Supplementary Information (SI) for Green Chemistry.
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Supporting Information for:

Multicolor-Tunable Ultralong Room Temperature Phosphorescence Based on Cyclodextrin Metal-Organic Frameworks

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Author Contributions:

Y.C. and J.G. conceptualized the project. J.Z. prepared the samples, performed the experiments and characterization, wrote the manuscript, drew the figure and organized the supporting information. J.T. and Y.Z. analyzed and discussed the results together. Y.C. and J.G. revised the manuscript. J.G. acquired funding for the whole study. All authors commented on the manuscript.

Supplement Files Involve:

- **A PDF File** (Supplementary text with experimental information, figure and tables)
- **Movies, MP4 File**

- Movies about afterglow of CD-MOF⊃BTP single crystal (Movie_S1.mp4)
- Movies about afterglow of CD-MOF⊃BTP (Movie_S2.mp4)
- Movies about afterglow of *γ*-CD⊃BTP (Movie_S3.mp4)
- Movies about afterglow of CD-MOF⊃BMTP (Movie_S4.mp4)
- Movies about afterglow of CD-MOF⊃BTP&Flu, [TP]:[Flu] is 10:1 (Movie_S5.mp4)
- Movies about afterglow of CD-MOF⊃BTP&RhB, [TP]:[RhB] is 25:1 (Movie_S6.mp4)

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Chemicals and Instruments

All reagents were commercially available and used as received without further purification. Food grade *γ*-cyclodextrin (*γ*-CD, 98%), Triphenylenylboronic acid (BTP, 98%), Triphenylene (TP, 98%), 4,4,5,5-TetraMethyl-2-(3-triphenylen-2-yl-phenyl)-[1,3,2] dioxaborolane (BMTP, 98%), Rhodamine B (RhB, 95%) and fluorescein sodium (Flu, 97%) were purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd. Potassium hydroxide (KOH, 95%) was purchased from Energy Chemical. Methanol (MeOH, 99.5%) and dichloromethane (99.5%) were purchased from Jiangtian Chemical. All the experiments used distilled water.

The X-ray powder diffraction data were collected using a Rigaku D/max 2500 (Rigaku, Japan). The absorption spectra of both solid and liquid samples were measured on UV-VIS-NIR spectrophotometer (Perkin Elmer). The luminescent spectra and quantum yield of the solid samples were measured using a FLS 1000 (Edinburgh Instruments) configured with an integrated sphere. The images after microscope magnification were taken using a stereo scan microscopy (Nikon SMZ745T). Part of the samples were ground using a planetary ball mill (Chuangde CLD-QM-3SP04).

Detailed Experimental Procedures

1. **Preparation of CD-MOF⊃BTP:** *γ*-CD (280 mg, 0.216 mmol), 130 mg KOH and BTP (10 mg, 0.0367 mmol) were dissolved in 10.0 mL water and then filtered through 0.22 μm filter into glass bottle with proper size. MeOH (about 10 mL) in a bigger beaker was allowed to vaper-diffuse into this solution at room temperature during several (3-5) days. Single crystals appeared at the bottom of the bottle, washed with MeOH and allowed to dry in air.
2. **Preparation of CD-MOF⊃TP:** *γ*-CD (280 mg, 0.216 mmol), 130 mg KOH were dissolved in 10.0 mL water and then filtered through 0.22 μm filter into glass bottle with proper size. TP (8.37 mg, 0.0367 mmol) was dissolved in $CHCl_3$ (1 mL) to form a clear solution, on which was carefully put on the top of the above aqueous solution. MeOH (about 10 mL) in a bigger beaker was allowed to vaper-diffuse into this solution at room temperature during several (3-5) days. Single crystals appeared at the liquid surface junction, washed with MeOH and allowed to dry in air.
3. **Preparation of CD-MOF⊃BMTP:** *γ*-CD (280 mg, 0.216 mmol), 130 mg KOH were dissolved in 10.0 mL water and then filtered through 0.22 μm filter into glass bottle with proper size. BMTP (13 mg, 0.0367 mmol) was dissolved in $CHCl_3$ (1 mL) to form a clear solution, on which was carefully put on the top of the above aqueous solution. MeOH (about 10 mL) in a bigger beaker was allowed to vaper-diffuse into this solution at room temperature during several (3-5) days. Single crystals appeared at the liquid surface junction, washed with MeOH and allowed to dry in air.
4. **Preparation of CD-MOF⊃BTP&Flu:** *γ*-CD (280 mg, 0.216 mmol), 130 mg KOH and BTP (10 mg, 0.0367 mmol) were dissolved in 10.0 mL different molar Flu water solution ($\text{BTP}_{(0.0367\ \text{mmol})}$: Flu = 50:1, 30:1, 10:1) and then filtered through 0.22 μm filter into glass bottle with proper size. MeOH (about 10 mL) in a bigger beaker was allowed to vaper-diffuse into this solution at room temperature during several (5-7) days. Single crystals appeared at the bottom of the bottle, washed with MeOH and allowed to dry in air.
5. **Preparation of CD-MOF⊃BTP&RhB:** *γ*-CD (280 mg, 0.216 mmol), 130 mg KOH and TP (10 mg, 0.0367 mmol) were dissolved in 10.0 mL different molar RhB water solution ($\text{BTP}_{(0.0367\ \text{mmol})}$: RhB = 25:1, 15:1, 5:1) and then filtered through 0.22 μm filter into glass bottle with proper size. MeOH (about 10 mL) in a bigger beaker was allowed to vaper-diffuse into this solution at room temperature (about 25°C) during several (5-7) days. Single crystals appeared at the bottom of the bottle, washed with MeOH and allowed to dry in air.
6. **Preparation of *γ*-CD⊃BTP:** *γ*-CD (280 mg, 0.216 mmol), BTP (10 mg, 0.0367 mmol) and 100 μL water were placed in an agate jar together with agate beads and were grinded at a rate of 1200 rpm for 7h by the use of a high-speed vibration mill. The solid mixture was dissolved in 10 mL water and filtered by a membrane filter (0.2 μm) into a glass bottle with proper size. Subsequently, the filtrate is dried to obtain ***γ*-CD⊃BTP** solid powder.
7. **Preparation of ZIF-8⊃BTP:** 200 mg zinc acetate was dissolved well in 25 mL ethanol under stirring. After adding 25 mL ethanol solution of 820 mg methylimidazole and BTP solution (10 mg BTP, 2 ml ammonia solution, 8 ml ethanol), the stirring was stopped. ZIF-8⊃BTP was collected via ultracentrifugation after 20 hours.

