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Supplementary Information

Ligand-driven self-assembly of iodine-based Cd(II) complexes via dissolution-recrystallization structural transformation

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Synthesis of $[Cd(I)(I_3)(phen)_2]I_2$ (5)

The synthetic procedure for **5** is similar to that for **2**, except EtOAc, i-PrOH or i-BuOH (0.01 M, 6 mL) was used as the solvent instead of MeOH or EtOH. After 3 days, the brown polycrystals of **5** were collected (9.3 mg, 63% yield based on **1**). Anal. Calcd for $CdC_{24}H_{16}N_4I_6$ (fw = 1234.25): C, 23.35; H, 1.31; N, 4.54. Found: C, 24.21; H, 1.33; N, 4.67. FT-IR (ATR, cm^{-1}): 1621(w), 1421(s), 840(s), 721(s).

Synthesis of $[Cd(I)_2(phen)_2]I_2$ (6)

The synthetic procedure for **6** is similar to that for **2**, except PrOH or BuOH (0.01 M, 6 mL) was used as the solvent instead of MeOH or EtOH. After 3 days, the brown polycrystals of **6** were collected (6.9 mg, 59% yield based on **1**). Anal. Calcd for $CdC_{24}H_{16}N_4I_4$ (fw = 980.44): C, 29.40; H, 1.64; N, 5.71. Found: C, 28.37; H, 1.54; N, 5.78. FT-IR (ATR, cm^{-1}): 1621(w), 1422(s), 840(s), 721(s).

Synthesis of $[Cd(I)(I_3)(phen)_{1.5}]$ (7)

The synthetic procedure for **7** is similar to that for **2**, except DCM (0.01 M, 6 mL) was used as the solvent instead of MeOH or EtOH. After 2 days, the dark brown block solid of **7** was collected (6.7 mg, 63% yield based on **1**). Anal. Calcd for $CdC_{18}H_{12}N_3I_4$ (fw = 890.34): C, 24.28; H, 1.36; N, 4.72. Found: C, 25.07; H, 1.34; N, 5.13. FT-IR (ATR, cm^{-1}): 1620(w), 1422(s), 841(s), 721(s).

Synthesis of $[Cd(AS)_2(phen)](I_2)_2$ (8)

The synthetic procedure for **8** is similar to that for **2**, except Hx (0.01 M, 6 mL) was used as the solvent instead of MeOH or EtOH. After 3 days, the brown solid of **8** was collected (10.2 mg, 77% yield based on **1**). Anal. Calcd for $CdC_{26}H_{20}N_4O_6I_4$ (fw = 1104.49): C, 28.27; H, 1.83; N, 5.07. Found: C, 28.10; H, 1.70; N, 5.47. FT-IR (ATR, cm^{-1}): 3460-3360(w), 1618(s), 1421(s), 840(s), 722(s).

Table S1. Selected bond distances (Å) for **2**.

Cd1—N3	2.355(4)
Cd1—N4	2.374(4)
Cd1—N2	2.381(4)
Cd1—N1	2.406(4)
Cd1—I4	2.8051(6)
Cd1—I1	3.0359(7)

Table S2. Selected bond angles (°) for **2**.

N3—Cd1—N4	70.50(14)	N2—Cd1—I4	103.88(9)
N3—Cd1—N2	152.22(14)	N1—Cd1—I4	92.25(9)
N4—Cd1—N2	90.37(13)	N3—Cd1—I1	105.74(11)
N3—Cd1—N1	91.00(14)	N4—Cd1—I1	88.3(1)
N4—Cd1—N1	94.98(14)	N2—Cd1—I1	93.2(1)
N2—Cd1—N1	70.19(13)	N1—Cd1—I1	163.05(9)
N3—Cd1—I4	96.89(9)	I4—Cd1—I1	88.417(16)
N4—Cd1—I4	165.53(10)		

Table S3. Intermolecular hydrogen bond lengths (Å) and angles (°) for **2**.

