Electronic Supplementary Information (ESI)

Stepwise formation of heteronuclear coordination networks based on quadruple-bonded dimolybdenum units containing formamidinate ligands †

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Experimental Details

General Procedures. Elemental analyses were obtained from a HERAEUS VaruoEL analyzer. The IR spectra (KBr disk) were recorded on a Jasco FT/IR-460 plus spectrometer. Powder X-ray diffraction measurements were carried out on a PANalytical PW3040/60 X'Pert Pro diffractometer and Bruker D2 PHASER X-ray Diffractometer.

Materials. The reagents 4-aminopyridine was purchased from Alfa Aesar, mercury (II) chloride, mercury (II) bromide were from ACROS, mercury (II) iodide from Sigma-Aldrich, and triethyl orthoformate from Sigma-Aldrich Co. Tetrahydrofuran and acetonitrile were purchased from Merck & Co., Inc.

Preparation of $[Mo_2(4\text{-pyf})_4]$, 1. A freshly prepared suspension of [Li(4-pyf)] (0.40 g, 2.02 mmol of 4-Hpyf and 0.8 mL of ^{n}BuLi 2.5 M in 20 mL of THF) was added dropwise to a solution of $[Mo_2(OAc)_4]$ (0.22 g, 0.51 mmol) in 10 mL of THF at -78 ^{o}C. The mixture was then stirred at room temperature for 24 h to yield a deep brown solution and precipitate. The solvent was reduced and diethylether added to induce more precipitate. The precipitate was then filtered and 50 mL of dichloromethane was added to dissolve the precipitate to give a yellow solution. The solution was then layered with diethylether and yellow plate crystals were found after five days. The crystals were then collected, washed with diethylether and dried in vacuum. Yield: 0.36 g (73 %). Anal. Calcd. for $C_{44}H_{36}N_{16}Mo_2$: C, 53.88; H, 3.70; N, 22.85. Found: C, 53.96; H, 3.53; 22.79. ^{1}H NMR (400 MHz, δ, ppm in $CDCl_3$): 8.73 (s, 1 H, C-*H*), 8.24 (d, 4 H, py), 6.13 (d, 4 H, py). IR (KBr disk, cm^{-1}): 1588 (m), 1528 (s), 1486 (m), 1419 (w), 1322 (m), 1244 (m), 1213 (m), 993 (w), 944 (m), 857 (m), 820 (m), 670 (m), 548 (w), 516 (w).

Preparations of $[Mo_2(4\text{-pyf})_4(HgX_2)_2\cdot(MeOH)]_n$, X = Br, 2, and I, 3. A methanol solution of $HgBr_2$ (0.34 g, 0.94 mmol) or HgI_2 (0.41 g, 0.90 mmol) was layered on the top of a dichloromethane solution of **1** (0.30 g, 0.31 mmol). After a week, plate yellow crystals were found at the interface. The crystals were collected, washed with dichloromethane (20 ml*2), methanol (20 ml*2) and diethylether (50 ml*2), and then dried under reduced pressure. Yield: 0.44 g (80 %) for **2**. Anal. Calcd. for $C_{22.5}H_{20}N_8MoHgBr_2O_{0.5}$: C, 31.18; H, 2.33; N, 12.93. Found: C, 30.38; H, 2.06; N, 12.15%. Yield: 0.37 g (61 %) for **3**. Anal. Calcd. for $C_{22.5}H_{20}N_8O_{0.5}MoHgI_2$: C, 28.13; H, 2.10; N, 11.66. Found: C, 28.55; H, 1.98; N, 11.97%. IR (KBr disk, cm^{-1}): 3517 ($HgBr_2$, w), 3041 (w), 1599 ($HgBr_2$, s), 1530 (s), 1488 (s), 1428 (m), 1321 (s), 1253 (m), 1210 (s), 1059 (m), 1011 (m), 944 (m), 860 (m), 822 (m), 729 (w), 673 (m), 655 (m), 549 (w), 511 ($HgBr_2$, m), 435 (w), for **2**. IR (KBr disk, cm^{-1}): 3855 (HgI_2, w), 3041 (w), 1597 (HgI_2, m), 1529 (s), 1488 (s), 1428 (m), 1321 (HgI_2, s), 1252 (m), 1211 (s), 1058 (m), 1010 (m), 943 (m), 860 (HgI_2, m), 821 (w), 672 (m), 655 (m), 550 (m), for **3**.

Preparations of $[Mo_2(4\text{-pyf})_4(HgCl_2)_{3.6}]_n$, (4).

An acetonitrile solution of $HgCl_2$ (0.50 g, 1.84 mmol) was layered on the top of a dichloromethane solution of **1** (0.30 g, 0.31 mmol). After two weeks, arborization like of sorrel crystals were found. The crystals were collected, washed with dichloromethane (20 ml*2), acetonitrile (20 ml*2) and diethylether (50 ml*2), and then dried under reduced pressure. Yield: 0.31 g (51 %). Anal. Calcd. for $C_{22}H_{18}N_8MoHg_{1.8}Cl_{3.6}$: C, 26.99; H, 1.85; N, 11.44. Found: C, 26.54; H, 1.85; N, 11.93%. IR (KBr disk, cm^{-1}): 3058 ($HgCl_2$, m), 1607 ($HgCl_2$, m), 1529 ($HgCl_2$, s), 1490 ($HgCl_2$, s), 1437 (w), 1321 (s), 1258 (w), 1211 (s), 1062 (m), 1015 (m), 944 (m), 825 ($HgCl_2$, w), 675 (w), 548 (w), 475 (w).

Table S1. Various experiments for complexes **2**, **3** and **4**.

Complex **2**

$Mo_2(4\text{-pyf})_4$		$HgBr_2$		ratio	Yield
MW = 980.77		MW =360.40		$HgX_2/[(Mo_2(4\text{-pyf}_4)]$	$[Mo_2(4\text{-pyf})_4(HgBr_2)_2\cdot CH_3OH]_n$
0.30g	0.31mmol	0.11g	0.31mmol	1	0.037g, 7%
0.30g	0.31mmol	0.22g	0.61mmol	2	0.069g, 13%
0.30g	0.31mmol	0.34g	0.94mmol	3	0.44g, 80%
0.30g	0.31mmol	0.45g	1.25mmol	4	0.43g, 78%

Complex **3**

$Mo_2(4\text{-pyf})_4$		HgI_2		ratio	Yield
		MW = 454.40		$HgI_2/[(Mo_2(4\text{-pyf}_4)]$	$[Mo_2(4\text{-pyf})_4(HgI_2)_2\cdot CH_3OH]_n$
0.30g	0.31mmol	0.14g	0.31mmol	1	0.012g, 2%
0.30g	0.31mmol	0.28g	0.62mmol	2	0.16g, 27%
0.30g	0.31mmol	0.41g	0.90mmol	3	0.37g, 61%
0.30g	0.31mmol	0.56g	1.23mmol	4	0.35g, 59%

Complex **4**

$Mo_2(4\text{-pyf})_4$		$HgCl_2$		ratio	Yield
		MW = 271.50		$HgCl_2/[(Mo_2(4\text{-pyf}_4)]$	$[Mo_2(4\text{-pyf})_4(HgCl_2)_{3.6}]_n$
0.30g	0.31mmol	0.08g	0.29mmol	1	0.025g, 4%
0.30g	0.31mmol	0.17g	0.63mmol	2	0.058g, 10%
0.30g	0.31mmol	0.25g	0.92mmol	3	0.17g, 28%
0.30g	0.31mmol	0.30g	1.10mmol	3.6	0.16g, 26%
0.30g	0.31mmol	0.34g	1.25mmol	4	0.24g, 39%
0.30g	0.31mmol	0.42g	1.55mmol	5	0.26g, 42%
0.30g	0.31mmol	0.50g	1.84mmol	6	0.31g, 51%

Table S2. Molar rations of Hg to Mo, X to Hg and X to Mo. (X= Br, **2**; I, **3** and Cl, **4)**

	Hg/Mo		X/Hg		X/Mo	
Complex	Expected	SEM-EDS	Expected	SEM-EDS	Expected	SEM-EDS
2	1	1.05	2	2.12	2	2.22
3	1	1.04	2	2.22	2	2.31
4 round 1	1.8	1.76	2	2.30	3.6	4.04
4 round 2	1.8	1.76	2	1.89	3.6	3.34
4 round 3	1.8	1.82	2	1.97	3.6	3.59

Fig. S1. Simulated and experimental powder XRD patterns for **2**.

