



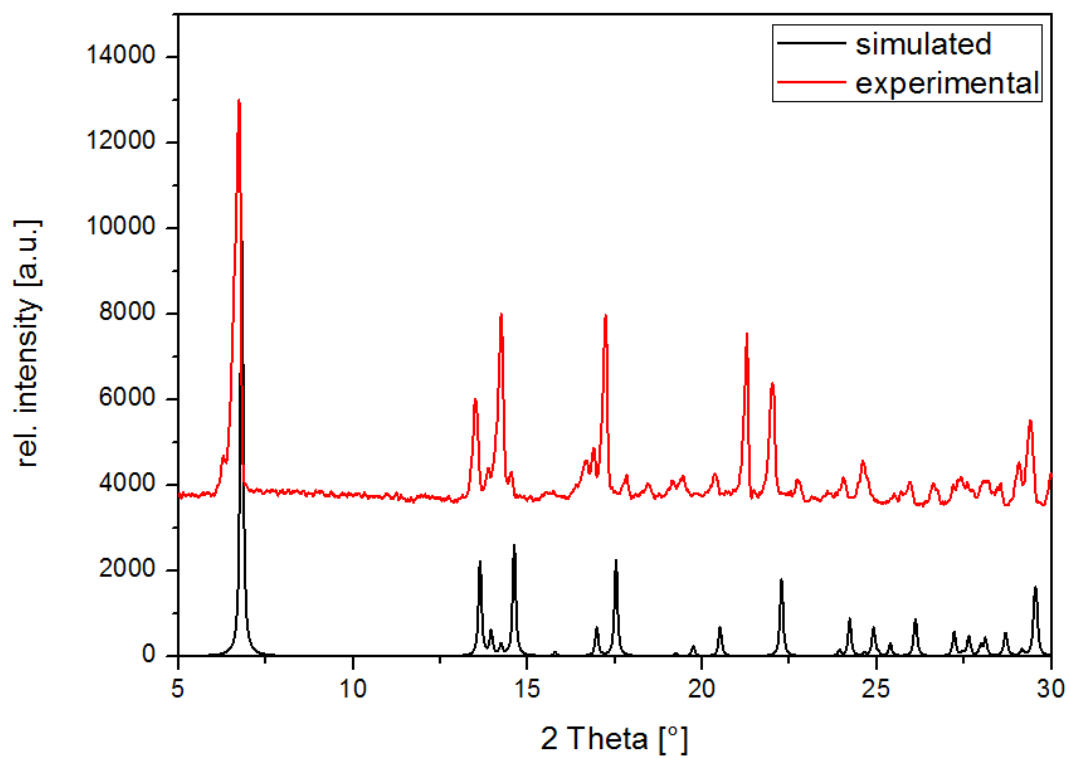
STRUCTURAL SCIENCE  
CRYSTAL ENGINEERING  
MATERIALS

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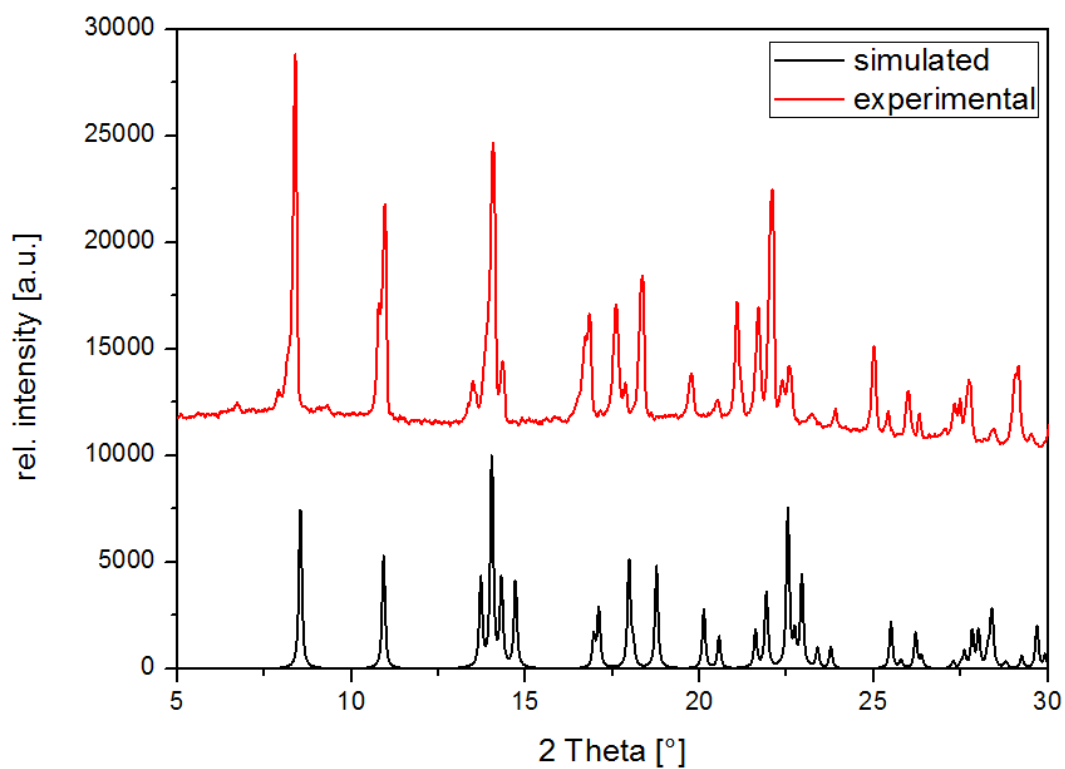
**Supporting information for article:**

**3-(Pyridin-4-yl)acetylacetonate: a donor ligand towards mercury(II) halides and a versatile linker for complex materials**

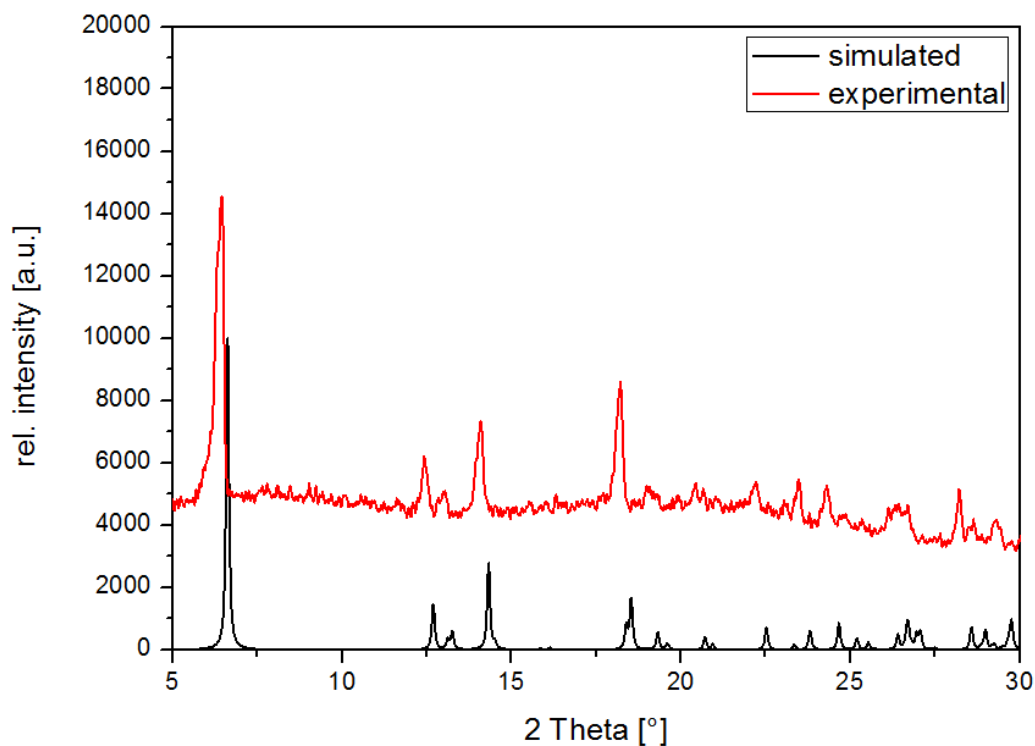
**Khai-Nghi Truong, Carina Merckens and Ulli Englert**