D−H···A	**d(D−H)/Å**	**d(H···A)/Å**	**d(D···A)/Å**	**<(DHA)/°**
C(15)−H(15)···I(2)	0.95	3.06	3.982(7)	165

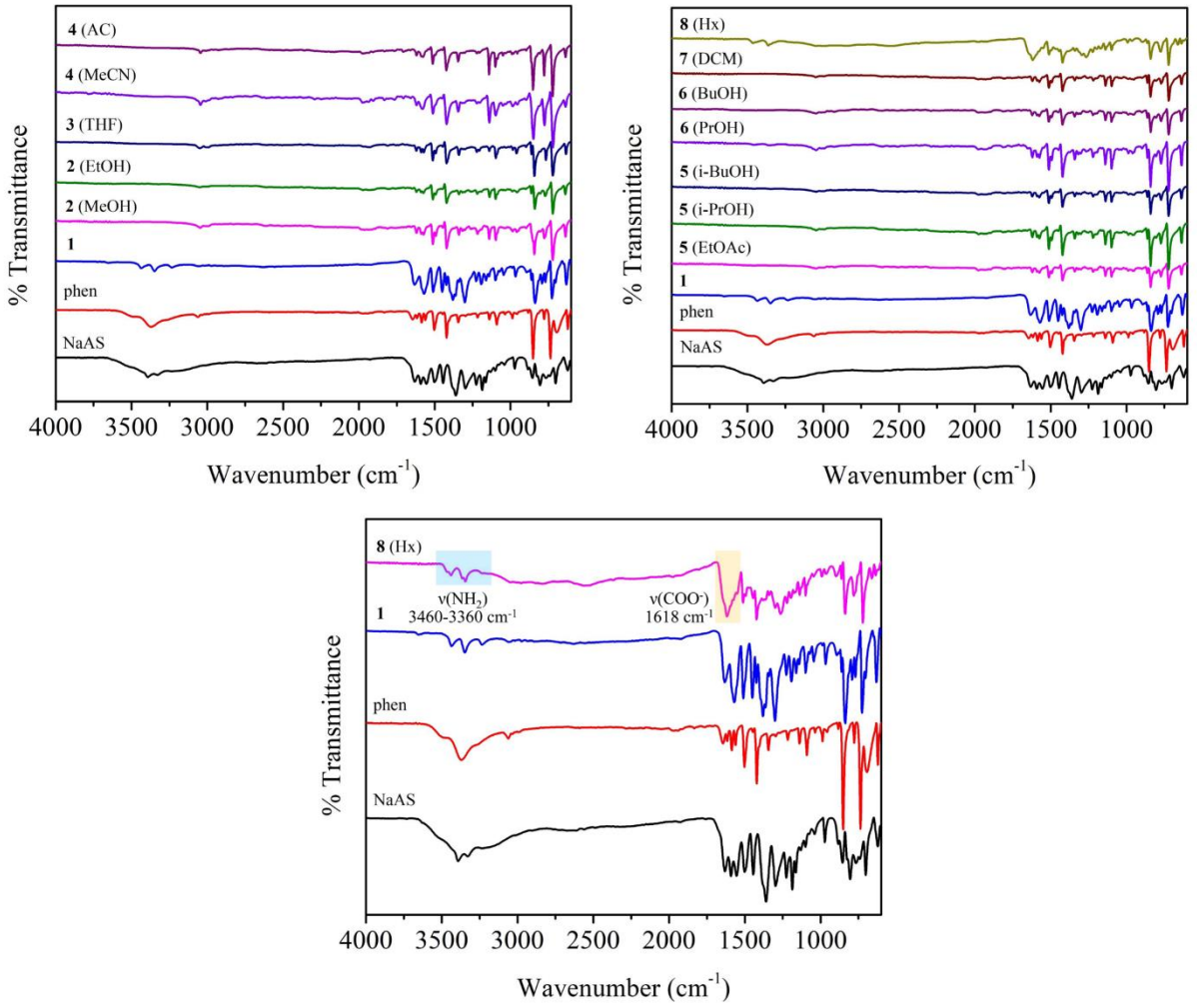
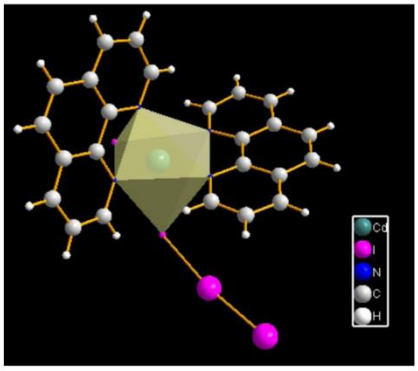
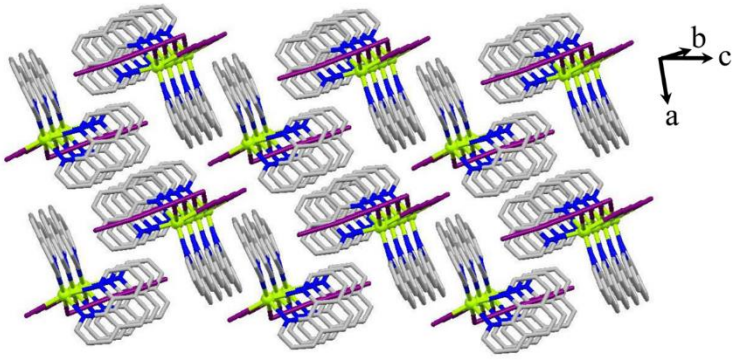


