

Supplementary Information

Highly luminescent olefin-linked covalent organic frameworks

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Experimental Details

Characterization. Proton nuclear magnetic resonance (^1H NMR) analysis was conducted on a Bruker Advance III 400 (400 MHz) NMR spectrometer. Fourier-transform infrared (FT-IR) spectrum was obtained by a Dell model II TENROS infrared spectrometer. Powder X-ray diffraction (PXRD) results were performed using X'Pert³ Powder X by directly depositing COF powder on glass substrates. Elemental analysis (EA) was performed on an ELEMENTAR Vario Micro elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under the protection of nitrogen at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from $20\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$. High-resolution transmission electron microscopy (HR-TEM) was carried out on a JEM 2100F high-resolution microscopy. All the COF samples were prepared through drop super-sonicated acetone suspensions of samples onto copper grids. Scanning electron microscope (SEM) images of COF samples were recorded on a Hitachi model S-4800 with an accelerating voltage of 3.0 kV. All the COF samples were prepared through drop super-sonicated acetone suspensions of samples onto substrates, then followed by gold coating. Nitrogen sorption isotherms were measured on BELSORP-max II at 77 K. Brunauer-Emmett-Teller (BET) theory is used to evaluate the surface area of all COF samples. The pore volume was calculated from the sorption curve by using the non-local density functional theory (NLDFT) model. Electronic absorption spectra were recorded on a JASCO model V-670 spectrophotometer. Fluorescence spectra and absolute quantum yield were recorded on a JASCO model FP-6600 spectrofluorometer, equipped with integral sphere. Time-resolved fluorescence spectroscopy were conducted on a Hamamatsu model compact fluorescence lifetime spectrometer C11367 (Quantaurs-Tau) that contains a light-emitting diode (LED) pulsed light source, monochromator, PMT (photomultiplier tube), iris (aperture) for adjusting light level, and filter for cutting excitation light. The COF samples were irradiated with internal LED at 365 nm.

Computational Calculation. The molecular modeling of TFB-TEXDP-COF was reconstructed using the density-functional tight-binding (DFTB) method, including the UFF (Universal Force Field) dispersive interactions. The calculations were performed with the DFTB+ program package version 19.1.^[S1] The PXRD data were analyzed by Pawley refinement using Reflex, which is a commercial software package for crystallographic structural analysis implemented in MS modeling version 4.4 (Accelrys Inc.). Unit cell dimensions were solved manually using coordinates from the obtained PXRD pattern positions. Pawley refinement was then performed, and the lattice parameters were iteratively optimized until the R_{WP} values converged.

Stability test. The COFs samples (100 mg) were sonicated and dispersed in different solvents, including hexane, THF, MeOH, DMF, DMSO, trifluoroacetic acid (TFA), triethyl-amine (TEA), H₂O (25 and 100 °C), aqueous HCl (12 M) and NaOH (14 M) solutions for one month. Before PXRD and nitrogen sorption analysis, the precipitates were collected by centrifugation and then washed with anhydrous tetrahydrofuran (3 × 10 mL) and acetone (3 × 10 mL) and then dried at 120 °C under vacuum overnight.

Fluorescence spectroscopy. The solid samples of COFs were packed on a round quartz plate (diameter = 20 mm, thickness = 5 mm) in solid-state fluorescence sample holder. The fluorescence spectra were recorded under emission mode (sensitivity: medium, response: 0.2 s) with specific excitation wavelength at the absorption band. The excitation and emission bandwidths were fixed for all spectra.

Fluorescence quantum yield measurement. The solid samples of COFs were grinded and filled into a high precision cell (thickness = 4 mm). The cell was placed into the integral sphere equipped on the spectrofluorometer. The fluorescence spectra were recorded under emission mode (excitation bandwidth = 3 nm, emission bandwidth = 2 nm, sensitivity: high, response: 0.2 s) with specific excitation wavelength. The background spectra were recorded under the same condition with blank cell. The fluorescence quantum yields were calculated with the Spectra Manager™ Suite Spectroscopy Software.

Time-resolved fluorescence spectroscopy. The decay curves were conducted on a Hamamatsu model compact fluorescence lifetime spectrometer C11367 (Quantaaurus-Tau) that contains a light-emitting diode (LED) pulsed light source, monochromator, PMT (photomultiplier tube), iris (aperture) for adjusting light level, and filter for cutting excitation light.