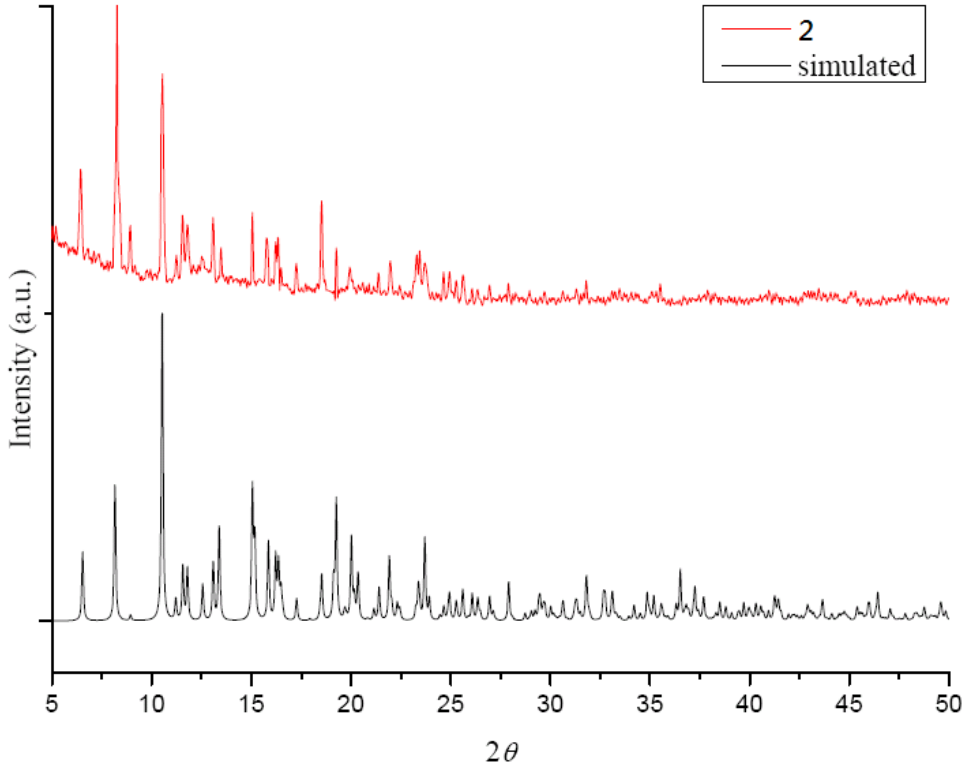


Fig. S2. Simulated and experimental powder XRD patterns for **3**.

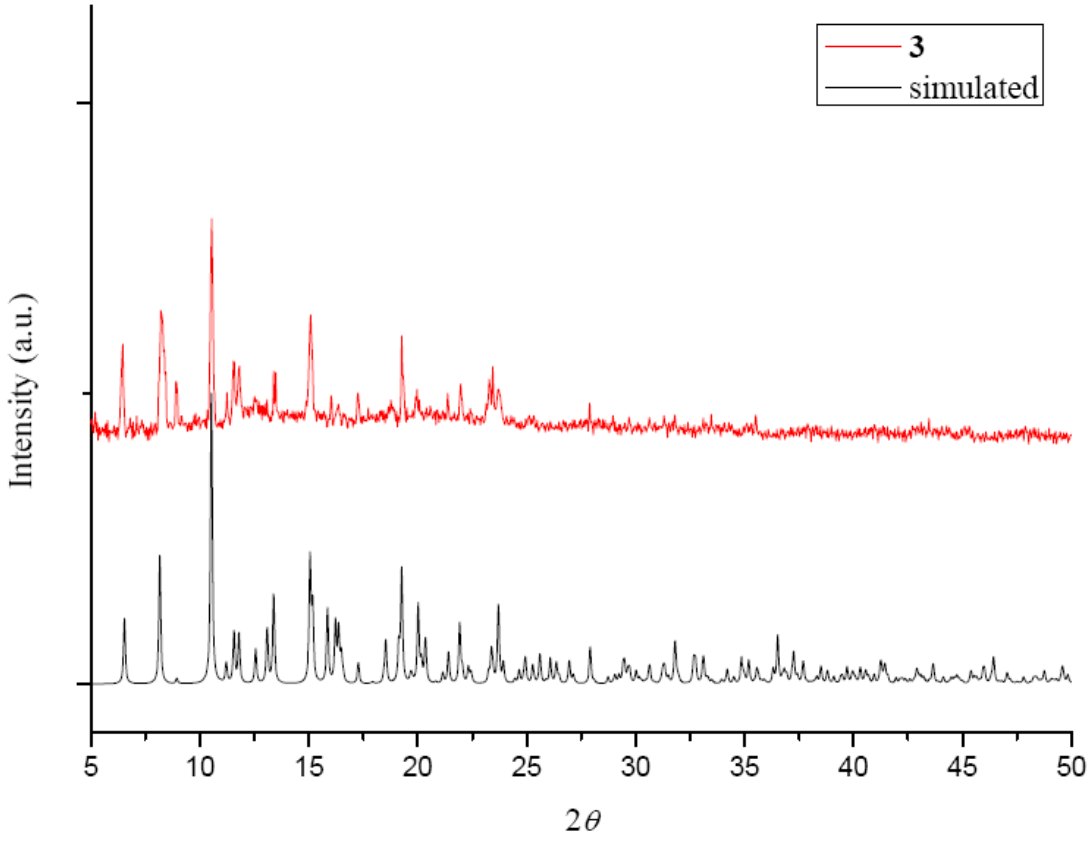


Fig. S3. Simulated and experimental powder XRD patterns for **4**.

