

Supplementary Information

Crystalline hydrogen-bonded organic framework for air-tolerant triplet–triplet annihilation upconversion

Qiaoyu Zhang^{a,c}, Guiwen Luo^{a,c}, Rui Hu^b, Guoqiang Yang^{b,c}, Jinping Chen^a, Tianjun Yu^a, Yi Zeng^{*,a,c}, Yi Li^{a,c}

^a Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

*E-mail: zengyi@mail.ipc.ac.cn

Experimental methods

¹H NMR spectra were recorded with a Bruker Avance II-400 (400 MHz) spectrometer. High-resolution mass spectroscopy (HRMS) was performed by a 9.4T Solarix Fourier Transform Ion Cytroic Resonance Mass Spectrometer (FT-ICR-MS). UV-visible absorption spectra and emission spectra were recorded by using a Shimadzu UV-2550PC spectrophotometer and a Hitachi F-4600 spectrometer, respectively. Upconversion emission of samples was obtained by Princeton Instrument PIXIS100 CCD coupled to an Acton SP2150i spectrometer. The excitation light source was a continuous-wave (CW) laser MRL-III-532L from Changchun New Industries Optoelectronics Tech. Co. Ltd. The power of the excitation laser was measured using an Ophir Nova II power meter with a PD300-3W photodetector. The upconversion emission, phosphorescence, and fluorescence decays were recorded by an Edinburgh FLS1000 spectrometer with a time-correlated single photon counting (TCSPC) method. UV-Vis diffuse reflectance spectra of solid materials were recorded on an Agilent Cary 7000 UV-Vis-NIR spectrophotometer. A suitable single crystal was selected on an XtaLAB Synergy R, HyPix diffractometer. The crystal was kept at 170.00(12) K during data collection. Using Olex2,¹

the structure was solved with the SHELXT² structure solution program using Intrinsic Phasing and refined with the SHELXL³ refinement package using Least Squares minimisation. XRD spectra were measured with a Bruker D8 Focus X-ray diffractometer equipped with CuK α 1 radiation (1.54184 Å).

UC quantum yield measurement

The upconversion quantum yields of solid samples were measured in an integrating sphere (Labsphere 4P-GPS-053-SL) coupled to a Princeton Instrument Acton SP2500 spectrometer with a Princeton Instrument PIX-100B CCD as the detector according to the technique reported previously.⁴ The solid UC sample was sealed between two coverslips with epoxy adhesive and then placed in the sphere for quantum yield measurement. The UC quantum yield, Φ_{UC} , was calculated by equation $\Phi_{UC} = I_{UC}/(I_0 - I)$, where I_{UC} is the integral intensity of the upconversion spectrum collected from the integrating sphere, I_0 is the integral intensity of the excited laser exiting the integrating sphere by passing through the blank area without UC samples, and I is the integral intensity of the laser when exciting the solid upconversion sample. Φ_{UC} of the solid samples is the average of six independent tests.

Emission lifetime measurement

The UC emission decay profiles are fitted by the multiexponential function:

$$I(t) = A + \sum_{i=1}^n B_i e^{(-t/\tau_i)}$$

where I is the emission decay data, τ_i is the lifetime, and B_i is the pre-exponential factor. When the decay of the data follows a mono-exponential decay, the equation simplifies to $I(t) = A + B e^{-(t/\tau)}$.