Materials. All of the chemicals and reagents are commercially available from Adams, Aldrich, J&K Scientific, TCI chemicals and used without further purification. 1,4-distyrylphenylene (DTP) and 1,3,5-trivinylbenzene (TVB) were synthesized according to literature methods.^[S2,S3]

Synthesis of TFB-TEXDP-COF. TFB (3.24 mg, 0.02 mmol) and TEXDP (11.3 mg, 0.03 mmol) were added into dioxane (2 mL) solution in a 10 mL Pyrex tube. Then potassium tert-butoxide (6.76 mg, 0.06 mmol) was added to the solution as a base catalyst. The tube was degassed by three freeze-pump-thaw cycles. After that, the tube was sealed off and heated to 100 °C for 5 days. The precipitates were collected by centrifugation and then washed with tetrahydrofuran (3 × 10 mL), acetone (3 × 10 mL), and water (3 × 10 mL). The powder was dried at 80 °C under vacuum overnight to give TFB-TEXDP-COF in a yield of 84 %.

Structural Characterization

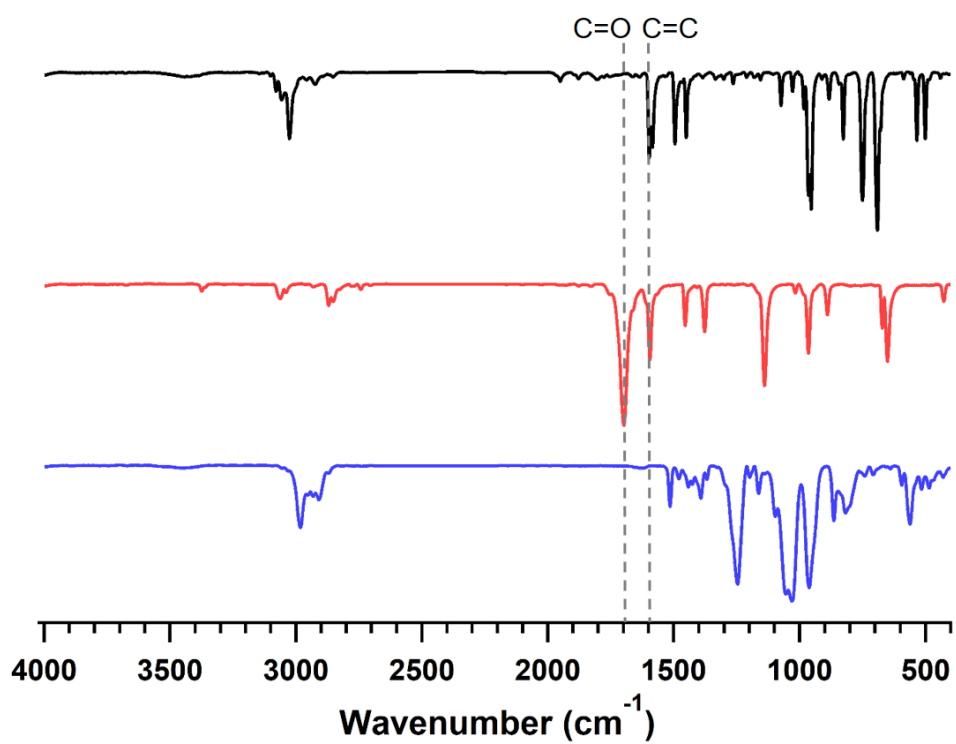


Figure S1. FT-IR spectra of TFB-TEXDP-COF (black curve), TFB (red curve), and TEXDP (blue curve).

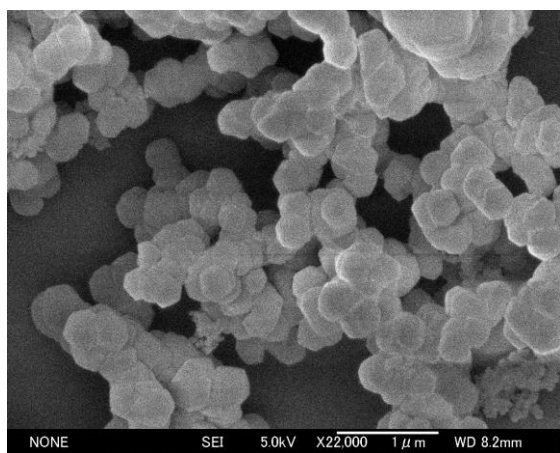


Figure S2. FE-SEM image of TFB-TEXDP-COF.