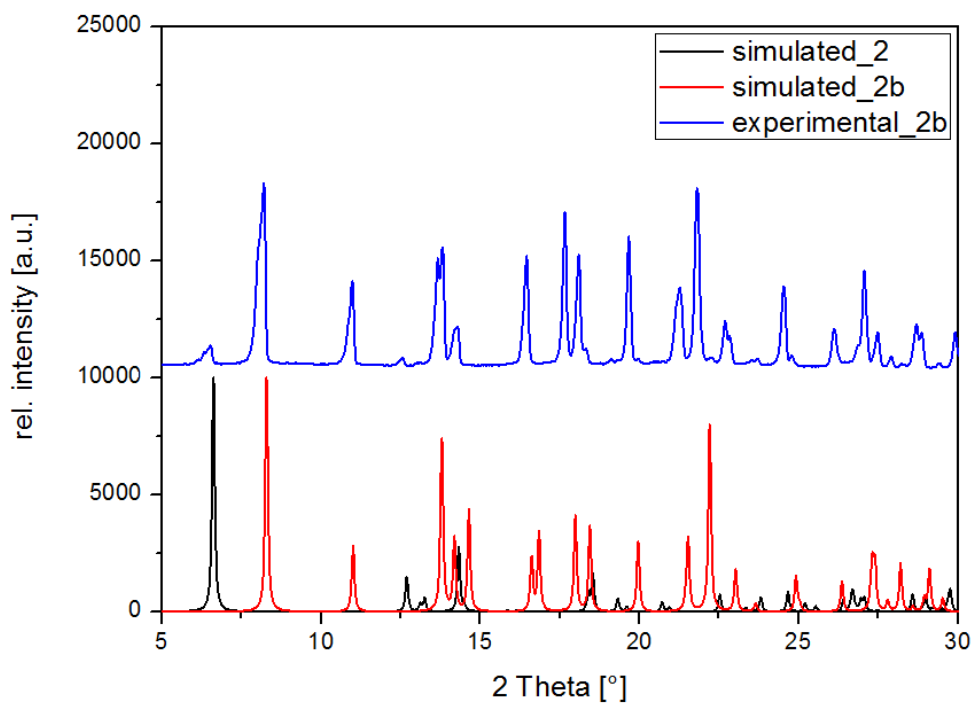
**Figure S1** Experimental (red) and simulated (black) powder pattern for (1a).



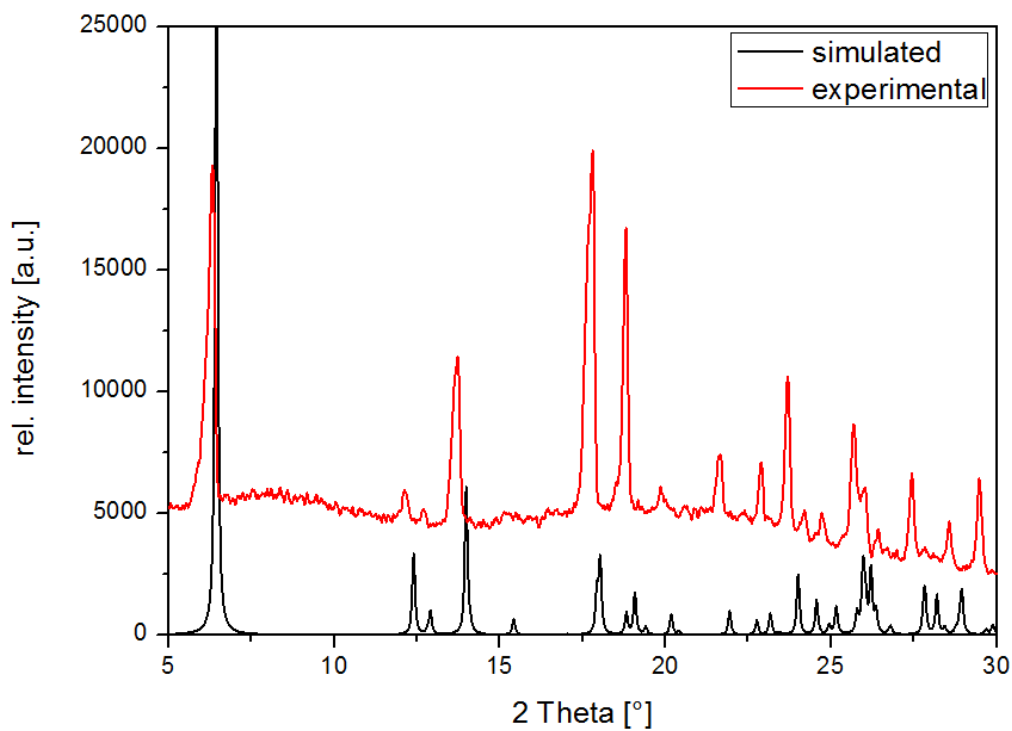
**Figure S2** Experimental (red) and simulated (black) powder pattern for (1b).



