

Multiple Stimulus Responsive Co-AIE framework Materials with Reversible Solvatochromic and Thermochromic Behaviors: Molecular design, synthesis and characterization

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Supporting Information

Materials and Methods

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) and Lambda 35 UV/VIS Spectrometer (200-800 nm, in form of liquid sample). X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu $K\alpha$ radiation, in the range $5^\circ < 2\theta < 50^\circ$, 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 $^\circ\text{C}$. The photoluminescent spectra 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). The $^1\text{H-NMR}$ spectra were measured on Nuclear Magnetic Resonance Spectrometer (Bruker Avance II 400).

Synthesis of 4',4''',4''''',4''''''''-(ethene-1,1,2,2-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylic acid) (H_4tcbpe)¹

Weigh 4,4'-dibromobenzophenone (6.8 g, 20 mmol) and zinc powder (5.6 g, 86 mmol) into a 250 mL two-necked flask, add 100 mL of tetrahydrofuran (THF) to obtain a gray cloudy solution. The flask was then placed in an ice-water bath atmosphere, fully cooled, and N_2 was continuously purged for 30 min. Drop 9-10 mL of titanium tetrachloride (TiCl_4) with a rubber tip dropper. During the addition process, it can be found that white mist emerges from the flask and a yellow solid is produced. During this period, nitrogen gas is continuously introduced, and then the device is transferred to the oil. The mixture was refluxed at 85 $^\circ\text{C}$ for 24 h in a bath, and cooled to obtain a black solution after the reaction. The solution was fully cooled to room temperature,

the tetrahydrofuran solvent was evaporated with a rotary evaporator, and the solid after rotary evaporation was dissolved with chloroform (CHCl_3) to obtain a black solution, which was extracted with saturated brine and concentrated hydrochloric acid, and the lower layer was separated and combined. The yellow organic phase was dried with anhydrous sodium sulfate for 12 h. Suction filtration to separate the desiccant to obtain a light-yellow transparent solution. Rotary evaporated and concentrated to the remaining 5-8 mL of solution. Column chromatography was performed with n-hexane, concentrated under reduced pressure, and dried to obtain 1,1,2,2-tetrakis(4-bromophenyl)ethylene as a white solid (M1).

Weigh the above-obtained M1 sample (1.5 g, 2.3 mmol), 4-methoxycarbonyl phenylboronic acid (2.5 g, 14 mmol), cesium fluoride (4.2 g, 28 mmol) in a 250 mL two-necked flask and place it in oil Stir in the bath, remove excess air, and protect with nitrogen for about 10 minutes; measure and add 150 mL of dry ethylene glycol dimethyl ether (DME) to the two-necked bottle, continue to protect with nitrogen for 10 minutes, and obtain a colorless transparent. Then, tetrakis(triphenylphosphine)palladium (0.2 g, 0.2 mmol) was added to the system as the catalyst for the reaction, and the whole process was heated to reflux at 65 °C for 48 h under nitrogen protection. The dark brown reaction solution was fully cooled to room temperature, and the ethylene glycol dimethyl ether solvent was evaporated under reduced pressure. The obtained solid was dissolved in dichloromethane to obtain a brownish-yellow solution, which was extracted with water. Dry over sodium sulfate for 12 h. The above solution was suction filtered to obtain a brown-yellow transparent solution, and the dichloromethane solvent was evaporated under reduced pressure to obtain a brown solid. The brown solid was then recrystallized from acetone to give M2 as a dark green solid.

Weigh M2 (1.0 g), 1 g of solid sodium hydroxide, and 105 mL of mixed solution ($\text{THF} : \text{CH}_3\text{OH} : \text{H}_2\text{O} = 1:1:1(\text{v}:\text{v}:\text{v})$) in a 250 mL two-necked flask, and heat at 90 °C for 12 h, a pale yellow clear solution was obtained. Then the reaction solution was fully cooled to room temperature, and the insoluble was filtered off, acidified with 6 mol/L hydrochloric acid to pH=1, filtered, washed and dried to obtain 4', 4''', 4''''', 4''''''-(ethylene-1,1,2,2-tetrayl)tetrakis[1,1'-biphenyl]-4-carboxylic acid (H_4tcbpe) yellow

