

Anion-induced structural diversity in cadmium coordination polymers of 4-aminobenzonitrile: a structural and DFT study

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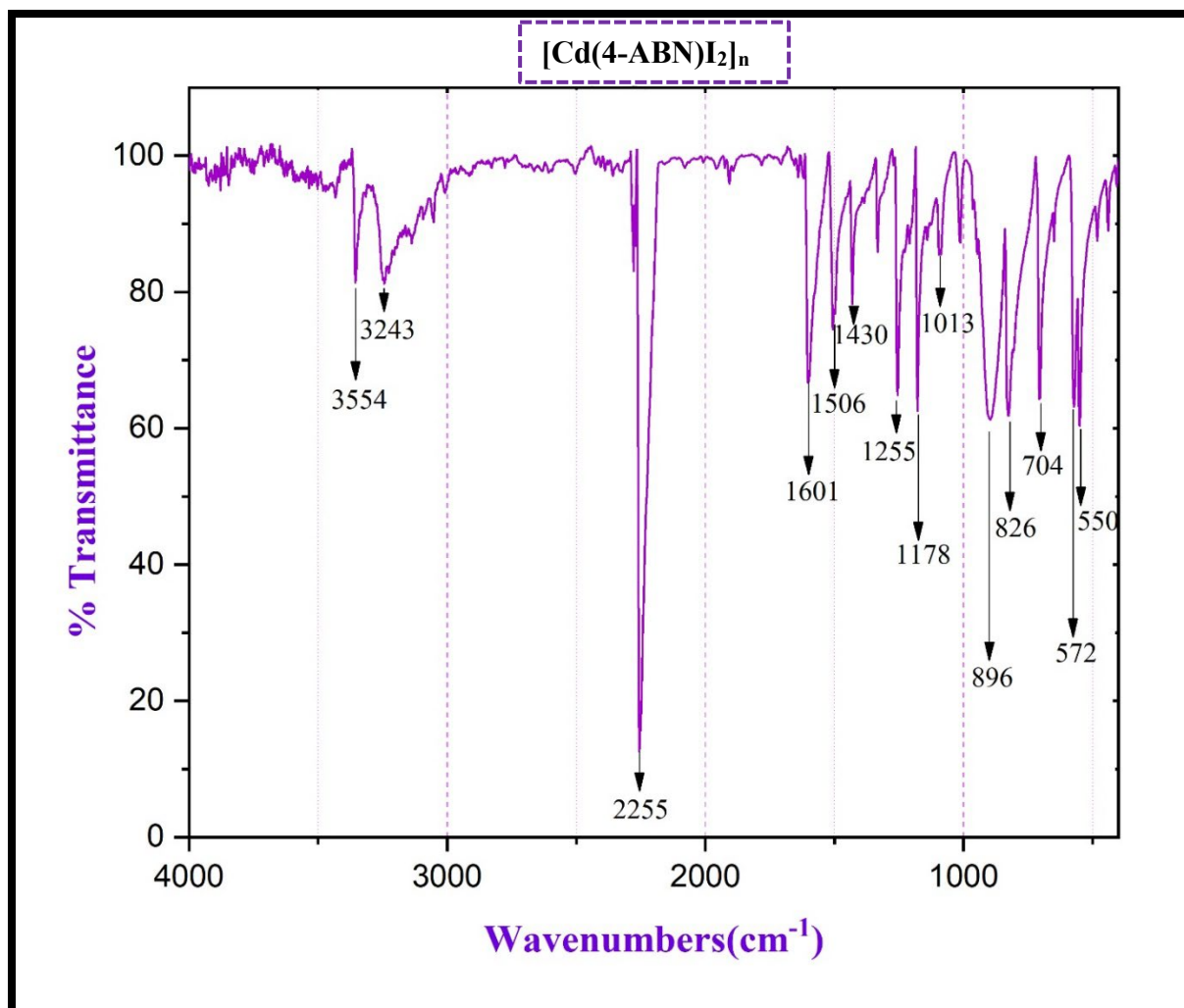


Figure S1. FT-IR spectrum of compound **1** in KBr pellet.

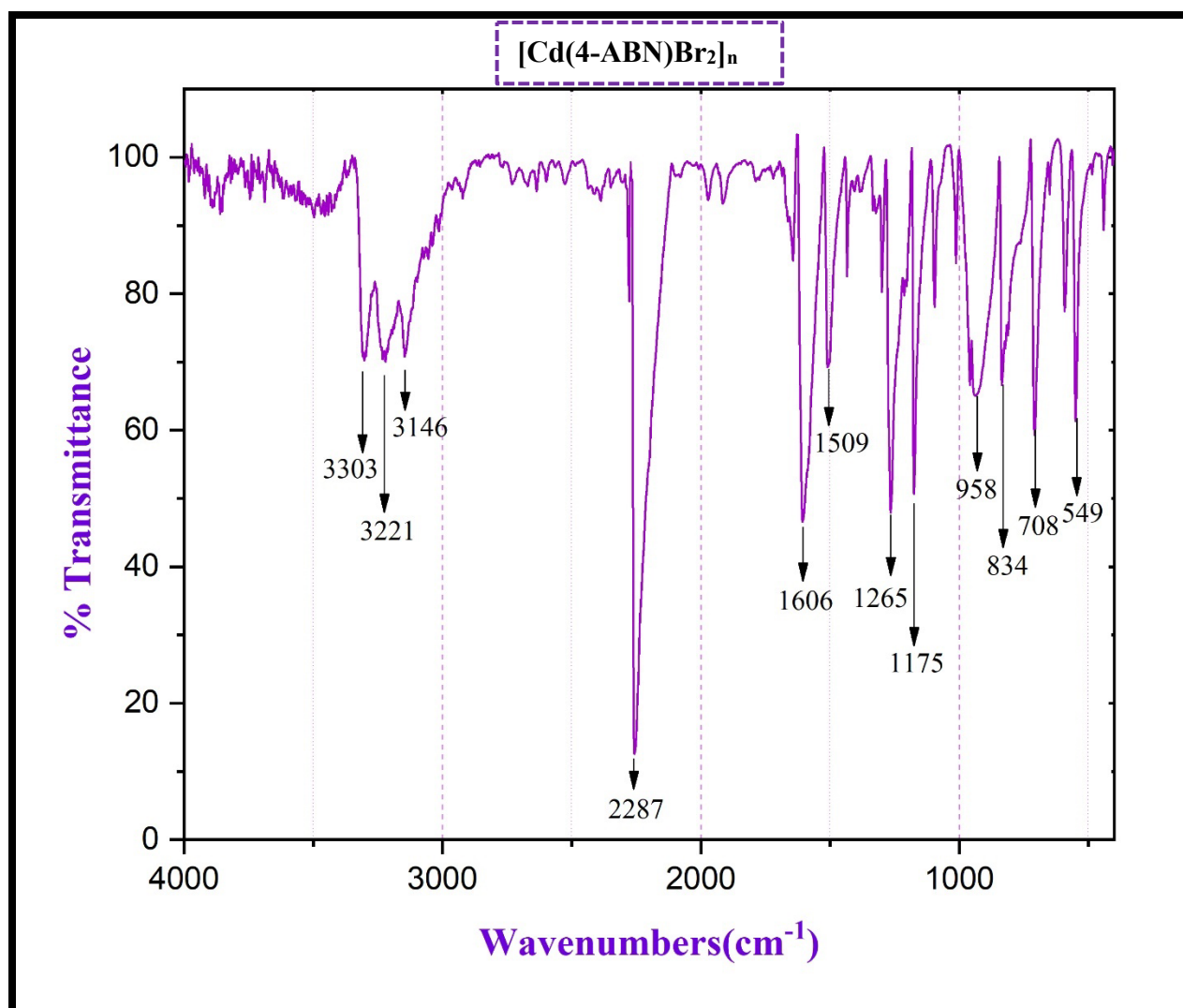


Figure S2. FT-IR spectrum of compound **2** in KBr pellet.