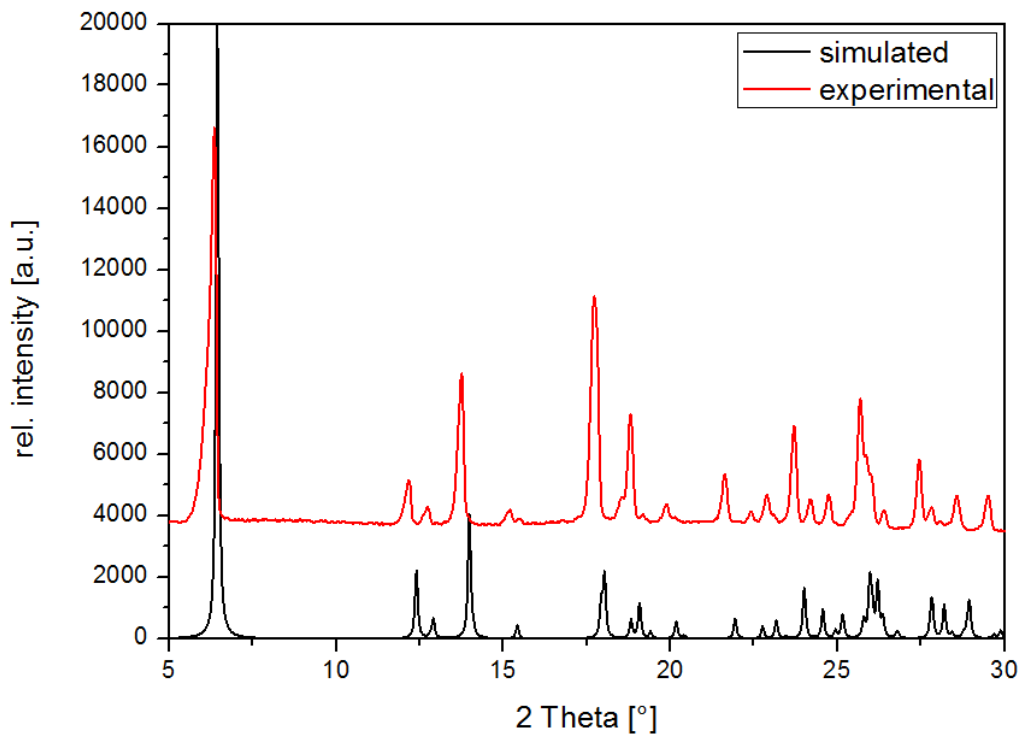
**Figure S3** Experimental (red) and simulated (black) powder pattern for (2).



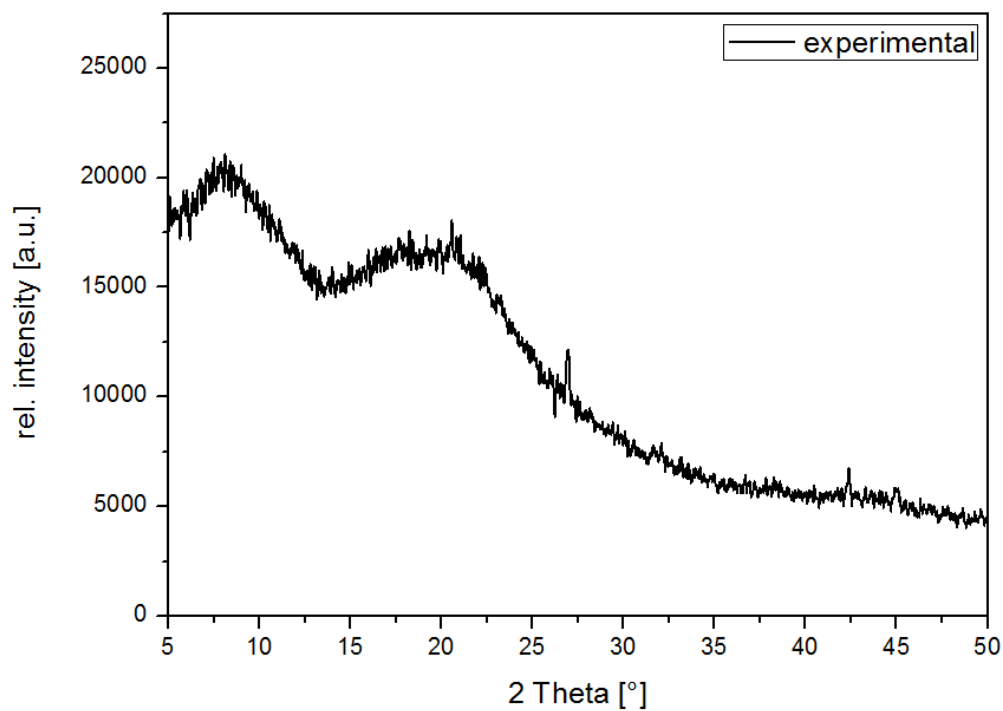
**Figure S4** Experimental (blue) powder diffraction pattern for (2b) reveals the co-existence of (2) (simulated, black) and (2b) (simulated, red).



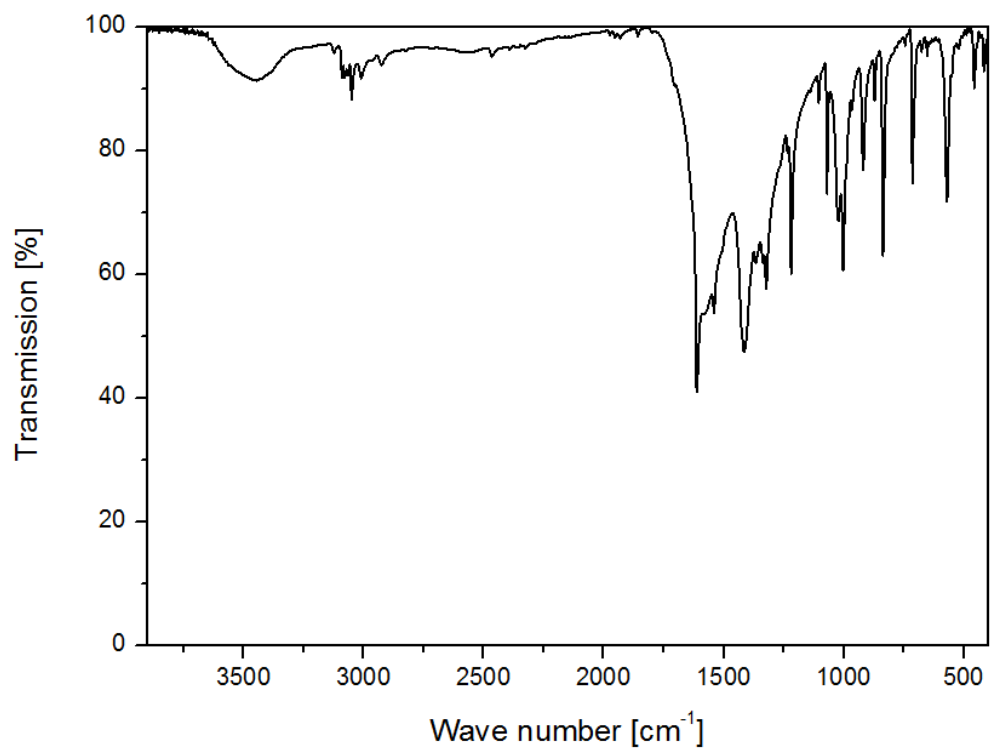
**Figure S5** Experimental (red) and simulated (black) powder pattern for (3), 1:1 ligand to metal ratio.



