 1610, 1576, 1518, 1408, 1373, 1333, 1274, 1136, 1090, 1057, 959, 943, 908, 868, 808, 758, 735, 702, 679, 658, 648, 627, 557, 534, 511, 484, 444, Anal. Calcd for  $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})]_2$  ( $\text{Re}_6\text{C}_{126}\text{H}_{84}\text{N}_{46}\text{O}_{18}$ ): C, 35.50%, H, 1.79%, N, 16.56%, Found: C, 35.99%, H, 1.39%, N, 16.20%, ESI-mass (MeCN):  $m/z = 3045$  ( $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})]_2^+$ )

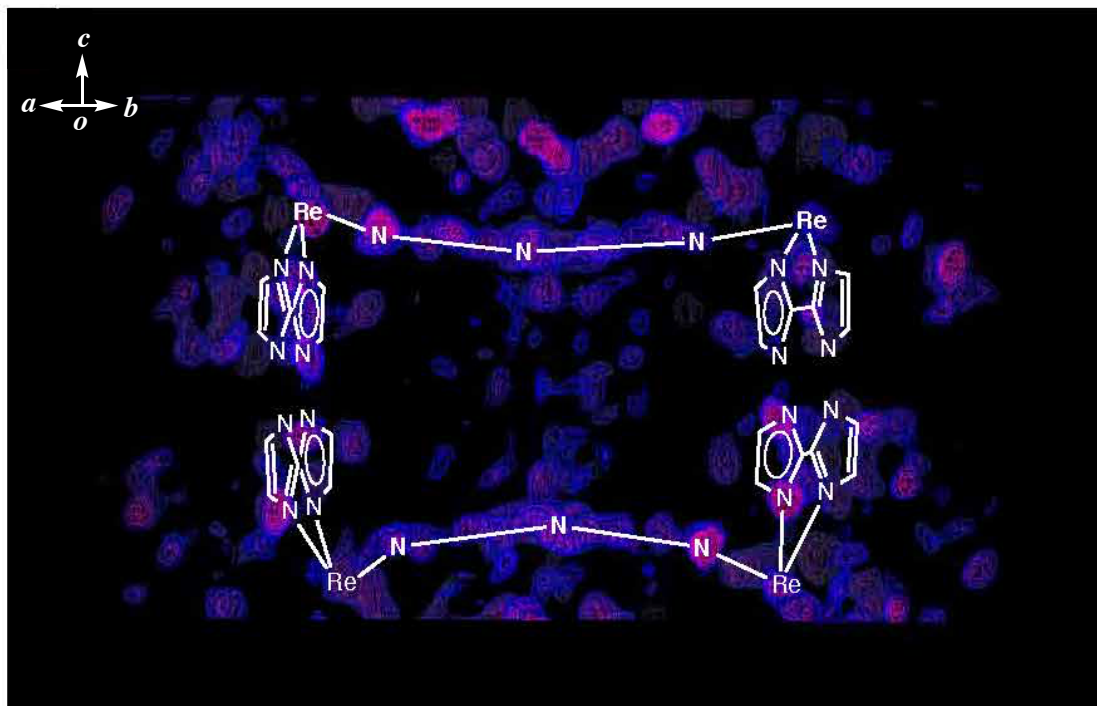
$[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim})\}_3(\text{tpta})]_2$  (**1'**)

$[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim})\}_3(\text{tpta})]_2$  (**1**) (0.20 g, 0.06 mmol) were heavily ground by a agate mortar for 40 min. The ground crystals were changed at the slightly red color. The XRD pattern was shown to be an amorphous state of **1'**. IR (KBr/cm<sup>-1</sup>): 3128, 2026, 1895, 1616, 1577, 1523, 1375, 1221, 1140, 1060, 808, 758, 702, 648, 555, Anal. Calcd for  $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})]_2$  ( $\text{Re}_6\text{C}_{126}\text{H}_{84}\text{N}_{46}\text{O}_{18}$ ): C, 35.50%, H, 1.79%, N, 16.56%, Found: C, 35.50%, H, 1.12%, N, 16.14%, ESI-mass (MeCN):  $m/z = 3045$  ( $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{bim})\}_3(\text{tpta})]_2^+$ )

**Crystal structure of**  $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim})\}_3(\text{tpta})]_2$  (**1**):  $\text{C}_{114}\text{H}_{102}\text{N}_{36}\text{O}_{18}\text{Cl}_{24}\text{Re}_6$ ,  $M = 4232.32$ , *Trigonal*, space group  $R\bar{3}c$  (#167),  $T = 173$  K,  $a = 16.902(2)$  Å,  $b = 16.902(2)$  Å,  $c = 83.022(10)$  Å,  $V = 20539(6)$  Å<sup>3</sup>,  $Z = 6$ ,  $F(000) = 24480$ ,  $D_{\text{calc}} = 2.053$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 58.29$  cm<sup>-1</sup>, radiation = 0.71073 Å,  $R_1 = 0.0744$  for  $I > 2.0\sigma(I)$ ,  $wR_2 = 0.2211$  for all data (4038 reflections  $2\theta < 50.05^\circ$ ), GOF = 1.173 (262 parameters). The maximum and minimum peaks in the final differential map were 2.137 and  $-1.706$  e<sup>-</sup>/Å<sup>3</sup>, respectively.

The SQUEEZE program was used to treat highly disordered solvent molecules in the channels of this crystal ( $R_1 = 0.0659$  for  $I > 2.0\sigma(I)$ ,  $wR_2 = 0.1816$ , GOF = 1.115). The maximum and minimum peaks in the final differential map were 2.043 and  $-1.755$  e<sup>-</sup>/Å<sup>3</sup>, respectively.

Diffraction data for crystals **1** were measured on a Brüker APEX CCD-detector X-ray diffractometer with monochromatized Mo K $\alpha$  radiation from a rotating anode source apparatus. Data reduction, structure solution and refinement, and all the necessary computational data processes were carried out using the APEX, SAINT, and SHELXTL programs<sup>40</sup>. All H atoms were fixed onto the coordinates and refined with isotropic temperature factors during calculation of the X-ray structures. Crystallographic data, excluding the structure data, have been deposited with the Cambridge Crystallographic Data Centre (CCDC), in the form of supplementary publication numbers CCDC 2047520 of **1**. A copy of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Direct Line: +44 1223 762910, Fax: +44 (0) 1223-336033, or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].