Characterization

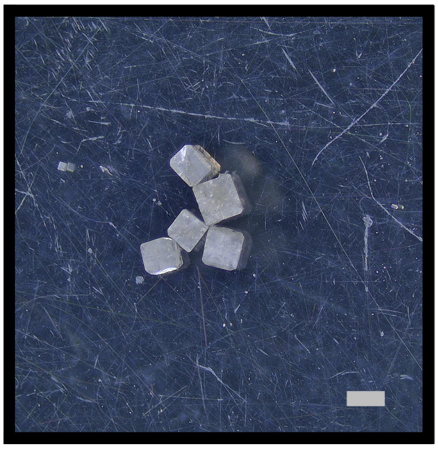

Fig. S1 Microphotographs of CD-MOF⊃BTP. Scar bar: 100 μm.

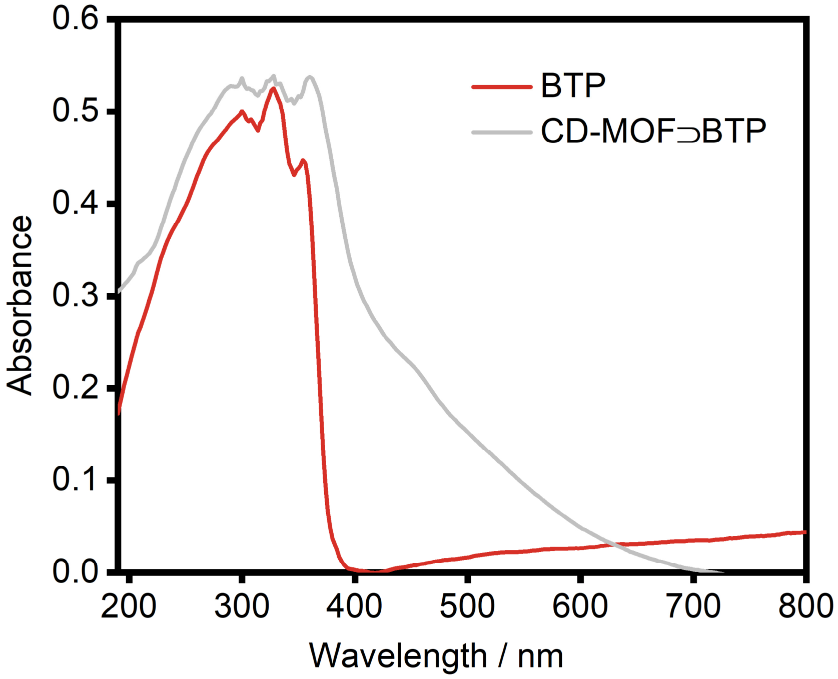

Fig. S2 UV-Vis diffuse reflectance spectroscopy of BTP and CD-MOF⊃BTP.

The absolute photoluminescence quantum yields (PLYQ) of solid-state compounds were measured using an absolute photoluminescence (PL) quantum yield spectrometer equipped with an integrating sphere under ambient conditions. The phosphorescence quantum yields of the compounds were obtained from the following equation:

$$\emptyset_{phos} = \frac{B}{A} \times \emptyset_{PL}$$

where A and B represent the integral areas of total photoluminescence and phosphorescence spectra, respectively.

For samples exhibiting clearly separated dual emission (fluorescence + phosphorescence), time-delayed detection can distinguish the components (NATURE MATERIALS | VOL 20 | NOVEMBER 2021 | 1539–1544). In our work, the photoluminescence spectrum shows a single dominant peak. Therefore, we used the Levenberg-Marquardt algorithm to separate the peaks based on the maximum emission peak positions of fluorescence (437 nm) and phosphorescence (487 nm). The phosphorescence contribution ratio was calculated from the integrated areas of the deconvoluted peaks. The total quantum yield ($\emptyset_{PL}$) was obtained through the integration program included in software Fluoracle.

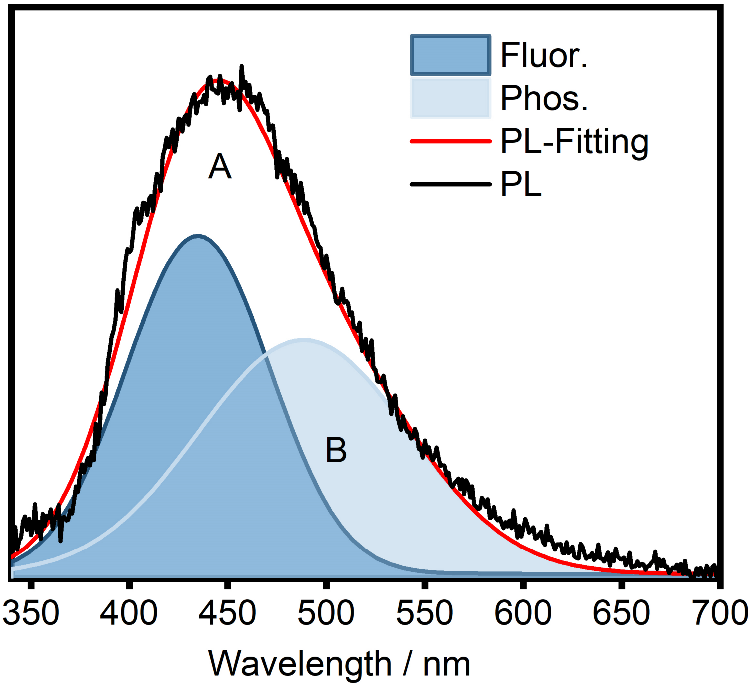

Fig. S3 Photoluminescence spectra of CD-MOF⊃BTP under ambient conditions.

