Electronic Supplementary Information

Controlling pseudopolymorphism *via* robust and repetitive solvent-containing supramolecular interactions in urea-based isostructural coordination polymers

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List of Supporting Information provided in this file

Synthesis of 1,3-di(pyridin-4-yl)urea (4bpu) ligand:

The **4bpu** ligand was synthesized according to the reported procedure.[1] Isonicotinic acid hydrazide (3 mmol, 410 mg) was dissolved in 10 ml 25% aq. HCl at 0 °C and $NaNO_2$ (5 mmol, 350 mg) dissolved in 5 mL ice cold water was added to it with stirring. Stirring was continued for 1 h, maintaining the temperature below 5 °C. The solution was neutralized by adding solid Na_2CO_3 and extracted with 65 ml toluene. The organic extracts were dried over Na_2SO_4 and filtered. 4-aminopyridine (3 mmol, 282 mg) was added to the filtrate and refluxed for 12 h. The precipitate was filtered and dried to afford **4bpu** in 70% yield. mp: 206-208 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) (Fig. S1a): δ= 7.47(d, 4H), 8.42(d, 4H), 9.36(s, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) (Fig. S1b): δ= 122.97, 146.45, 150.70, 152.26. IR data (KBr pellet, cm^{-1}) (Fig. S2): 3402(m), 3079(m), 1940(w), 1831(w), 1739(s), 1640(m), 1604(s), 1586(s), 1537(m), 1517(s), 1496(m), 1423(m), 1335(m), 1325(m), 1286(m), 1245(m), 1191(m), 1004(m), 898(w), 828(s), 791(m), 737(m), 657(w), 645(w), 527(s).

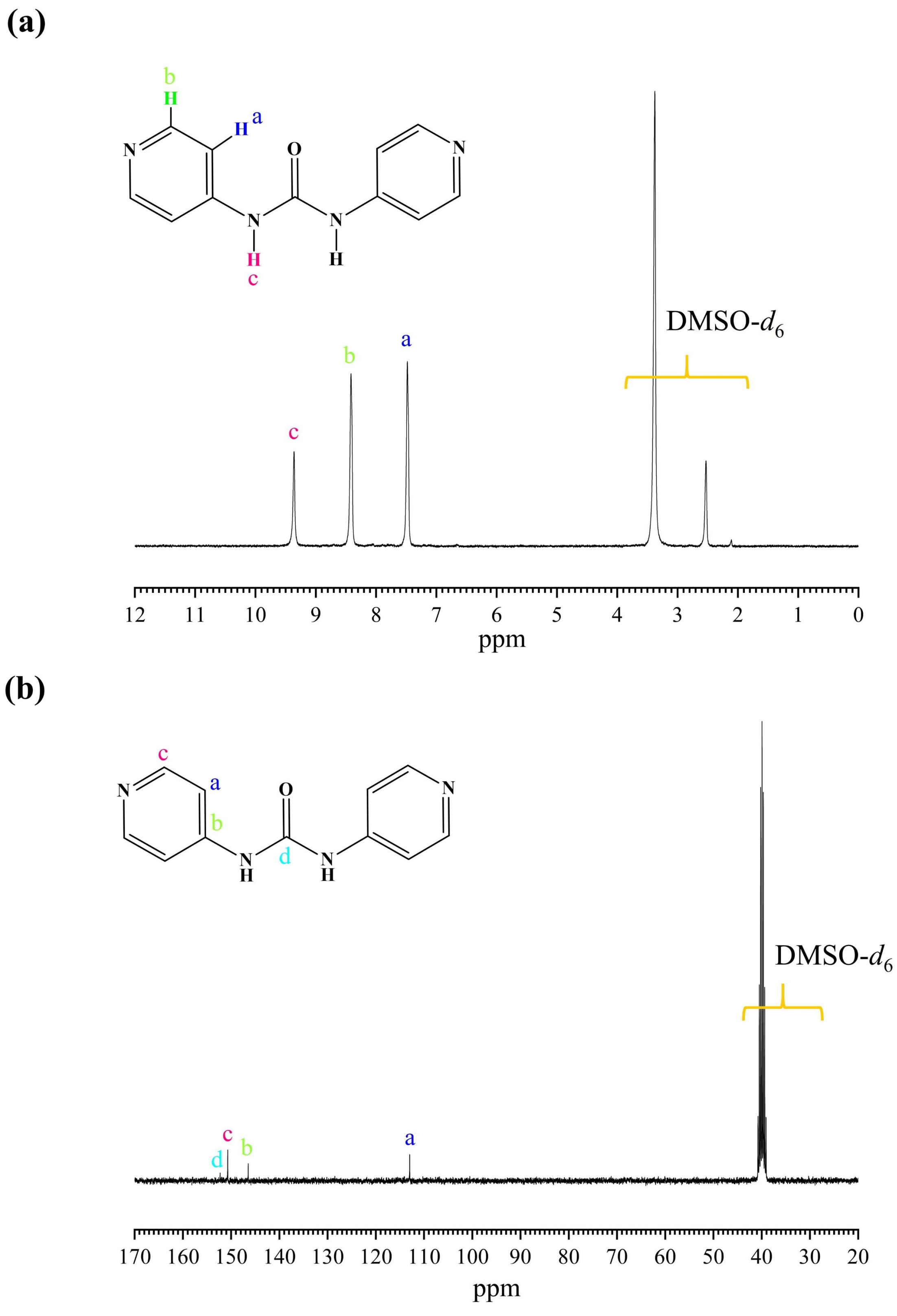


Fig. S1 (a) ^{1}H NMR spectrum of **4bpu** in DMSO-d_6, 300 MHz and

(b) ^{13}C NMR spectrum of **4bpu** in DMSO-d_6, 75 MHz.

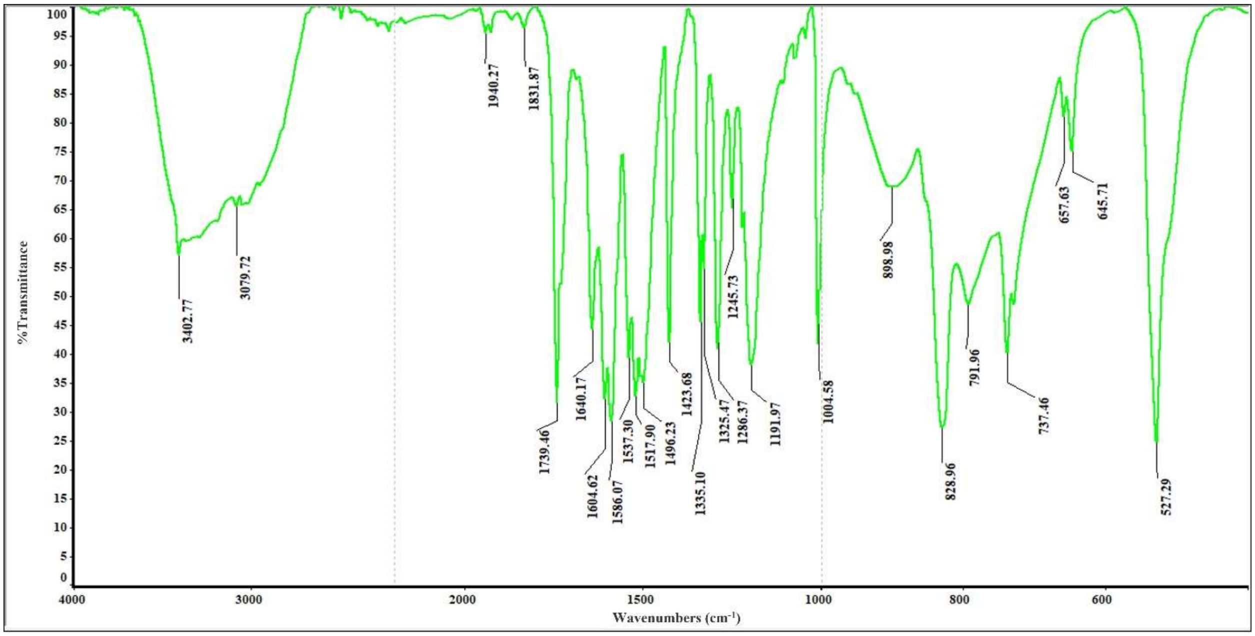


Fig. S2 FT-IR spectrum of **4bpu** ligand in KBr pellet.

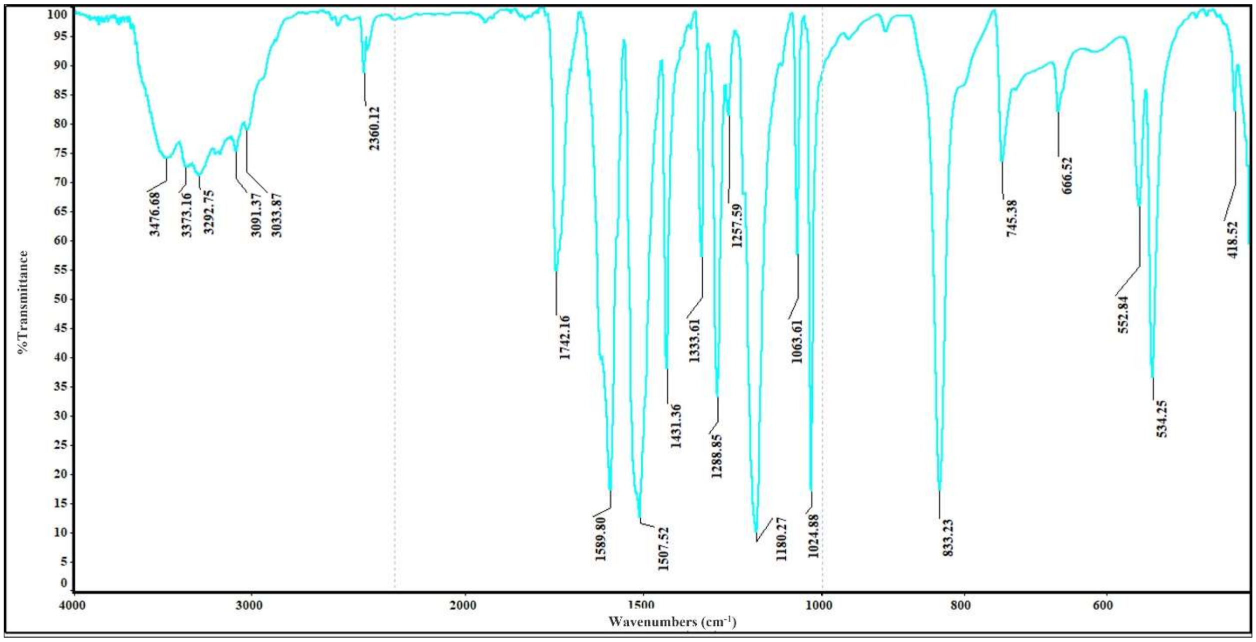


Fig. S3 FT-IR spectrum of **Zn-MeOH** in KBr pellet.