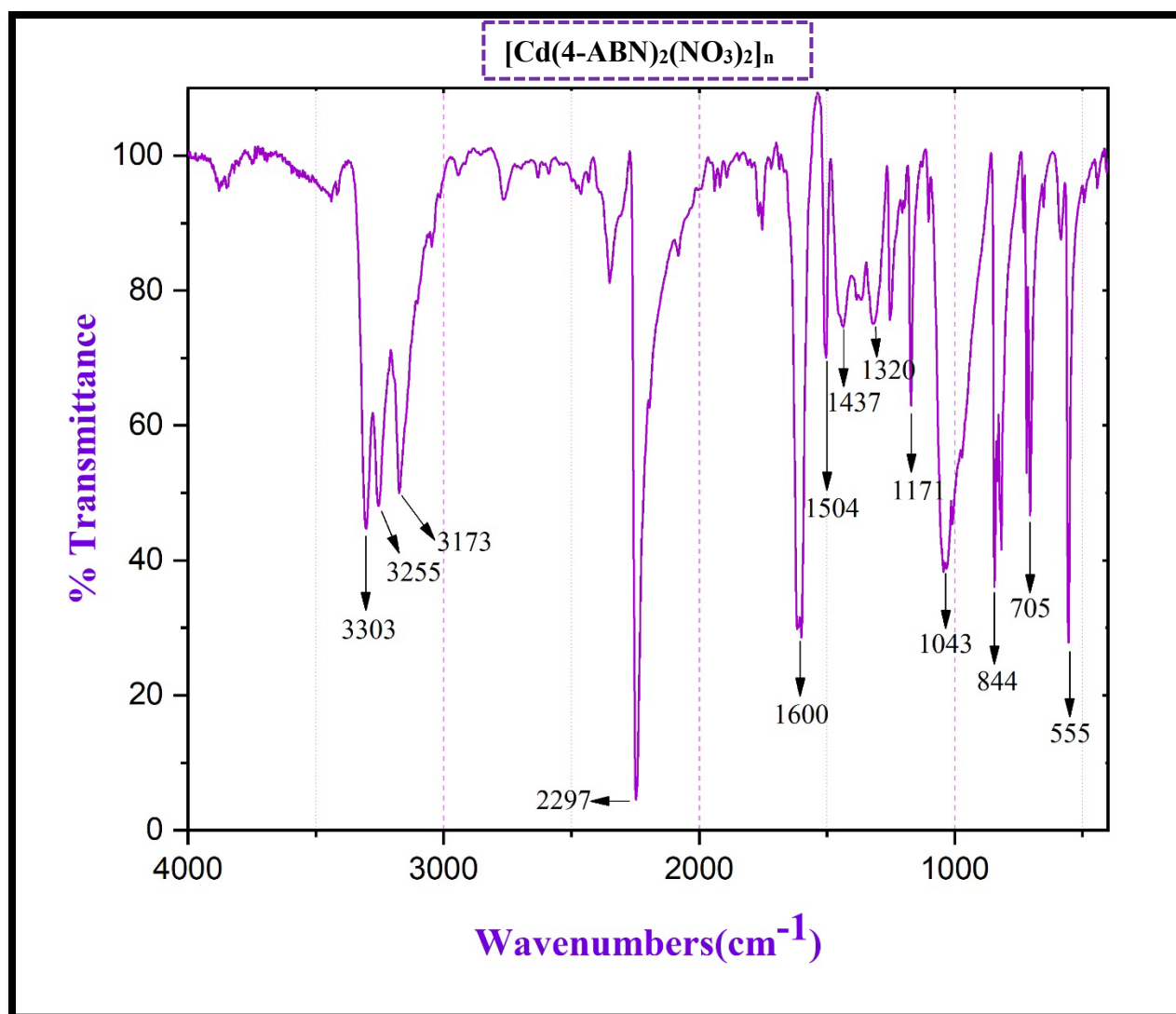


Figure S3. FT-IR spectrum of compound **3** in KBr pellet.

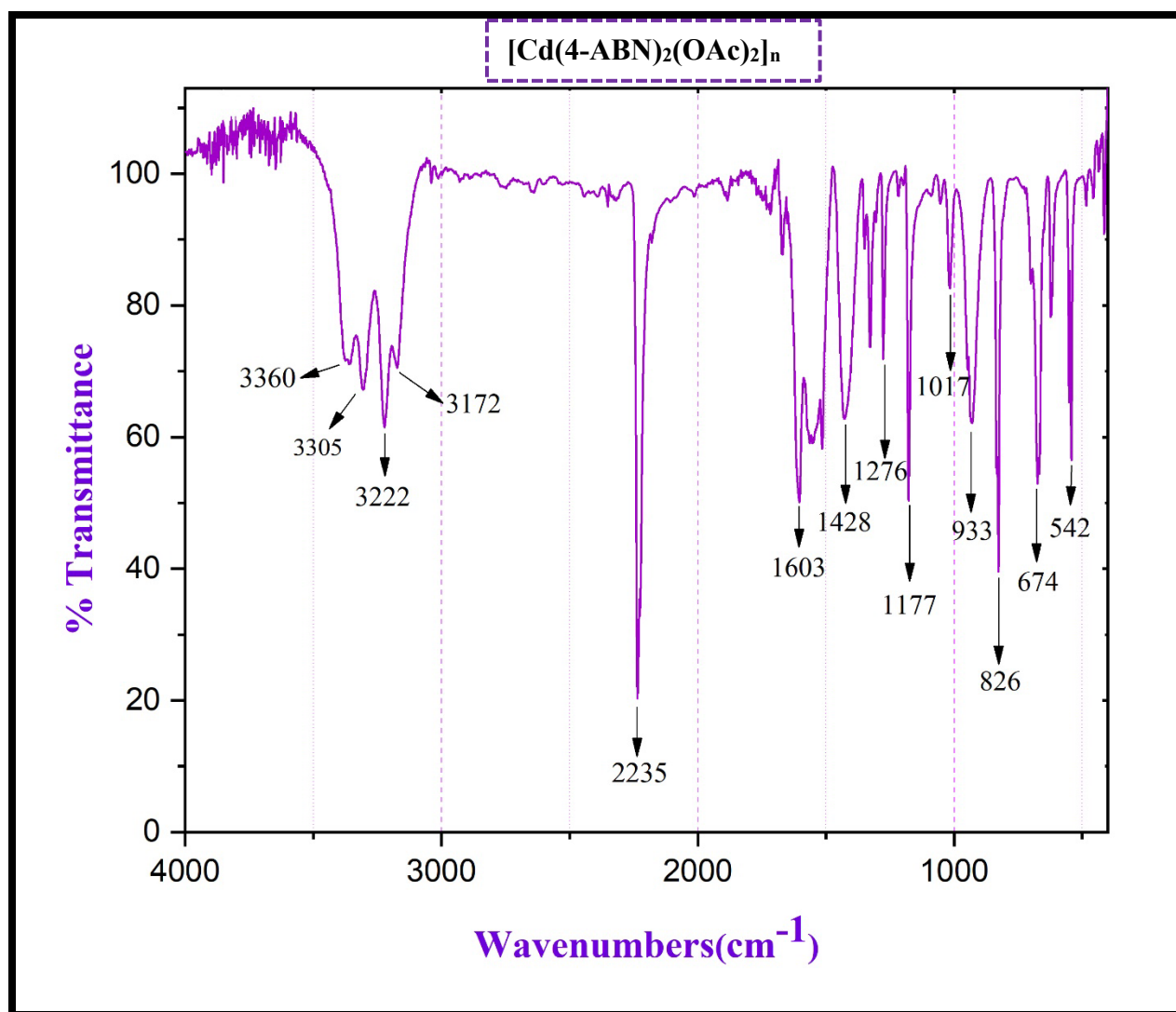


Figure S4. FT-IR spectrum of compound **4** in KBr pellet.

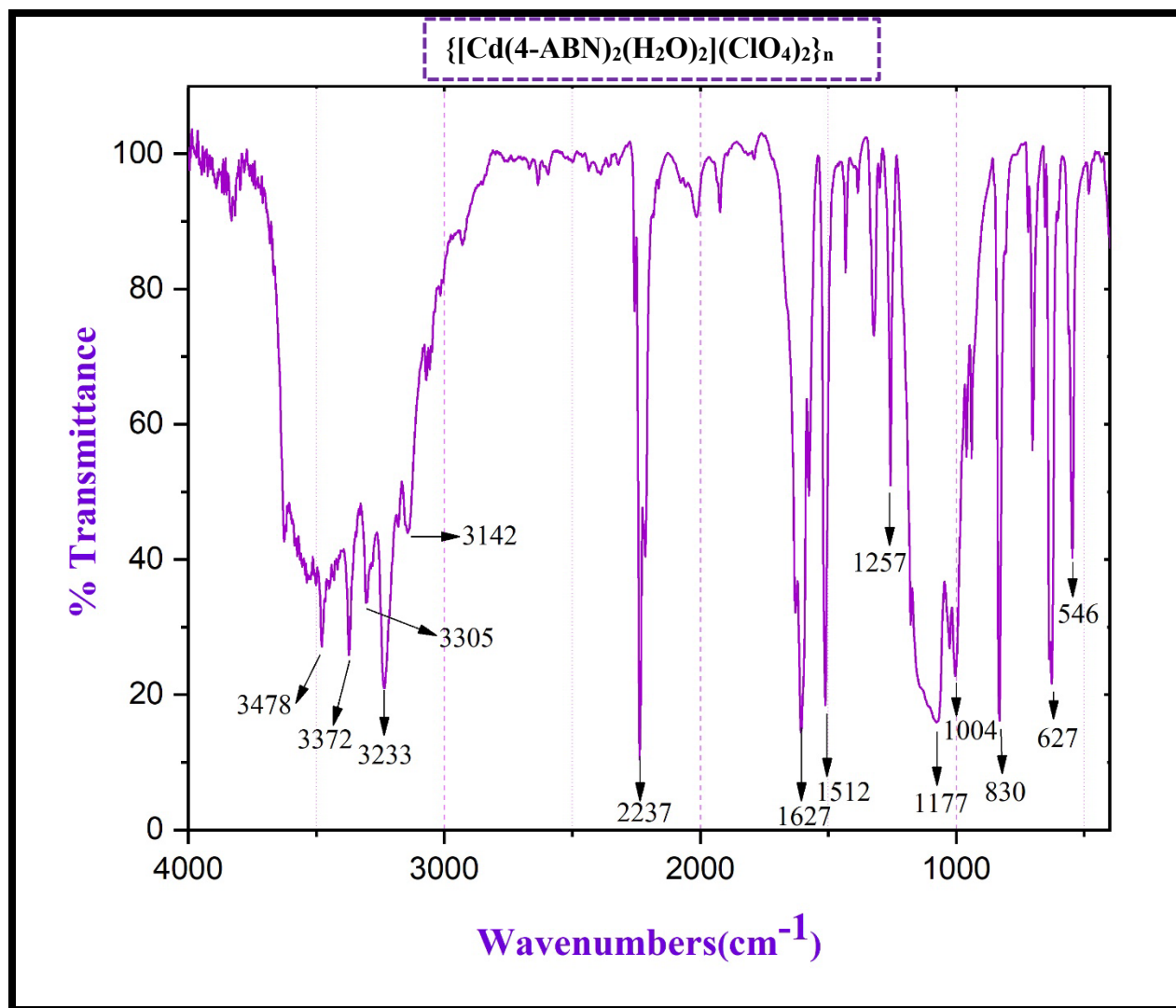


Figure S5. FT-IR spectrum of compound 5 in KBr pellet.

