Supplementary Informantion

Linear-light controlled reverse electron transfer in a 3-D pyromelliticdiimide-based photo-/thermochromic cadmium(II) coordination polymer

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1. Experimental section

1.1 Synthesis of 1

Dissolve 4-PMPMD (20 mg, 0.05mmol) in 5 mL DMF solution, heat and stir until clarified, add $Cd(NO_3)_2 \cdot 4H_2O$ (46 mg, 0.15mmol) and terephthalic acid (25 mg, 0.15mmol) and stir for another 10 minutes. The solution is colorless transparent liquid. The solution was transferred to a 15 mL reactor and put into an oven at 60 ℃ for 5 days, After cooling to room temperature, light yellow transparent flaky crystals were obtained, washed in DMF, filtered and dried in 38.6% yield (based on 4-PMPMD). Anal. calcd (%) for $C_{30}H_{19}CdN_4O_8$: C , 53.26; H , 2.81; N , 8.29%. Found: C , 53.25; H , 2.97; N , 8.26%. IR data (KBr, cm^{-1}): 3428(s), 3057(m), 2926(w), 1955(w), 1775(m), 1722(s), 1665(s), 1614(w), 1557(s), 1505(w), 1382(s), 1225(w), 1155(w), 1110(s), 1091(s), 1015(m), 938(s), 837(s), 785(w), 747(m), 722(m), 658(w), 630(m), 575(w), 556(w), 511(m), 472(w).

1.2 Materials and methods

All reagents and solvents were purchased from commercial sources without further purification. The 4-PMPMD ligand was synthesised by methods based on the literature.[1] A 300w mercury (Hg) lamp (~ 365 nm)/xenon lamp (>420 nm) system with temperature control was used to prepare the coloured samples, and the distance between the samples and the Hg/xenon lamps were both about 25 cm. Elemental analyses (C, H, N) were made on a PerkinElmer 240 elemental analyser. Thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) was performed using a HCT-2 thermogravimetric analyzer under the protection of nitrogen atmosphere with a temperature range of 30-800 ℃, a ramp rate of 10 ℃ min^{-1}, and a flow rate of 100 cm^3 min^{-1}.Time-dependent UV-Vis absorption spectra were recorded at room temperature using a METASH UV-9000S UV-Vis spectrophotometer equipped with an integrating sphere and a glass slide coated with barium sulfate as a reference standard. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku UItima IV-185 diffractometer at room temperature, and simulated PXRD patterns were derived based on single-crystal data using the free Mercury software. Fourier transform infrared (FT-IR) spectra were measured in the range of 4000-500 cm^{-1} using a Nicolet 5DX spectrometer with KBr pressed flakes as substrate. Electron paramagnetic resonance (EPR) spectra were performed on a Bruker A300-10/12 EPR spectrometer at room temperature.

1.3 Single crystal X-ray structure determination and refinement

Single crystals of **1** were attached to the glass fiber surface with glue and crystal data were collected by using a graphite monochromator (Mo Kα, λ = 0.71073 Å) on a Bruker D8 Venture diffractometer. The

absorption correction in the SCALE3 ABSPACK scaling algorithm is carried out by applying the spherical harmonic function.[2] The structure of **1** was solved by the direct method and refined on the basis of F^2 by full-matrix least-squares refinements with the Olex2 program.[3-4] All non-hydrogen atoms were refined by anisotropic thermal parameters, while all hydrogen atoms were calculated and added based on theoretical positions. The crystallographic data, selected bond lengths and bond angles are recorded in Tables S2-S3. CCDC 2054370 contains the supplementary crystallographic data for **1**.

2. Figures

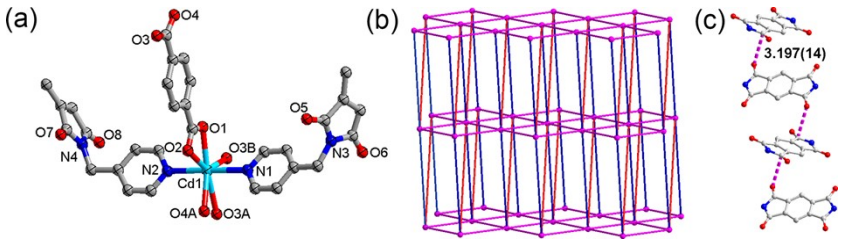

Fig. S1 The asymmetric unit of **1** (symmetry codes A, x, -1.5-y, 0.5+z, B, -1-x, -0.5+y, -1.5-z, C, -x, -2-y, -1-z, D, -2-x, -2-y, -2-z). (b) Schematic description of the 3-D framework with the 8-connected topological network of **1**. (c) The lone pair-π interaction in **1**. All hydrogen atoms and partial pyridylmethyl groups are omitted for clarity.