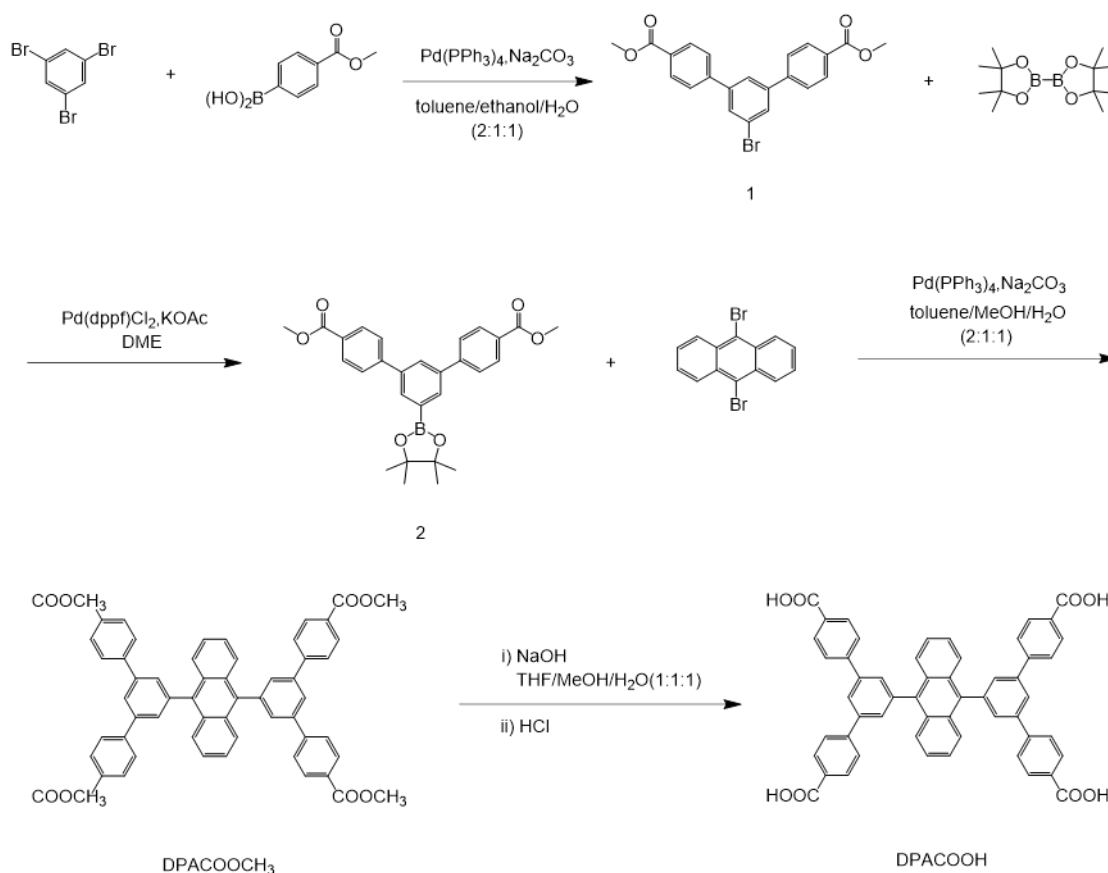
The triplet lifetime of DPACOOH τ_T is estimated from the decay time constant of upconverted emission according to the approximate relationship $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_T)$ in the longer timescale region, where the TTA decay become negligible relative to the spontaneous decay of the triplets and τ_{UC} is the time constant of UC decay in the longer time region. τ_{UC} of the HOF and powder samples was estimated to be 103 and 107 μ s, respectively, by fitting the tail of the UC emission kinetics (Fig. S8d). The τ_T in the HOF and powder samples was then estimated to be 206 and 214 μ s, respectively

Absorption coefficient estimation

α is the absorption coefficient that describes the intensity attenuation of the light passing through the sample ($I = I_0 e^{-\alpha L}$), where I_0 is the incident intensity, I is the transmittance intensity, and L is the optical path length. In the HOF and powder samples, DPACOOH is considered as a solid solvent and the concentration of PtOEP in DPACOOH/PtOEP (2500/1) is about 338 μ M. The absorption coefficient of PtOEP in DEF solvents was measured and multiplied by the corresponding concentration multipliers to obtain the absorption coefficients

of the solids (36.5 cm^{-1} in the samples).

Material synthesis



Scheme S1. The synthesis route of DPACOOH.

(1) Synthesis of Compound 1

Tribromobenzene (2 g, 6.35 mmol), p-methoxycarbonyl phenylboronic acid (2.86 g, 15.88 mmol), sodium carbonate (3.37 g, 31.77 mmol), 26 mL toluene, 13 mL ethanol, and 13 mL water were added to a Schlenk bottle. Then tetrtriphenylphosphine palladium (220 mg, 0.19 mmol) was added to the Schlenk bottle under N_2 protection and a three-cycle free-pump-thaw deoxygenation was carried out. The reaction was heated to $95 \text{ }^\circ\text{C}$ and refluxed for 12 h. After the reaction was completed, the reaction mixture was extracted with ethyl acetate and water for three times. The organic layer was dried with anhydrous magnesium sulfate. The crude product was purified by silica gel column chromatography by using dichloromethane and petroleum ether as eluents to yield compound 1 (yield: 44%). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.4 \text{ Hz}$, 4H), 7.76 (d, $J = 9.3 \text{ Hz}$, 3H), 7.68 (d, $J = 7.7 \text{ Hz}$, 4H), 3.96 (s, 6H). HRMS (m/z): calculated for $\text{C}_{22}\text{H}_{17}\text{O}_4\text{Br} = 424.03$, found 424.03.

(2) Synthesis of Compound 2

Compound 1 (500 mg, 1.18 mmol), 4,4,4',4',5,5,5',5'-Octamethyl-2,2'-bi(1,3,2-dioxaborolane) (328 mg, 1.30 mmol), potassium acetate (346 mg, 3.53 mmol) and 1, 2-dimethoxy-ethane 20 mL were added to a Schlenk bottle. Pd(dppf)Cl₂ (26 mg, 0.035 mmol) was added to the bottle under N₂ protection and a three-cycle free-pump-thaw deoxygenation was carried out. The reaction was heated to 120 °C and refluxed for 12 h. After the reaction was completed, the reaction mixture was diluted with 1, 2-dimethoxy-ethane and filtered through diatomite to remove insoluble inorganic salt impurities and concentrated to brown crude products.