**Figure S1.**

Electron density in the nano-porous space of  $[\{\text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim})\}_3(\text{tapa})]_2$  (1). The six confined  $(\text{CH}_2\text{Cl})_2$  appear fuzzy and are not captured in this space. Accordingly, the electron densities of six  $(\text{CH}_2\text{Cl})_2$  cannot almost observe in the space.

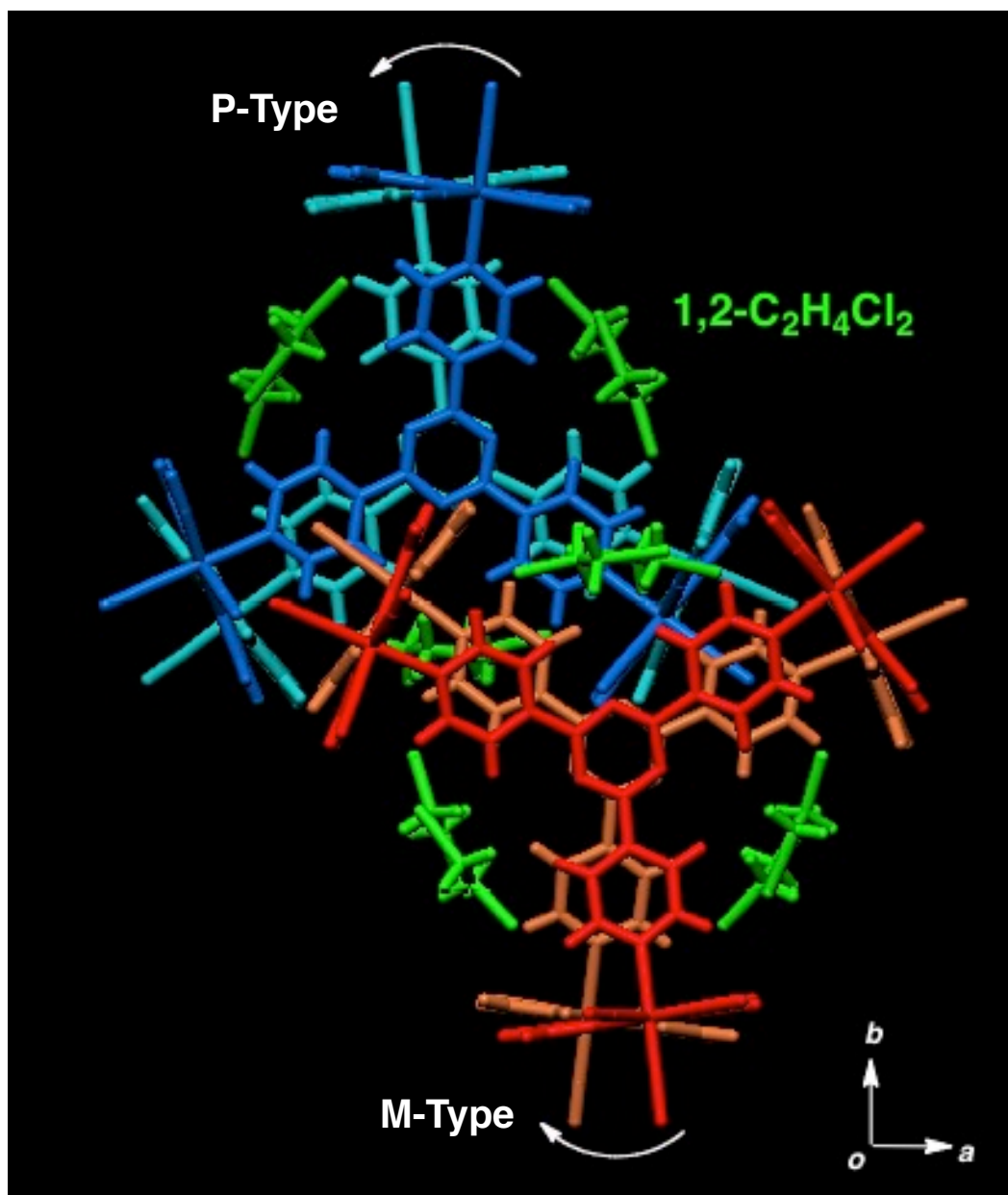


Figure S2.

View of the crystal structure of 1 along the  $c$  axis, showing the two chiral forms:  $P$ -type (coloured in blue and cyan) and  $M$ -type (red and orange). Green: six  $(\text{CH}_2\text{Cl})_2$  molecules that are not confined in the cavity.