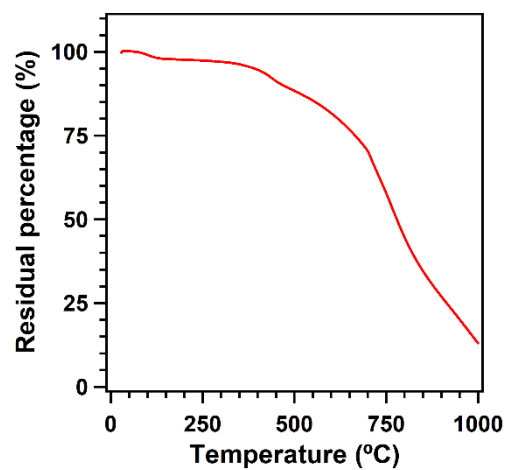


Figure S3. TGA profile of TFB-TEXDP-COF under nitrogen atmosphere.

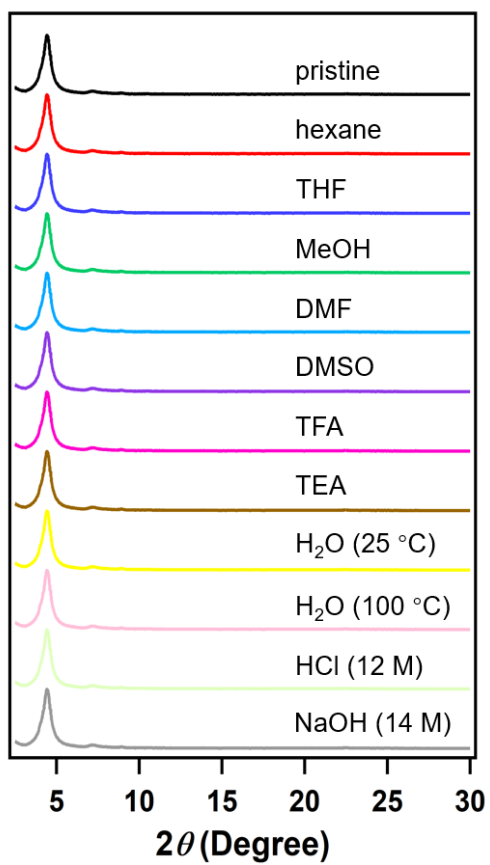


Figure S4. PXRD patterns of TFB-TEXDP-COF samples after treatment in different solutions.

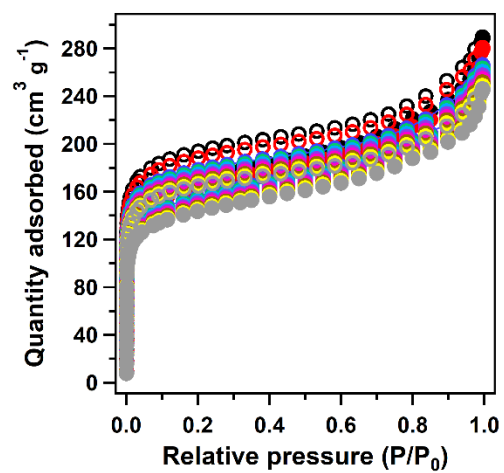


Figure S5. Nitrogen sorption isotherms of TFB-TEXDP-COF samples after treatment in different solutions.

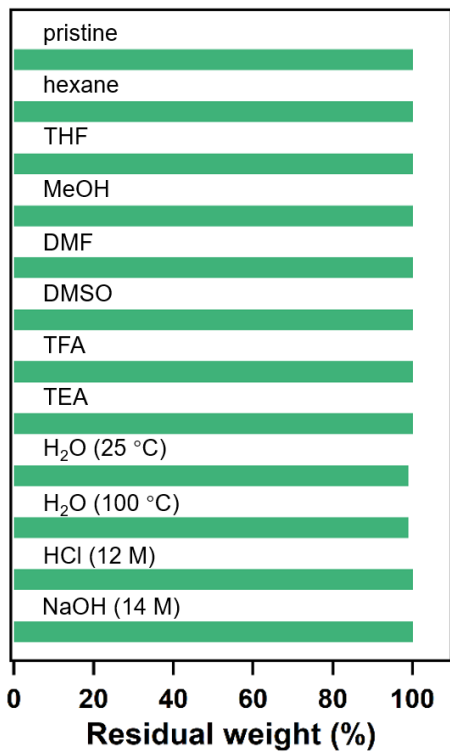


Figure S6. Residual weight percentage of TFB-TEXDP-COF samples after treatment in different solutions.

