

Supplementary Information

Reversible uptake of HgCl₂ in a porous coordination polymer based on the dual functions of carboxylate and thioether

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Experimental details

General Procedure.

Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich) and used without further purification. Elemental analysis was performed by a Vario EL III CHN elemental analyzer. FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. The metal ions ratios were measured using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer. Thermal analysis (TG) was carried out in a nitrogen stream using WRT-2P Thermal analysis equipment with a heating rate of 5 °C min⁻¹. X-ray powder diffraction patterns of the bulk samples (the powder samples were spread onto a glass slides for data collection) were collected at room temperature on a Siemens D500 powder diffractometer (Cu K α , $\lambda = 1.5418 \text{ \AA}$).

Single crystal XRD analyses (data collection, structure solution and refinement) were conducted on a Bruker AXS SMART APEX CCD system using Mo K α ($\lambda=0.71073 \text{ \AA}$) radiation at 100(2) K. All absorption corrections were performed using the SADABS program. The structures were solved and refined by full-matrix least-squares on Fo2 using SHELXL 6.14 (Bruker AXS Inc., Madison, Wisconsin: USA, 2003). The treatment for the HgCl₂ components in the HgCl₂-loaded crystal of Pb(TMBD)·HgCl₂ involves the use of the SQUEEZE program. The HgCl₂ parts of the structure were found to be

severely disordered and refinement attempts under inclusion of the HgCl₂ component were not successful. Hg and Cl atoms were disordered over each one to three or more positions with anisotropic displacement parameters that indicated correlation between the disordered moieties and/or additional dynamic disorder of the atom. Possible presence of solvent molecules in addition to Hg and Cl atoms can not be excluded as a possibility. Any atoms in the voids were thus omitted from the structural model and only the host net Pb(TMBD) was refined. Due to the large residual electron density some restraints were applied in this model for methyl carbon atom position and some anisotropic displacement parameters, ADPs. This model was then used as the starting point for a dataset corrected for the residual electron density using the SQUEEZE procedure implemented in the program Platon (40M-version 180209, A. L. Spek, 1980-2009). The residual electron density per void was 658 electrons (or 5.77 molecules of HgCl₂ per void). Each of the two voids per unit cell void is about 839 Å³ large or 14% of the unit cell volume. The structure was then re-refined, the restraints applied before could now be omitted, and the SQUEEZE procedure was then repeated using this improved structural model with the original hkl file. This slightly more reliable new hkl file was then used for the final refinement cycles to obtain the final structural model and the cif file corrected for the electron density of the ill defined HgCl₂ molecules in the voids.

From the squeeze file we obtain the following data:

```
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 0.500 0.000 0.047 839 658 ''
2 0.000 0.500 -0.014 839 658 ''
```

Such dense electron count is beyond the account of the solvent molecules, and strongly points to the presence of much heavier elements (i.e., HgCl₂).

Finally, a refinement was made with zero cycles with the new res file and the old uncorrected hkl file, in order to generate a difference res file, and to better assess the residual electron density peaks from the HgCl₂ components. The difference res file is included as part of the ESI. The following major residual electron density peaks (larger than 10 electrons per Å³, thus larger than could be caused by atoms of the solvents used) were obtained:

```
Q1  1  0.745800  0.000000 -0.011900 10.500000  0.050000  48.92
Q2  1  0.936300  0.500000  0.259900 10.500000  0.050000  22.48
Q3  1  0.733300  0.000000  0.092000 10.500000  0.050000  12.54
Q4  1  0.849600  0.452200  0.754400 11.000000  0.050000  12.14
Q5  1  0.862300  0.417500  0.694100 11.000000  0.050000  10.33
```

In Fig. S4, the structural information obtained from the difference res file is presented with the major Q peaks included.

Synthesis of the TMBD ligand. This is based on a reported method (*Inorg. Chem.*, 2008, **47**, 7459)

Preparation of guest-free samples of 1: Guest-free samples of **1** were obtained by heating the as-synthesized crystals **1** at 200 °C under a vacuum created by a mechanical pump for five hours. Chemical analysis of the product yields the following: calcd for $C_{12}H_{12}O_4PbS_4$, corresponding to Pb(TMBD): [C (25.94%), H (2.18%)]; found [C (25.83), H (2.50%)]. IR (ν/cm^{-1}): 2984w, 2916m, 1534s, 1421s, 1299s, 1096w, 974m, 852w, 800w, 700w, 606m. See also the IR spectra below.

