Electronic Supplementary Information

Phenoxazine-Based Covalent Organic Frameworks as A Turn-Off Fluorescent Probe for Trace Water Detection in Organic Solvents

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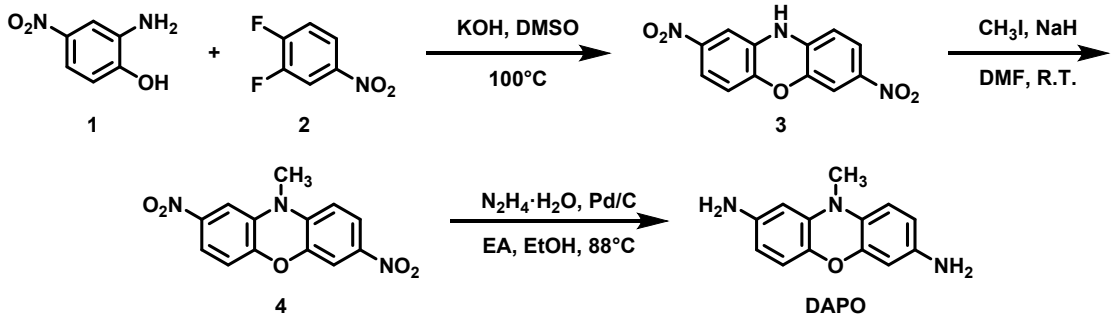
Materials and general procedures

Tetrahydrofuran (THF), methanol (MeOH), hexane, ethyl acetate (EA), dichloromethane (DCM), petroleum ether (PE), $CHCl_3$, hydrazine hydrate ($N_2H_4 \cdot H_2O$) and potassium hydroxide (KOH) were purchased from Nanjing WANQING chemical Glass ware & Instrument. Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile were purchased from J&K. 1,2-Dichlorobenzene (*o*-DCB) and *n*-butanol were purchased from Energy Chemical. 1,3,5-Trimethylbenzene (Mesitylene) were purchased from Aladdin. THF were dried by distillation from Na/benzophenone. All other chemicals were obtained from commercial sources. Unless stated otherwise, the reactions were performed under an atmosphere of dry nitrogen. 2,4,6-Tris(4-formyphenyl)benzene (TFPB)[1] and 2,4,6-tris(4-formylphenyl)triazine (TFPT)[2] were synthesized according to a literature procedure.

All liquid state NMR measurements were performed on a JEOL ECZ 400S 400 MHz spectrometer (magnetic field 9.4 T). Chemical shifts (δ) are given in ppm relative to TMS. PXRD patterns were recorded on a Rigaku Smart Lab 3kW with a scanning speed of 20° min^{-1} and a step size of 0.02° in 2θ. TGA experiments were performed on a Rigaku Smart Lab 3kWunder air from room temperature to 800 °C at a ramp rate of 10 °C/min. SEM images were recorded on a Quanta 250 FEG scanning electron microscope. FT-IR spectra were measured on a ThermoFisher IS10 FT-IR with pure KBr pellets. Nitrogen sorption isotherms were measured at 77 K with a Quantachrome Autosorb-iQ3 analyzer. Before measurement, the samples were degassed in vacuum at 130 °C for 24 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using solid density functional theory (QSDFT), the pore size distribution was derived from the sorption curve. The absorption spectra were recorded on a UV-vis-NIR Lambda 950 spectrophotometer (PerkinElmer, American). The fluorescence measurements were carried out on an F-4600 spectrofluorometer (Lengguang Technology, China).

Synthetic procedure

Synthesis of 2,7-diamine-10-methyl-phenoxazine (DAPO).[3]



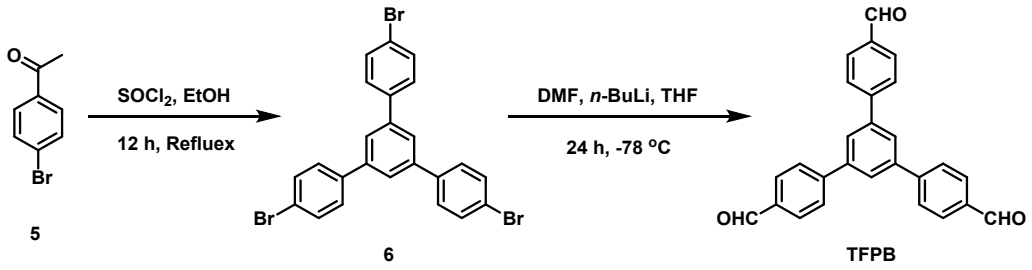
Synthesis of 2,7-dinitro-10H-phenoxazine (3): A mixture of 2-amino-4-nitrophenol (154.2 mg, 1 mmol), KOH (1.18 g, 21 mmol) and DMSO (15 mL) was charged in a 250 mL three-necked flask under nitrogen atmosphere, then 3,4-difluoronitrobenzene (1.1 mL, 0.1192 g, 1 mmol) was added dropwise to the reaction mixture and stirred at 100 °C for 24 h. The mixture was quenched using the water (100 mL) with stirring. The crude product was collected by precipitated and washed with water. The crude product was refluxed in chloroform and filtered while it hot and collected the red solid 2,7-dinitro-10H-phenoxazine (2.31 g, 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.74 (s, 1H), 7.74 (dd, J = 8.8, 2.5 Hz, 1H), 7.58 (dd, J = 8.8, 2.7 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.25 (d, J = 2.7 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.56 (d, J = 8.8 Hz, 1H).

Synthesis of 2,7-dinitro-10-methyl-phenoxazine (4): A solution of 2,7-dinitro-10H-phenoxazine (2.73 g, 10 mmol) in DMF (60 mL) with CH_3I (1.22 mL, 2.8 g, 20 mmol) and NaH (0.36 g, 15 mmol) was stirred at room temperature for 20 h. After the complete addition, the water was added to the reaction mixture with stirring. Then the orange color solids precipitated was filtered and washed with water. The solids were dried under reduced pressure to give the pure product as orange color solid (2.71 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.93 (dd, J = 8.9, 2.6 Hz, 1H), 7.81 (dd, J = 8.7, 2.5 Hz, 1H), 7.63 (d, J = 2.6 Hz, 1H), 7.51 (d, J = 2.5 Hz, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.66 (d, J = 8.9 Hz, 1H), 3.27 (s, 3H).

