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Supporting information

The first 2,6-di(1,6-naphthyridin-2-yl)pyridine-based redox photochromic coordination polymer platform with selective vapochromism for trolamine

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Experimental

Materials and methods

All raw materials were commercially purchased from either J&K Scientific and/or Tianjin Chemical Reagent Factory, and used as received without further purification. Doubly deionized water was employed during the synthesis. 2,6-Di(1,6-naphthyridin-2-yl)pyridine (L) was prepared according to the literature procedures.[1] Elemental analyses for C, H, and N were carried out with a CE–440 (Leeman–Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar–370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiment was performed on a Shimadzu simultaneous DTG–60A compositional analysis instrument from room temperature to 786 ^oC (for **1** and **2**) or 800 ^oC (for **3**) under N_2 atmosphere at a heating rate of 5 ^oC min^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu $K\alpha$ radiation (λ = 1.5406 Å), with a scan speed of 0.1 sec/step and a step size of 0.01^o in 2θ. The simulated PXRD pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. The electron spin resonance (ESR) characterization was recorded in the X band using the crystalline samples on a Brucker (EMXplus6-1) spectrometer at room temperature. The visible light-induced photochromism was carried out by a continuous wavelength-irradiation Xenon lamp (Beijing, 300 W) with a 420 nm cut-off filter (420 nm – 780 nm, 100 mW·cm^{-2}). The UV light was generated by a hand-held UV lamp (365 nm, 10 mW·cm^{-2}). The photographs for the crystals of **1**–**3** are taken on an optical microscope (Zeiss stemi 2000-cs). UV-vis diffuse reflectance spectra (DRS) were carried out on a U-4100 UV-vis spectrophotometer (HITACHI) equipped with an integrating sphere assembly. Photographs of the vapochrosim before and after sensing ammonia vapors were taken by A710-IS Canon camera.

Synthesis of {[$Cd_4(H_2O)_4(L)_2(BDC)_4$]·DMF·4H_2O}$_n$ (1)

$Cd(NO_3)_2·4H_2O$ (30.8 mg, 0.10 mmol), L (10.1 mg, 0.03 mmol), and H_2BDC (16.6 mg, 0.10 mmol) were dispersed in a mixed DMF-H_2O-C_2H_5OH solution (v:v:v = 1:2:2, 5.0 mL). The resulting mixture was sealed in a Teflon-lined stainless steel vessel (23.0 mL) and heated at 80 ^oC for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 0.8 $^oC·h^{-1}$, yellow block-shaped crystals suitable for X-ray analysis were obtained directly, washed with cold water, and dried in air. Yield: 15% on the basis of L ligand. Calcd. for $C_{77}H_{65}Cd_4N_{11}O_{25}$: C, 46.38; H, 3.29; N, 7.73%. Found: C, 46.36; H, 3.31; N, 7.72%. FT-IR (KBr, cm^{-1}): 3202 (br), 3082(w), 1663 (w), 1616 (s), 1559 (s), 1492 (s), 1442 (w), 1379 (s), 1249 (w), 1223 (w), 1134 (w), 1093 (w), 1084 (w), 1043 (w), 1011 (w), 960 (w), 903 (w), 834 (m), 783 (w), 748 (m), 679 (w), 641 (w), 565 (w), 511 (w), 425 (w).

Synthesis of {[$Cd_2(L)_2(BDC)_2$]·2H_2O·H_2BDC}$_n$ (2)

Colorless block-shaped crystals of **2** were generated by adopting the procedures similar to those of **1** except that the volume ratio of the mixed solvent was change to 3:1:1 for DMF, water and ethanol (5.0 mL), and the solvothermal temperature was elevated to 120 ^oC. Yield: 25% on the basis of L ligand. Calcd. for $C_{66}H_{44}Cd_2N_{10}O_{14}$: C, 55.59; H, 3.11; N, 9.82%. Found: C, 55.60; H, 3.10; N, 9.83%. FT-IR (KBr, cm^{-1}): 3376 (br), 3069 (w), 1701 (m), 1666 (m), 1613 (m), 1559 (s), 1496 (m), 1439 (w), 1375 (s), 1299 (w), 1245 (w), 1223 (w), 1128 (w), 1100 (w), 1081 (w), 1040 (w), 1011 (w), 960 (w), 891 (w), 834 (m), 786 (w), 742 (m), 675 (w), 641 (w), 562 (w), 517 (w), 425 (w).

Synthesis of {[$Cd_8(H_2O)_4(L)_4(BDC)_8$]·6DMF·10H_2O}$_n$ (3)

The synthetic procedures of **3** were similar to those of **1** except that the volume ratio of the mixed solvent was changed to 3:1:1 (DMF:H_2O:C_2H_5OH). Pale yellow block-shaped crystals suitable for single-crystal X-ray analysis were obtained directly, washed with cold water and dried in air. Yield: 8% on the basis of L ligand. Calcd. for $C_{166}H_{154}Cd_8N_{26}O_{52}$: C, 46.98; H, 3.66; N, 8.58%. Found: C, 46.95; H, 3.64; N, 8.59%. FT-IR (KBr, cm^{-1}): 3398 (br), 3066 (w), 1657 (m), 1616 (m), 1565 (s), 1499 (m), 1442 (w), 1394 (s), 1312 (w), 1242 (w), 1220 (w), 1188 (w), 1131 (w), 1103 (w), 1081 (w), 1040 (w), 1011 (w), 960 (w), 903 (w), 884 (w), 827 (m), 745 (m), 679 (w), 660 (w), 555 (w), 514 (w).