Sorption of HgCl₂. A mixture of evacuated sample of **1** (10.0 mg), HgCl₂ (20.0 mg), and benzene solvent (1.0 mL) was sealed in a Pyrex glass tube, heated in an oven at 100 °C for 48 h, and then cooled to room temperature over 12 hrs. The impregnated product was obtained by filtration and washing with THF three times (14.5 mg, yield 97.4%). Chemical analysis of the product $C_{12}H_{12}Cl_2HgO_4PbS_4$, corresponding to Pb(TMBD)·HgCl₂, yields the following: calcd [C (17.42%), H (1.46%)], found: [C (17.57), H (1.71%)]. The sample of Pb(TMBD)·HgCl₂ was also dissolved in the concentrated HNO₃ by heating at 80 °C, and the ensuing ICP elemental analysis yielded a Hg/Pb molar ratio of 1.06. The HgCl₂ was depleted from the host framework by the following procedure: a mixture of Pb(TMBD)·HgCl₂ (10.0 mg) and acetonitrile (2.0 mL) in a sealed small vial was heated at 60 °C for 3 days and cooled to room temperature. The product was filtrated and washed with fresh acetonitrile and then dried in air overnight. Chemical analysis of the product $C_{12}H_{14}Cl_{0.42}Hg_{0.21}O_5PbS_4$, corresponding to Pb(TMBD)·0.21HgCl₂·H₂O, yields the following: calcd [C (22.85%), H (2.24%)], found: [C (22.75), H (2.36%)]. ICP elemental analysis yields an Hg/Pb molar ratio of 0.21.

Preparation of MOF-5 samples and treatment with HgCl₂. The samples of MOF-5 and activated MOF-5 were synthesized and prepared according to the literature (*Science*, 2002, **295**, 469). The procedure for treating the activated MOF-5 with HgCl₂ is same as that for the preparation of Pb(TMBD)·HgCl₂. ICP elemental analysis yields a molar ratio Zn/Hg = 658:1, indicating minimal absorption of the Hg species by the MOF-5 sample.

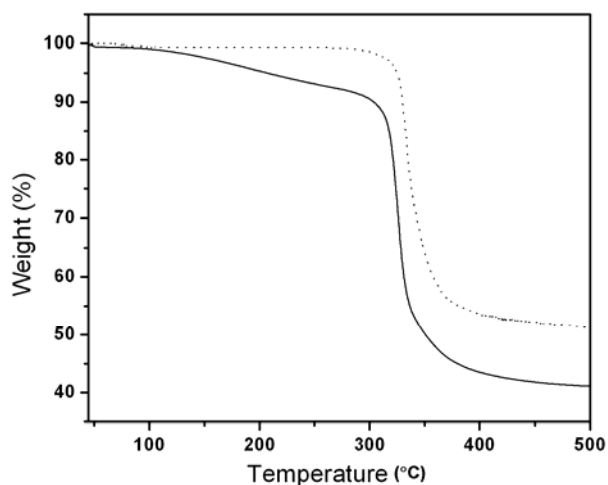


Fig. S1 Thermogravimetric analysis (TGA) plots for an as-made solid sample of **1** (solid line), and a guest-free sample of **1** (dotted line). The guest-free sample was generated by heating the as-made sample at 200 °C in vacuo.

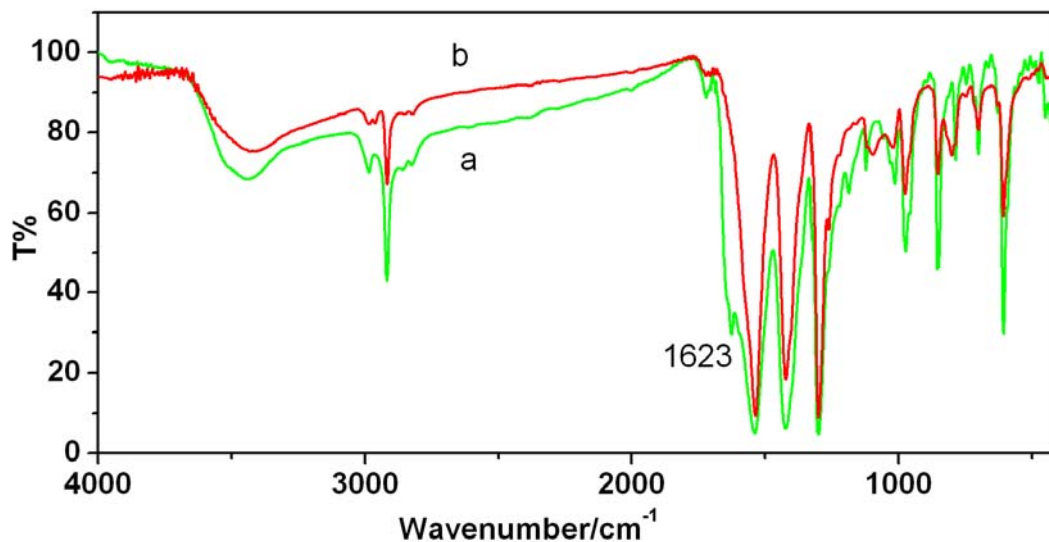


Fig. S2 The IR spectra of (a) an as-made sample of **1**, $(\text{Pb}_3(\text{TMBD})_3 \cdot 2\text{DMA} \cdot 0.79\text{H}_2\text{O})$, and (b) a guest-free sample, $\text{Pb}(\text{TMBD})$. The 1623 peak in spectrum (a) arises from the C=O stretching of the DMA guests. This peak is absent in spectrum b. The guest-free sample was generated by heating the as-made sample at 200 °C in vacuo.