Note: The total photoluminescence is 15.47%, in which the phosphorescent region accounted for 0.53.

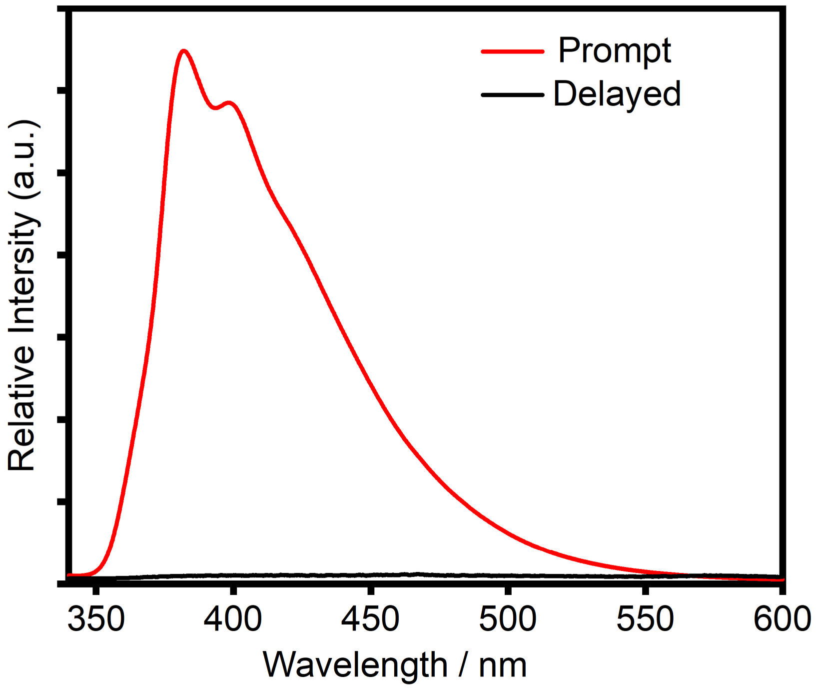

Fig. S4 Photoluminescence spectra of BTP under ambient conditions.

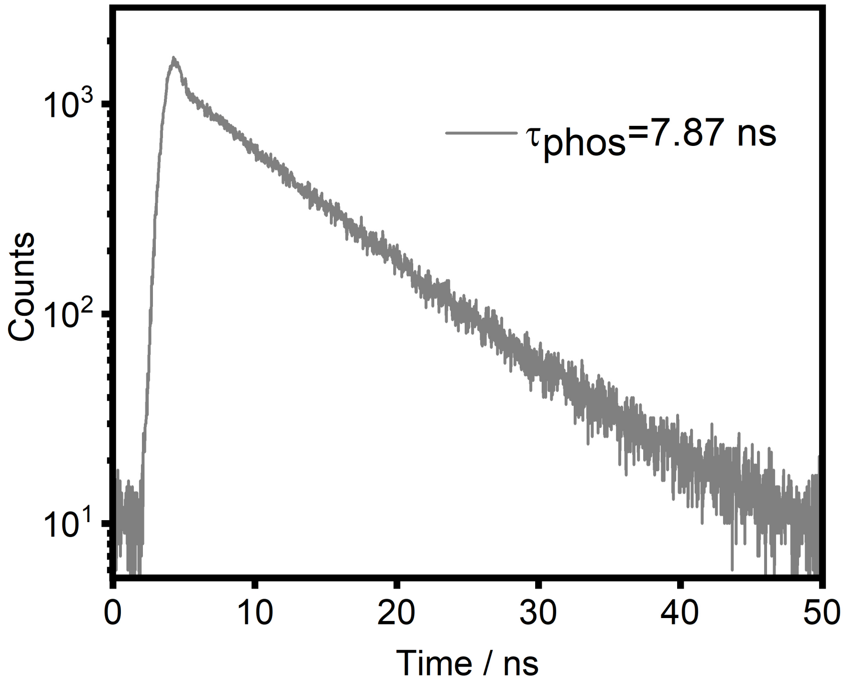

Fig. S5 Time-resolved decay spectra of BTP.

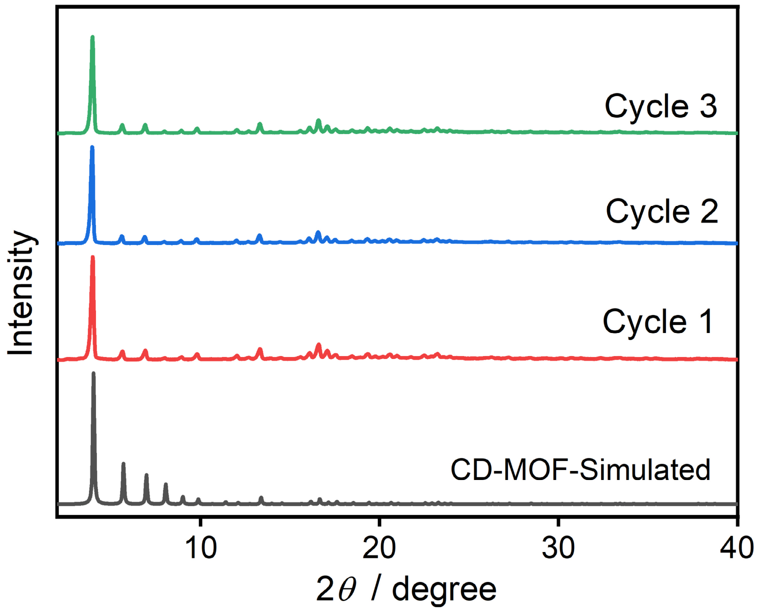

Fig. S6 X-ray powder diffraction pattern of recrystallized CD-MOF ⊃BTP. Simulated based on available single-crystal structure from the Cambridge structure database, CCDC 2209020.

