

Supporting Information

Tunable Photo/Thermochromic Properties of Cd(II)-Viologen Coordination Polymers Modulated by Coordination Modes for Flexible Imager Film and Anti-counterfeiting

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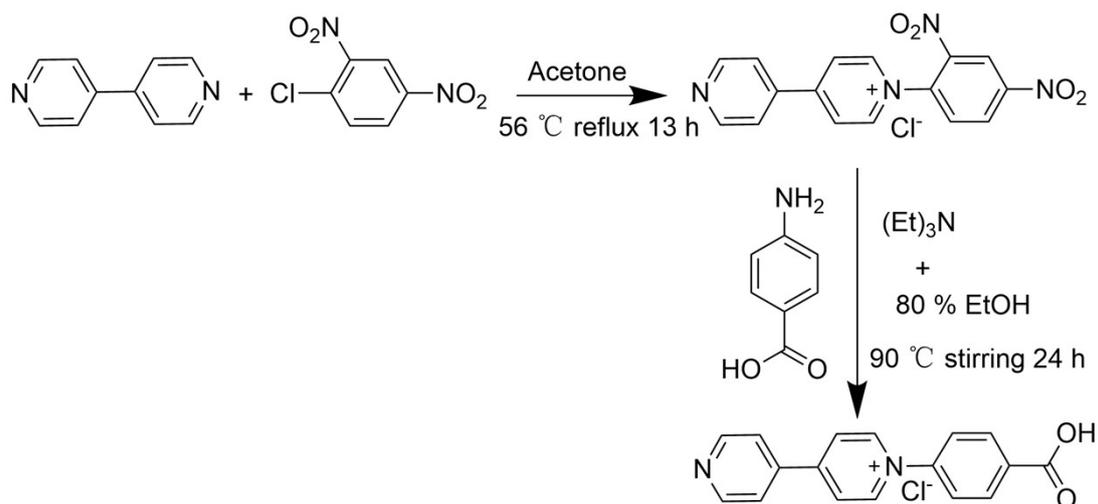
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Synthesis of 1-(4-Carboxyphenyl)-4,4'-bipyridinium·Cl (HCPB·Cl)

4,4'-Bipyridine (3.5 g, 22.5 mmol) and 2,4-dinitrochlorobenzene (3.0 g, 15 mmol) were dissolved in 25 ml of acetone and refluxed for 13 h at 56 °C. The mixture was cooled to room temperature, and the precipitate was filtered and washed several times with methylene chloride and dried under vacuum to give 1-(2,4-dinitrophenyl)-4,4'-bipyridinium·Cl as a grey powder.

1-(2,4-Dinitrophenyl)-4,4'-bipyridinium·Cl (0.65 g, 2.0 mmol) and 4-aminobenzoic acid (0.41 g, 3.0 mmol) were dissolved in 80% ethanol (50 mL), then 2.5 mmol of triethylamine was added. The reaction mixture was stirred at 90 °C for 24 hours. The precipitate was filtered, recrystallized from ethanol, and dried under vacuum to give HCPB·Cl as a reddish-brown powder.



Scheme S1. The synthesis process of HCPB·Cl.

Table S1. Crystallographic data for **1** and **2**.

<i>Compound</i>	<i>1</i>	<i>2</i>
Formula	C ₆₈ H ₅₄ Cd ₄ N ₄ O ₂₅	C ₃₄ H ₃₀ CdClN ₅ O ₁₂
Fw	1776.79	848.48
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> /(Å)	9.4800(13)	13.6920(4)
<i>b</i> /(Å)	21.078(3)	18.1108(5)
<i>c</i> /(Å)	17.495(3)	18.0526(7)
<i>α</i> (°)	90	90
<i>β</i> (°)	104.272(9)	131.224(2)
<i>γ</i> (°)	90	90
<i>V</i> /(Å ³)	3388.0(9)	3367.0(2)
<i>Z</i>	4	4
Temperature/(K)	293.17	100.7
ρ_{calc} (g/cm ³)	1.742	1.630
<i>F</i> (000)	1776.0	1144.0
μ /(mm ⁻¹)	10.652	0.724
Reflections collected	18963	20759
Independent reflections	5926	7854
R1 [<i>I</i> ≥ 2σ (<i>I</i>)]	0.0463	0.0408
wR ₂ [all data]	0.1237	0.1032
GOF on <i>F</i> ²	1.037	1.053

Table S2. Hydrogen bond distances (Å) of compounds **1**.