Fig. S1 FT-IR spectra of **2-8** obtained by the different solvents in comparison with the original **1**, and free AS and phen ligands.



(a)



(b)

Fig. S2 (a) Coordination environment around Cd(II) center of **2**, showing an octahedral geometry. (b) 3D supramolecular framework of **2**.

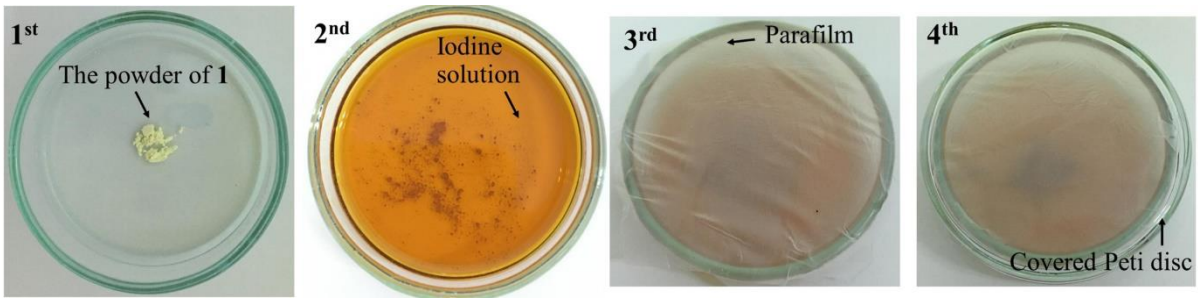


Fig. S3 Experimental set up for following the DRST process. The ground powder of **1** (10 mg) was firstly placed into the Peti disc. Then, 6 mL of iodine solution was added. Parafilm was used to cover the reaction first, then closed by another Peti disc. All covers were removed at different time intervals, and the image of crystal growth was immediately captured under an optical microscope.

Table S4. Details of the direct synthesis of **2-4** at room temperature.

Reactants	**I_2 solutions (0.01 M, 6 mL)**	**Reaction time**	**Final products***
CdI_2:phen (0.012:0.024 mmol)	MeOH	1 day	unidentified brown solid **(A)**
	EtOH	1 day	unidentified brown solid **(B)**
	THF	1 day	yellow polycrystals **(C)**
	MeCN	4 days	mixture of yellow and brown polycrystals **(D)**
	AC	4 days	pale yellow polycrystals **(E)**

*The final products were confirmed by PXRD.

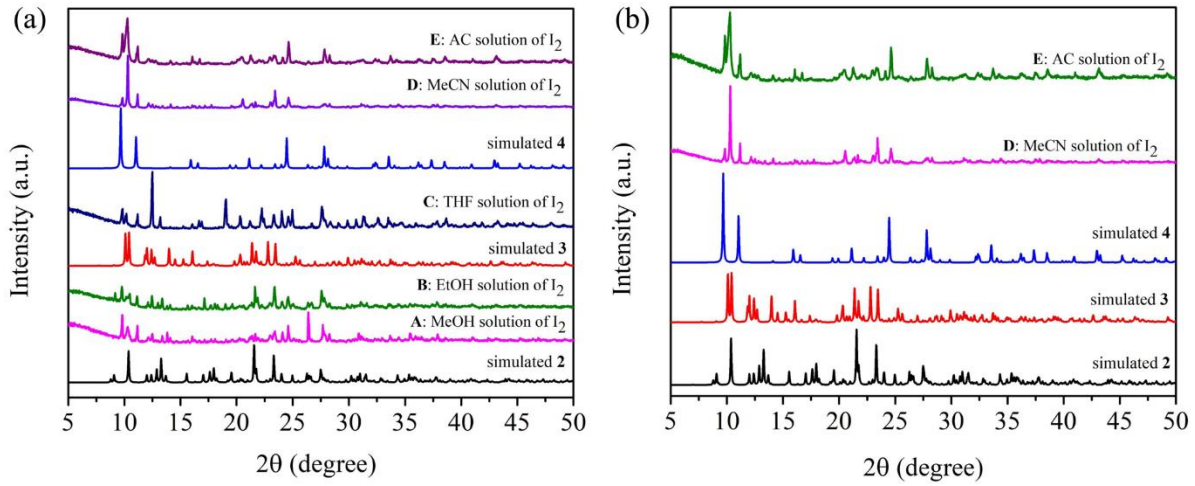


Fig. S4 PXRD patterns of the final products synthesized by using CdI_2 and phen as precursors in I_2 solutions compared with the simulated patterns of complexes **2-4**.