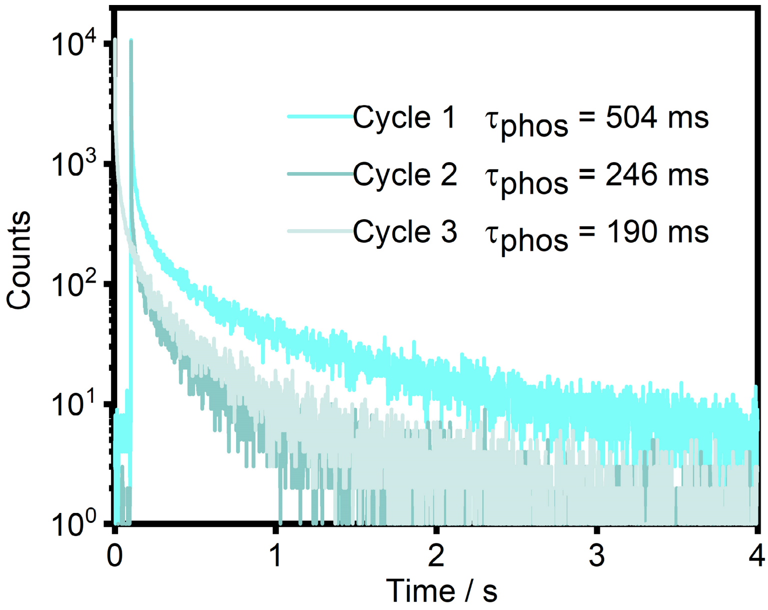

Fig. S7 Time-resolved decay spectra of different recrystallized samples.

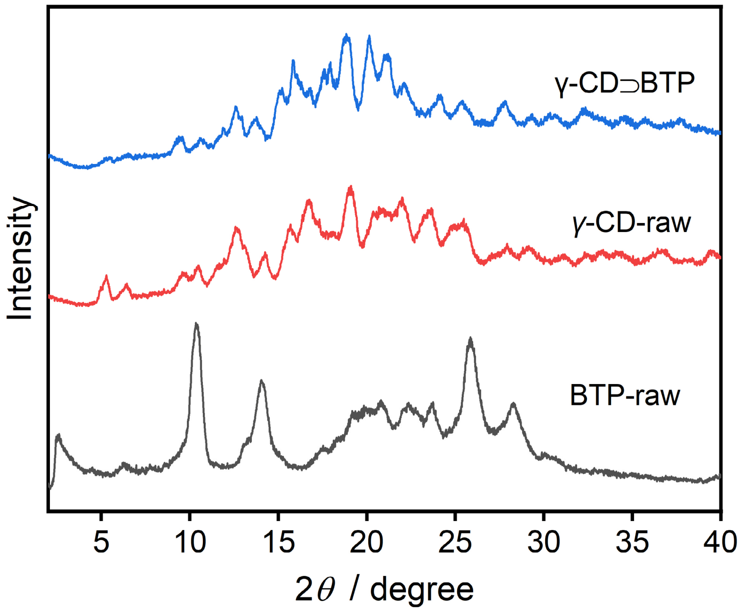

Fig. S8 X-ray powder diffraction pattern of BTP, *γ*-CD and *γ*-CD⊃BTP.

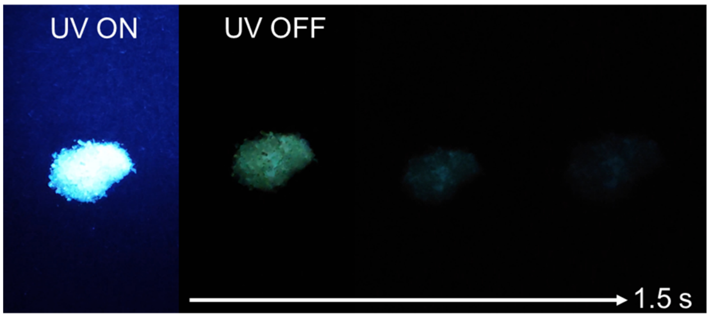

Fig. S9 The afterglow photographs of CD-MOF⊃BMTP under ambient condition.

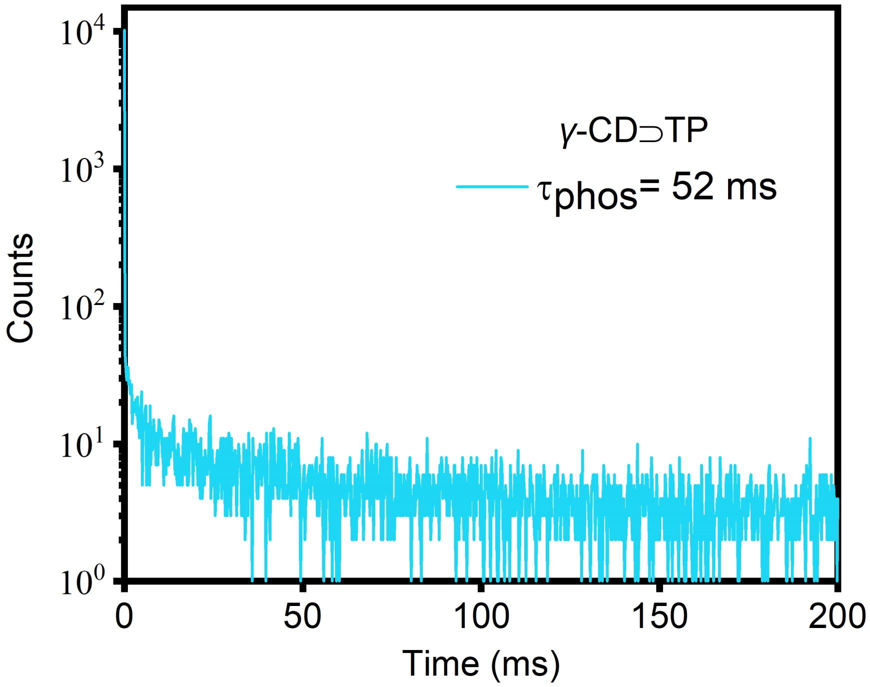

Fig. S10 Time-resolved decay spectra of γ-CD⊃BTP under ambient conditions.

