Supporting Information

Multi-stimulus responsive properties of Cd-MOF based on tetraphenylethylene

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Materials and Instrumentation

The elemental analysis was carried out on a Perkin-Elmer 240C automatic analyzer. Infrared spectra were measured on a Bruker AXSTENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 400-4000 cm^{-1} at room temperature. UV-vis spectra were recorded on JASCOV-570 spectrometer (200-800 nm, in form of solid sample). X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu Kα radiation, in the range $5° < 2\theta < 50°$, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step. Thermogravimetric analysis (TG) was performed on a Perkin Elmer Diamond TG/DTA under the conditions of the N_2 atmosphere in the temperature range from 30 to 800 °C. The photoluminescent spectra, photoluminescence quantum yield (PLQY), and fluorescence lifetime of the coordination polymers were measured on a HORIBA Fluoromax-4-TCSPC spectrofluorometer equipped with Spectra LED Pulsed LED sources at room temperature (200-1000 nm). In addition, PLQY was measured with the use of an integrating sphere. The inner surface of the integrating sphere shell is coated with barium sulfate-based materials or special materials of Spectralon, which have total reflection characteristics and can capture light entering and exiting the sphere. By measuring the spectra of the fluorescent substance and the blank cavity separately, the fluorescence emission (Ec) and scattering (Lc) of the fluorescent substance, as well as the emission (Ea) and scattering (La) of the blank cavity are measured. The fluorescence quantum yield is calculated according to the following formula.

$$\Phi_f = \frac{E_c - (1 - A)\cdot E_b}{L_a \cdot A} = \frac{E_c - E_a}{L_a - L_c}$$

E_b: Fluorescence integration of fluorescent substances due to indirect luminescence from the integrating sphere; A: Absorption value of fluorescent substance at excitation wavelength.

Reagent and Chemicals

Cadmium(II) nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] was purchased from Damao Chemical Reagent Factory. DMF (N,N'-dimethylformamide), zinc powder were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous ethanol was purchased from

Tianjin Fuyu Fine Chemical Co., Ltd. Cesium fluoride (CsF) was purchased from Shanghai Macklin Biochemical Co., Ltd. 4,4'-Dibromobenzophenone was purchased from Shanghai Haohong Biomedical Technology Co., Ltd. Methyl 4-boronobenzoate acid was purchased from Shanghai boka Chemical Technology Co., Ltd. 1,2-Dimethoxyethane and poly(methyl methacrylate) (PMMA) were purchased from shanghai Aladdin Biochemical Technology Co., Ltd. Methanol (MeOH), tetrahydrofuran (THF), n-Hexane and dichloromethane (DCM) were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Hydrochloric acid, chloroform, and acetonitrile (CH_3CN) were purchased Tianjin Kemio Chemical Reagent Co., Ltd. Polydimethylsiloxane (PDMS) was purchased from Dongguan Yihui Adhesive Co., Ltd. All water used is deionized water. All chemical reagents were at least of analytical grade and were directly used without further purification. And the ligand H_4tcbpe was synthesized with the reference to literature[1]. And the LEDs were purchased from Taobao network.

Synthesis method of Cd-tcbpe with "one pot"

8.1 mg of H_4tcbpe ligand and 30.8 mg of cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] were dissolved in a mixture of 1 mL DMF and 0.5 mL ethanol, heated at 85℃ for 12 h, and repeatedly washed with pure DMF solvent, and dried at room temperature to obtain pale yellow block crystals **Cd-tcbpe**. Yield: 28.6% (based on H_4tcbpe).

X-ray crystallographic determination

Single crystal X-ray reflection data was collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with Mo-Kα (λ = 0.71073 Å) radiation. A semiempirical absorption correction was applied by the program SADABS. The program suite SHELXL-2018[2, 3] and OLEX 2[4] platform was used for space-group determination (XPREP), direct method structure solution (XS) and least-squares refinement (XL). Non-hydrogen atoms were refined with anisotropic displacement parameters in the final cycles. DELU commands were applied to Cd3 atom. Besides, the 'OMIT' command were used to remove the bad reflections in the structure; due to

the serious disorder of the solvent molecules, the 'SQUEEZE' command was used to deal with disorder of solvent DMF molecules in **Cd-tcbpe**. For **Cd-tcbpe**, we found four alert level B "D-H Bond Without Acceptor O5-H5A, O5-H5B, O7-H7A, O7-H7B" by checkcif in the structure. It can be attributed that O5-H5A, O5-H5B, O7-H7A, O7-H7B are part of water molecules or from water molecules that is likely disordered/on a partially occupied site and for the last one. And we also found one alert level B "Low 'MainMol' Ueq as Compared to Neighbors of Cd3" by checkcif in the structure of **Cd-tcbpe**. It could be attributed that the Cd3 atom may show some disorder. "Missing # of FCF Reflection(s) Below Theta(Min). 16 Note" was found in the checkcif of **Cd-tcbpe**. The reason might be that beamstop theta-min limit set too high, large unit-cell etc. The details of the crystal parameters, data collection, and refinement for **Cd-tcbpe** are summarized in Table S1, and selected bond lengths and angles with their estimated standard deviations are listed in Table S2. CCDC 2284476 contains crystallographic data for this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic data of **Cd-tcbpe***

Complex	**Cd-tcbpe (SQUEEZE)**
Formula	$C_{84}H_{59}Cd_3NO_{15}$
Molecular weight	1659.52
Crystal system	Orthorhombic
Space group	*Pbcn*
a/Å	17.7252(4)
b/Å	41.8784(10)
c/Å	34.5610(8)
α/(°)	90
β/(°)	90
γ (°)	90
V (Å^3)	25654.7(10)
Z	8
D_{calc}/(g·cm^{-3})	0.859
F(000)	6672.0
μ / mm^{-1}	0.532
2θ range/(°)	4.398-50.748
Reflections collected	166964
Independent reflections [I>2σ(*I*)]	23522
Parameters	789
Goodness of fit	1.022
R_1[a]	0.0487(0.0678)[b]
wR_2[a]	0.1317 (0.1458)[b]
Δ(*ρ*) (e Å^{-3})	1.27 and -0.67