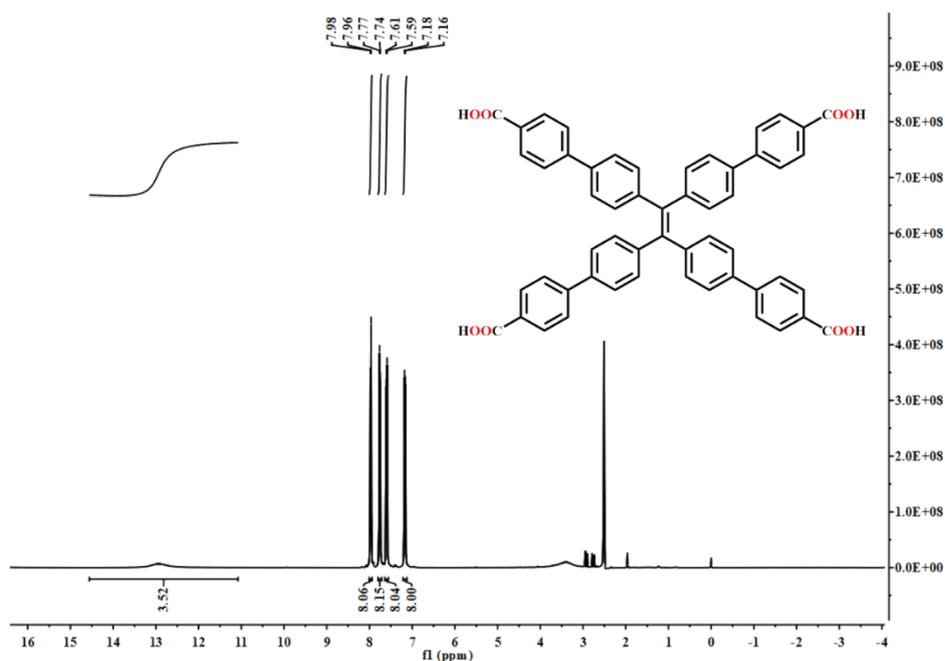


Figure S2 The ^1H -NMR spectrum of H_4tcbpe

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 $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. A semiempirical absorption correction was applied by the program SADABS. The program suite SHELXL-2018^{2, 3} and OLEX 2 platform⁴ 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. PART commands were employed on lattice ligand tcbpe^{4-} (C9, C10, C12), where ISOR commands were also applied to C9B and C12B atom. Besides, the ‘OMIT 0 52’ 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 DMA and H_2O molecules in **Co-tcbpe**. For **Co-tcbpe**, we found two alert level B “D-H Bond Without Acceptor O3-H3, O4-H4B” by checkcif in the structures. It can be attributed that O3-H3, O4-H4B, are part of water molecules or from water molecules that is likely disordered/on a partially occupied site and for the last one. The details of the crystal parameters, data collection, and refinement for **Co-tcbpe** are summarized in Table S1, and selected bond

lengths and angles with their estimated standard deviations are listed in Table S2. CCDC 2193387 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 for the **Co-tcbpe***

Complex	Co-tcbpe (SQUEEZE)
Formula	C ₅₄ H ₄₂ Co ₃ O ₁₄
Molecular weight	1091.66
Crystal system	Orthorhombic
Space group	<i>Imma</i>
<i>a</i> /Å	43.283(3)
<i>b</i> /Å	28.3063(18)
<i>c</i> /Å	6.3675(4)
α /(°)	90
β /(°)	90
γ (°)	90
V (Å ³)	7801.3(9)
Z	4
D _{calc} /(g·cm ⁻³)	0.929
F(000)	2236.0
μ / mm ⁻¹	0.673
2 θ range/(°)	4.738-51.996
Reflections collected	42401
Independent reflections [$I > 2\sigma(I)$]	3954
Parameters	203
Goodness of fit	1.117
R ₁ ^a	0.0832 (0.1242) ^b
wR ₂ ^a	0.1883 (0.1990) ^b
$\Delta(\rho)$ (e Å ⁻³)	0.44 and -0.60

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

Table S2 The selected bonds (Å) and angle (°) of **Co-tcbpe**

Co-tcbpe
Selected bonds (Å)

Co1-O3 ^{#3}	2.0459(4)	Co1-O3	2.0458(4)
Co1-O2 ^{#2}	2.1208(3)	Co1-O2 ^{#4}	2.1208(3)
Co1-O2 ^{#6}	2.1208(3)	Co1-O2 ^{#5}	2.1208(3)
Co2-O3	2.0578(3)	Co2-O3 ^{#2}	2.0579(3)
Co2-O1	2.0888(3)	Co2-O1 ^{#5}	2.0889(4)
Co2-O4 ^{#5}	2.1364(4)	Co2-O4	2.1364(4)
C14-C14 ^{#8}	1.3056(17)	C14-C11 ^{#7}	1.5120(7)
C3-C4	1.3881(8)	C1-O1	1.2498(6)
Selected angle (°)			
O3-Co1-O3 ^{#3}	180.0	O3-Co1-O2 ^{#2}	85.31(12)
O3 ^{#3} -Co1-O2 ^{#2}	94.69(12)	O3-Co1-O2 ^{#4}	94.69(12)
O3 ^{#3} -Co1-O2 ^{#5}	85.31(12)	O2 ^{#4} -Co1-O2 ^{#6}	89.0(2)
O3-Co2-O4 ^{#5}	94.31(15)	O3 ^{#2} -Co2-O1	96.78(16)
O3 ^{#2} -Co2-O4 ^{#5}	177.20(16)	C1-O2-Co1 ^{#1}	134.7(3)
O3 ^{#4} -Co1-O3	180.0	C26 ^{#5} -C26-C12 ^{#6}	122.4(6)
O1-C1-O2	125.5(4)	C14 ^{#8} -C14-C11 ^{#7}	122.7(4)
C11 ^{#7} -C14-C11	114.6(7)	C4-C3-C2	119.6(5)

***Co-tcbpe**: #1 x, y, z+1; #2 -x+1/2, -y-1/2, -z+1/2; #3 -x+1/2, -y-1/2, -z-1/2; #4 x, y, z-1; #5 -x+1/2, y, -z+1/2; #6 x, -y-1/2, z-1; #7 -x, y, z; #8 -x, -y-1, -z+2.