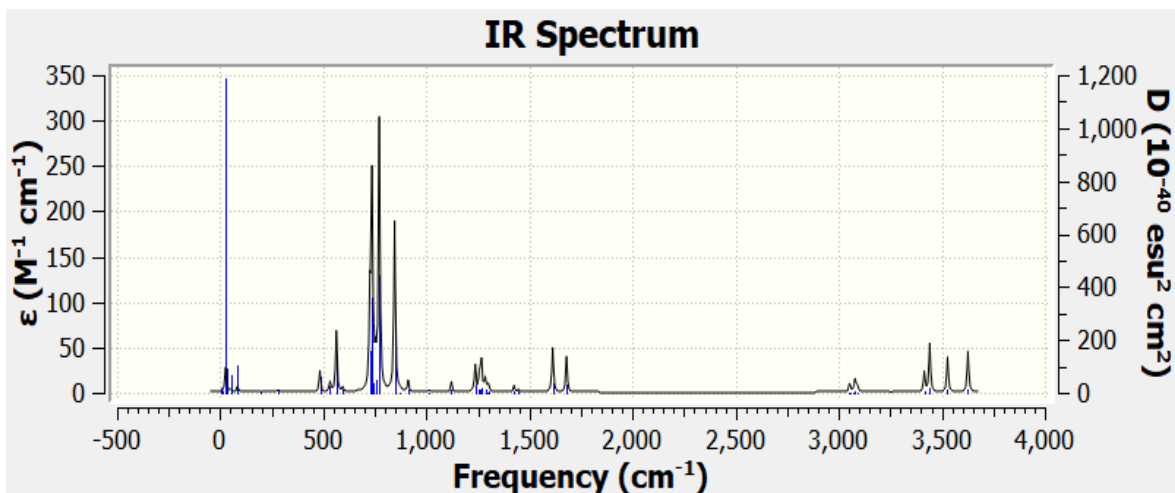


Figure S6. Theoretical calculated FT-IR spectrum of compound 1.

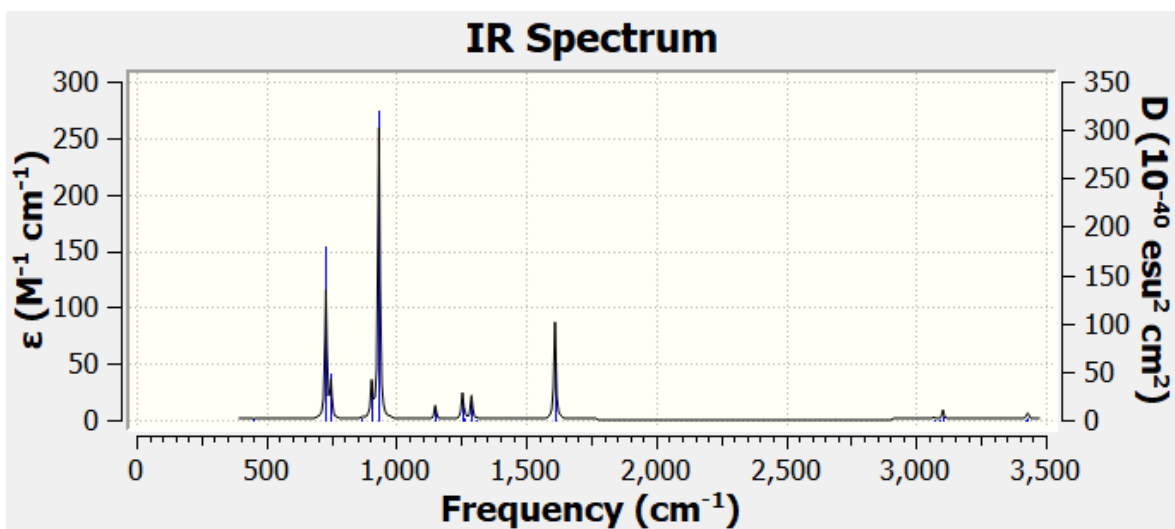


Figure S7. Theoretical calculated FT-IR spectrum of compound 2.

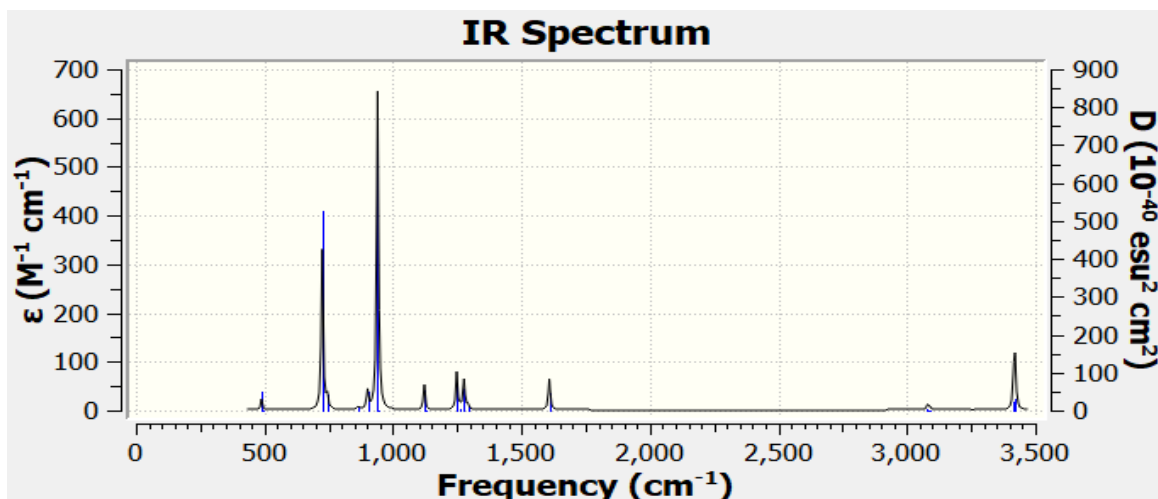


Figure S8. Theoretical calculated FT-IR spectrum of compound 3.

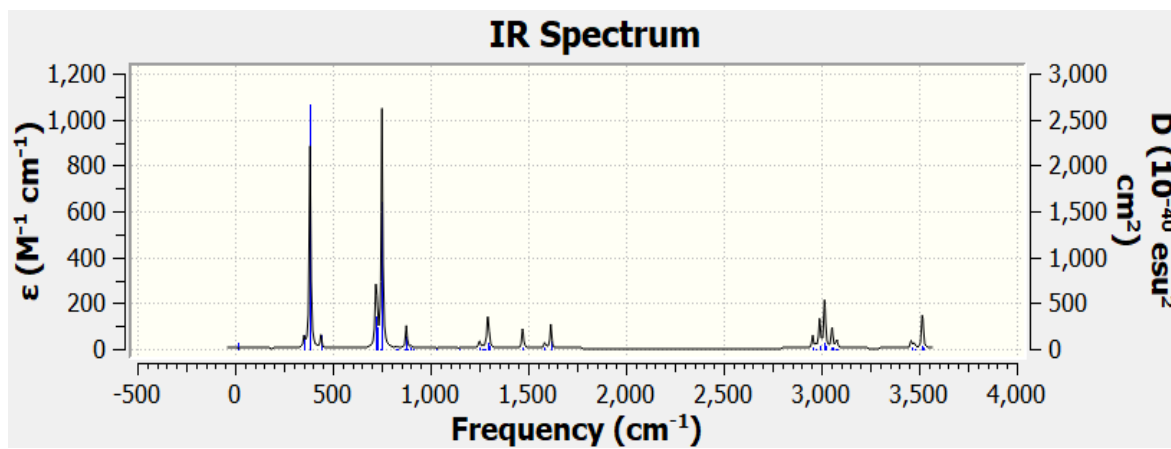


Figure S9. Theoretical calculated FT-IR spectrum of compound 4.

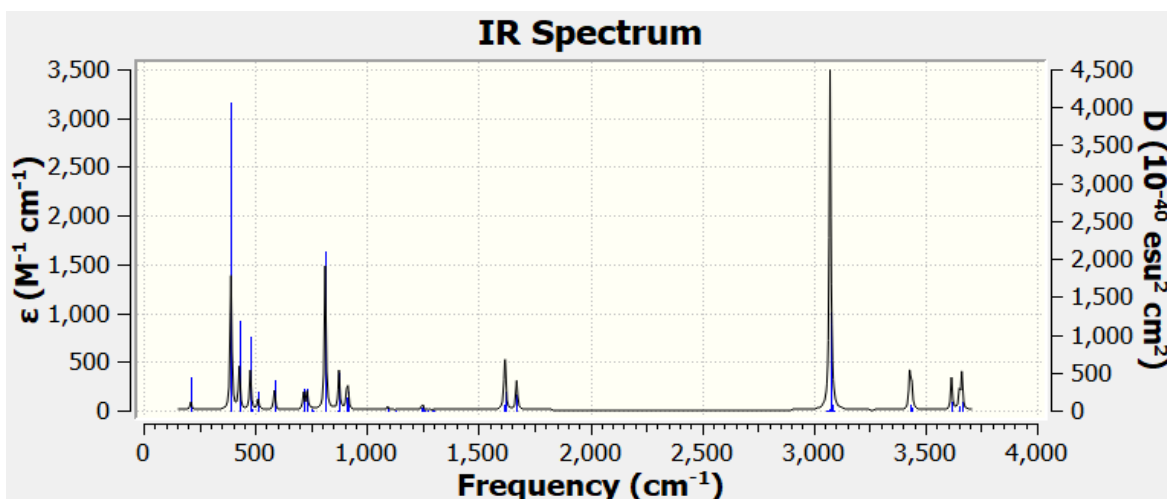


Figure S10. Theoretical calculated FT-IR spectrum of compound 5.