Synthesis of 2,7-diamine-10-methyl-phenoxazine (DAPO): A mixture of 2,7-dinitro -10-methyl-phenoxazine (862.5 mg, 3 mmol), 10 % Pd/C (70 mg, 90 mmol), $N_2H_4{\cdot}H_2O$ (5.15 mL), ethyl acetate (10 mL) and ethanol (30 mL) were placed in a hydrothermal reactor and heated to 88 °C for 24 h. The reaction mixture was then filtered to remove the Pd/C, and the filtrate was distilled to remove some solvent. The precipitate was collected dried under vacuum and depurated by silica gel column using

EA:PE = 1.5:1 as eluent under nitrogen atmosphere to give the pure product DAPO (260.2 mg, 38.2%). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 6.41 (d, J = 8.4 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 6.08 (dd, J = 8.4, 2.4 Hz, 1H), 6.03 (d, J = 2.4 Hz, 1H), 5.94 (d, J = 2.4 Hz, 1H), 5.83 (dd, J = 8.4, 2.4 Hz, 1H), 4.66 (s, 2H), 4.63 (s, 2H), 2.89 (s, 3H).

Synthesis of 2,4,6-tris(4-formyphenyl)benzene (TFPB).

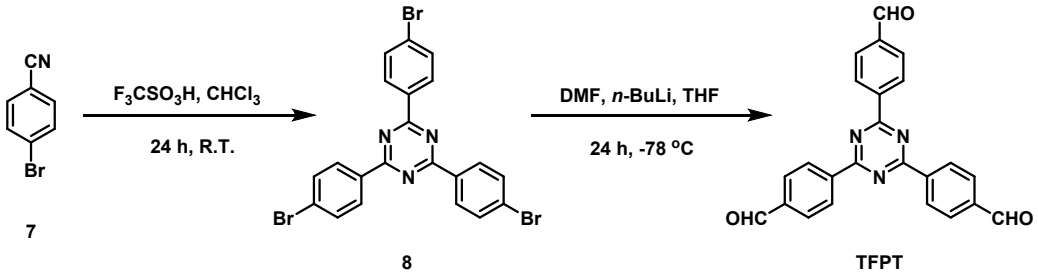


Synthesis of 2,4,6-tris(4-bromophenyl)benzene (5): A 100 mL two-neck flask was charged with 4-bromoacetophenone (10 g, 50.2 mmol) in dry ethanol (30 mL) in an ice bath at nitrogen atmosphere. The flask was connected to a reflux condenser and the exhaust was filtered through an alkaline water solution. Under vigorous stirring thionyl chloride (16.4 g, 10 mL, 138 mmol) was added via a dropping funnel over 1 h. The solution naturally warm up to ambient temperature and stirred overnight at 60 °C. Afterwards, the suspension was cooled in an ice bath and water (20 mL) was added carefully while stirring. The precipitate was collected and washed with water and hot ethanol, until the filtrate remained colorless. Drying under reduced pressure afforded 2,4,6-tris(4-bromophenyl)benzene (TFPB, 6.7 g, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.69 (s, 3H), 7.61 (d, J = 8.5 Hz, 6H), 7.53 (d, J = 8.5 Hz, 6H).

Synthesis of 2,4,6-tris(4-formyphenyl)benzene (TFPB): A solution of 2,4,6-tris(4-bromophenyl)benzene (740 mg, 1.36 mmol) in THF (100 mL) was stirred at -78 °C under dry N_2 and treated dropwise with a solution of *n*-BuLi (2.5 M in hexane, 3.2 mL, 8.16 mmol). The temperature risen to -60 °C and stirred for 3 h obtaining green solution and then DMF (1.26 mL, 16.32 mmol) was added dropwise. The mixture was stirred overnight while the temperature risen to 25 °C. The milky opaque mixture was added 2 M aqueous HCl, and the volatiles were partially removed by evaporation under reduced pressure. The remaining aqueous concentrate was extracted with CH_2Cl_2, and the combined organic extracts were washed with water and brine, and dried over $MgSO_4$, and filtered. Volatiles were removed by evaporation under reduced pressure, and the crude yellow product was

further purified by silica gel column using CH_2Cl_2:PE = 4:1 as eluent to afford colorless crystals TFPB (200 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.11 (s, 3H), 8.03 (d, J = 8.3 Hz, 6H), 7.91 (s, 3H), 7.88 (d, J = 8.3 Hz, 6H).

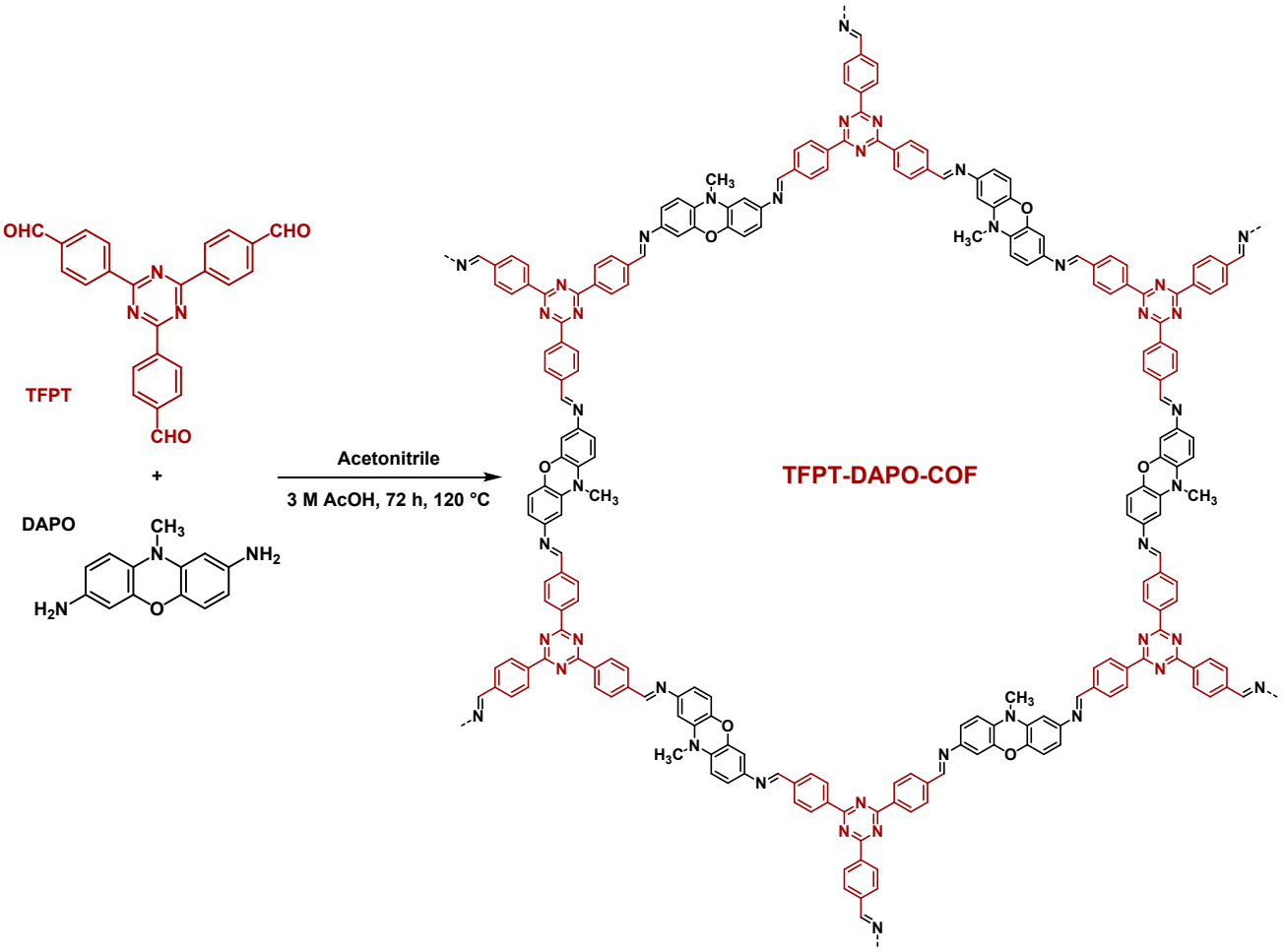
Synthesis of 2,4,6-tris(4-formyphenyl)triazine (TFPT).