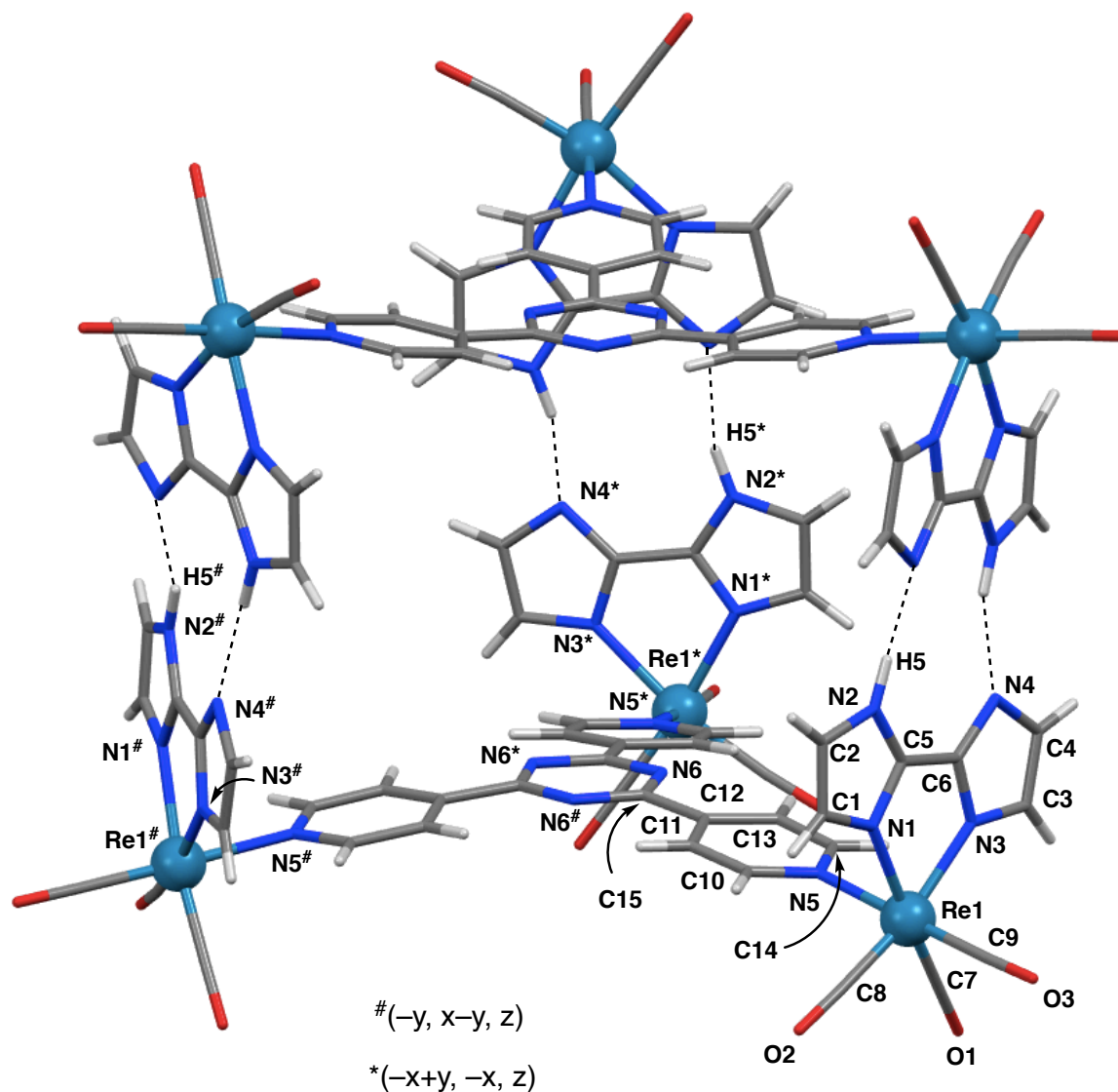
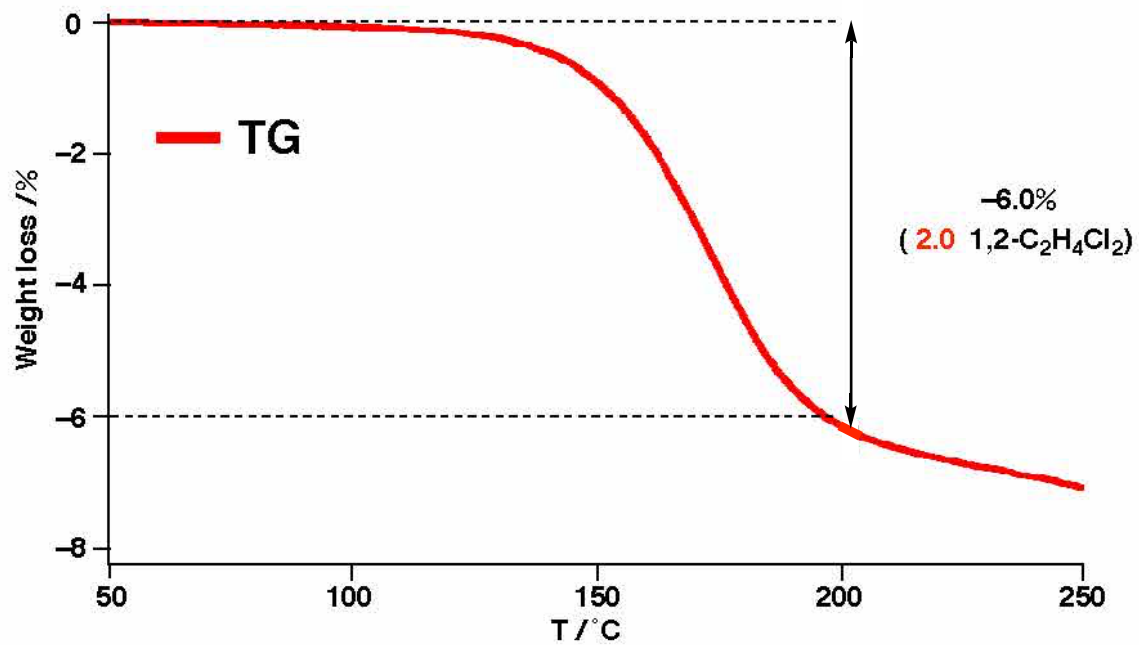


Figure S3.

Molecular structure of  $[\{\text{Re}(\text{CO})_3(\text{Hbim})\}_3(\text{tapa})]_2$  (1) with the atom numbering scheme.



**Figure 4S.**

TG data for the crystals of 1 after drying in vacuo at 25 °C for 12 h. The loss of two (CH<sub>2</sub>Cl)<sub>2</sub> was observed until 200 °C.