<i>Hydrogen Bond</i>	<i>Distance</i>
C1-H1...O5	2.590(6)
C5-H5...O2	2.770(5)
C5-H5...O4	3.282(4)
C5-H5...O7	3.102(7)
C7-H7...O1	2.977(2)
C7-H7...O8	2.280(0)
C7-H7...O9	3.134(1)
C8-H8...O4	2.252(4)
C8-H8...O5	2.985(6)

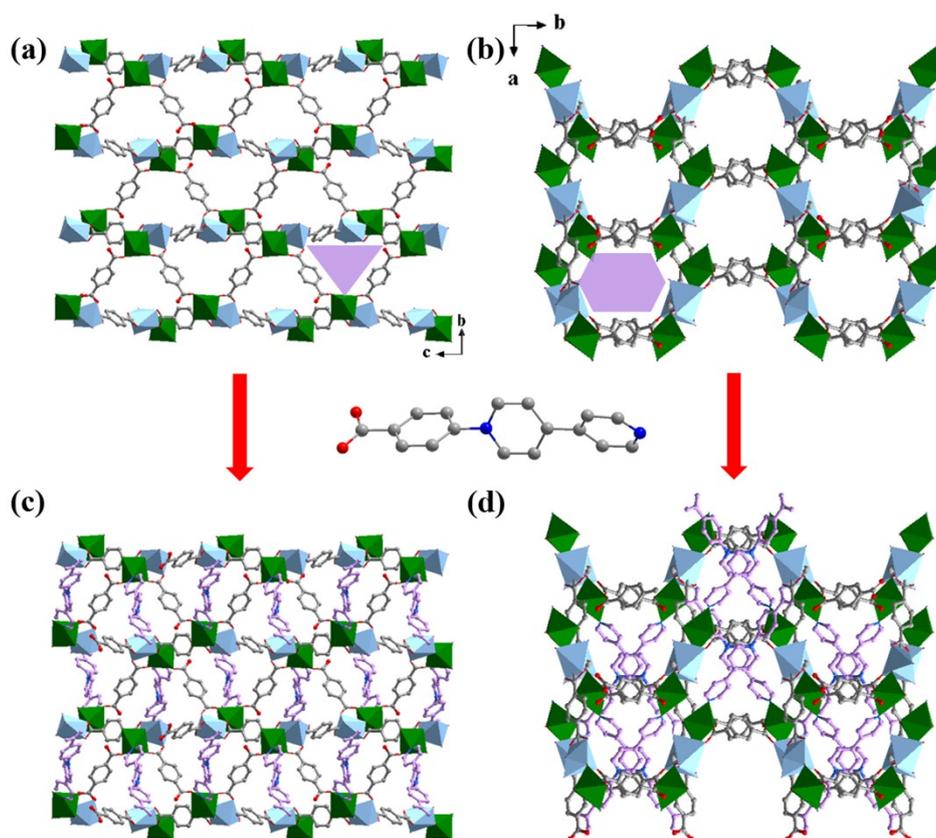


Fig. S1 View of the [Cd₄(BDC)₄(H₂O)₂]_n 3D architecture constructed: the triangular channel along the a-axis (a) and the hexagonal channel along the c-axis (b). The 3D structure of **1** along the a-axis (c) and c-axis (d).