(3) Synthesis of DPACOOCH₃

Compound 2 (500 mg, 1.06 mmol), 9,10-dibromoanthracene (142 mg, 0.42 mmol), sodium carbonate (224 mg, 2.12 mmol), and a mixed solvent (toluene 20 mL, methanol 10 mL, water 10 mL) were added to a Schlenk bottle. Tetrtriphenylphosphine palladium (15 mg, 0.013 mmol) was added to the Schlenk bottle under N₂ protection and a three-cycle free-pump-thaw deoxygenation was carried out. The reaction was heated to 95 °C and refluxed for 12 h. After the reaction was completed, the solid mixture was obtained by filtration with the Brinelli funnel. Then the solid mixture was dissolved in chloroform and dried with anhydrous magnesium sulfate. The crude product was recrystallized by chloroform to yield white products (yield: 72.4%). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 7.4 Hz, 8H), 8.09 (s, 2H), 7.83 (d, J = 8.4 Hz, 16H), 7.43 (s, 4H), 3.95 (s, 12H). HRMS (m/z): calculated for C₅₈H₄₂O₈ = 866.29, found 866.29.

(4) Synthesis of DPACOOH

DPACOOCH₃ (150 mg, 0.17 mmol), sodium hydroxide (138 mg, 3.46 mmol), and mixed solvent (tetrahydrofuran 6 mL, methanol 6 mL, water 6 mL) were added to a round-bottom flask, heated to 90°C and refluxed for about 5 h. After the reaction was completed, the reaction mixture was concentrated. The mixture was acidified using 1 mol/L HCl, and the precipitate was separated by centrifugation. ¹H NMR (400 MHz, DMSO) δ 13.03 (s, 4H), 8.35 (s, 2H), 8.07 (s, 16H), 7.90 (s, 4H), 7.85 – 7.68 (m, 4H), 7.51 (d, J = 6.1 Hz, 4H). HRMS (m/z): calculated for C₅₈H₃₄O₈ = 810.23, found 810.22.

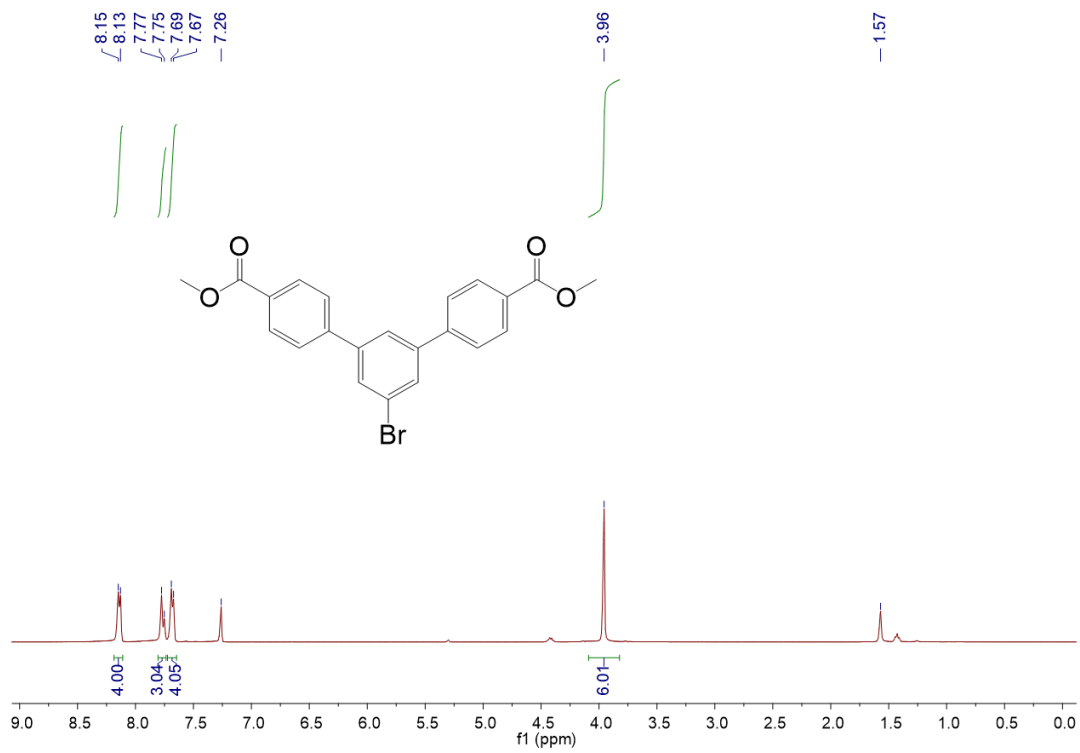


Fig. S1. ¹H NMR spectrum of Compound 1.