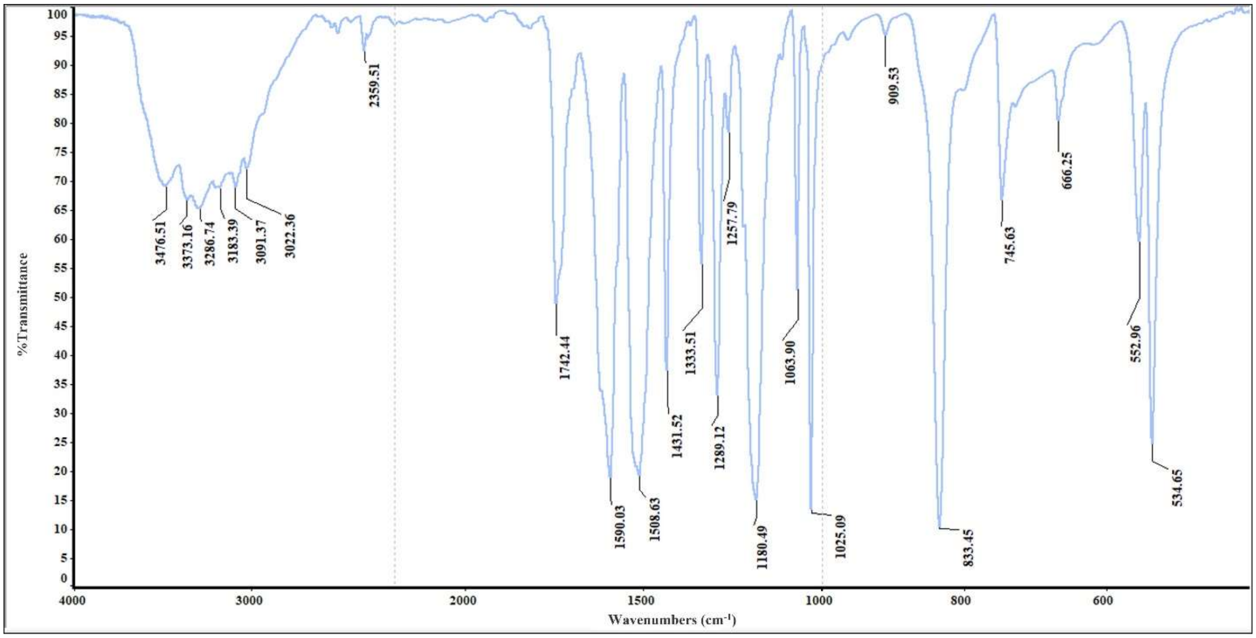


Fig. S4 FT-IR spectrum of **Zn-EtOH** in KBr pellet.

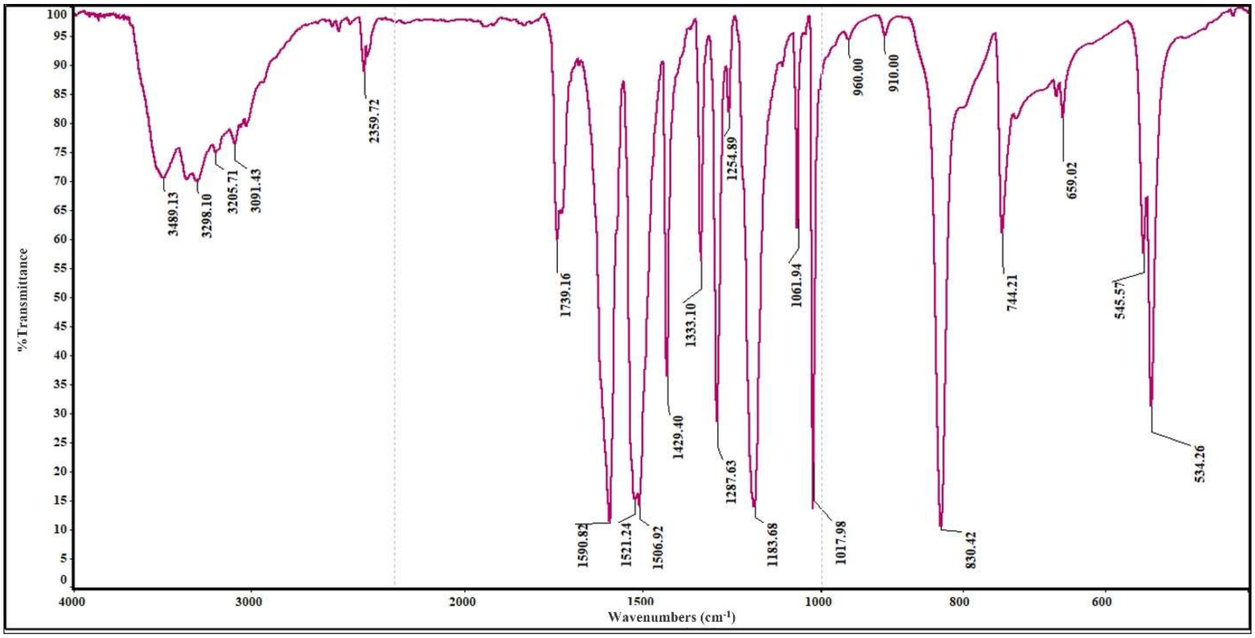


Fig. S5 FT-IR spectrum of **Cd-MeOH** in KBr pellet.

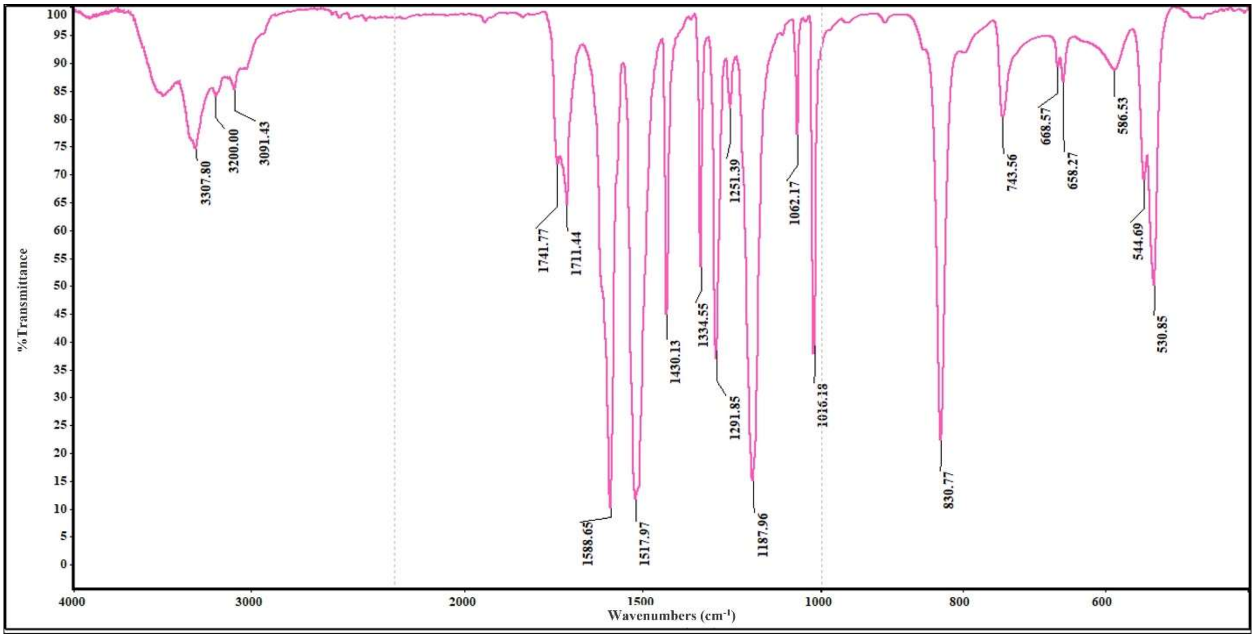


Fig. S6 FT-IR spectrum of **Cd-EtOH** in KBr pellet.

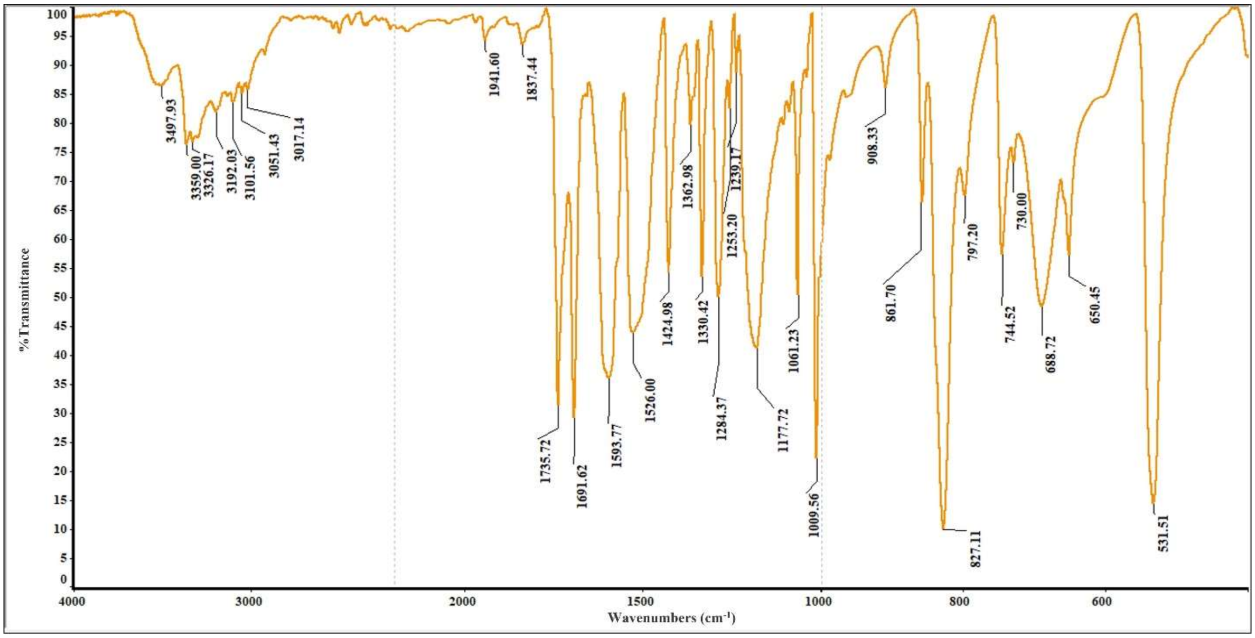


Fig. S7 FT-IR spectrum of **Hg-MeOH** in KBr pellet.

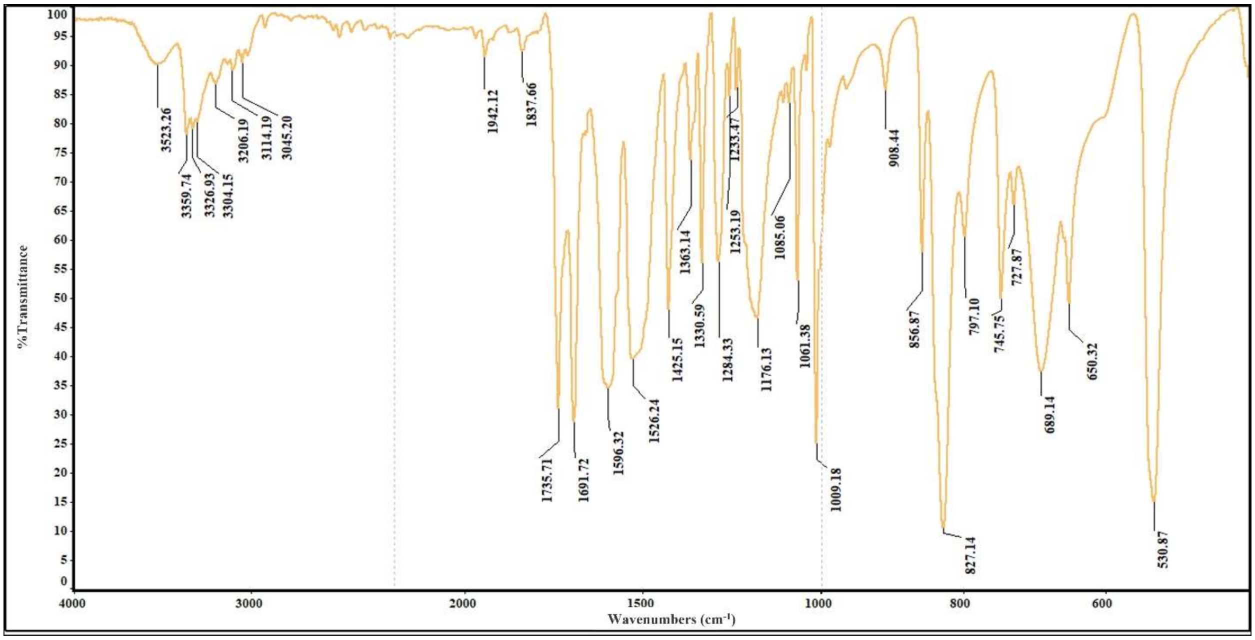


Fig. S8 FT-IR spectrum of **Hg-EtOH** in KBr pellet.