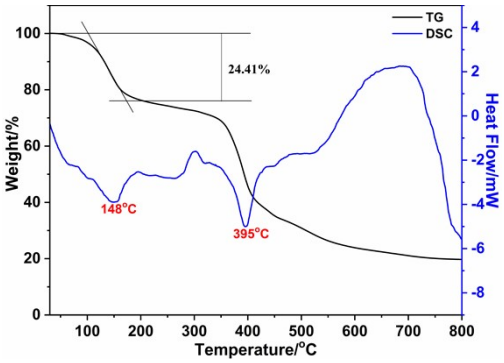

Fig. S2 Thermo-gravimetric (TG) and Differential scanning calorimetry (DSC) curves of **1**

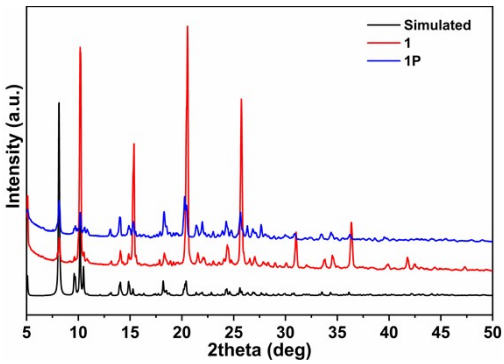

Fig. S3 Powder X-ray diffraction (PXRD) patterns for **1** and **1P** at room temperature.

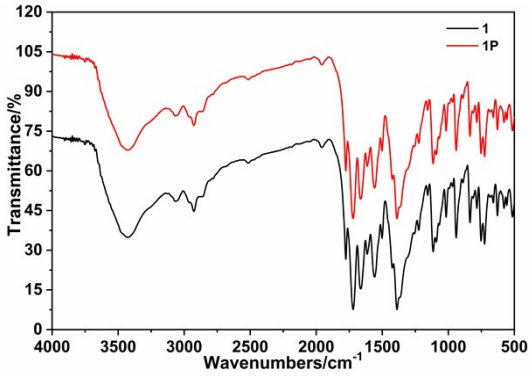

Fig. S4 IR spectra of **1**

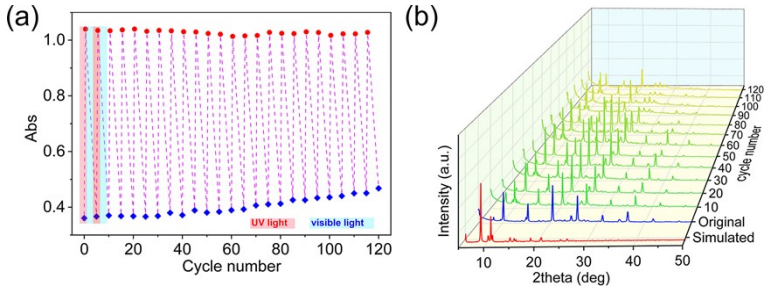

Fig. S5 (a) The switching cycles of forward and reverse ET reactions of **1** by alternating UV and visible light irradiation. (b) PXRD patterns during the processes of all-optical switch.

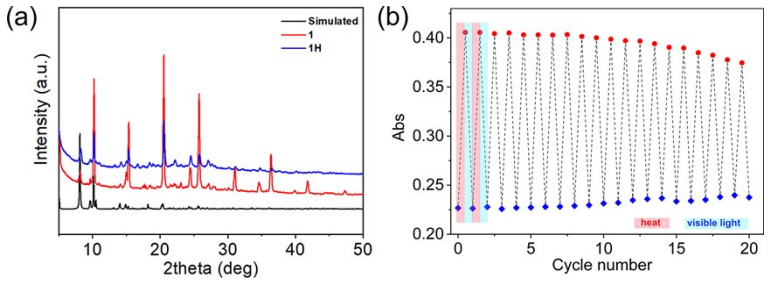

Fig. S6 (a) PXRD patterns of **1** and **1H** at room temperature. (b) The switching cycles of bidirectional ET reactions of **1** upon alternate excitation by heating and visible light irradiation.