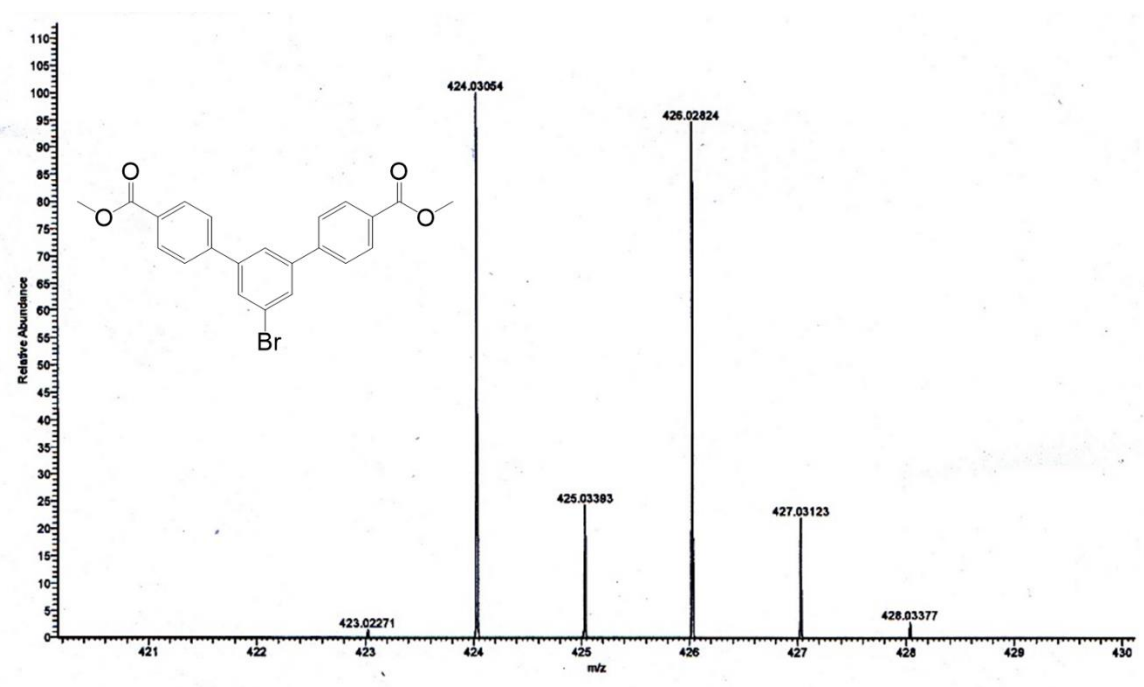


Fig. S2. MALDI-MS spectrum of Compound 1.

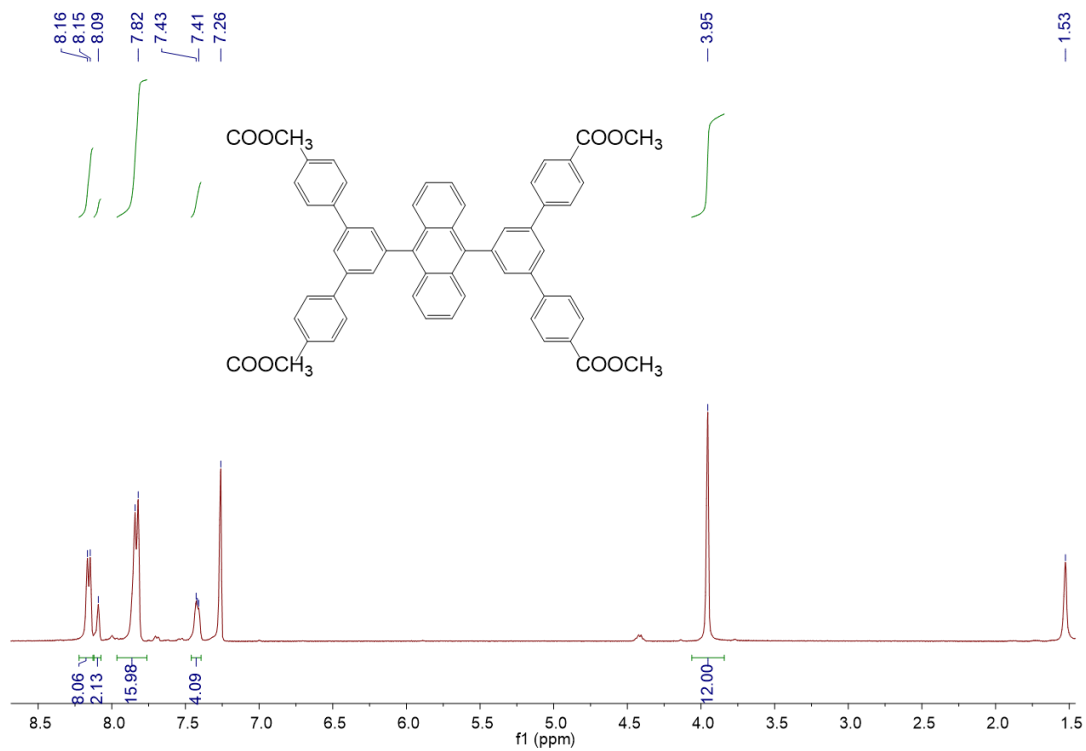


Fig. S3. ¹H NMR spectrum of DPACOOCH₃.