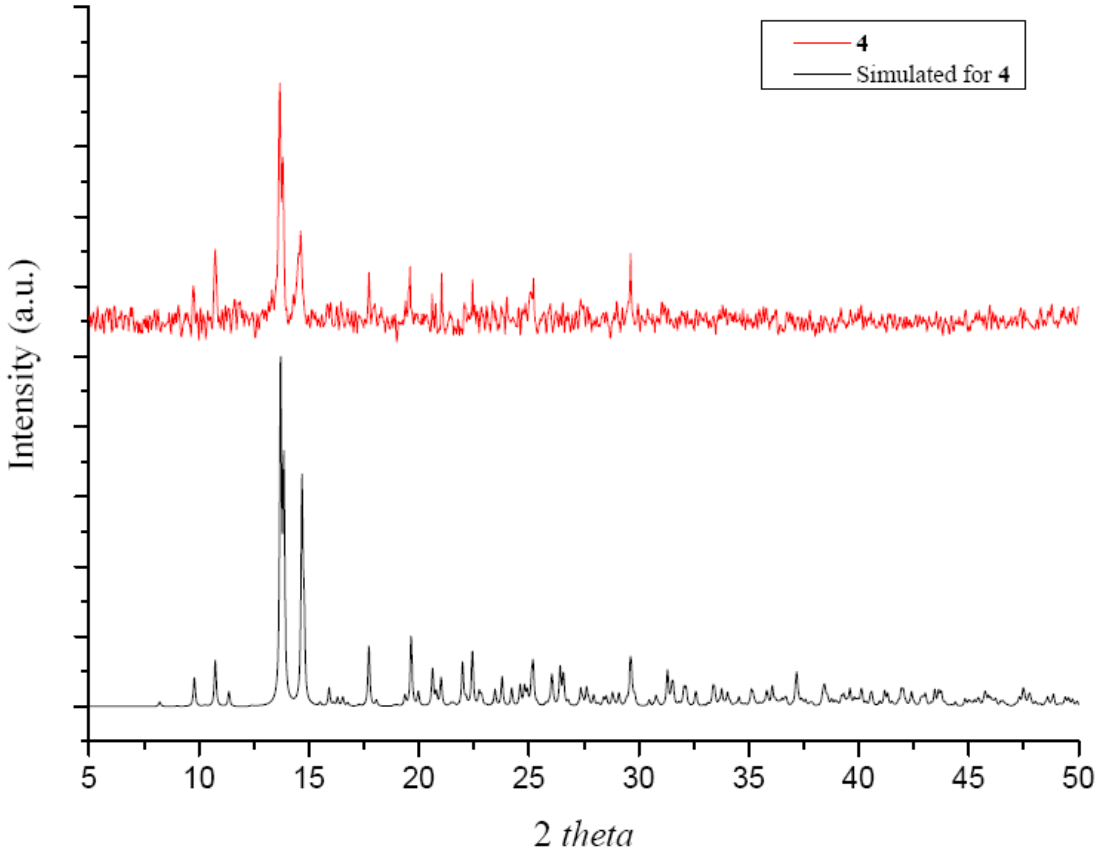
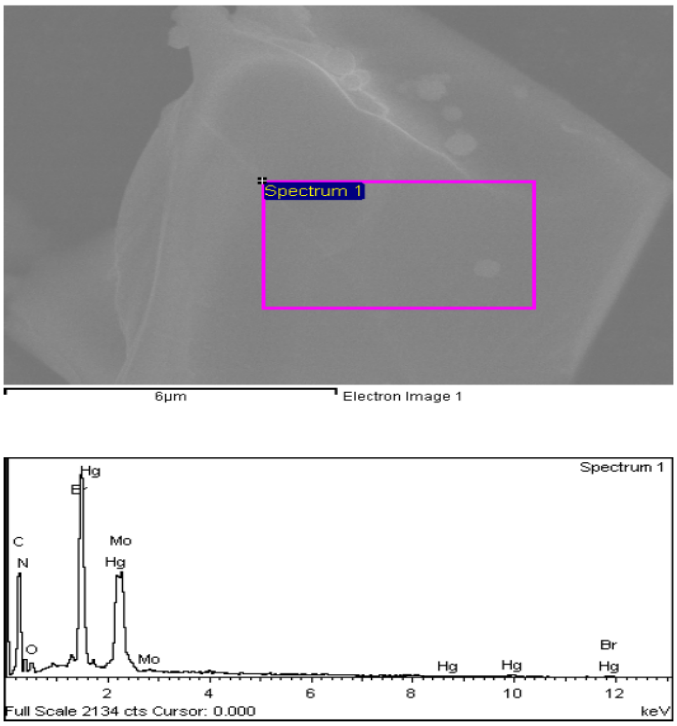
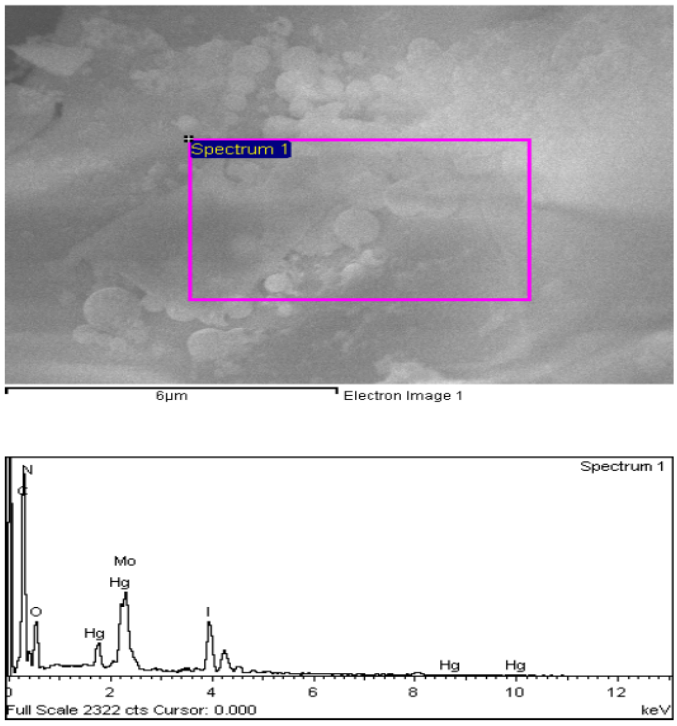


Fig. S4. The SEM image and EDS spectrum for (a) complex **2** and (b) complex **3**.



Element	Weight%	Atomic%
C K	34.33	65.25
N K	12.08	19.70
O K	3.46	4.94
Br L	18.41	5.26
Mo L	9.97	2.37
Hg M	21.75	2.48
Totals	100.00	

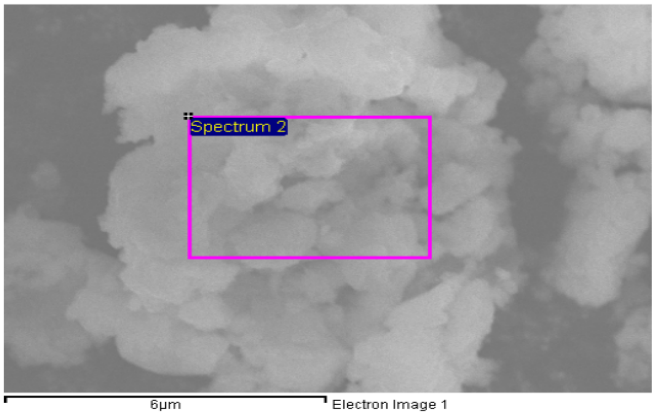
(a)

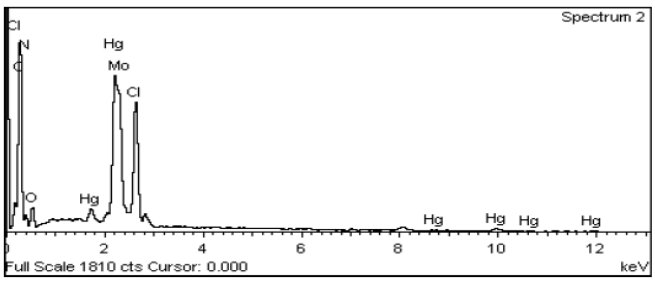


Element	Weight%	Atomic%
C K	37.30	61.32
N K	13.02	18.35
O K	12.09	14.92
Mo L	6.03	1.24
I L	18.41	2.86
Hg M	13.15	1.29
Totals	100.00	

(b)

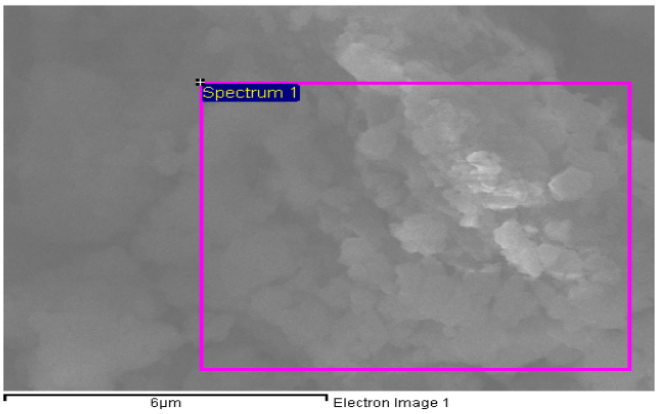
Fig. S5. The SEM images and EDS spectra of complex **4**, which were obtained from three different experiments.