Structural Characterization

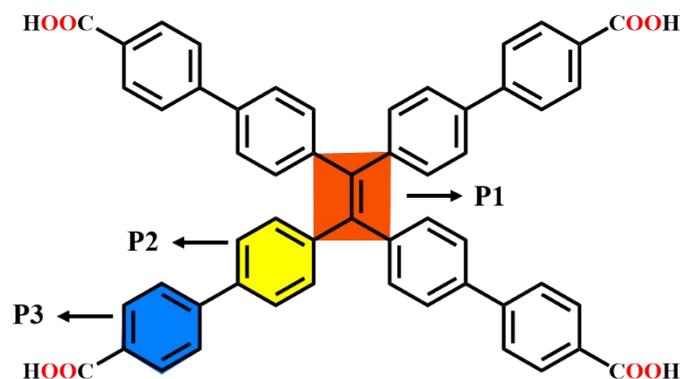


Figure S3 Plane definitions within the structure of H₄tcbpe: Orange plane P1 is defined by the two C atoms forming the central C=C double bond and four C atoms surround them; The yellow and blue phenyl rings define the P2 and P3 plane crossing them, respectively

Table S3 Gradual decrease of mass of a sample of Co-tcbpe recorded in the TGA experiment

Segment	Upper limit	Loss of mass from TGA	Description
A	194 °C	26.16%	DMA and H ₂ O in the hydrophobic pores
B	524 °C	23.33%	Coordinated H ₂ O, bridging OH ⁻ anion and partly framework
C	560 °C	9.4%	Framework decomposition
D	-	-	Mineralized sample

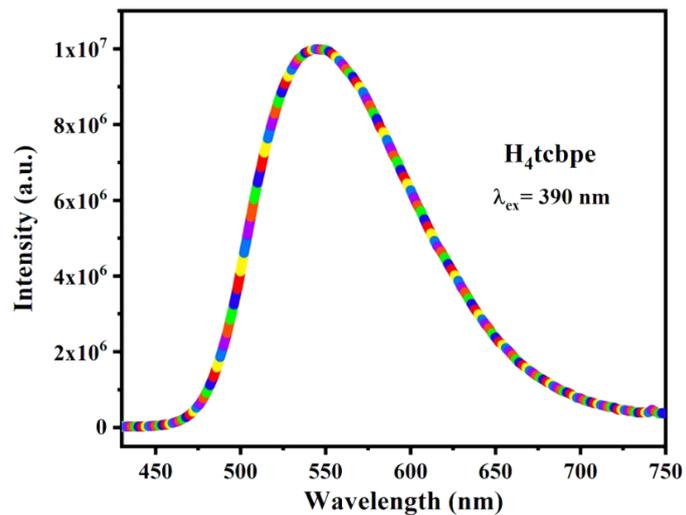


Figure S4 The solid fluorescence emission spectrum of H₄tcbpe ligand ($\lambda_{\text{ex}}=390$ nm)

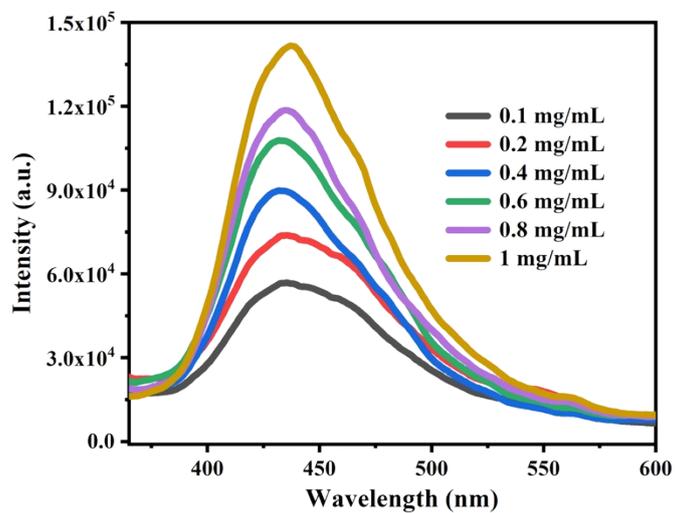


Figure S5 The AIE effect of Co-tcbpe in EtOH solvent ($\lambda_{\text{ex}}=320$ nm)

Solvatochromic Behavior

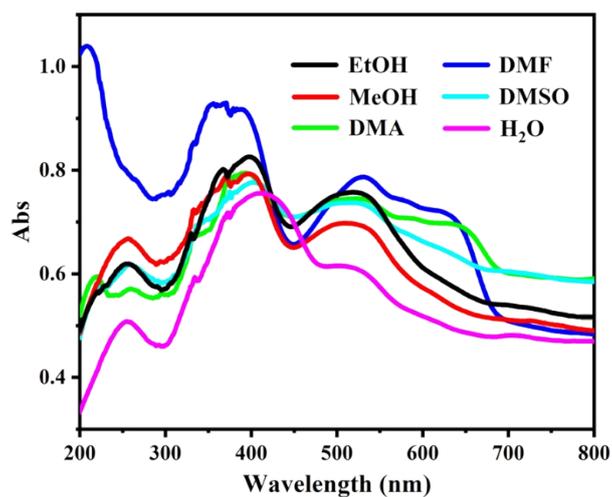


Figure S6 The UV-vis spectra of **Co-tcbpe** detailed with different solvents

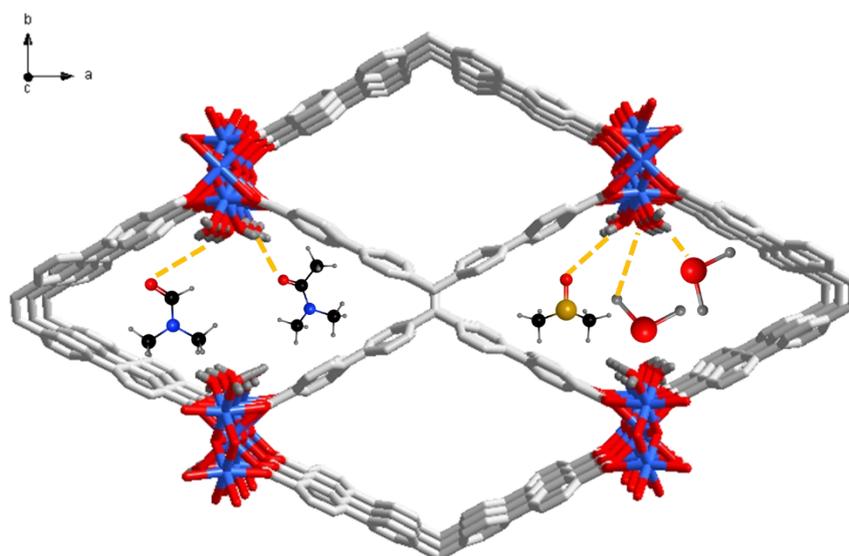


Figure S7 Schematic diagram of hydrogen bonding interaction between different solvent molecules and coordinated water molecules in the **Co-tcbpe** structure.