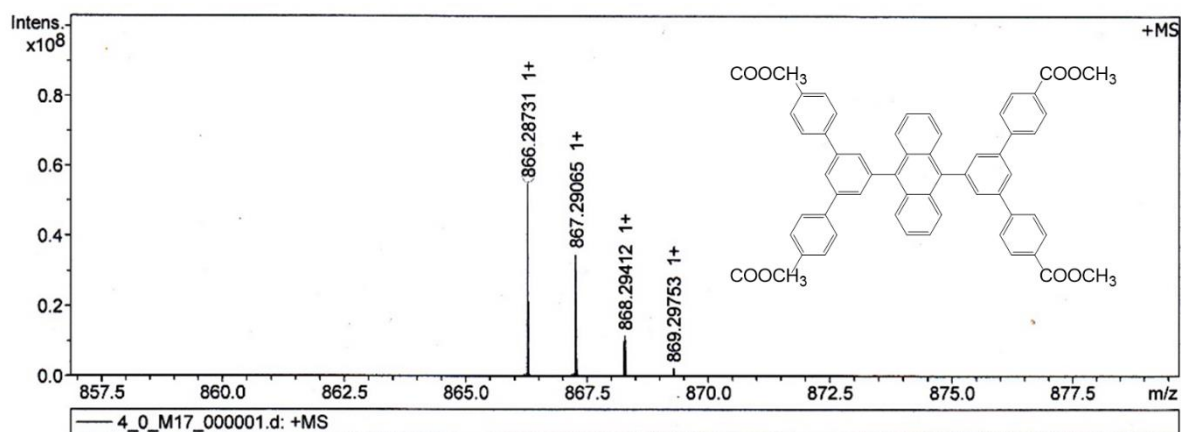


Fig. S4. MALDI-MS spectrum of DPACOOCH₃.

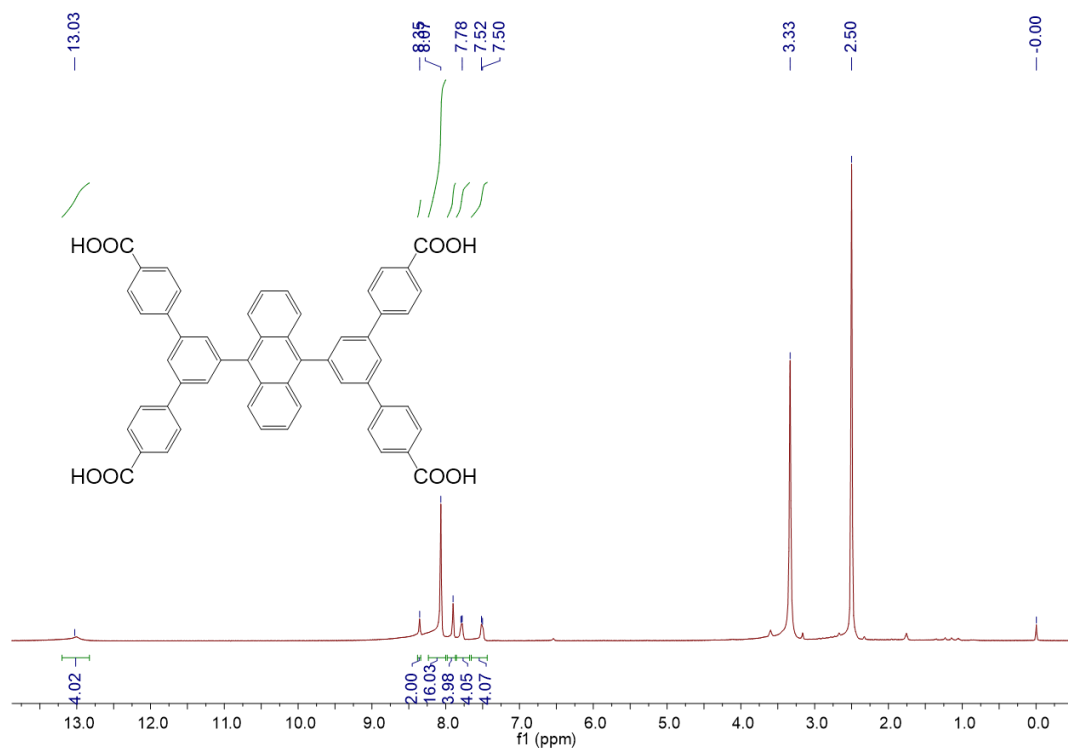


Fig. S5. ¹H NMR spectrum of DPACOOH.