(a): after vacuum drying sample at 25 °C of 1

(b): crystalline compounds of 1

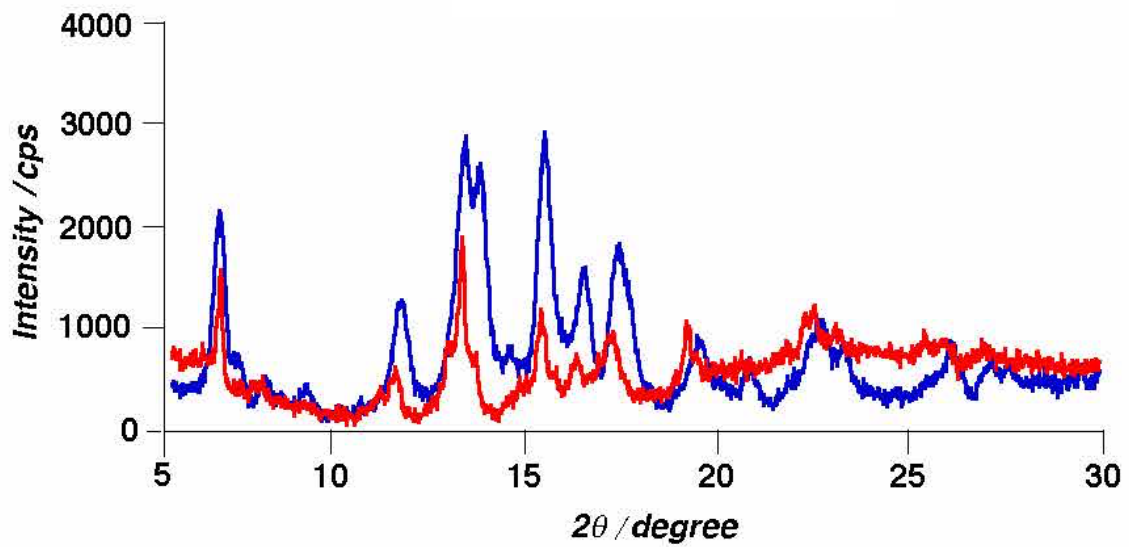
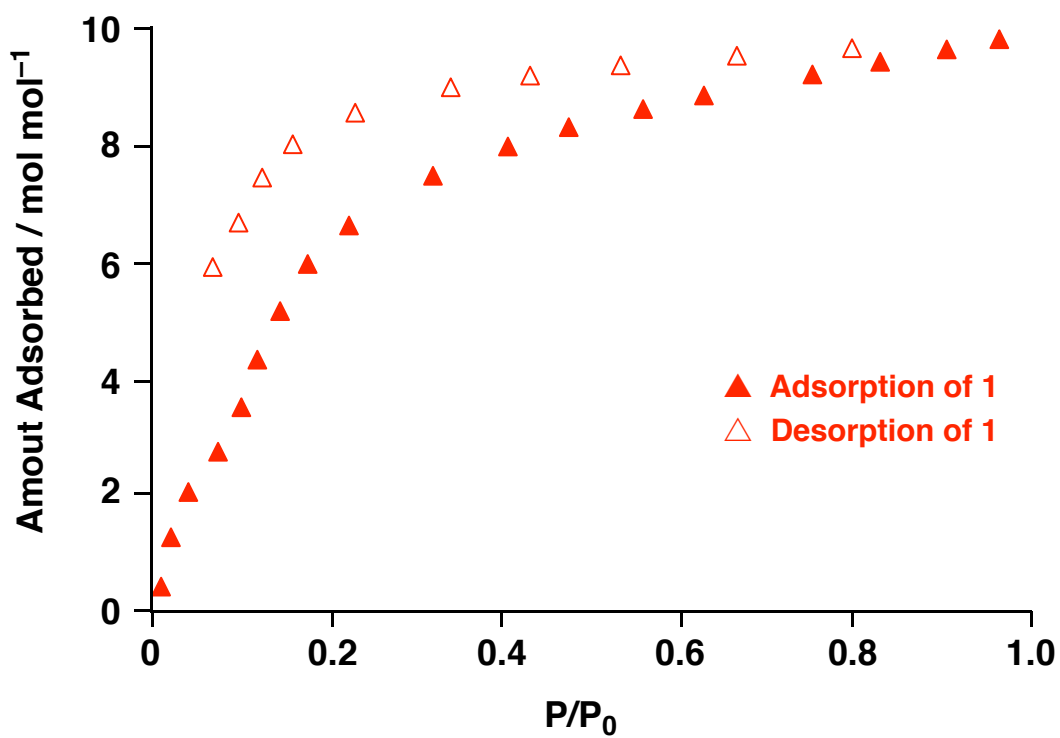


Figure S5.

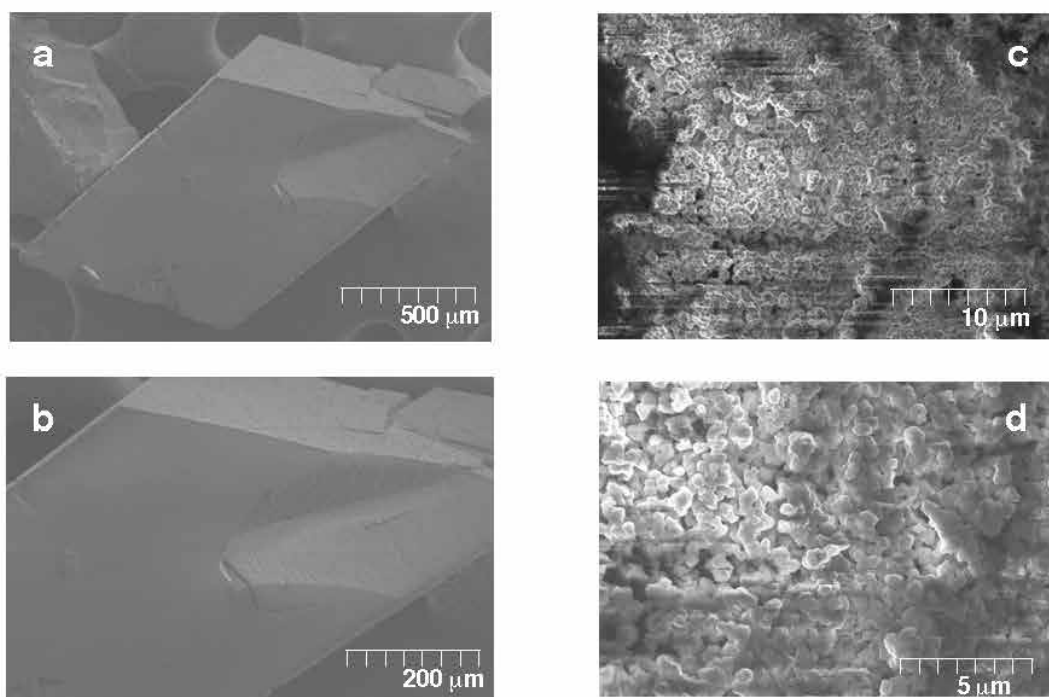
XRD patterns of (a) sample of 1 after vacuum drying at 25 °C and (b) the corresponding crystalline sample before drying.





