Supporting Information

The impact of metal ions on photoinduced electron-transfer properties: four photochromic metal-organic frameworks based on a naphthalene diimide chromophore

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Table S1 Selected bond lengths (Å) and angles (°) for **1**-**4**.

Compound **1**

Zn(1)-O(3)#1	2.030(3)	O(3)#2-Zn(1)-O(3)#1	87.3(2)
Zn(1)-O(3)#2	2.030(3)	O(3)#1-Zn(1)-O(6)#3	158.11(13)
Zn(1)-O(6)#3	2.034(3)	O(3)#2-Zn(1)-O(6)#3	87.44(13)
Zn(1)-O(6)	2.034(3)	O(3)#1-Zn(1)-O(6)	87.44(13)
Zn(1)-O(7)	1.950(4)	O(3)#2-Zn(1)-O(6)	158.11(13)
Zn(2)-O(4)#1	2.049(2)	O(6)-Zn(1)-O(6)#3	89.60(17)
Zn(2)-O(4)#2	2.049(2)	O(7)-Zn(1)-O(3)#2	101.42(13)
Zn(2)-O(5)	2.014(3)	O(7)-Zn(1)-O(3)#1	101.42(13)
Zn(2)-O(5)#3	2.013(3)	O(7)-Zn(1)-O(6)	100.45(12)
Zn(2)-O(8)	1.946(4)	O(7)-Zn(1)-O(6)#3	100.45(12)
O(4)#1-Zn(2)-O(4)#2	90.11(15)	O(5)-Zn(2)-O(4)#2	158.59(13)
O(5)#3-Zn(2)-O(4)#2	87.55(12)	O(5)#3-Zn(2)-O(4)#1	158.59(13)

O(5)-Zn(2)-O(4)#1	87.55(12)	O(5)#3-Zn(2)-O(5)	86.9(2)
O(8)-Zn(2)-O(4)#1	100.23(12)	O(8)-Zn(2)-O(4)#2	100.23(12)
O(8)-Zn(2)-O(5)#3	101.12(13)	O(8)-Zn(2)-O(5)	101.12(13)

Compound **2**

Cd(1)-O(5)	2.231(2)	O(5)-Cd(1)-O(5)#1	109.31(13)
Cd(1)-O(5)#1	2.231(2)	O(5)-Cd(1)-O(7)	142.09(8)
Cd(1)-O(7)	2.384(2)	O(5)#1-Cd(1)-O(7)	88.99(10)
Cd(1)-O(7)#1	2.384(2)	O(5)#1-Cd(1)-O(7)#1	142.09(8)
Cd(1)-O(8)	2.376(2)	O(5)-Cd(1)-O(7)#1	88.98(10)
Cd(1)-O(8)#1	2.376(2)	O(5)-Cd(1)-O(8)#1	120.53(8)
O(5)#1-Cd(1)-O(8)#1	87.25(8)	O(5)#1-Cd(1)-O(8)	120.53(8)
O(5)-Cd(1)-O(8)	87.25(8)	O(7)#1-Cd(1)-O(7)	96.38(15)
O(8)-Cd(1)-O(7)	55.13(8)	O(8)#1-Cd(1)-O(7)	92.38(8)
O(8)-Cd(1)-O(7)#1	92.38(8)	O(8)#1-Cd(1)-O(7)#1	55.13(8)
O(8)-Cd(1)-O(8)#1	133.13(12)		

Compound **3**

Ca(1)-O(2)	2.418(2)	O(2)-Ca(1)-Cl(1)	84.38(6)
Ca(1)-O(3)#2	2.357(3)	O(3)#2-Ca(1)-Cl(1)	165.06(9)
Ca(1)-O(9)#3	2.330(2)	O(3)#2-Ca(1)-O(2)	82.95(9)
Ca(1)-O(12)#1	2.331(2)	O(9)#3-Ca(1)-Cl(1)	87.84(6)
Ca(1)-O(15)	2.268(3)	O(9)#3-Ca(1)-O(2)	168.13(8)
Ca(1)-Cl(1)	2.7708(11)	O(9)#3-Ca(1)-O(3)#2	105.86(10)
Ca(2)-O(4)#4	2.300(3)	O(9)#3-Ca(1)-O(12)#1	74.86(8)
Ca(2)-O(9)#5	2.300(3)	O(12)#1-Ca(1)-Cl(1)	97.09(7)
Ca(2)-O(10)#5	2.455(2)	O(12)#1-Ca(1)-O(2)	114.97(9)
Ca(2)-O(11)	2.436(2)	O(12)#1-Ca(1)-O(3)#2	81.21(10)
Ca(2)-O(12)	2.561(2)	O(15)-Ca(1)-Cl(1)	95.46(10)
Ca(2)-O(13)	2.339(3)	O(15)-Ca(1)-O(2)	85.48(11)
Ca(2)-O(14)	2.280(3)	O(15)-Ca(1)-O(3)#2	91.40(13)
O(4)#4-Ca(3)-O(12)	84.63(11)	O(15)-Ca(1)-O(9)#3	86.34(10)
O(9)#5-Ca(3)-O(12)	67.82(7)	O(15)-Ca(1)-O(12)#1	156.90(11)

O(10)#5-Ca(3)-O(12)	119.71(8)	O(4)#4-Ca(2)-O(9)#5	86.91(10)
O(11)-Ca(3)-O(10)#5	171.38(9)	O(4)#4-Ca(2)-O(10)#5	96.70(10)
O(13)-Ca(3)-O(9)#5	83.82(10)	O(4)#4-Ca(2)-O(11)	86.85(10)
O(13)-Ca(3)-O(11)	92.80(11)	O(4)#4-Ca(2)-O(12)	84.52(9)
O(14)-Ca(3)-O(4)#4	97.53(16)	O(4)#4-Ca(2)-O(13)	169.10(11)
O(14)-Ca(3)-O(10)#5	92.35(13)	O(9)#5-Ca(2)-O(12)	67.79(7)
O(10)#5-Ca(2)-O(9)#5	52.23(7)	O(10)#5-Ca(2)-O(12)	119.73(7)
O(11)-Ca(2)-O(9)#5	120.39(7)	O(11)-Ca(2)-O(10)#5	171.35(8)
O(11)-Ca(2)-O(12)	52.61(7)	O(13)-Ca(2)-O(9)#5	83.83(9)
O(13)-Ca(2)-O(10)#5	82.15(10)	O(13)-Ca(2)-O(11)	92.86(10)
O(13)-Ca(2)-O(12)	86.65(10)	O(14)-Ca(2)-O(4)#4	97.46(14)
O(14)-Ca(2)-O(9)#5	144.63(11)	O(14)-Ca(2)-O(10)#5	92.42(11)
O(14)-Ca(2)-O(11)	94.94(11)	O(14)-Ca(2)-O(12)	147.45(11)
O(14)-Ca(2)-O(13)	93.42(15)		