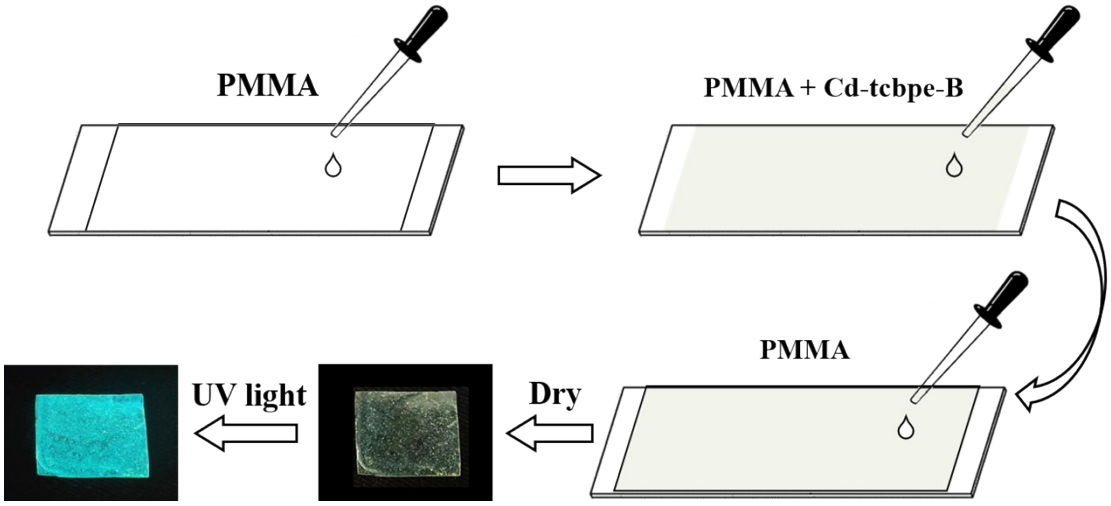
* a. $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=(\Sigma(w(F_o^2-F_c^2)^2/\Sigma(w(F_o^2)^2)^{1/2}$; b. [$F_o>4\sigma(F_o)$]; b. based on all data.

Table S2 Selected bonds (Å) and angle (°) of **Cd-tcbpe**

Cd-tcbpe			
Selected bonds (Å)			
Cd1-O3	2.2078(3)	Cd1-O3$^{\#3}$	2.3078(3)
Cd1-O1$^{\#3}$	2.2724(3)	Cd1-O1	2.2724(3)
Cd1-O2$^{\#3}$	2.5509(3)	Cd1-O2	2.5509(3)
Cd2-O12$^{\#1}$	2.2253(3)	Cd2-O9$^{\#6}$	2.2320(3)
Cd2-O4	2522(3)	Cd2-O5	2.3091(4)
Cd2-O6	2.3541(3)	Cd2-O2	2.3557(3)
Cd3-O18	2.1933(3)	Cd3-O13$^{\#3}$	2.2364(3)
Cd3-O11$^{\#10}$	2.2740(3)	Cd3-O7	2.2773(4)
Cd3-O14$^{\#9}$	2.3218(3)	Cd3-O6$^{\#6}$	2.3573(3)
Cd4-O10$^{\#12}$	2.2272(3)	Cd4-O10$^{\#11}$	2.2272(3)
Cd4-O15	2.2556(3)	Cd4-O15$^{\#3}$	2.2556(3)
Cd4-O14	2.5996(3)	Cd4-O14$^{\#3}$	2.5997(3)
Selected angle (°)			
O14-Cd4-O14$^{\#3}$	116.98(12)	O10$^{\#12}$-Cd4-O14	120.28(11)
O10$^{\#12}$-Cd4-O10$^{\#11}$	83.70(18)	O15-Cd4-O14$^{\#3}$	85.05(12)
O2$^{\#3}$-Cd1-O2	133.40(12)	O3-Cd1-O2$^{\#3}$	115.38(11)
O3-Cd1-O1	149.14(12)	O1-Cd1-O2	53.57(11)
O14$^{\#9}$-Cd3-O6$^{\#6}$	83.62(11)	O13#13-Cd3-O14$^{\#9}$	176.12(11)
O13$^{\#13}$-Cd3-O7	89.24(15)	O7-Cd3-O6$^{\#6}$	169.93(14)
O12$^{\#1}$-Cd2-O4	172.54(12)	O9$^{\#6}$-Cd2-O6	94.66(14)
O5-Cd2-O2	86.92(17)	O5-Cd2-O6	174.45(17)
C73-C72-C77	120.0	C14-C28-C29	122.7(3)
C56-N1-C57	117.7(5)	C17-C18-C19	120.0

Cd-tcbpe: #1: x-1/2, -y+3/2, -z+1; #2: -x+1/2, y+1/2, z; #3: -x+1, y, -z+3/2; #4: x-1/2, y+1/2, -z+3/2; #5: x, y-1, z; #6: -x+1, -y+1, -z+1; #7: x-1/2, -y+1/2, -z+1; #8: -x+3/2, y+1/2, z; #9: x+1/2, -y+3/2, -z+1; #10: x+1/2, -y+1/2, -z+1; #11: x, y+1, z; #12: -x+1, y+1, -z+3/2; #13: -x+3/2, y-1/2, z; #14: -x, y, -z+3/2

Preparation route of Cd-tcbpe-B@PMMA film



Scheme S1 Preparation route of **Cd-tcbpe-B**@PMMA film

Synthesis Discussion

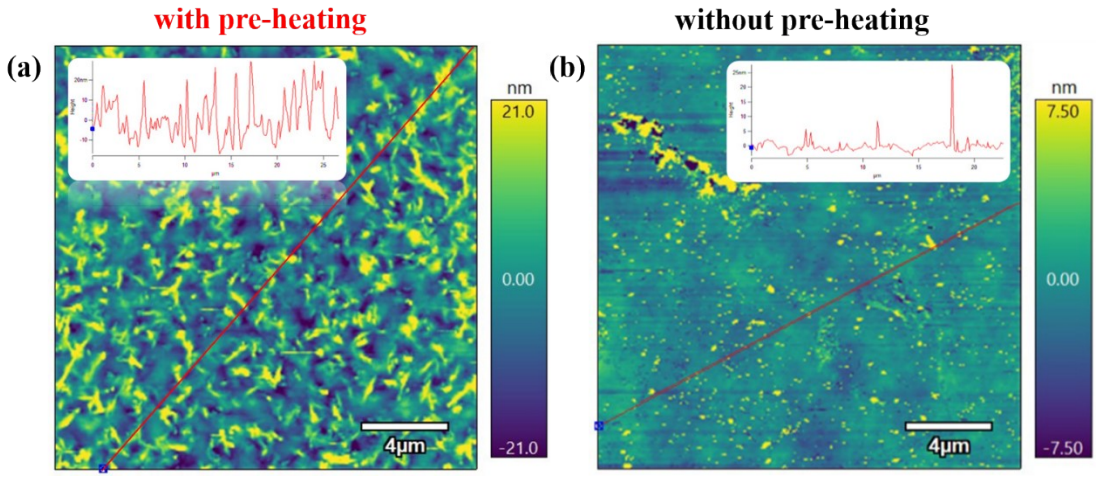


Figure S1 (a) AFM images of the preheating solution in "two step" method and (b) without preheating solution in "one pot" method