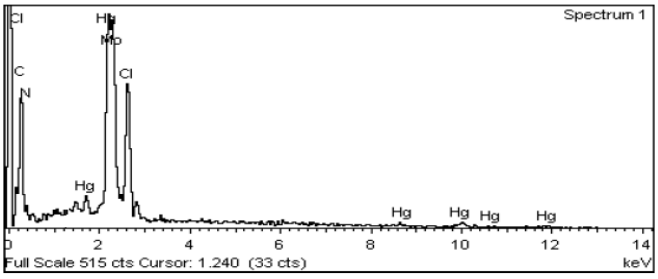




Element	Weight%	Atomic%
C K	52.47	67.67
N K	16.91	18.71
O K	10.34	10.01
Cl K	4.89	2.14
Mo L	3.30	0.53
Hg M	12.09	0.93
Totals	100.00	

(a)

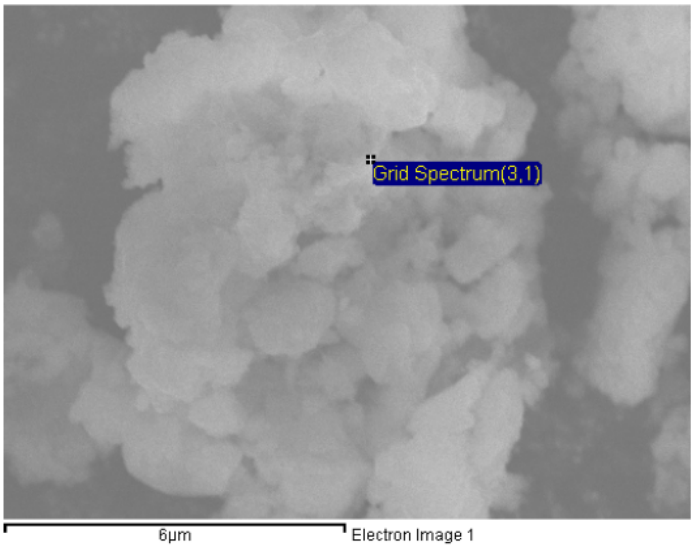


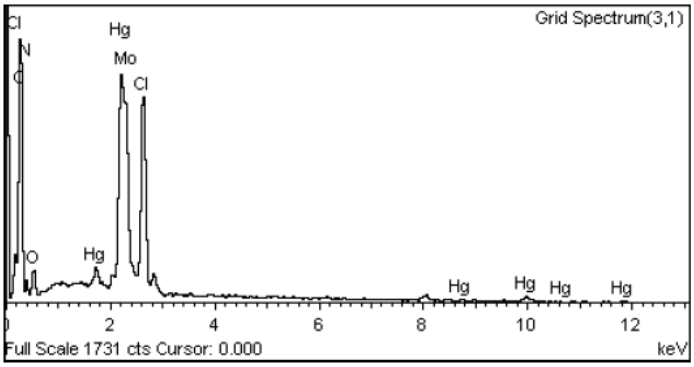


Element	Weight%	Atomic%
C K	38.34	67.67
N K	14.22	21.53
Cl K	9.88	5.91
Mo L	8.01	1.77
Hg M	29.55	3.12
Totals	100.00	

(b)

Fig. S5. The SEM images and EDS spectra of complex **4**, which were obtained from three different experiments. (cont.)

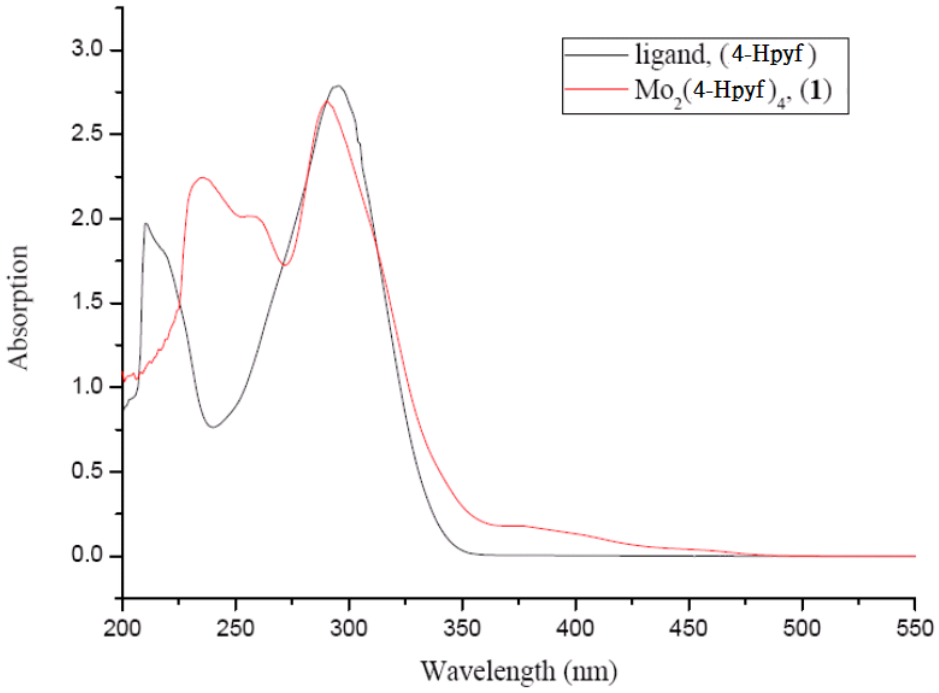




Element	Weight%	Atomic%
C K	41.89	76.30
N K	5.54	8.66
O K	2.23	3.05
Cl K	10.88	6.71
Mo L	8.22	1.87
Hg M	31.24	3.41
Totals	100.00	

(c)

Fig. S6. The UV-vis spectra for 4-Hpyf and complex **1** in CH_2Cl_2.