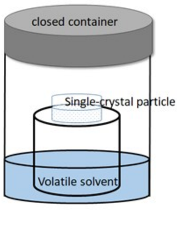
X-ray data collection and structure determination

Diffraction intensities for **1**–**3** are collected respectively on a Bruker APEX-II QUAZAR diffractometer equipped with graphite-monochromated Mo *K*α radiation with a radiation wavelength of 0.71073 Å by using the φ-ω scan technique at 296 K (for both **1** and **2**) and at 293 K (for **3**). There is no evidence of crystal decay during data collection. Semi-empirical multi-scan absorption corrections are applied by SADABS[2] and the program SAINT[3] is used for integration of the diffraction profiles. The structures are solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.[4] Anisotropic thermal parameters are assigned to all non-H atoms. The organic H atoms are generated geometrically. The number of the disordered solvent molecules is speculated based on the electron counts calculated by PLATON software.[5] The summary of the crystallographic data for **1**–**3** is listed in Table S1. The selected bond lengths and angles as well as the hydrogen-bonding parameters are shown in Table S2–S5. CCDC 1897628–1897630 for **1**–**3** contain supplementary crystallographic data for this paper. These data can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U. K.

Photochromic and vapochromic experiments

Well-crushed single-crystals of **1** (40.0 mg) were dispersed in ethanol (1.0 mL), and the resulting dispersion has been ultra-sonicated for at least 30 minutes to ensure the homogeneity. Then, a piece of filter paper was soaked in the dispersion. After complete drying under ambient conditions, the filter paper was covered by a paper with hollowed-out "TJNU" letters and irradiated by hand-portable UV lamp. The photograph of the filter paper was taken before and after UV irradiation.

The vapochromic experiments were conducted in a sealed glass bottle containing volatile analyte (5.0 mL) and one crystalline sample (3.0 mg, Scheme S1). The optical image of the crystalline sample in the absence and presence of volatile vapor is taken at different periods of time. The recyclability of **1** and **3** on the vapochromism has been carried out by consequently irradiating the vapochromic sample for 10 min and exposing in the trolamine vapor for 50 min.



Scheme S1 The equipment for the vapochromism of **1**–**3**.

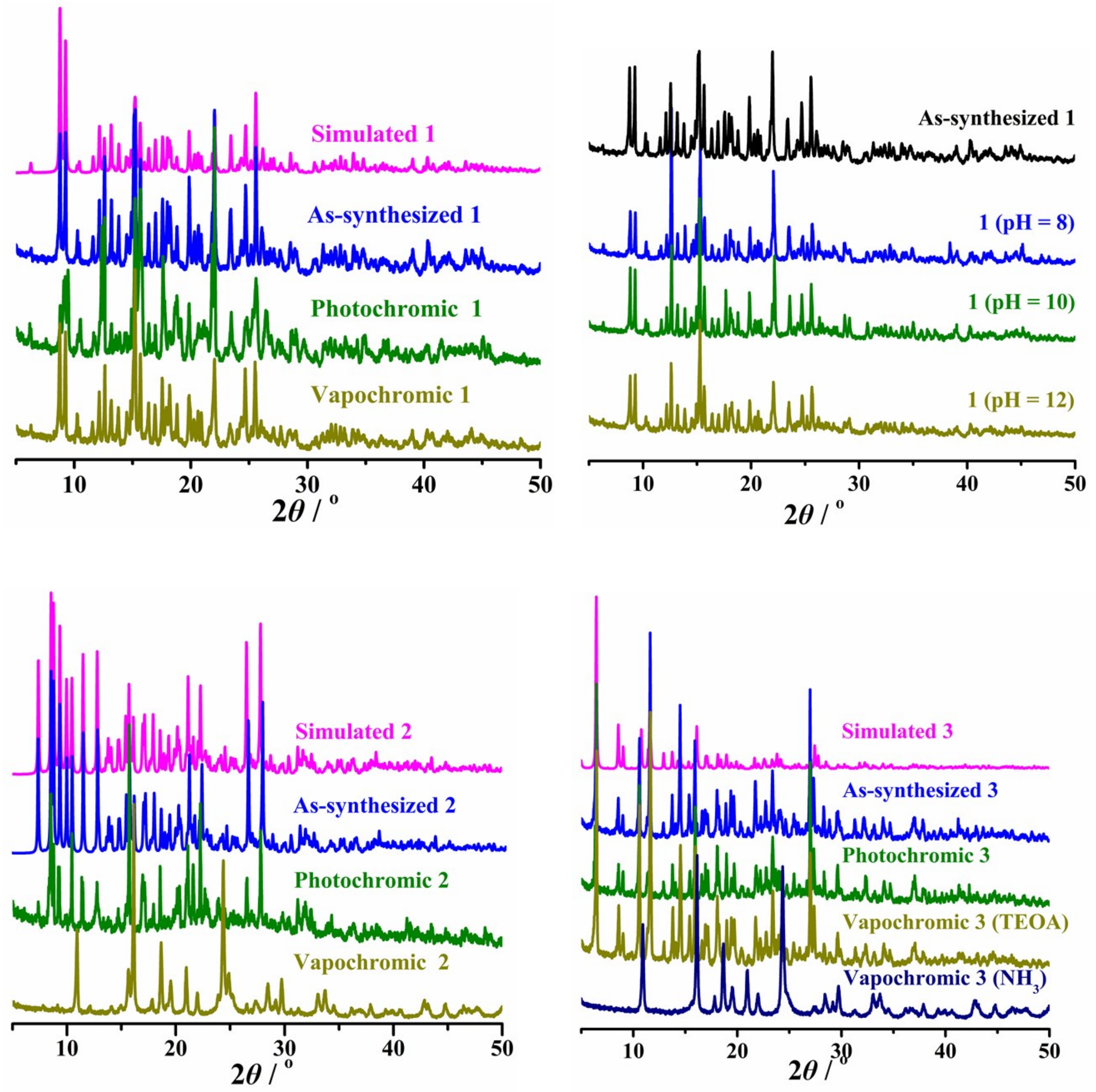
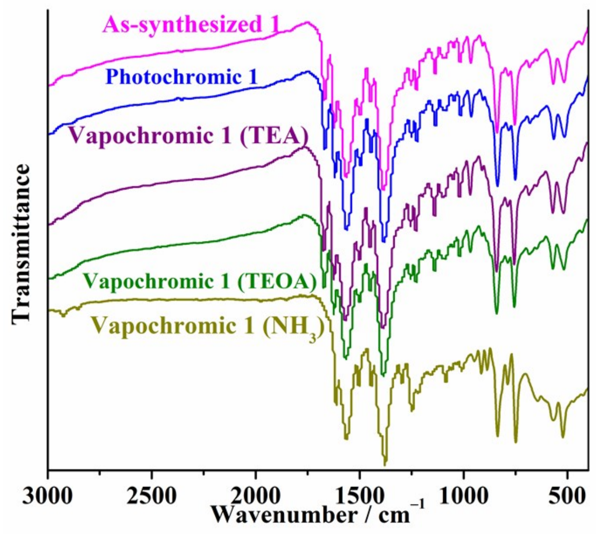
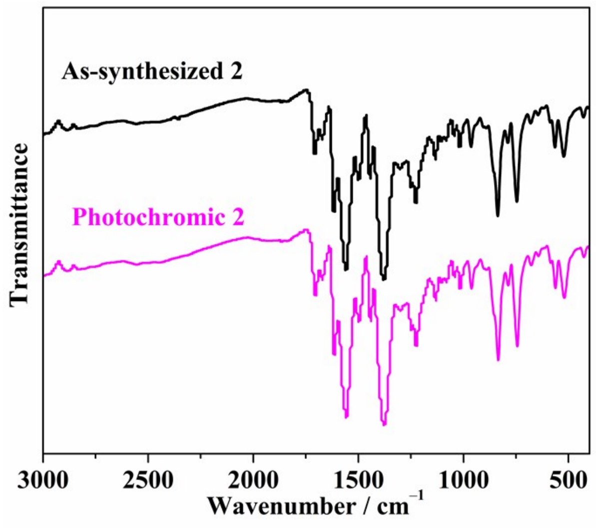