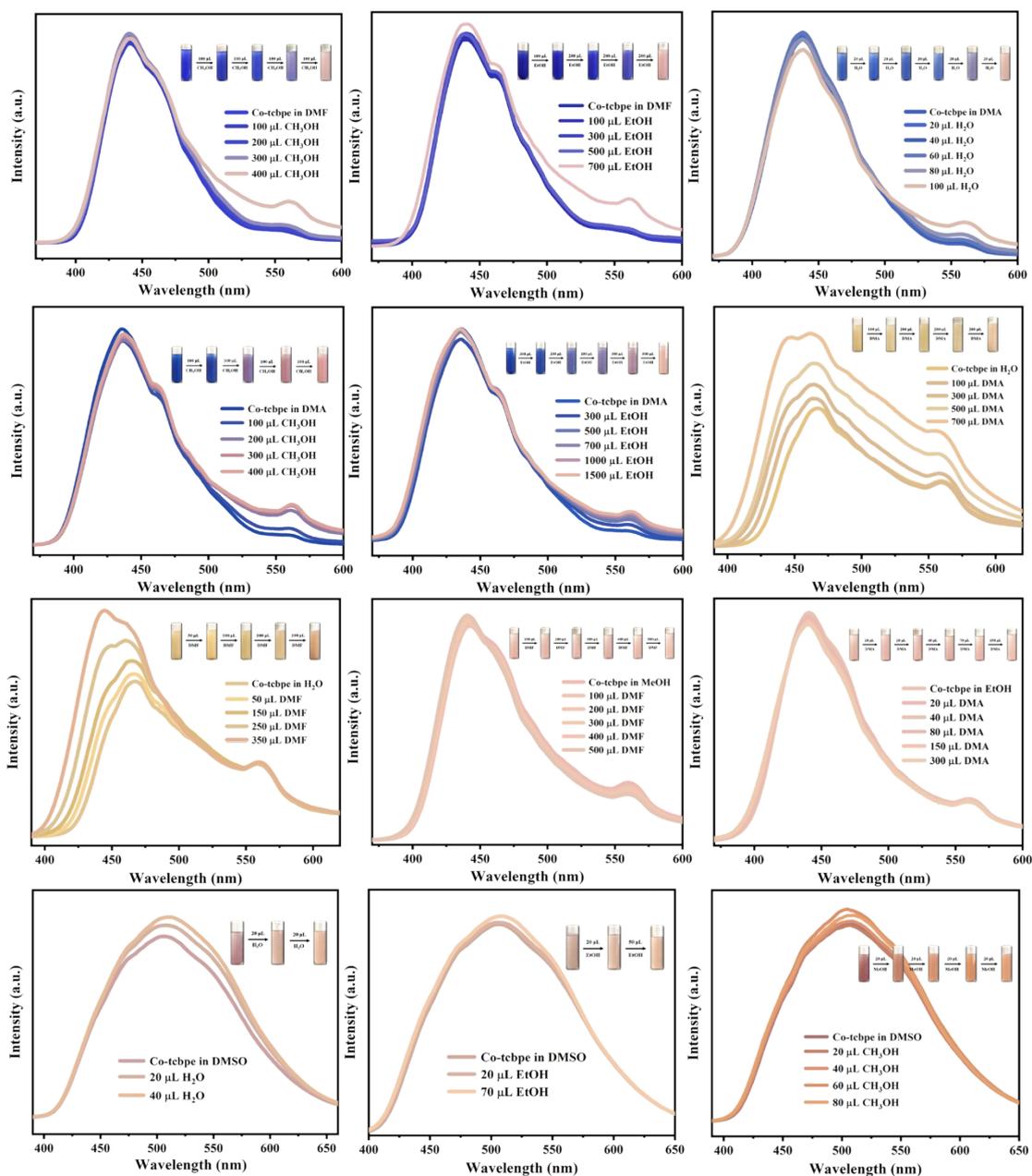


Figure S8 Change of the fluorescence spectra of the Co-tcbpe in six different solutions before and after adding different volumes of other solvents

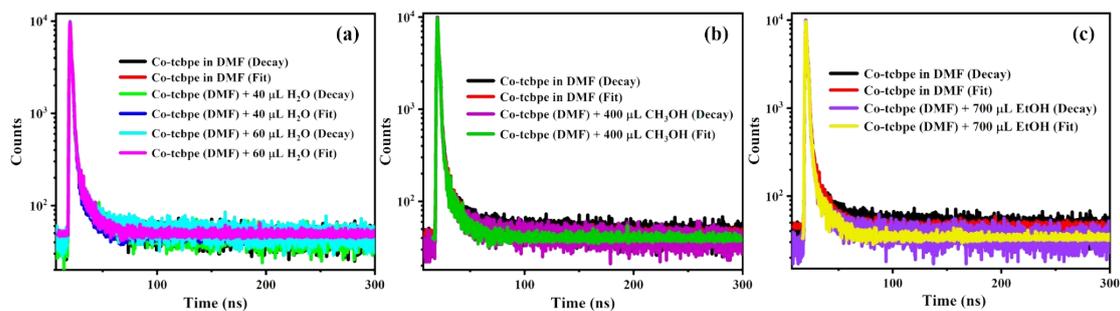


Figure S9 The fluorescence lifetime of Co-tcbpe in DMF before and after adding H_2O (a),