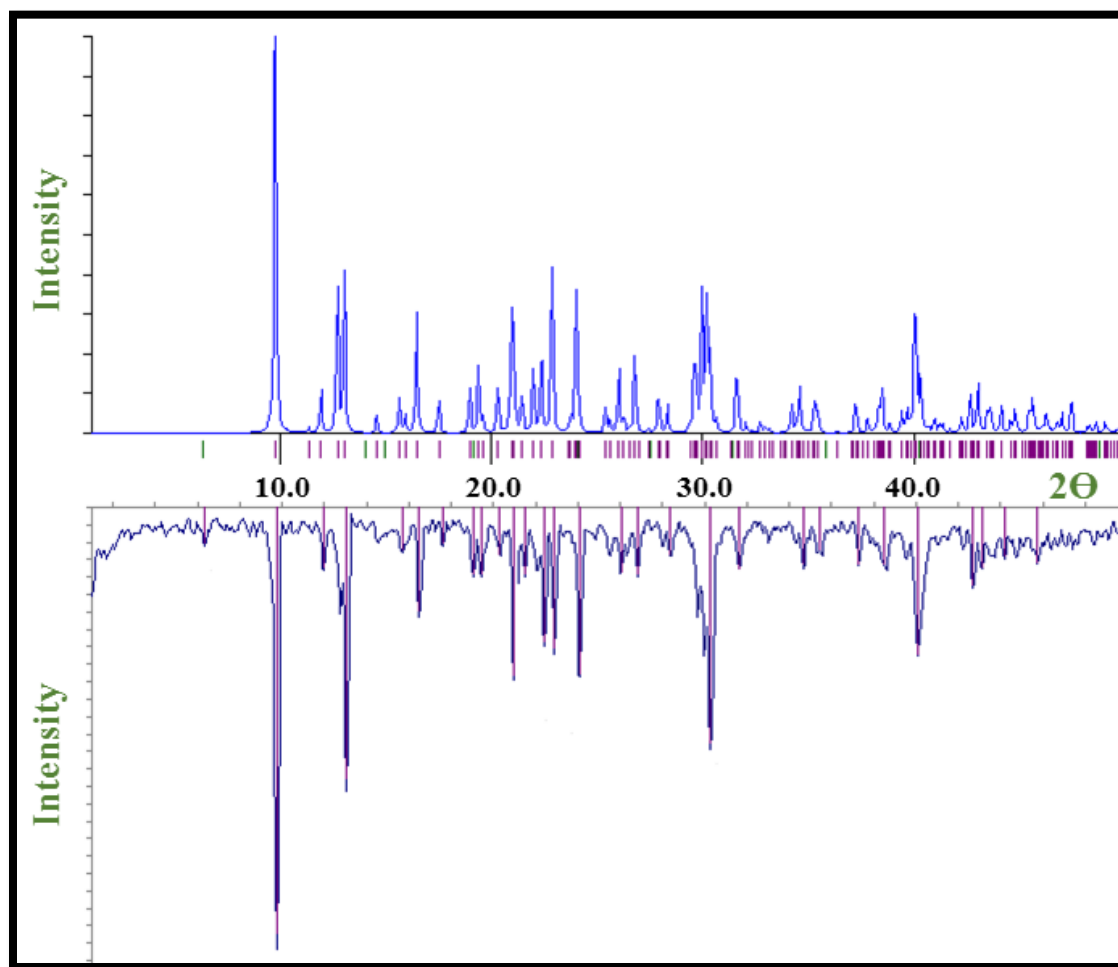


Figure S11. PXRD patterns of compound 1: (top) simulated, (bottom) synthesized.

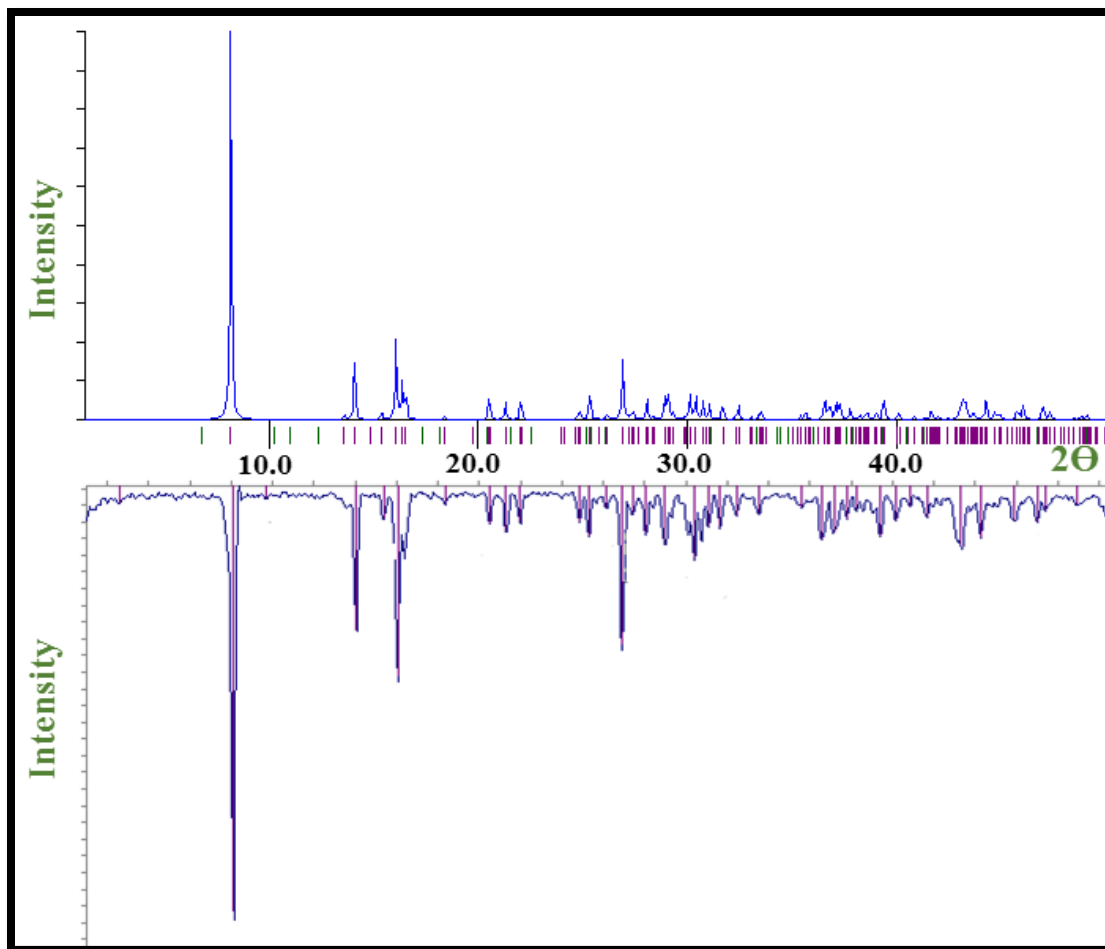


Figure S12. PXRD patterns of compound 2: (top) simulated, (bottom) synthesized.

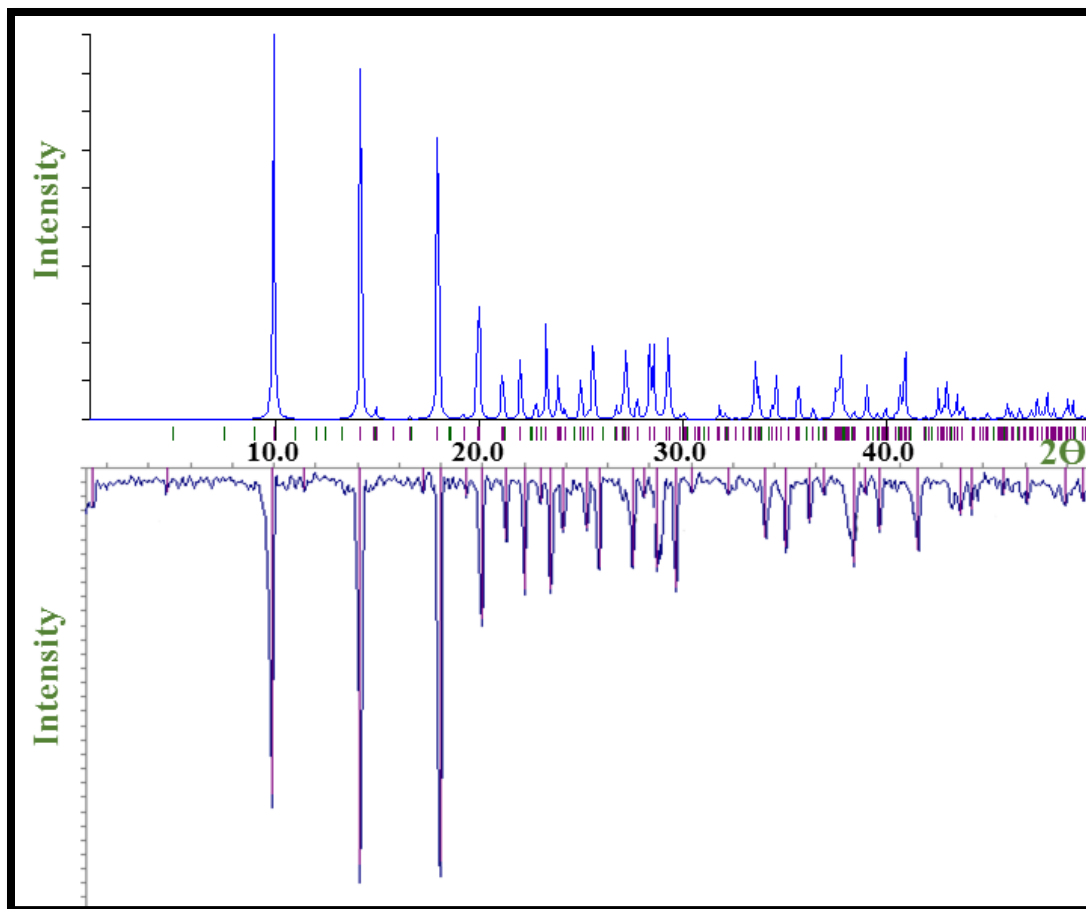


Figure S13. PXRD patterns of compound 3: (top) simulated, (bottom) synthesized.