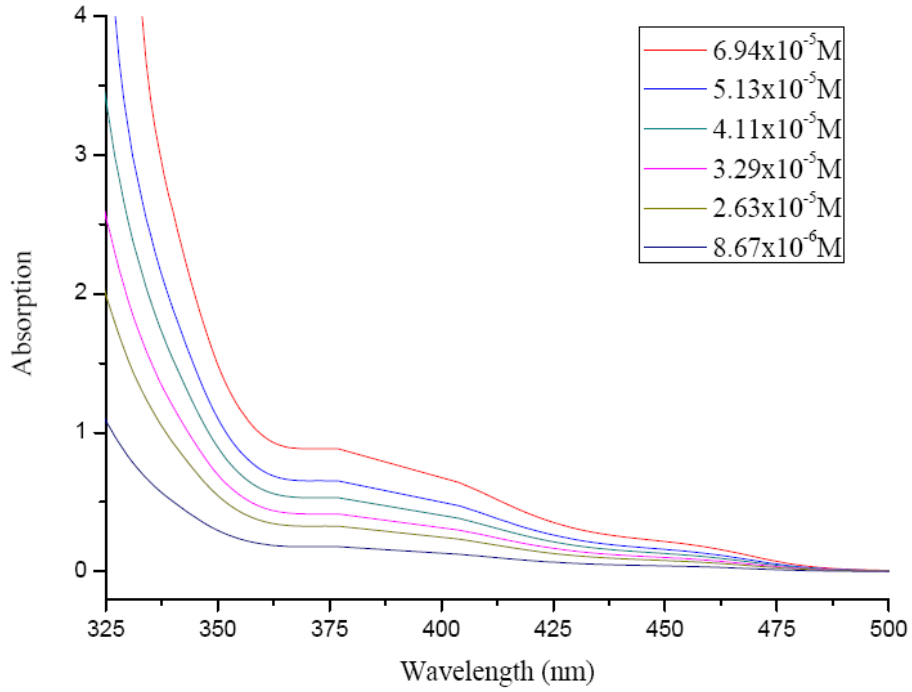


Fig. S7. The UV-vis spectra of HgX_2 (X = Cl, Br, I) in MeOH.

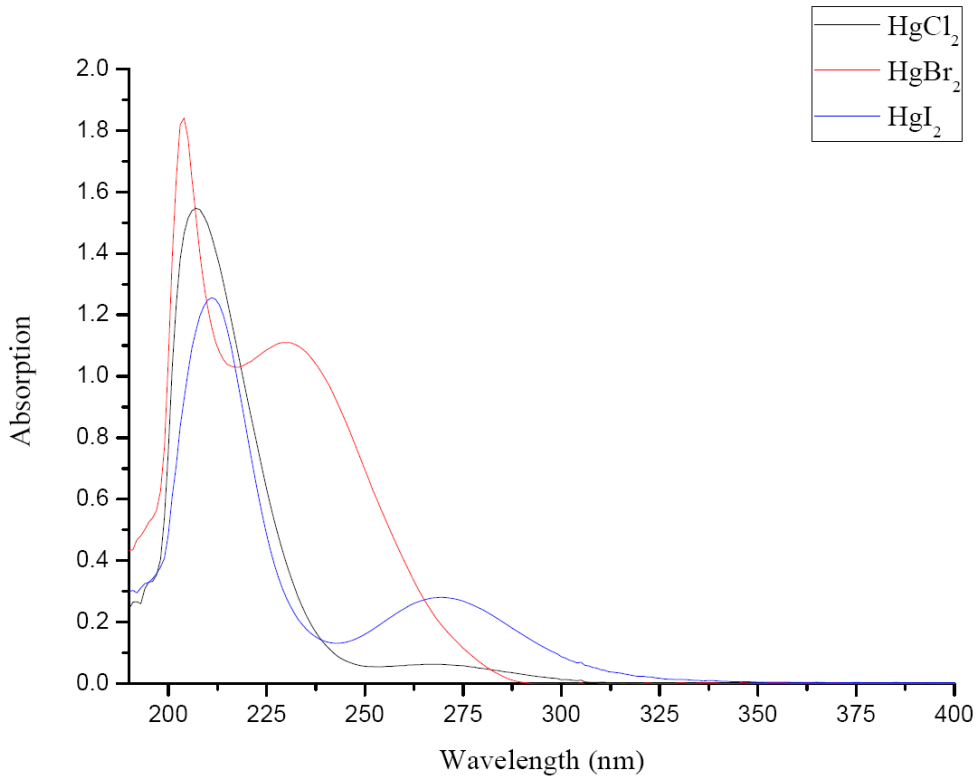


Fig. S8. The solid state UV-vis spectra of 4-Hpyf.

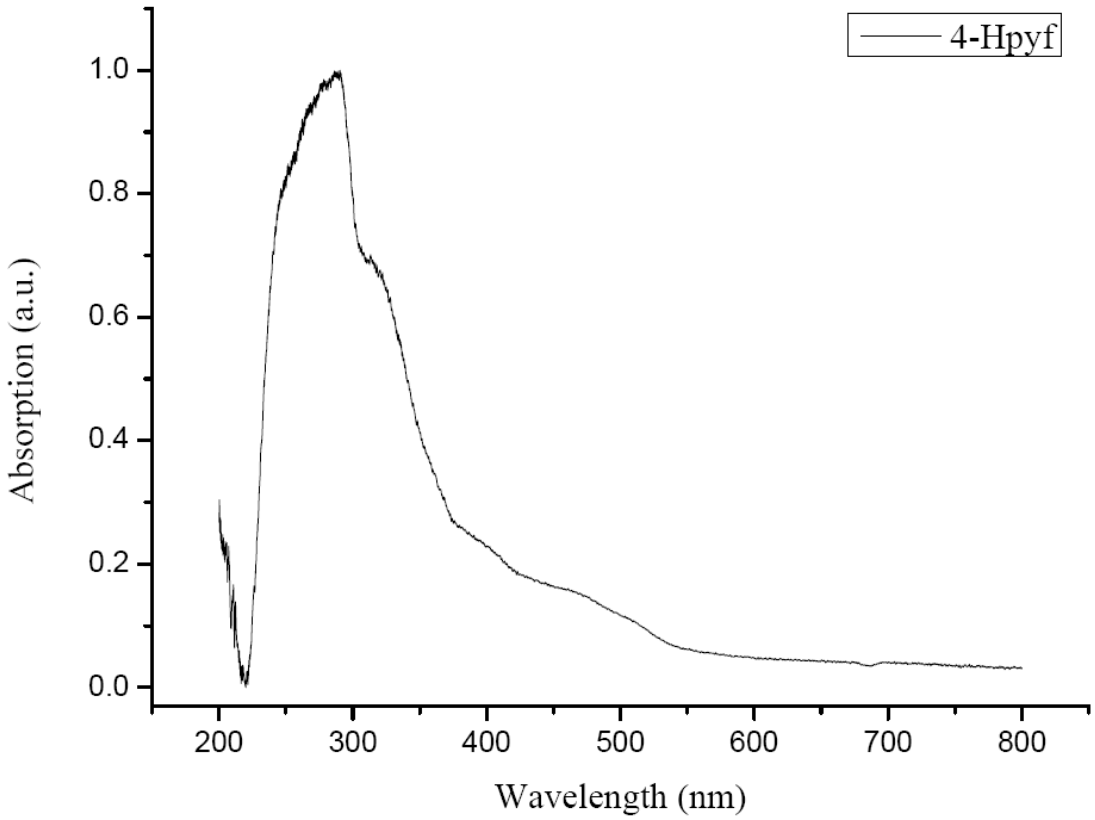


Fig. S9. The solid state UV-vis spectra of HgX_2 (X = Cl, Br, I).