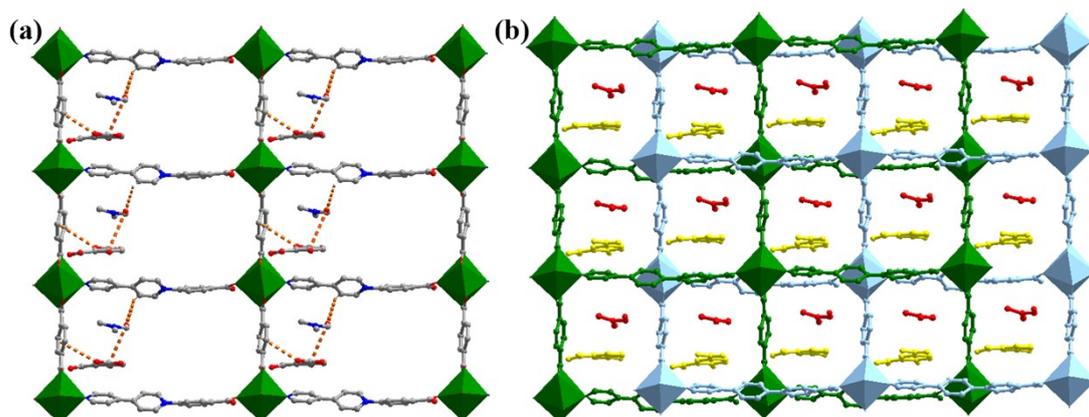


Fig. S2 (a) The interactions between free molecules and the 2D layer in **2**. (b) 2-fold interpenetrated of 2D layer accompanied by free molecules.

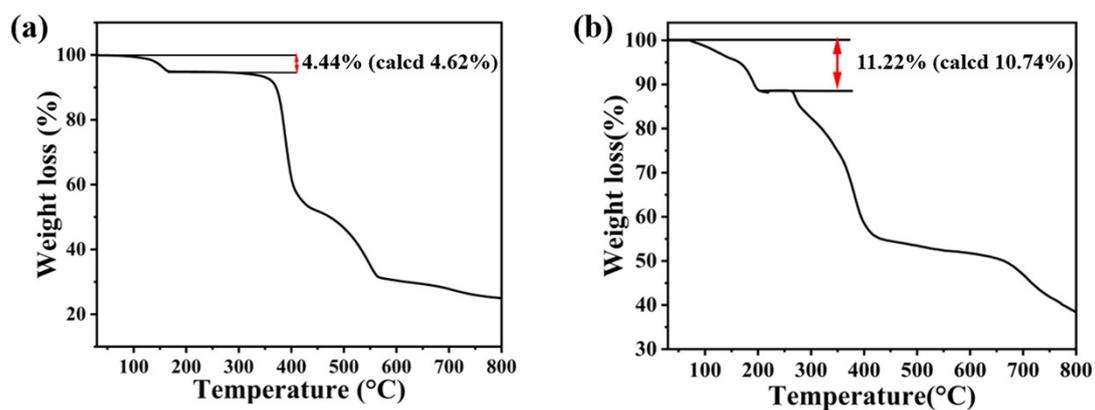


Fig. S3 The TG plots for **1** (a) and **2** (b).

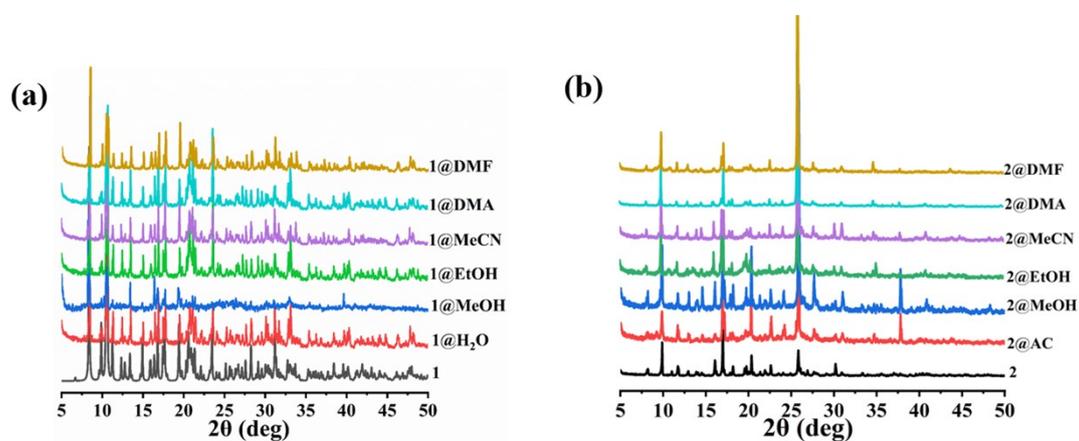


Fig. S4 PXRD patterns of **1** (a) and **2** (b) immersed in different solutions.