Compound **4**

Ba(1)-O(1)#1	2.727(7)	O(1)#1-Ba(1)-O(2)#1	47.63(19)
Ba(1)-O(2)#1	2.807(6)	O(1)#1-Ba(1)-O(23)#2	147.2(2)
Ba(1)-O(3)	2.714(7)	O(1)#1-Ba(1)-O(24)#2	132.87(19)
Ba(1)-O(22)#2	2.672(7)	O(1)#1-Ba(1)-O(25)	69.8(4)
Ba(1)-O(23)#3	2.765(7)	O(1)#1-Ba(1)-O(26)	111.6(2)
Ba(1)-O(24)#3	2.847(7)	O(1)#1-Ba(2)-O(27)#3	72.5(2)
Ba(1)-O(25)	2.737(18)	O(2)#1-Ba(1)-O(24)#2	172.1(2)
Ba(1)-O(26)	2.897(8)	O(2)#1-Ba(1)-O(26)	66.8(2)
Ba(1)-O(27)#4	2.845(8)	O(2)#1-Ba(1)-O(27)#3	119.8(2)
Ba(2)-O(2)#1	2.683(7)	O(3)-Ba(1)-O(1)#1	108.16(19)
Ba(2)-O(3)	2.807(7)	O(3)-Ba(1)-O(2)#1	75.5(2)
Ba(2)-O(4)	2.829(9)	O(3)-Ba(1)-O(23)#2	103.4(2)
Ba(2)-O(21)#5	2.795(9)	O(3)-Ba(1)-O(24)#2	98.0(2)
Ba(2)-O(22)#5	2.745(6)	O(3)-Ba(1)-O(25)	139.0(4)
Ba(2)-O(24)#2	2.694(6)	O(3)-Ba(1)-O(26)	65.1(2)
Ba(2)-O(26)	2.884(7)	O(3)-Ba(1)-O(27)#3	139.4(2)

Ba(2)-O(27)	2.874(8)	O(22)#4-Ba(1)-O(1)#1	79.8(2)
Ba(2)-O(28)	2.876(9)	O(22)#4-Ba(1)-O(2)#1	100.60(19)
Ba(3)-O(9)#7	2.731(10)	O(22)#4-Ba(1)-O(3)	70.7(2)
Ba(3)-O(10)#7	2.888(10)	O(22)#4-Ba(1)-O(23)#2	119.6(2)
Ba(3)-O(11)	2.716(8)	O(22)#4-Ba(1)-O(24)#2	72.72(18)
Ba(3)-O(14)	2.685(8)	O(22)#4-Ba(1)-O(25)	142.7(4)
Ba(3)-O(15)#6	2.897(11)	O(22)#4-Ba(1)-O(26)	135.7(2)
Ba(3)-O(16)#6	2.753(10)	O(22)#4-Ba(1)-O(27)#3	69.6(2)
Ba(3)-O(22)#29	2.905(11)	O(23)#2-Ba(1)-O(2)#1	137.3(2)
Ba(3)-O(31)#6	2.861(12)	O(23)#2-Ba(1)-O(24)#2	47.98(19)
Ba(4)-O(10)#7	2.666(8)	O(23)#2-Ba(1)-O(26)	74.2(2)
Ba(4)-O(11)	2.824(11)	O(23)#2-Ba(1)-O(27)#3	89.2(2)
Ba(4)-O(12)	2.850(11)	O(24)#2-Ba(1)-O(26)	114.9(2)
Ba(4)-O(13)#7	2.795(10)	O(25)-Ba(1)-O(2)#1	74.7(4)
Ba(4)-O(14)#7	2.801(10)	O(25)-Ba(1)-O(23)#2	80.7(4)
Ba(4)-O(15)	2.715(9)	O(25)-Ba(1)-O(24)#2	113.1(4)
Ba(4)-O(29)	2.969(12)	O(25)-Ba(1)-O(26)	77.4(4)
Ba(4)-O(30)	2.860(11)	O(25)-Ba(1)-O(27)#3	80.6(4)
Ba(4)-O(31)	2.887(14)	O(27)#3-Ba(1)-O(24)#2	62.4(2)
O(27)#3-Ba(1)-O(26)	154.3(2)	O(2)#1-Ba(2)-O(3)	76.0(2)
O(2)#1-Ba(2)-O(4)	122.0(2)	O(2)#1-Ba(2)-O(21)#5	82.2(3)
O(2)#1-Ba(2)-O(22)#5	90.4(2)	O(2)#1-Ba(2)-O(24)#4	69.0(2)
O(2)#1-Ba(2)-O(26)	68.5(2)	O(2)#1-Ba(2)-O(27)	131.8(2)
O(2)#1-Ba(2)-O(28)	152.5(3)	O(3)-Ba(2)-O(4)	46.6(2)
O(3)-Ba(2)-O(26)	64.2(2)	O(3)-Ba(2)-O(27)	112.4(2)
O(3)-Ba(2)-O(28)	121.1(2)	O(4)-Ba(2)-O(26)	78.1(3)
O(4)-Ba(2)-O(27)	85.3(3)	O(4)-Ba(2)-O(28)	75.6(2)
O(21)#5-Ba(2)-O(3)	138.2(2)	O(21)#5-Ba(2)-O(4)	132.8(3)
O(21)#5-Ba(2)-O(26)	74.8(2)	O(21)#5-Ba(2)-O(27)	108.8(2)
O(21)#5-Ba(2)-O(28)	70.9(3)	O(22)#5-Ba(2)-O(3)	162.07(19)

O(22)#5-Ba(2)-O(4)	147.4(2)	O(22)#5-Ba(2)-O(21)#5	48.3(2)
O(22)#5-Ba(2)-O(26)	121.9(2)	O(22)#5-Ba(2)-O(27)	68.2(2)
O(22)#5-Ba(2)-O(28)	76.1(2)	O(24)#4-Ba(2)-O(3)	89.98(19)
O(24)#4-Ba(2)-O(4)	111.9(3)	O(24)#5-Ba(2)-O(21)#5	114.8(2)
O(24)#5-Ba(2)-O(22)#5	74.0(2)	O(24)#5-Ba(2)-O(26)	134.3(2)
O(24)#5-Ba(2)-O(27)	63.8(2)	O(24)#5-Ba(2)-O(28)	127.4(3)
O(27)-Ba(2)-O(26)	159.2(3)	O(27)-Ba(2)-O(28)	65.2(3)
O(28)-Ba(2)-O(26)	98.2(3)	O(9)#7-Ba(3)-O(10)#7	47.9(3)
O(9)#7-Ba(3)-O(15)#6	132.4(3)	O(9)#7-Ba(3)-O(16)#6	150.1(4)
O(9)#7-Ba(3)-O(29)	112.1(3)	O(9)#7-Ba(3)-O(31)#6	72.0(3)
O(10)#7-Ba(3)-O(15)#6	173.6(2)	O(10)#7-Ba(3)-O(29)	67.7(3)
O(11)-Ba(3)-O(9)#7	108.8(3)	O(11)-Ba(3)-O(10)#7	75.8(3)
O(11)-Ba(3)-O(16)#6	100.4(3)	O(11)-Ba(3)-O(29)	67.0(3)
O(11)-Ba(3)-O(31)#6	139.3(4)	O(14)-Ba(3)-O(9)#7	80.0(3)
O(14)-Ba(3)-O(10)#7	99.6(3)	O(14)-Ba(3)-O(11)	69.1(3)
O(14)-Ba(3)-O(15)#6	74.8(3)	O(14)-Ba(3)-O(16)#6	117.9(3)
O(14)-Ba(3)-O(29)	136.1(3)	O(14)-Ba(3)-O(31)#6	71.1(4)
O(15)#6-Ba(3)-O(29)	114.1(3)	O(16)#6-Ba(3)-O(15)#6	45.6(3)
O(16)#6-Ba(3)-O(10)#7	138.5(3)	O(16)#6-Ba(3)-O(29)	72.9(4)
O(16)#6-Ba(3)-O(31)#6	90.6(4)	O(31)#6-Ba(3)-O(10)#7	119.6(3)
O(31)#6-Ba(3)-O(15)#6	61.9(3)	O(31)#6-Ba(3)-O(29)	152.4(4)
O(10)#7-Ba(4)-O(11)	77.7(3)	O(10)#7-Ba(4)-O(12)	123.0(3)
O(10)#7-Ba(4)-O(13)#7	81.4(4)	O(10)#7-Ba(4)-O(14)#7	88.1(3)
O(10)#7-Ba(4)-O(15)	68.9(3)	O(10)#7-Ba(4)-O(29)	69.6(3)
O(10)#7-Ba(4)-O(30)	154.0(3)	O(10)#7-Ba(4)-O(31)	131.0(3)
O(11)-Ba(4)-O(12)	46.0(3)	O(11)-Ba(4)-O(29)	64.8(3)
O(11)-Ba(4)-O(30)	119.9(3)	O(11)-Ba(4)-O(31)	112.2(3)
O(12)-Ba(4)-O(29)	77.7(3)	O(12)-Ba(4)-O(30)	74.6(3)
O(12)-Ba(4)-O(31)	86.0(3)	O(13)#7-Ba(4)-O(11)	139.1(3)
O(13)#7-Ba(4)-O(12)	133.0(4)	O(13)#7-Ba(4)-O(14)#7	46.8(3)