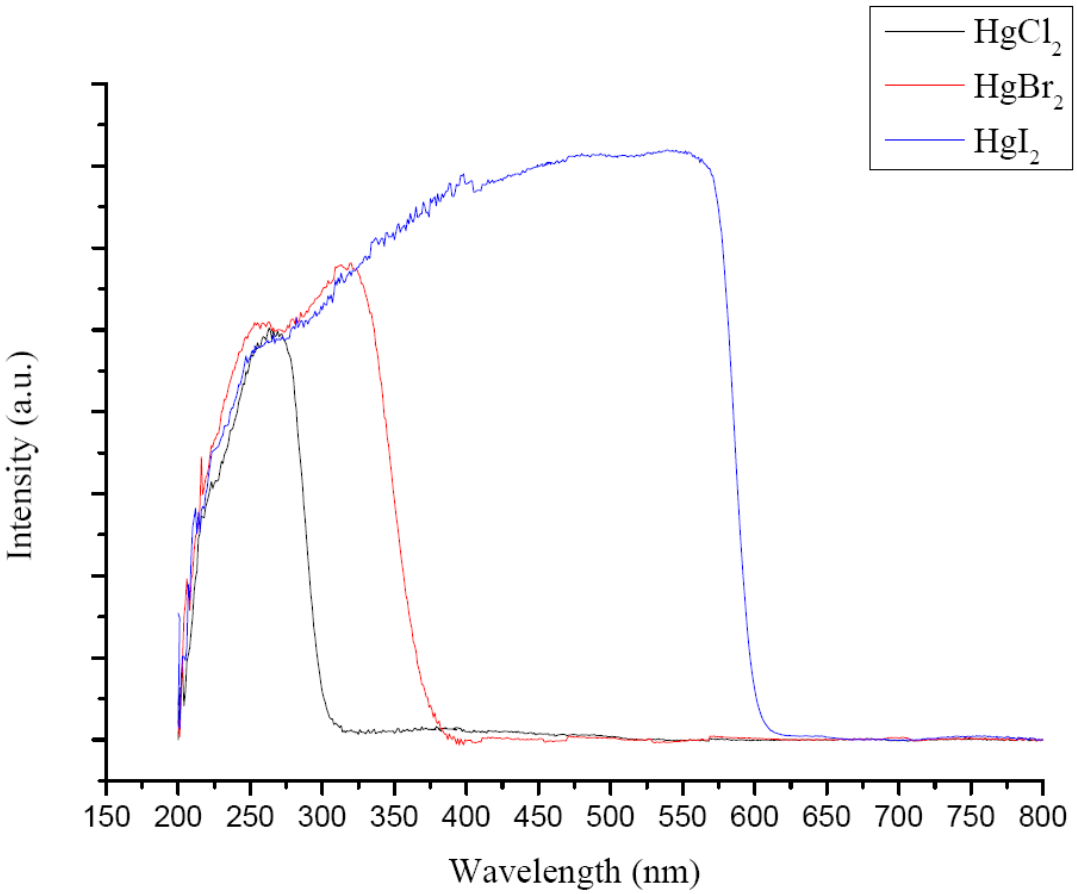


Fig. S10. The solid state UV-vis spectra of **1** – **4**.

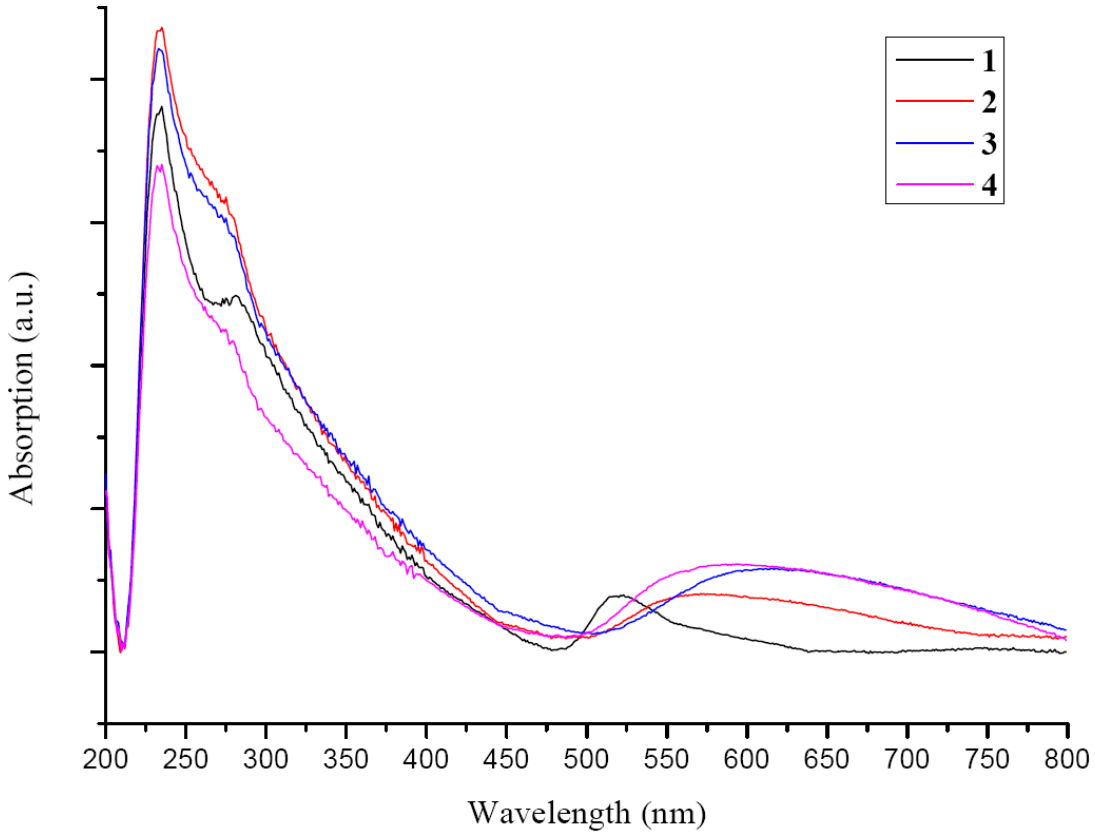


Fig. S11. An ORTEP diagram showing the structure of **1**.