Fig. S1 Simulated and experimental PXRD patterns for **1**–**3**.





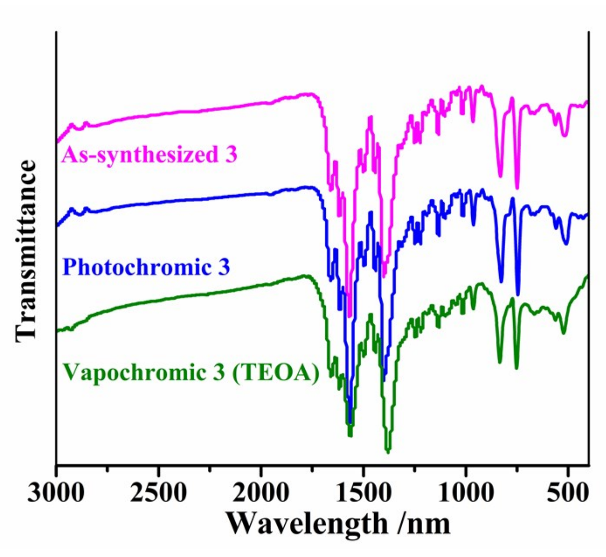


Fig. S2 FT-IR spectra for the as-synthesized, photochromic, and/or vapochromic samples of **1**–**3**.

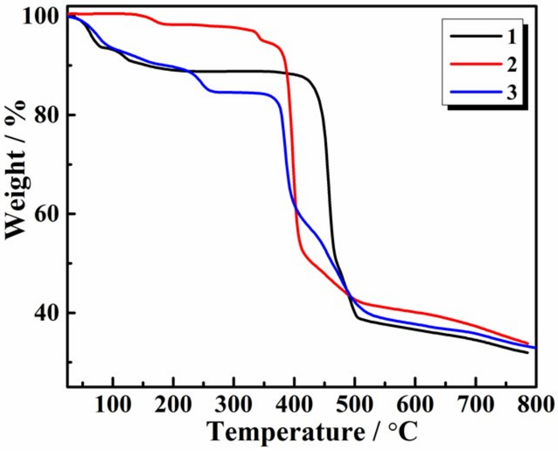


Fig. S3 TG curves for **1**–**3**.

Table S1 Crystal and structure refinement data for **1**–**3** [a]