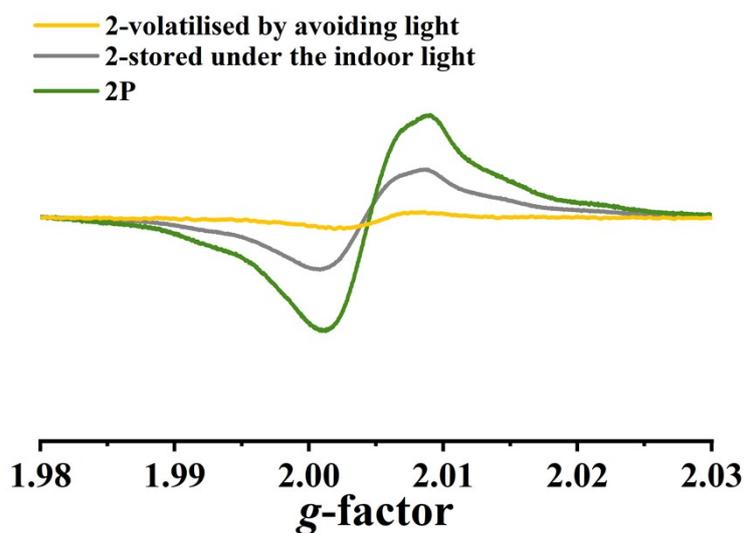


Fig. S5 The EPR spectra of **2** volatilized by avoiding light, stored under the indoor light for several months, and irradiated by UV light.