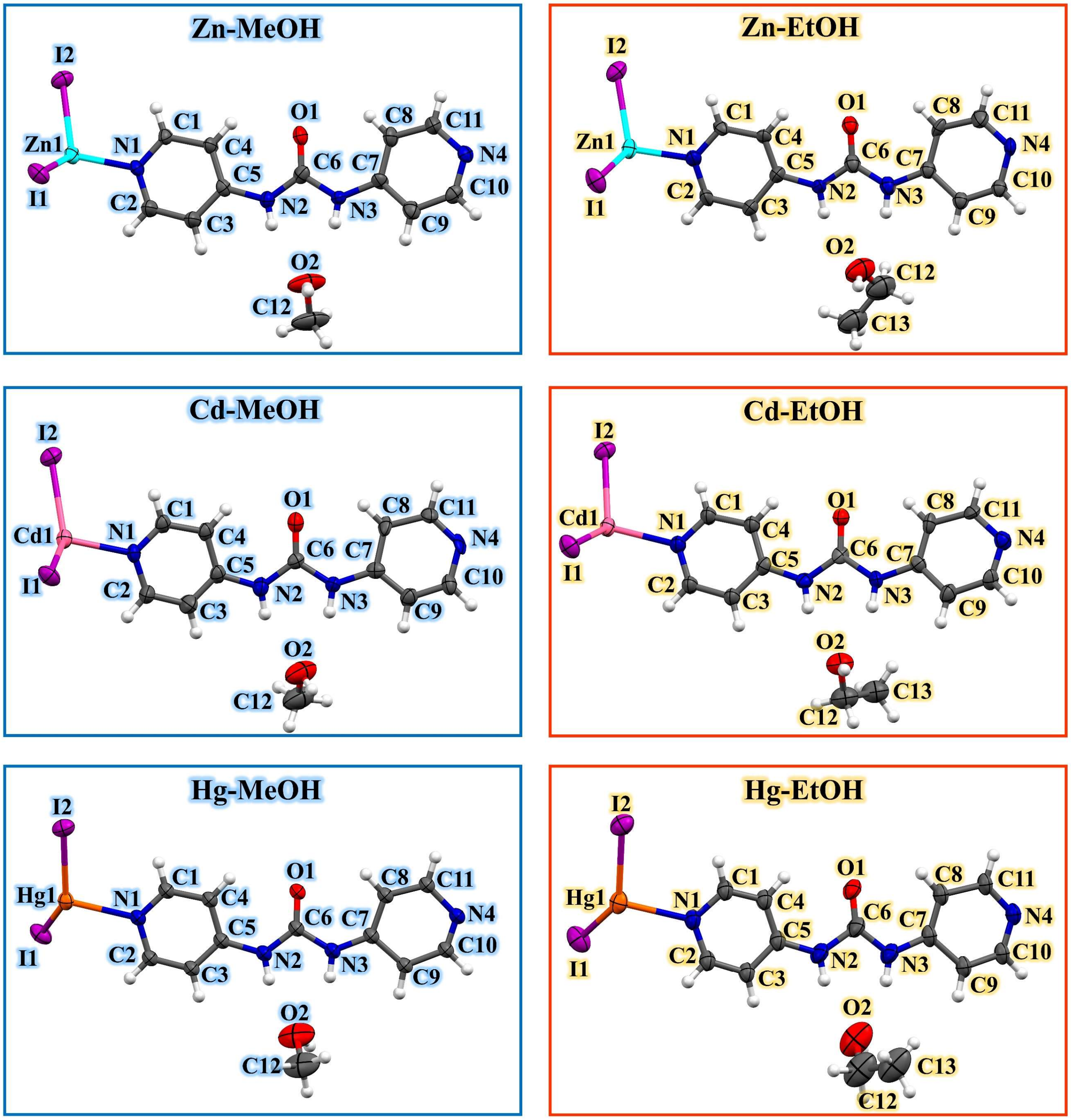


Fig. S9 ORTEP diagram of the coordination environment around metal centers with atom labeling scheme in compounds **M-MeOH** and **M-EtOH** (M= Zn, Cd and Hg). Thermal ellipsoids are at the 30% probability level. Color code: Zn, light blue; Cd, pink; Hg, orange; O, red; N, blue; C, grey; I, purple and H, white.

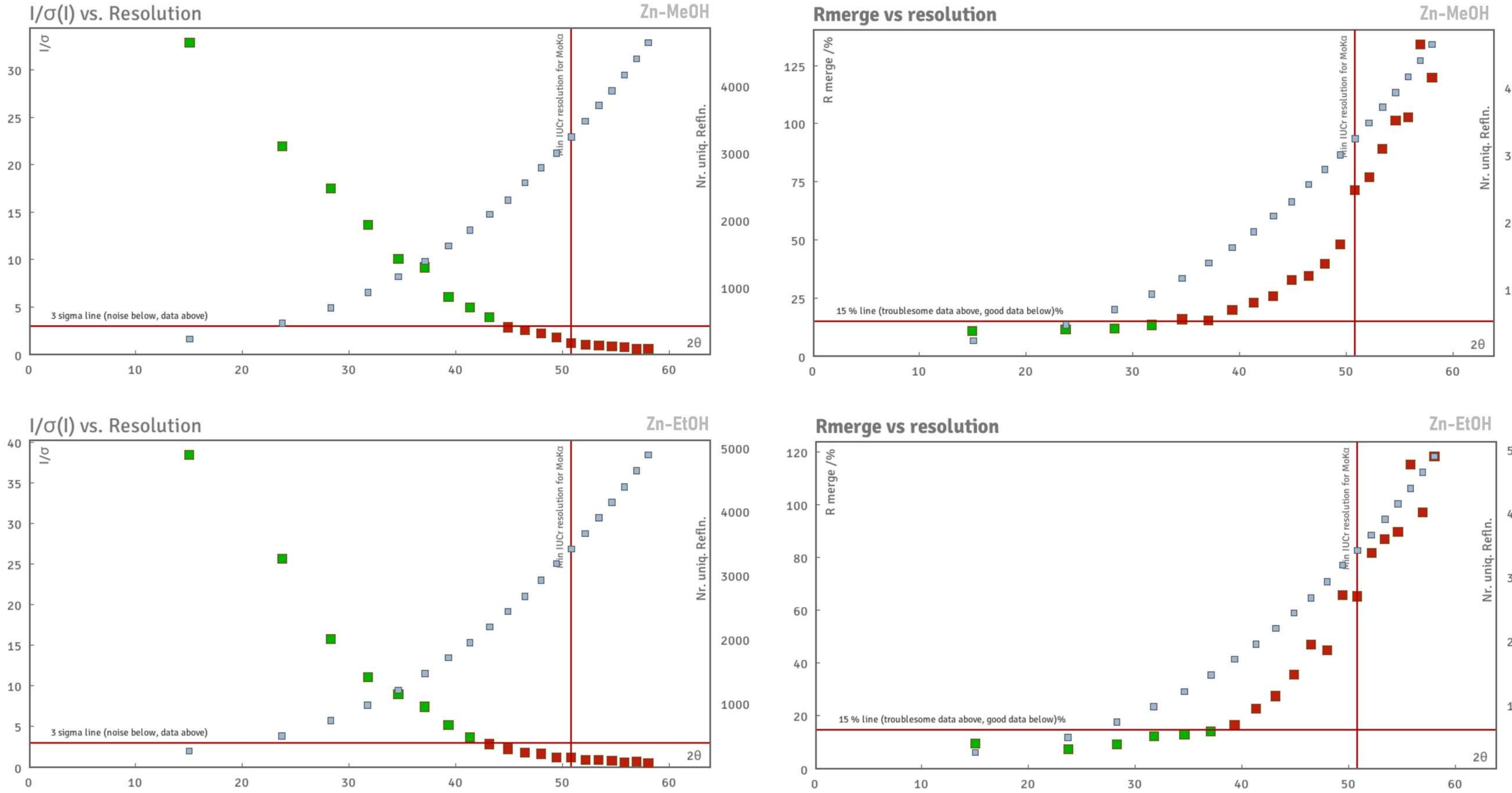


Fig. S10 I/σ(I) vs. Resolution and Rmerge vs. Resolution plots for **Zn-MeOH** and **Zn-EtOH**.