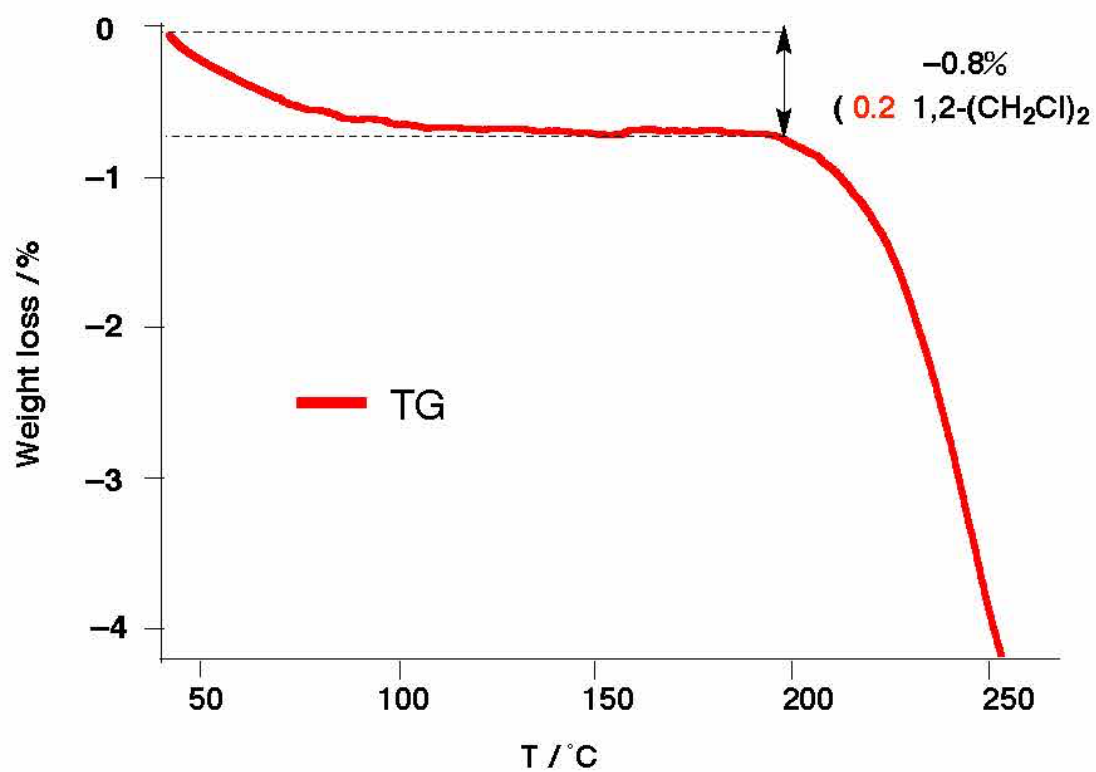
**Figure S6.**

**Adsorption and desorption of (CH<sub>2</sub>Cl)<sub>2</sub> in crystals of 1 after vacuum-drying at 25 °C. The saturated (CH<sub>2</sub>Cl)<sub>2</sub> adsorption is 10 mol/mol.**



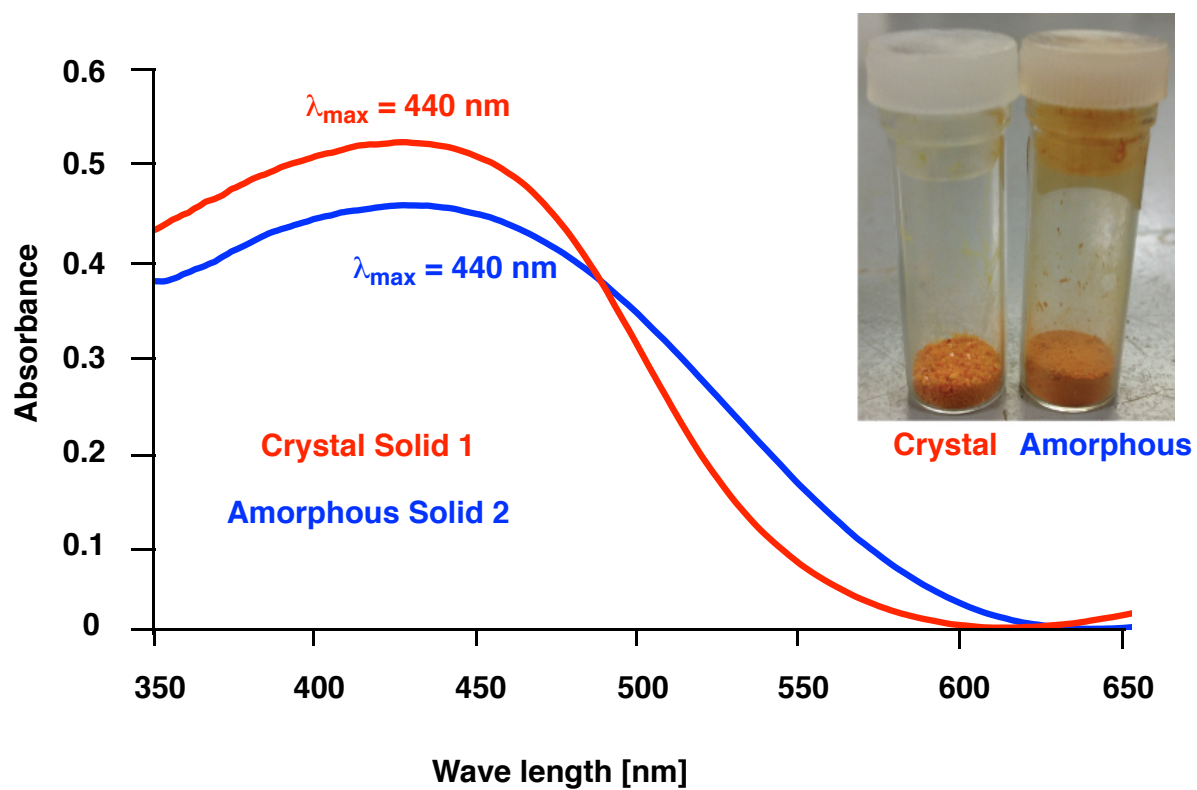
**Figure S7.**

**SEM images of (a, b) the crystal form of 1, and (c, d) the powdered form after grinding by a mortar for 40 min. XRD pattern of the ground sample shows a certain amount of the amorphous state.**



**Figure S8.**

TG results for the amorphous solid of 1, which included almost no (CH<sub>2</sub>Cl)<sub>2</sub>.



**Figure S9.**

Solid state reflection absorption spectra for the crystal of 1 (red) and the amorphous solid obtained by grinding 1 by a mortar for 40 min (blue).