CH₃OH (b) and EtOH (c)

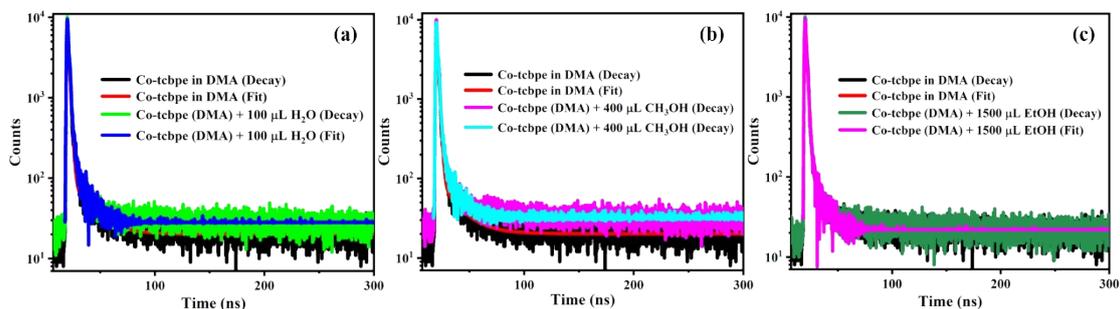


Figure S10 The fluorescence lifetime of Co-tcbpe in DMA before and after adding H₂O (a), CH₃OH (b) and EtOH (c)

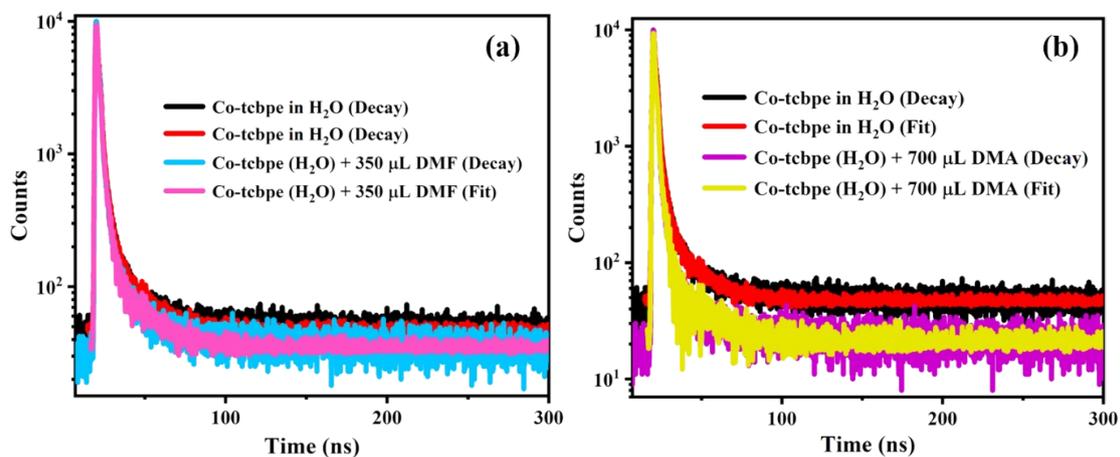


Figure S11 The fluorescence lifetime of Co-tcbpe in H₂O before and after adding DMF (a) and DMA (b)

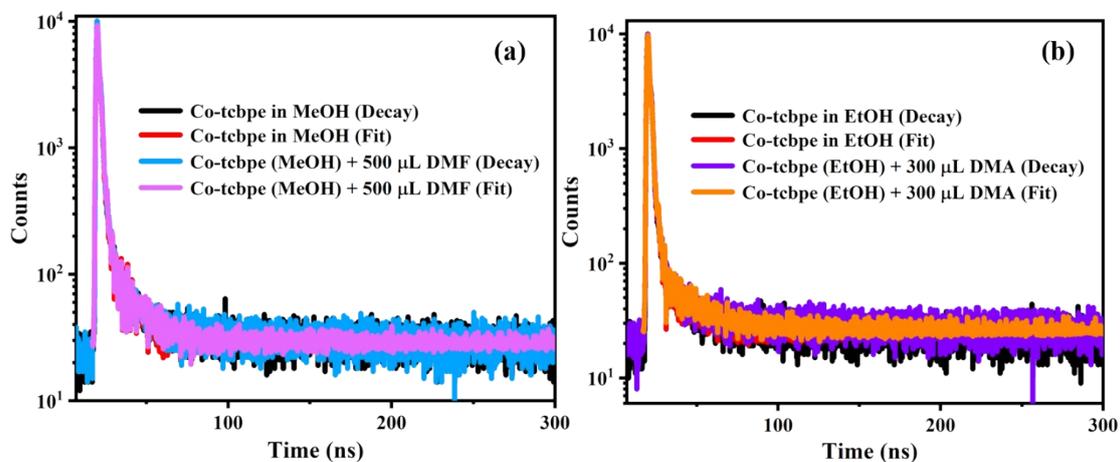


Figure S12 The fluorescence lifetime of Co-tcbpe in MeOH and EtOH before and after adding

DMF (a) DMA (b)