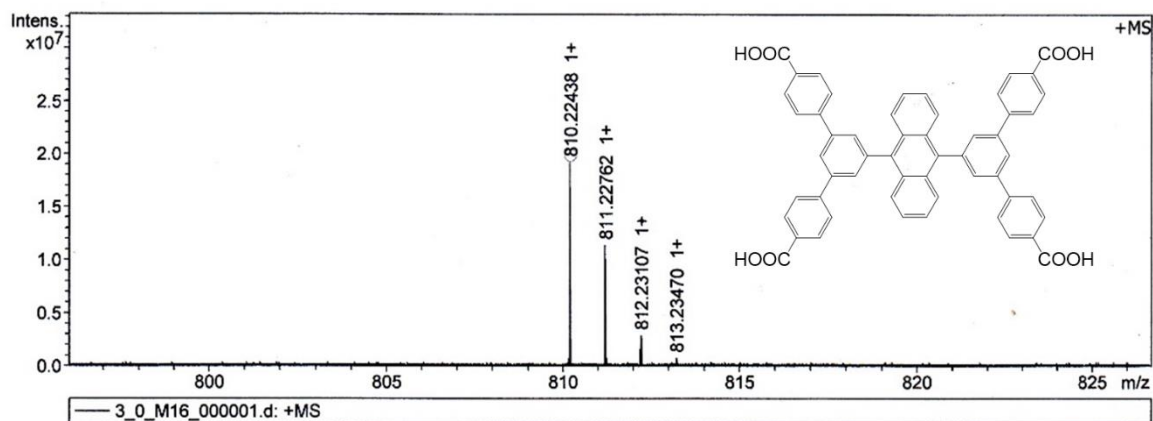


Fig. S6. MALDI-MS spectrum of DPACOOH.

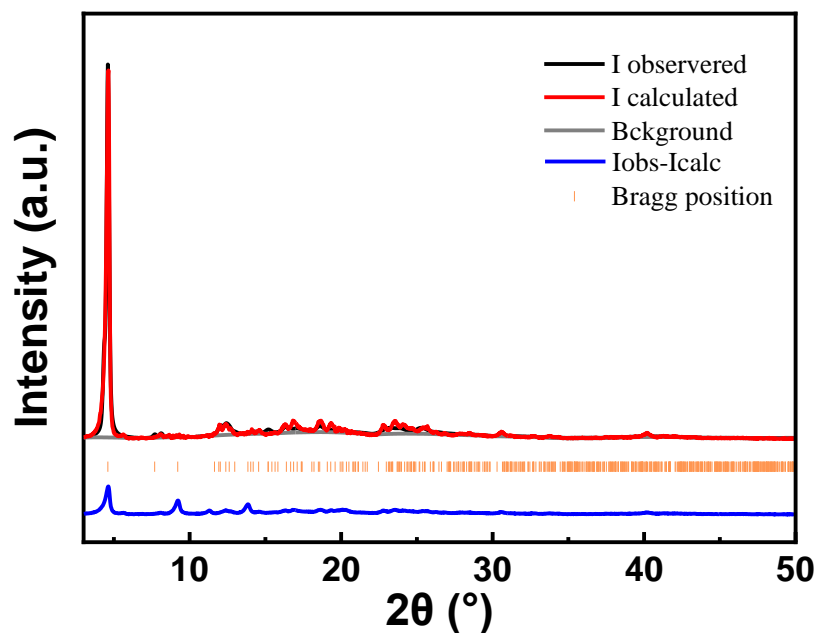


Fig. S7. Whole profile pattern matching using the Rietveld method for the synthesized HOF, indicating the phase purity of the synthesized HOF. The diffraction peak of HOF at 4.6 deg corresponding to the pore size of 1.9 nm, is the same as that obtained from the simulation of DPACOOH single crystal structure, and the peaks at 9.2 and 13.8 deg in Fig. 4a correspond to the multistage diffraction. After removing these two peaks, the XRD data were refined. Rietveld refinement was done on the XRD patterns using TOPAS software.

