

# Solvent diffusion and binding in a 'nonporous' molecular crystal

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## 1. Materials and Methods

X-ray powder diffraction experiments were carried out on a Bruker D8 Advance instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a point detector. Thermogravimetric analysis was carried out using a TA Instruments Q500 thermogravimetric analyser. The balance and sample were purged with dry N $_2$  gas flowing at rates of 50 and 70 cm $^3$ .min $^{-1}$ . Samples were heated at a rate of either 5 or 10 °C.min $^{-1}$ .

## 2. Synthesis

### [Cd $_2$ L $_2$ Br $_4$ ] $\cdot$ 2MeOH (**2** $\cdot$ **2MeOH**)

0.02 mmol L (6.85 mg) were dissolved in 3 ml chloroform and layered with a 4 ml buffer layer followed by 0.02 mmol CdBr $_2$  $\cdot$ 4H $_2$ O (6.9 mg) dissolved in 3 ml methanol. After 4 days, colourless plates were afforded and the structure was elucidated by single-crystal diffraction.

### [Cd $_2$ L $_2$ I $_4$ ] $\cdot$ CH $_2$ Cl $_2$ (**3** $\cdot$ **CH $_2$ Cl $_2$** )

0.02 mmol L (6.85 mg) were dissolved in 3 ml dichloromethane and layered with 0.02 mmol CdI $_2$  (7.32 mg) dissolved in 3 ml acetonitrile. After 10 days colourless plates had grown and these were suitable for single-crystal diffraction studies.

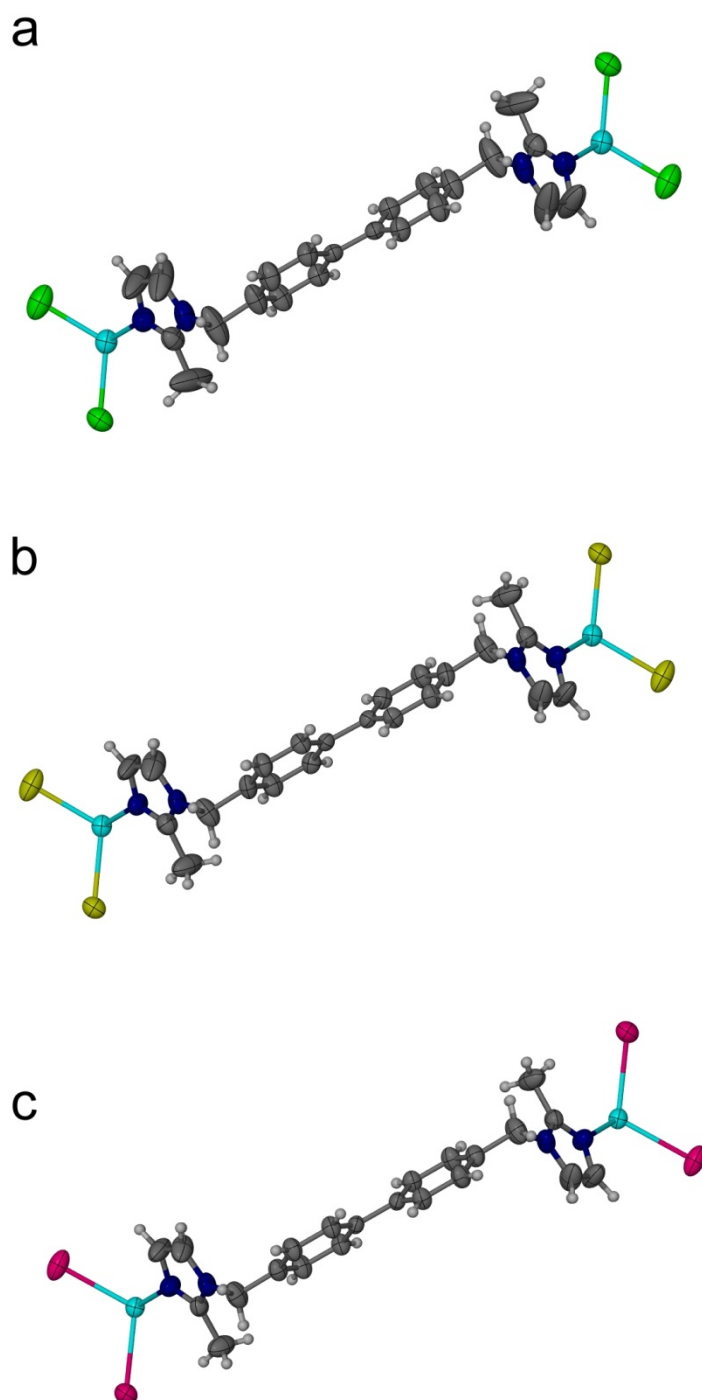
### [Cd $_2$ L $_2$ I $_4$ ] $\cdot$ CH $_3$ Cl (**3** $\cdot$ **CHCl $_3$** )