Synthesis of 2,4,6-tris(4-bromolphenyl)triazine[4]*:* 4-bromobenzonitrile (3.0 g, 16.5 mmol) mixed in $CHCl_3$ (40 mL) at 0 ºC. A $CHCl_3$ solution (30 mL) containing CF_3SO_3H (8 mL, 89 mmol) was added slowly at 0 ºC. The solution was stirred at room temperature for 20 h. The reaction was poured into ice water and then quenched by addition of $NaHCO_3$ aqueous solution. Then the formed precipitate was collected by filtration and washed with water and CH_3OH. After vacuum drying, 2,4,6-tris(4-bromolphenyl)triazine was provided (2.03 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.61 (d, J = 8.3 Hz, 6H), 7.71 (d, J = 8.3 Hz, 6H).

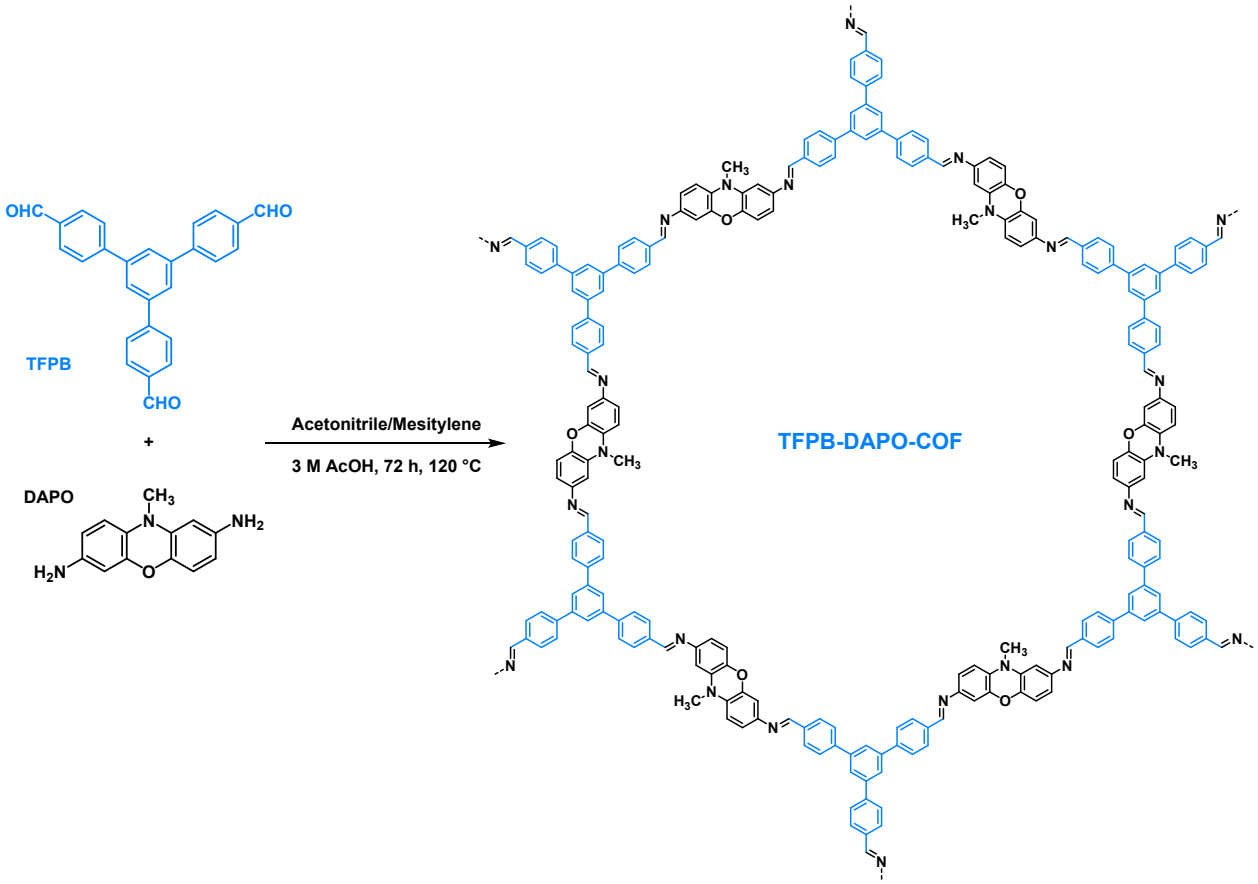
Synthesis of 2,4,6-tris(4-formyphenyl)triazine (TFPT)：Into a Schlenk tube containing 2,4,6-tris(4-bromolphenyl)triazine (817 mg, 1.5 mmol), and THF (100 mL), *n*-BuLi (3.6 mL, 9 mmol) was added slowly at -78 ºC. The solution was stirred for 3 h at -60 ºC, and was added DMF (1.38 mL, 18 mmol). The mixture was stirred overnight while the temperature risen to 25 °C. The resultant reaction mixture was stirred for 2 h. The mixture was added 2 M HCl, and the volatiles were partially removed by evaporation under reduced pressure. The remaining aqueous concentrate was extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, and dried over $MgSO_4$, and filtered. Volatiles were removed by evaporation under reduced pressure, and the crude light-yellow product was further depurated by recrystallization using CH_2Cl_2. The desired product was purified by column chromatography (CH_2Cl_2: PE = 2:1), and was obtained as the white solid TFPT (213 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.20 (s, 3H), 8.96 (d, J = 8.2 Hz, 6H), 8.13 (d, J = 8.2 Hz, 6H).

Synthesis of TFPT-DAPO-COF.



