## Supplementary Information

# Reversible single-crystal to single-crystal transformations in a Hg(II) derivative. 1D-polymeric chain ⇌ 2D-networking as a function of temperature

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**Table S1** Selected bond lengths (Å) and angles (°) for **1, 4** and **1** (Regenerated)

| Bond lengths (Å) | **1**(X=Cl) | **4** | **1**(X=Cl) **(Regenerated)** |
|---|---|---|---|
| Hg(1)-N(1) | 2.220(3) | 2.143(6) | 2.194(8) |
| Hg(1)-X(1) | 2.3629(10) | 2.316(2) | 2.353(3) |
| Hg(1)-X(2)#1 | | 2.8408(19) | |
| Hg(1)-X(2) | 2.7858(10) | 2.885(2) | 2.777(3) |
| Hg(1)-X(3) | 2.4980(10) | | 2.492(3) |
| Hg(2)-N(2) | 2.209(3) | | 2.212(8) |
| Hg(2)-X(4) | 2.3798(10) | 2.3300(18) | 2.365(3) |
| Hg(2)-X(3) | 2.7533(10) | 2.3512(19) | 2.743(3) |
| Hg(2)-X(2)#1 | 2.4987(10) | | 2.490(3) |
| Hg(2)-X(2) | | 2.756(2) | |
| Hg(2)-X(3)#2 | | 2.8575(19) | |
| Bond angles (°) | | | |
| N(1)-Hg(1)-X(1) | 133.93(10) | 157.48(17) | 133.7(3) |
| N(1)-Hg(1)-X(3) | 105.24(10) | | 105.2(3) |
| X(1)-Hg(1)-X(3) | 119.16(4) | | 119.56(11) |
| N(1)-Hg(1)-X(2) | 92.59(9) | 97.00(17) | 91.8(2) |
| N(1)-Hg(1)-X(2)#1 | | 97.47(16) | |
| X(1)-Hg(1)-X(2) | 96.43(4) | 98.59(7) | 96.59(10) |
| X(1)-Hg(1)-X(2)#1 | | 101.28(7) | |
| X(2)#1-Hg(1)-X(2) | | 79.90(6) | |
| X(3)-Hg(1)-X(2) | 93.17(3) | | 93.40(9) |
| N(2)-Hg(2)-X(4) | 133.48(9) | | 133.2(2) |
| N(2)-Hg(2)-X(2)#1 | 107.32(9) | | 107.4(2) |
| X(4)-Hg(2)-X(2)#1 | 116.57(4) | 94.71(7) | 116.84(11) |
| N(2)-Hg(2)-X(3) | 95.22(9) | | 95.1(2) |
| X(4)-Hg(2)-X(3) | 95.87(4) | 161.85(8) | 95.73(9) |
| X(3)-Hg(2)-X(2) | | 102.61(7) | |
| X(2)#1-Hg(2)-X(3) | 94.63(3) | 94.04(6) | 94.58(9) |
| Hg(2)#2-X(2)-Hg(1) | 98.14(3) | | 98.04(9) |
| Hg(1)-X(3)-Hg(2) | 96.37(3) | | 96.40(9) |
| Cl(4)-Hg(2)-Cl(3)#2 | | 96.29(6) | |
| Cl(3)-Hg(2)-Cl(3)#2 | | 87.97(6) | |
| Hg(2)-Cl(2)-Hg(1)#1 | | 127.27(7) | |
| Hg(2)-Cl(2)-Hg(1) | | 117.13(7) | |
| Hg(1)#1-Cl(2)-Hg(1) | | 100.10(6) | |
| Hg(2)-Cl(3)-Hg(2)#2 | | 92.03(6) | |

**Table S2** Selected bond lengths (Å) and angles (°) for **2** and **3**

| Bond length (Å)/ | **2(X=Br)** | **3(X=I)** |
|---|---|---|
| Hg(1)-N(1) | 2.253(8) | 2.303(7) |
| Hg(1)-X(1) | 2.4815(11) | 2.6429(6) |
| Hg(1)-X(2) | 2.9325(10) | 3.0824(6) |
| Hg(1)-X(3) | 2.5812(10) | 2.7406(6) |
| Hg(2)-N(2) | 2.246(8) | 2.285(6) |
| Hg(2)-X(4) | 2.4930(10) | 2.6528(6) |
| Hg(2)-X(3) | 2.9063(10) | 3.0591(6) |
| Hg(2)-X(2)#1 | 2.5879(10) | 2.7553(6) |
| Bond angle (°) | | |
| N(1)-Hg(1)-X(1) | 129.8(2) | 127.15(19) |
| N(1)-Hg(1)-X(3) | 105.8(2) | 105.45(19) |
| X(1)-Hg(1)-X(3) | 123.40(4) | 124.82(2) |
| N(1)-Hg(1)-X(2) | 91.2(2) | 92.38(17) |
| X(1)-Hg(1)-X(2) | 96.45(3) | 100.88(2) |
| X(3)-Hg(1)-X(2) | 91.70(4) | 91.442(18) |
| N(2)-Hg(2)-X(4) | 129.1(2) | 126.52(16) |
| N(2)-Hg(2)-X(2)#1 | 107.7(2) | 106.31(17) |
| X(4)-Hg(2)-X(2)#1 | 121.33(4) | 124.02(2) |
| N(2)-Hg(2)-X(3) | 94.64(19) | 94.97(17) |
| X(4)-Hg(2)-X(3) | 95.94(3) | 99.554(19) |
| X(2)#1-Hg(2)-X(3) | 92.48(3) | 92.301(18) |

| | | |
|---|---|---|
| Hg(2)#2-X(2)-Hg(1) | 95.10(3) | 93.438(18) |
| Hg(1)-X(3)-Hg(2) | 94.52(3) | 94.742(18) |