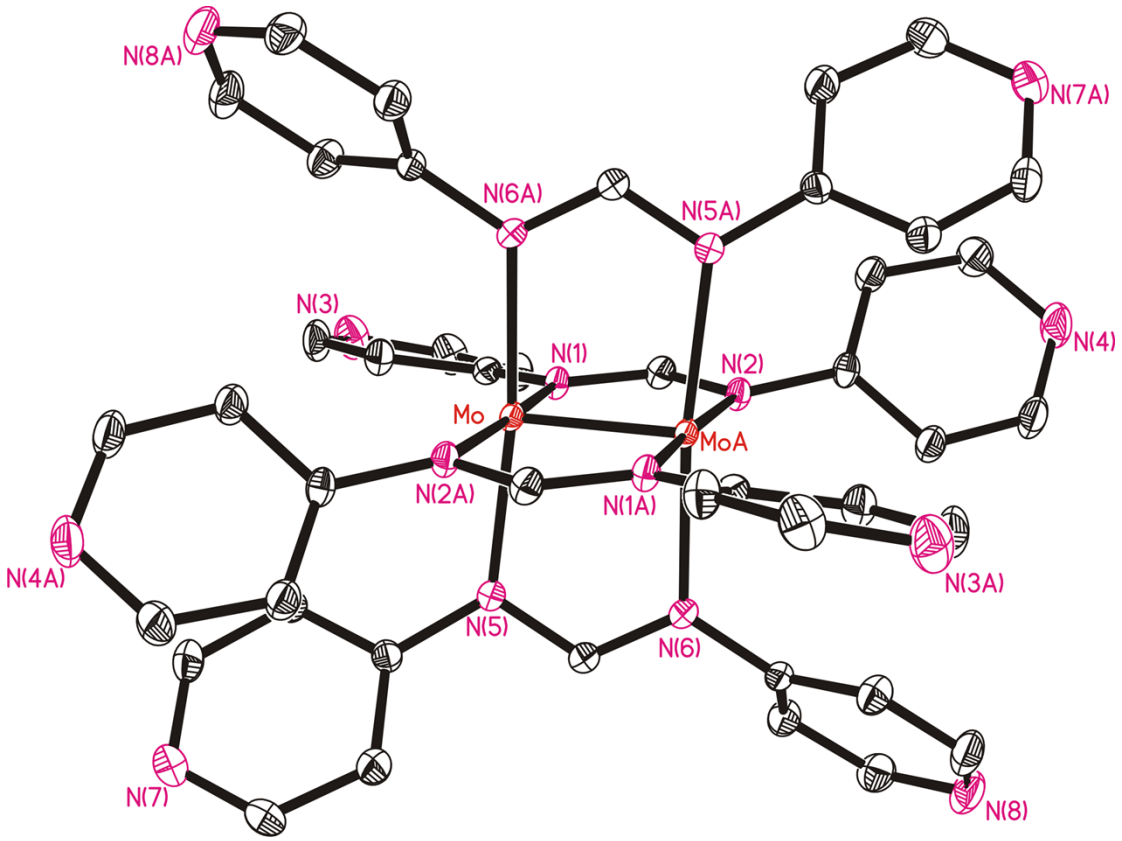


Fig. S12. An ORTEP diagram showing the coordination environments about the Mo(II) ions in **2**.

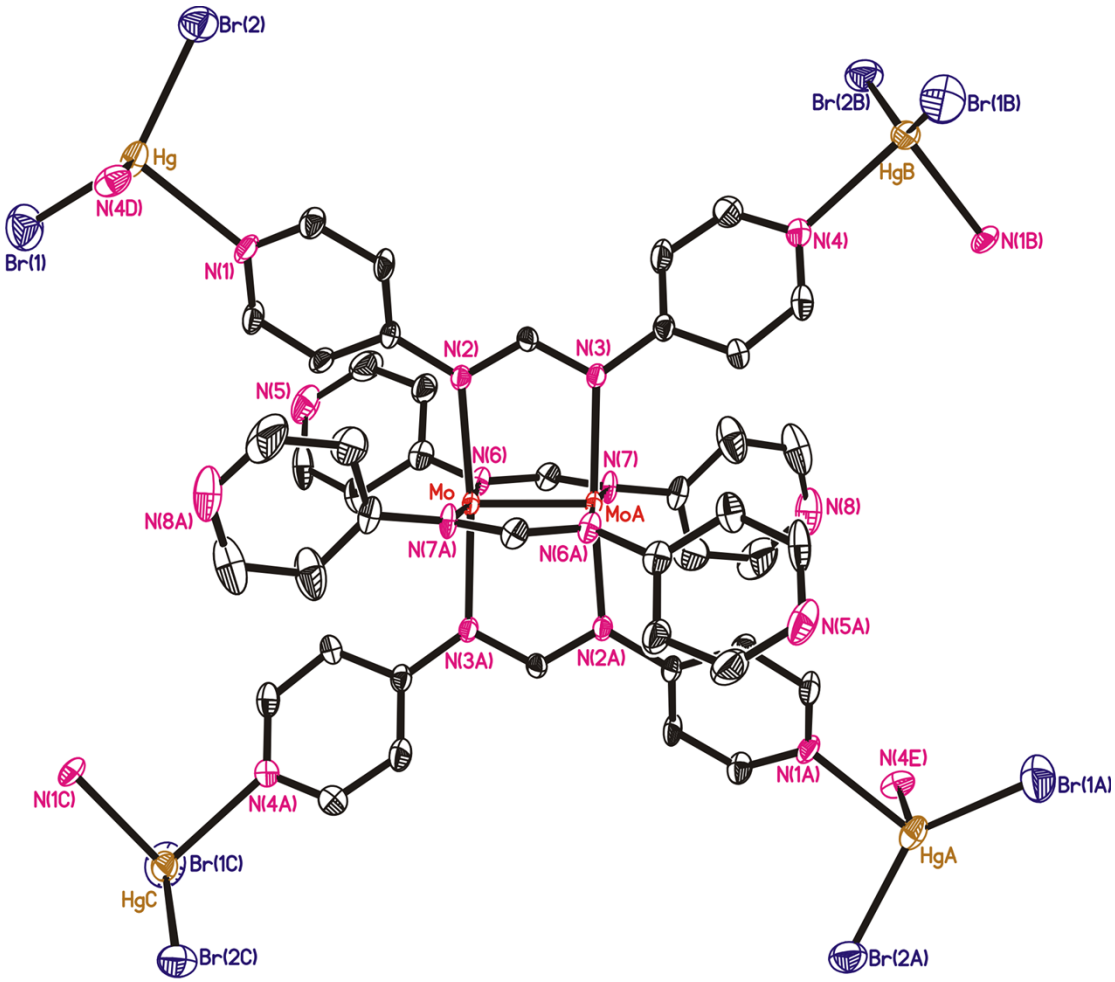


Fig. S13. An ORTEP diagram showing the coordination environments about the Mo(II) ions in **3**.