A 10 mL Schlenk tube was charged with 2,7-diamine-10-methyl-phenoxazine (DAPO, 10.2 mg, 0.045 mmol), 2,4,6-tris(4-formylphenyl)triazine (TFPT, 11.8 mg, 0.03 mmol) and CH_3CN (1 mL). The mixture was sonicated for 10 min to get a homogenous dispersion. Then, AcOH (3 M, 0.3 mL) was added and the vial was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and heated left undisturbed for 3 days at 120 °C. The yielded brown precipitate was centrifugation and washed with DMF and THF, separately. The collected powder was dried at 110 °C under vacuum for 12 h to give red powder (18 mg, 88%).

Synthesis of TFPB-DAPO-COF.



A 10 mL Schlenk tube was charged with 2,7-diamine-10-methyl-phenoxazine (DAPO, 20.4 mg, 0.09 mmol), 2,4,6-tris(4-formylphenyl)benzene (TFPB, 23.4 mg, 0.06 mmol) and CH_3CN/Mesitylene (1:1 v/v, 2 mL). The mixture was sonicated for 10 min to get a homogenous dispersion. Then, AcOH (3 M, 0.6 mL) was added and the vial was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and heated left undisturbed for 3 days at 120 °C. The yielded brown precipitate was centrifugation and washed with DMF and THF, separately. The collected powder was dried at 110 °C under vacuum for 24 h to give a yellow powder with (34 mg, 84%).

Detection of water in organic solvents

A certain amount of TFPT-DAPO-COF (1.000 mg) was ultrasonically dispersed in 10 mL of organic solvent, different volumes of water were added into this suspension. A 1 mL sample of the above-obtained solution was added to a clean quartz cell (1 × 1 cm^2) with slight shaking. The corresponding fluorescence spectra upon excitation at 507 nm were recorded.

The relationship between the quenching rate and water content

From the results of the fluorescence spectra, we estimated the ability of the COFs in detecting trace amount of water in organic solvents by using the Stern-Volmer equation shown below:

$$I_0/I = 1+K[Q]$$

where K was the quenching constant; [Q] was the volume percentage of water; I_0 was the initial luminescent intensity of luminescence material in organic solvent without water and I was the luminescent intensity of the luminescence material in organic solvent with different contents of water.

The detection limit calculated by:

$$LOD = 3S/K$$

where S is the standard deviation for THF solution of COF without adding water; K is the quenching constant, which was obtained by the slope of the Stern-Volmer curve at low water content.

Supporting figure

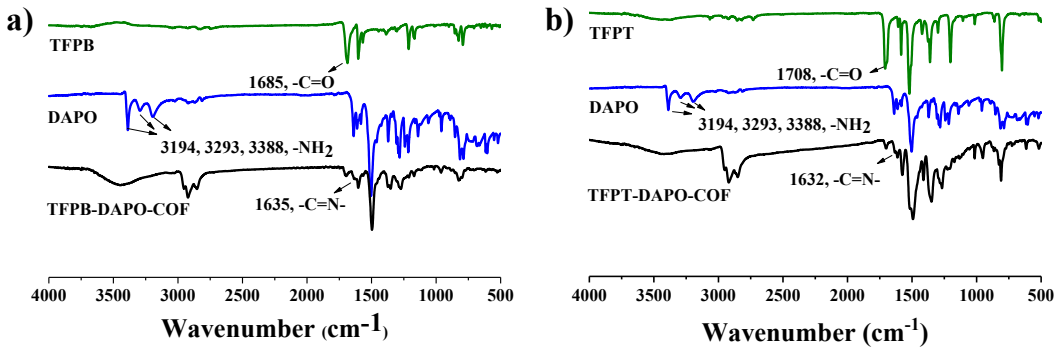


Figure S1. a) FT-IR spectra of TFPB (green), DAPO (blue) and TFPB-DAPO-COF (black); b) FT-IR spectra of TFPT (green), DAPO (blue) and TFPT-DAPO-COF (black).

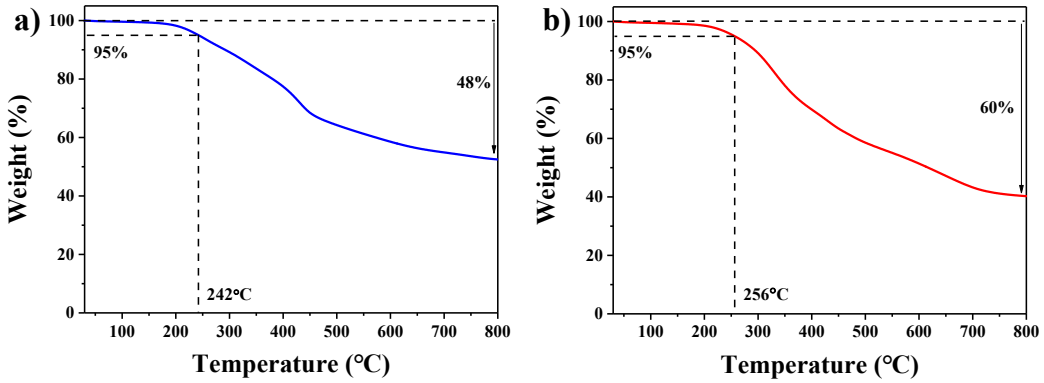


Figure S2. Thermogravimetric analysis of (a) TFPB-DAPO-COF and (b) TFPT-DAPO-COF under a nitrogen atmosphere with a heating rate of 10 °C/min.