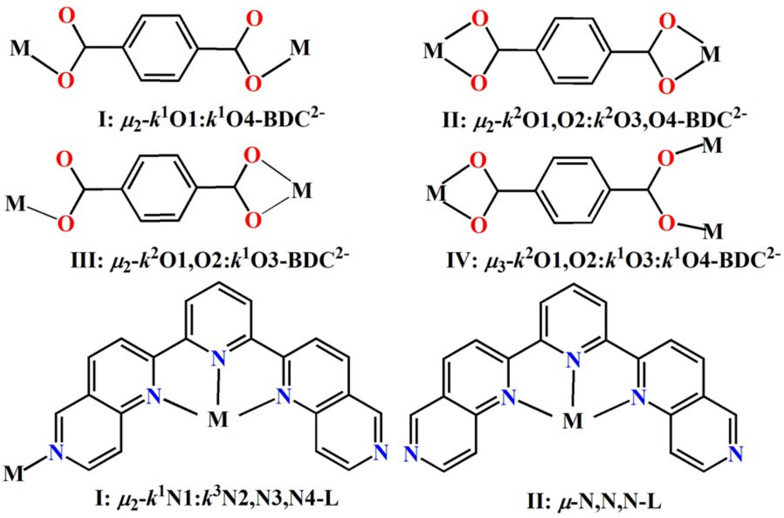
	1	**2**	**3**
empirical formula	$C_{77}H_{65}Cd_4N_{11}O_{25}$	$C_{66}H_{44}Cd_2N_{10}O_{14}$	$C_{166}H_{154}Cd_8N_{26}O_{52}$
F_w	1994.00	1425.91	4244.34
cryst size (mm)	0.22 ×0.21 × 0.18	0.22 × 0.21 × 0.18	0.25 × 0.22 × 0.20
cryst syst	triclinic	triclinic	monoclinic
space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$
a (Å)	11.2201(15)	12.027(3)	18.7384(8)
b (Å)	13.1513(17)	13.525(4)	20.6651(8)
c (Å)	14.668(2)	19.934(6)	12.0896(4)
α (°)	94.253(2)	72.128(6)	90
β (°)	103.553(2)	88.935(6)	103.421(4)
γ (°)	111.125(2)	68.331(6)	90
V (Å^3)	1932.5(4)	2851.5(14)	4553.6(3)
Z	1	2	1
D_c (g cm^{-3})	1.713	1.661	1.548
h / k / l	–11, 14/–16, 15/–16, 18	–15, 8/–16, 12/–25, 24	–22, 22/–19, 24/–14, 13
F(000)	996.0	1436.0	2132.0
μ (mm^{-1})	1.173	0.827	1.002
reflections collected / unique	11336 / 7899	16664 / 11673	21581 / 8016
R_{int}	0.0151	0.0654	0.0387
data / restraints / params	7899 / 65 / 563	11673/ 0 / 833	8016 / 58 / 597
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0317, 0.0808	0.0801, 0.1863	0.0455, 0.1135
R_1, wR_2 (all data)	0.0385, 0.0844	0.1719, 0.2257	0.0583, 0.1231
GOF on F^2	1.061	0.937	1.042
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	0.962, –0.677	1.76, –1.68	1.08, –1.14

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (deg) for **1**[a]

Cd–D	*d* (Cd–D)	Cd–D	*d* (Cd–D)
Cd(1)–O(1)	2.211(2)	Cd(2)–O(4)$^{\#1}$	2.182(2)
Cd(1)–N(3)	2.307(2)	Cd(2)–O(9)	2.307(2)
Cd(1)–O(6)	2.306(2)	Cd(2)–O(10)	2.336(2)
Cd(1)–N(2)	2.374(2)	Cd(2)–O(7)	2.395(3)
Cd(1)–N(4)	2.418(3)	Cd(2)–O(8)	2.411(3)
Cd(1)–O(5)	2.551(2)	Cd(2)–N(1)	2.428(3)
D–Cd–D′	∠DCdD′	D–Cd–D′	∠DCdD′
O(1)–Cd(1)–O(5)	133.70(9)	O(4)$^{\#1}$–Cd(2)–O(7)	124.78(10)
O(1)–Cd(1)–O(6)	84.15(9)	O(4)$^{\#1}$–Cd(2)–O(8)	89.25(10)
O(1)–Cd(1)–N(2)	115.79(10)	O(4)$^{\#1}$–Cd(2)–O(9)	145.57(9)
O(1)–Cd(1)–N(3)	130.98(9)	O(4)$^{\#1}$–Cd(2)–O(10)	88.51(9)
O(1)–Cd(1)–N(4)	91.01(10)	O(4)$^{\#1}$–Cd(2)–N(1)	98.90(10)
O(6)–Cd(1)–O(5)	53.11(8)	O(7)–Cd(2)–O(8)	53.37(9)
O(6)–Cd(1)–N(2)	107.42(9)	O(7)–Cd(2)–N(1)	82.93(9)
O(6)–Cd(1)–N(3)	143.27(8)	O(8)–Cd(2)–N(1)	129.76(10)
O(6)–Cd(1)–N(4)	104.61(8)	O(9)–Cd(2)–O(7)	89.17(10)
N(2)–Cd(1)–O(5)	95.58(9)	O(9)–Cd(2)–O(8)	119.42(10)
N(2)–Cd(1)–N(4)	139.73(9)	O(9)–Cd(2)–O(10)	76.65(9)
N(3)–Cd(1)–O(5)	90.22(8)	O(9)–Cd(2)–N(1)	77.92(9)
N(3)–Cd(1)–N(2)	70.20(9)	O(10)–Cd(2)–O(7)	120.90(9)
N(3)–Cd(1)–N(4)	69.53(8)	O(10)–Cd(2)–O(8)	84.72(9)
N(4)–Cd(1)–O(5)	84.57(9)	O(10)–Cd(2)–N(1)	144.46(9)

[a] Symmetry codes: #1 $-x + 2, -y + 2, -z$.



I: μ_2-k^1O1:k^1O4-BDC^{2-}

II: μ_2-k^2O1,O2:k^2O3,O4-BDC^{2-}

III: μ_2-k^2O1,O2:k^1O3-BDC^{2-}

IV: μ_3-k^2O1,O2:k^1O3:k^1O4-BDC^{2-}

I: μ_2-k^1N1:k^3N2,N3,N4-L

II: μ-N,N,N-L

Fig. S4 Binding modes of L and BDC^{2-} ligands in **1**–**3**.