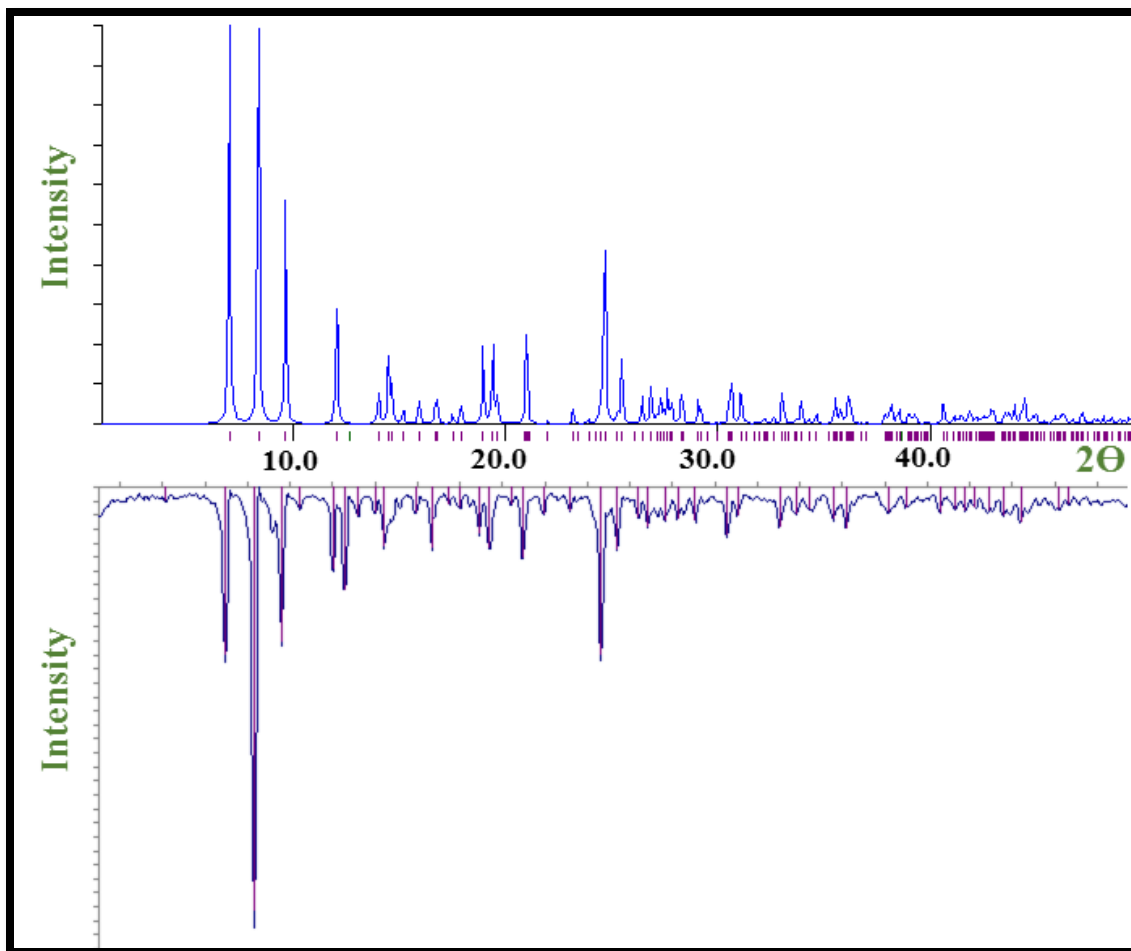


Figure S14. PXRD patterns of compound **4**: (top) simulated, (bottom) synthesized.

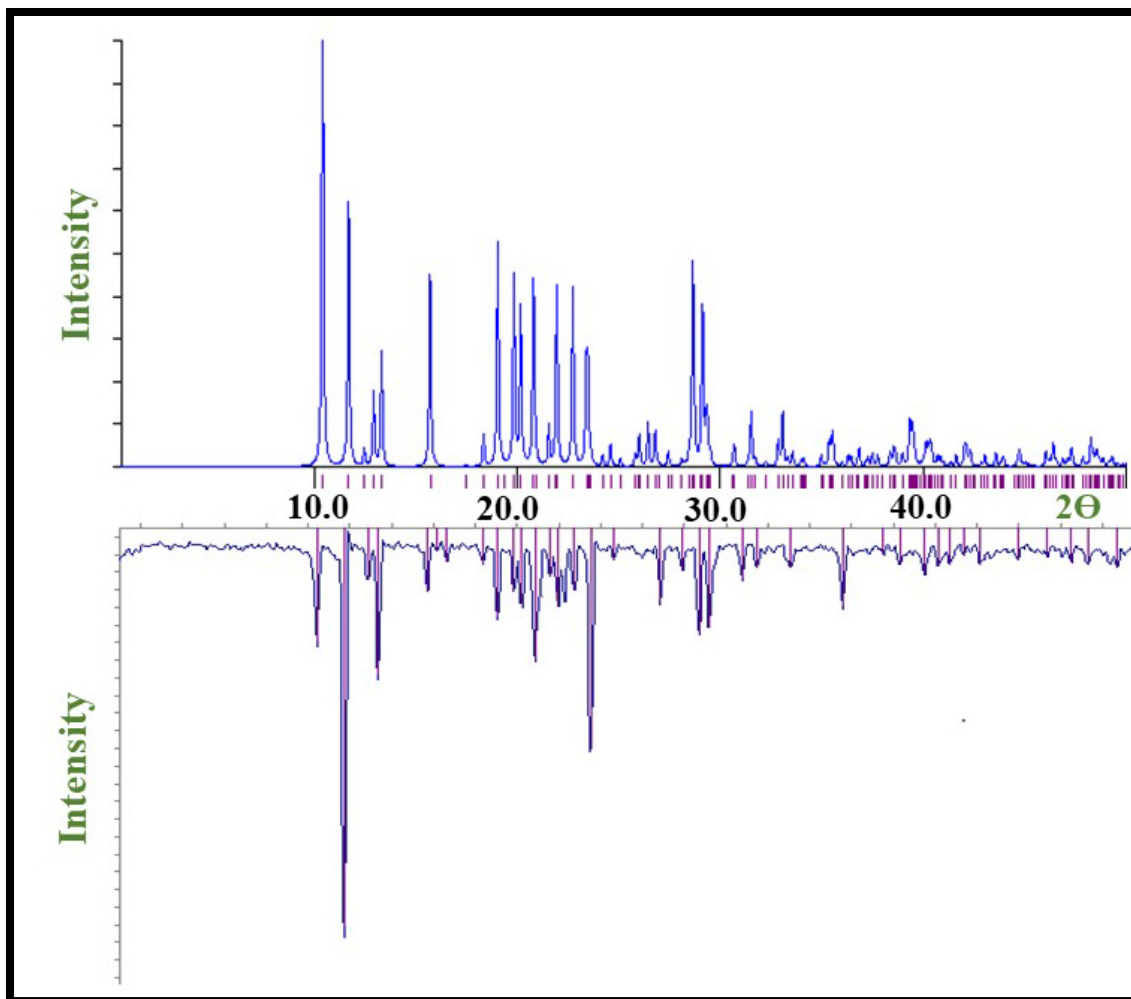


Figure S15. PXRD patterns of compound 5: (top) simulated, (bottom) synthesized.

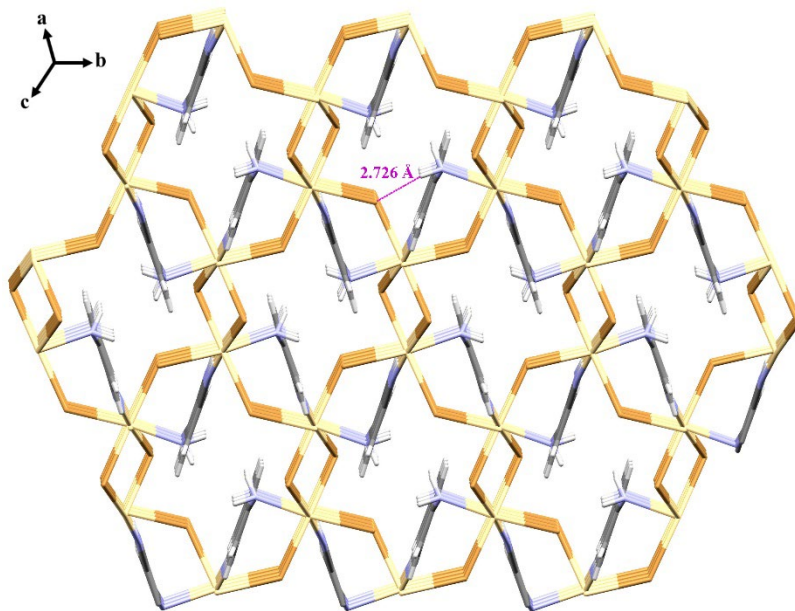


Figure S16. N–H···Br hydrogen bonding interaction which is shown in purple dashed lines in **2**.