**Table S3** Hydrogen bonding parameters (Å, $^{o}$ ) for **1, 4** and **1** (**Regenerated**).

| D-H...A | *d*(D...H) | *d*(D...A) | *d*(H...A) | ∠D-H...A |
|---|---|---|---|---|
| | | **1** | | |
| O1-H01A...O2(#1) | 0.840(4) | 2.665(6) | 1.879(4) | 153.14(30) |
| O2-H02A...O1(#1) | 0.840(4) | 2.665(6) | 1.919(4) | 145.59(29) |
| C7-H7A...Cl4(#0) | 0.990(4) | 3.672(4) | 2.768(1) | 152.10( 26) |
| C14-H14B...Cl1(#2) | 0.990(4) | 3.640(4) | 2.753(1) | 149.37( 25) |
| C4-H4...Cl1(#3) | 0.950(5) | 3.563(5) | 2.817(1) | 136.14(28) |
| C11-H11...Cl4(#4) | 0.950(4) | 3.551(4) | 2.841(1) | 132.43(26) |
| C6-H6A...O2(#5) | 0.990(4) | 3.708(6) | 2.724(4) | 172.23(26) |
| C13-H13B...O1(#4) | 0.990(4) | 3.646(5) | 2.665(4) | 170.94(25) |
| C2-H2...Cl3(#6) | 0.950(4) | 3.791(4) | 2.864(1) | 165.48(30) |
| | | **4** | | |
| O1-H101...Cl4 #1 | 0.840(9) | 2.522(2) | 3.288(9) | 152.13(50) |
| C4-H4...Cl1#2 | 0.950(7) | 2.964(2) | 3.584(8) | 124.08(50) |
| C4-H4...Cl3#2 | 0.950(7) | 2.984(2) | 3.815(8) | 146.82(54) |
| C7-H7B...Cl4#3 | 0.990(11) | 2.825(2) | 3.738(10) | 153.53(62) |
| | | **1 Regenerated** | | |
| O1-H01A...O2(#1) | 0.840(10) | 2.655(15) | 2.091(10) | 124.13(70) |
| O2-H102...O1(#1) | 0.840(8) | 2.655(14) | 2.183(10) | 115.5168) |
| C7-H7A...Cl4(#0) | 0.990(11) | 3.684(11) | 2.772(3) | 153.33(64) |
| C14-H14B...Cl1(#2) | 0.990(11) | 3.620(11) | 2.718(3) | 151.63(68) |
| C4-H4...Cl1(#3) | 0.950(14) | 3.575(16) | 2.826(3) | 136.46(89) |

| | | | | |
|---|---|---|---|---|
| C11-H11...Cl4(#4) | 0.950(9) | 3.557(10) | 2.849(3) | 132.19(60) |
| C6-H6A...O2(#5) | 0.990(10) | 3.733(15) | 2.749(10) | 172.59(65) |
| C13-H13B...O1(#4) | 0.990(10) | 3.651(13) | 2.670(9) | 171.12(66) |
| C2-H2...Cl3(3) (#6) | 0.950(11) | 3.800(12) | 2.871(2) | 165.91(82) |

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**Symmetry ;**

For **1** and **1 Regenerated:**

x, y, z (#0)

-x+1,-y,-z(#1)

x+1,+y,+z(#2)

x,+y+1,+z(#3)

x,+y-1,+z(#4)

x-1,+y+1,+z(#5)

-x+1, -y+1, -z+1 (#6)

For **4:** x+1,+y,+z(#1)

x,+y-1,+z(#2)

-x+1,-y+1,-z+2(#3)

Short contacts for **1**

2.6551 (50) O1 - O2_$2

2.7021 (82) O1 - O1_$1

2.6551 (50) O2 - O1_$2

2.7026 (75) O2 - O2_$3

Short contacts for **1 Regenerated**

2.6547 (123)  O1 - O2_$2

2.6841 (189)  O1 - O1_$1

2.6547 (124)  O2 - O1_$2

2.6869 (197)  O2 - O2_$3

Symmetry:

$1 -X, -Y+1, -Z

$2 -X+1, -Y, -Z

$3 -X+1, -Y-1, -Z

**Table S4** Hydrogen bonding parameters (Å, $^{o}$ ) for **2** and **3**

| D-H...A | *d*(D...H) | *d*(D...A) | *d*(H...A) | ∠D-H...A |
|---|---|---|---|---|
| | | **2** | | |
| O1-H01A...O2(#1) | 0.840(9) | 2.701(13) | 1.968(9) | 145.31(63) |
| O2-H02A...O1(#1) | 0.840(4) | 2.701(13) | 1.964(9) | 146.06(65) |
| C7-H7A...Br4(#0) | 0.990(10) | 3.777(10) | 2.871(1) | 152.59(60) |
| C14-H14B...Br1(#2) | 0.990(9) | 3.726(9) | 2.832(1) | 150.54( 56) |
| C4-H4...Br1(#3) | 0.950(13) | 3.752(12) | 2.980(1) | 139.32(71) |
| C11-H11...Br4(#4) | 0.950(9) | 3.719(10) | 2.986(1) | 134.95(62) |
| C6-H6A...O2(#5) | 0.990(10) | 3.791(13) | 2.804(9) | 173.19(61) |
| C13-H13B...O1(#4) | 0.990(4) | 3.689(12) | 2.704(8) | 173.14(58) |
| | | **3** | | |
| O1-H01A...O2(#1) | 0.840(7) | 2.718(10) | 2.018(7) | 140.43(51) |
| O2-H02B...O1(#1) | 0.840(7) | 2.718(10) | 1.954(7) | 150.86(52) |
| C7-H7A...I4 (#0) | 0.990(4) | 3.672(4) | 2.769(1) | 151.89( 26) |
| C14-H14B...I1(#2) | 0.990(4) | 3.640(4) | 2.754(1) | 149.22( 25) |
| C4-H4...I1(#3) | 0.950(5) | 3.563(5) | 2.817(1) | 136.14(28) |
| C11-H11...I4(#4) | 0.950(4) | 3.551(4) | 2.840(1) | 132.43(26) |
| C6-H6A...O2(#5) | 0.990(9) | 3.938(11) | 2.954(7) | 172.35(51) |
| C13-H13B...O1(#4) | 0.990(7) | 3.843(10) | 2.861(6) | 171.20(48) |

**Symmetry ;**

For **2-3:**

x, y, z (#0)

-x+1,-y,-z(#1)

x+1,+y,+z(#2)

x,+y+1,+z(#3)

x,+y-1,+z(#4)

x-1,+y+1,+z(#5)

Short contacts for **2**

3.6622 (15) Br3...Br3_$4

2.7015 (109) O1 - O2_$2

2.7252 (159) O1 - O1_$1

2.7015 (109) O2 - O1_$2

2.7138 (180) O2 - O2_$3

Short contacts for **3**

3.8156 (7) I3...I3_$4

2.7185 (95) O1 - O2_$2

2.7415 (132) O1 - O1_$1

2.7185 (95) O2 - O1_$2

2.7236 (138) O2 - O2_$3

Symmetry:

$1 -X, -Y+1, -Z

$2 -X+1, -Y, -Z

$3 -X+1, -Y-1, -Z

$4 -x+1,-y,-z+1

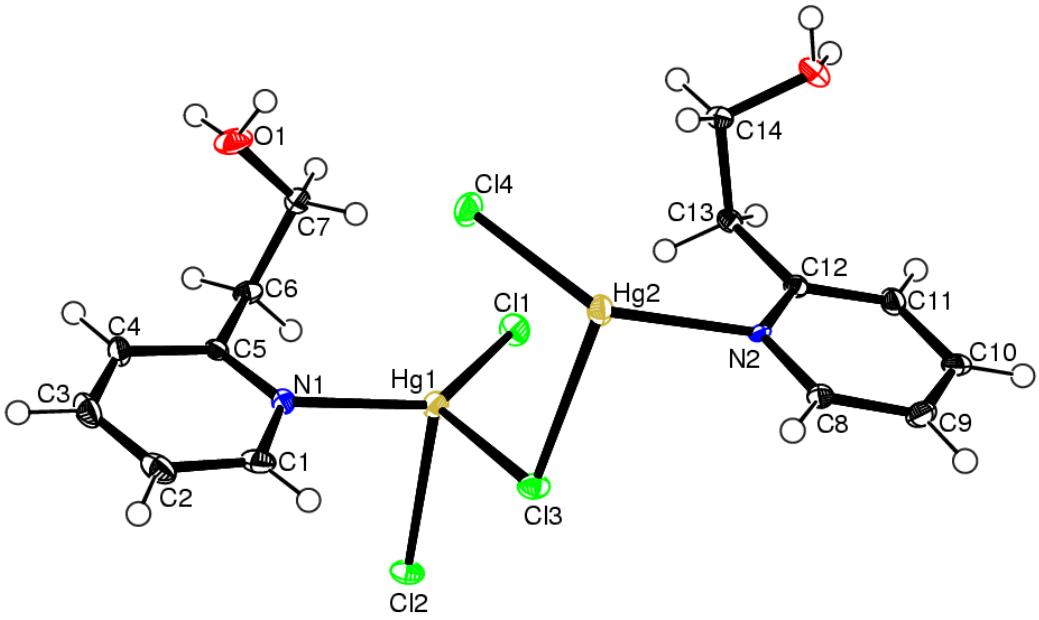


**Fig. S1** ORTEP drawing of **1** showing the molecule in the asymmetric unit with anisotropic displacement parameters are drawn at 50% probability.

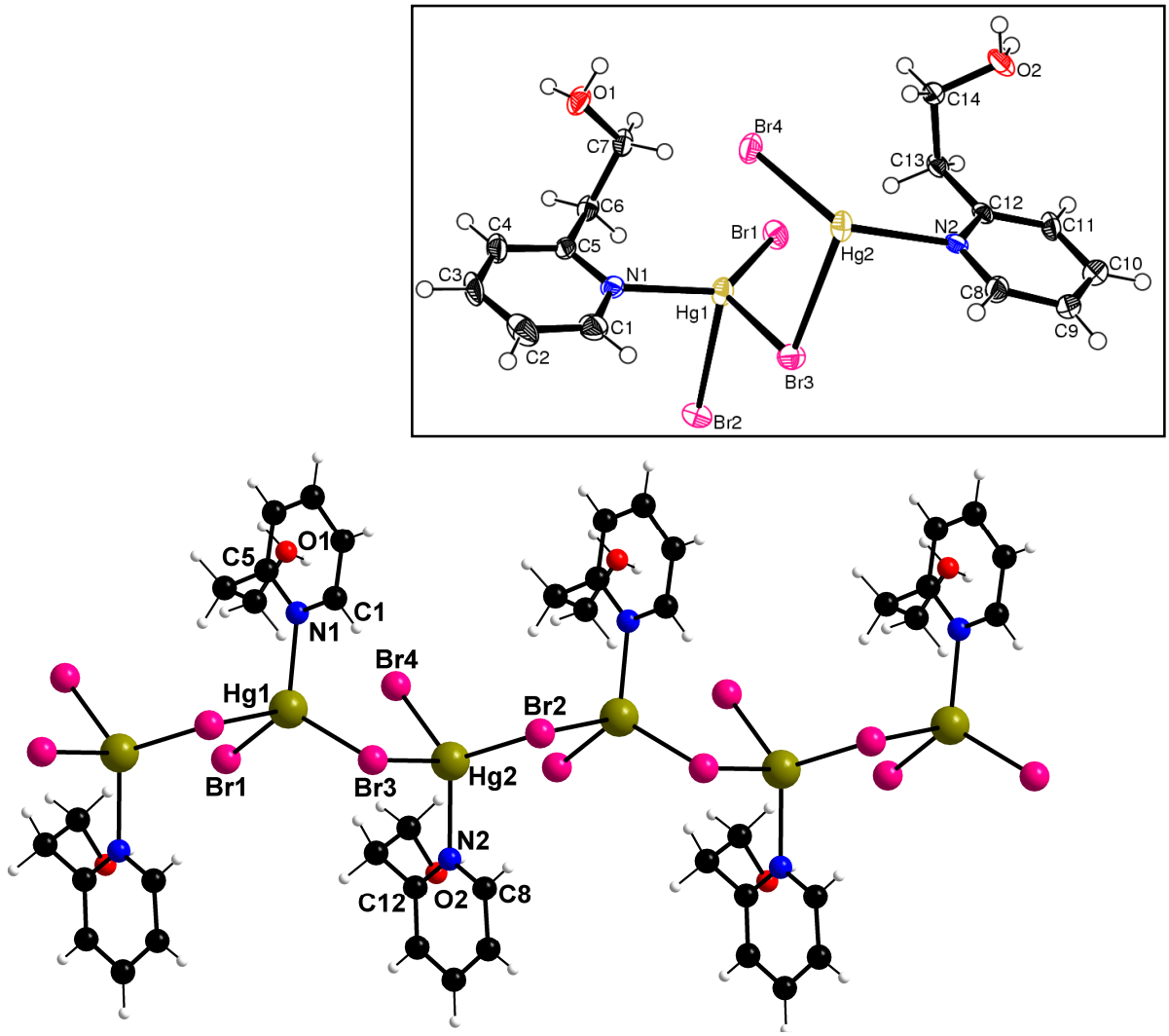


**Fig. S2** Perspective view of the 1D-coordination polymeric chain in **2**. Insert shows the ORTEP drawing of **2** showing the molecule in the asymmetric unit with anisotropic displacement parameters are drawn at 50% probability.