Structural description of Cd-tcbpe

Single-crystal X-ray diffraction analysis demonstrated that **Cd-tcbpe** crystalizes in orthorhombic crystal system, *Pbcn* space group. In its asymmetric unit, there are four Cd^{2+} ions, one and a half of deprotonated $tcbpe^{4-}$ ligand, one coordinated DMF molecule and two coordinated water molecules. Among them, the crystallographic

occupancy of Cd1 and Cd4 is 0.5. Four metal Cd^{2+} ions exhibit two different coordination environments: Cd1, Cd4 coordinate with six carboxyl oxygen atoms from four $tcbpe^{4-}$ ligands, forming a twisted octahedral configuration; And Cd2 and Cd3 compose another octahedral configuration with four carboxyl oxygen atoms from four ligands, one coordinated H_2O molecule, and a coordinated DMF molecule, respectively (Figure S2a). Moreover, H_4tcbpe ligand is completely deprotonation in coordination process, and form two different connection modes: μ_8-$\eta^1\eta^1\eta^1\eta^1\eta^1\eta^1\eta^1\eta^1$ and μ_8-$\eta^1\eta^2\eta^1\eta^2\eta^1\eta^2\eta^1\eta^2$ (Figure S2b). These [CdO6] metal polyhedrons are linked to form an infinitely extending spiral chain structure along the b-axis direction by the carboxyl groups in H_4tcbpe ligand, as shown in Figure S2d. Each of spiral chain structure is connected by ligands to form a three-dimensional network structure with large pore structure (Figure S2c). A 54.1 % solvent accessible volume calculated by OLEX 2. And simplify the $tcbpe^{4-}$ ligand as an 8-c node, metal Cd^{2+} as a 4-c node, resulting in a 4-node (4^2, 8^2-c net), the point symbol for net is $\{4^{12}.6^{14}.8^2\}2\{4^4.6^2\}6\{4^8.6^{12}.8^8\}$ (Figure S2e).

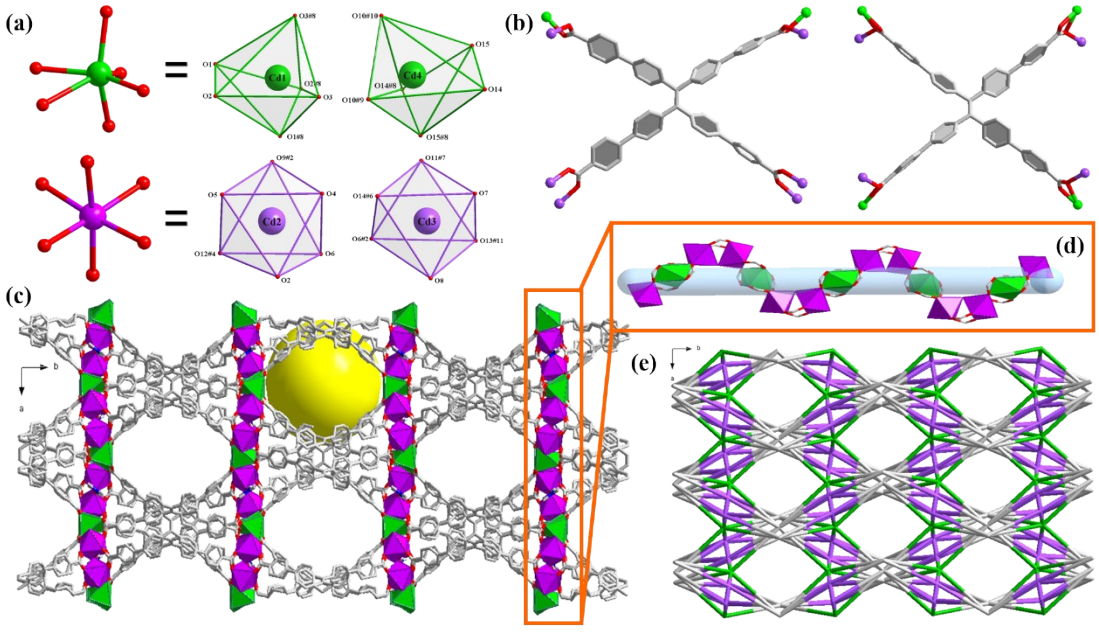


Figure S2 (a) Coordination environment of four Cd^{2+} ions; (b) Two different connected mode of H_4tcbpe ligand; (c) Three-dimensional network of **Cd-tcbpe**; (d) 1D spiral chain structure; (e) Simplified topological structure of **Cd-tcbpe**

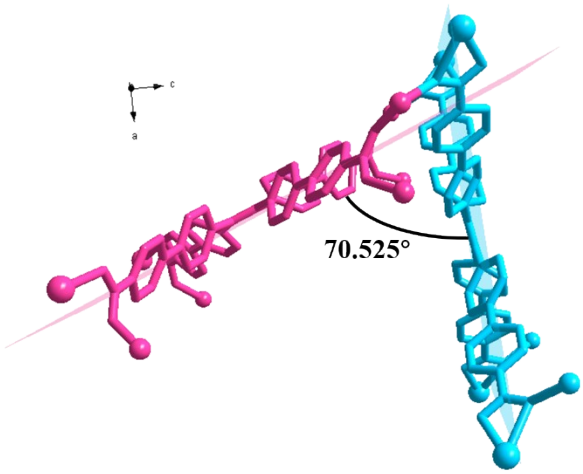


Figure S3 Formation of spatial expression of ligand with two different coordination modes