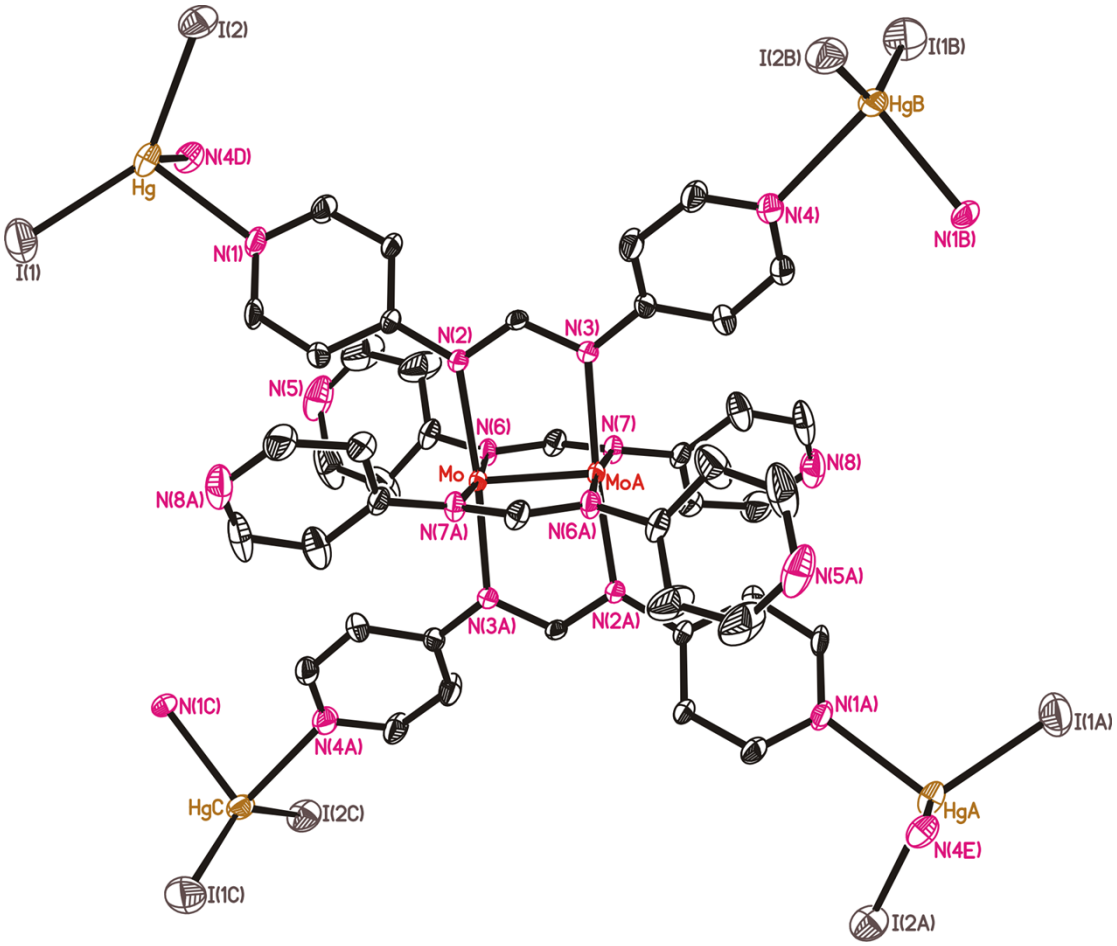


Fig. S14a. An ORTEP diagram showing the coordination environments about the Mo(II) ions in **4**. The disordered atoms are connected by the dashed lines.

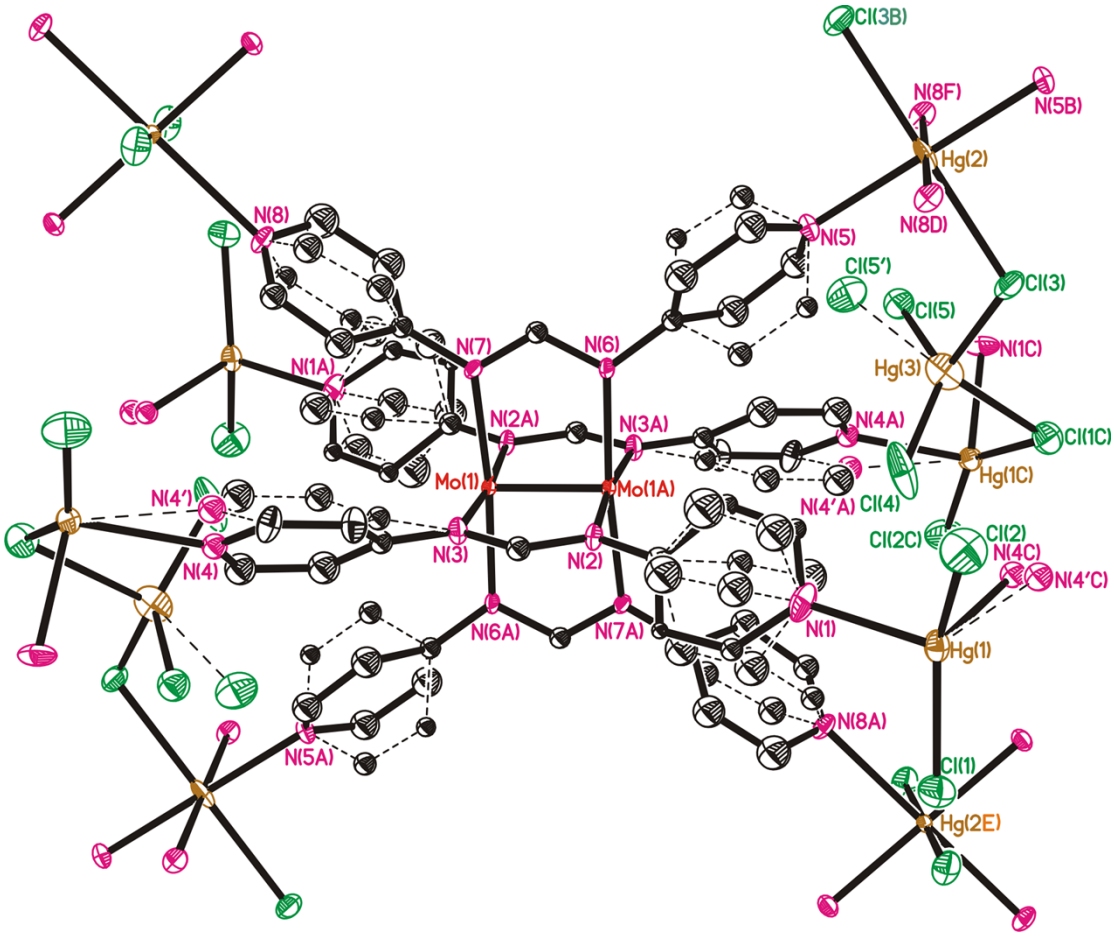
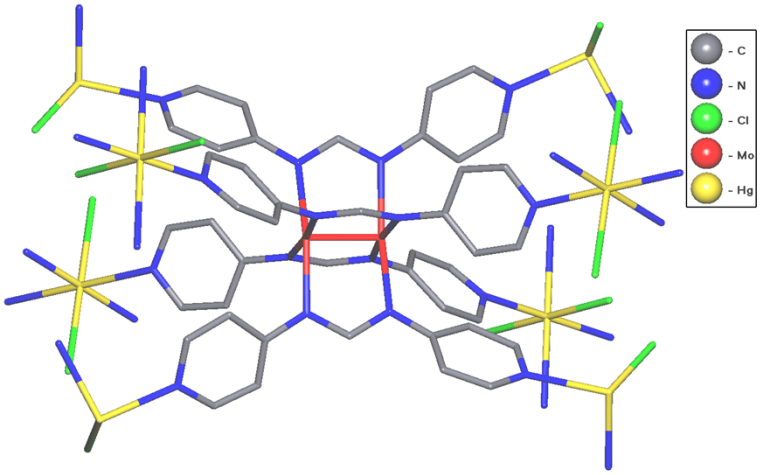
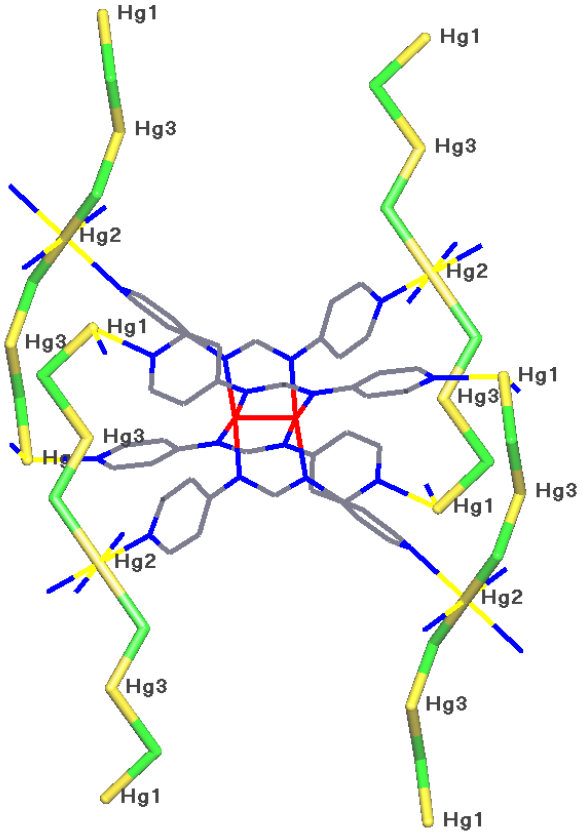


Fig. S14b. Two views of the coordination of the Mo2 dimer in **4** showing also the pentanuclear Hg chains (the disorder on N,C has been removed for better view).

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