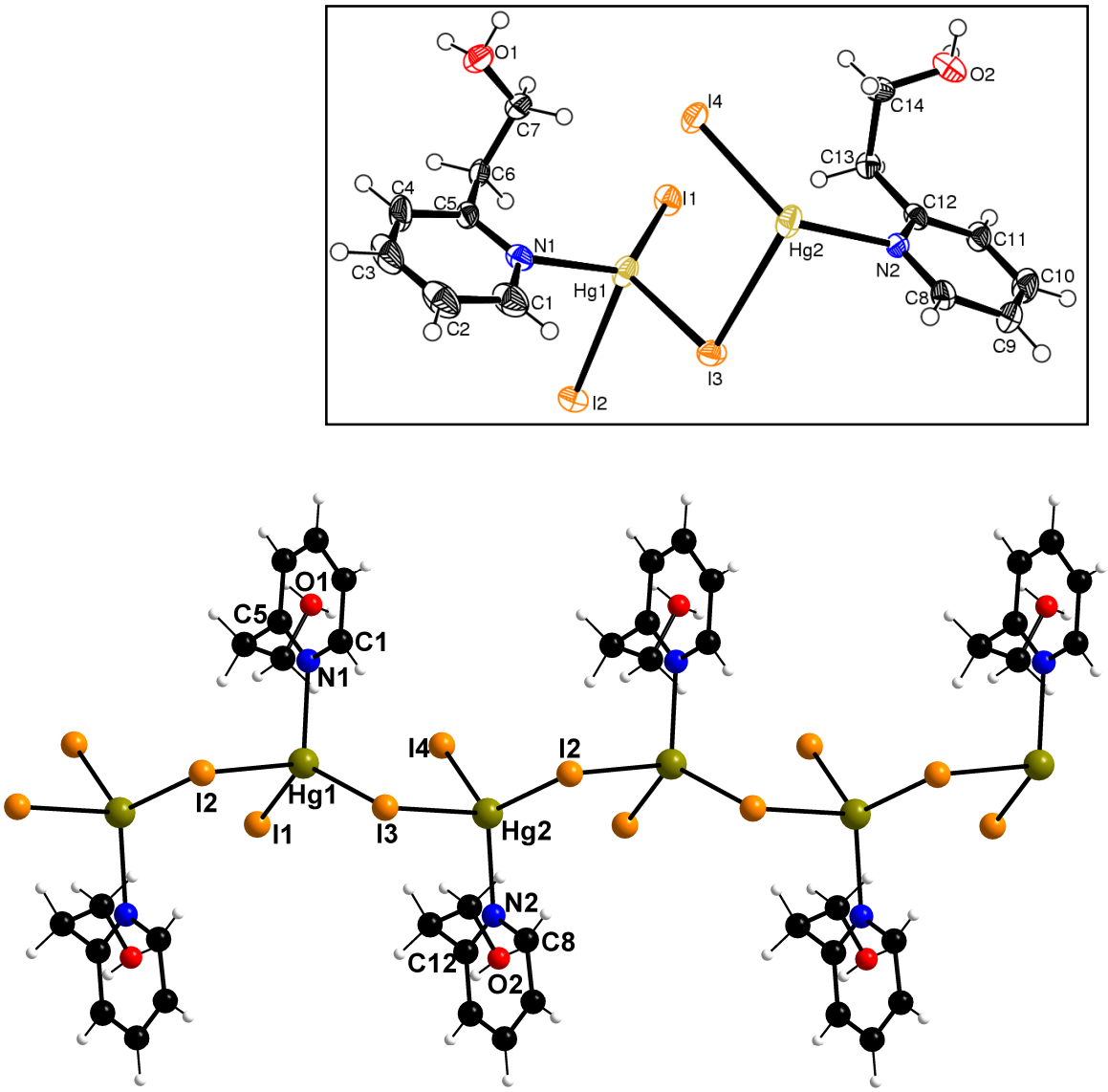


**Fig. S3** Perspective view of the 1D-coordination polymeric chain in **3**. Insert shows the ORTEP drawing of **3** showing the molecule in the asymmetric unit with anisotropic displacement parameters are drawn at 50% probability.