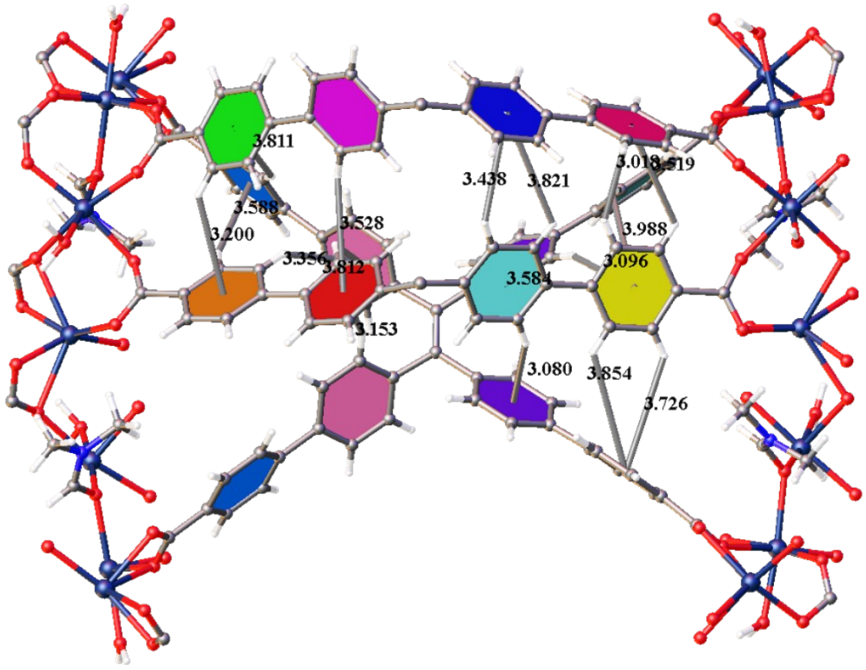


Figure S4 C-H···π intermolecular interaction in **Cd-tcbpe** structure

Table S3 C-H···π interaction in the structure of **Cd-tcbpe**

X-H···Cg (Å)	H···Cg (Å)	X···Cg (Å)	X-H···Cg (°)
C20-H20···Cg1$^{\#6}$	3.439	3.717	142.60(3)
C19-H19···Cg1$^{\#6}$	3.821	4.346	143.69 (4)
C26-H26···Cg2$^{\#6}$	3.018	3.785	138.82(10)

C25-H25···Cg2$^{\#6}$	3.519	4.036	150.24(12)
C31-H31···Cg3$^{\#6}$	3.528	4.324	146.52(4)
C37-H37···Cg4$^{\#6}$	3.200	3.925	124.56(6)
C77-H77···Cg3$^{\#4}$	3.153	3.868	35.31(4)
C61-H61···Cg5$^{\#2}$	3.988	4.633	37.37(3)
C66-H66···Cg5$^{\#2}$	3.096	3.967	28.25(13)
C67-H67···Cg6$^{\#2}$	3.584	4.383	152.12(5)
C79-H79···Cg7$^{\#1}$	3.811	4.586	123.20(3)
C76-H76···Cg4$^{\#4}$	3.401	4.161	4.16(5)
C17-H17···Cg8$^{\#a}$	3.080	3.916	35.87(3)
C22-H22···Cg9$^{\#a}$	3.854	4.500	5.5(2)
C23-H23···Cg9$^{\#a}$	3.726	4.435	59.89(8)
C6-H6···Cg10$^{\#b}$	3.356	4.087	152.70(4)
C13-H13···Cg10$^{\#b}$	3.812	4.478	139.19(4)
C7-H7···Cg11$^{\#b}$	3.588	4.469	123.49(4)

Symmetry codes: #1: x-1/2, -y+3/2, -z+1; #2: -x+1/2, y+1/2, z; #4: x-1/2, y+1/2, -z+3/2; #6: -x+1, -y+1, -z+1; #a: x+1/2, -1/2+y, 3/2-Z; #b: 1/2-x, y-1/2, z; Cg1 is the centroid of C46, C45, C44, C43, C43, and C47; Cg2 is the centroid of C52, C51, C50, C49, C48, and C53; Cg3 is the centroid of C12, C11, C10, C9, C8, and C13; Cg4 is the centroid of C6, C5, C4, C3, C2, and C7; Cg5 is the centroid of C21, C22, C23, C24, C25, and C26; Cg6 is the centroid of C15, C16, C17, C18, C19, and C20; Cg7 is the centroid of C35, C36, C37, C38, C39, and C40; Cg8 is the centroid of C70, C69, C68, C67, C66, and C65; Cg9 is the centroid of C63, C62, C37, C61, C60, and C64; Cg10 is the centroid of C72, C73, C74, C75, C76, and C77; Cg11 is the centroid of C78, C79, C80, C81, C82, and C83.

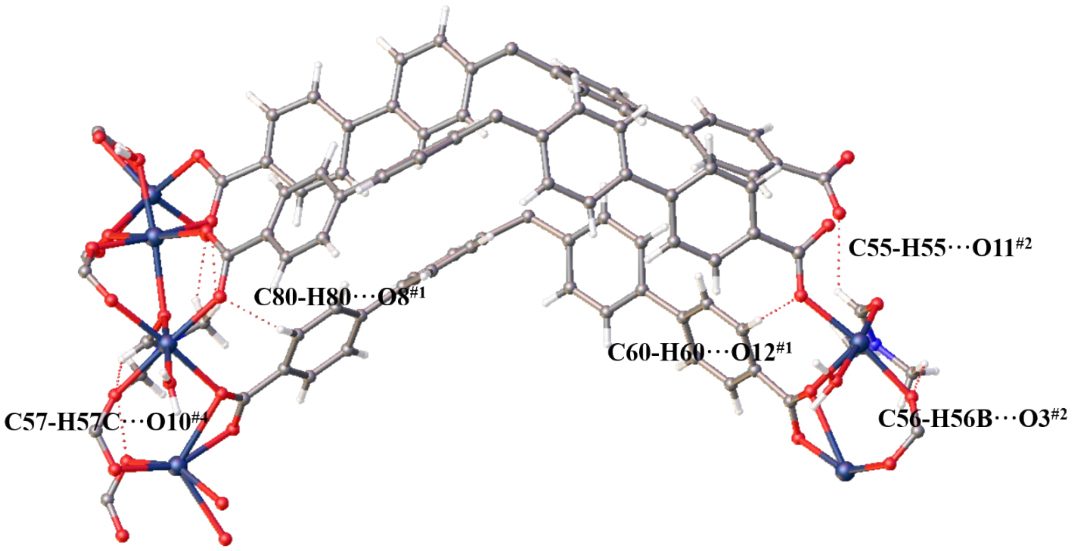


Figure S5 C-H···O hydrogen bond interactions in **Cd-tcbpe** structure

Table S4 Hydrogen bonding interaction in the structure of **Cd-tcbpe**

	D-H	H···A	D···A	<(DHA)
C80-H80···O8#1	0.93	2.42	3.283(4)	154.7
C60-H60···O12#1	0.93	2.36	3.291(4)	177.5
C55-H55···O11#2	0.93	2.35	2.950(6)	122.2
C56-H56B···O3#2	0.96	2.33	3.227(7)	154.5
C57-H57C···O10#4	0.96	2.55	3.251(7)	130.3

#1: x-1/2, -y+3/2, -z+1; #2: -x+1/2, y+1/2, z; #4: x-1/2, y+1/2, -z+3/2

DFT calculation

In DFT calculation of **Cd-tcbpe**, the calculated model was constructed from the corresponding crystallographic structure, where the metals were deleted and hydrogen atoms were added to make it neutral. Then the added H atoms were optimized using DFT for Gaussian 09[5] at the level of B3LYP/6-31G* with the other parts fixed at their reported crystallographic positions.