3. Tables

Table S1 Summary of the bifunctional photo-/thermochromic materials based on ET.

Electron donor	Electron acceptor	Stimuli	Coloration			Decoloration[a]		References
			Initial color	Saturated color	Saturated time	Dark/Heat	Time	
Cl, Br	4, 4′-bipyridine derivatives	light	pale yellow	blue	—	120 °C or dark	1h or 3 d	5
			yellow	blue-green	—	dark	3 d	

		heat	pale yellow	blue	100 °C 30 min	120 °C or dark	1h or 5 d	
			yellow	blue	100 °C 30 min	dark	5 d	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	light orange	dark grey blue	15 min	dark	1 d	6
		heat	light orange	yellow	98 °C 6 min	dark	—	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	yellow	light green	4 min	dark	—	7
			yellow	darker yellow	2 h	—	—	
		heat	yellow	light green	170 °C	—	—	
carboxylate O atom	4, 4′-bipyridine derivatives	light	yellow	blue	2 min	dark	Several minutes	8
		heat	yellow	blue	vacuum (below 100 °C)	decrease temperature	—	
anionic framework	4, 4′-bipyridine derivatives	light	colorless	blue	5 min	—	—	9
		heat	colorless	blue	300 °C 3 h	—	—	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	light yellow	dark green	5 min	dark	1 d	10
			light yellow	light green	10 min	100 °C	30 min	
		heat	light yellow	dark green	90 °C 30min	dark	—	
inorganic anionic framework	4, 4′-bipyridine derivatives	light	pale yellow	steel grey	30 min	dark	4 months	11
		heat	pale yellow	black green	300 °C 30min	dark	4 months	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	colorless	navy	90 s	180 °C	30 min	12
			colorless	blue	120 s	120 °C	30 min	
		heat	colorless	sky blue	120 °C 10 min	180 °C	10 min	
N_3^- anions	4, 4′-bipyridine derivatives	light	yellow	green	5 min	dark	1 week	13
		heat	yellow	green	70 °C	dark	1 week	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	pale yellow	dark green	—	170 °C	30 min	14
			light green	blue green	—	—	—	
		heat	light green	blue green	—	—	—	
O atoms from H_2pma^{2-}	4, 4′-bipyridine derivatives	light	colorless	blue	5 min	dark	24 h	15
		heat	colorless	light blue	52 °C 3 min	dark	22 h	
O atoms in POMs	4, 4′-bipyridine derivatives	light	blue	black	2 s	dark	11-16 d	16
			brown	dark brown	15 s			

			yellow	green	7 s			
		heat	blue	dark blue	120 °C	RT	6 h	
the carboxyl O atom and Cl^-	4, 4′-bipyridine derivatives	light	white	light blue	3 s	dark or 60 °C	48 h or 6 h	17
		heat	white	light green	150 °C 2 h	water	—	
O atoms in POMs	4, 4′-bipyridine derivatives	light	yellow-green	dark-green	3 min	dark	—	18
			yellow	turquoise	5 min	dark	—	
		heat	yellowish-green	yellow	180 °C	RT	5 min	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	colorless	light blue	45 min	dark	—	19
		heat	colorless	light yellow	130 °C	cannot be completely converted	—	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	light yellow	blue	40 s	100 °C	1 h	20
			white	cyan blue	60 s	100 °C	1 h	
		heat	light yellow	light blue	110 °C 10 min	170 °C	10 min	
the host *β*-CD	4, 4′-bipyridine derivatives	light	grayish white	dark gray,	3 min	dark	—	21
			white	dark blue	2 min	dark	48 h	
		heat	white	green	100 °C	RT relative humidity of 75%	5 h	
						RT relative humidity of 33%	24 h	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	yellow	blue	5 min	dark	3 weeks	22
			yellow	blue	5 min	dark	5 d	
		heat	yellow	blue	90 °C	dark	3 weeks	
			yellow	blue	90 °C	dark	5 d	
carboxylate O atoms	4, 4′-bipyridine derivatives	light,	yellow	blue	20 min	dark or 120 °C	14 d or 4 h	23
		heat	yellow	blue	110 °C	120 °C	—	
carboxylate O atoms	4, 4′-bipyridine derivatives	light	colorless	cyan	10 s	dark or 50-100 °C	2 h or 30 min	24
			pink	purple	40 s	dark	5 d	
			colorless	pink	130 °C 20 min	dark	1 d	
		heat	pink	blue	180 °C	without decoloration	2 months	
			blue	brown	240 °C 30 min	without decoloration	2 months	

Table S2 Crystallographic data and refinement of compound **1**.