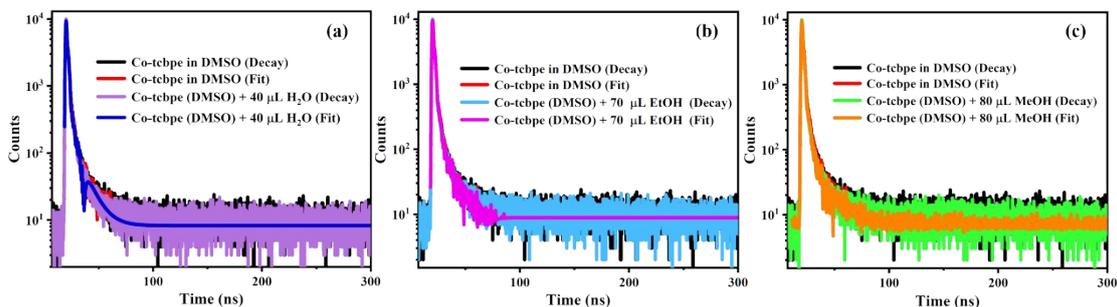


Figure S13 The fluorescence lifetime of **Co-tcbpe** in DMSO before and after adding H₂O (a), EtOH (b) and MeOH (c)

Table S4 The fluorescence lifetime of **Co-tcbpe** in six different organic solvents before and after adding other solvents

	Lifetime (ns)	Average lifetime (s)
Co-tcbpe in DMF	$\tau_1=0.2940$; $\tau_2=3.241$; $\tau_3=0.3918$	3.352×10^{-10}
Co-tcbpe in DMF + 60 μL H ₂ O	$\tau_1=2.886$; $\tau_2=0.2900$; $\tau_3=0.2874$	2.887×10^{-10}
Co-tcbpe in DMF + 400 μL MeOH	$\tau_1=3.100$; $\tau_2=0.3081$; $\tau_3=0.2774$	2.922×10^{-10}
Co-tcbpe in DMF + 700 μL EtOH	$\tau_1=0.3426$; $\tau_2=3.019$; $\tau_3=0.3197$	3.3166×10^{-10}
Co-tcbpe in DMA	$\tau_1=1.559$; $\tau_2=1.505$; $\tau_3=17.06$	1.550×10^{-9}
Co-tcbpe in DMA + 100 μL H ₂ O	$\tau_1=3.018$; $\tau_2=0.3130$; $\tau_3=0.3122$	3.126×10^{-10}
Co-tcbpe in DMA + 400 μL MeOH	$\tau_1=0.3823$; $\tau_2=3.127$; $\tau_3=0.3748$	3.788×10^{-10}
Co-tcbpe in DMA + 1500 μL EtOH	$\tau_1=0.3051$; $\tau_2=3.053$; $\tau_3=0.4523$	3.646×10^{-10}
Co-tcbpe in H ₂ O	$\tau_1=0.3531$; $\tau_2=4.760$; $\tau_3=0.3377$	3.454×10^{-10}
Co-tcbpe in H ₂ O + 350 μL DMF	$\tau_1=5.105$; $\tau_2=0.3497$;	3.506×10^{-10}

	$\tau_3=0.3514$	
Co-tcbpe in H ₂ O + 700 μ L DMA	$\tau_1=0.3118; \tau_2=0.3101;$ $\tau_3=5.784$	3.109×10^{-10}
Co-tcbpe in EtOH	$\tau_1=0.4107; \tau_2=0.3762;$ $\tau_3=4.483$	3.938×10^{-10}
Co-tcbpe in EtOH + 300 μ L DMA	$\tau_1=0.2547; \tau_2=0.4692;$ $\tau_3=4.432$	3.235×10^{-10}
Co-tcbpe in MeOH	$\tau_1=0.3449; \tau_2=3.470;$ $\tau_3=0.3350$	3.401×10^{-10}
Co-tcbpe in MeOH + 500 μ L DMF	$\tau_1=0.3753; \tau_2=3.815;$ $\tau_3=0.3521$	3.638×10^{-10}
Co-tcbpe in DMSO	$\tau_1=1.030; \tau_2=5.525;$ $\tau_3=0.2074$	2.830×10^{-10}
Co-tcbpe in DMSO + 40 μ L H ₂ O	$\tau_1=1.883; \tau_2=9.608;$ $\tau_3=0.1153$	1.508×10^{-10}
Co-tcbpe in DMSO + 70 μ L EtOH	$\tau_1=0.9860; \tau_2=4.926;$ $\tau_3=0.1898$	2.593×10^{-10}
Co-tcbpe in DMSO + 80 μ L MeOH	$\tau_1=1.088; \tau_2=0.2013;$ $\tau_3=5.760$	2.770×10^{-10}