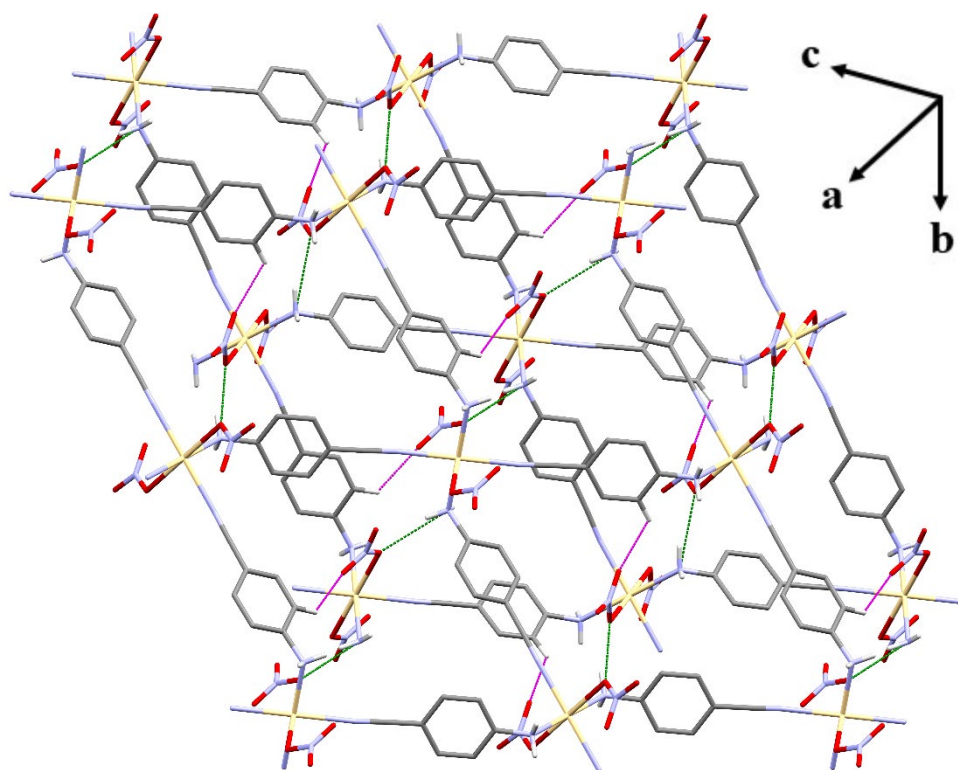


Figure S17. (a) N–H···O and C–H···O hydrogen bonding interactions between AB layers in compound **3** which is shown as green and purple dashed lines, respectively.

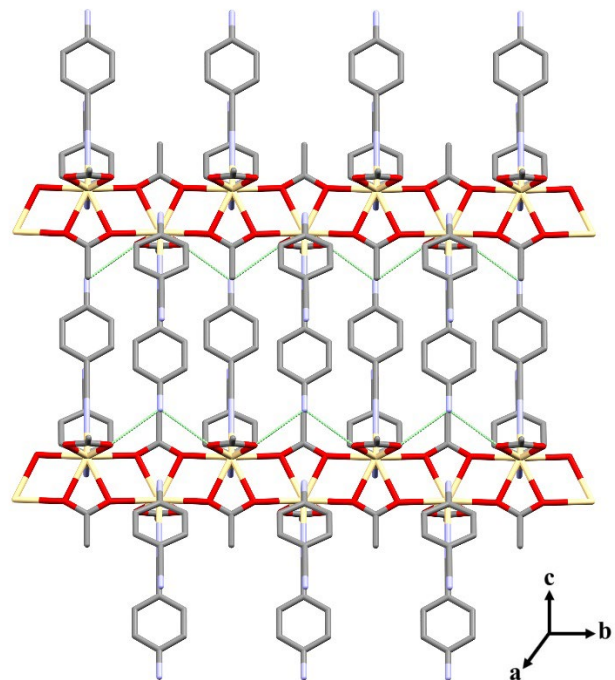


Figure S18. C-H...O hydrogen bond between adjacent chains in **4**.

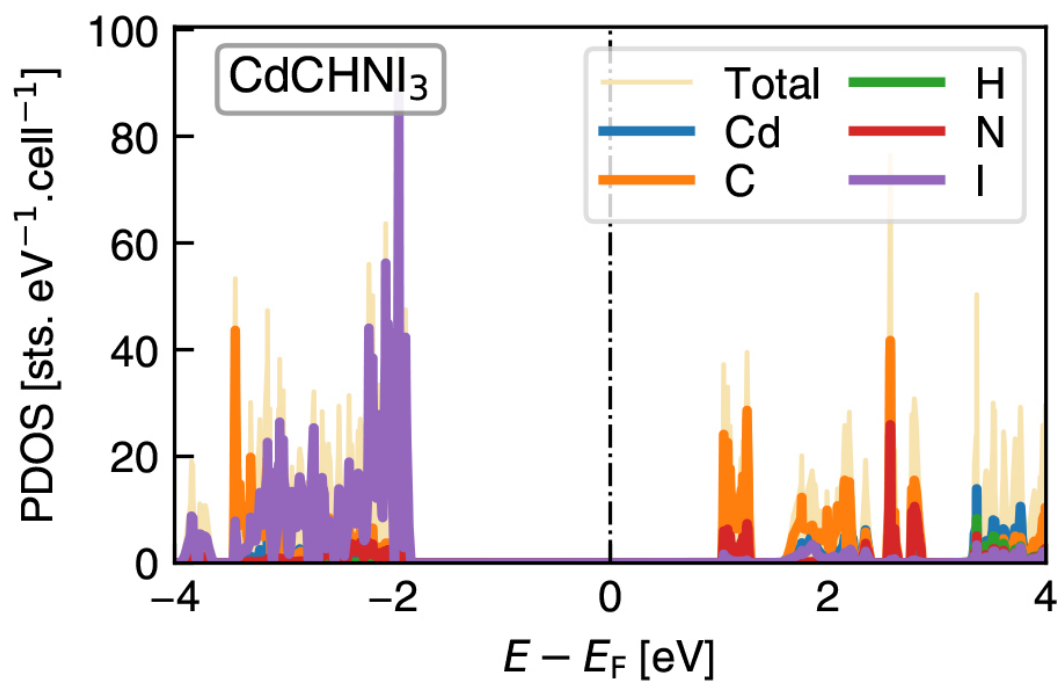


Figure S19. Projected density of states (PDOS) of compound **1**.

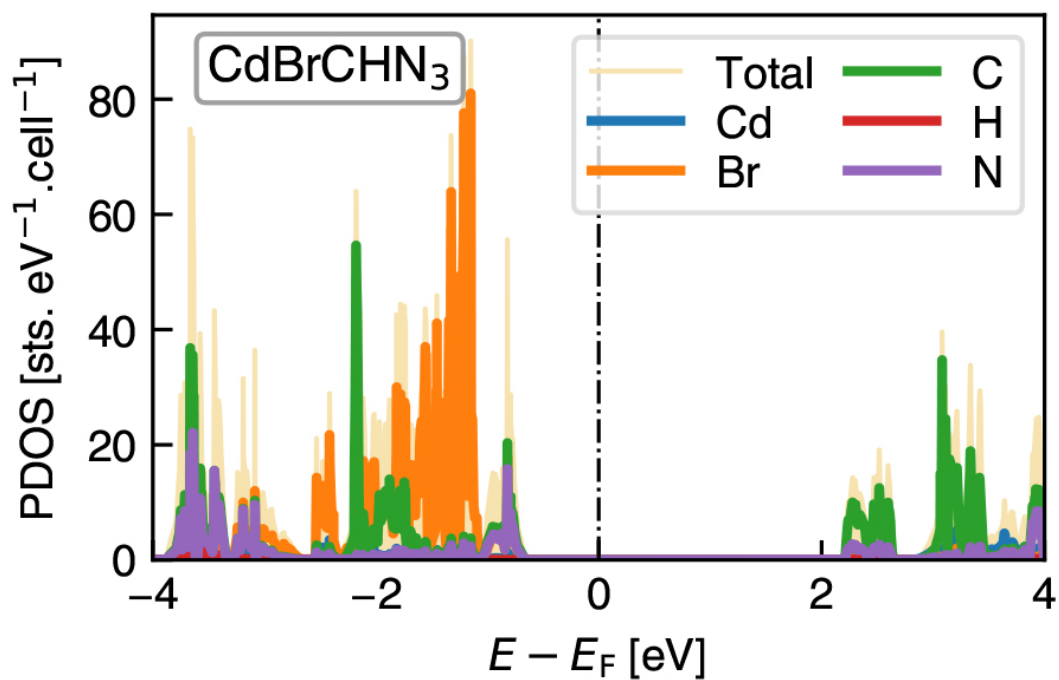


Figure S20. Projected density of states (PDOS) of compound 2.