O(13)#7-Ba(4)-O(29)	75.1(3)	O(13)#7-Ba(4)-O(30)	72.9(4)
O(13)#7-Ba(4)-O(31)	108.0(4)	O(14)#7-Ba(4)-O(11)	162.0(2)
O(14)#7-Ba(4)-O(12)	148.8(3)	O(14)#7-Ba(4)-O(29)	120.6(3)
O(14)#7-Ba(4)-O(30)	77.3(3)	O(14)#7-Ba(4)-O(31)	69.1(3)
O(15)-Ba(4)-O(11)	88.5(3)	O(15)-Ba(4)-O(12)	110.5(3)
O(15)-Ba(4)-O(13)#7	116.0(3)	O(15)-Ba(4)-O(14)#7	75.9(3)
O(15)-Ba(4)-O(29)	134.4(3)	O(15)-Ba(4)-O(30)	126.3(4)
O(15)-Ba(4)-O(31)	63.8(3)		

Symmetry transformations used to generate equivalent atoms: for **1**: #1 -1/2+x, 3/2-y, 1-z. #2 -1/2+x, 3/2-y, -1/2+z #3 +x, +y, 1/2-z #4 1/2+x, 3/2-y, 1-z #5 1-x, 1-y, 1-z; for **2**: #1 1-x, +y, 1/2-z. #2 3/2-x, 3/2-y, 3/2-z #3 2-x, 1-y, 1-z; for **3**: #1 1-x, 2-y, -z. #2 1-x,3-y,-1-z #3 -x, 2-y, -z #4 +x, -1+y, 1+z #5 1+x, +y, +z #6 +x, 1+y, -1+z #7 -1+x, +y, +z; for **4**: #1 1-x, 1/2+y, 3/2-z. #2 +x, +y, 1+z #3 1-x, -1/2+y, 1/2-z #4 1-x, -1/2+y, 3/2-z #5 1-x, 1/2+y, 1/2-z #6 -x, -1/2+y, 1/2-z #7 -x, 1/2+y, 1/2-z.

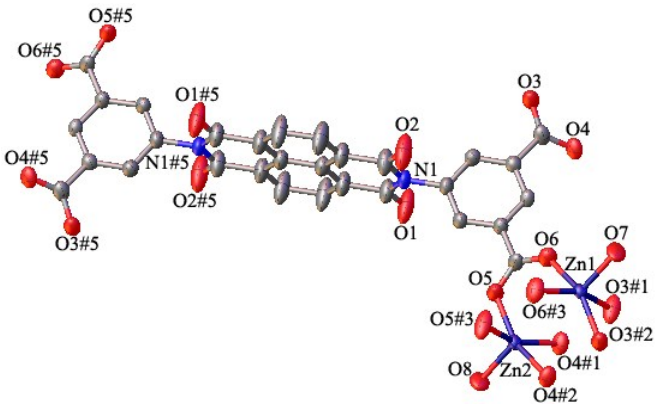


Fig. S1 Coordination environment of the Zn(II) atoms in **1**. (Symmetry codes: [#1]-1/2+x, 3/2-y, 1-z; [#2]-1/2+x, 3/2-y, -1/2+z; [#3]+x, +y, 1/2-z; [#5]1-x, 1-y, 1-z).

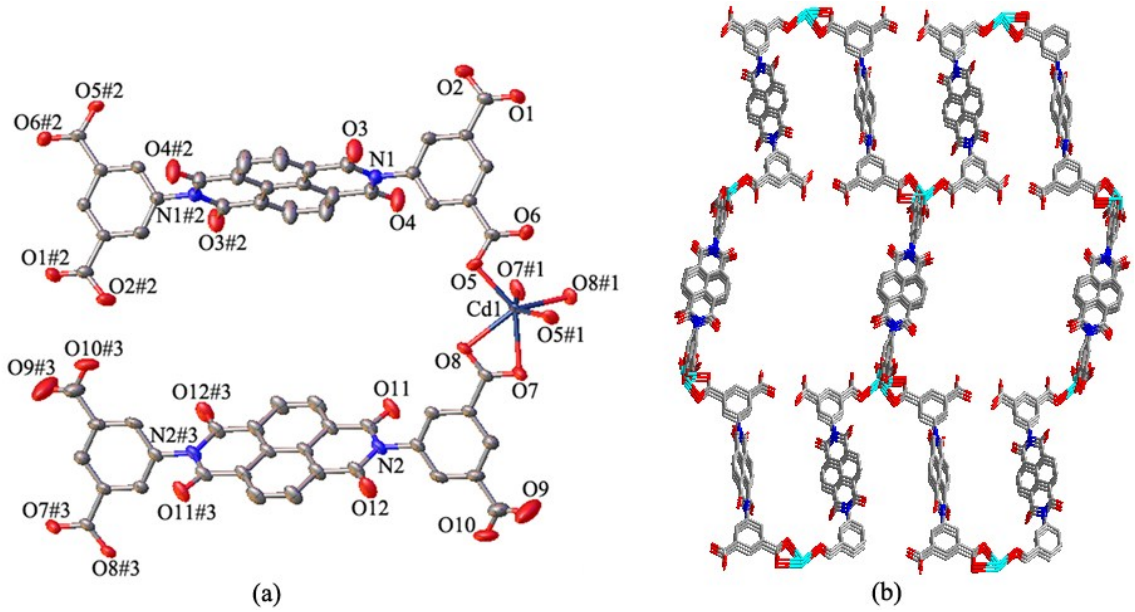


Fig. S2 (a) Coordination environment of the Cd(II) atoms in **2**. (with hydrogen atoms and free DMF omitted for clarity) (Symmetry codes: [#1]1-x, +y, 1/2-z; [#2]3/2-x, 3/2-y, 3/2-z; [#3]2-x, 1-y, 1-z). (b) View of a single 3D framework in **2**.