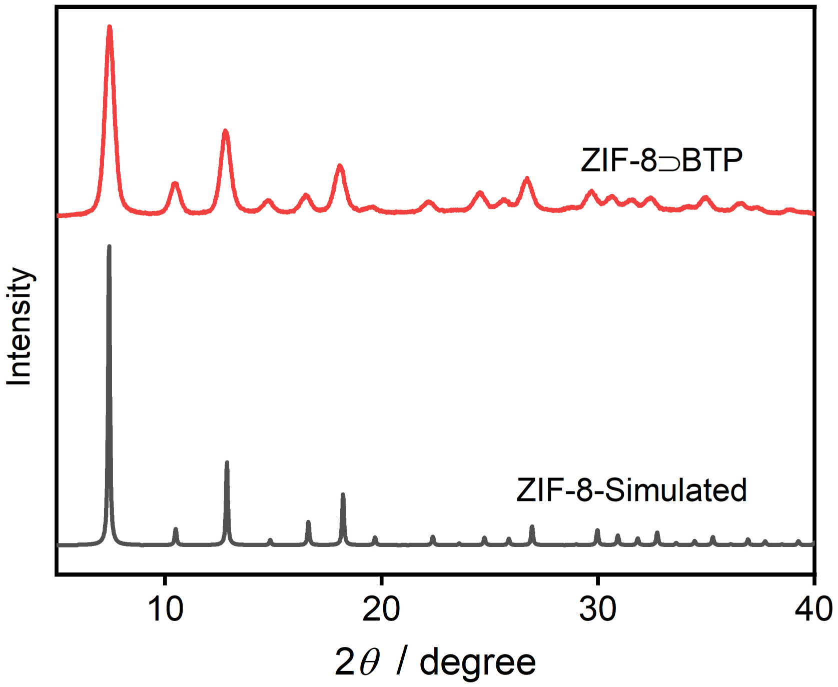

Fig. S11 X-ray powder diffraction pattern of ZIF-8⊃BTP. Simulated based on available single-crystal structure from the Cambridge structure database, CCDC 864309.

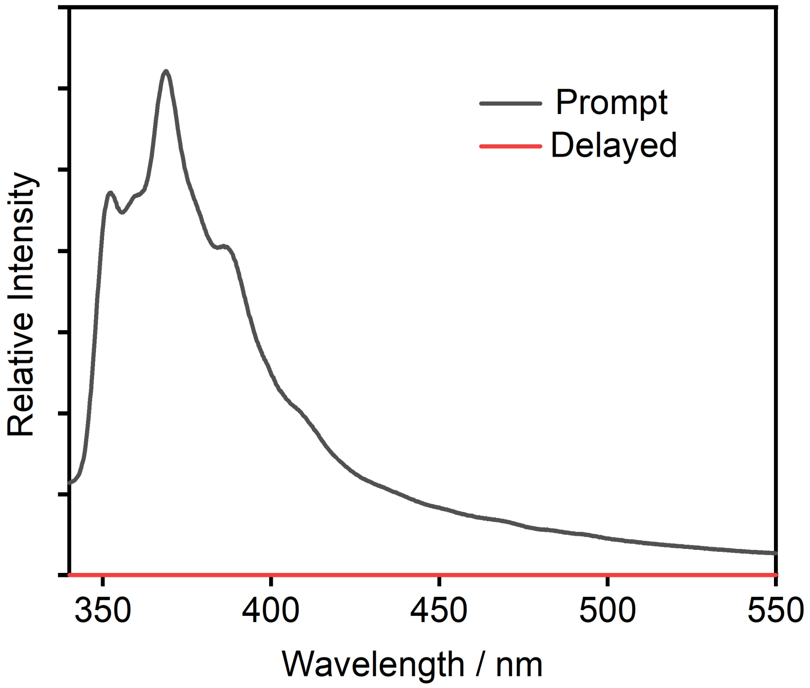

Fig. S12 Photoluminescence spectra of ZIF-8⊃ BTP crystals under ambient conditions.

Table S1. Performance Comparison of CD-MOF with MOF-Based RTP Systems

Organic ligands	Coordinating metals	Synthesis condition	Lifetime (RT) (ms)	Quantum yield (%)	Reference
γ-cyclodextrin	K^+	H_2O and Methanol, RT	553	8.19	This work
Terephthalic acid	Zn^{2+}	DMF, 100°C	472	4.76	*Chem.Sci.*, **2016**, 7, 4519–4526
Modified Isophthalic acid	Al^{3+}	DMF and H_2O, 135°C	101	4.4	*ACS Materials Lett.* **2023**, 5, 2691−2699
3,3′-bipyridyl	Zn^{2+}	DMF and Methanol, 70°C	180	/	*J.Am.Chem.Soc.* **2025**, 147, 10530−10539
4,5-imidazoledicarboxylic acid	Li^+	DEF and H_2O, 100°C	299	4.91	*Sci China Chem*, **2025**, 68
1H-1,2,4-triazole-3,5-dicarboxylic acid	Na^+	Methanol and H_2O, RT	378.9	5.04	*Chem.Eur.J.* **2025**, 31,e202402715
4,5-imidazoledicarboxylic formic acid	Ca^{2+}	DMF, 120°C	645	/	*Inorg. Chem.* **2021**, 60, 10075−10078
5-fluoronicotinic acid	Ca^{2+}	DMF / CH_3CN, 140°C	264	/	*Inorg. Chem.* **2024**, 63, 21336−21344
Formic acid	Lu^{3+}	H_2O, 95°C	110.1	/	*J. Mater. Chem. C*, **2025**, 13, 1157–1164
5-bromoisophthalic acid	Zn cluster	H_2O, 150°C	7.041	11.12	*ACS Appl. Mater. Interfaces* **2018**, 10, 34377−34384
Camphoric acid 1,1,2,2-tetra(pyridin-4-yl)ethene)	Zn^{2+}	DMA / Benzyl alcohol / H_2O, 100°C	340	75.39	*Adv. Funct. Mater.* **2023**, 33, 2300105