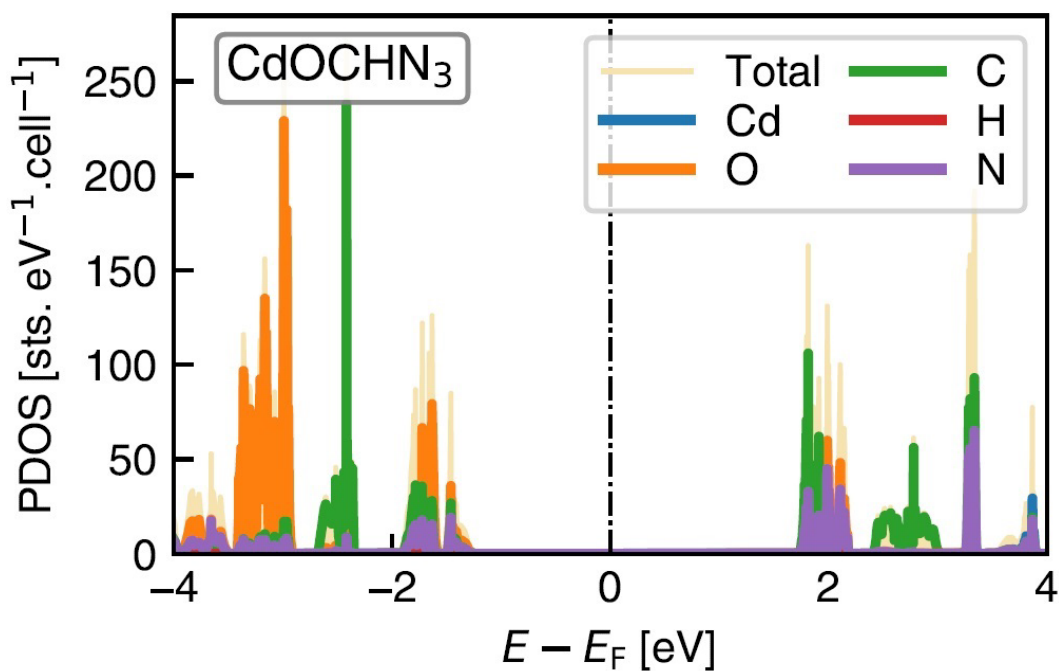


Figure S21. Projected density of states (PDOS) of compound 3.

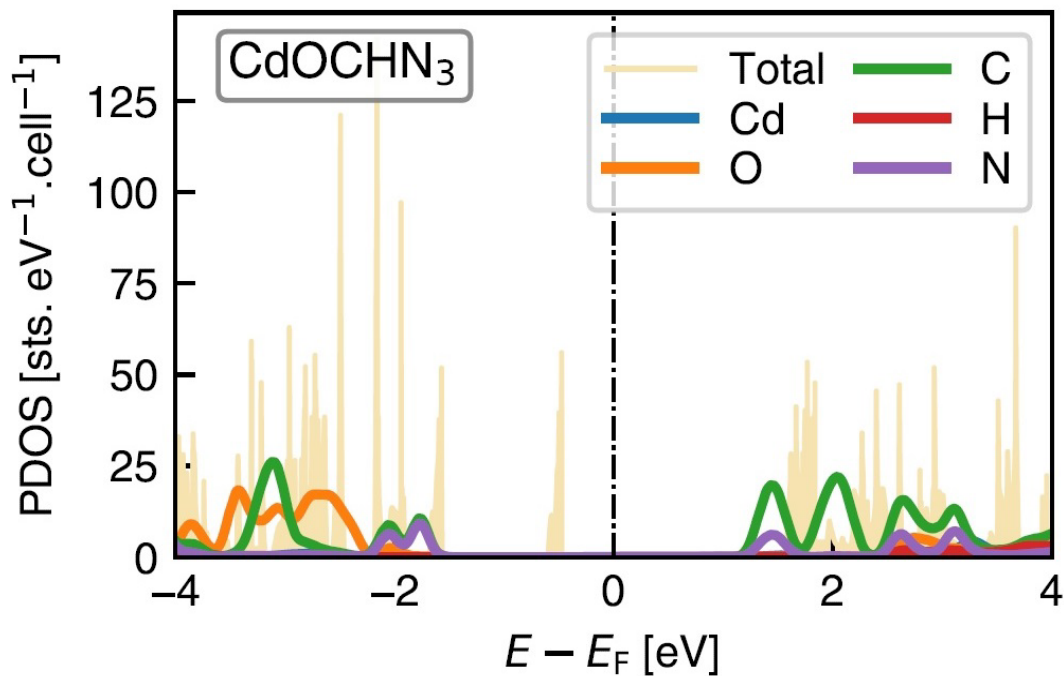


Figure S22. Projected density of states (PDOS) of compound 4.

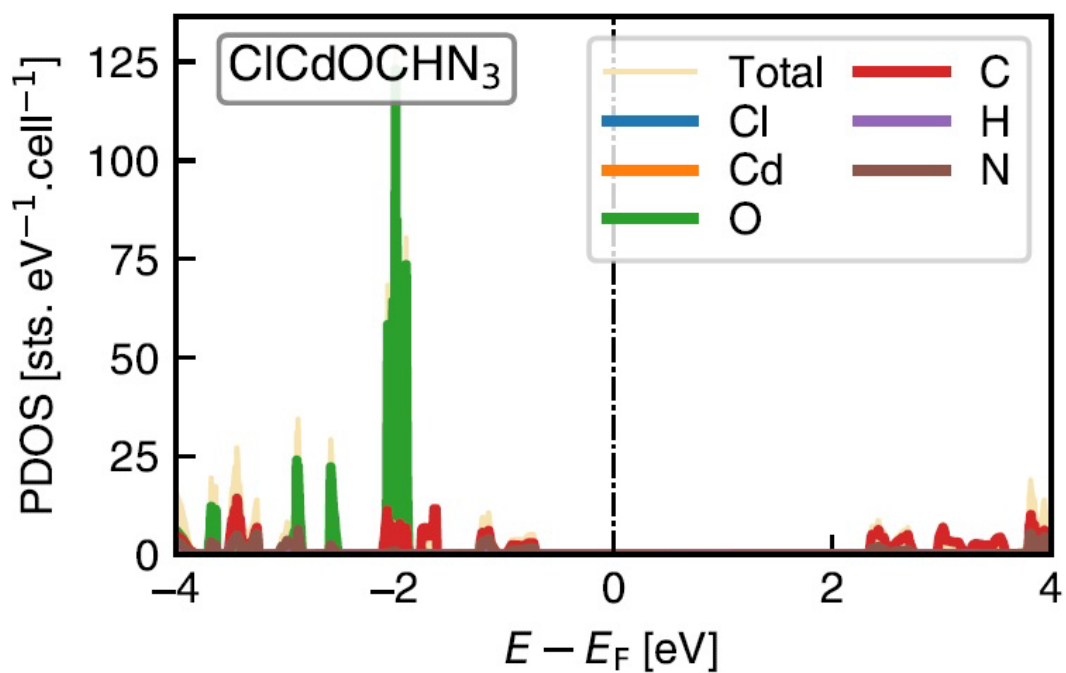


Figure S23. Projected density of states (PDOS) of compound 5.

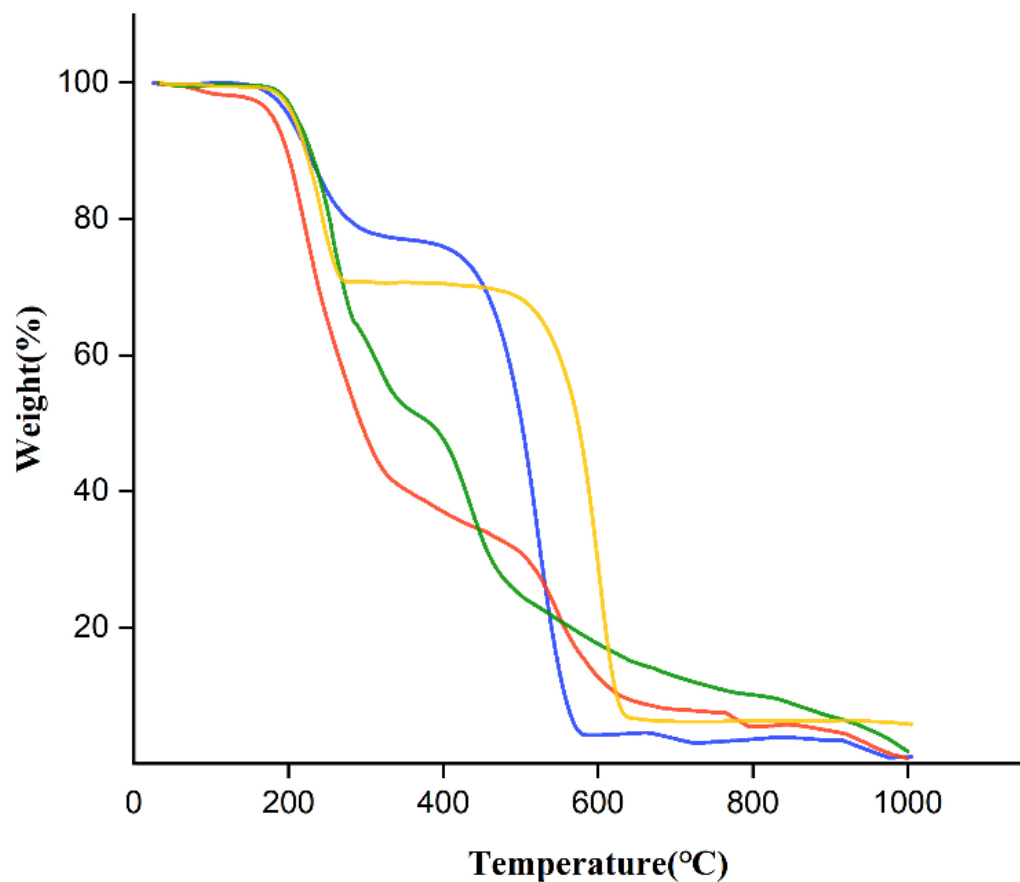


Figure S24. TGA curves of compound **1** (blue), **2** (yellow) under Ar atmosphere and **3** (green), **4** (orange) under N₂ atmosphere.