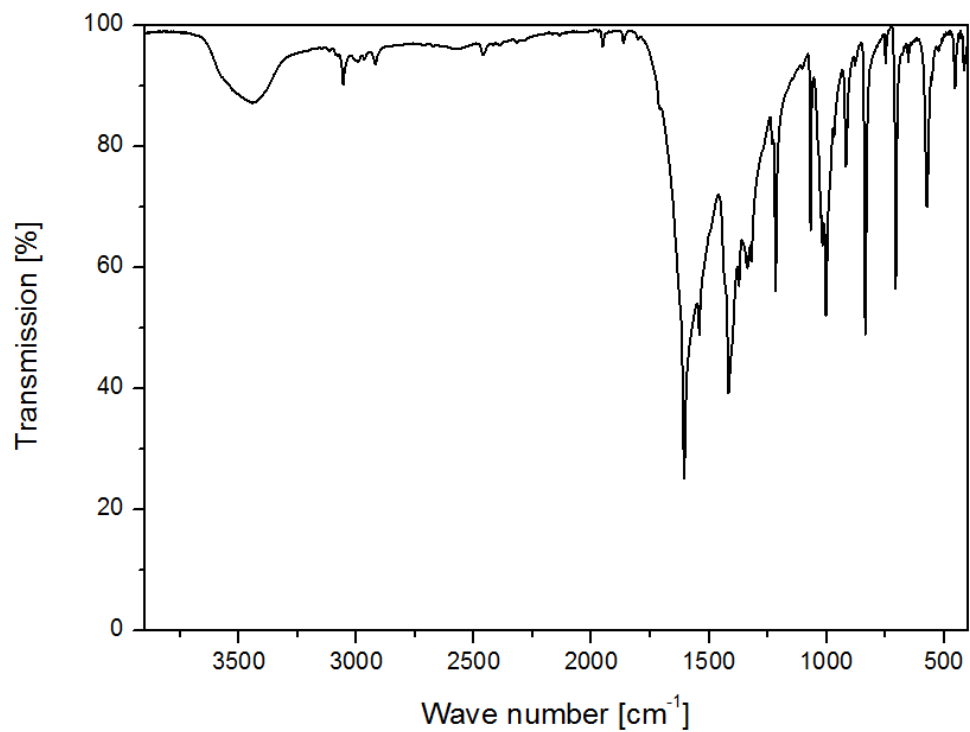
**Figure S6** Experimental (red) and simulated (black) powder pattern for (3), 2:1 ligand to metal ratio.



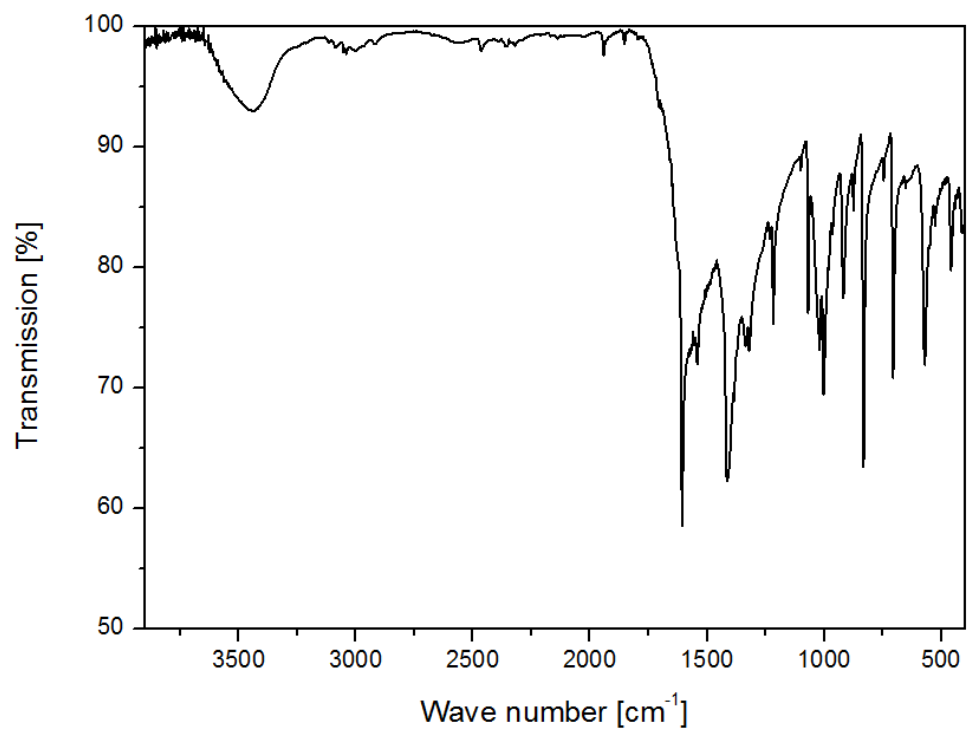
**Figure S7** Attempted transformation experiment of (2b) to (2): Essentially amorphous solid after annealing *in vacuo* at 135 °C.



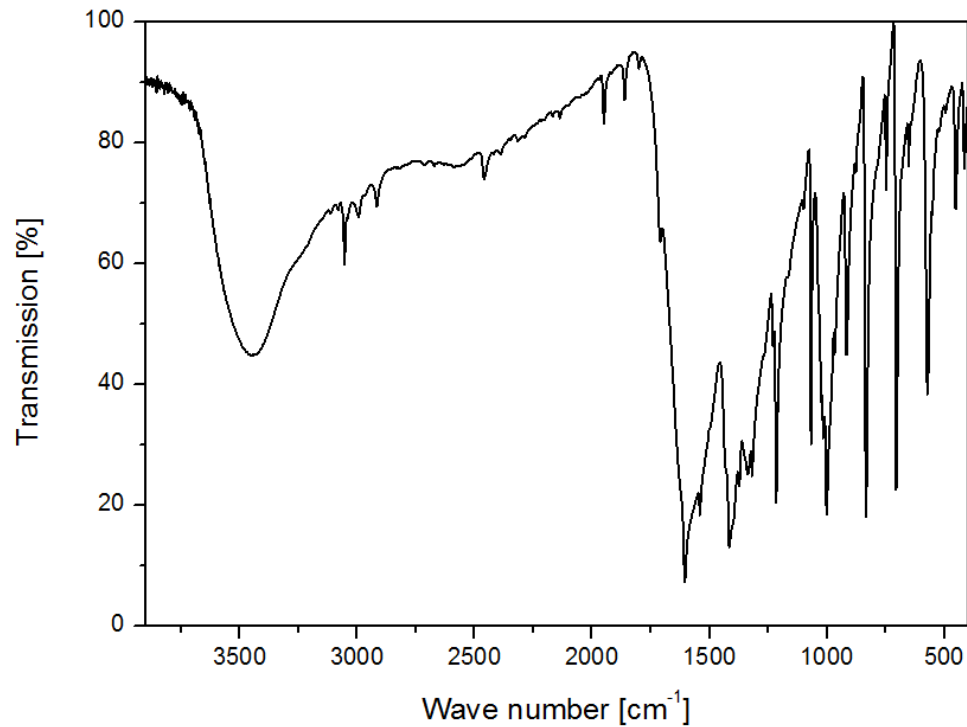
**Figure S8** Infrared spectrum of (1a).