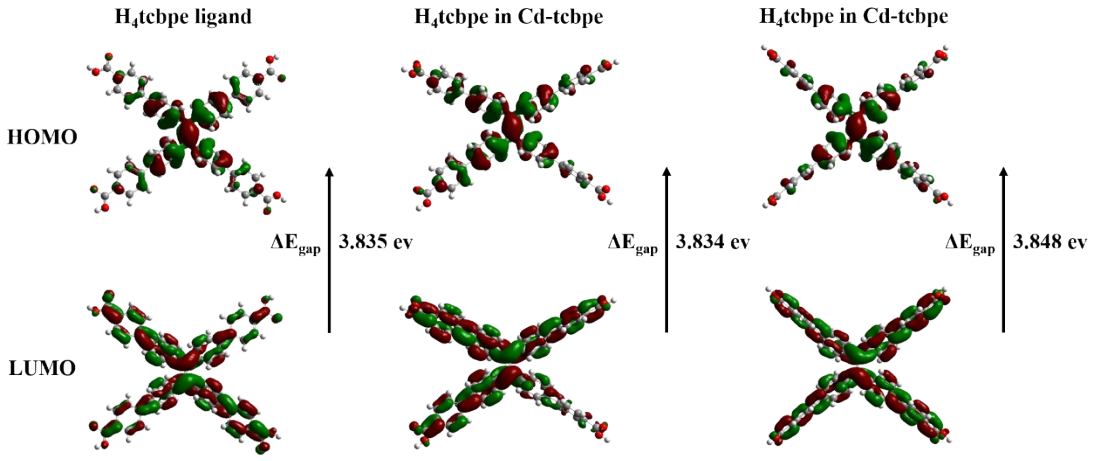


Figure S6 HOMO and LUMO energy level[5] of H_4tcbpe in free conformation[1] and **Cd-tcbpe** conformation

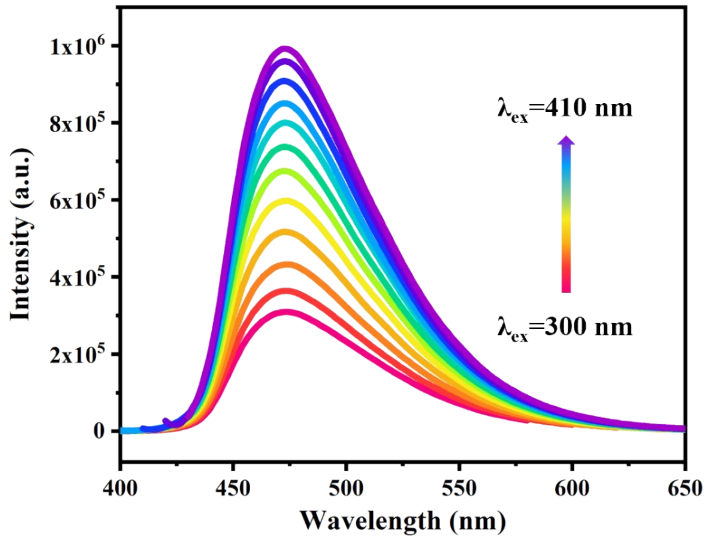


Figure S7 Fluorescence emission spectra of **Cd-tcbpe** at different excitation wavelength from 300 nm to 410 nm (1 nm: 1 nm)

Mechanochromic luminescence behavior of Cd-tcbpe

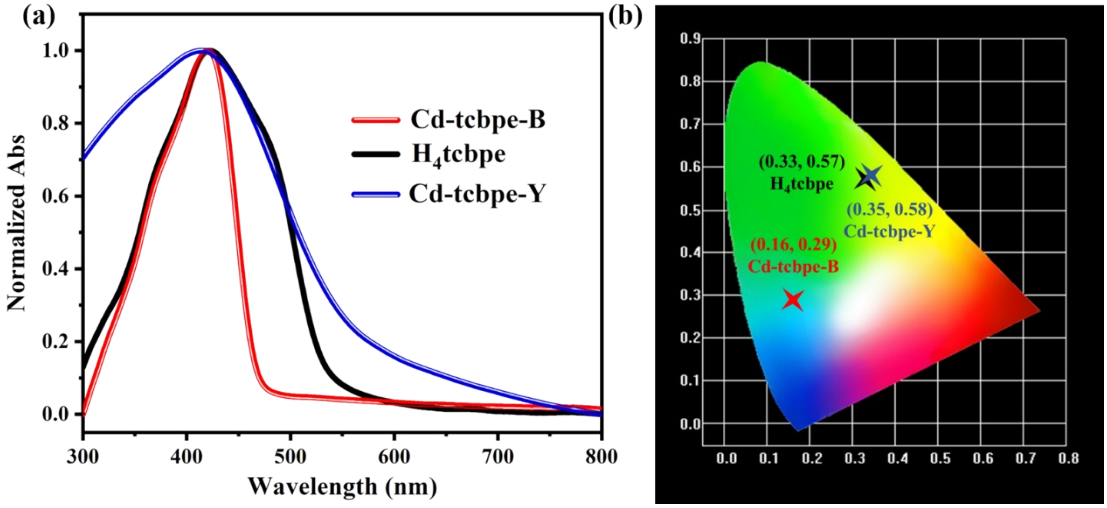


Figure S8 (a) UV-vis spectra of **Cd-tcbpe-B**, **Cd-tcbpe-Y** and H_4tcbpe; (b) CIE coordinates of **Cd-tcbpe-B**, **Cd-tcbpe-Y** and H_4tcbpe

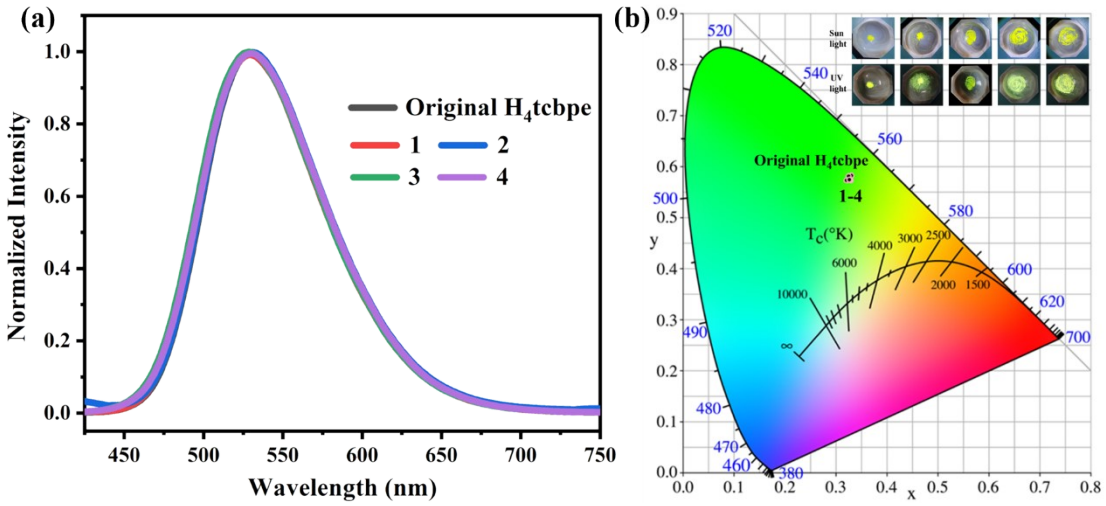


Figure S9 (a) Fluorescence emission spectra of H_4tcbpe with the process of grinding; (b) Changes of CIE coordinates with the process of grinding