Table S1. Selected bond lengths (Å) and angles (°) for compound **1**.

Cd(1)-N(2) ^{#1}	2.368(14)	N(2) ^{#1} -Cd(1)-N(1) ^{#3}	94.3(4)
Cd(1)-N(1)	2.470(9)	N(2) ^{#1} -Cd(1)-N(1)	85.0 (4)
Cd(1)-I(1)	2.8815(14)	N(2) ^{#1} -Cd(1)-I(1)	169.9(3)
Cd(2)-I(2)	2.7243(13)	N(1)-Cd(1)-N(1) ^{#3}	179.1 (6)
Cd(2)-I(1)	2.8555(14)	N(1)-Cd(1)-I(1)	88.7(3)
N(2) ^{#1} -Cd(1)-N(2) ^{#2}	80.3(6)	N(2) ^{#2} -Cd(1)-I(1)	92.3 (3)
Symmetry codes; #1: x, -y+1, z-1/2, #2: -x+1, -y+1, -z+1, #3: -x+1, y, -z+1/2			

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

Cd(1)-N(2) ^{#1}	2.357(12)	N(2) ^{#1} -Cd(1)-Br(2) ^{#2}	88.8(4)
Cd(1)-N(1)	2.404(14)	N(1)-Cd(1)-Br(2) ^{#2}	85.6(4)
Cd(1)-Br(1)	2.737(2)	Br(1)-Cd(1)-Br(2) ^{#2}	171.20(6)
Cd(1)-Br(2) ^{#2}	2.738(2)	N(2) ^{#1} -Cd(1)-Br(2)	175.9(4)
Cd(1)-Br(2)	2.747(18)	N(1)-Cd(1)-Br(2)	86.3(3)
Cd(1)-Br(1) ^{#3}	2.755(2)	Br(1)-Cd(1)-Br(2)	93.93(6)
N(2) ^{#1} -Cd(1)-N(1)	90.4(5)	Br(2) ^{#2} -Cd(1)-Br(2)	93.39(6)
N(2) ^{#1} -Cd(1)-Br(1)	83.6(4)	N(2) ^{#1} -Cd(1)-Br(1) ^{#3}	91.7(4)
N(1)-Cd(1)-Br(1)	90.0(4)	N(1)-Cd(1)-Br(1) ^{#3}	174.4(4)
Symmetry codes; #1: -x+1, y-1/2, -z+3/2, #2: -x, -y, -z+1, #3: -x, y-1/2, -z+3/2			

Table S3. Selected bond lengths (Å) and angles (°) for compound **3**.

Cd(1)-N(1)	2.338(6)	N(1)-Cd(1)-O(1)	83.8(2)
Cd(1)-O(1)	2.341(6)	O(1) ^{#1} -Cd(1)-O(1)	180.0(2)
Cd(1)-N(2) ^{#2}	2.405(5)	N(1) ^{#1} -Cd(1)-N(2) ^{#2}	89.1(2)
N(1) ^{#1} -Cd(1)-N(1)	180.0	N(1)-Cd(1)-N(2) ^{#2}	90.9(2)
N(1)-Cd(1)-O(1) ^{#1}	96.2(2)	O(1) ^{#1} -Cd(1)-N(2) ^{#2}	100.3(2)
Symmetry codes; #1: -x+2, -y, -z+1, #2: x, -y+1/2, z+1/2			

Table S4. Selected bond lengths (Å) and angles (°) for compound **4**.

Cd(1)-O(2)	2.457(2)	N(4)-Cd(1)-O(1)	91.87(14)
Cd(1)-N(4)	2.367(4)	N(1)-Cd(1)-O(1)	153.28(7)
Cd(1)-N(1)	2.388(5)	O(1) ^{#2} -Cd(1)-O(1)	52.26(14)
Cd(1)-O(1)	2.448(3)	N(4)-Cd(1)-O(2)	153.27(6)
N(1)-Cd(1)-O(2) ^{#1}	76.60(7)	N(1)-Cd(1)-O(2)	81.83(12)
N(4)-Cd(1)-N(1)	93.69(17)	O(1) ^{#2} -Cd(1)-O(2) ^{#2}	81.51(10)
O(1) ^{#2} -Cd(1)-O(2) ^{#3}	78.04(10)	O(1)-Cd(1)-O(2) ^{#2}	103.97(10)
N(1)-Cd(1)-O(1) ^{#2}	153.28(7)	O(1) ^{#2} -Cd(1)-O(2) ^{#1}	130.01(10)
O(1)-Cd(1)-O(2)	81.51(10)	O(2)-Cd(1)-O(2) ^{#1}	69.37(9)
N(4)-Cd(1)-O(2) ^{#1}	83.93(6)	O(2) ^{#2} -Cd(1)-O(2) ^{#1}	120.03(6)
Symmetry codes; #1: -x+2, -y, -z+1, #2: x, -y+1/2, z, #3: -x+2, y+1/2, -z+1			

Table S5. Selected bond lengths (Å) and angles (°) for compound **5**.

Cd(1)-N(2)	2.296(4)	N(1) ^{#1} -Cd(1)-N(1) ^{#3}	180.0
Cd(1)-O(1)	2.300(4)	O(1)-Cd(1)-O(1) ^{#2}	180.0
Cd(1)-N(1) ^{#1}	2.373(4)	N(2)-Cd(1)-O(1) ^{#2}	91.11 (17)
Cl(1)-O(2)	1.302(6)	N(2)-Cd(1)-N(1) ^{#1}	94.24 (13)
Cl(1)-O(4)	1.377(7)	N(2) ^{#2} -Cd(1)-N(1) ^{#1}	85.76 (13)
Cl(1)-O(3)	1.412(6)	O(1)-Cd(1)-N(1) ^{#1}	94.59 (16)
Cl(1)-O(5)	1.417(6)	O(1) ^{#2} -Cd(1)-N(1) ^{#1}	85.42 (16)
N(2)-Cd(1)-N(2) ^{#2}	180.0	N(2)-Cd(1)-O(1)	88.89 (17)
Symmetry codes; #1: -x, -y+1, -z, #2; -x, -y+1, -z+1, #3: x, y, z+1			

Table S6. Hydrogen bond parameters (D-H...A) for compound **2**.

D-H...A	d (D-H)/Å	d (H...A)/Å	d (D...A)/Å	<(DHA)/°
N(1)-H(1A)...Br(1) ^{#1}	0.87(2)	2.73(6)	3.541(15)	156(13)
Symmetry codes; #1: -x, y+1/2, -z+3/2				

Crystal structure determination and refinement for 1-5:

Single-crystal X-ray diffraction measurement for compounds was performed on a STOE IPDS- II diffractometer with graphite-monochromated Mo-K α radiation. Single crystals of **1-5** were mounted on glass fiber and used for data collection. Cell constant and an orientation matrix were obtained from a least-square refinement of the diffraction data from 6127, 4378, 4707, 4474, 4053 reflections for **1-5**, respectively. All data were collected at room temperature to a maximum 2 θ value of 25° for **1-5**. Diffraction data were collected in a series of ω scans in 1° oscillation and integrated using the Stoe X-AREA¹ software package. Numerical absorption correction was applied using X-RED² and X-SHAPE³ software. The data were corrected for Lorentz and polarizing effects. The structures were solved using direct methods⁴ and analysis of subsequent difference Fourier maps and then refining F² using a full-matrix least-squares procedure with anisotropic displacement parameters.⁵ Crystal data and refinement for compounds **1-5** are summarized in Table 1. The atomic factors used were taken from the international tables for X-ray crystallography.⁶ All improvements were performed using the X-STEP 32 crystallographic software package.⁷

Computational methods

We used ultrasoft pseudopotentials of the Vanderbilt type⁸⁻⁹ using kinetic energy and charge density cutoff energy of 50 and 500 Ry. The Brillouin zone was sampled with 2×2×1 Monkhorst–Pack¹⁰ *k*-point meshes and three times higher for the non-self-consistent calculations. The molecular crystal was fully relaxed for the lattice vectors and atomic positions until the force on each atom was less than 1 mRy/Å. In molecular crystals, van der Waals (vdW) forces are crucial, which dominate large-distance intermolecular interactions but are missing in standard DFT, with uncontrolled errors in the optimal geometry. A previous study using fingerprint analysis¹¹ demonstrated that molecular crystals relaxed with vdW–DF–ob86 functional have the best agreement with the experimental structure parameters. Therefore, in the present study, we employed the vdW–DF–ob86 (optB86b–vdW) scheme¹²⁻¹³ enabling accurate treatments of weak interactions in crystals. The vibrational frequencies were calculated by Gaussian 03 using B3LYP/6-31+G* for light elements and B3LYP/SDD for cadmium and iodide.¹⁴

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