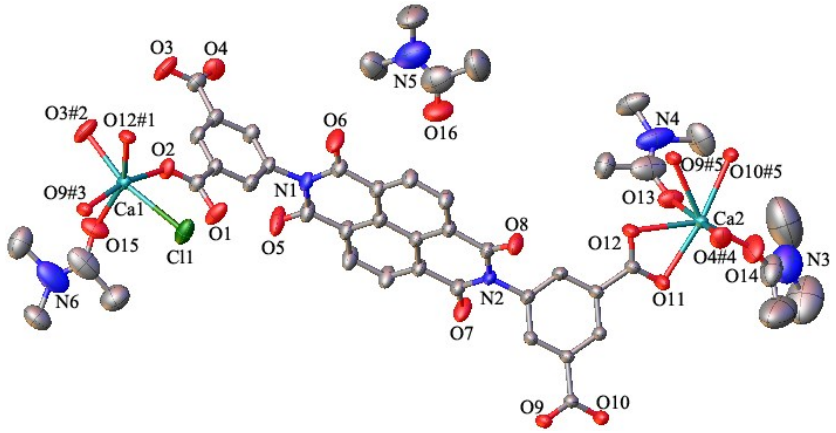


Fig. S3 Coordination environment of the Ca(II) atoms in **3**. (Symmetry codes: [#1]1-x, 2-y, -z. [#2]1-x,3-y,-1-z [#3]-x, 2-y, -z [#4]+x, -1+y, 1+z [#5]1+x, +y, +z).

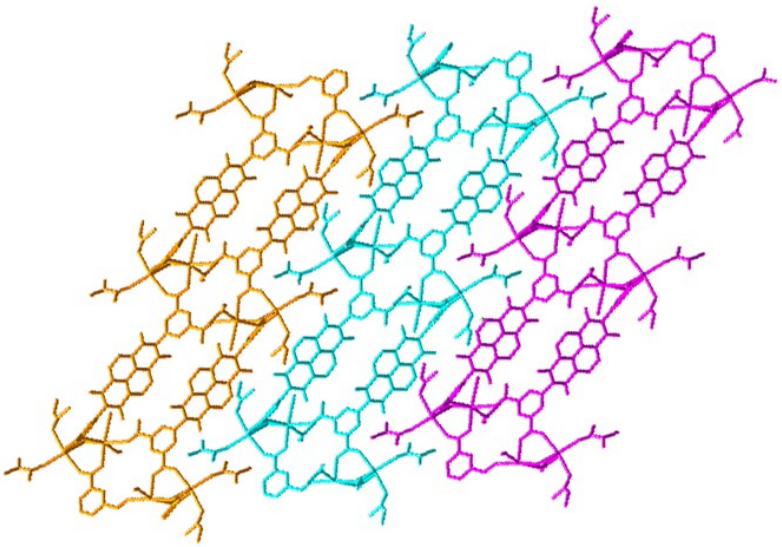


Figure S4 View of the 2D → 3D interdigitated array of **3**.

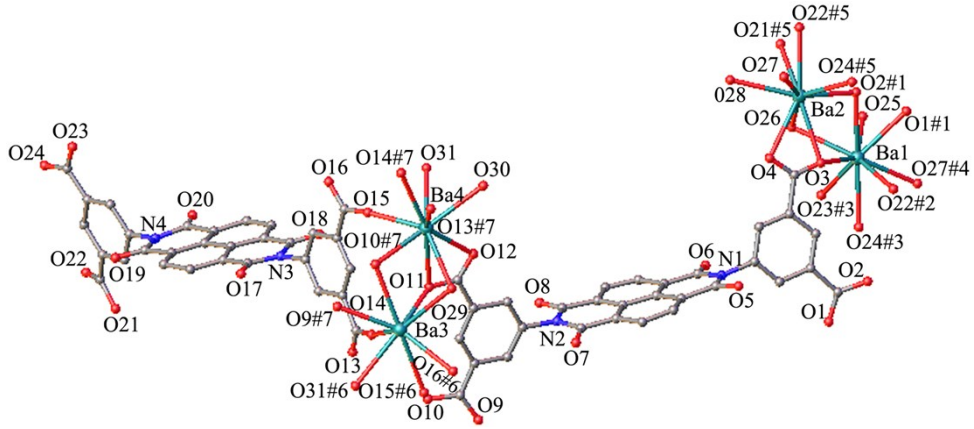
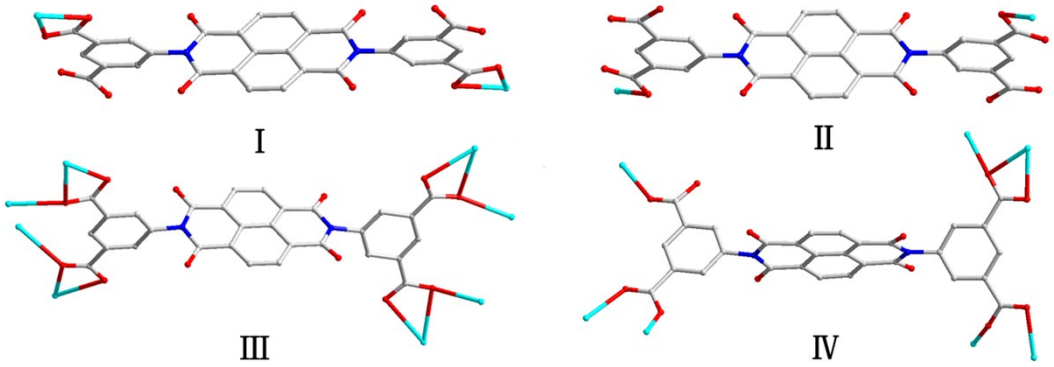


Fig. S5 (a) Coordination environment of the Ba(II) atoms in **4**. (Symmetry codes: #1 1-x, 1/2+y, 3/2-z. #2 +x, +y, 1+z #3 1-x, -1/2+y, 1/2-z #4 1-x, -1/2+y, 3/2-z #5 1-x, 1/2+y, 1/2-z #6 -x, -1/2+y, 1/2-z #7 -x, 1/2+y, 1/2-z).



Scheme S1 Coordination modes of the BINDI ligand in compounds **1**–**4**.

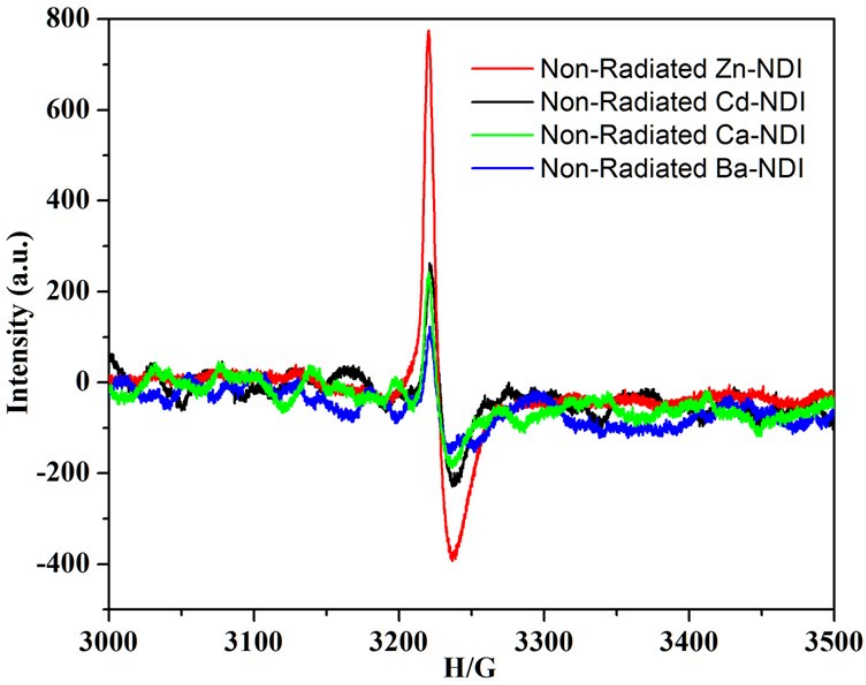


Fig. S6 The semi-quantitative ESR spectra of compounds **1-4** before photoirradiation.