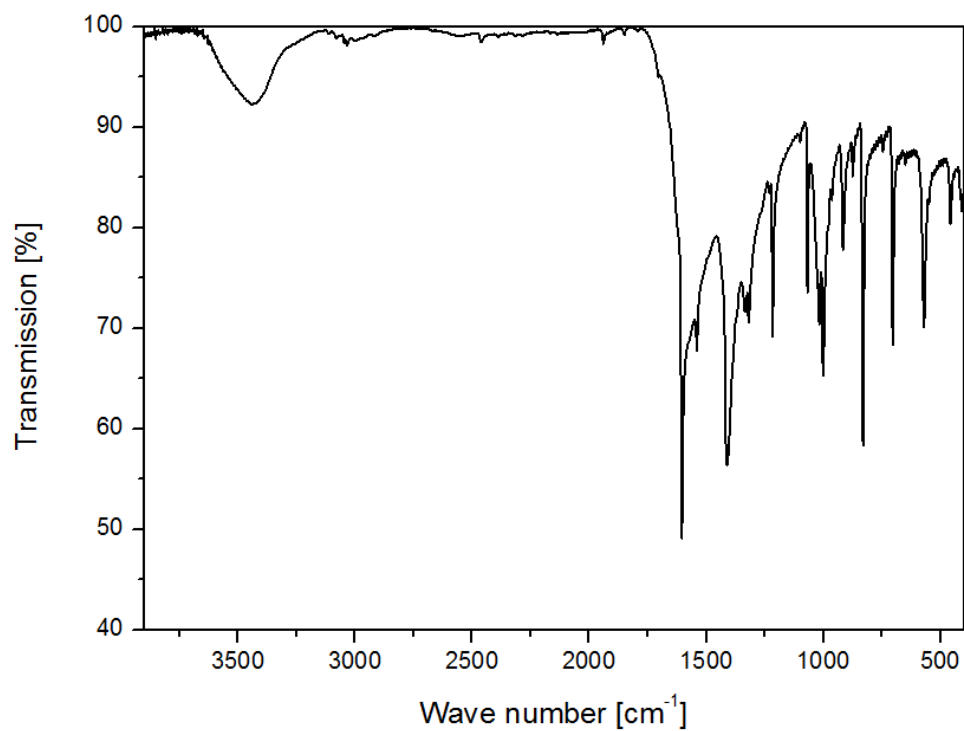
**Figure S9** Infrared spectrum of (1b).



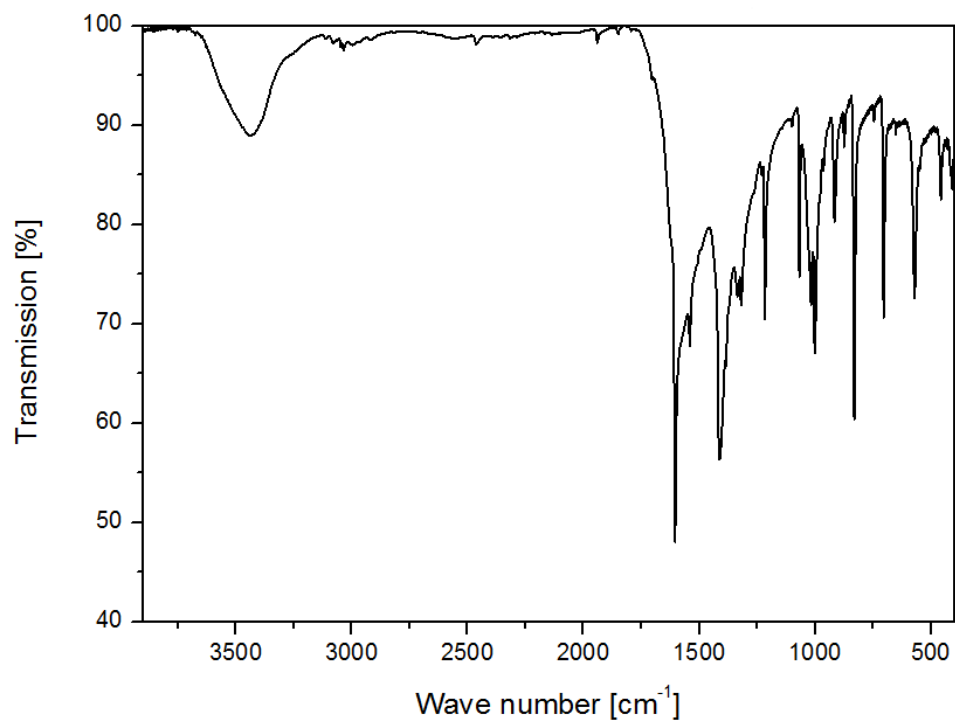
**Figure S10** Infrared spectrum of (2).