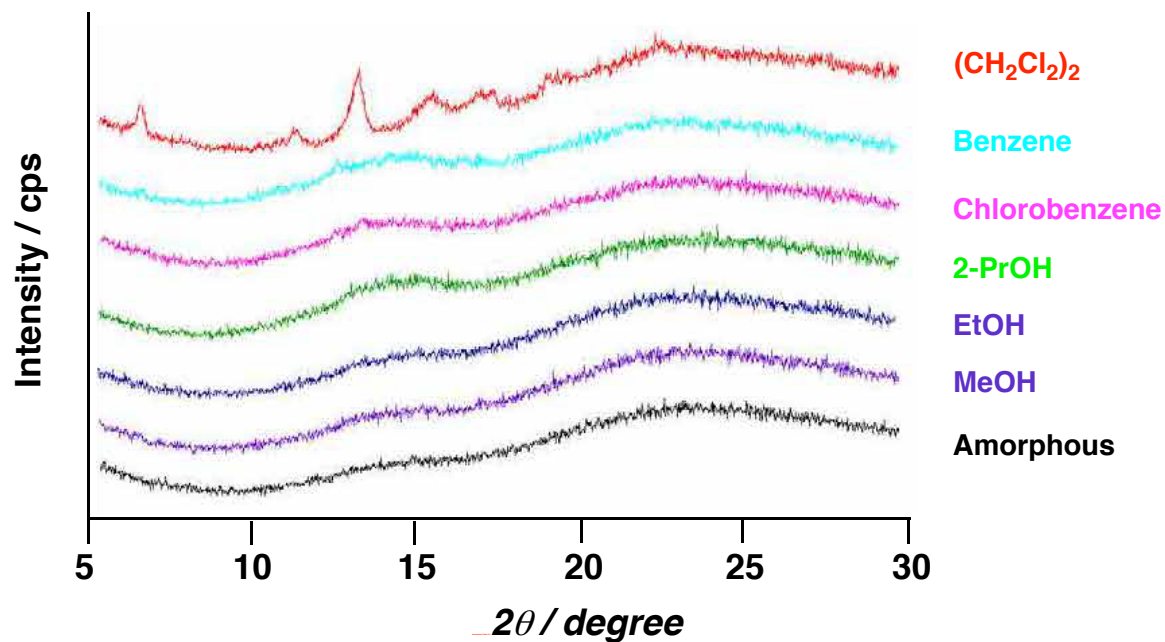


Figure S10.

XRD patterns for the amorphous solid of 1 after 3-day exposure to the vapour of different organic solvents: (CH<sub>2</sub>Cl)<sub>2</sub>, benzene, chlorobenzene, 2-PrOH, EtOH, and MeOH. The XRD pattern of the sample prior to vapour exposure is also shown.

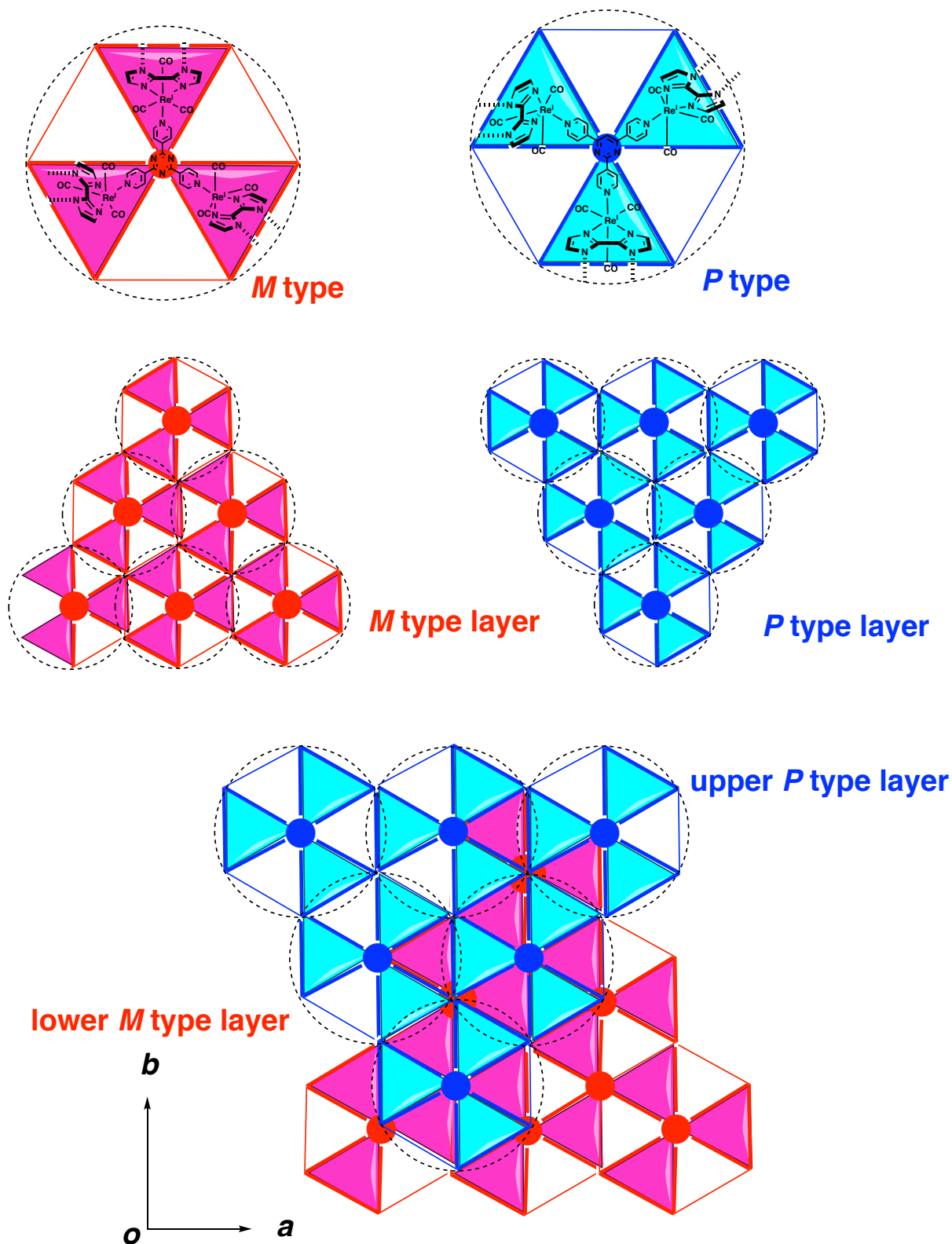


Figure S11.