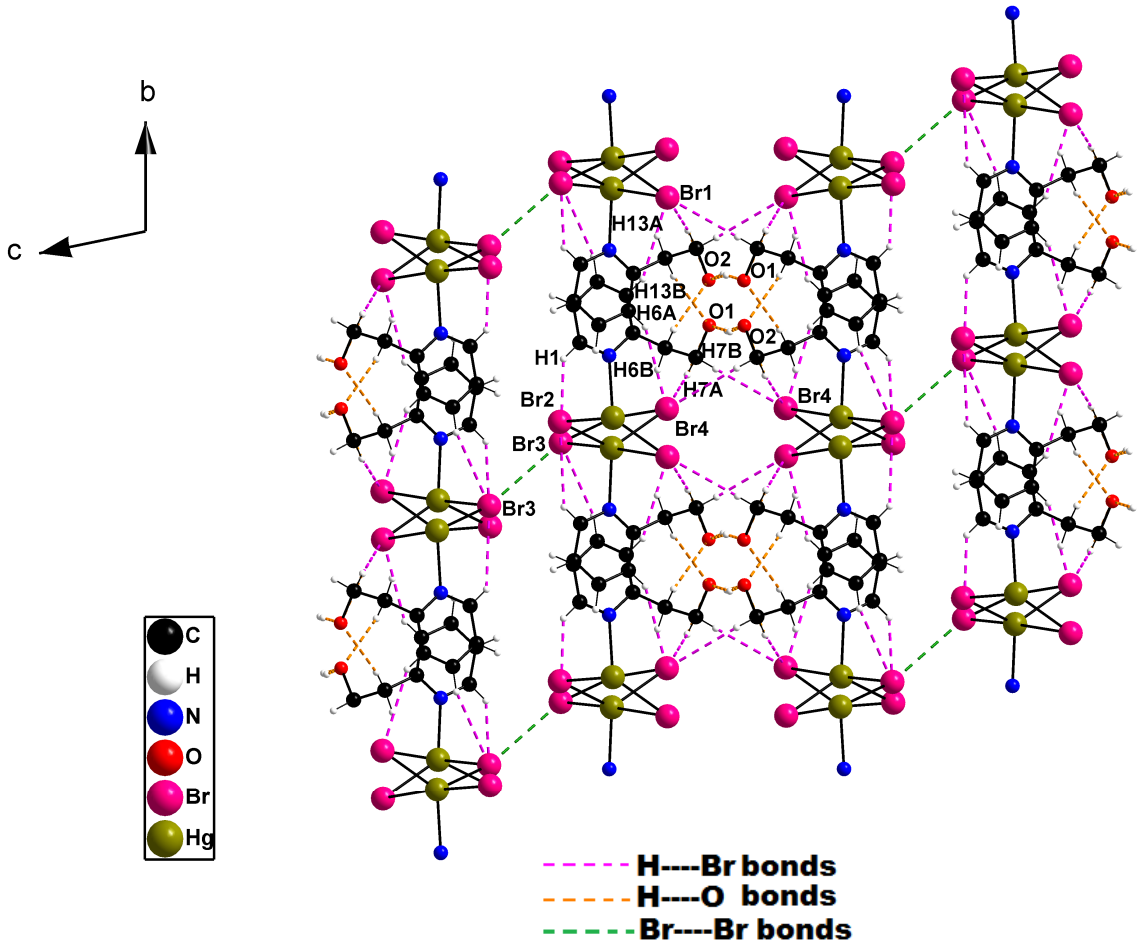


**Fig. S4** Packing diagram of the hydrogen bonded 2D network in **2** along the *a*-axis.

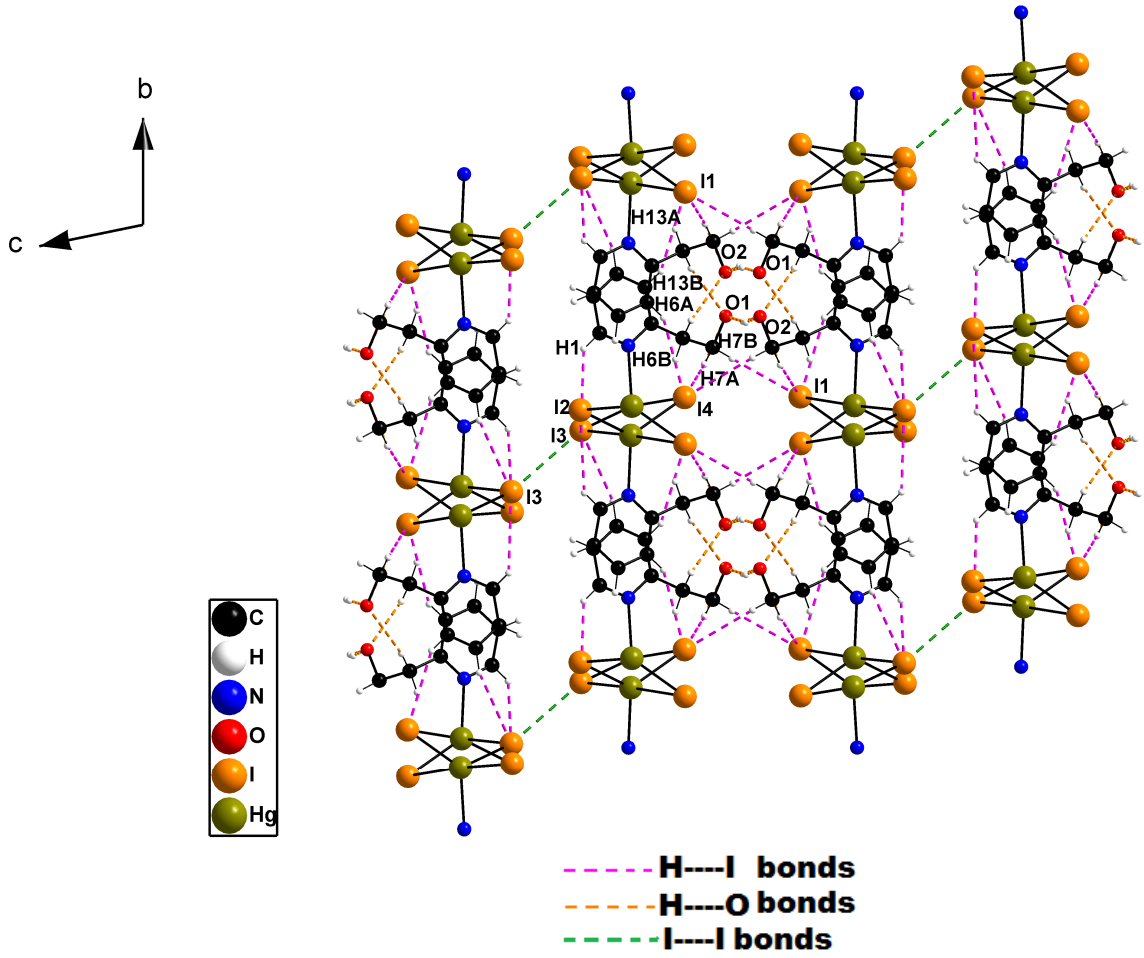


**Fig. S5** Packing diagram of the hydrogen bonded 2D network in **3** along the *a*-axis.

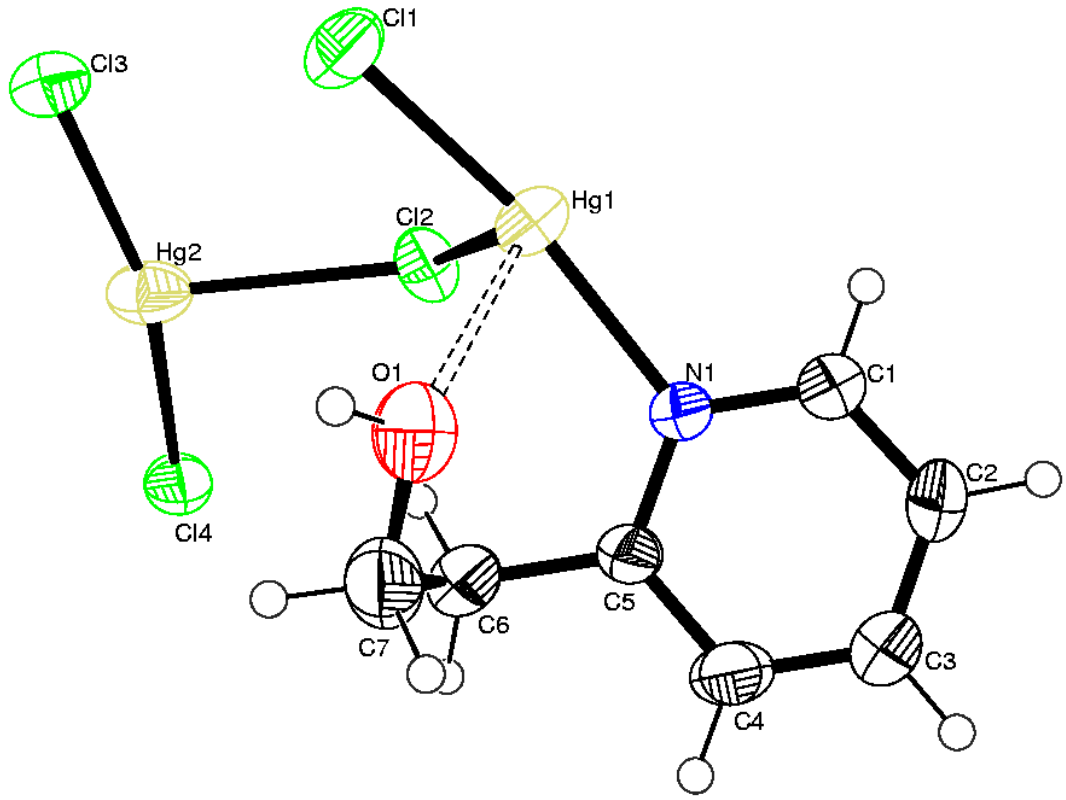


**Fig. S6** ORTEP drawing of **4** showing the molecule in the asymmetric unit with anisotropic displacement parameters are drawn at 50% probability.