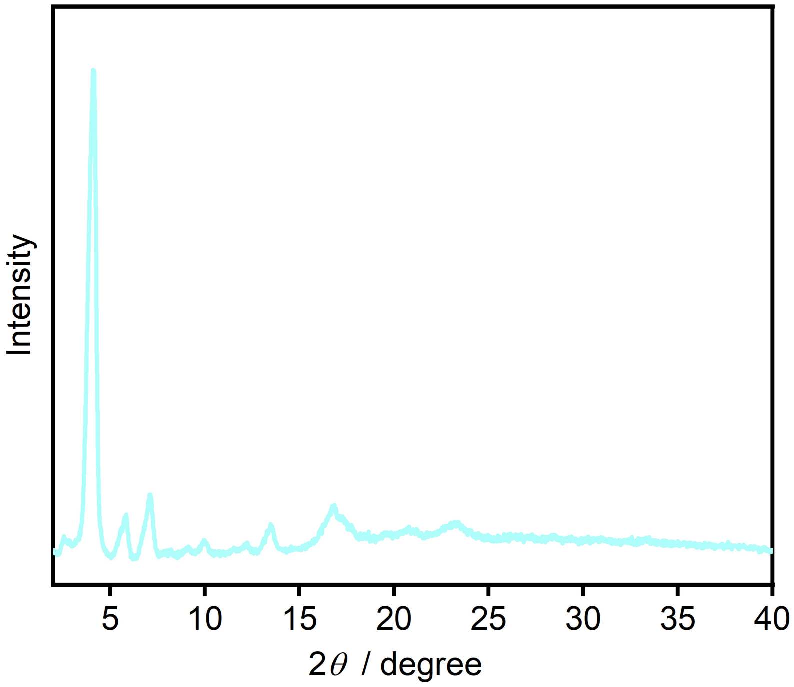

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Fig. S13 X-ray powder diffraction pattern of CD-MOF⊃TP.

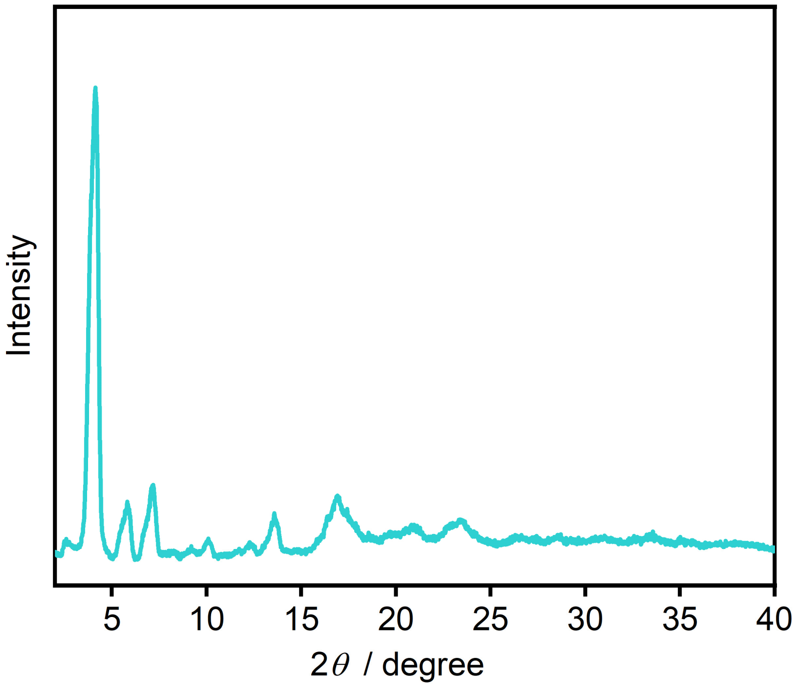

Fig. S14 X-ray powder diffraction pattern of CD-MOF⊃BMTP.

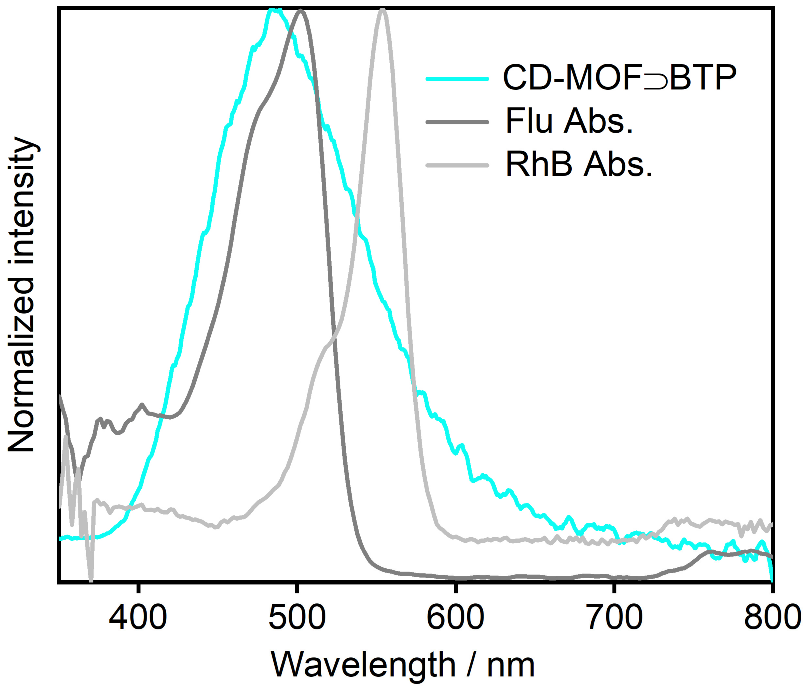

Fig. S15 Normalized phosphorescence spectrum of CD-MOF⊃BTP (blue line) and normalized absorption spectra of Flu (gray line) and RhB (light gray line) in aqueous solution.(0.00010 mol/L for Flu and RhB)