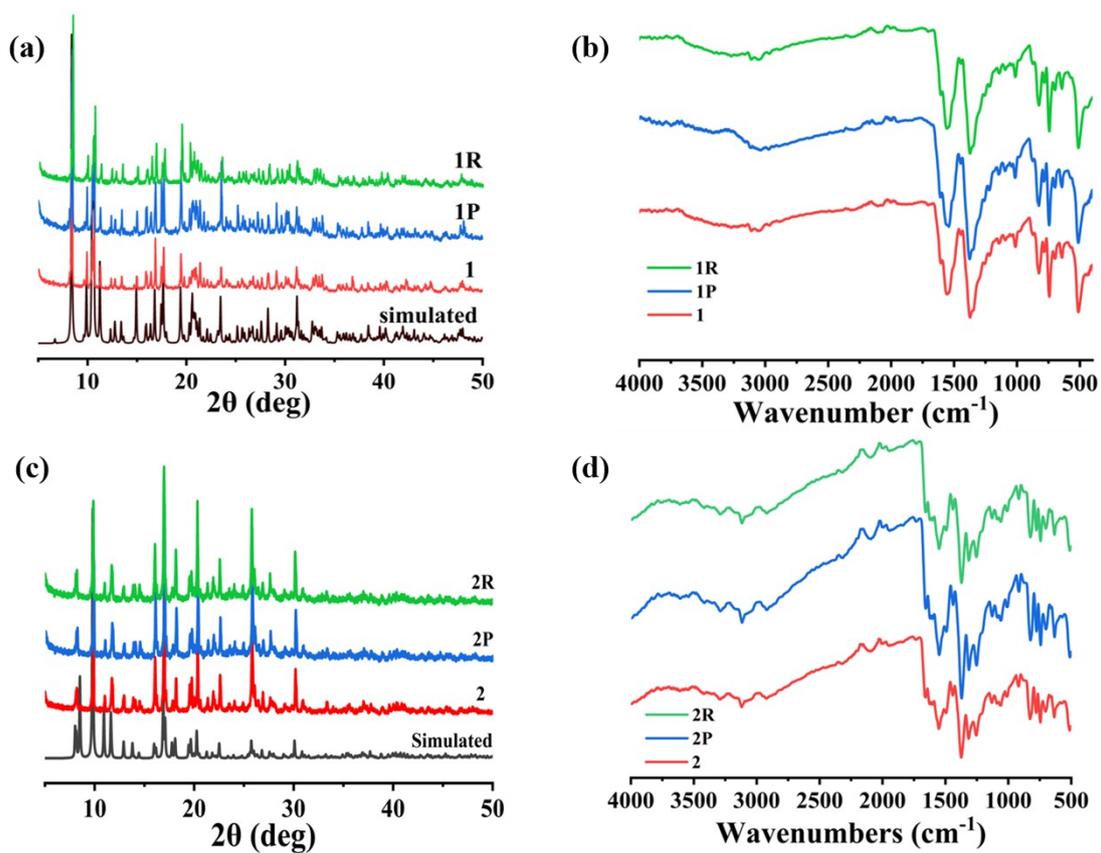


Fig. S6 Simulated, experimental, photochromic, and decolored PXRD patterns of **1** (a) and **2** (c). IR spectra of **1** (b) and **2** (d) before and after coloration.

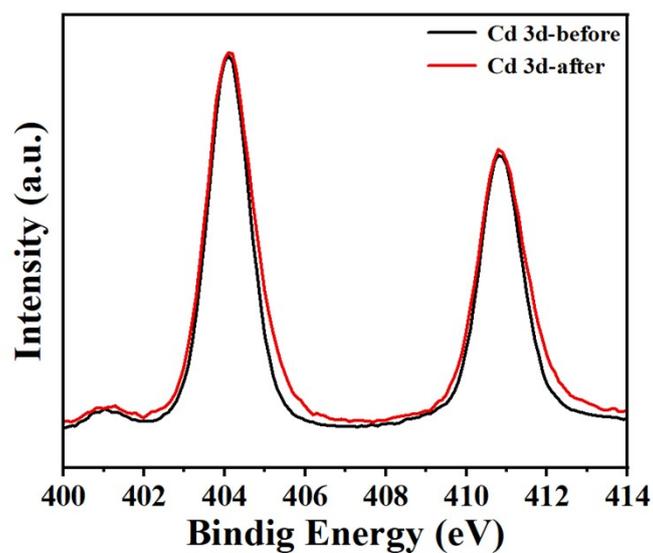


Fig. S7 Cd 3d XPS core-level spectra of **1** before and after irradiation by UV light.

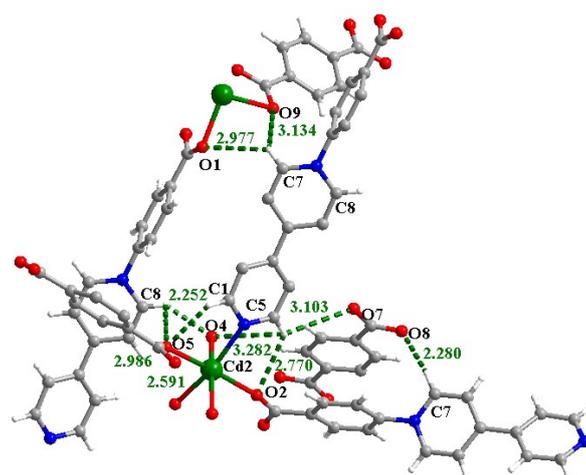


Fig. S8 The distances between the hydrogen atom at the α -carbon atom of the pyridinium group and the carboxylate O atom in **1**.