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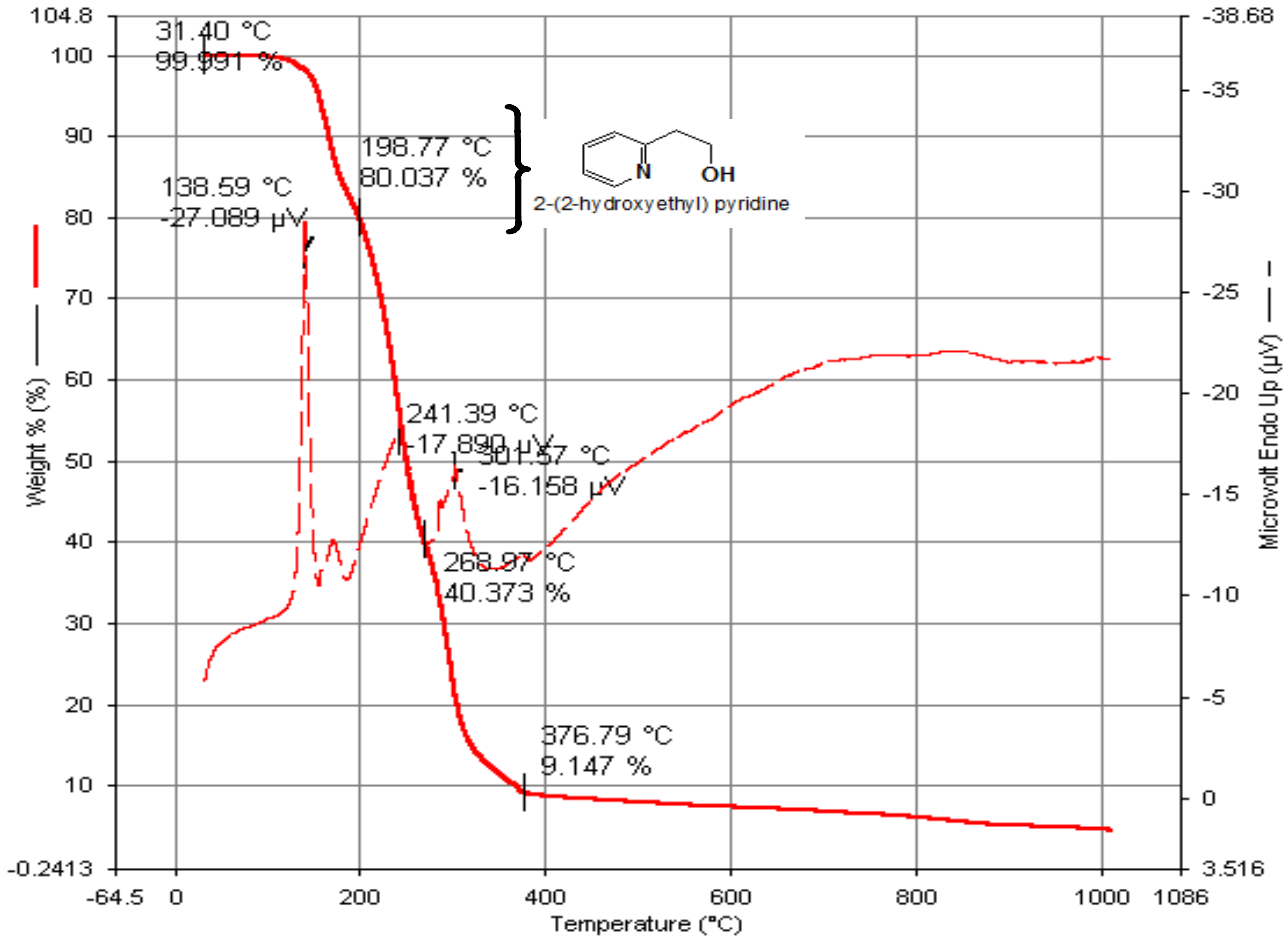
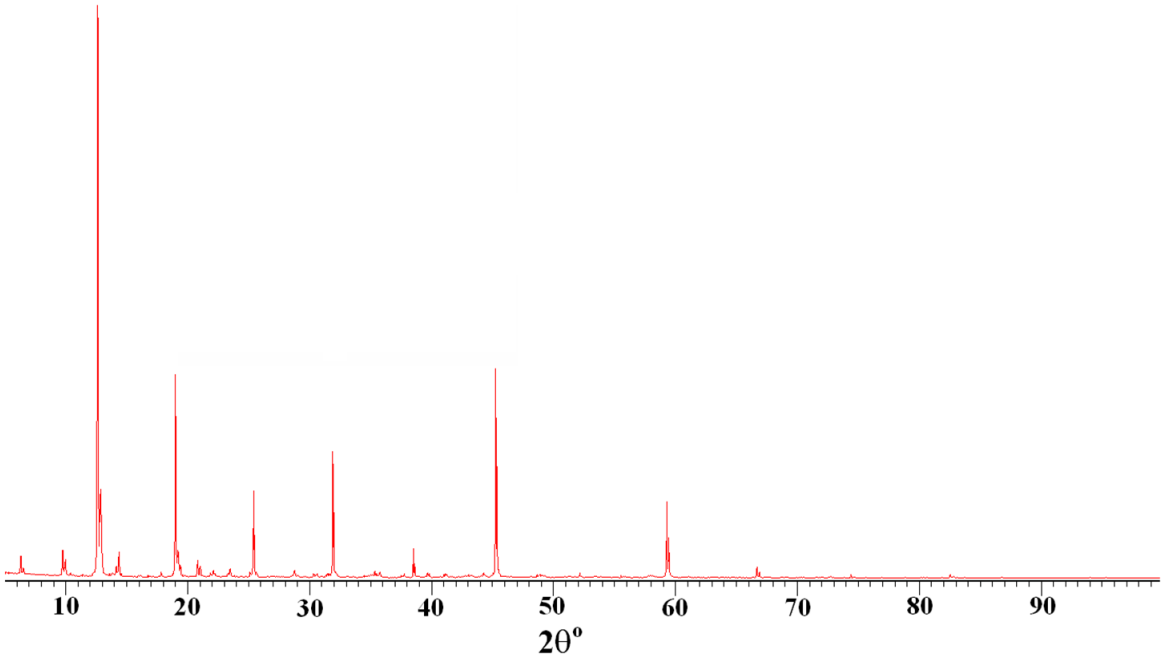