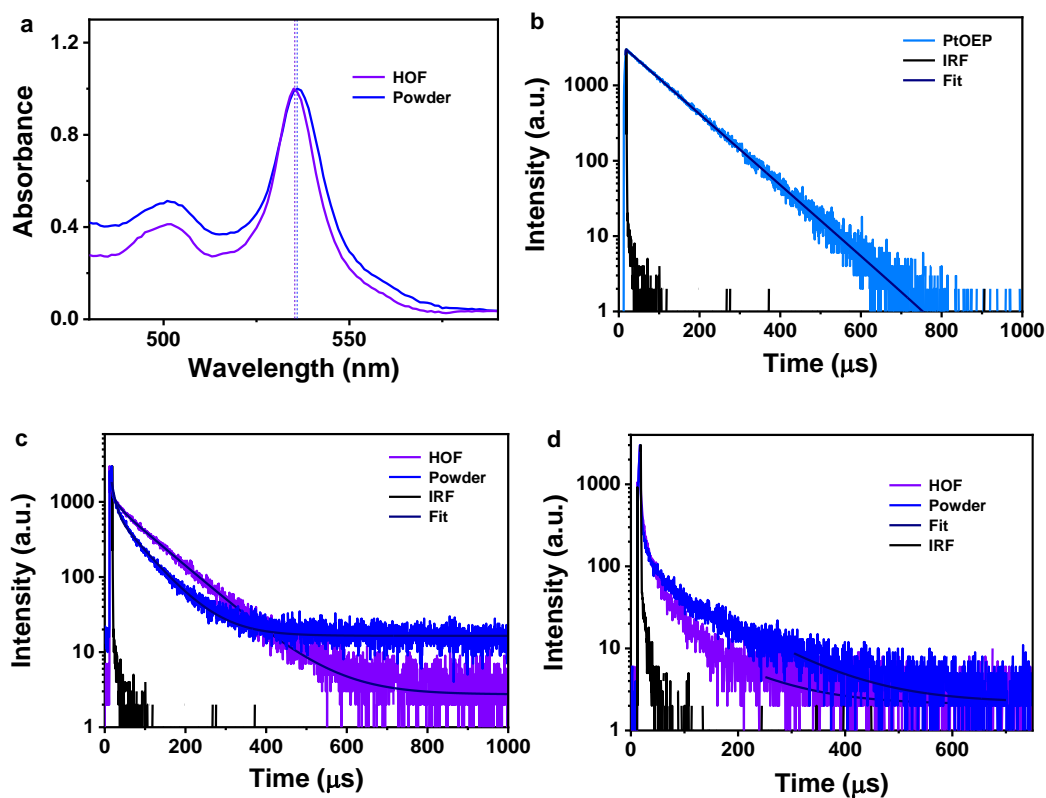


Fig. S8. (a) Normalized UV-Vis diffuse reflectance spectra of DPACOOH/PtOEP (2500/1 molar ratio) HOF and powder samples. (b) Phosphorescence lifetime of sensitizer PtOEP doped in polystyrene (0.03%wt, comparable to the weight doping ratio of DPACOOH/PtOEP of 2500/1). The solid line is the fit to the data giving a τ_0 of 92.3 μs . (c) The phosphorescence decays DPACOOH/PtOEP HOF and powder samples. Corresponding fitting of the data gives the lifetime of PtOEP after quenching of 13.9 and 9.1 μs in HOF and powder samples, respectively. (d) UC emission decays of DPACOOH/PtOEP HOF and powder samples. In the longer time region, the TTA decay become negligible relative to the spontaneous decay of the triplets. The triplet lifetime of DPACOOH τ_T can be estimated from the decay time constant of upconverted emission according to the approximate relationship $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_T)$. τ_{UC} of the HOF and powder samples was determined be 103 and 107 μs , respectively, by fitting the tail of the UC emission kinetics. τ_T in the HOF and powder samples was then estimated to be 206 and 214 μs , respectively.