Compound	**1**
CCDC code	2054370
Temperature (K)	273
Empirical formula	$C_{30}H_{18}CdN_4O_8$
Formula weight	674.88
Crystal size (mm^3)	0.314 × 0.197 × 0.041
Crystal system	monoclinic
Space group	*P*21*/c*
a (Å)	20.341(10)
b (Å)	13.506(6)
c (Å)	21.538(8)
α (°)	90
β (°)	121.24(3)
γ (°)	90
V ($Å^3$)	5059(4)
Z	4
D_c ($g\ cm^{-3}$)	0.886
F(000)	1352.0
$\mu(mm^{-1})$	0.464
ϑ range (°)	4.984 to 52
Reflections collected	35329
Unique reflections	9465
R_{int}	0.1146
Goodness-of-fit on F^2	1.040
R_1/wR_2, $[I \geq 2\sigma(I)]$[a,b]	0.0968/0.2607
R_1/wR_2, (all data)	0.1391/0.2939
$\Delta\rho_{max}/\Delta\rho_{min}$ (e $Å^{-3}$)	2.06/-1.53

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

Table S3 Selected bond lengths (Å) and angles (°) for compound **1**.

Compound **1**			
Cd1-O1	2.314(5)	C3-C4	1.346(14)
Cd1-O2	2.552(5)	C3-C6	1.520(13)
Cd1-O3#1	2.392(5)	C4-C5	1.345(14)
Cd1-O3#2	2.592(4)	C7-C8	1.430(15)
Cd1-O4#2	2.317(17)	C8-C9	1.382(14)
Cd1-N1	2.353(7)	C8-C11#3	1.339(15)
Cd1-N2	2.338(7)	C9-C10	1.494(15)
Cd1-O4A#2	2.380(12)	C9-C11	1.491(16)
O1-C23	1.258(8)	C12-C13	1.301(14)
O2-C23	1.243(8)	C13-C14	1.345(13)
O3-C30	1.260(9)	C14-C15	1.403(14)
O4-C30	1.240(19)	C14-C17	1.516(13)
O5-C10	1.194(12)	C15-C16	1.351(13)
O6-C7	1.227(15)	C18-C19	1.507(13)
O7-C21	1.238(12)	C19-C20	1.340(13)
O8-C18	1.209(12)	C19-C22#4	1.383(14)
N1-C1	1.313(11)	C20-C21	1.487(12)
N1-C5	1.278(11)	C20-C22	1.391(14)
N2-C12	1.341(12)	C23-C24	1.525(8)
N2-C16	1.315(10)	C24-C25	1.419(10)
N3-C6	1.499(14)	C24-C29	1.369(9)
N3-C7	1.434(14)	C25-C26	1.385(9)
N3-C10	1.348(15)	C26-C27	1.411(9)
N4-C17	1.449(13)	C27-C28	1.383(9)
N4-C18	1.400(14)	C27-C30	1.527(8)
N4-C21	1.383(14)	C28-C29	1.402(10)
C1-C2	1.333(13)	C30-O4A	1.273(12)
O1-Cd1-O2	53.55(16)	O6-C7-C8	131.4(13)
O1-Cd1-O3#1	164.26(15)	C8-C7-N3	105.4(11)
O1-Cd1-O3#2	87.52(15)	C9-C8-C7	109.7(10)
O1-Cd1-O4#1	144.0(4)	C11#5-C8-C7	126.1(11)
O1-Cd1-N1	90.3(2)	C11#5-C8-C9	124.1(10)