Table S5. Details of the direct synthesis of **2-4** at room temperature.

Reactants	**Solvents**	**Reaction time**	**Final products***
CdI_2:phen (0.012:0.024 mmol)	MeOH	1 day	white polycrystals **(F)**
	EtOH	1 day	white polycrystals **(G)**
	THF	1 day	white polycrystals **(H)**
	MeCN	4 days	white polycrystals **(I)**
	AC	4 days	white polycrystals **(J)**

*The final products were confirmed by PXRD.

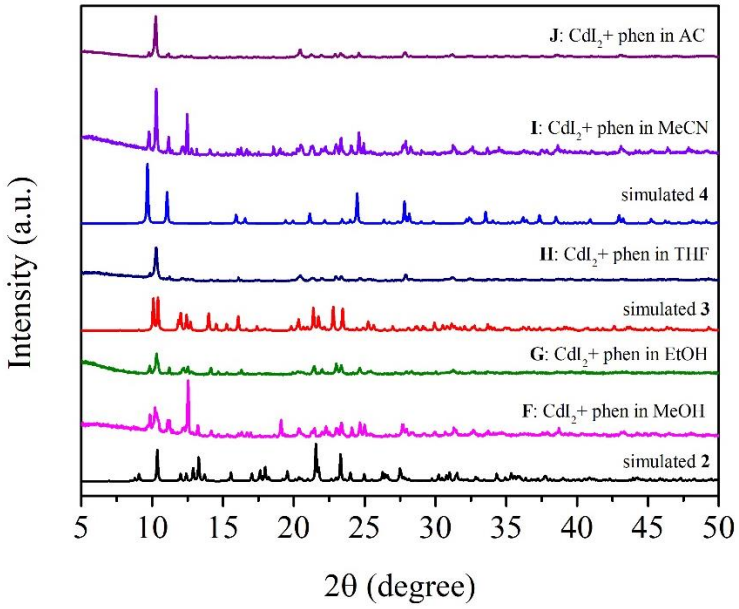


Fig. S5 PXRD patterns of the final products synthesized by using CdI_2 and phen as precursors in different pure solvents compared with the simulated patterns of complexes **2-4**.

Table S6. The synthetic detail of **2-4** by using the starting complexes without AS ligand at room temperature.

Reactants	**I_2 solutions (0.01 M, 6 mL)**	**Reaction time**	**Final products***
Complex **2** (10 mg)	THF	1 day	unidentified black solid **(K)**
	MeCN	4 days	clear brown solution
	AC	4 days	clear brown solution
Complex **3** (10 mg)	MeOH	1 day	unidentified brown solid **(L)**
	EtOH	1 day	unidentified dark brown solid **(M)**
	MeCN	4 days	clear brown solution
	AC	4 days	clear brown solution
Complex **4** (10 mg)	MeOH	1 day	yellow powder of **4** (**N**-MeOH)
	EtOH	1 day	yellow powder of **4** (**N**-EtOH)
	THF	1 day	yellow powder of **4** (**N**-THF)

*The final products were confirmed by PXRD.