0.02 mmol L (6.85 mg) were dissolved in 3 ml chloroform and layered with 0.02 mmol CdI $_2$  (7.32 mg) dissolved in 3 ml methanol. After a month, colourless plates were afforded and the structure was elucidated by single-crystal diffraction.

## 3. Single-Crystal X-ray Diffraction

Intensity data were collected on a Bruker SMART Apex CCD diffractometer<sup>1</sup> using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The temperature of the crystals was controlled using an Oxford Cryostream Cooler. Data reduction was carried out by means of a standard procedure using the APEX II software. Where necessary, systematic errors in the intensity data were corrected for using SADABS. The structures were solved by direct

methods using SHELXS-97.<sup>2</sup> All atoms were located by this method. All ordered non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on  $F^2$  using SHELXL-97<sup>2</sup> within the X-Seed<sup>3</sup> environment. Where appropriate, the hydrogen atoms were placed in calculated positions using riding models and assigned isotropic thermal parameters 1.2 times those of their parent atoms for CH<sub>2</sub>, aromatic C and O-H groups, or 1.5 times those of their parent atoms for CH<sub>3</sub> groups. In special cases, hydrogen atoms were located in difference electron density maps and their isotropic thermal parameters were refined freely. Molecular graphics were produced using the program POV-Ray.<sup>4</sup>



**Fig. S1** Atomic displacement (50% probability) plot of a) **1**, b) **2** and c) **3** using intensity data collected with the crystal under vacuum at 293 K. The projection is along [010] and provide a clue to the mechanism of gas transport through the seemingly nonporous material. The

imidazole moieties seem to experience a relatively high degree of motion, as does the halide ion guarding a potential channel that might momentarily form between two neighbouring voids. Overall, it seems that the methylene groups serve as joints that enable the imidazole groups to pivot in order to allow solvent diffusion from one void to the next.<sup>5</sup>

Crystal data for **1·CS<sub>2</sub>**: C<sub>44.87</sub>H<sub>44</sub>Cd<sub>2</sub>Cl<sub>4</sub>N<sub>8</sub>S<sub>1.74</sub>, *M* = 1117.71, colourless block, 0.27 × 0.18 × 0.15 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 17.790(2), *b* = 15.5454(17), *c* = 9.3054(10) Å, *β* = 114.886(2)°, *V* = 2334.5(4) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.590 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1122.2, Bruker APEX CCD area-detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 100(2)K, 2 $\theta$ <sub>max</sub> = 55.0°, 7314 reflections collected, 2737 unique (*R*<sub>int</sub> = 0.0174). Final *Goof* = 1.105, *RI* = 0.0427, *wR2* = 0.1063, *R* indices based on 2606 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 147 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu$  = 1.259 mm<sup>-1</sup>.