**Figure S11** Infrared spectrum of (2b).

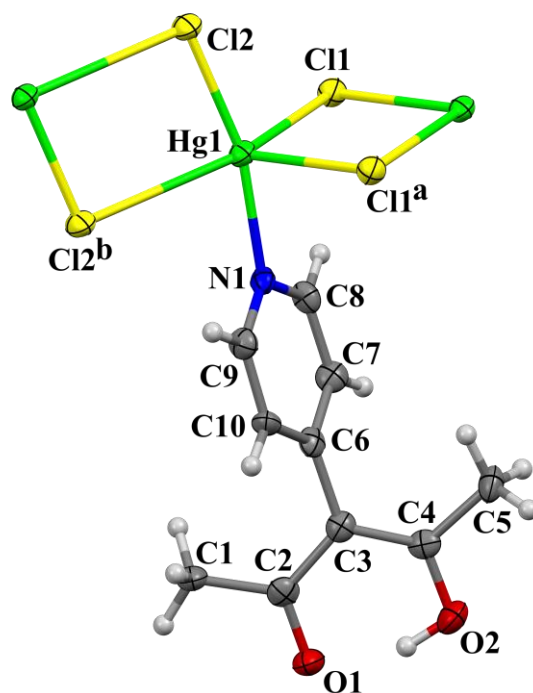


**Figure S12** Infrared spectrum of (3), 1:1 ligand to metal ratio.

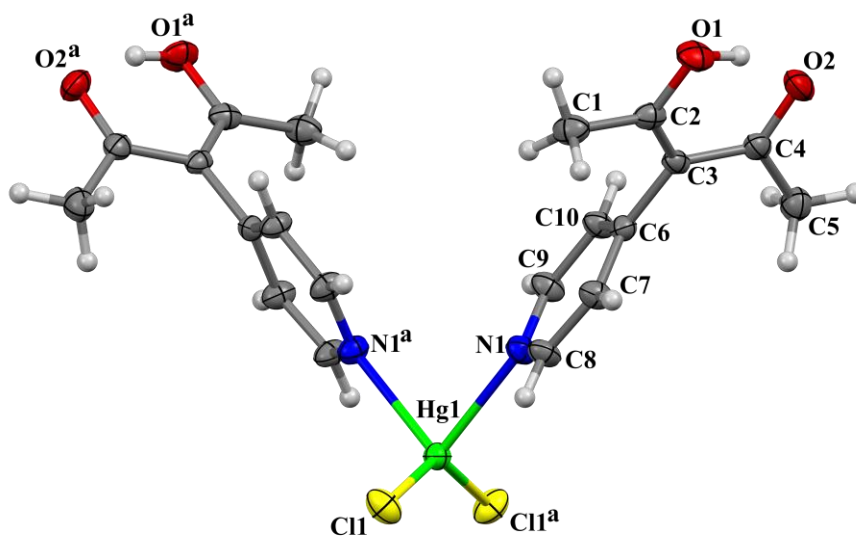


**Figure S13** Infrared spectrum of (3), 2:1 ligand to metal ratio.

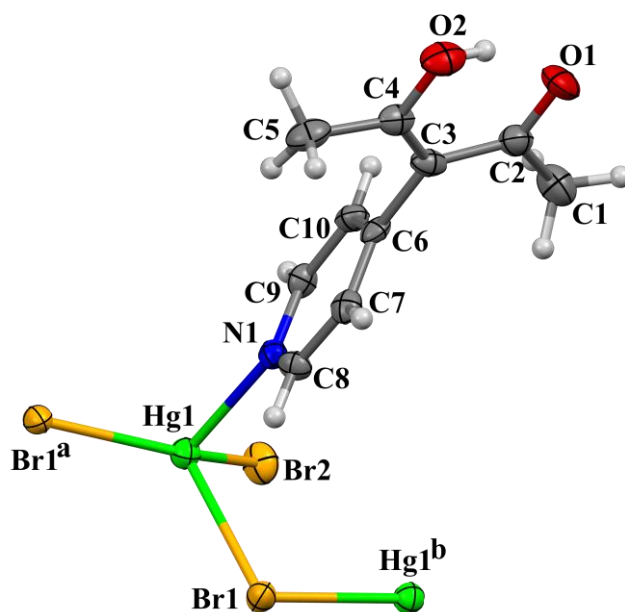




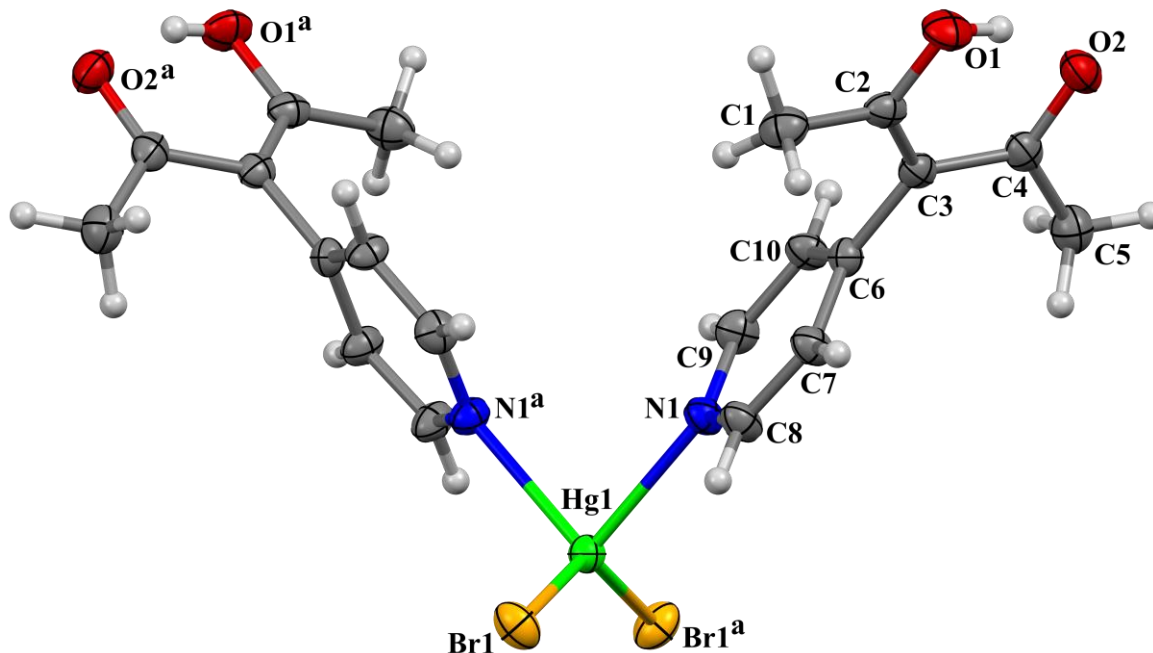
**Figure S14** Displacement ellipsoid plot of the asymmetric unit of (1a). Ellipsoids are drawn at 70 % probability level (symmetry operations: a:  $-x, -y, 1-z$ ; b:  $1-x, -y, 2-z$ ).



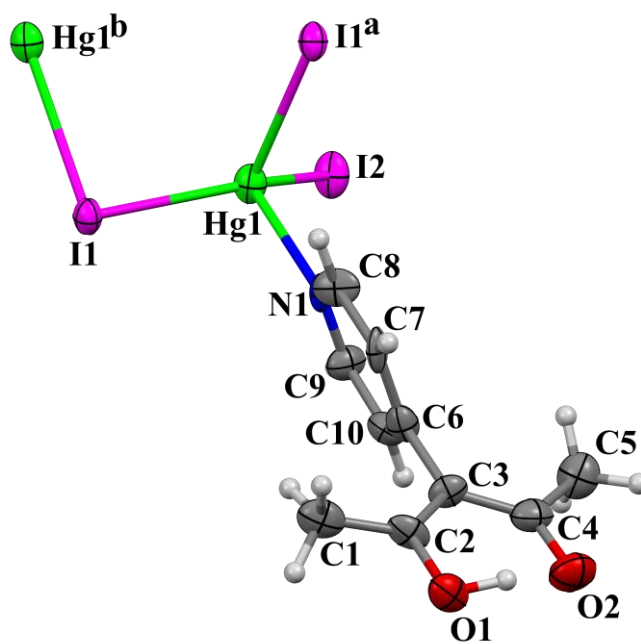
**Figure S15** Displacement ellipsoid plot of the asymmetric unit of (1b). Ellipsoids are drawn at 70 % probability level (symmetry operation: a:  $1-x, y, 3/2-z$ ).