Thermochromic Behavior

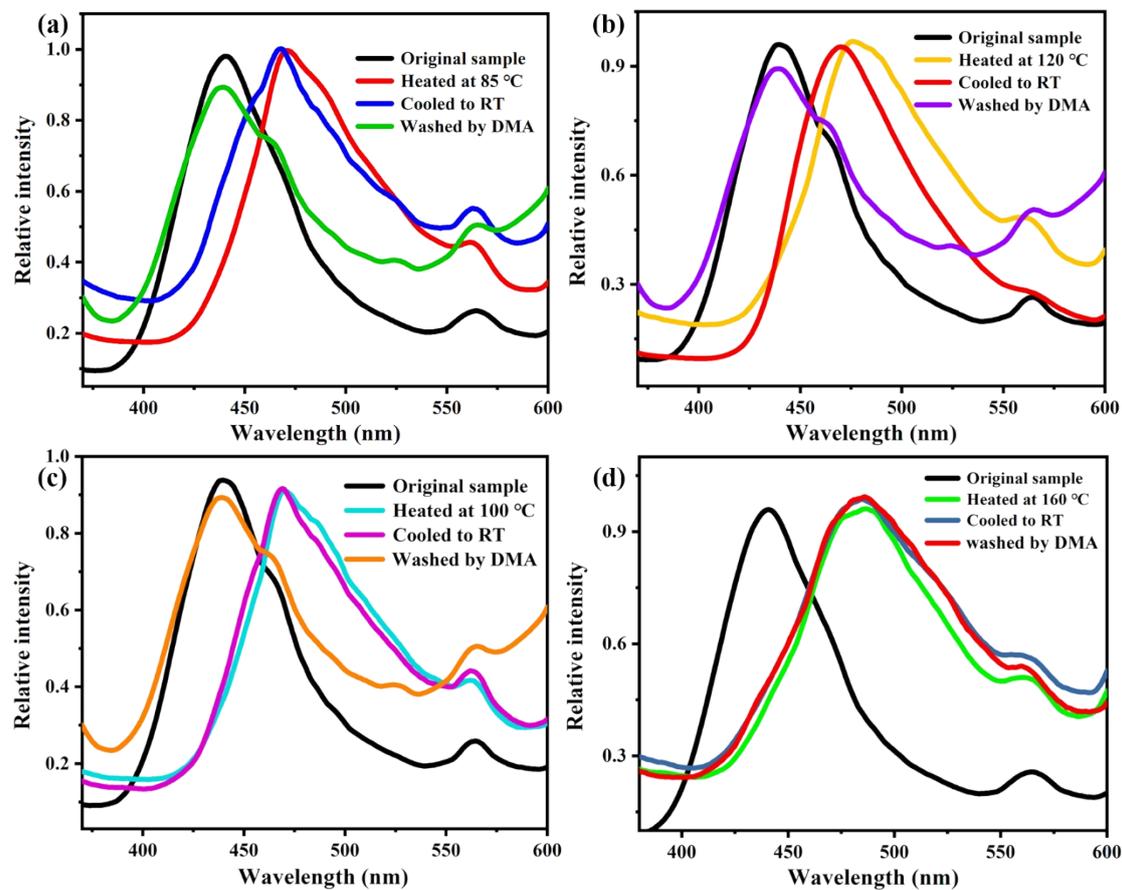


Figure S14 The fluorescence spectra of the original and treated under different conditions of **Co-tcbpe**

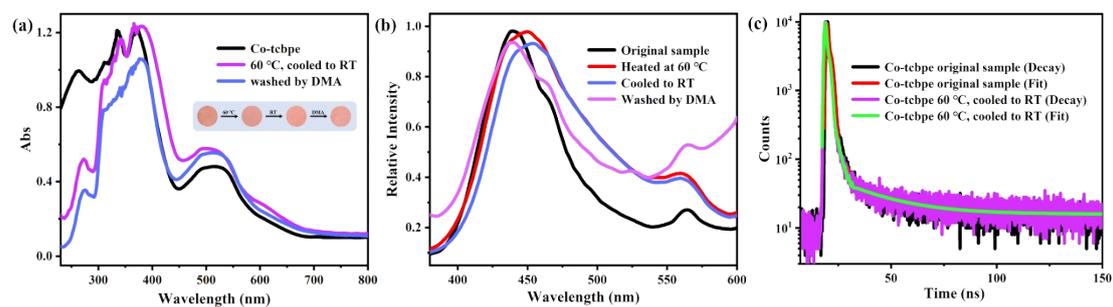


Figure S15 The UV-Vis spectra (a), fluorescence emission spectrum (b) and fluorescence lifetime (c) of **Co-tcbpe** before and after being heated at 60 °C