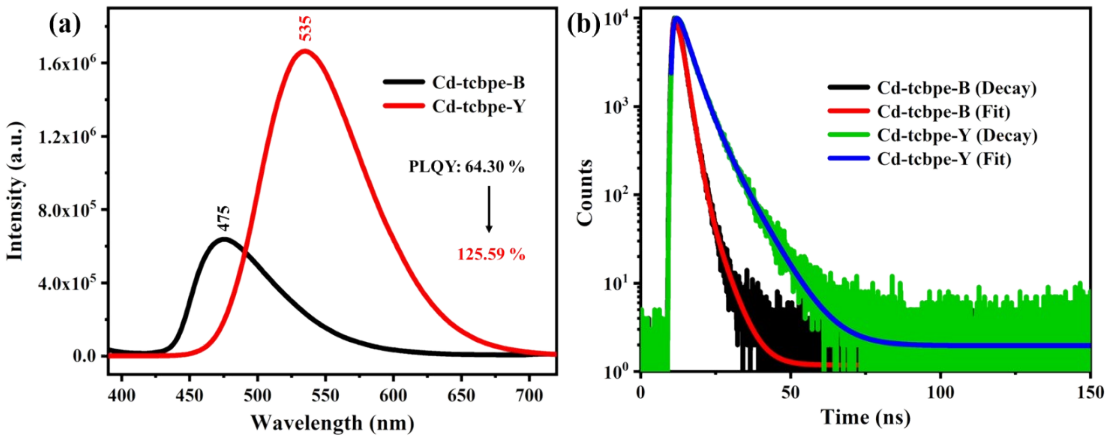


Figure S10 (a) Change of fluorescence emission spectra of **Cd-tcbpe-B** and **Cd-tcbpe-Y**; (b) Fluorescence lifetimes of **Cd-tcbpe-B** and **Cd-tcbpe-Y**

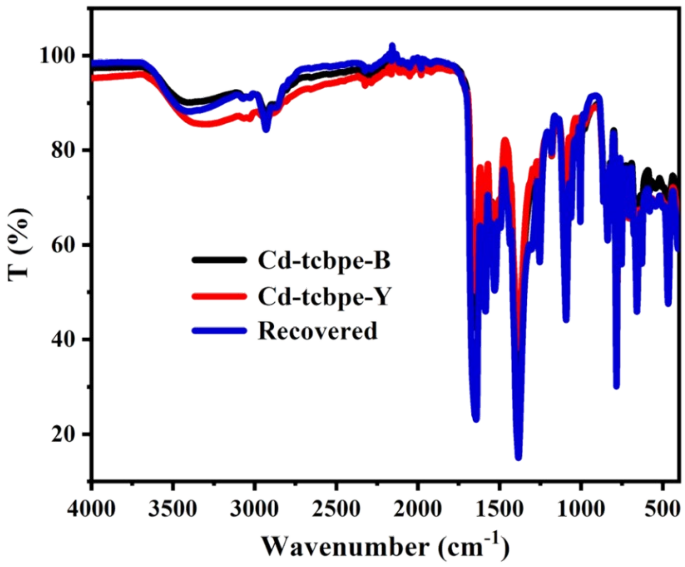


Figure S11 FT-IR spectra of **Cd-tcbpe-B**, **Cd-tcbpe-Y** and the recovered sample

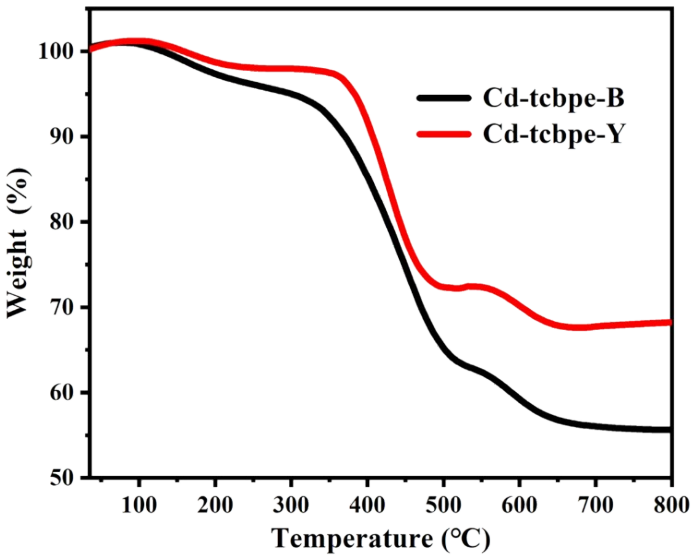


Figure S12 TGA curves of **Cd-tcbpe-B** and **Cd-tcbpe-Y**

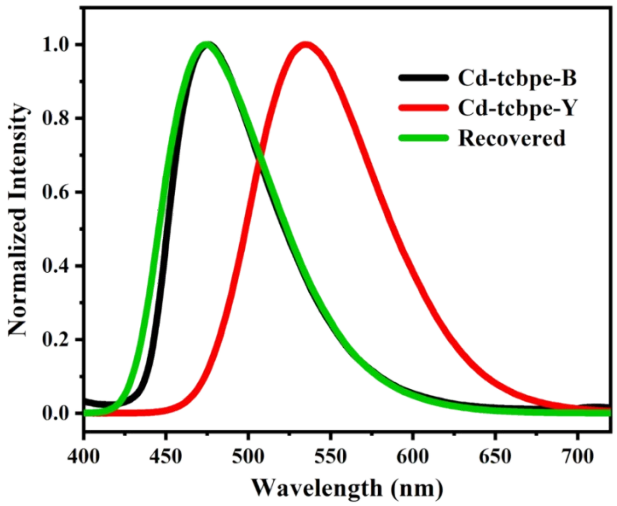


Figure S13 Changes of normalized fluorescence spectra of **Cd-tcbpe-B**, **Cd-tcbpe-Y** and the recovered sample

Preparation of paper-based material of Cd-tcbpe-B

The 40 mg **Cd-tcbpe-B** complex was spread evenly on the filter paper with adhesive, and it is important to ensure that there are excess complex residues on the surface of the filter paper.