The schematic representations of the crystal structure for *P* type and *M* type isomers: The *P* type and *M* type isomers are separated to the alternative 2-D sheet structures along the *ab* plane. The sheets of the *P* type and *M* type isomers stack along the *c* axis.

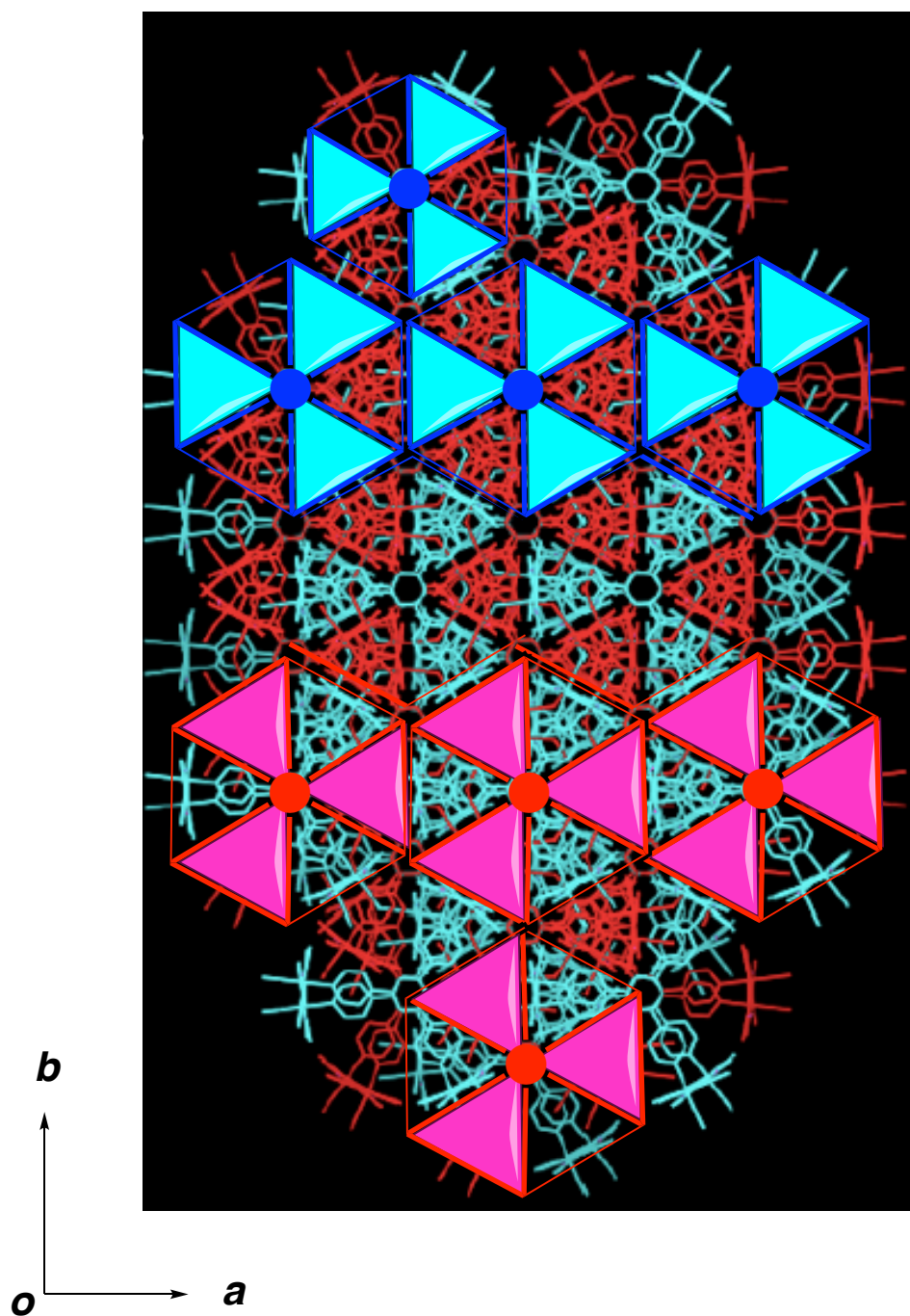
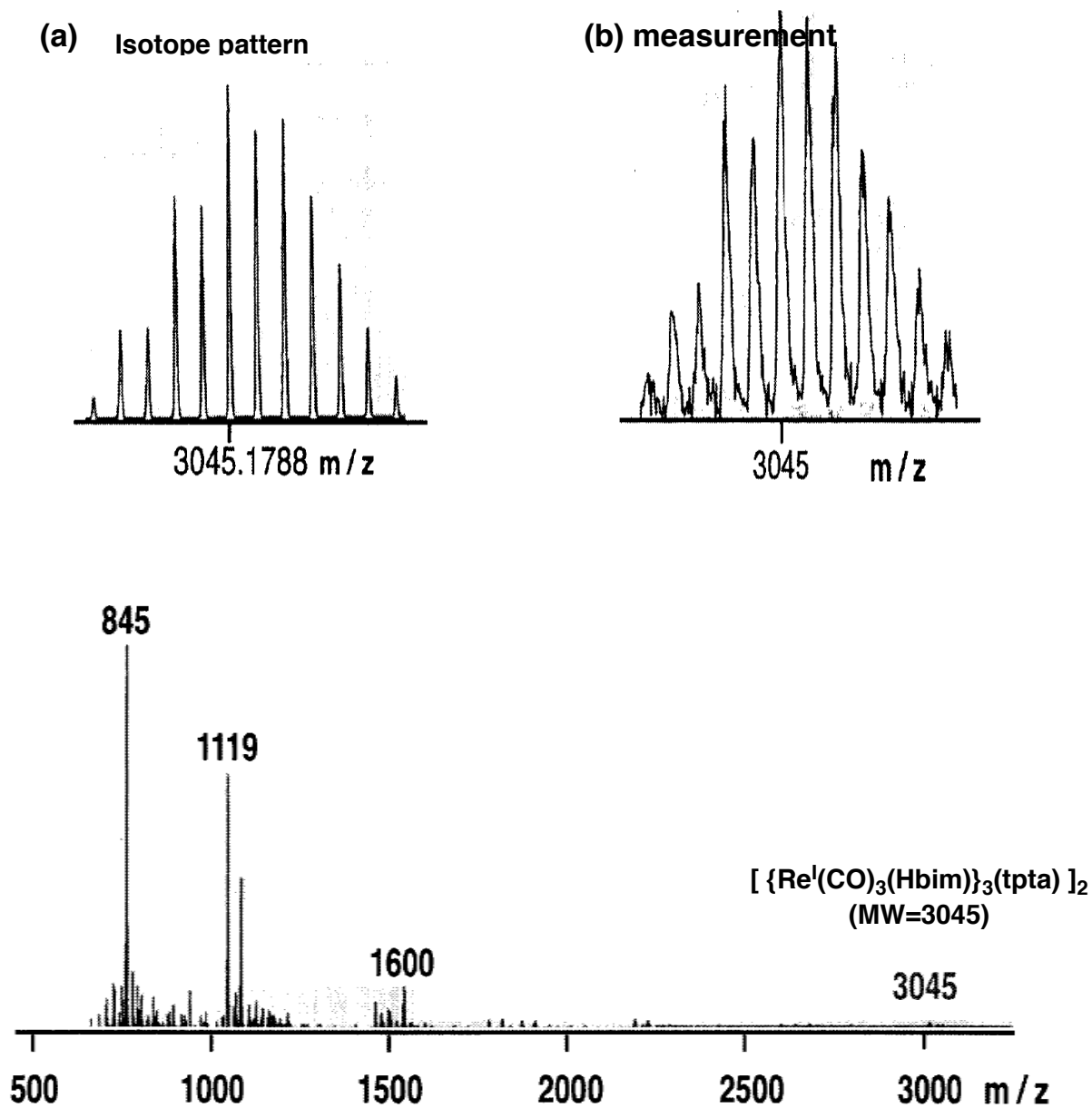