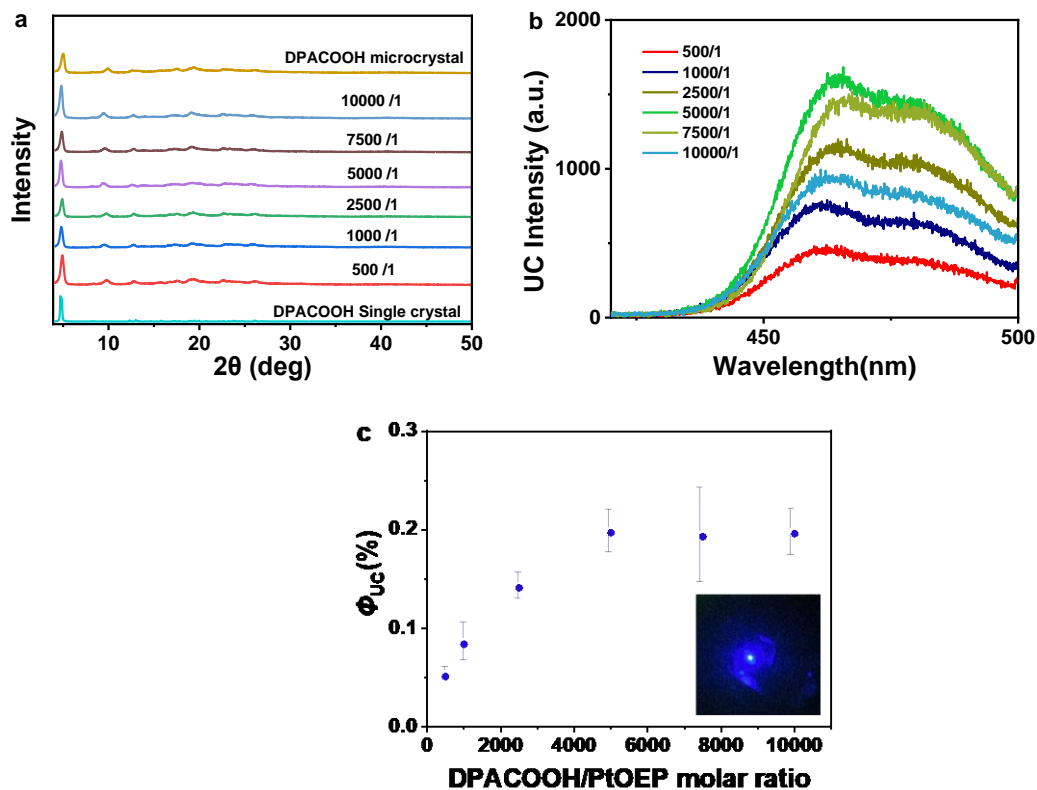


Fig. S9. (a) X ray diffraction patterns of DPACOOH single crystal and DPACOOH/PtOEP microcrystals. Upconversion luminescence spectra (b) and upconversion quantum yield (c) of HOF with different ratios of PtOEP under 532 nm laser irradiation (Power density 810 mW/cm^2). Inset is a photograph of the HOF (DPACOOH/PtOEP = 5000/1) taken by a 470 nm band-pass filter.

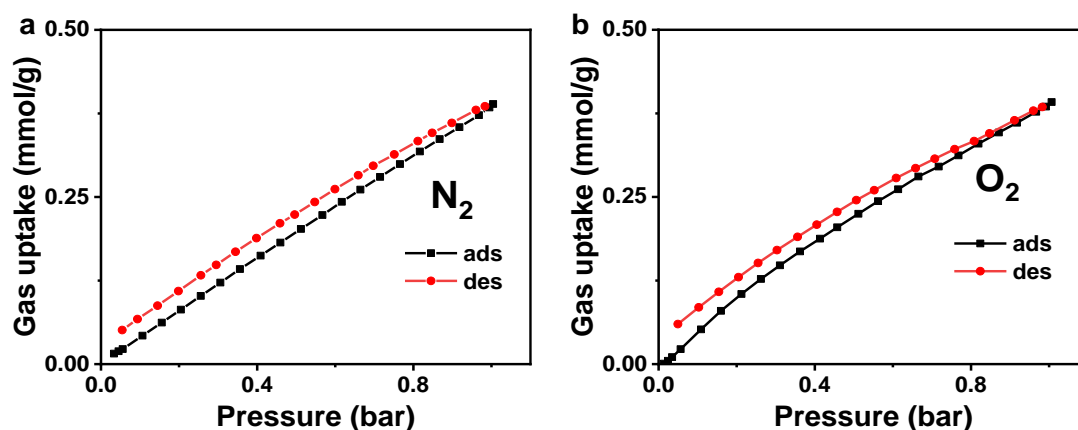


Fig. S10 N_2 and O_2 adsorption isotherms (273 K) of as-synthesized HOF. Henry's constant was estimated to be $0.38 \text{ mmol}^{-1} \text{ g}^{-1} \text{ bar}^{-1}$ for N_2 and $0.39 \text{ mmol}^{-1} \text{ g}^{-1} \text{ bar}^{-1}$ for O_2 , respectively.

Table S1. Crystal data and structure refinement for DPACOOH

Empirical formula	C ₅₈ H ₄₆ O ₁₀
Formula weight	902.95
Temperature/K	170.00(12)
Crystal system	monoclinic
Space group	I2/a
a/Å	7.6531(5)
b/Å	20.7577(10)
c/Å	37.5707(13)
α /°	90
β /°	92.335(4)
γ /°	90
Volume/Å ³	5963.6(5)
Z	4
ρ_{calc} /cm ³	1.006
μ /mm ⁻¹	0.556
F(000)	1896.0
Crystal size/mm ³	0.15 × 0.02 × 0.01
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	4.708 to 153.974
Index ranges	-9 ≤ h ≤ 9, -25 ≤ k ≤ 17, -46 ≤ l ≤ 46
Reflections collected	19274
Independent reflections	5846 [R _{int} = 0.0555, R _{sigma} = 0.0499]

Data/restraints/parameters	5846/13/311
Goodness-of-fit on F^2	1.419
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1253$, $wR_2 = 0.3384$
Final R indexes [all data]	$R_1 = 0.1547$, $wR_2 = 0.3691$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.01/-0.49

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
2. G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.
3. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.
4. M. F. Wu, D. N. Congreve, M. W. B. Wilson, J. Jean, N. Geva, M. Welborn, T. Van Voorhis, V. Bulovic, M. G. Bawendi and M. A. Baldo, *Nat. Photonics*, 2016, **10**, 31-34.