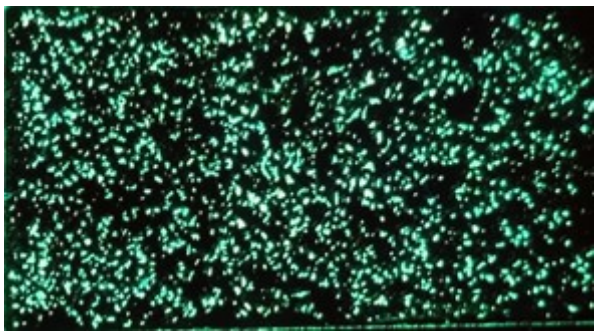


Figure S14 Image of **Cd-tcbpe-B** which was dispersed in PDMS

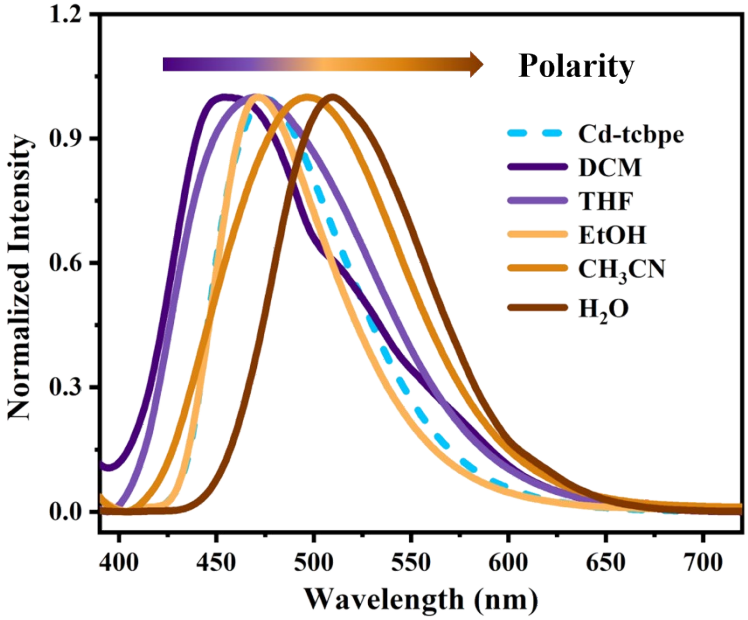


Figure S15 Fluorescence emission spectra of **Cd-tcbpe-B** with the increase of the polarity of the solvents

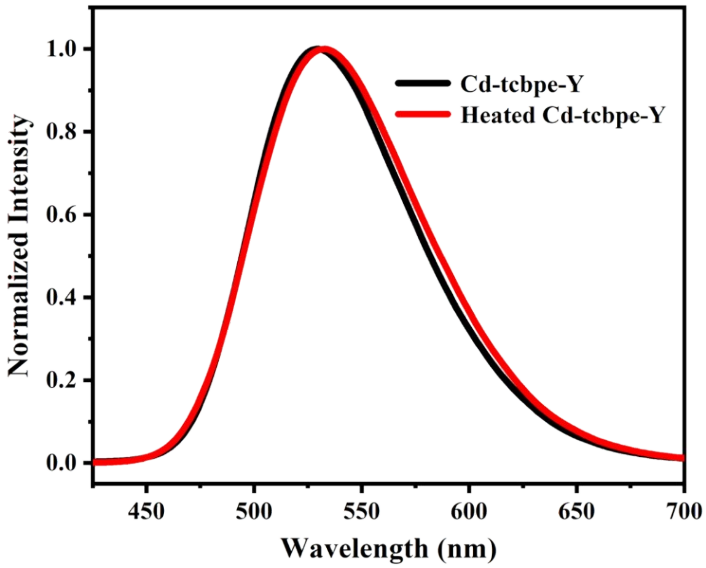


Figure S16 Fluorescence emission spectra of **Cd-tcbpe-Y** after being heated at 100 ℃

Hydrochromic luminescence behavior of Cd-tcbpe

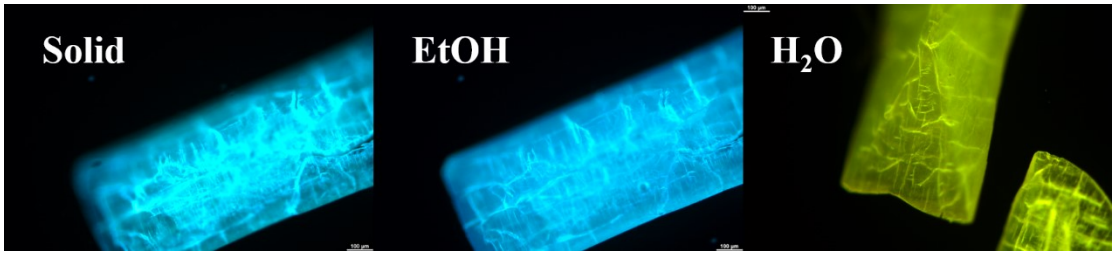


Figure S17 Fluorescence photographs of **Cd-tcbpe-B** under different stimulating conditions

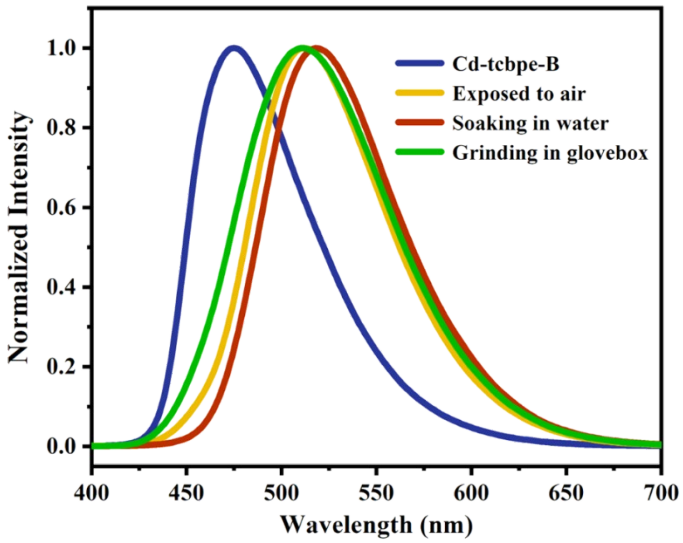


Figure S18 Fluorescence emission spectra of **Cd-tcbpe-B** under different stimulating conditions