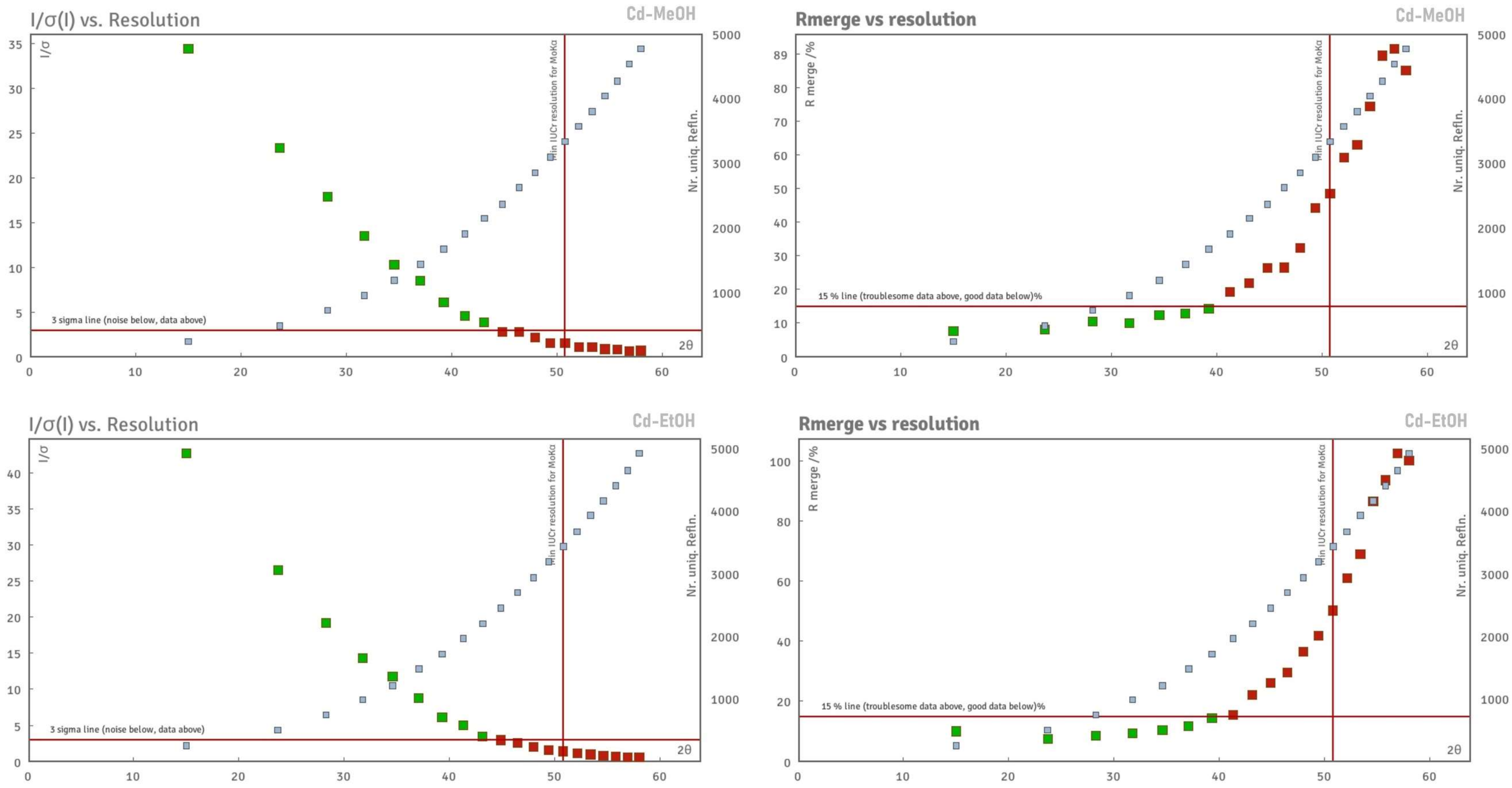


Fig. S11 I/σ(I) vs. Resolution and Rmerge vs. Resolution plots for **Cd-MeOH** and **Cd-EtOH**.

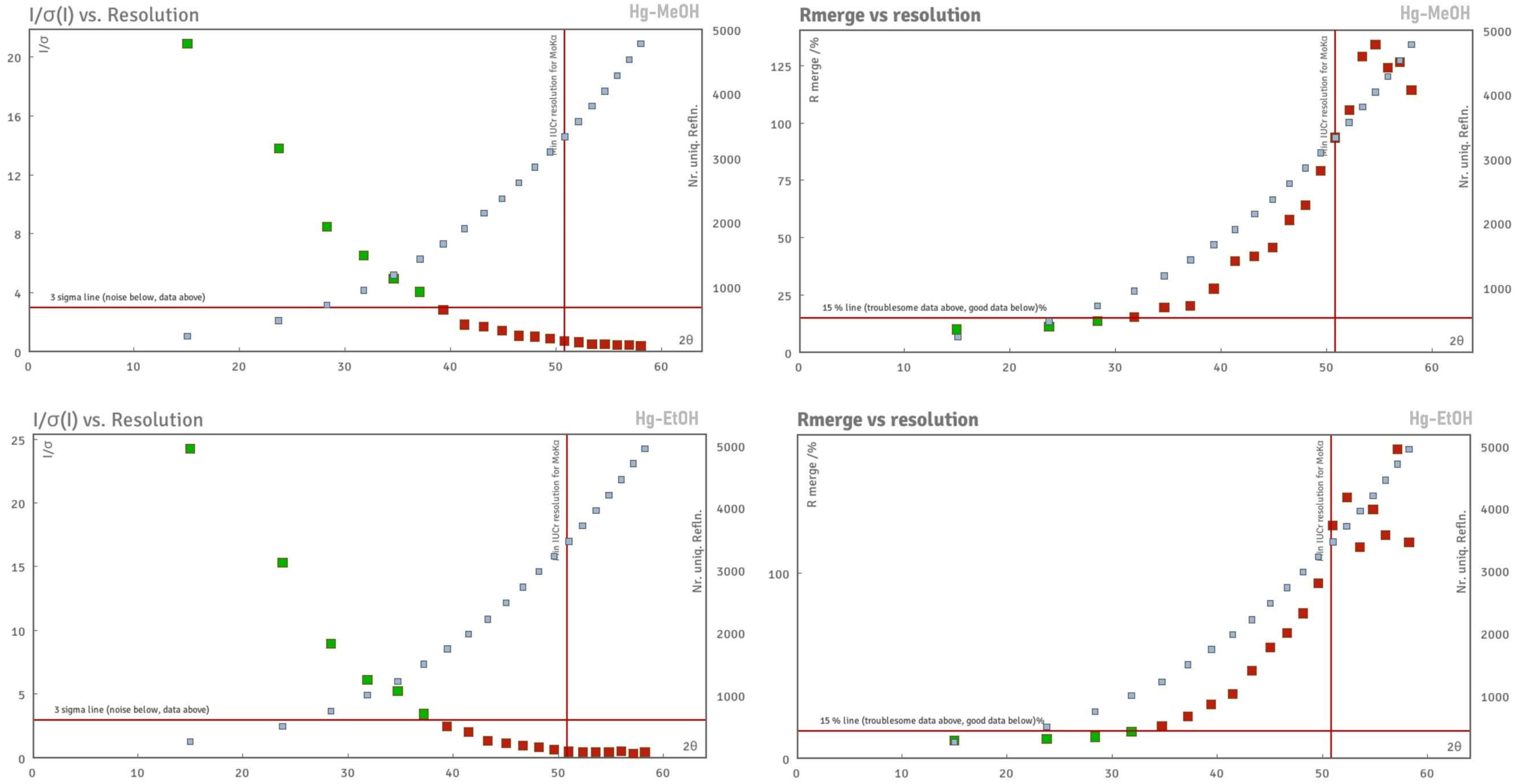
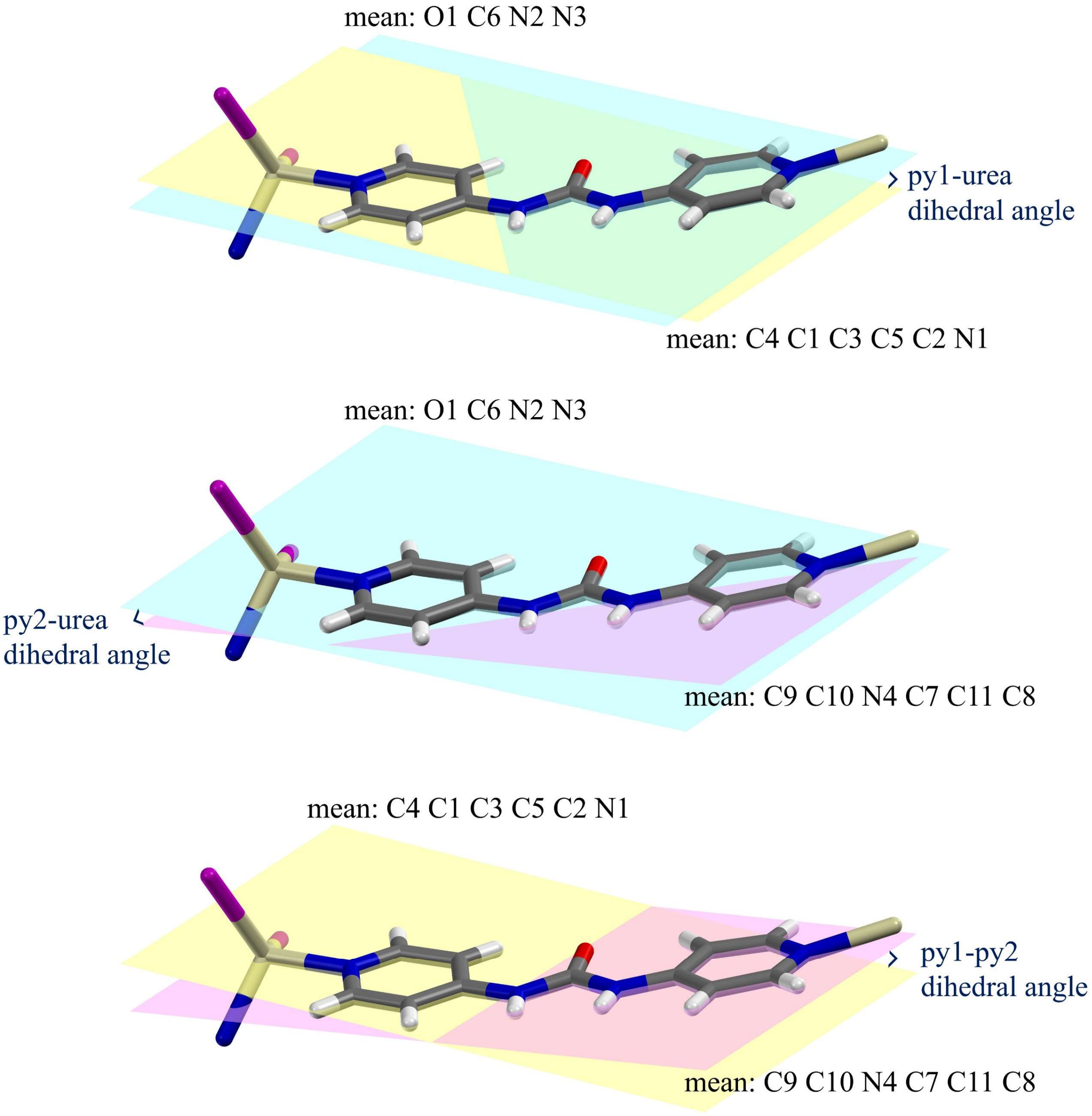


Fig. S12 I/σ(I) vs. Resolution and Rmerge vs. Resolution plots for **Hg-MeOH** and **Hg-EtOH**.



Compounds	**∠ Mean plane of py1 – urea [°]**	**∠ Mean plane of py2 – urea [°]**	**∠ Mean plane of py1 – py2 [°]**
Zn-MeOH	6.29	5.37	7.67
Cd-MeOH	7.22	6.21	10.00
Hg-MeOH	6.39	5.16	8.11
Zn-EtOH	6.64	5.63	9.25
Cd-EtOH	6.39	5.51	8.17
Hg-EtOH	7.24	5.57	6.77

Fig. S13 Dihedral angles between pyridyl-urea and pyridyl-pyridyl planes of ligand in compounds **M-MeOH** and **M-EtOH** (M=Zn, Cd and Hg).