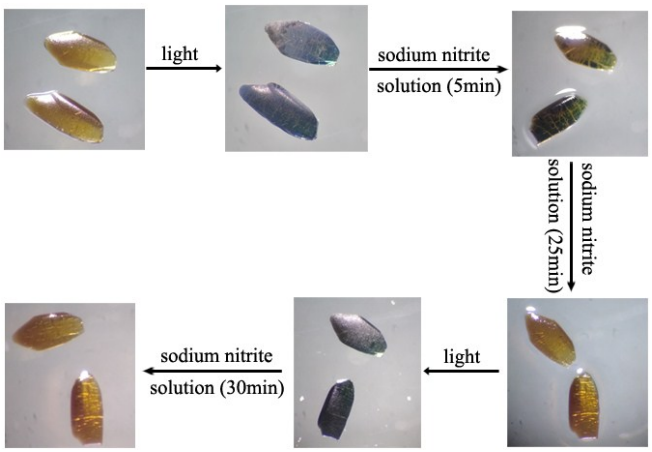


Fig. S7 The coloration and decoloration process of **1** from photographic images

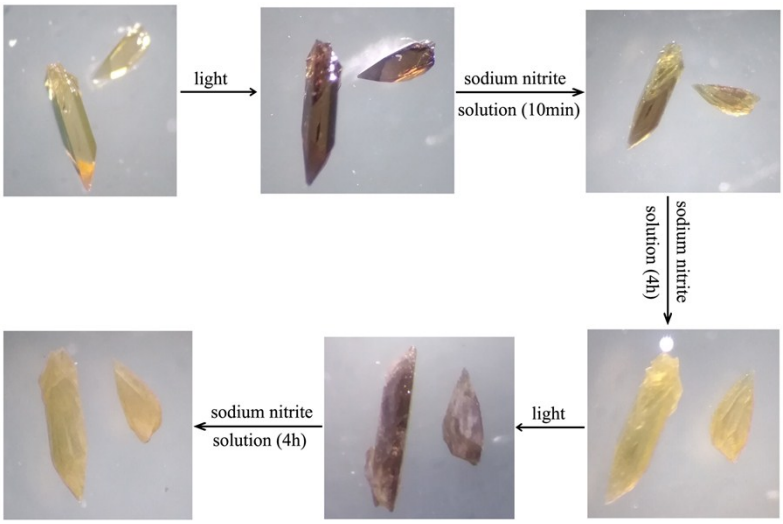


Fig. S8 The coloration and decoloration process of **2** from photographic images

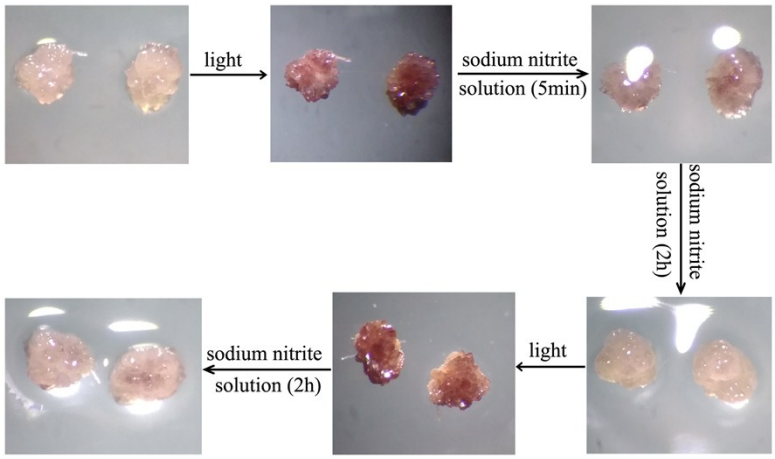


Fig. S9 The coloration and decoloration process of **3** from photographic images

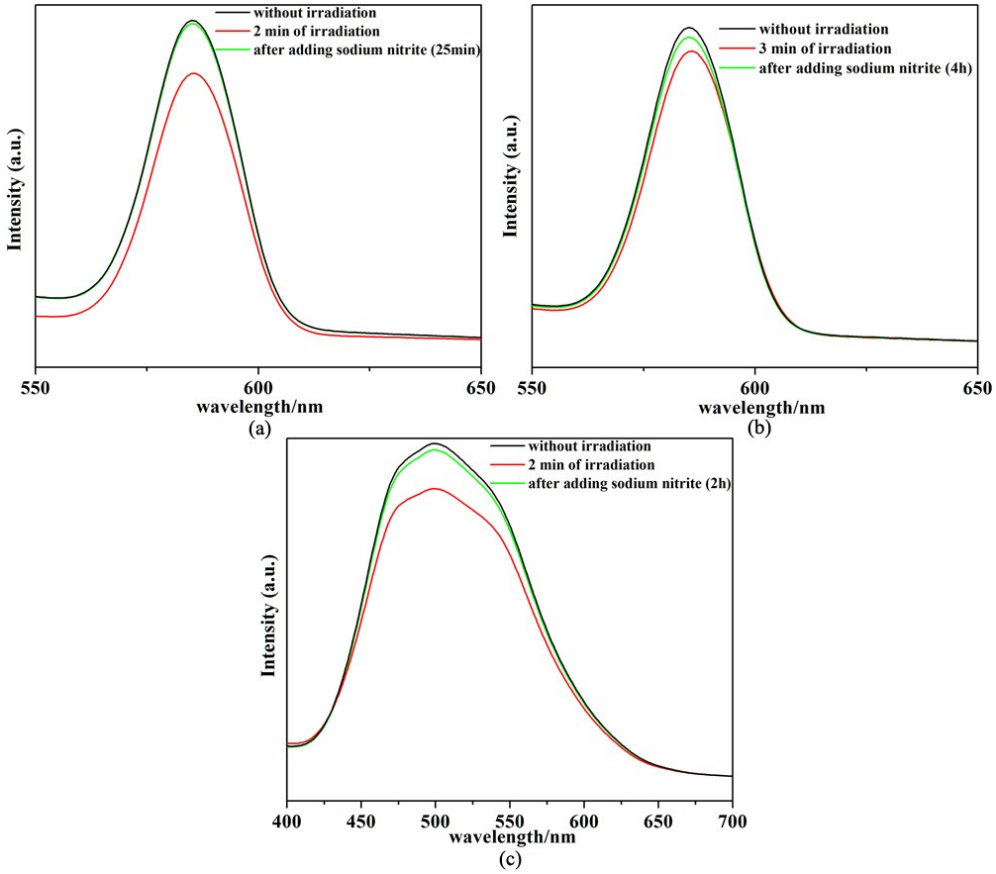


Fig. S10 The fluorescence responses of the irradiated samples of **1** (a), **2**(b), **3**(c) upon the addition of sodium nitrite solution.