O1-Cd1-N2	90.9(2)	C8-C9-C10	106.8(10)
O1-Cd1-O4A#1	142.6(3)	C8-C9-C11	121.9(10)
O2-Cd1-O3#1	142.10(15)	C11-C9-C10	131.3(10)
O3#2-Cd1-O2	141.06(15)	O5-C10-N3	123.6(11)
O3#2-Cd1-O3#1	76.83(15)	O5-C10-C9	129.7(13)
O4#1-Cd1-O2	90.8(5)	N3-C10-C9	106.7(10)
O4#1-Cd1-O3#1	51.7(4)	C8#5-C11-C9	113.9(11)
O4#1-Cd1-O3#2	127.9(5)	C13-C12-N2	125.1(9)
O4#1-Cd1-N1	84.7(8)	C12-C13-C14	123.9(12)
O4#1-Cd1-N2	95.2(8)	C13-C14-C15	112.3(9)
O4#1-Cd1-O4A#1	9.5(4)	C13-C14-C17	122.7(10)
N1-Cd1-O2	90.4(2)	C15-C14-C17	125.0(9)
N1-Cd1-O3#2	89.00(17)	C16-C15-C14	120.7(9)
N1-Cd1-O3#1	91.06(19)	N2-C16-C15	124.9(10)
N1-Cd1-O4A#1	94.1(6)	N4-C17-C14	113.2(10)
N2-Cd1-O2	91.3(2)	O8-C18-N4	123.7(10)
N2-Cd1-O3#1	87.44(19)	O8-C18-C19	131.4(11)
N2-Cd1-O3#2	89.69(18)	N4-C18-C19	104.9(9)
N2-Cd1-N1	178.2(2)	C20-C19-C18	119.4(9)
N2-Cd1-O4A#1	85.8(6)	C20-C19-C22#6	121.7(10)
O4A#1-Cd1-O2	89.2(3)	C22#6-C19-C18	128.8(10)
C23-O1-Cd1	96.9(4)	C19-C20-C21	107.5(9)
C23-O2-Cd1	86.2(4)	C19-C20-C22	123.6(9)
Cd1#3-O3-Cd1#4	103.17(15)	C22-C20-C21	128.9(10)
C30-O3-Cd1#4	87.0(4)	O7-C21-N4	124.6(9)
C30-O3-Cd1#3	169.6(4)	O7-C21-C20	127.6(10)
C30-O4-Cd1#4	100.7(10)	N4-C21-C20	107.5(9)
C1-N1-Cd1	121.5(6)	C19#6-C22-C20	114.7(10)
C5-N1-Cd1	124.9(6)	O1-C23-C24	116.4(6)
C5-N1-C1	113.6(8)	O2-C23-O1	123.4(6)
C12-N2-Cd1	125.8(5)	O2-C23-C24	120.2(6)
C16-N2-Cd1	121.4(6)	C25-C24-C23	119.8(6)
C16-N2-C12	112.8(8)	C29-C24-C23	121.8(6)
C7-N3-C6	124.9(12)	C29-C24-C25	118.4(6)
C10-N3-C6	123.8(10)	C26-C25-C24	121.6(6)

C10-N3-C7	111.3(10)	C25-C26-C27	118.2(6)
C18-N4-C17	124.4(10)	C26-C27-C30	120.4(5)
C21-N4-C17	124.5(10)	C28-C27-C26	120.8(6)
C21-N4-C18	110.6(8)	C28-C27-C30	118.8(6)
N1-C1-C2	123.9(10)	C27-C28-C29	119.6(7)
C1-C2-C3	121.4(9)	C24-C29-C28	121.5(6)
C2-C3-C6	121.4(9)	O3-C30-C27	120.3(6)
C4-C3-C2	113.0(8)	O3-C30-O4A	122.8(7)
C4-C3-C6	125.5(9)	O4-C30-O3	119.0(10)
C5-C4-C3	119.5(10)	O4-C30-C27	119.4(10)
N1-C5-C4	127.8(10)	O4A-C30-C27	116.6(8)
N3-C6-C3	112.7(8)	C30-O4A-Cd1#4	96.5(8)
O6-C7-N3	123.0(13)		

symmetry codes: #1 +x, -3/2-y, 1/2+z; #2 -1-x, -1/2+y, -3/2-z; #3 -1-x, 1/2+y, -3/2-z; #4 +x, -3/2-y, -1/2+z; #5 -x, -2-y, -1-z; #6 -2-x, -2-y, -2-z

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