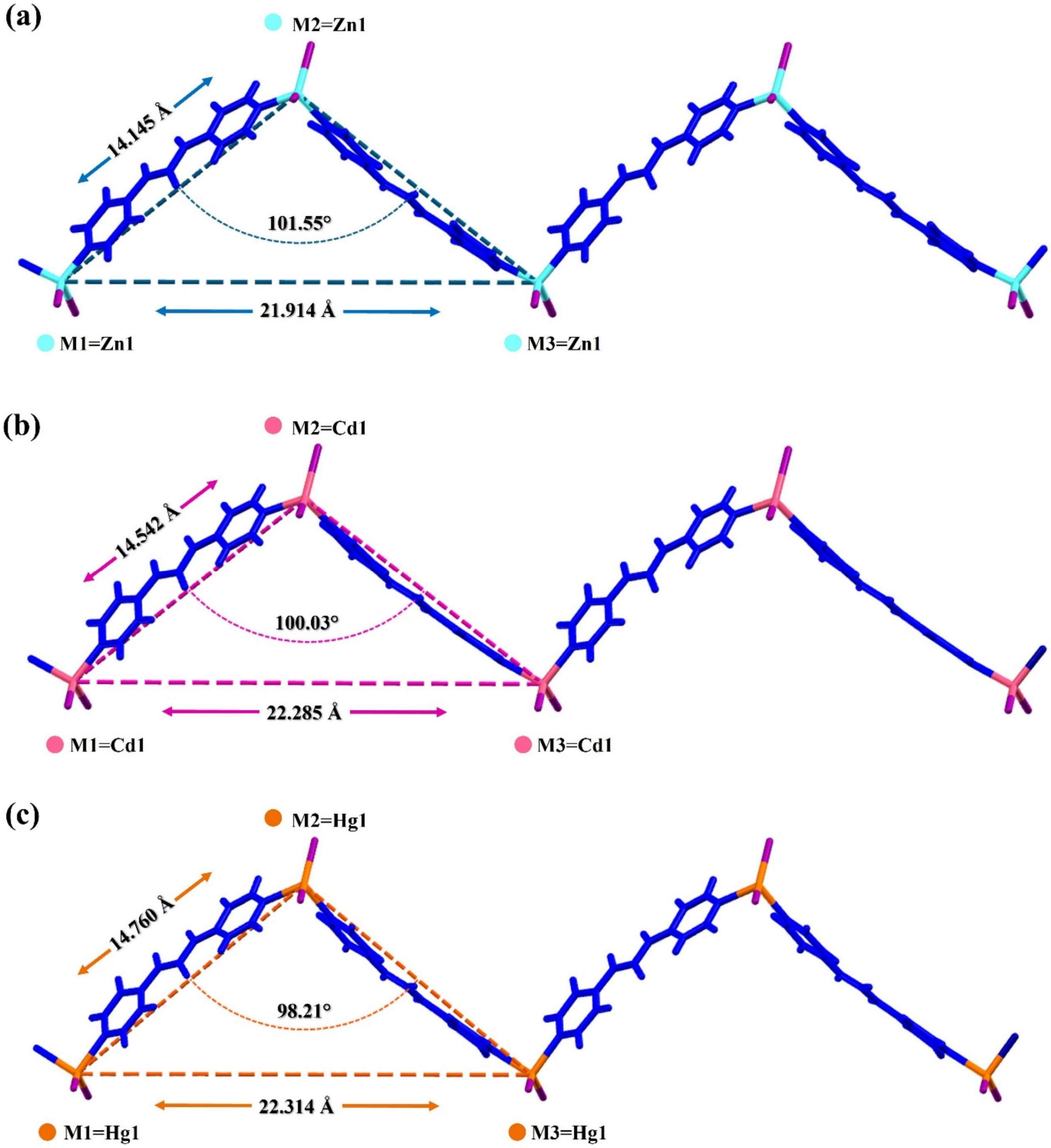


Fig. S14 M···M distances (D, d/ Å) and M···M···M angle (α/ deg.) in zig-zag chains of (a) **Zn-MeOH**, (b) **Cd-MeOH** and (c) **Hg-MeOH**.

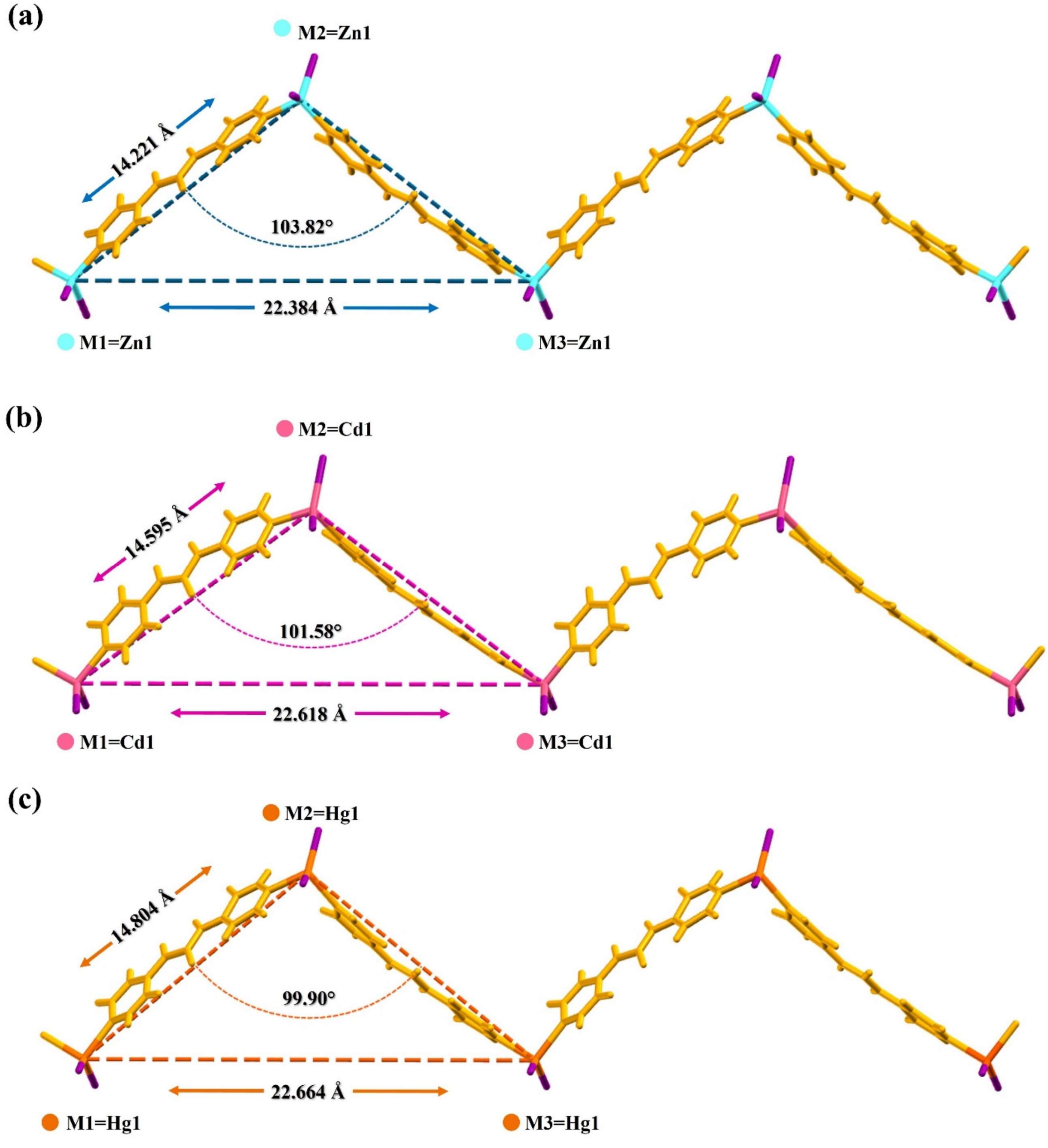


Fig. S15 M···M distances (D, d/ Å) and M···M···M angle (α/ deg.) in zig-zag chains of (a) **Zn-EtOH**, (b) **Cd-EtOH** and (c) **Hg-EtOH**.

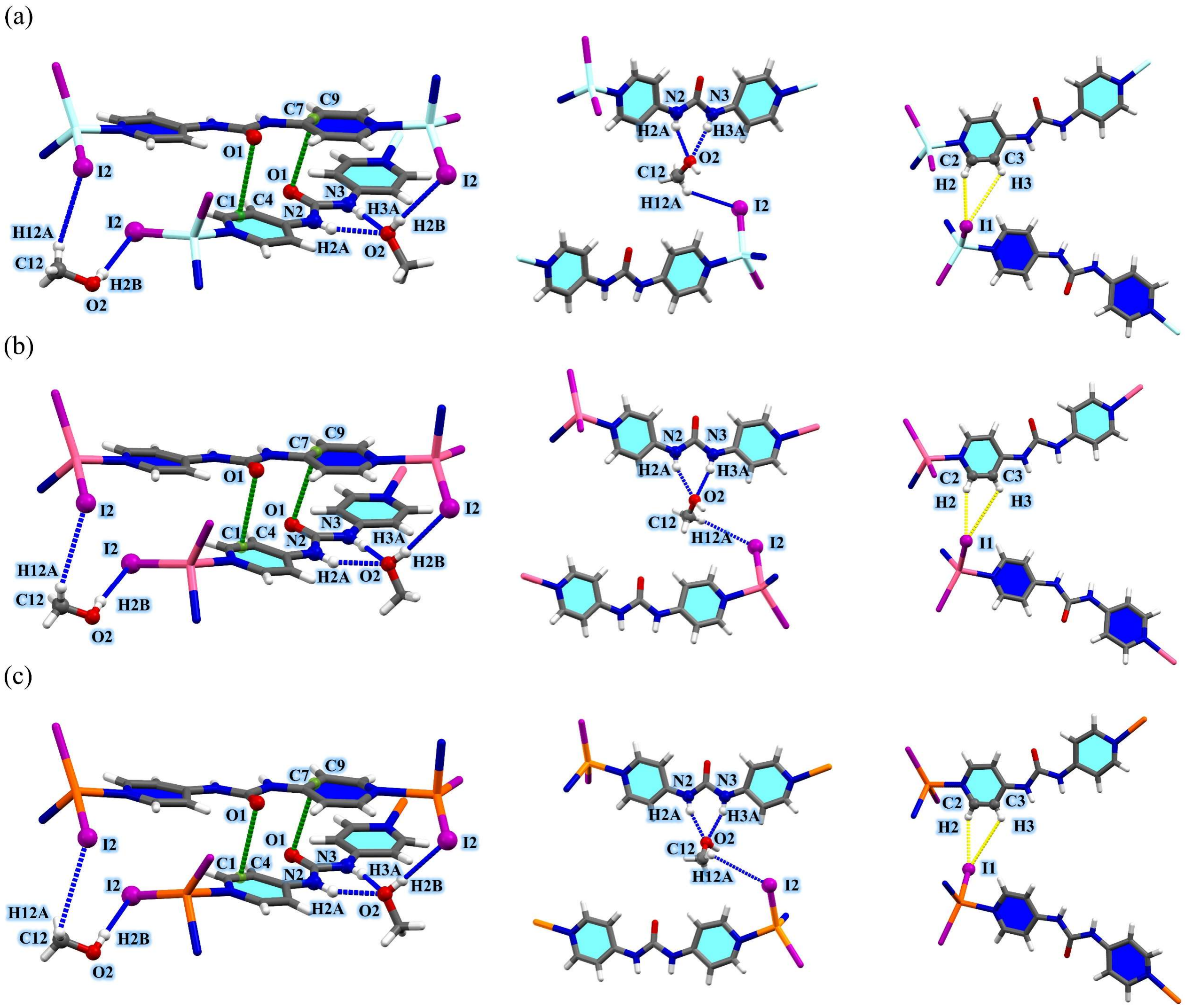


Fig. S16 Supramolecular interactions in compounds (a) **Zn-MeOH**, (b) **Cd-MeOH** and (c) **Hg-MeOH.**