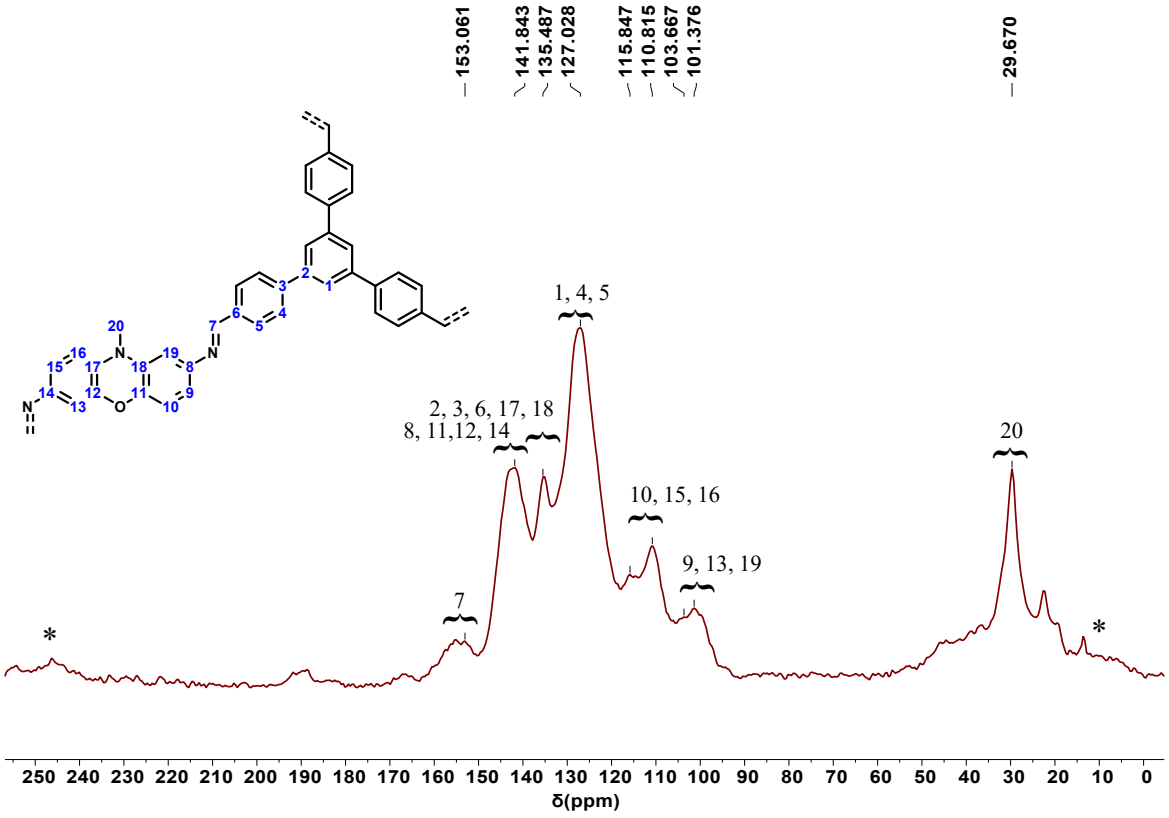


Figure S3. Solid-state ^{13}C NMR spectra and peak assignment for TFPB-DAPO-COF.

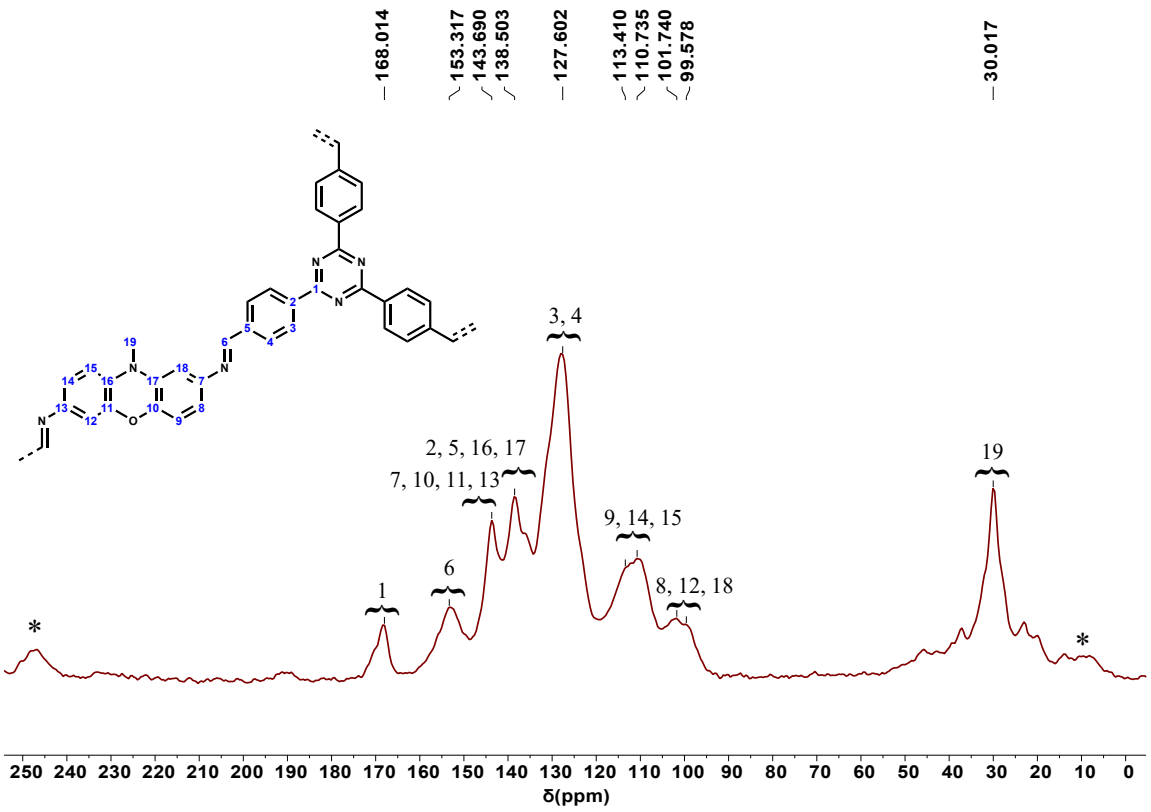


Figure S4. Solid-state ^{13}C NMR spectra and peak assignment for TFPT-DAPO-COF.

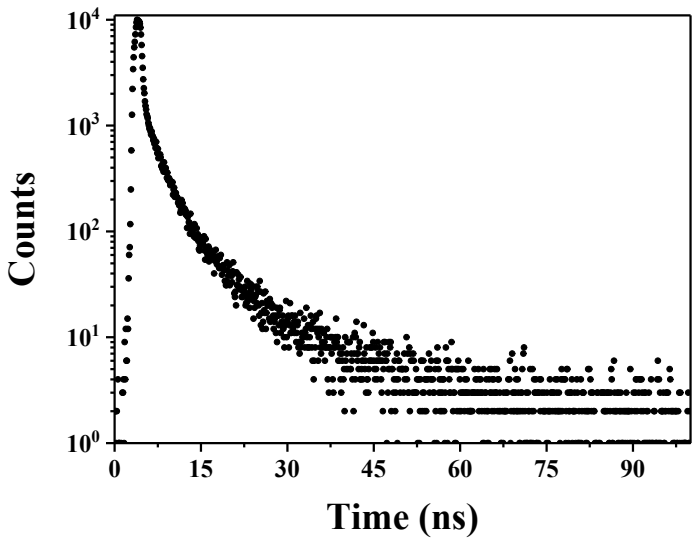


Figure S5. Photoluminescence decay curves of TFPT-DAPO-COF at room temperature.