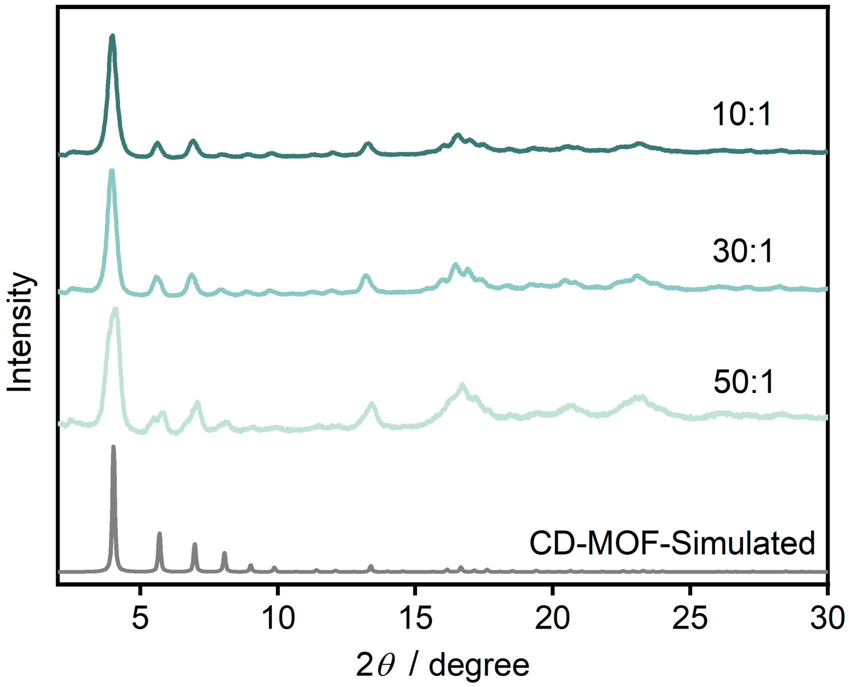

Fig. S16 X-ray powder diffraction pattern of CD-MOF⊃BTP&Flu with different fluorescein (Flu) concentrations.

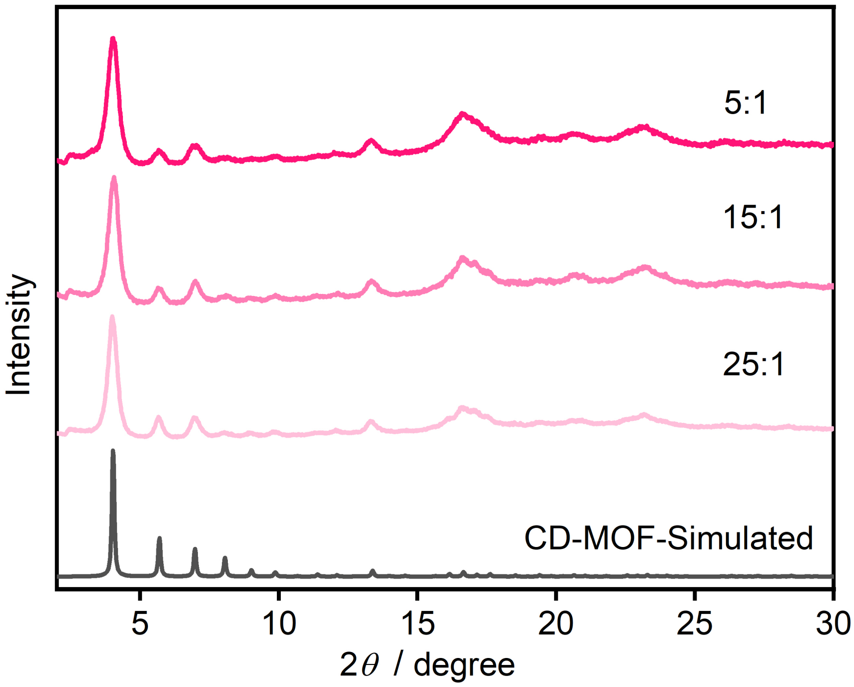

Fig. S17 X-ray powder diffraction pattern of CD-MOF⊃BTP&RhB with different rhodamine B (RhB) concentrations.

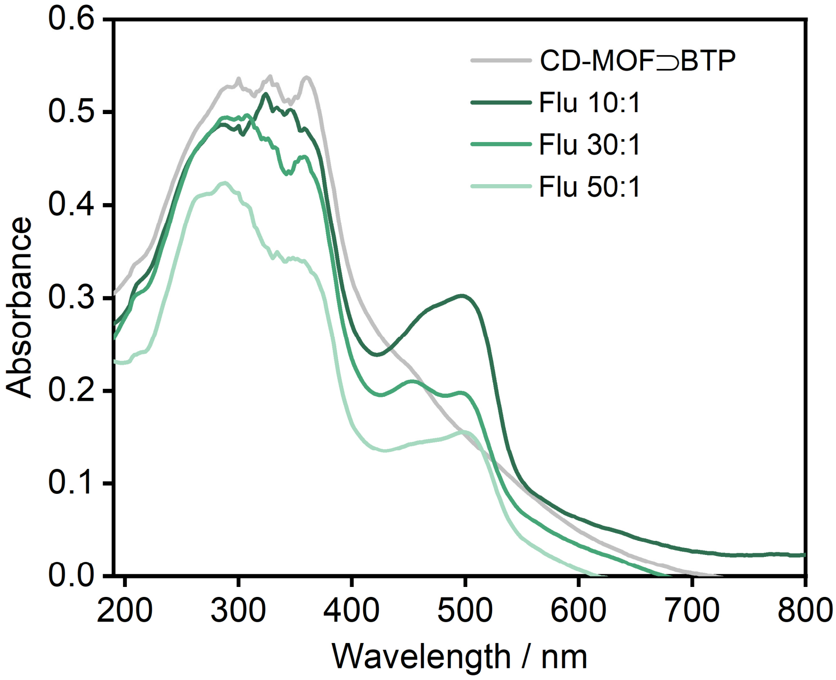

Fig. S18 UV-Vis diffuse reflectance spectroscopy of CD-MOF⊃BTP and CD-MOF⊃BTP with different sodium fluorescein (Flu) concentrations.