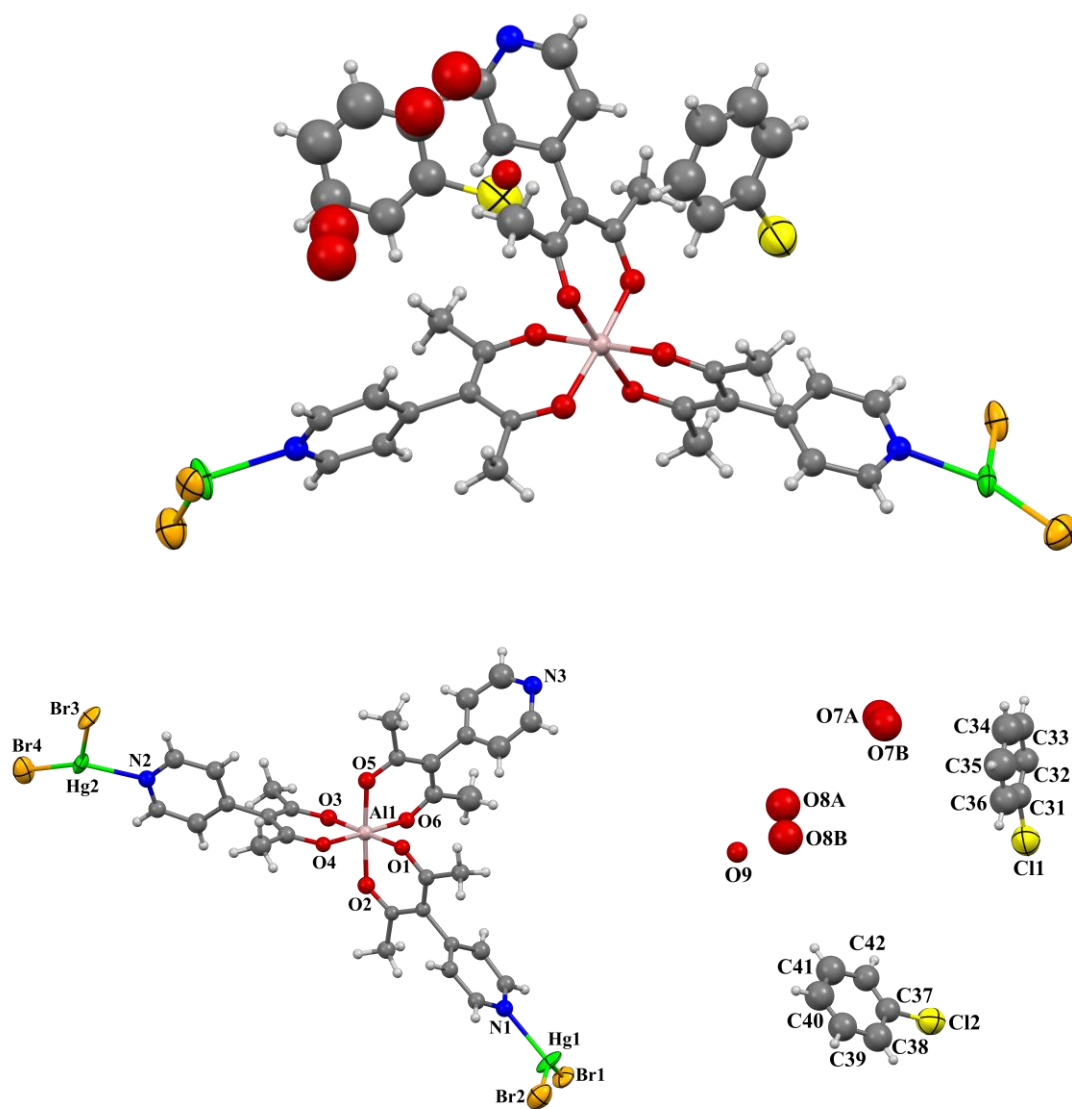
**Figure S16** Displacement ellipsoid plot of the asymmetric unit of (2). Ellipsoids are drawn at 70 % probability level (symmetry operations: a:  $1/2+x, y, 1/2-z$ ; b:  $-1/2+x, y, 1/2-z$ ).



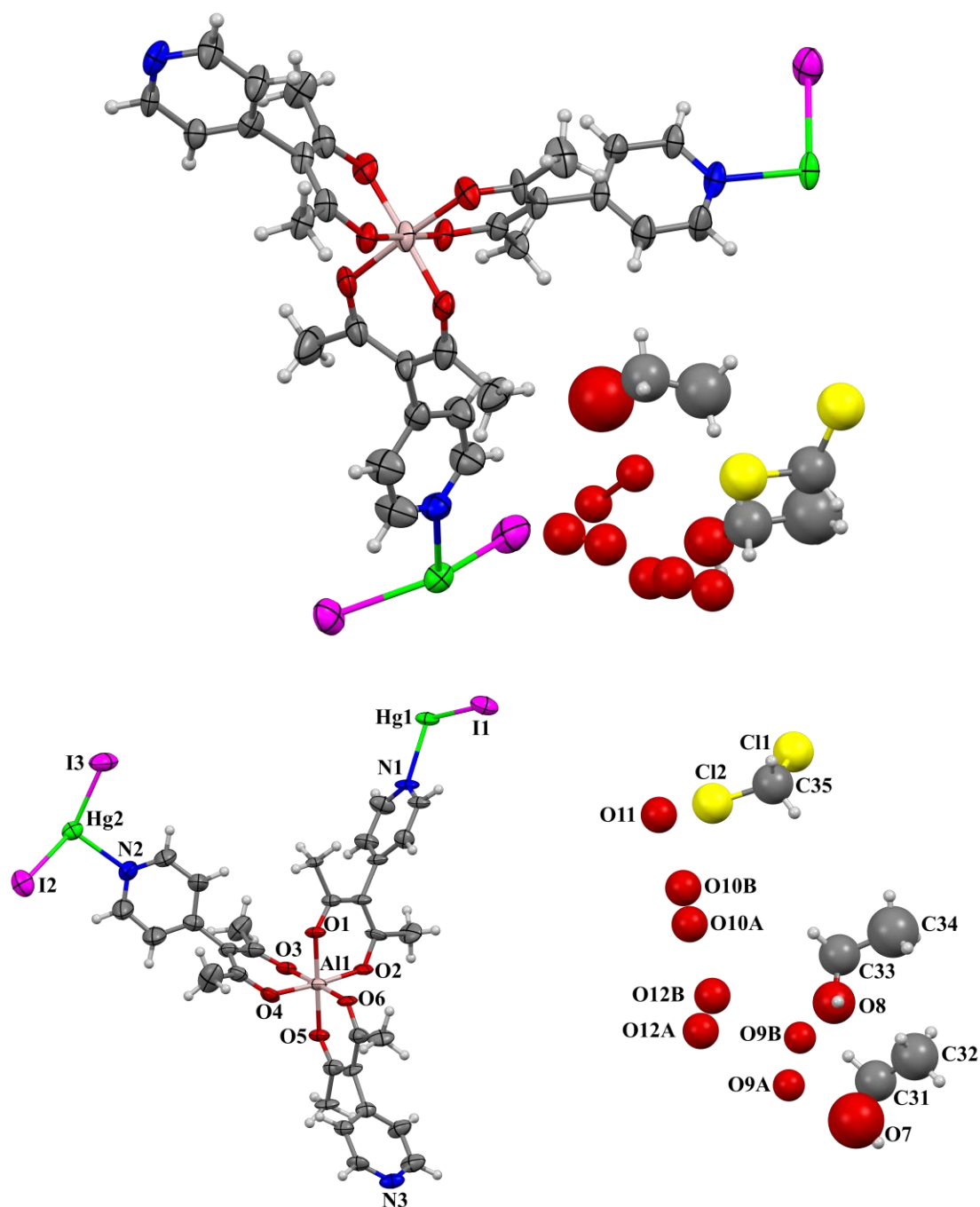
**Figure S17** Displacement ellipsoid plot of the asymmetric unit of (2b). Ellipsoids are drawn at 70 % probability level (symmetry operation: a:  $1-x, y, 3/2-z$ ).



**Figure S18** Displacement ellipsoid plot of the asymmetric unit of (3). Ellipsoids are drawn at 70 % probability level (symmetry operations: a:  $1/2+x, y, 1/2-z$ ; b:  $-1/2+x, y, 1/2-z$ ).



**Figure S19** Displacement ellipsoid plot of the asymmetric unit of (6c). Ellipsoids are drawn at 70 % probability level. The majority of (6c) was refined with isotropic displacement parameters (top: full asymmetric unit; bottom left: asymmetric unit of the framework; bottom right: co-crystallized solvent molecules).