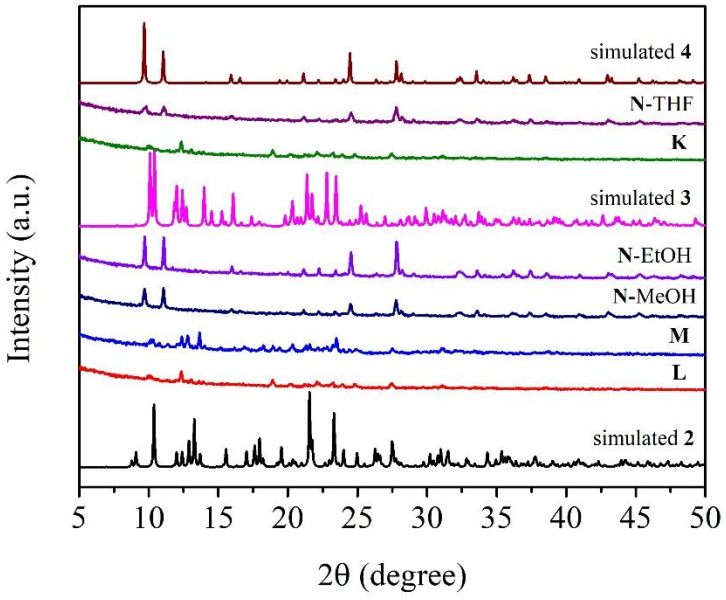


Fig. S6 PXRD patterns of the final products synthesized by using the starting complexes without AS ligand in I_2 solutions compared with the simulated patterns of complexes **2-4**.

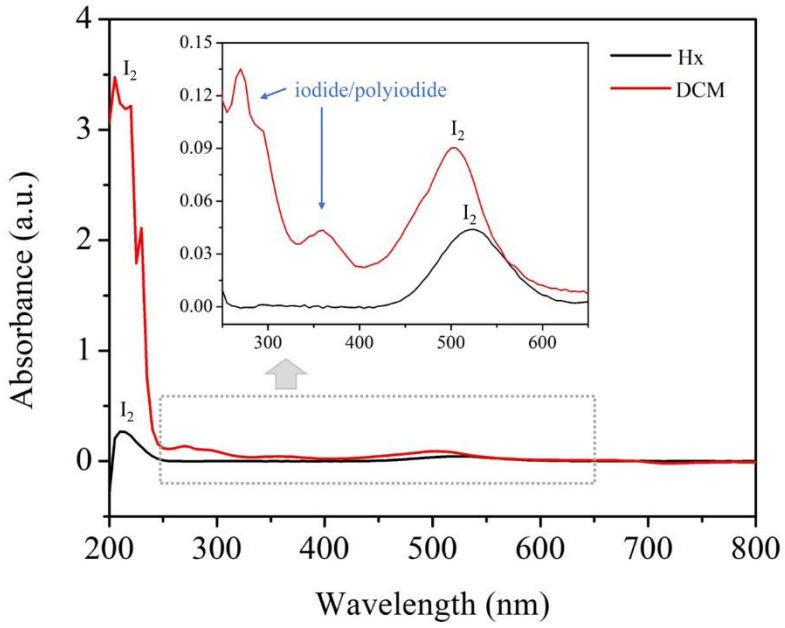


Fig. S7 UV-vis spectra of hexane (Hx) and dichloromethane (DCM) solutions of iodine. The absorption band appear around 204 and 500-520 nm belongs to the neutral I_2 molecules, and the bands at 288 and 360 nm are attributed to the iodide/polyiodide ions.

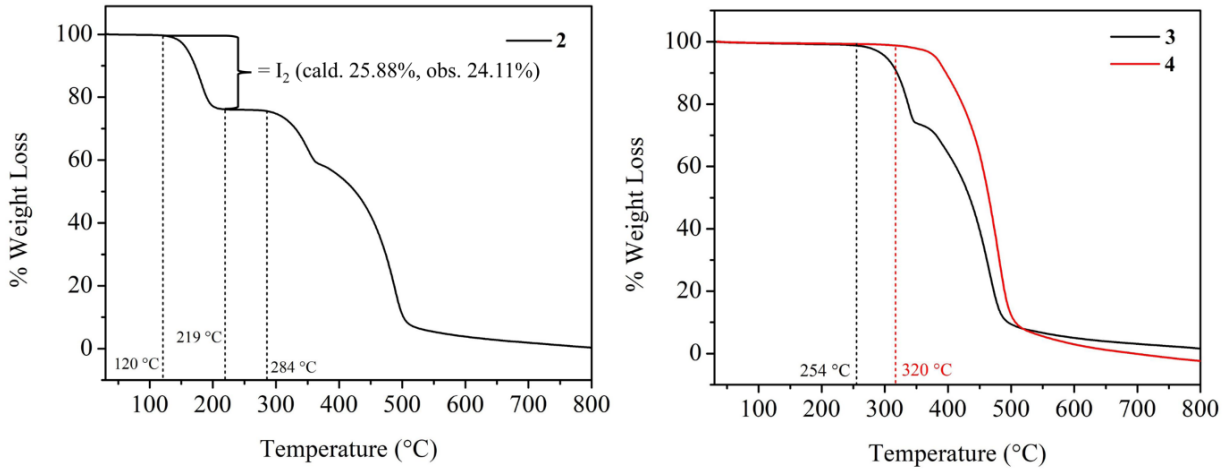


Fig. S8 TG curves of **2-4**.