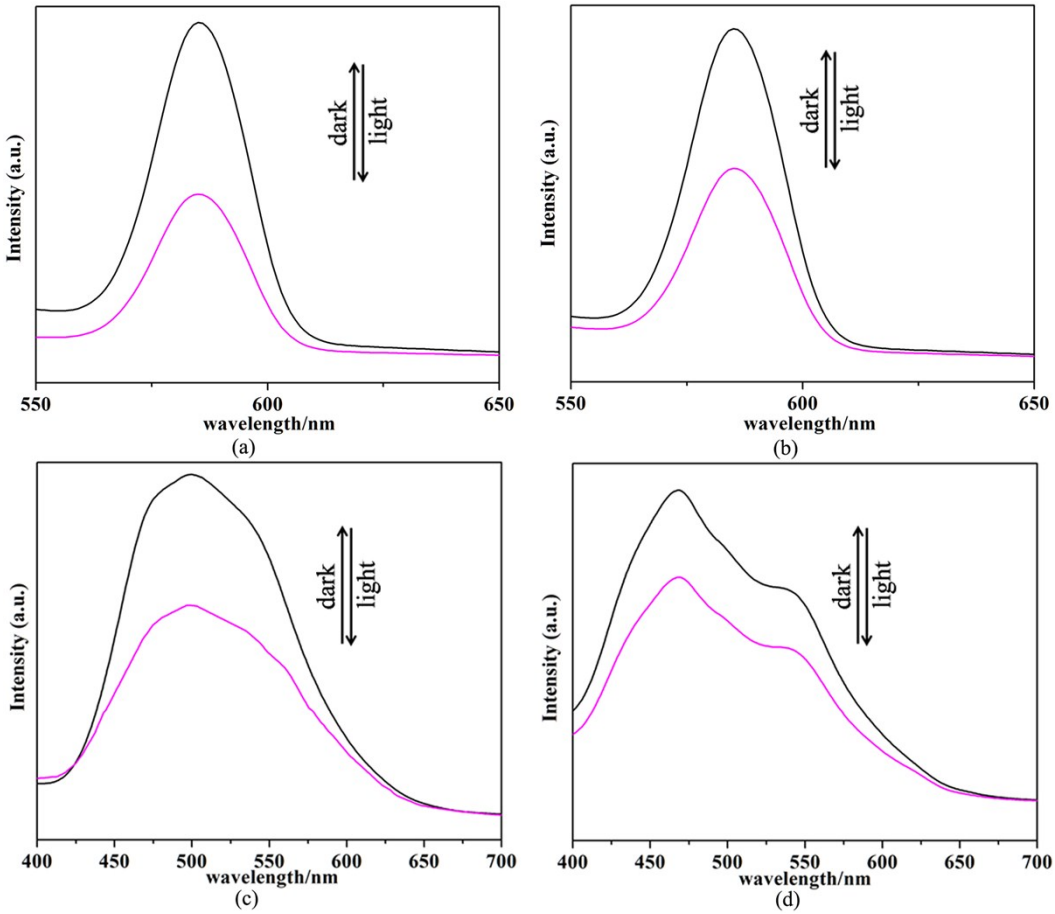


Fig. S11 The photoluminescence spectra for **1-4** before and after colour change.

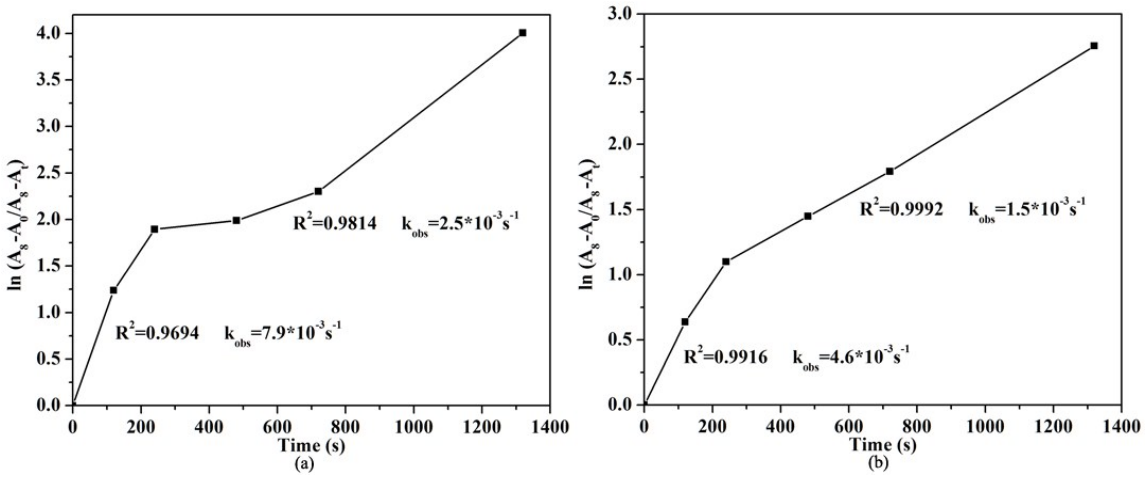


Fig. S12 Solid state first order rate plot of coloration: **3** (a), **4** (b). For **3**, the photochemical reaction can be separated into two stages. Firstly, it exhibits a rate constant with k_{obs} = 7.9 × 10^{-3} s^{-1}. The reaction rate constant decreases as time goes on, showing k_{obs} = 2.5 × 10^{-3} s^{-1}, at the second step. For **4**, the recation can also be separated into two stages. The reaction rate constant is 4.6 × 10^{-3} s^{-1} and 1.5 × 10^{-3} s^{-1} respectively due to its poor photosensitivity.

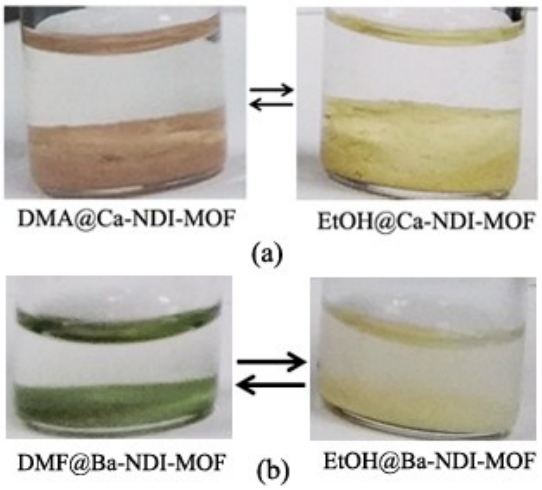


Fig. S13 Reversible solvent color change of **3** (a) and **4** (b).