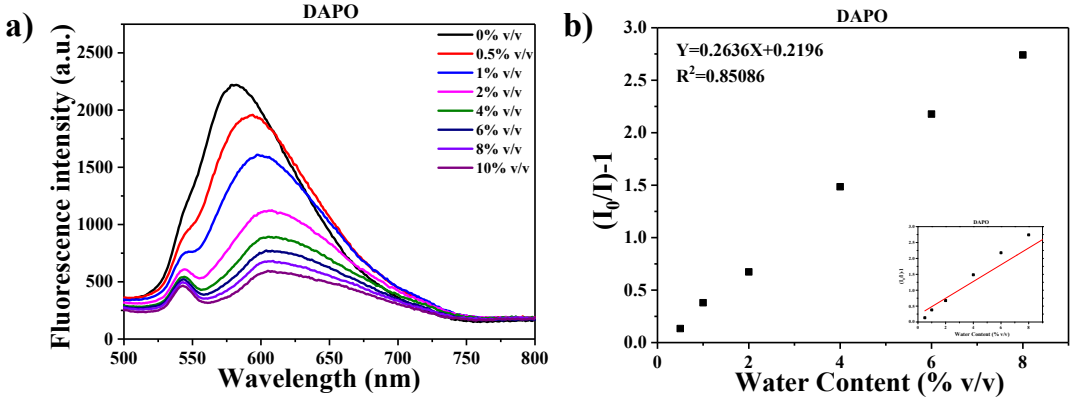


Figure S6. a) Fluorescence spectra of DAPO in THF with different water content (0-10% v/v); b) The linear correlation between the fluorescence of DAPO in THF and different water contents (0-10% v/v); The inset shows the linear correlation between 0-10% v/v.

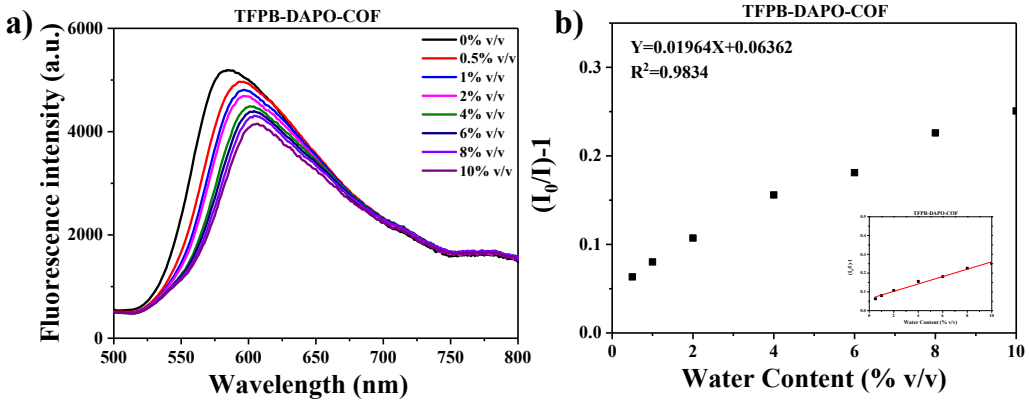


Figure S7. a) Fluorescence spectra of TFPB-DAPO-COF in THF with different water content (0-10% v/v); b) The linear correlation between the fluorescence of TFPB-DAPO-COF in THF and different water contents (0-10% v/v); The inset shows the linear correlation between 0-10% v/v.

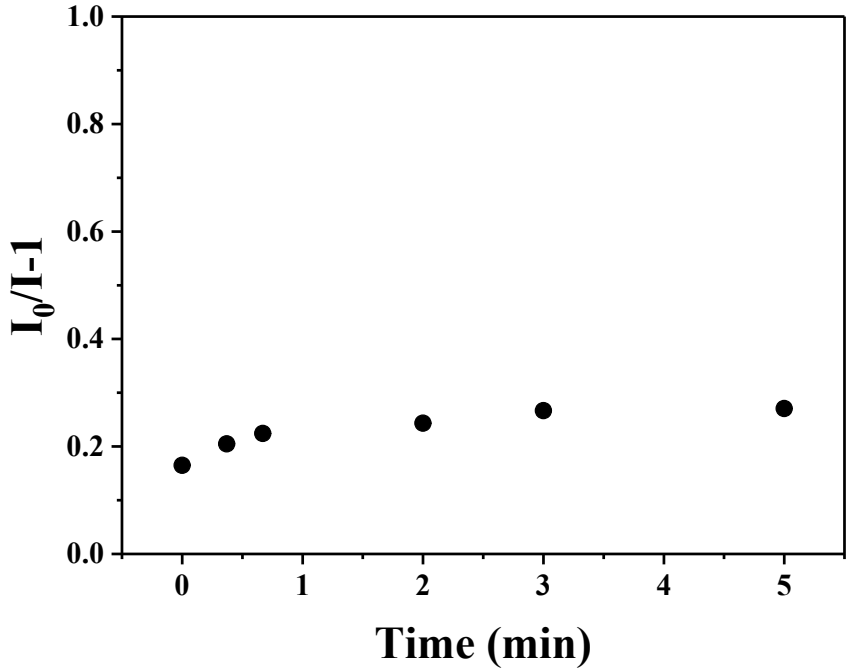


Figure S8. Effect of ultrasonication time on (I_0/I-1) of TFPT-DAPO-COF in THF with 1 wt% water.

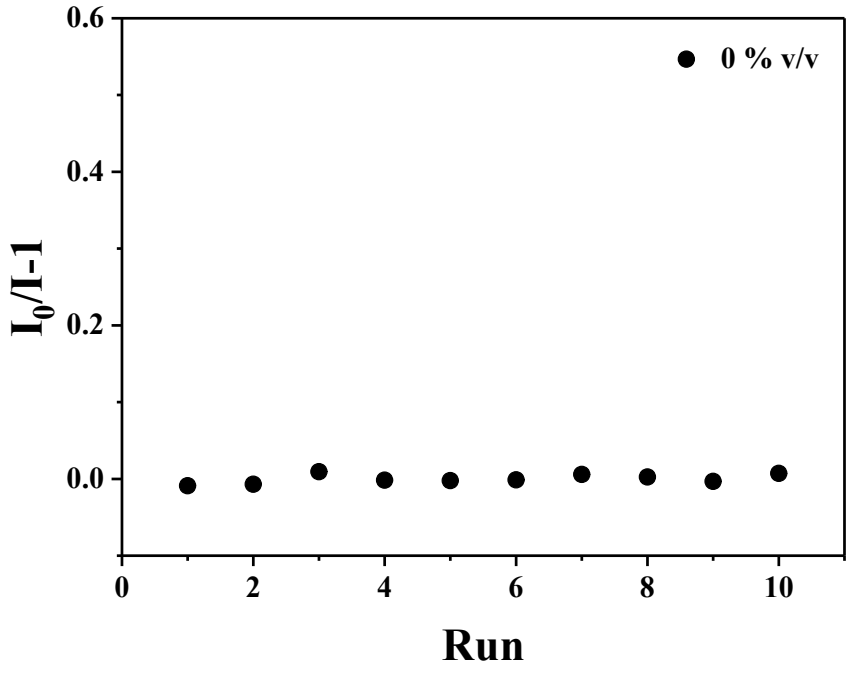


Figure S9. Relative standard deviations on (I_0/I-1) of TFPT-DAPO-COF for 10 replicate detections with 0% water in THF.