**Fig. S7** TGA of **1**, revealing initial 18% loss corresponds to the removal of hep-H ligand.

(a)




(b)

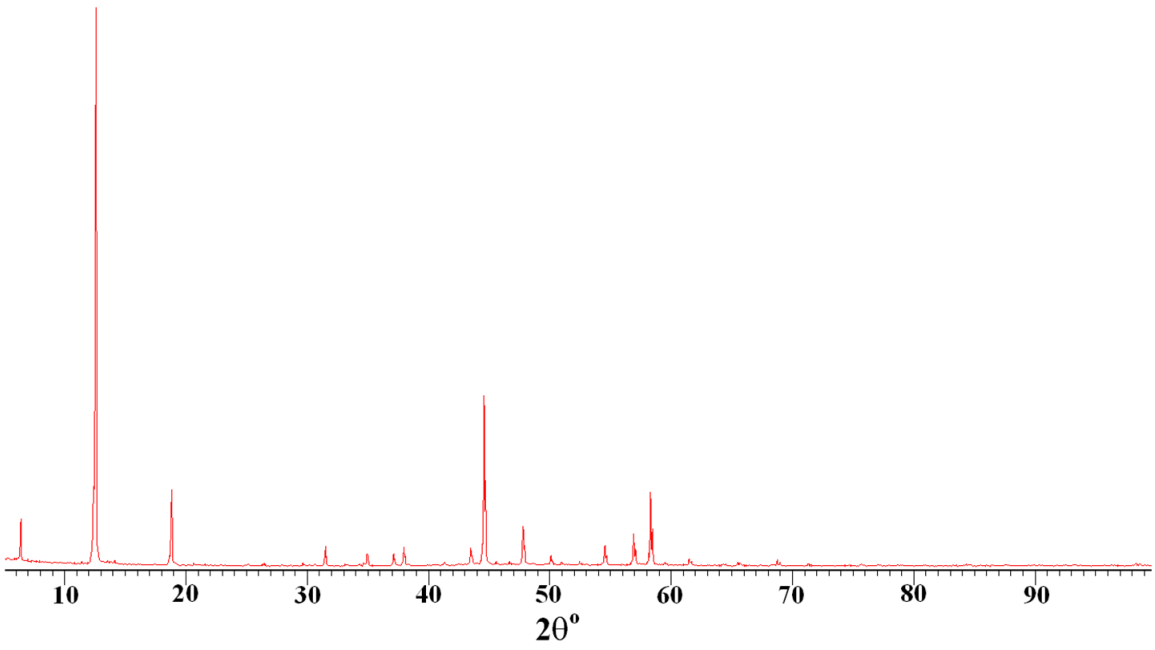



**Fig. S8** Powder XRD patterns for (a) **1** and (b) **2**.

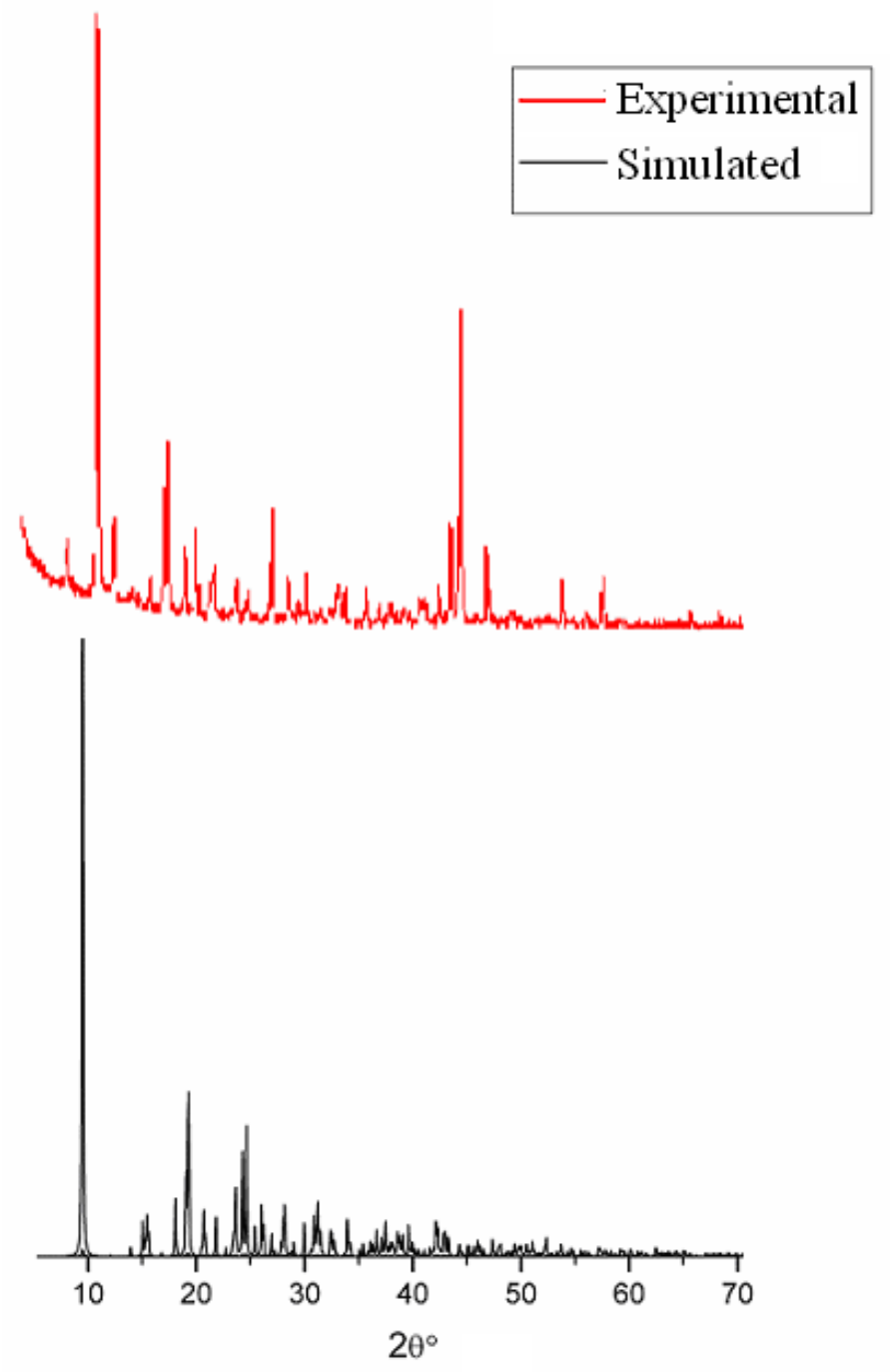



**Fig. 9** Powder XRD patterns for **4** simulated (black) and experimental (red).

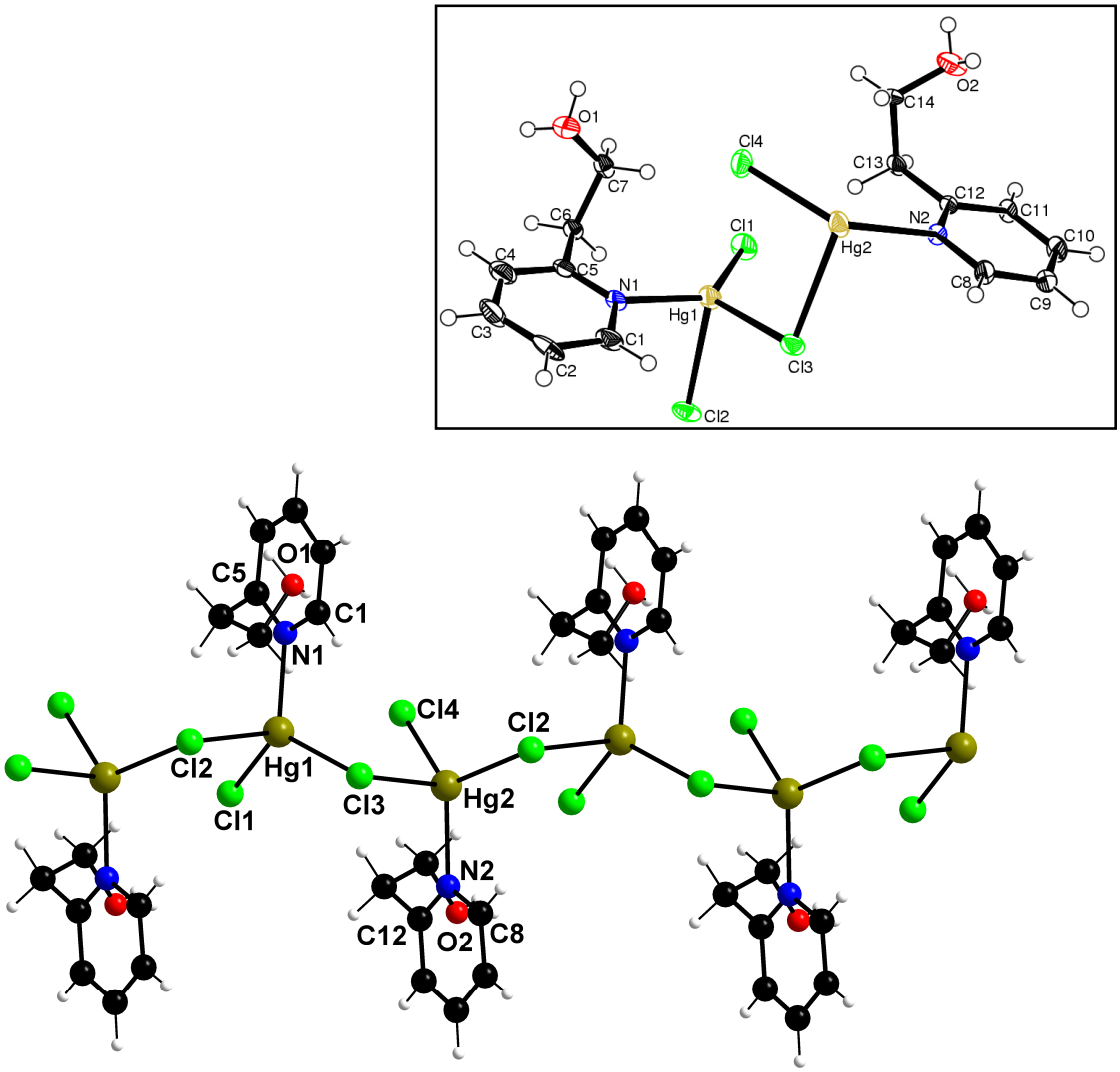
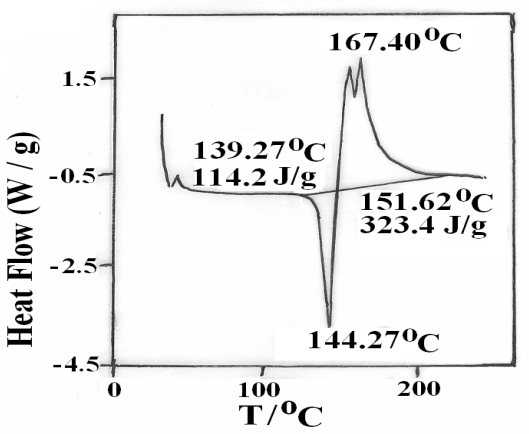