**Figure S20** Displacement ellipsoid plot of the asymmetric unit of (9d). Ellipsoids are drawn at 70 % probability level (top: full asymmetric unit; bottom left: asymmetric unit of the framework; bottom right: co-crystallized solvent molecules with isotropic displacement parameters).

## Refinement strategy

All bimetallic compounds (4c) - (9d) contain larger amounts of solvent molecules; their diffraction data suffer from partial desolvation, and structure models are affected by disorder in the solvent region. The six compounds adopt two different structure types, and a full structure model for only one compound within each isomorphous series is presented here.

Compounds (4c), (5c) and (6c) show a ratio of 2:1 between Hg(II) and the octahedrally coordinated trivalent cations. They are isomorphous, and their crystal data have been compiled in Table S1. A full structure model with atomic resolution in the solvent region is only reported for (6c).

Structure model for (6c): in order to avoid physically meaningless anisotropic displacement parameters (ADPs) and complicated split positions, only the most relevant scattering centers (Hg, Br, Cl) were assigned anisotropic displacement parameters and all other atoms were treated as isotropic. Two well-ordered chlorobenzene as well as three water molecules fit inside the voids of the asymmetric unit of (6c). Two of the three water oxygen atoms were assigned split positions, and no hydrogen atoms were assigned to the water molecules. In the final refinement cycles, an isotropic extinction parameter according to Larson (1970) converged to a value of 0.00137(2), and three reflections with large discrepancies between calculated and observed structure factors were omitted as outliers.

Compounds (7d), (8d) and (9d) show a ratio of 3:2 between Hg(II) and the octahedrally coordinated trivalent cations. They are isomorphous, and their crystal data have been compiled in Table S2. A full structure model with atomic resolution in the solvent region is only reported for (9d).

Structure model for (9d): ADPs were assigned to all atoms of the framework of the ladder structure; enhanced rigid bond restraints (Hirshfeld, 1976; Thorn *et al.*, 2012) with standard uncertainties of 0.005 Å<sup>2</sup> were applied for several atom pairs. Atoms associated with solvent molecules were assigned isotropic displacement parameters. According to a Difference Fourier map, the solvent region contains one well-ordered dichloromethane, two well-ordered ethanol and four water molecules; similar to (6c), most of the oxygen atoms associated with water molecules were refined with split positions.

For all compounds reported in the manuscript, the highest residual electron density fluctuations  $\Delta\rho_{\max}$  (maxima) and  $\Delta\rho_{\min}$  (minima) are associated with the mercury sites.

Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239-244.

Larson, A. C. (1970). *Crystallographic Computing*, 291-294.

Thorn, A., Dittrich, B., Sheldrick, G. M. (2012). *Acta Cryst.* **A68**, 448-451.

**Table S1** Crystal data and data collection parameters for compounds (4c)\*, (5c)\* and (6c).

Experiments were carried out at 100 K with Mo-K $\alpha$  radiation using a CCD area detector diffractometer (\* determination of only the isotropic framework without explicit treatment of the co-crystallized solvent molecules).

	(4c)*	(5c)*	(6c)
Crystal data			
Chemical formula	C <sub>60</sub> H <sub>60</sub> Cl <sub>8</sub> Fe <sub>2</sub> Hg <sub>4</sub> N <sub>6</sub> O <sub>12</sub>	C <sub>60</sub> H <sub>60</sub> Al <sub>2</sub> Cl <sub>8</sub> Hg <sub>4</sub> N <sub>6</sub> O <sub>12</sub>	C <sub>84</sub> H <sub>80</sub> Al <sub>2</sub> Br <sub>8</sub> Cl <sub>4</sub> Hg <sub>4</sub> N <sub>6</sub> O <sub>17</sub>
$M_r$	2254.85	2197.12	3082.94
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
$a, b, c$ (Å)	16.8958(11), 22.8992(13), 13.8455(17)	16.6273(13), 22.9667(16), 13.8451(10)	16.7982(18), 24.3995(19), 13.9346(15)
$\alpha, \beta, \gamma$ (°)	90, 110.860(4), 90	90, 109.902(9), 90	90, 107.435(4), 90
$V$ (Å <sup>3</sup> )	5005.4(3)	4971.3(8)	5448.9(9)
$Z$	2	2	2
$\mu$ (mm <sup>-1</sup> )	7.613	7.264	8.723
Crystal size (mm)	0.28 x 0.24 x 0.23	0.32 x 0.14 x 0.13	0.26 x 0.14 x 0.13
Crystal colour, shape	Red, rod	Colourless, rod	Colourless, rod
Data collection			
Absorption collection	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>
$T_{\min}, T_{\max}$	0.3297, 0.7452	0.1821, 0.7449	0.4432, 0.7454
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	26103, 8734, 6285	10903, 7004, 3959	66382, 11349, 6418
$R_{\text{int}}$	0.1023	0.1413	0.1564
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.5813	0.5412	0.6084

**Table S2** Crystal data and data collection parameters for compounds (7d)\*, (8d)\* and (9d).

Experiments were carried out at 100 K with Mo-K $\alpha$  radiation using a CCD area detector diffractometer (\* determination of only the isotropic framework without explicit treatment of the co-crystallized solvent molecules).

	(7d)*	(8d)*	(9d)
Crystal data			
Chemical formula	C <sub>60</sub> H <sub>60</sub> Br <sub>6</sub> Fe <sub>2</sub> Hg <sub>3</sub> N <sub>6</sub> O <sub>12</sub>	C <sub>60</sub> H <sub>60</sub> Fe <sub>2</sub> Hg <sub>3</sub> I <sub>6</sub> N <sub>6</sub> O <sub>12</sub>	C <sub>69</sub> H <sub>86</sub> Al <sub>2</sub> Cl <sub>2</sub> Hg <sub>3</sub> I <sub>6</sub> N <sub>6</sub> O <sub>23.18</sub>
$M_r$	2250.06	2532.03	2858.30
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>
$a, b, c$ (Å)	31.6013(17), 13.9035(11), 26.9928(16)	32.4346(14), 13.9168(14), 27.6445(12)	32.1651(19), 13.8294(12), 27.6145(16)
$\alpha, \beta, \gamma$ (°)	90, 125.353(3), 90	90, 125.772(5), 90	90, 124.917(3), 90
$V$ (Å <sup>3</sup> )	9672.4(15)	10124.293	10072.3(12)
$Z$	4	4	4
$\mu$ (mm <sup>-1</sup> )	7.561	8.435	6.533
Crystal size (mm)	0.19 x 0.17 x 0.17	0.18 x 0.16 x 0.13	0.28 x 0.20 x 0.17
Crystal colour, shape	Red, block	Red, block	Colourless, block
Data collection			
Absorption collection	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>
$T_{\min}, T_{\max}$	0.4339, 0.7447	0.3597, 0.7454	0.3177, 0.7452
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	19515, 5980, 4122	66382, 11349, 6418	51862, 9165, 6621
$R_{\text{int}}$	0.1031	0.1325	0.1258
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.5164	0.5423	0.5835