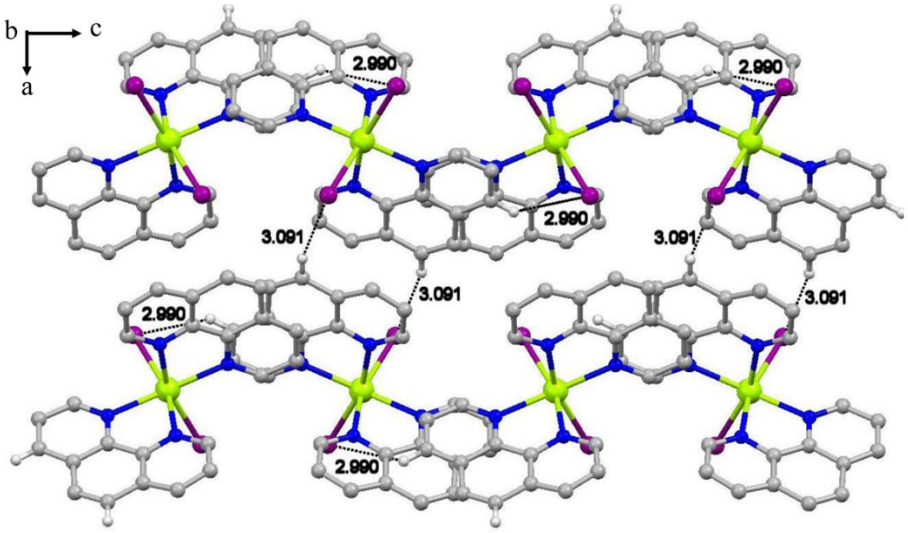


Fig. S9 3D supramolecular framework of **9** stabilized by weak I···H interactions with distances of 3.091 Å for I1···H16A and 2.990 Å for I1···H9A.[1]

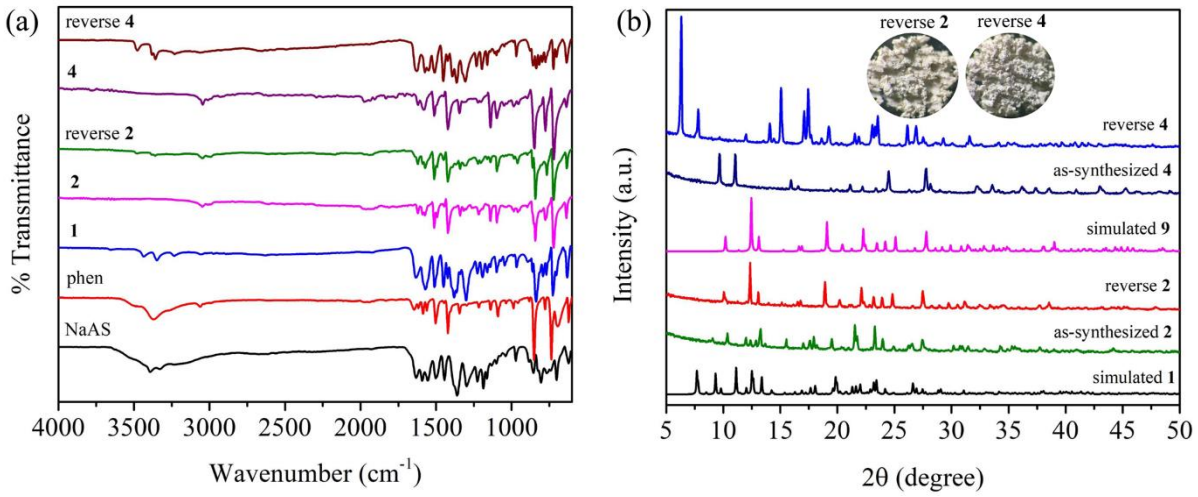


Fig. S10 (a) FT-IR spectra, and (b) PXRD patterns of **2** and **4** after reverse experiments.

Reference

1. Cao, M.-L.; Fang, X.; Yu, H.-Y.; Wang, J.-D. Diiodidobis(1,10-phenanthroline-κ^2N,N')cadmium(II). *Acta Crystallogr. E* **2007,** *63*, m1951.