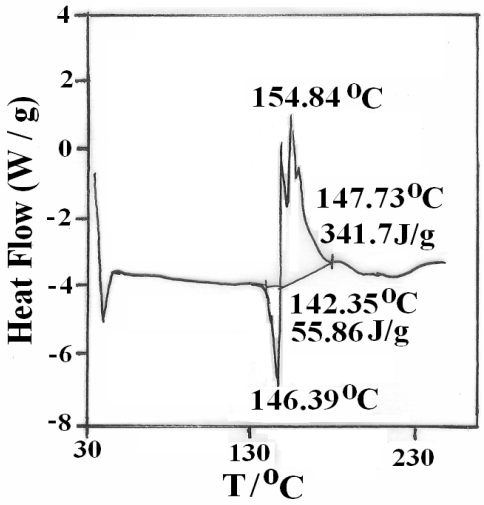



**Fig. S10** Perspective view of the 1D-coordination polymeric chain in **1-Regenerated**. Insert shows the ORTEP drawing of **1-Regenerated** showing the molecule in the asymmetric unit with anisotropic displacement parameters are drawn at 50% probability.

(a)




(b)




(c)

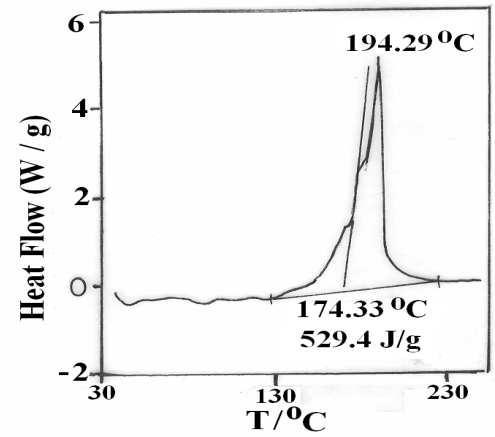



**Fig. S11** DSC: (a) **1**, (b) **2** and (c) **4**.