Crystal data for **2·2MeOH**: C<sub>46</sub>H<sub>52</sub>Br<sub>4</sub>Cd<sub>2</sub>N<sub>8</sub>O<sub>2</sub>, *M* = 1293.40, colourless prism, 0.28 × 0.21 × 0.18 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 17.179(2), *b* = 15.8014(19), *c* = 9.6965(11) Å, *β* = 114.179(2)°, *V* = 2401.3(5) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.789 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1272, Bruker APEX CCD area-detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 100(2)K, 2 $\theta$ <sub>max</sub> = 56.6°, 7519 reflections collected, 2861 unique (*R*<sub>int</sub> = 0.0239). Final *Goof* = 1.040, *RI* = 0.0331, *wR2* = 0.0815, *R* indices based on 2549 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 151 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu$  = 4.260 mm<sup>-1</sup>.

Crystal data for **2·vac**: C<sub>44</sub>H<sub>44</sub>Br<sub>4</sub>Cd<sub>2</sub>N<sub>8</sub>, *M* = 1229.31, colourless plate, 0.20 × 0.20 × 0.08 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 18.001(3), *b* = 15.844(3), *c* = 9.3530(15) Å, *β* = 114.239(3)°, *V* = 2432.4(7) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.678 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1200, Bruker APEX CCD area-detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 295(2)K, 2 $\theta$ <sub>max</sub> = 55.0°, 7578 reflections collected, 2848 unique (*R*<sub>int</sub> = 0.0406). Final *Goof* = 0.970, *RI* = 0.0454, *wR2* = 0.0937, *R* indices based on 1743 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 137 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu$  = 4.198 mm<sup>-1</sup>.

Crystal data for **2·CS<sub>2</sub>**: C<sub>44.87</sub>H<sub>44</sub>Br<sub>4</sub>Cd<sub>2</sub>N<sub>8</sub>S<sub>1.74</sub>, *M* = 1295.77, colourless plate, 0.25 × 0.10 × 0.04 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 17.478(2), *b* = 15.809(2), *c* = 9.3913(13) Å, *β* = 114.457(2)°, *V* = 2362.1(6) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.822 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1266.2, Bruker APEX CCD area-detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 100(2)K, 2 $\theta$ <sub>max</sub> = 55.0°, 7179 reflections collected, 2749 unique (*R*<sub>int</sub> = 0.0388). Final *Goof* = 1.046, *RI* = 0.0439, *wR2* = 0.0929, *R* indices based on 2197 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 147 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu$  = 4.414 mm<sup>-1</sup>.