Table S3 Hydrogen-bonding parameter (Å, °) for **1** and **2** [a]

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠DHA
1				
C(22)–H(22)···O(2)	0.93	2.32	3.208(5)	160
C(27)–H(27)···O(4)	0.93	2.55	3.091(5)	118
C(28)–H(28)···O(5)	0.93	2.35	3.238(5)	158
O10–H10A···N5[#1]	0.85	1.99	2.793	156
2				
C1–H1···O1[#1]	0.93	2.49	3.292	144
C7–H7···O6[#2]	0.93	2.28	3.003	134
C6–H6···N5[#4]	0.93	2.54	3.422	159
C19–H19···O5	0.93	2.36	3.253	161
C23–H23···O8[#3]	0.93	2.41	3.211	144

[a] Symmetry codes for **1**: [#1] $-1 + x, y, -1 + z$; [#2] $1 - x, 2 - y, -z$; For **2**: [#1] $2 - x, 1 - y, -z$; [#2] $3 - x, 1 - y, -z$; [#3] $x, -1 + y, 1 + z$; [#4] $1 + x, -1 + y, z$.

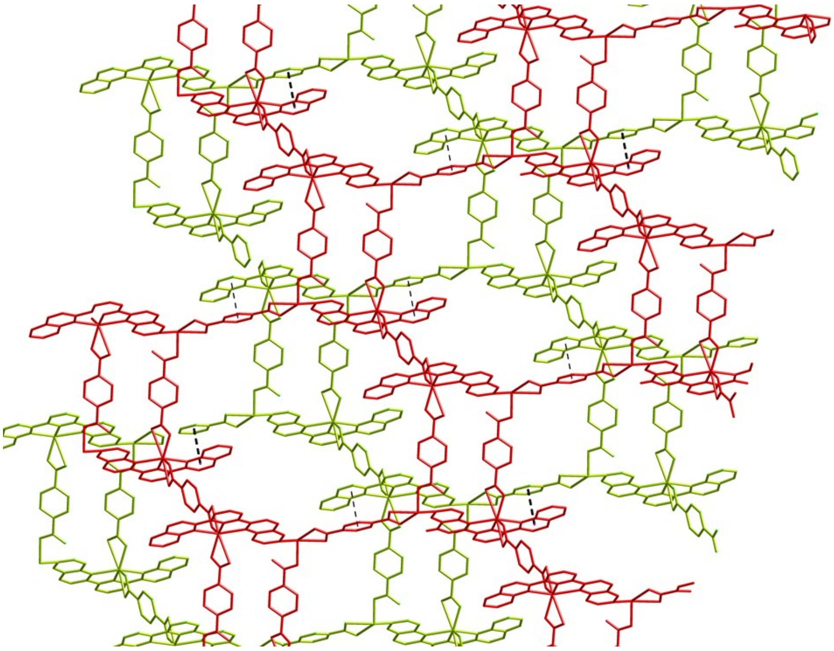
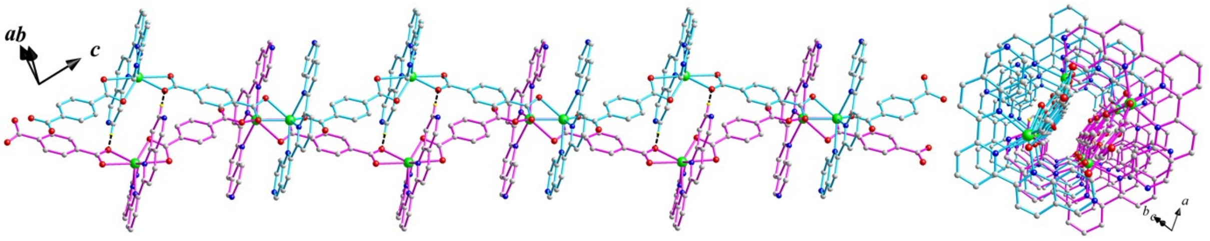


Fig. S5 Interlayer$\pi\cdots\pi$ stacking interaction in **1**.

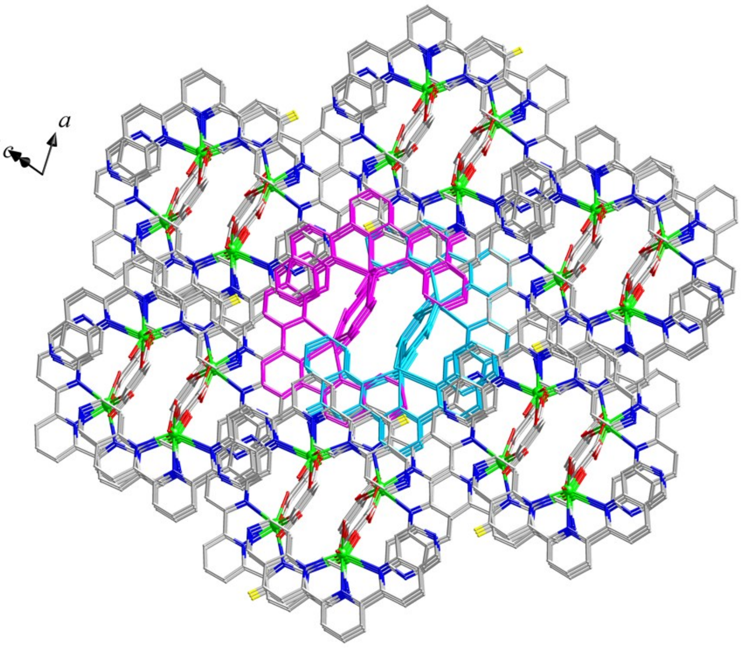
Table S4 Selected bond lengths (Å) and angles (°) for **2**[a]