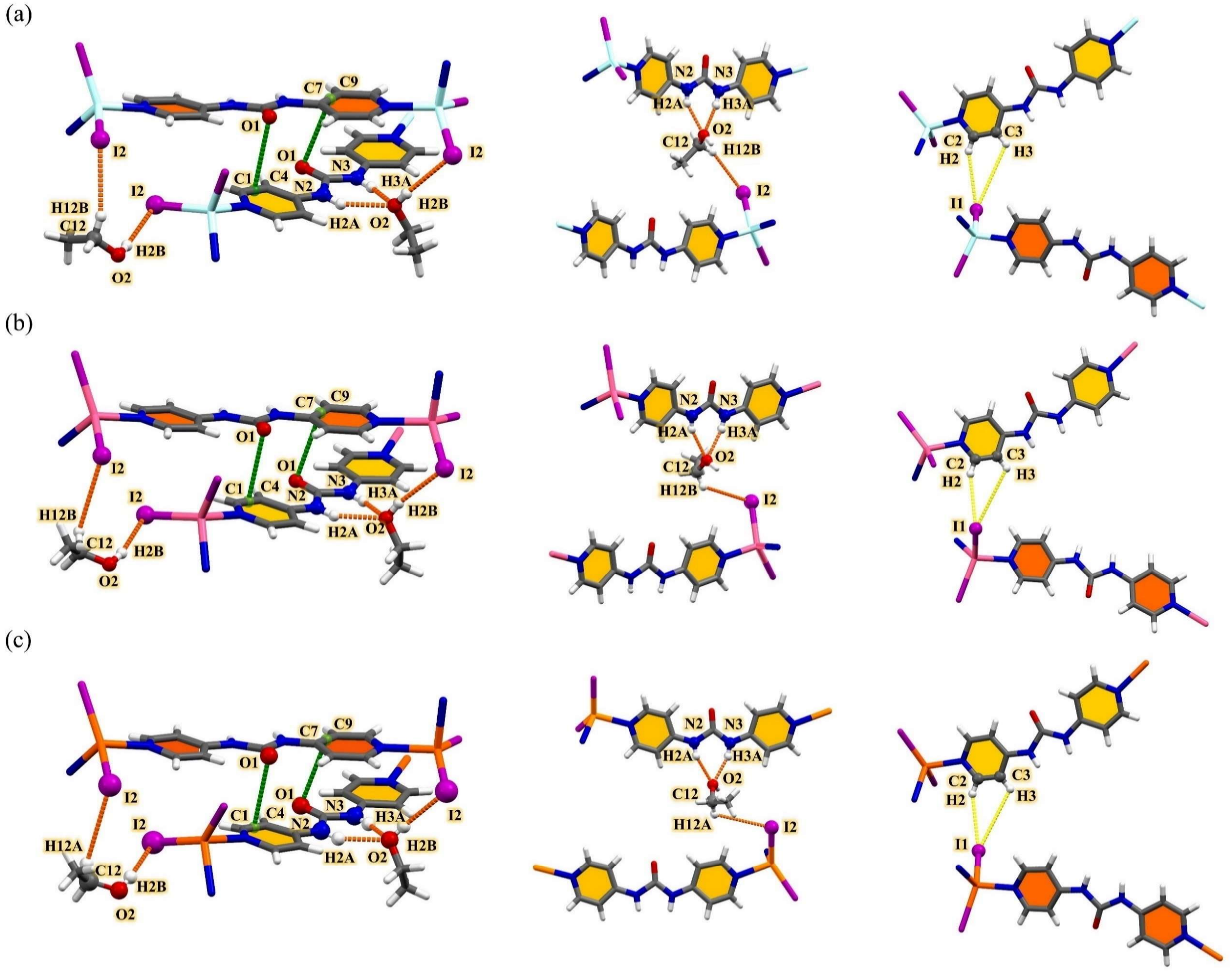


Fig. S17 Supramolecular interactions in compounds (a) **Zn-EtOH**, (b) **Cd-EtOH** and (c) **Hg-EtOH.**

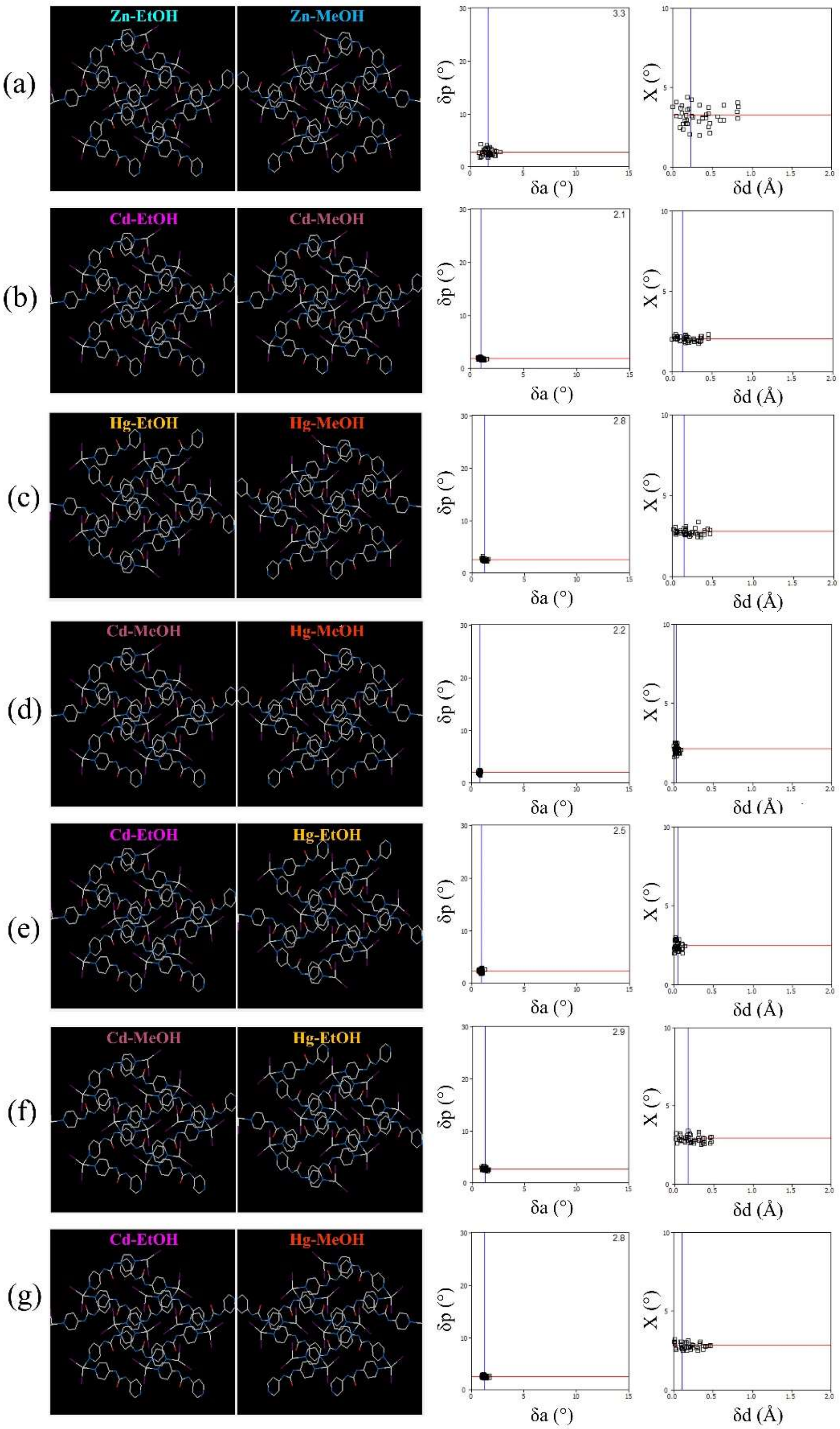


Fig. S18 3D supramolecular constructs obtained from XPac analysis for the isostructural pairs (a) **Zn-EtOH** and **Zn-MeOH**, (b) **Cd-EtOH** and **Cd-MeOH**, (c) **Hg-EtOH** and **Hg-MeOH**, (d) **Cd-MeOH** and **Hg-MeOH**, (e) **Cd-EtOH** and **Hg-EtOH**, (f) **Cd-MeOH** and **Hg-EtOH** and (g) **Cd-EtOH** and **Hg-MeOH**.

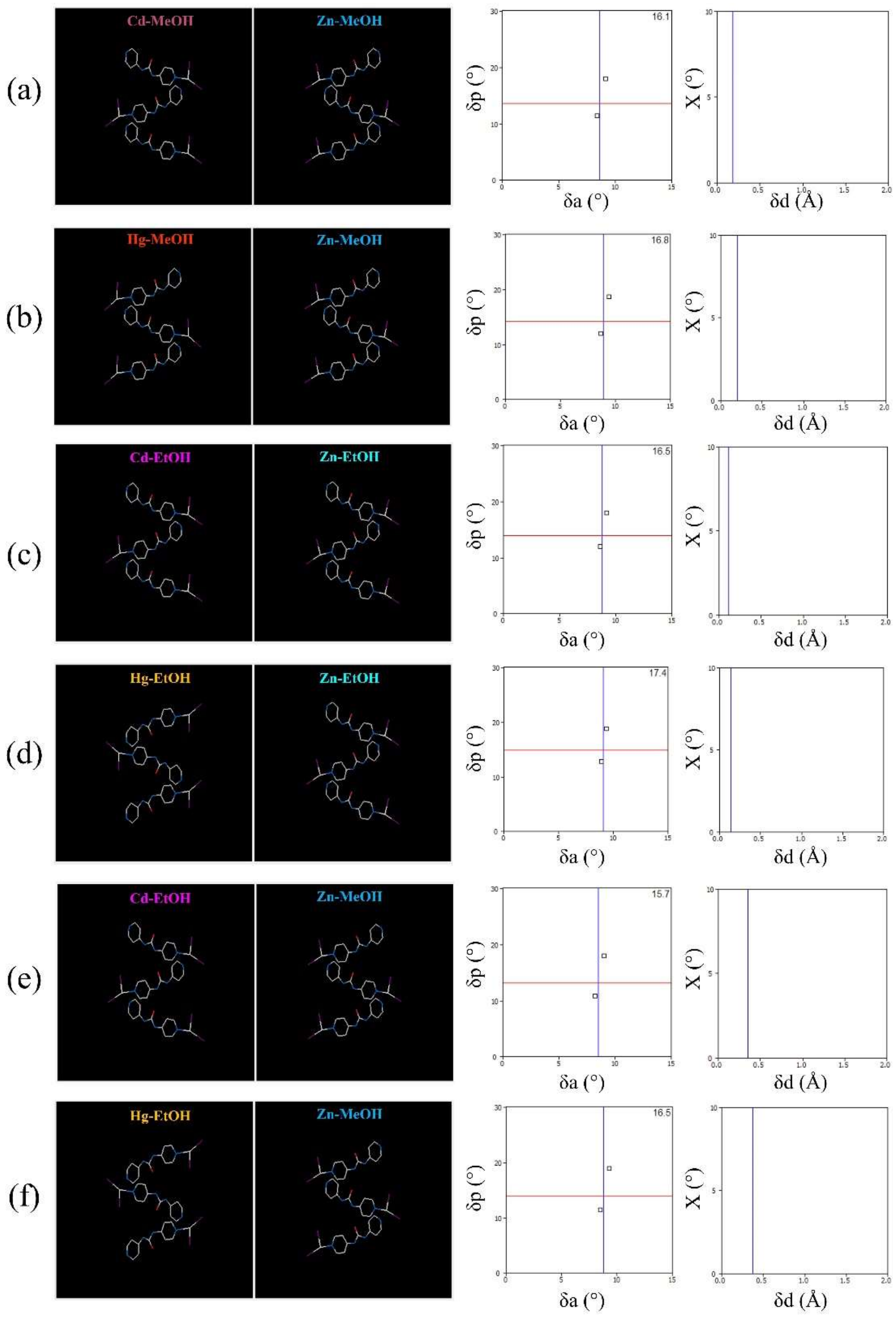


Fig. S19 1D supramolecular constructs obtained from XPac analysis for the isostructural pairs (a) **Cd-MeOH** and **Zn-MeOH**, (b) **Hg-MeOH** and **Zn-MeOH**, (c) **Cd-EtOH** and **Zn-EtOH**, (d) **Hg-EtOH** and **Zn-EtOH**, (e) **Cd-EtOH** and **Zn-MeOH** and (f) **Hg-EtOH** and **Zn-MeOH**.