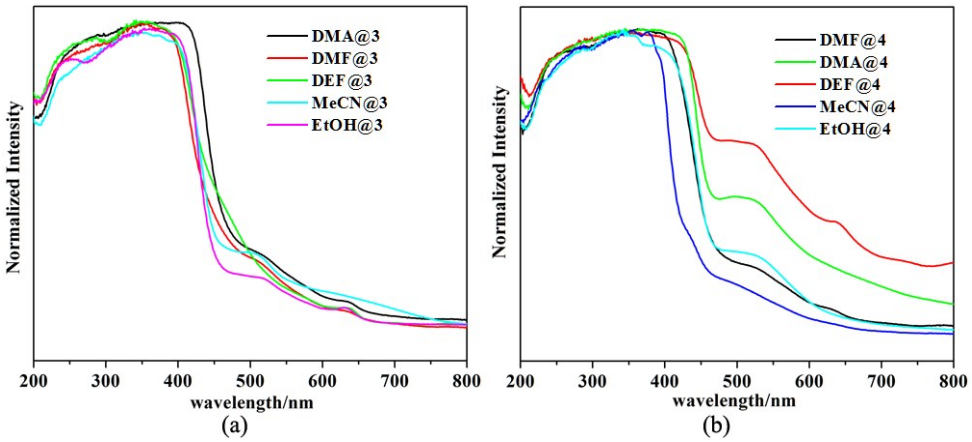


Fig. S14 Solid state UV-vis spectra of **3** (a) and **4** (b) soaked in different solvents

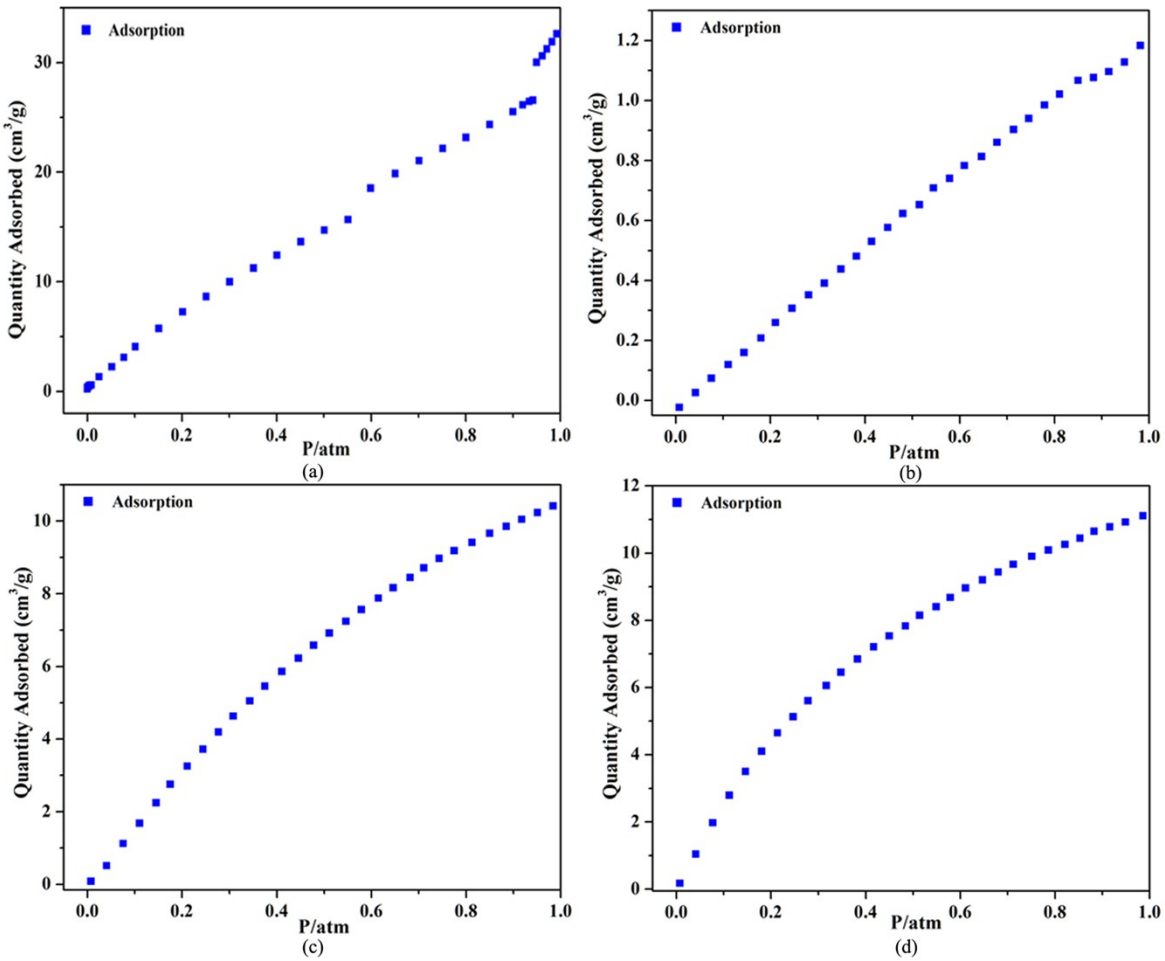


Fig. S15 Gas adsorptio isotherms of guest-free **1** (a) N_2 at 77.35 K, **1** (b) CO_2 at 273 K, **2** (a) CO_2 at 273 K, **4** (c) CO_2 at 273 K. The desolvated **1**, **2**, **4** shows CO_2 sorption with Langmuir surface area of ~ 20.442 m^2g^{-1}, ~ 117.012 m^2g^{-1}, ~ 104.521 m^2g^{-1}. The activated **1** exhibits N_2 sorption with Langmuir surface area of ~ 23.154 m^2g^{-1}. Confronted with these disappointing results, we think it may result from the traditional activation. In other words, the traditional thermal evacuation of solvent instead causes the collapse of interparticle micropores, which prevent micropores accessible to gas molecules.[1]

1. A. P. Nelson, O. K. Farha, K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 458.

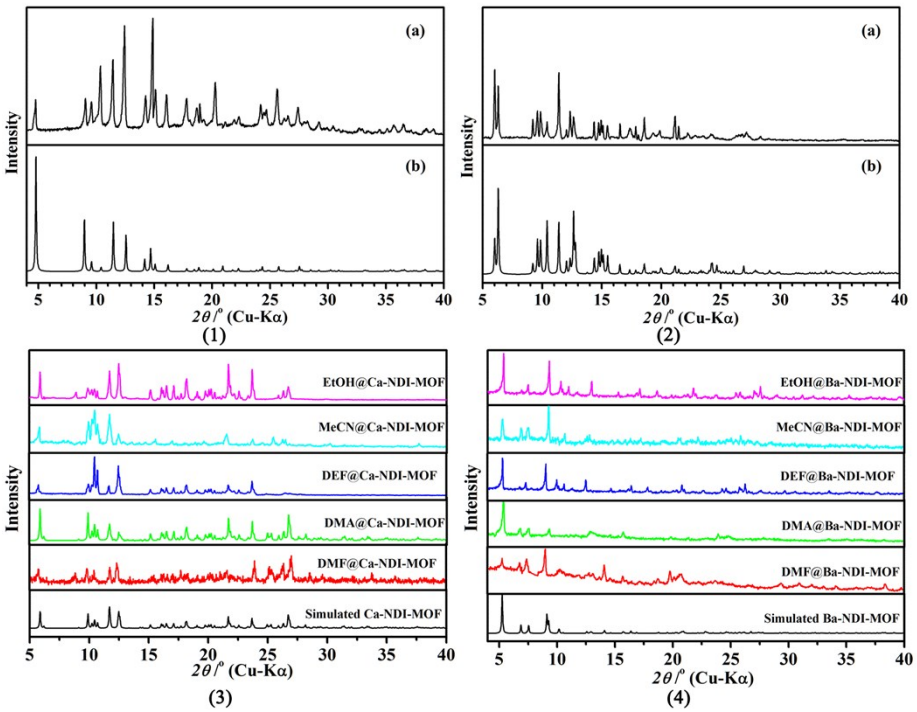


Fig. S16 The PXRD patterns for **1-2.** ((a): as-synthesized samples, (b): simulated one based on the single-crystal structure), PXRD pattern of solvent@**3** compared with the simulated pattern of **3**, and PXRD pattern of solvent@**4** compared with the simulated pattern of **4**.