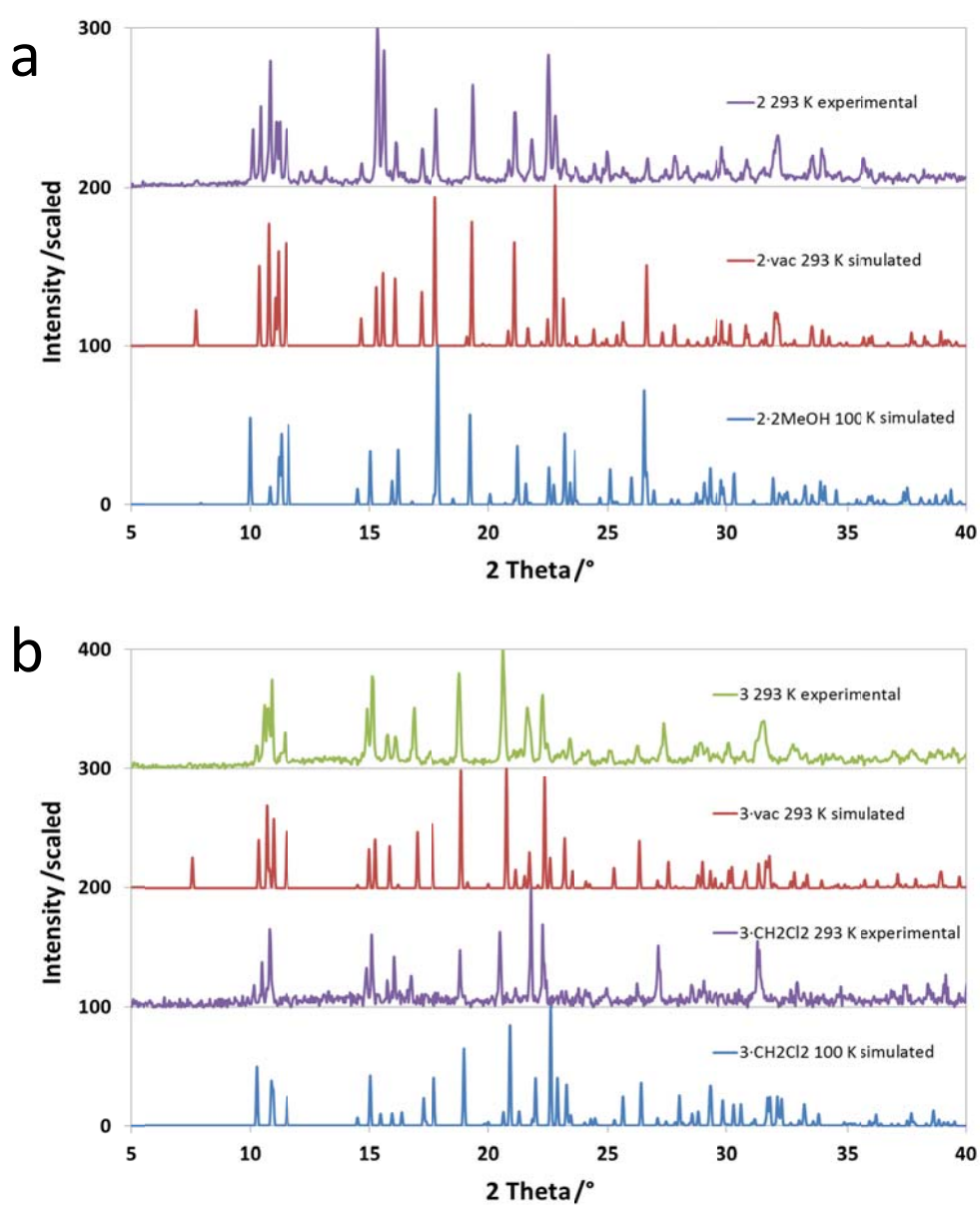
Crystal data for **3·CH<sub>2</sub>Cl<sub>2</sub>**: C<sub>45</sub>H<sub>46</sub>Cd<sub>2</sub>Cl<sub>2</sub>I<sub>4</sub>N<sub>8</sub>, *M* = 1502.20, colourless prism, 0.31 × 0.24 × 0.17 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 17.799(2), *b* = 16.188(2), *c* = 9.4162(12) Å, *β* = 113.843(2)°, *V* = 2481.6(5) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 2.010 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1428, Bruker APEX CCD area-detector, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 100(2)K, 2 $\theta$ <sub>max</sub> = 52.7°, 6979 reflections collected, 2547 unique (*R*<sub>int</sub> = 0.0219). Final *Goof* = 1.165, *RI* = 0.0311, *wR2* = 0.0674, *R* indices based on 2262 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 161 parameters, 4 restraints. Lp and absorption corrections applied,  $\mu$  = 3.493 mm<sup>-1</sup>.

Crystal data for **3·CHCl<sub>3</sub>**: C<sub>45</sub>H<sub>45</sub>Cd<sub>2</sub>Cl<sub>3</sub>I<sub>4</sub>N<sub>8</sub>, *M* = 1536.64, colourless shard, 0.23 × 0.19 × 0.10 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 18.281(3), *b* = 16.193(3), *c* = 9.2445(17) Å, β = 113.271(3)°, *V* = 2514.0(8) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 2.030 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1460, Bruker APEX CCD area-detector, MoKα radiation, λ = 0.71073 Å, *T* = 100(2)K, 2θ<sub>max</sub> = 52.7°, 7287 reflections collected, 2645 unique (*R*<sub>int</sub> = 0.0296). Final *Goof* = 1.109, *RI* = 0.0535, *wR2* = 0.1419, *R* indices based on 2353 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 158 parameters, 14 restraints. Lp and absorption corrections applied, μ = 3.502 mm<sup>-1</sup>.