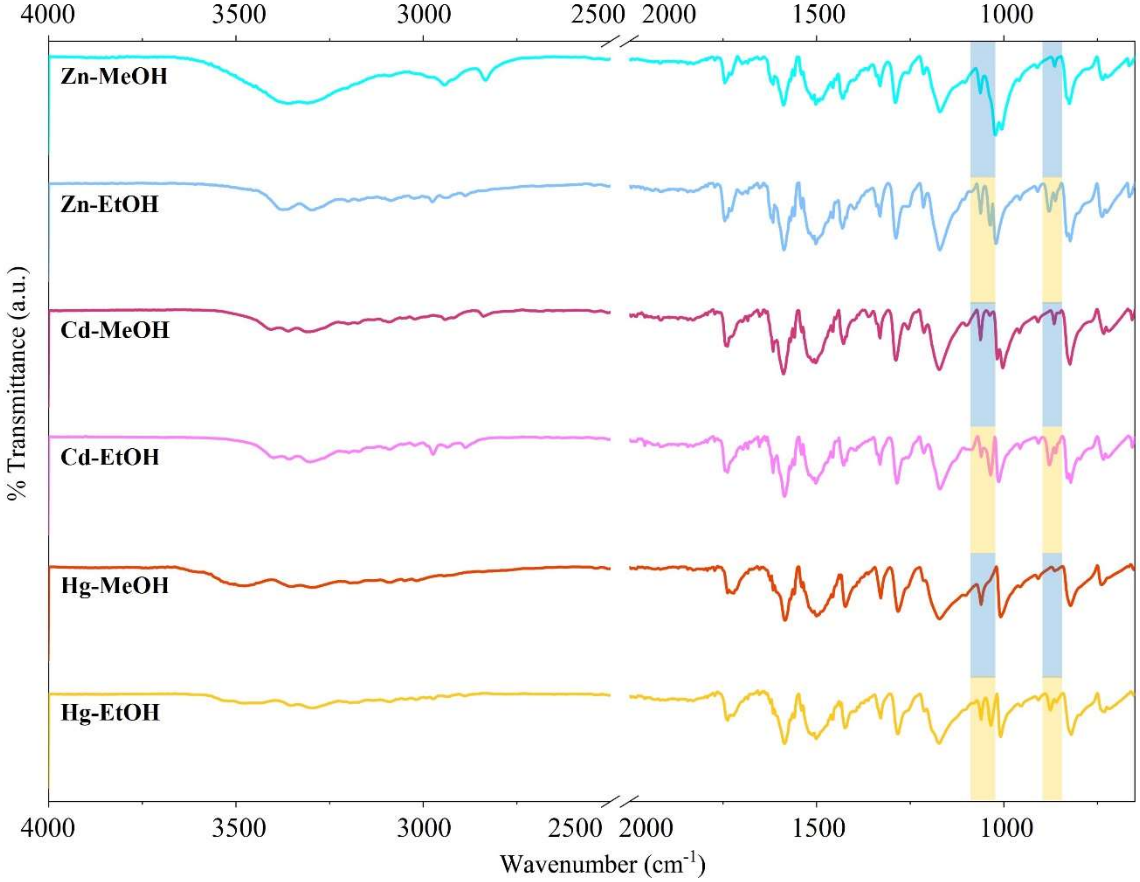


Fig. S20 ATR-FTIR spectra of compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

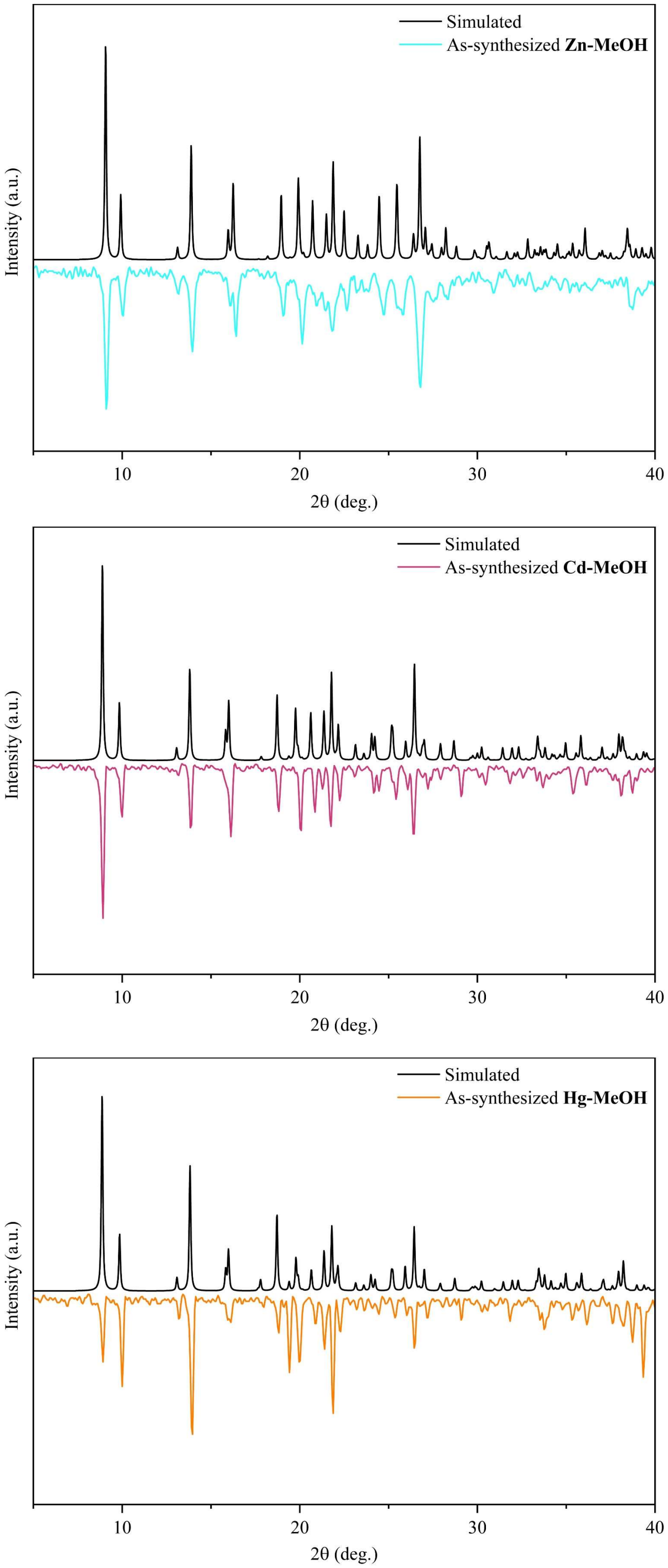


Fig. S21 PXRD patterns of **M-MeOH (**M = Zn, Cd and Hg). Black: Simulated from the X-ray single-crystal data; Cyan: observed for the as-synthesized **Zn-MeOH** solids, Purple: observed for the as-synthesized **Cd-MeOH** solids and Orange: observed for the as-synthesized **Hg-MeOH** solids.

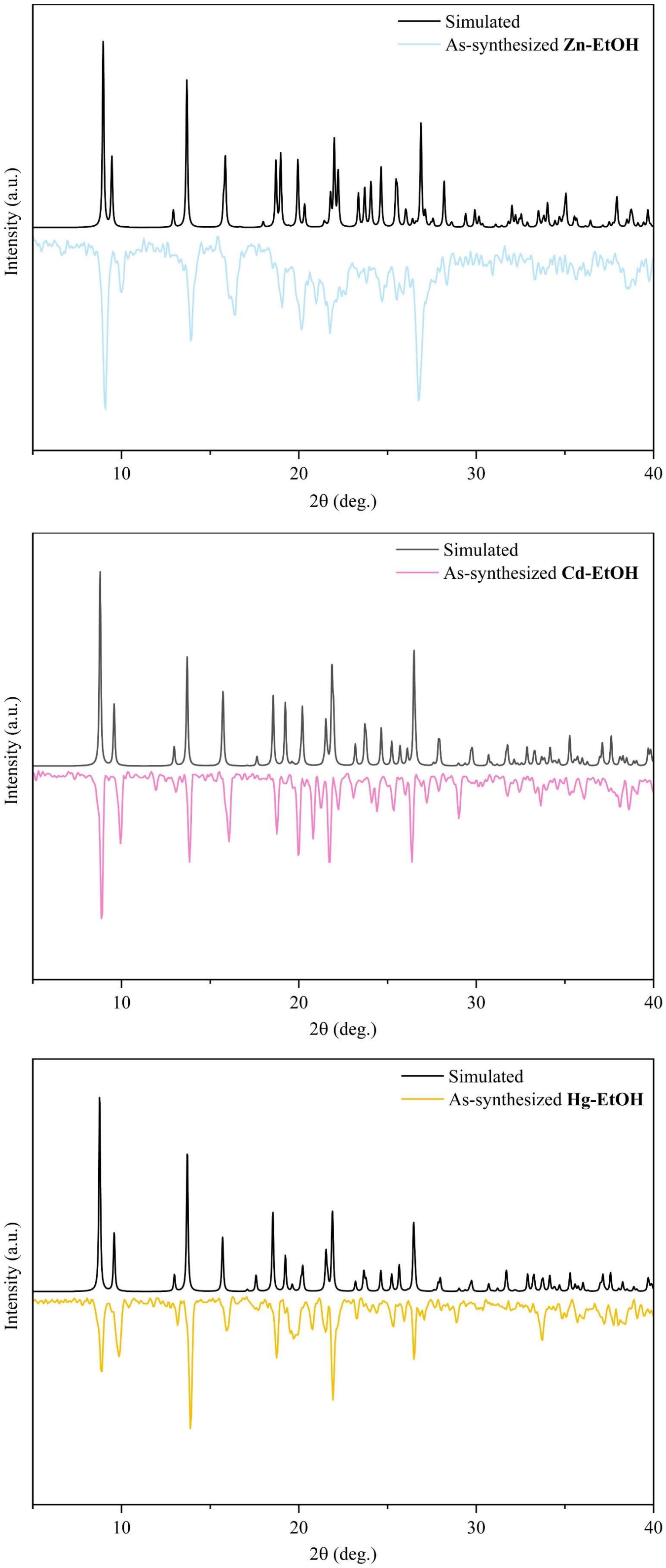


Fig. S22 PXRD patterns of **M-EtOH (**M = Zn, Cd and Hg). Black: Simulated from the X-ray single-crystal data; Light blue: observed for the as-synthesized **Zn-EtOH** solids, Pink: observed for the as-synthesized **Cd-EtOH** solids and Pale orange: observed for the as-synthesized **Hg-EtOH** solids.