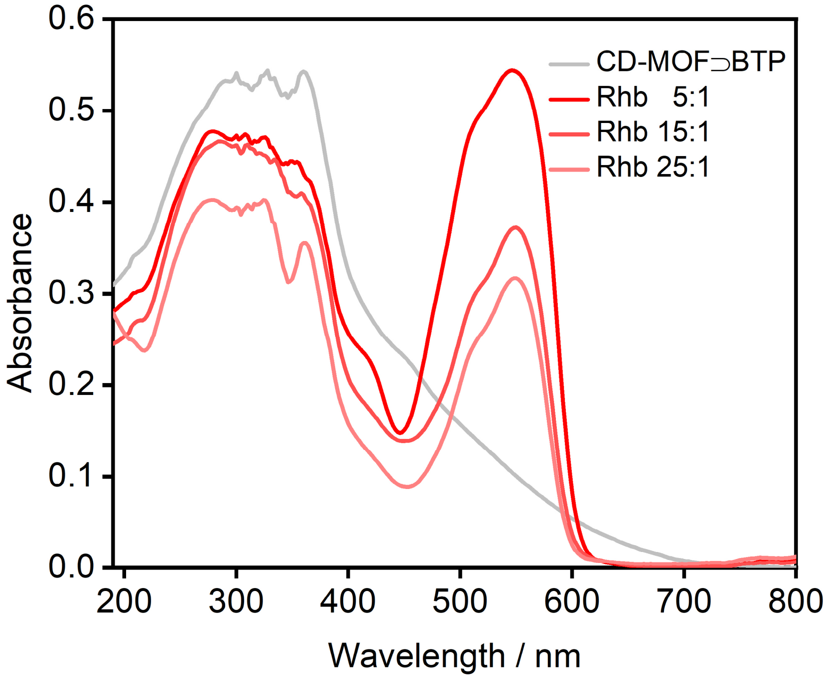

Fig. S19 UV-Vis diffuse reflectance spectroscopy of CD-MOF⊃BTP and CD-MOF⊃BTP with different rhodamine B (RhB) concentrations.

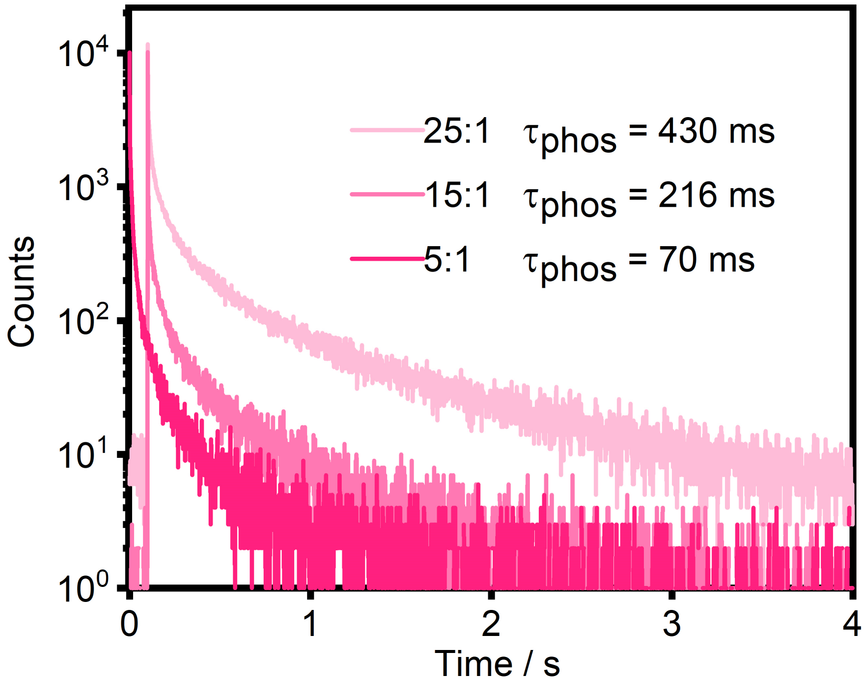

Fig. S20 Time-resolved decay spectra of CD-MOF⊃BTP&RhB with different RhB concentrations.

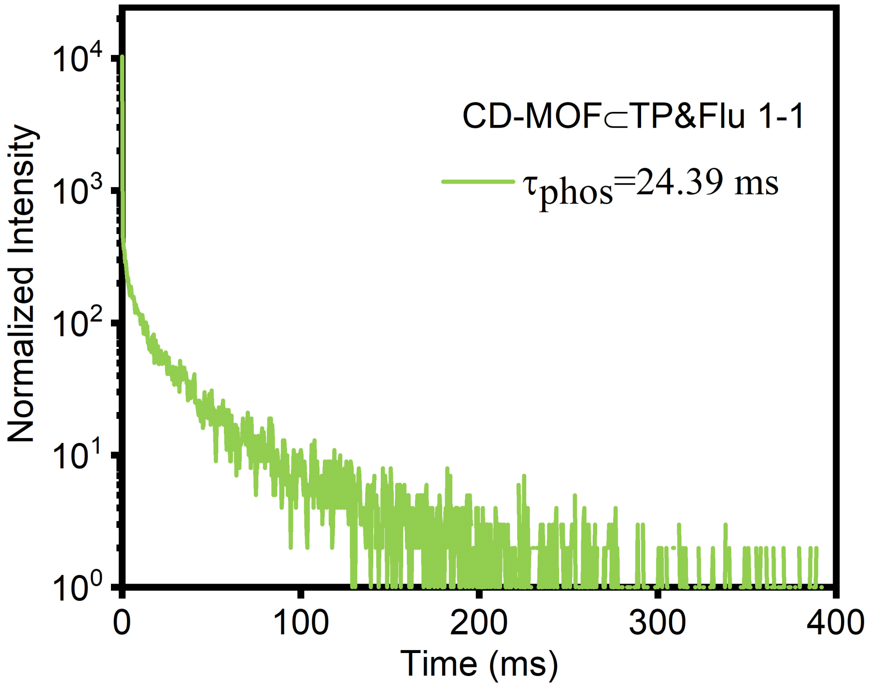

Fig. S21 Time-resolved decay spectra of CD-MOF⊃BTP&Flu, [TP]:[Flu] is 1:1.