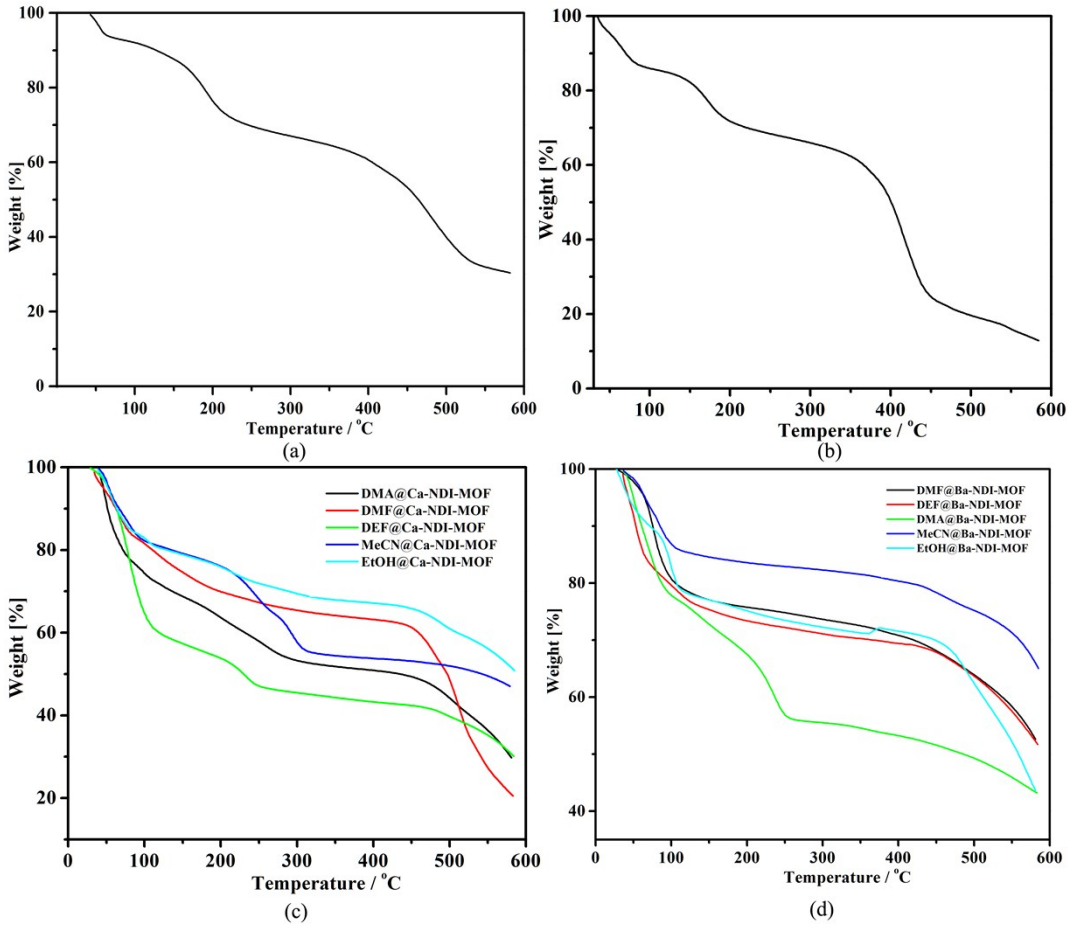


Fig. S17 The TG curves of **1** (a)**, 2** (b)**, 3** (c), 4 (d).

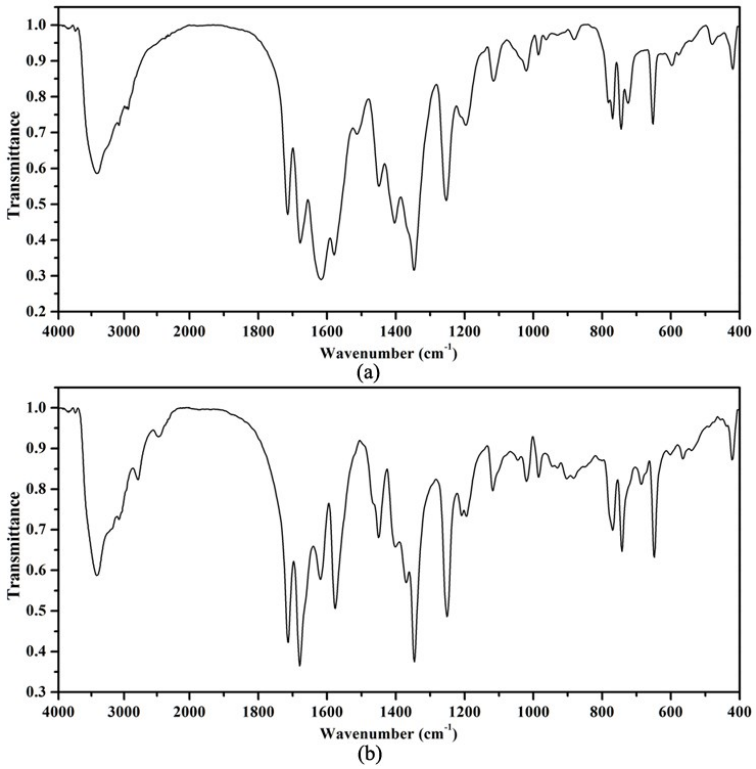


Fig. S18 The IR spectrum of **1** (a)**, 2** (b).

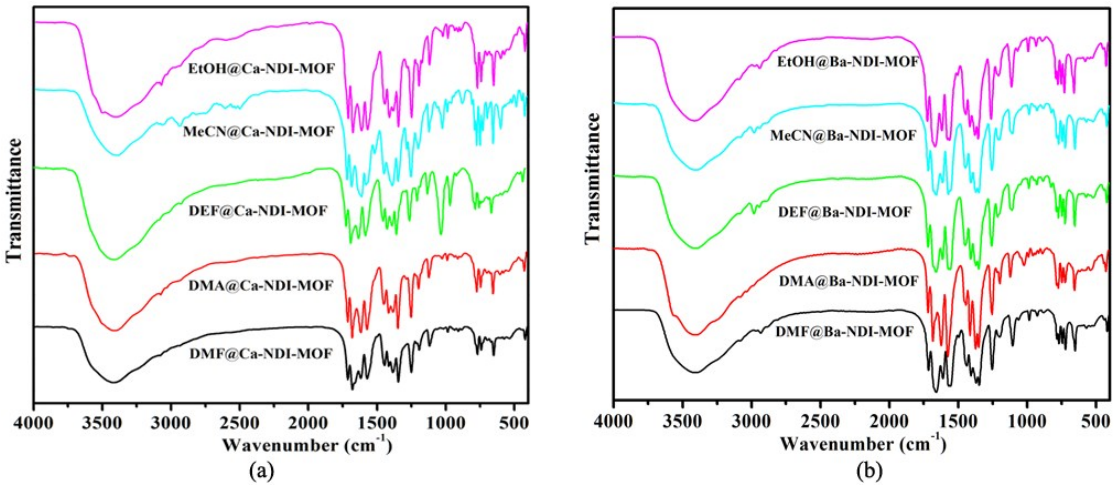


Fig. S19 The IR spectrum of **3** (a) and **4** (b) soaked in different solvents.