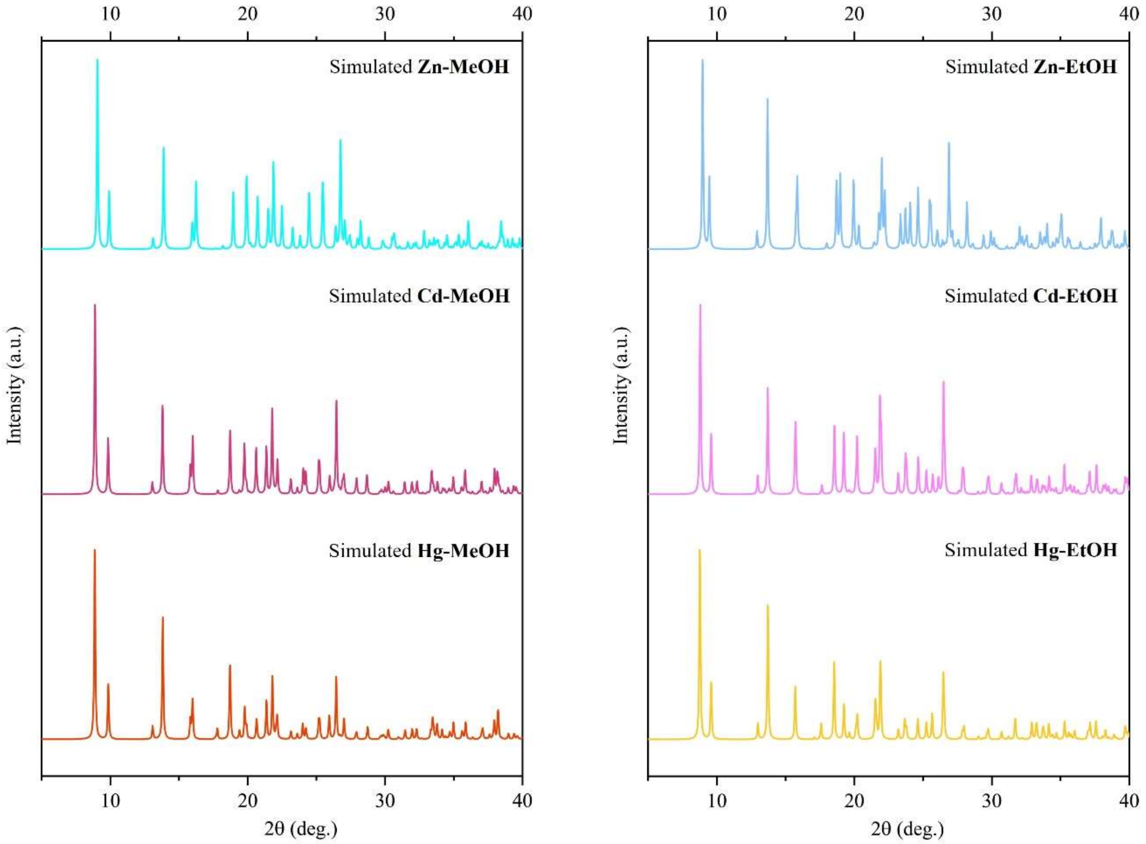


Fig. S23 Simulated PXRD patterns from the X-ray single-crystal data of compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

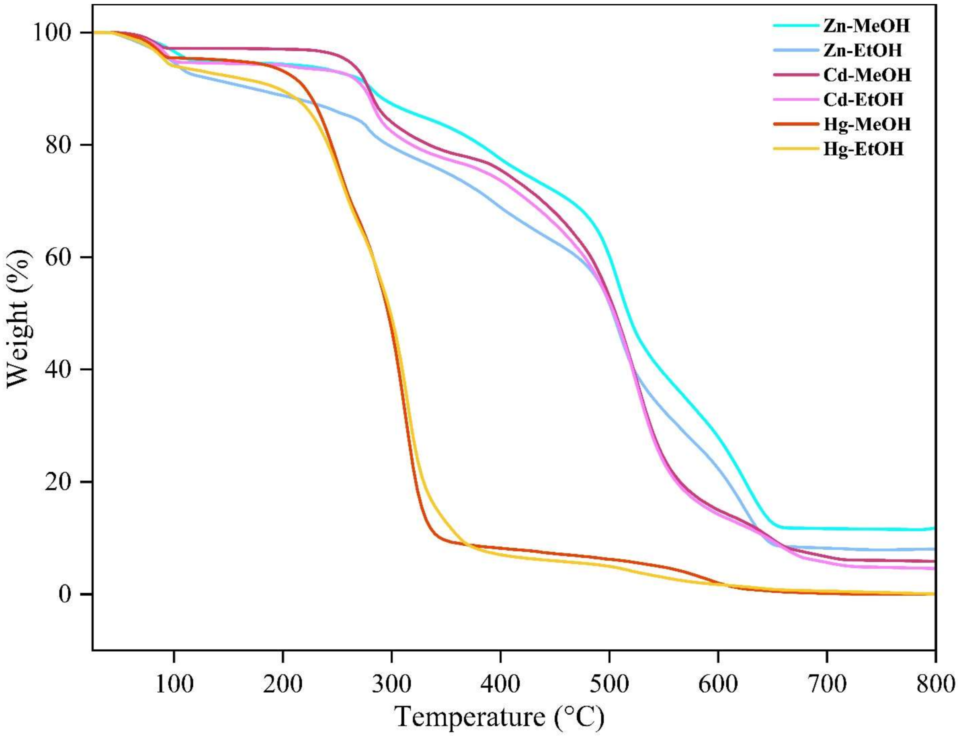


Fig. S24 TGA curves of compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

Table S1 Selected bond lengths [Å] and angles [°] for compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

Selected bond lengths [Å] and angles [°] for **Zn-MeOH**			
Zn(1)—I(1)	2.547(3)	I(1)—Zn(1)—N(1)	107.8(6)
Zn(1)—I(2)	2.575(4)	I(2)—Zn(1)—N(1)	108.2(5)
Zn(1)—N(1)	2.057(19)	I(1)—Zn(1)—N(4)$^{\#1}$	109.0(5)
Zn(1)—N(4)$^{\#1}$	2.041(17)	I(2)—Zn(1)—N(4)$^{\#1}$	106.4(5)
I(1)—Zn(1)—I(2)	121.43(11)	N(1)—Zn(1)—N(4)$^{\#1}$	102.4(7)
Symmetry code: #1: – x + 1/2, y – 1/2, z + 1/2			
Selected bond lengths [Å] and angles [°] for **Zn-EtOH**			
Zn(1)—I(1)	2.548(3)	I(1)—Zn(1)—N(1)	109.6(6)
Zn(1)—I(2)	2.559(4)	I(2)—Zn(1)—N(1)	108.0(5)
Zn(1)—N(1)	2.07(2)	I(1)—Zn(1)—N(4)$^{\#1}$	109.9(5)
Zn(1)—N(4)$^{\#1}$	2.055(17)	I(2)—Zn(1)—N(4)$^{\#1}$	106.2(6)
I(1)—Zn(1)—I(2)	119.63(13)	N(1)—Zn(1)—N(4)$^{\#1}$	102.1(8)
Symmetry code: #1: – x + 3/2, y – 1/2, z – 1/2			
Selected bond lengths [Å] and angles [°] for **Cd-MeOH**			
Cd(1)—I(1)	2.695(2)	I(1)—Cd(1)—N(1)	106.4(5)
Cd(1)—I(2)	2.712(3)	I(2)—Cd(1)—N(1)	105.3(5)
Cd(1)—N(1)	2.293(16)	I(1)—Cd(1)—N(4)$^{\#1}$	107.4(4)
Cd(1)—N(4)$^{\#1}$	2.041(17)	I(2)—Cd(1)—N(4)$^{\#1}$	104.3(5)
I(1)—Cd(1)—I(2)	129.57(8)	N(1)—Cd(1)—N(4)$^{\#1}$	100.2(6)
Symmetry code: #1: – x + 3/2, y – 1/2, z – 1/2			
Selected bond lengths [Å] and angles [°] for **Cd-EtOH**			
Cd(1)—I(1)	2.695(3)	I(1)—Cd(1)—N(1)	108.2(5)
Cd(1)—I(2)	2.712(3)	I(2)—Cd(1)—N(1)	106.3(5)
Cd(1)—N(1)	2.270(18)	I(1)—Cd(1)—N(4)$^{\#1}$	107.7(5)
Cd(1)—N(4)$^{\#1}$	2.266(19)	I(2)—Cd(1)—N(4)$^{\#1}$	104.8(5)
I(1)—Cd(1)—I(2)	126.50(8)	N(1)—Cd(1)—N(4)$^{\#1}$	100.2(7)
Symmetry code: #1: – x + 1/2, y – 1/2, z – 1/2			
Selected bond lengths [Å] and angles [°] for **Hg-MeOH**			
Hg(1)—I(1)	2.658(4)	I(1)—Hg(1)—N(1)	105.3(9)
Hg(1)—I(2)	2.659(4)	I(2)—Hg(1)—N(1)	101.2(9)
Hg(1)—N(1)	2.37(4)	I(1)—Hg(1)—N(4)$^{\#1}$	103.7(9)
Hg(1)—N(4)$^{\#1}$	2.39(4)	I(2)—Hg(1)—N(4)$^{\#1}$	104.8(9)
I(1)—Hg(1)—I(2)	139.13(16)	N(1)—Hg(1)—N(4)$^{\#1}$	94.1(14)
Symmetry code: #1: – x + 1/2, y – 1/2, z – 1/2			
Selected bond lengths [Å] and angles [°] for **Hg-EtOH**			
Hg(1)—I(1)	2.645(4)	I(1)—Hg(1)—N(1)	105.3(7)
Hg(1)—I(2)	2.665(4)	I(2)—Hg(1)—N(1)	102.5(8)
Hg(1)—N(1)	2.38(3)	I(1)—Hg(1)—N(4)$^{\#1}$	104.4(8)
Hg(1)—N(4)$^{\#1}$	2.38(3)	I(2)—Hg(1)—N(4)$^{\#1}$	103.5(8)
I(1)—Hg(1)—I(2)	137.43(15)	N(1)—Hg(1)—N(4)$^{\#1}$	96.7(11)
Symmetry code: #1: – x + 3/2, y – 1/2, z + 1/2			

Table S2 τ_4 parameter for compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

Compounds	τ_4 Parameter	Coordination geometry
Zn-MeOH	0.92	distorted trigonal-pyramidal
Zn-EtOH	0.93	distorted trigonal-pyramidal
Cd-MeOH	0.87	distorted trigonal-pyramidal
Cd-EtOH	0.89	distorted trigonal-pyramidal
Hg-MeOH	0.82	distorted trigonal-pyramidal
Hg-EtOH	0.83	distorted trigonal-pyramidal

Table S3 Temperature range and percentage of weight loss for MeOH and EtOH in compounds **M-MeOH** and **M-EtOH** (M = Zn, Cd and Hg).

Compounds	Temperature range (°C)	Calculated (%)	Observed (%)
Zn-MeOH	41-124	5.66	5.20
Zn-EtOH	38-128	7.95	8.10
Cd-MeOH	35-94	5.23	2.81
Cd-EtOH	30-112	7.36	5.32
Hg-MeOH	30-108	4.57	4.58
Hg-EtOH	35-111	6.45	6.30

X-ray crystallography

The crystallographic data for compounds were collected on a STOE IPDS-II diffractometer with graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å). Single crystals with appropriate dimensions were chosen under a polarizing microscope and were mounted onto a glass fiber for data collection. Cell constants and orientation matrices for data collection were obtained by least-square refinement of the diffraction data. All diffraction data were collected at 298(2) K in a series of ω scans in 1° oscillations and was integrated using the Stoe X-AREA[2] software. A numerical absorption correction was applied using X-RED[3] and X-SHAPE[4] software. The reflection data were corrected for Lorentz and polarizing effects. The structures were solved by direct methods[5] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[6] All the hydrogen atoms attach to carbon atoms in compounds were added in idealized positions. The atomic factors were taken from International Tables for X-ray Crystallography.[7] All refinements were performed using the X-STEP32 crystallographic software package.[8]

References

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