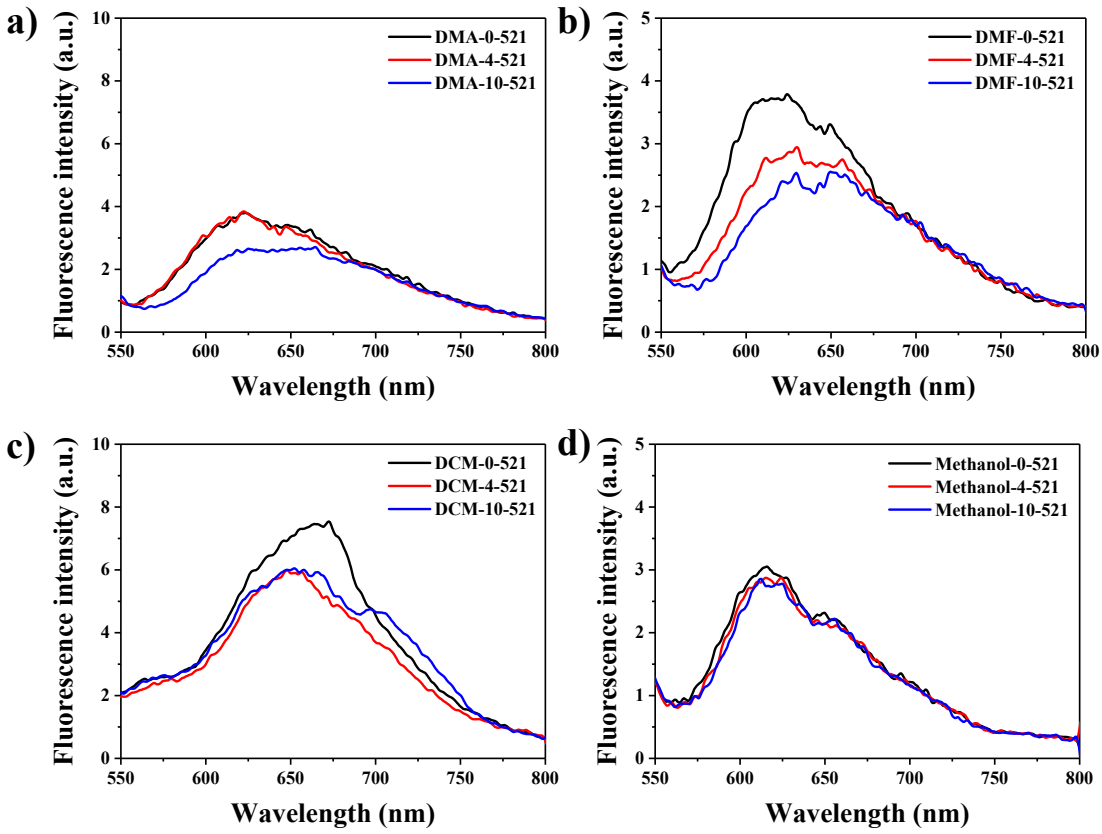


Figure S10. Under the excitation wavelength of 521nm, Fluorescence emission spectra of TFPT-DAPO-COF in some kinds of organic solvents with different water content (0-10% v/v), a) DMA; b) DMF; c) DCM; d) Methanol

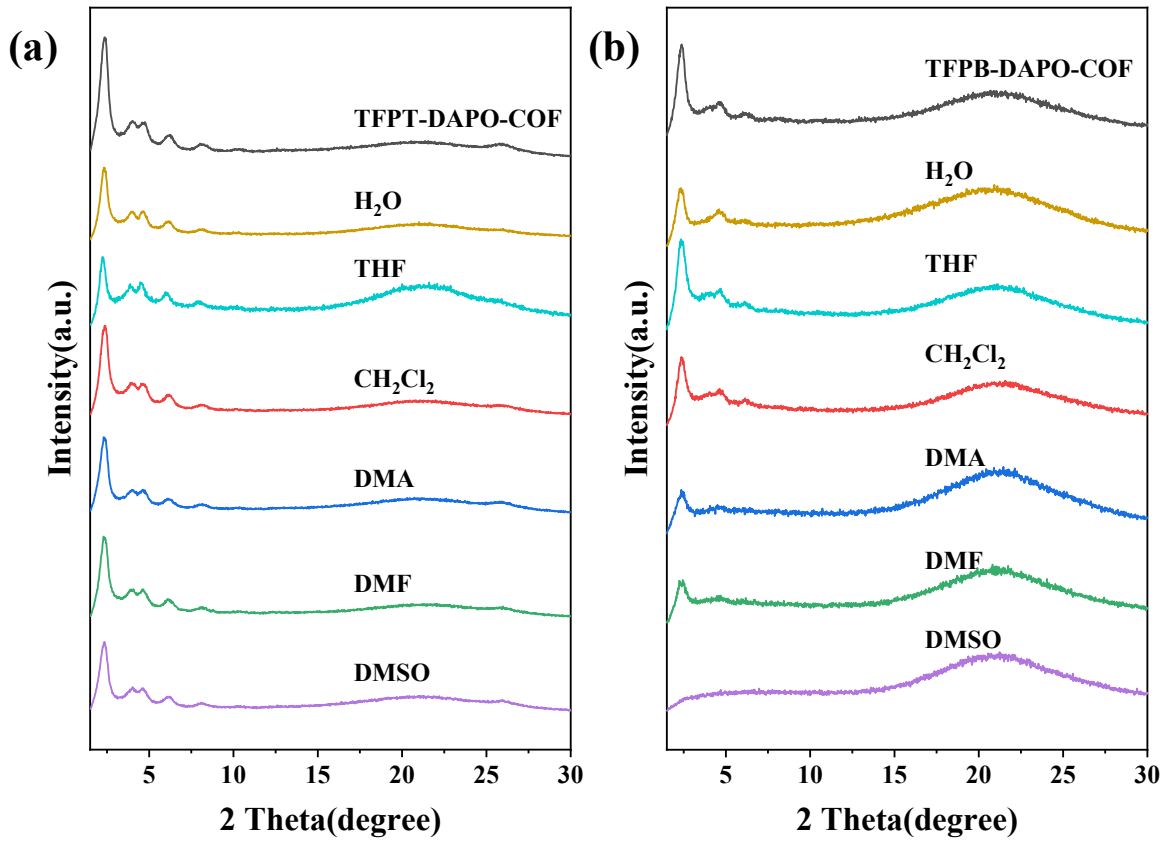


Figure S11. Chemical stability tests of the (a)TFPT-DAPO-COF and (b) TFPB-DAPO-COF. The samples were each exposed to identical conditions for 24 h (10 mg COFs in 4 mL solvents).