Cd–D	*d* (Cd–D)	Cd–D	*d* (Cd–D)
Cd(1)–O(1)	2.268(7)	Cd(2)–O(8)$^{\#1}$	2.214(6)
Cd(1)–O(5)	2.300(7)	Cd(2)–N(8)	2.325(8)
Cd(1)–N(3)	2.323(8)	Cd(2)–O(4)	2.350(6)
Cd(1)–N(2)	2.401(7)	Cd(2)–N(9)	2.390(9)
Cd(1)–O(6)	2.483(7)	Cd(2)–N(7)	2.418(10)
Cd(1)–N(4)	2.484(8)	Cd(2)–O(3)	2.515(8)
Cd(1)–O(2)	2.596(7)		
D–Cd–D′	∠DCdD′	D–Cd–D′	∠DCdD′
O(1)–Cd(1)–O(2)	51.6(2)	N(3)–Cd(1)–N(4)	67.8(3)
O(1)–Cd(1)–O(5)	85.6(2)	N(4)–Cd(1)–O(2)	104.3(3)
O(1)–Cd(1)–O(6)	138.8(3)	O(4)–Cd(2)–O(3)	52.5(3)
O(1)–Cd(1)–N(2)	123.2(3)	O(4)–Cd(2)–N(7)	108.9(3)
O(1)–Cd(1)–N(3)	120.9(3)	O(4)–Cd(2)–N(9)	84.3(3)
O(1)–Cd(1)–N(4)	90.1(3)	O(8)$^{\#1}$–Cd(2)–O(3)	88.1(3)
O(5)–Cd(1)–O(2)	129.5(3)	O(8)$^{\#1}$–Cd(2)–O(4)	130.0(2)
O(5)–Cd(1)–O(6)	54.3(2)	O(8)$^{\#1}$–Cd(2)–N(7)	96.0(3)
O(5)–Cd(1)–N(2)	109.5(2)	O(8)$^{\#1}$–Cd(2)–N(8)	135.9(2)
O(5)–Cd(1)–N(3)	149.7(2)	O(8)$^{\#1}$–Cd(2)–N(9)	105.0(3)
O(5)–Cd(1)–N(4)	100.6(3)	N(7)–Cd(2)–O(3)	86.6(3)
O(6)–Cd(1)–N(4)	88.8(3)	N(8)–Cd(2)–O(3)	130.6(3)
N(2)–Cd(1)–O(2)	80.9(2)	N(8)–Cd(2)–O(4)	93.7(3)
N(2)–Cd(1)–O(6)	83.6(3)	N(8)–Cd(2)–N(7)	70.5(3)
N(2)–Cd(1)–N(4)	135.7(3)	N(8)–Cd(2)–N(9)	69.5(3)
N(3)–Cd(1)–O(2)	80.7(3)	N(9)–Cd(2)–O(3)	128.8(3)
N(3)–Cd(1)–O(6)	96.5(3)	N(9)–Cd(2)–N(7)	138.5(3)
N(3)–Cd(1)–N(2)	69.8(3)		

[a] Symmetry codes: $^{\#1}$ x, $y - 1$, $z + 1$.



(a)



(b)

Fig. S6 (a) An entangled pair of **2** by interchain C–H···O contacts viewed from two orthogonal directions. (b) Three-dimensional supramolecular packing of **2** formed by interpair C–H···O and C–H···N hydrogen-bonding interactions.

Table S5 Selected bond lengths (Å) and angles (°) for **3**[a]

Cd–D	*d* (Cd–D)	Cd–D	*d* (Cd–D)
Cd(1)–O(1)	2.616(3)	Cd(1)–O(2)	2.228(3)
Cd(1)–O(3)	2.264(4)	Cd(1)–O(4)	2.562(4)
Cd(1)–N(2)	2.357(4)	Cd(1)–N(3)	2.286(4)
Cd(1)–N(4)	2.390(4)	Cd(2)–O(5)	2.184(3)
Cd(2)–O(6)$^{\#1}$	2.356(3)	Cd(2)–O(7)$^{\#2}$	2.223(4)
Cd(2)–O(8)$^{\#2}$	2.591(4)	Cd(2)–O(9)	2.384(4)
Cd(2)–N(5)	2.361(4)		
D–Cd–D’	∠DCdD’	D–Cd–D’	∠DCdD’
O(2)–Cd(1)–O(1)	53.48(11)	O(2)–Cd(1)–O(3)	84.75(13)
O(2)–Cd(1)–O(4)	129.62(13)	O(2)–Cd(1)–N(2)	116.55(14)
O(2)–Cd(1)–N(3)	141.32(13)	O(2)–Cd(1)–N(4)	94.12(12)
O(3)–Cd(1)–O(1)	136.88(13)	O(3)–Cd(1)–O(4)	53.95(13)
O(3)–Cd(1)–N(2)	96.82(15)	O(3)–Cd(1)–N(3)	133.61(14)
O(3)–Cd(1)–N(4)	110.41(13)	N(2)–Cd(1)– O(1)	93.58(12)
N(2)–Cd(1)–O(4)	97.73(13)	N(2)–Cd(1)–N(4)	140.85(15)
N(3)–Cd(1)–O(1)	89.24(12)	N(3)–Cd(1)–O(4)	82.89(13)
N(3)–Cd(1)–N(2)	70.48(16)	N(3)–Cd(1)–N(4)	70.38(14)
N(4)–Cd(1)–O(1)	85.49(11)	N(4)–Cd(1)–O(4)	77.86(12)
O(5)–Cd(2)–O(6)$^{\#1}$	96.11(13)	O(5)–Cd(2)–O(7)$^{\#2}$	140.44(13)
O(5)–Cd(2)–O(8)$^{\#2}$	90.44(12)	O(5)–Cd(2)–O(9)	81.86(14)
O(5)–Cd(2)–N(5)	131.88(14)	O(6)$^{\#1}$–Cd(2)–O(8)$^{\#2}$	91.14(12)
O(6)$^{\#1}$–Cd(2)–N(5)	89.90(12)	O(7)$^{\#2}$–Cd(2)–O(6)$^{\#1}$	99.54(14)
O(7)$^{\#2}$–Cd(2)–O(8)$^{\#2}$	53.33(13)	O(7)$^{\#2}$–Cd(2)–O(9)	88.72(15)
O(7)$^{\#2}$–Cd(2)–N(5)	84.41(14)	O(9)–Cd(2)–O(8)$^{\#2}$	99.76(14)
N(5)–Cd(2)–O(8)$^{\#2}$	137.27(12)	N(5)–Cd(2)–O(9)	83.50(14)