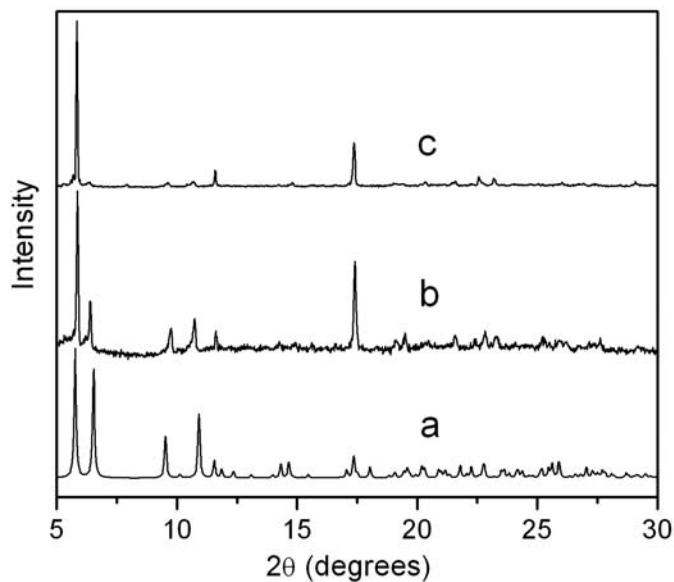


Fig. S3 X-ray powder patterns ($\text{Cu K}\alpha$, $\lambda=1.5418 \text{ \AA}$) of **1**. (a) Calculated pattern from the single crystal structure of **1** (data collected at 100 K); (b) observed from an as-synthesized sample of **1** at 298 K; (c) observed from a guest-free sample of **1** at 298 K. The guest-free sample was generated by heating the as-made sample at 200 °C in vacuo.

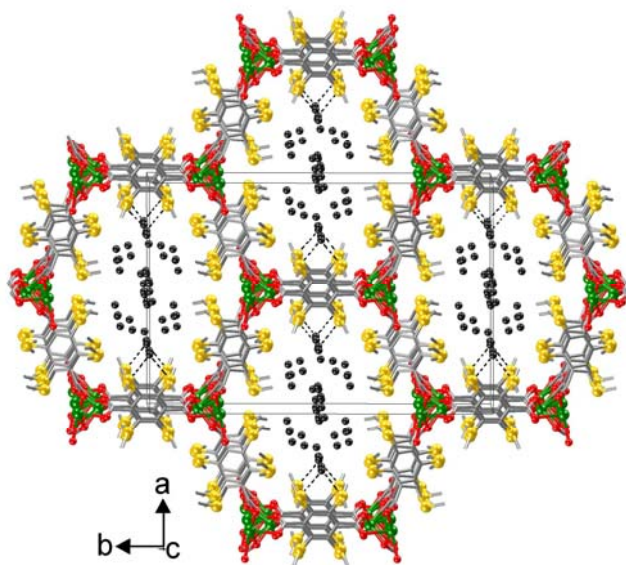


Fig. S4 View of the PbTMBD network of $\text{Pb}(\text{TMBD})\cdot\text{HgCl}_2$ along the channel direction, with major residual electron density peaks (Q peaks, $48.92\text{-}5.03\text{ e}/\text{\AA}^3$) included as black spheres. The dotted line features a distance of 2.685 \AA between the first Q peak ($48.92\text{ e}/\text{\AA}^3$) and two sulfur atoms from the host net. Green spheres, Pb; red spheres, O; yellow spheres, S.

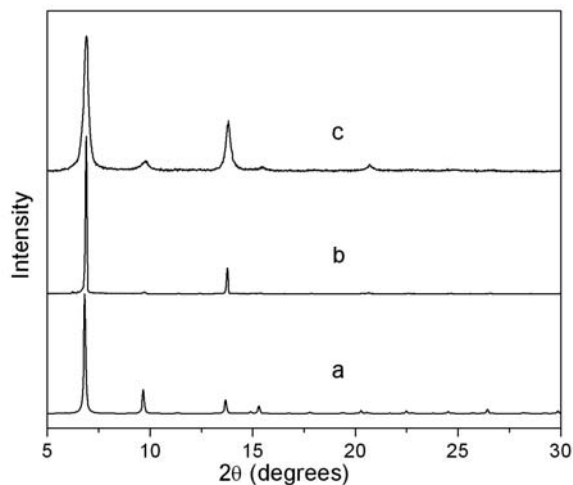


Fig. S5 X-ray diffraction patterns ($\text{Cu K}\alpha$, $\lambda=1.5418$) of MOF-5: (a) calculated from the single-crystal structure with random orientation of crystallites observed for a powder solid sample of MOF-5; (b) observed for a powder solid sample of activated MOF-5; (c) observed for a powder solid sample after treating with HgCl_2 .



Fig. S6 Photographs of single crystals of as-made **1** (left; size: $0.19 \times 0.06 \times 0.05 \text{ mm}^3$) and an HgCl_2 -loaded sample of $\text{PbTMBD} \cdot \text{HgCl}_2$ (right; size: $0.27 \times 0.11 \times 0.09 \text{ mm}^3$).