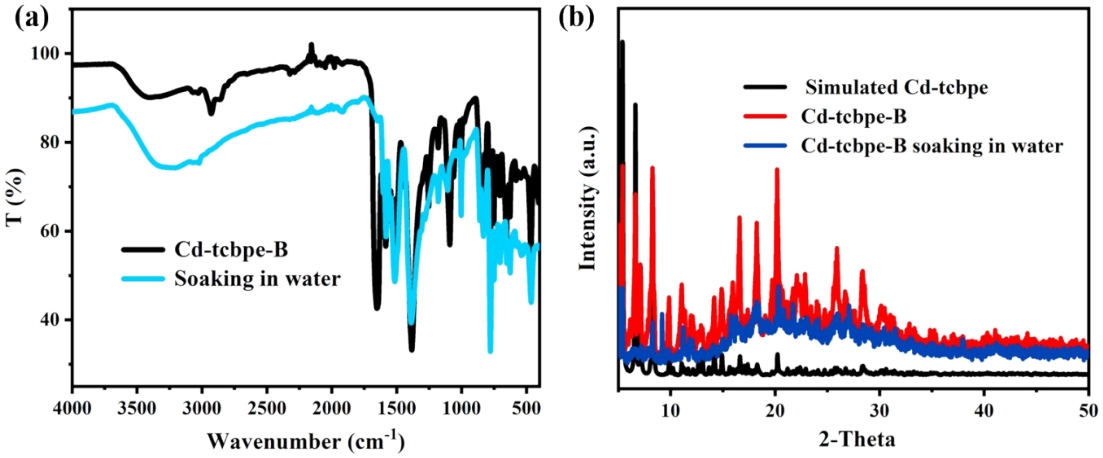


Figure S19 FT-IR spectra and PXRD pattern of **Cd-tcbpe-B** soaking in water

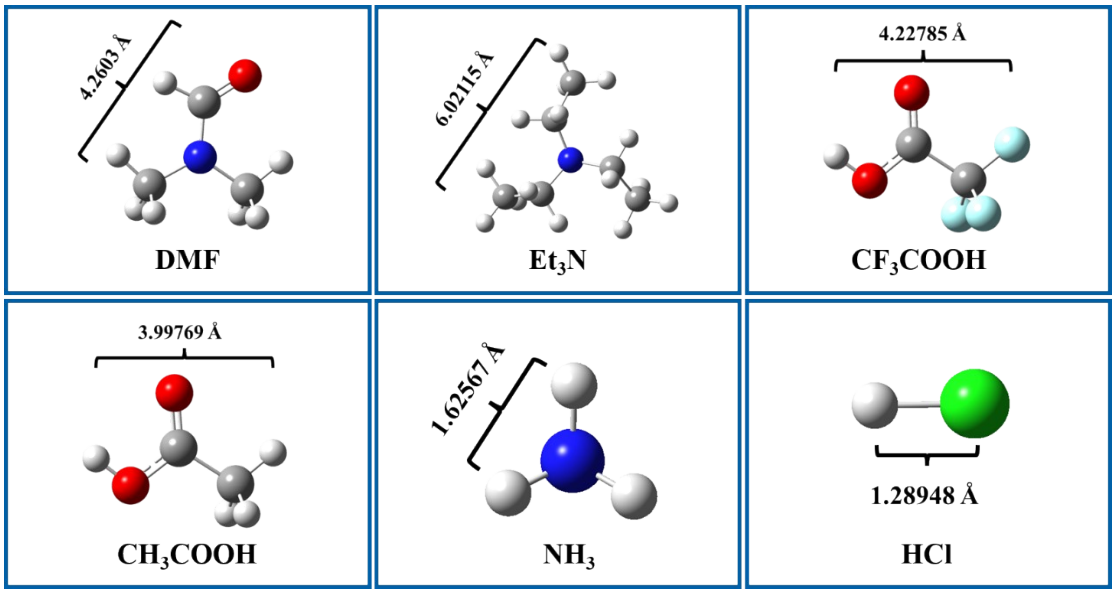


Figure S20 Sizes of six organic small molecules[5]

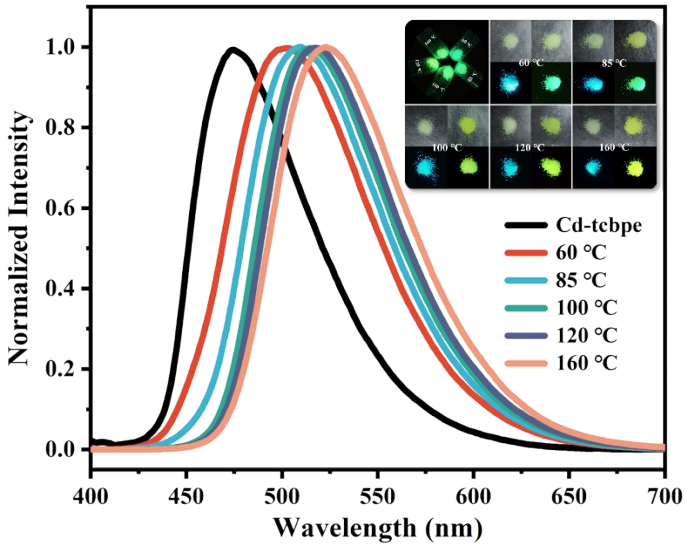


Figure S21 Fluorescence emission of **Cd-tcbpe** after heating at different temperatures for 1 hour

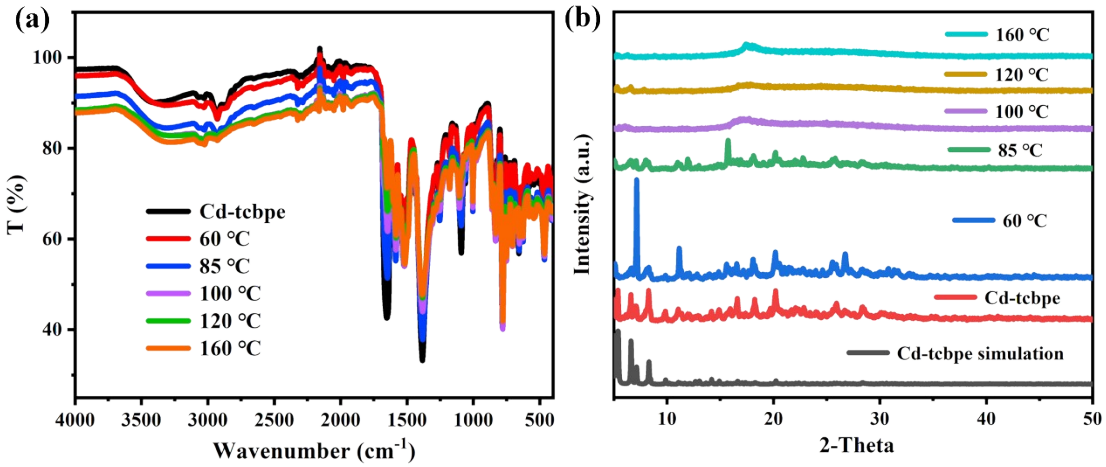


Figure S22 IR spectra (a) and PXRD patterns (b) of **Cd-tcbpe** after heating at different temperatures for 1 hour

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