[a] Symmetry codes: $\#^1$ – *x*, 1 – *y*, 1 – z; $\#^2$ – *x*,– 1/2 + *y*, 3/2 – *z*.

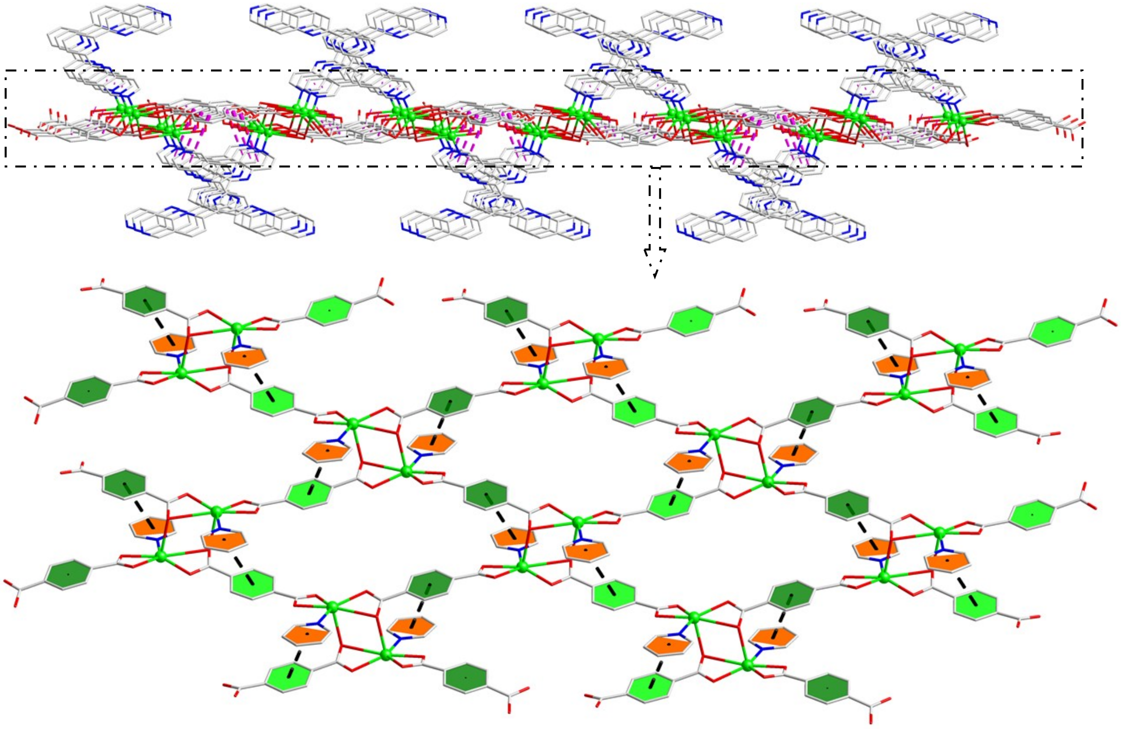


Fig. S7 Intramolecular π···π interaction between BDC^{2-} and pyridyl moiety of L ligand in **3** viewed from two different directions.

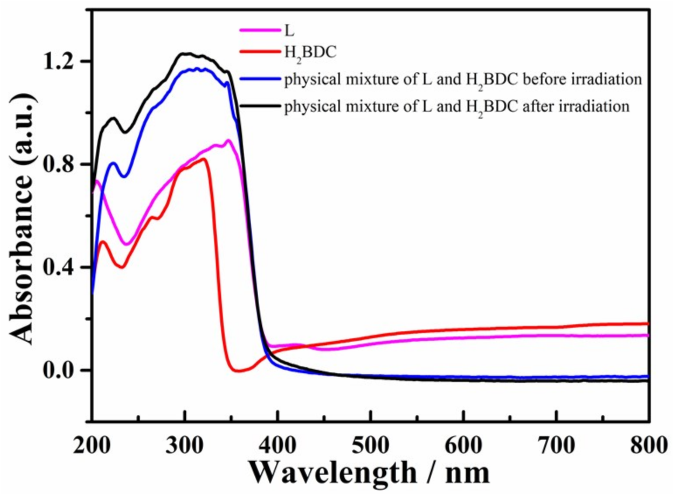


Fig. S8 Diffuse reflectance UV-vis spectra of H_2BDC, L and their physical mixture of the both ligands.