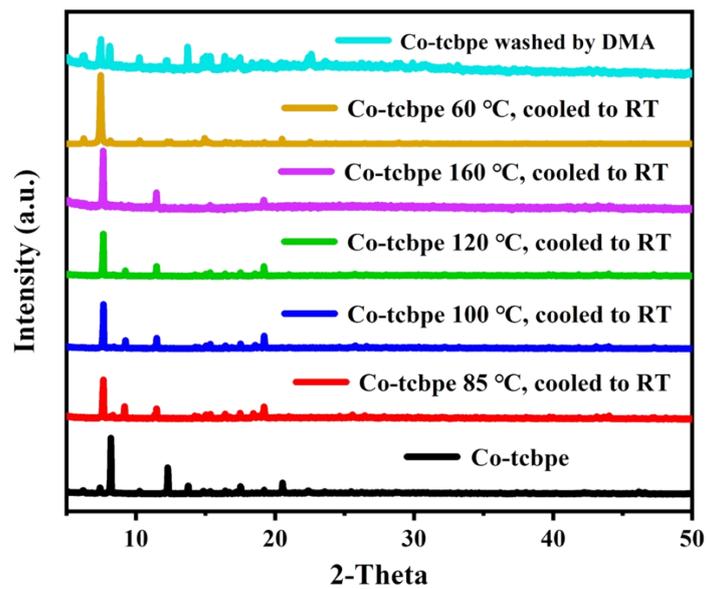


Figure S16 The PXR D spectra of **Co-tcbpe** after being heated and cooled to RT

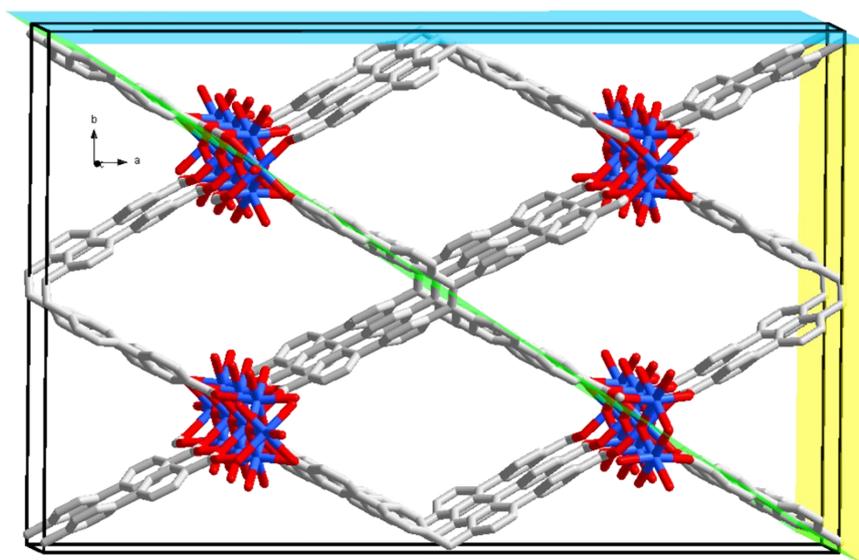


Figure S17 Perspective view of lattice planes (010) (in blue), (100) (in yellow) and (110) (in green) for **Co-tcbpe** along the [001] axis (hydrogen atoms are omitted for clarity)

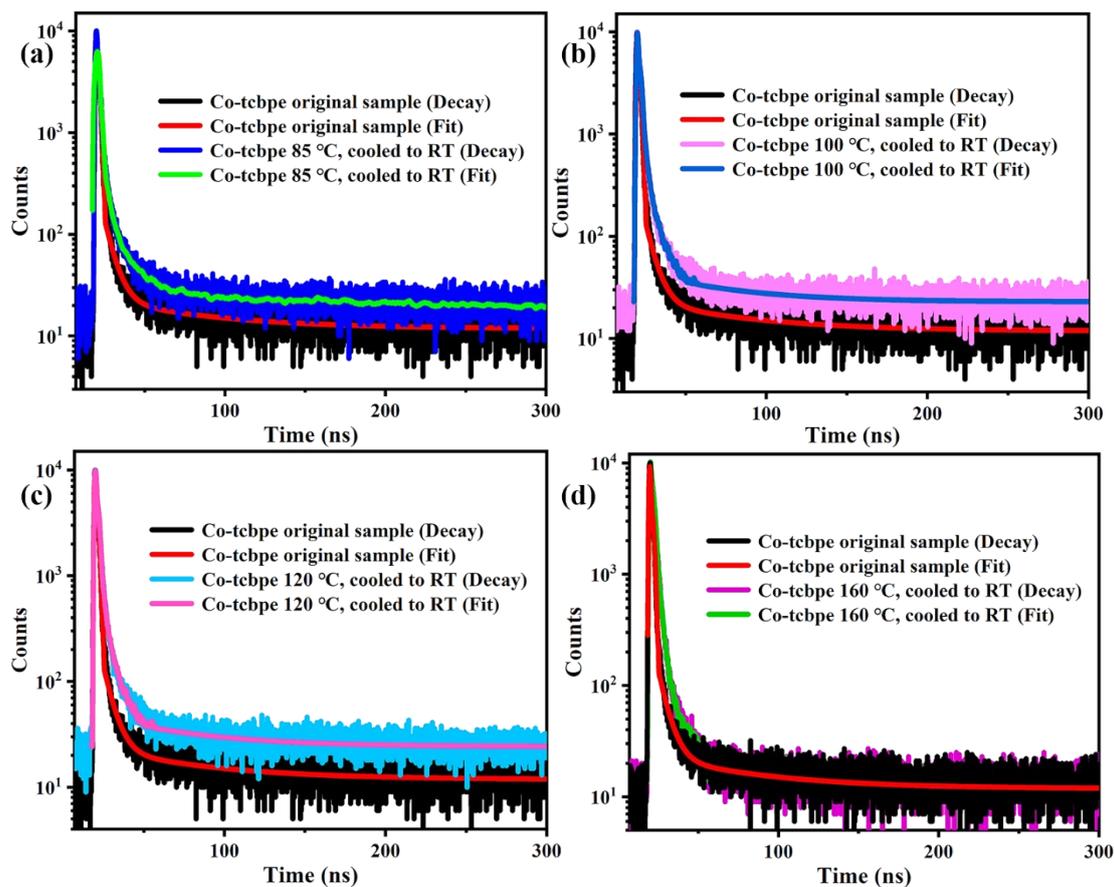


Figure S18 The fluorescence lifetime of **Co-tcbpe** before and after being heated by different temperature

Table S5 The fluorescence lifetime under different conditions samples of **Co-tcbpe**

Sample	Lifetime (ns)	Average lifetime (s)
Co-tcbpe	$\tau_1=5.714; \tau_2= 62.00, \tau_3= 0.4534$	4.660×10^{-11}
Co-tcbpe 60 °C, cooled to RT	$\tau_1= 0.1340; \tau_2= 1.039; \tau_3= 22.36$	1.549×10^{-10}
Co-tcbpe 85 °C, cooled to RT	$\tau_1= 5.388, \tau_2= 722.4; \tau_3= 0.1557$	1.991×10^{-10}
Co-tcbpe 100 °C, cooled to RT	$\tau_1= 1.079; \tau_2= 51.50; \tau_3= 0.1303$	1.530×10^{-10}
Co-tcbpe 120 °C, cooled to RT	$\tau_1= 1.049; \tau_2= 54.26; \tau_3= 0.1240$	1.408×10^{-10}
Co-tcbpe 160 °C, cooled	$\tau_1= 0.04437; \tau_2= 1.131; \tau_3= 8.627$	5.422×10^{-11}

References

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