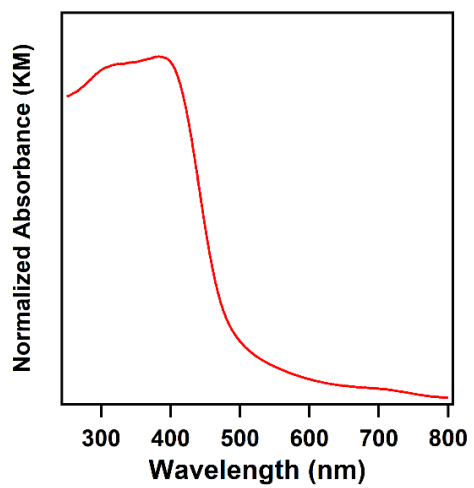


Figure S7. UV-vis K/M spectrum of solid-state TFB-TEXDP-COF.

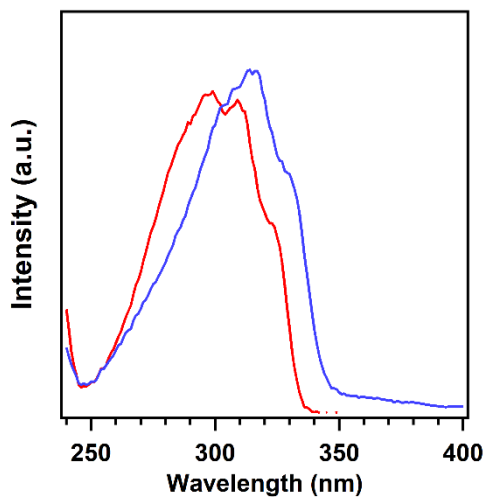


Figure S8. UV-vis K/M spectra of solid-state DTP (red curve) and TVB (blue curve).

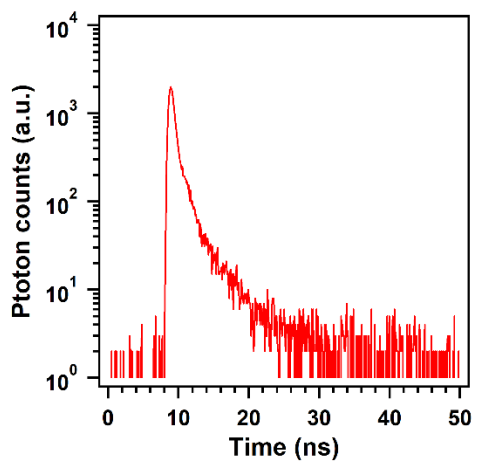


Figure S9. Fluorescence decay spectrum of DTP.

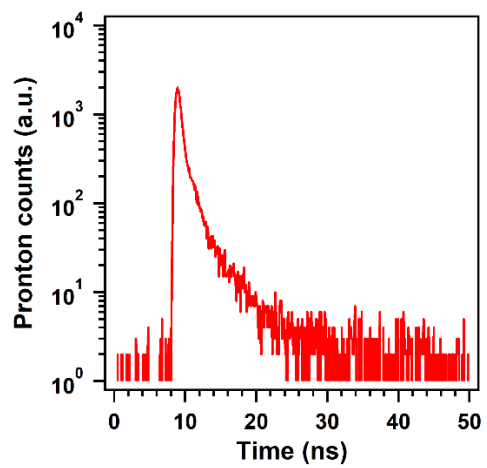


Figure S10. Fluorescence decay spectrum of TVB.

Table S1. Atomistic coordinates for the AA stacking mode of TFB-TEXDP-COF (space group: P6/M).

Atom	x	y	z
C1	0.26275	0.62628	0.5
C2	0.30319	0.59659	0.5
C3	0.41908	0.60812	0.5
C4	0.4008	0.54304	0.5
C5	0.45135	0.5214	0.5
C6	0.42946	0.45272	0.5
C7	0.47533	0.42984	0.5
H8	0.27903	0.5395	0.5
H9	0.34523	0.50308	0.5
H10	0.45659	0.37356	0.5
H11	0.47465	0.64808	0.5
H12	0.37335	0.41451	0.5

Table S2. Elemental analysis of TFB-TEXDP-COF.

COFs		C (%)	H (%)
TFB-TEXDP-COF	Calculated	93.4	6.6
	Found	92.8	7.1

Supporting References

- S1. B. Aradi, B. Hourahine, T. Frauenheim, DFTB+, a sparse matrix-based implementation of the DFTB Method. *J. Phys. Chem. A* 2007, **111**, 5678–5684.
- S2. D. L. Pastoetter, Y. Liu, M. A. Addicoat, S. Paasch, A. Dianat, D. Bodesheim, A. L. Waentig, S. Xu, M. Borrelli, A. Croy, M. Richter, E. Brunner, G. Cuniberti and X. Feng. *Chem. Eur. J.* 2022, **28**, e2021045.
- S3. A. R. Chaudhary and A. V. Bedekar. *Synthetic Commun.* 2012, **42**, 1778–1785.