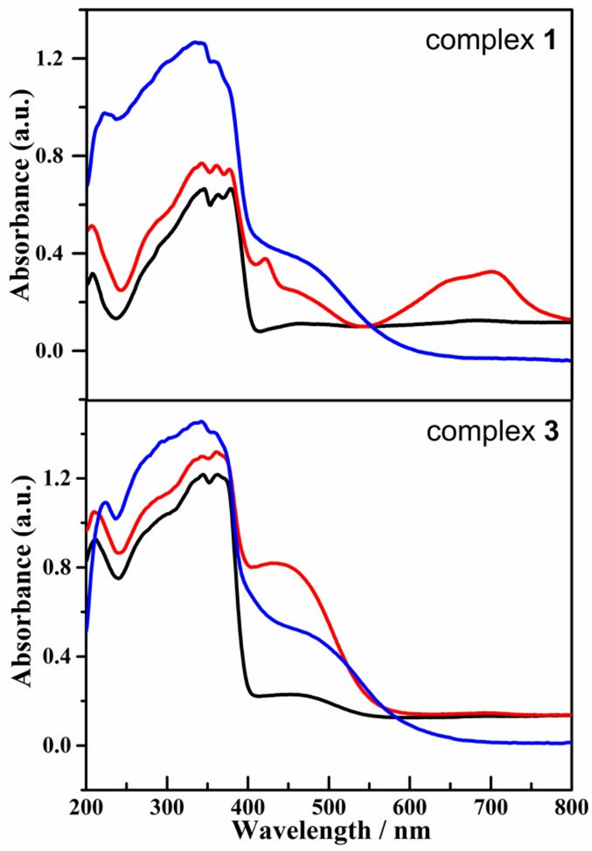


Fig. S9 Diffuse reflectance UV-vis spectra for the as-prepared sample (black solid line), photochromic (red solid line) and vapochromic (blue solid line) **1** and **3**.

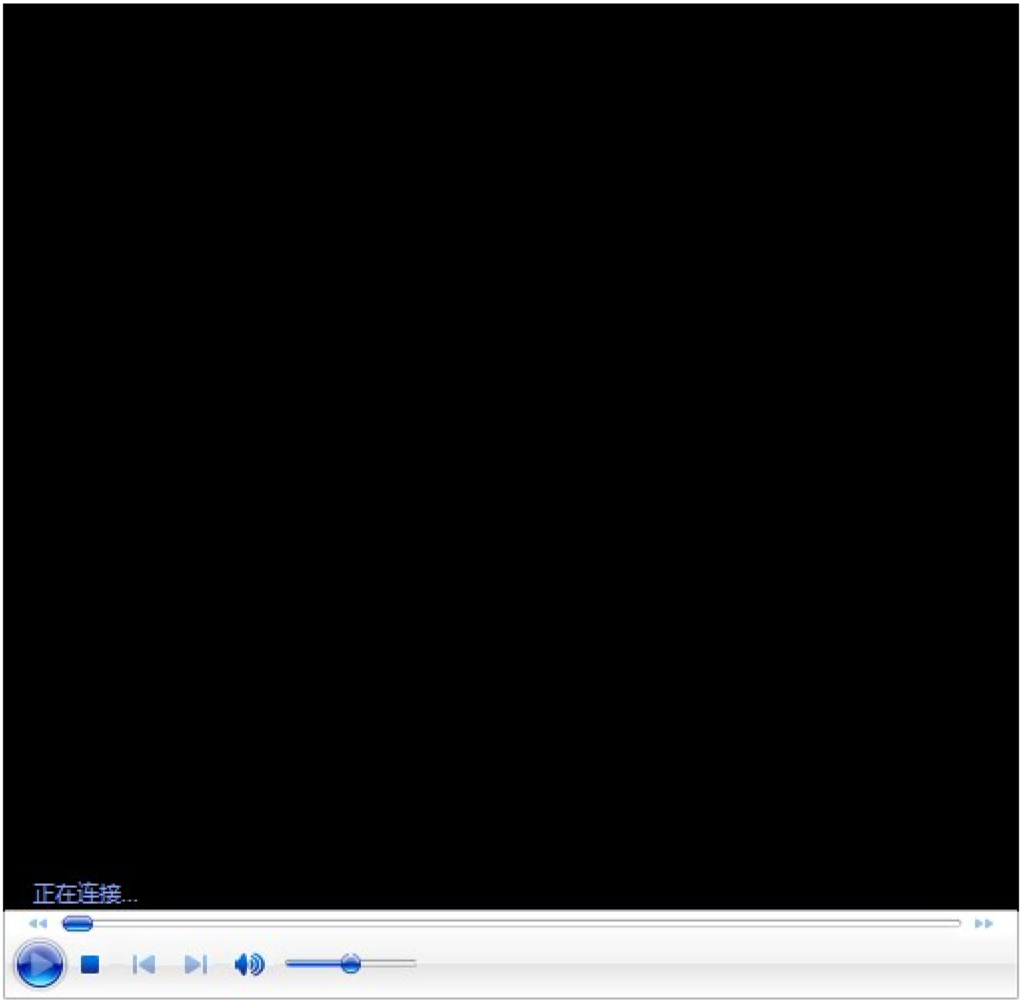


Fig. S10 Video recording the photochromism of **1**.

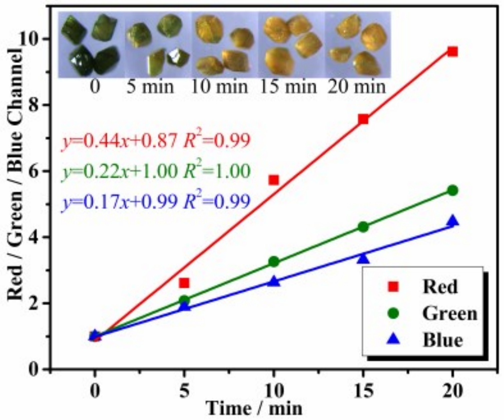


Fig. S11 Time-dependent color change of **1** upon exposing in TEOA vapor.

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