Crystal data for **3·vac**: C<sub>44</sub>H<sub>44</sub>Cd<sub>2</sub>I<sub>4</sub>N<sub>8</sub>, *M* = 1417.27, colourless prism, 0.25 × 0.22 × 0.13 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 18.081(2), *b* = 16.3388(18), *c* = 9.3220(10) Å, β = 113.628(2)°, *V* = 2523.1(5) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.865 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1344, Bruker APEX CCD area-detector, MoKα radiation, λ = 0.71073 Å, *T* = 295(2)K, 2θ<sub>max</sub> = 52.7°, 7407 reflections collected, 2674 unique (*R*<sub>int</sub> = 0.0164). Final *Goof* = 1.098, *RI* = 0.0520, *wR2* = 0.1430, *R* indices based on 2348 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 137 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.327 mm<sup>-1</sup>.

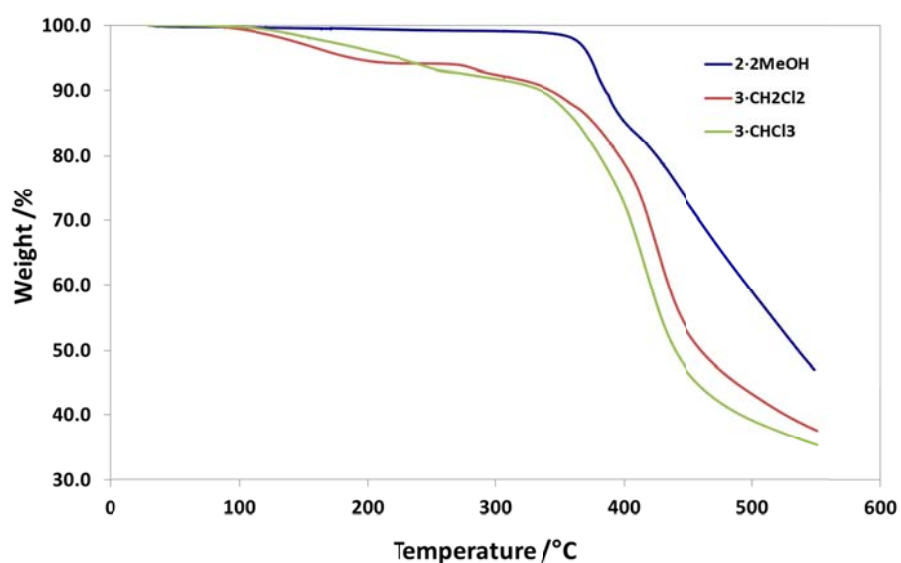
Crystal data for **3·CS<sub>2</sub>**: C<sub>44.76</sub>H<sub>44</sub>Cd<sub>2</sub>I<sub>4</sub>N<sub>8</sub>S<sub>1.52</sub>, *M* = 1474.97, colourless prism, 0.27 × 0.24 × 0.13 mm<sup>3</sup>, monoclinic, space group *C2/m* (No. 12), *a* = 17.584(3), *b* = 16.190(3), *c* = 9.4187(15) Å, β = 113.809(2)°, *V* = 2453.3(7) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.997 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1401, Bruker APEX CCD area-detector, MoKα radiation, λ = 0.71073 Å, *T* = 100(2)K, 2θ<sub>max</sub> = 52.7°, 7094 reflections collected, 2593 unique (*R*<sub>int</sub> = 0.0340). Final *Goof* = 1.347, *RI* = 0.0775, *wR2* = 0.1562, *R* indices based on 2347 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 147 parameters, 12 restraints. Lp and absorption corrections applied, μ = 3.509 mm<sup>-1</sup>.

#### 4. Powder X-Ray Diffraction



**Fig. S2** A comparison of the powder pattern of sublimed **2** used for gas sorption experiments and a pattern simulated from **2·vac·293K**.

## 5. Thermal Analysis



**Fig. S3** Thermogravimetric analysis of sublimed **2** and **2**·CO<sub>2</sub> grown from supercritical CO<sub>2</sub>.

## 6. References

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