Figure S12

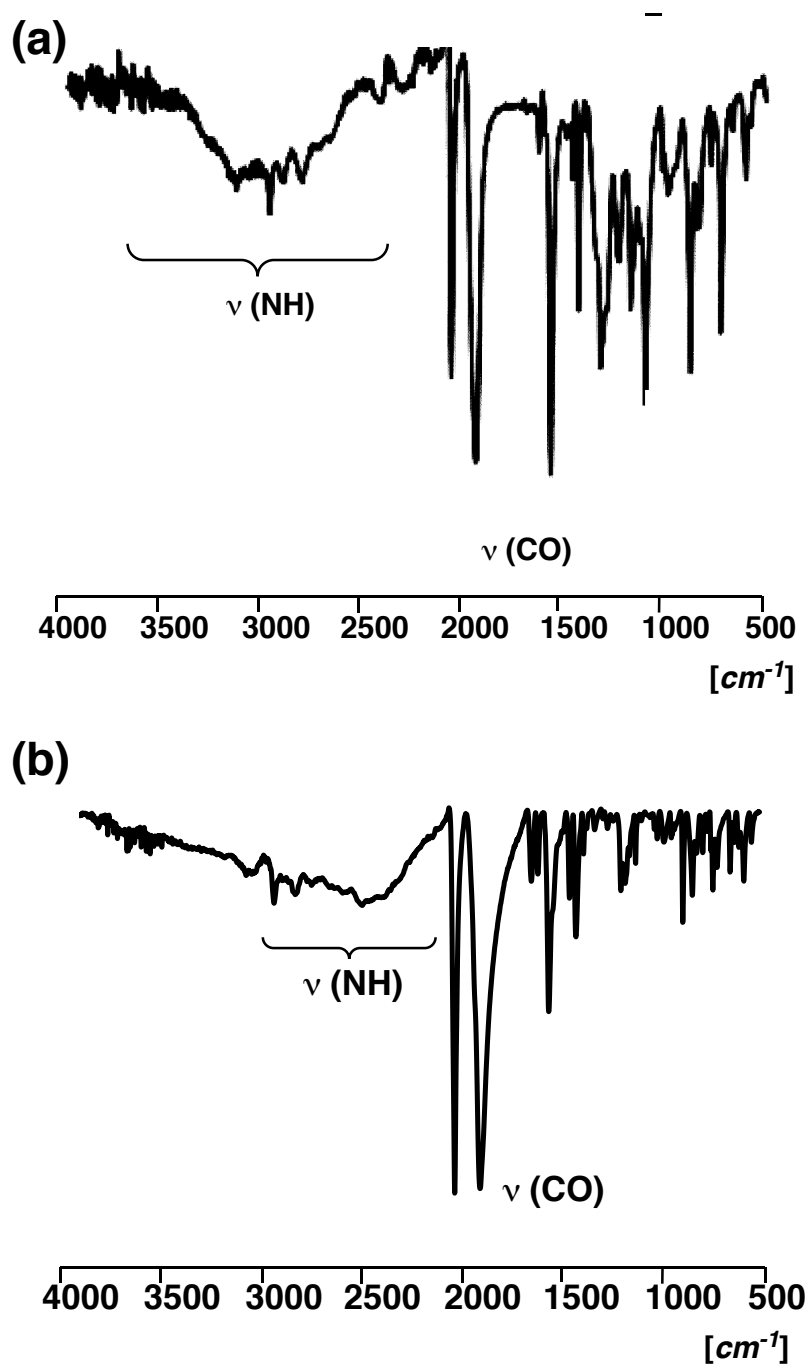
Schematic representation of stacking structure of 1 along the c axis. The 2-D sheet structures are shown in 2-D arrangements of the hexagonal tessellation of only the *P* or *M* type isomers along the ab plane



**Figure S13**

ESI-mass spectrum of  $[ \{ \text{Re}^{\text{I}}(\text{CO})_3(\text{Hbim}) \}_3(\text{tpta}) ]_2$  (a) a calculated isotope pattern, (b) a spectrum pattern of ESI (in MeCN)





**Figure S14**

IR spectra of the protonated trinuclear Re complex of 1 and the deprotonated hexanuclear Re one of 2: The hydrogen bonding regions of  $n(\text{NH})$  are changed around 3000  $\text{cm}^{-1}$  and 2500  $\text{cm}^{-1}$ , respectively.