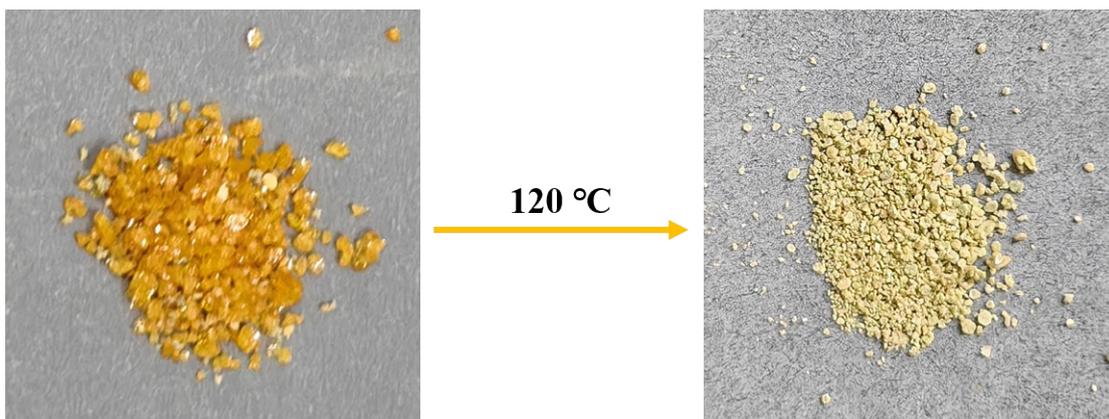


Fig. S9 Photographs of crystal sample **1** heated at 120 °C for 30 minutes.

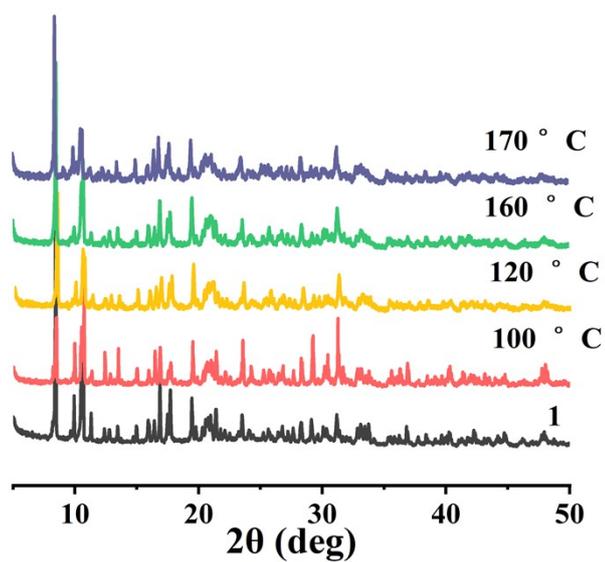


Fig. S10 PXRD patterns of **1** heated at 100 °C, 120 °C, 160 °C, and 170 °C.

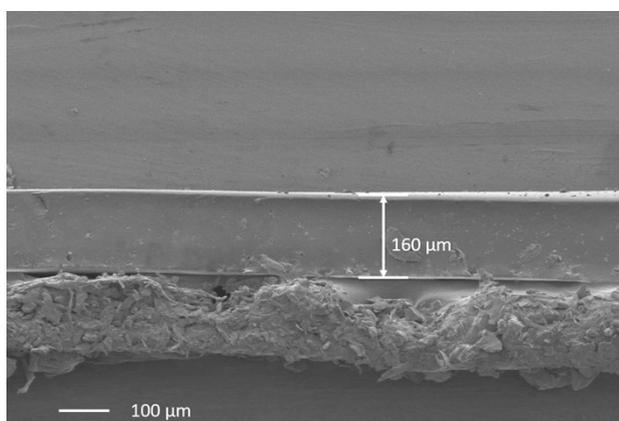


Fig. S11 The SEM photos of the profile for **1@PDMS** film.

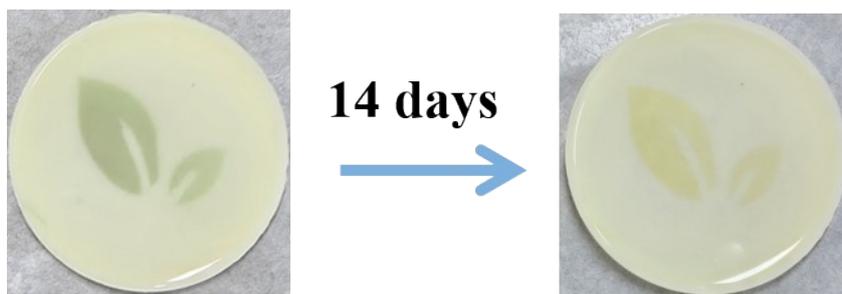


Fig. S12 The photochromism imaging for the flexible film after 4 min UV illuminated and placed in the dark for 14 days.