Supporting tables

Table S1. Various probes for sensing water in organic solvent.

Materials	solvents	Linear range	LOD	Ref.
GSH-$_L$-CuNCs	DMF	1.4× 10^{-3}-1.0× 10^{-2}% v/v	4.2 × 10^{-4} % v/v	5
	CH_3CN	7.0× 10^{-4}-1.0×10^{-2}% v/v	2.0 × 10^{-4} % v/v	
	THF	5.0× 10^{-4}-1.0×10^{-2}% v/v	1.6 × 10^{-4} % v/v	
Tb^{3+}@p-CDs/MOF	EtOH	0-30 % v/v	2.8× 10^{-1}% v/v	6
	DMF	0-30 % v/v	3.3× 10^{-1}% v/v	
	Cyclopropane	0-40 % v/v	2.5× 10^{-1}% v/v	
o-CDs	Acetone	/	1.9× 10^{-1}% v/v	7
	THF	/	1.3× 10^{-1}% v/v	
	CH_3CN	/	1.8× 10^{-1}% v/v	
Eu-MOF	DMF	5.0× 10^{-2}-6% v/v	2.0× 10^{-2}% v/v	8
TzDa	IPA	1.1-7.7% wt	8.5× 10^{-2}% wt	9
	Acetone	0.1-5.1 % wt	2.2× 10^{-2}% wt	
	THF	0.5-5.1% wt	2.6× 10^{-2}% wt	
	Ethanol	0.4-2.5% wt	3.4× 10^{-2}% wt	
	EA	0.6-3.2% wt	6.0× 10^{-3}% wt	
TAPT-BMTA-COF	CH_3CN	0.33-5% v/v	1.2× 10^{-1}% v/v	10
DAPO	THF	1-8% v/v	7.4× 10^{-2}% v/v	*This work*
TFPB-DAPO-COF	THF	1-8% v/v	3.2% v/v	
TFPT-DAPO-COF	THF	0.1-0.4% v/v	6.56× 10^{-2}% v/v	

Table S2. Fractional atomic coordinates for the unit cell of TFPT-DAPO-COF with AA stacking.

P6/m							
a = 45.630 Å, b = 45.595 Å, c = 2.00 Å, α = β = 90°, γ = 59.934°							
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
H1	6.45107	-5.30600	0.00000	C25	6.51550	-5.19438	0.00000
H2	6.47244	-5.26323	0.00000	C26	6.52740	-5.17074	0.00000
H3	6.36571	-5.17778	0.00000	C27	6.50360	-5.13490	0.00000
H4	6.34434	-5.22055	0.00000	C28	6.46790	-5.12292	0.00000
H5	6.38030	-5.39912	0.00000	C29	6.45599	-5.14678	0.00000
H6	6.42306	-5.46316	0.00000	C30	6.57476	-5.15873	0.00000
H7	6.50839	-5.44180	0.00000	C31	6.55095	-5.12289	0.00000
H8	6.46563	-5.37777	0.00000	C32	6.50385	-5.55152	0.00000
H9	6.28723	-5.23485	0.00000	C33	6.49195	-5.57516	0.00000
H10	6.22299	-5.21358	0.00000	C34	6.51576	-5.61100	0.00000
H11	6.24441	-5.32025	0.00000	C35	6.55146	-5.62276	0.00000
H12	6.30850	-5.34177	0.00000	C36	6.56336	-5.59912	0.00000
H13	6.41328	-5.16591	0.00000	C37	6.53956	-5.56328	0.00000
H14	6.52031	-5.50158	0.00000	C38	6.52766	-5.67048	0.00000
H15	6.53438	-5.22276	0.00000	C39	6.56336	-5.68224	0.00000
H16	6.44902	-5.09454	0.00000	C40	6.51576	-5.69412	0.00000
H17	6.42765	-5.13731	0.00000	C41	6.53956	-5.72996	0.00000
H18	6.46360	-5.56563	0.00000	C42	6.57526	-5.74172	0.00000
H19	6.59172	-5.60865	0.00000	C43	6.58717	-5.71808	0.00000
H20	6.54906	-5.54443	0.00000	C44	6.61046	-5.17071	0.00000
H21	6.48740	-5.68459	0.00000	C45	6.62236	-5.14685	0.00000
H22	6.53005	-5.74880	0.00000	C46	6.59856	-5.11123	0.00000
H23	6.61552	-5.72761	0.00000	C47	6.56286	-5.09925	0.00000
H24	6.62934	-5.19909	0.00000	C48	6.64617	-5.09935	0.00000
H25	6.65071	-5.15632	0.00000	C49	6.65807	-5.07549	0.00000

H26	6.54398	-5.07087	0.00000	C50	6.69377	-5.08747	0.00000
H27	6.66505	-5.12773	0.00000	C51	6.70567	-5.06361	0.00000
H28	6.71265	-5.11585	0.00000	C52	6.68187	-5.02798	0.00000
H29	6.73402	-5.07307	0.00000	C53	6.64617	-5.01600	0.00000
H30	6.62729	-4.98762	0.00000	C54	6.63427	-5.03987	0.00000
H31	6.60592	-5.03040	0.00000	C55	6.69352	-5.00400	0.00000
H32	6.69806	-4.89450	0.00000	C56	6.74113	-4.99212	0.00000
H33	6.65530	-4.83047	0.00000	C57	6.68162	-4.94452	0.00000
H34	6.56996	-4.85182	0.00000	C58	6.65782	-4.90889	0.00000
H35	6.61273	-4.91586	0.00000	C59	6.66972	-4.88503	0.00000
H36	6.55807	-4.79239	0.00000	C60	6.64591	-4.84941	0.00000
H37	6.79113	-5.05878	0.00000	C61	6.61021	-4.83743	0.00000
H38	6.85537	-5.08004	0.00000	C62	6.59831	-4.86129	0.00000
H39	6.83394	-4.97337	0.00000	C63	6.62211	-4.89691	0.00000
H40	6.76971	-4.95211	0.00000	C64	6.58641	-4.80181	0.00000
H41	6.89342	-5.02117	0.00000	C65	6.77683	-5.00410	0.00000
H42	6.95788	-5.14220	0.00000	C66	6.80063	-5.03994	0.00000
H43	7.00044	-5.05682	0.00000	C67	6.83634	-5.05170	0.00000
H44	6.93648	-5.03540	0.00000	C68	6.84824	-5.02806	0.00000
H45	7.07677	-5.23752	0.00000	C69	6.82444	-4.99222	0.00000
H46	7.14078	-5.25865	0.00000	C70	6.78873	-4.98046	0.00000
H47	7.11933	-5.15199	0.00000	C71	6.88395	-5.04004	0.00000
H48	7.18363	-5.27312	0.00000	C72	6.94345	-5.08764	0.00000
H49	6.61914	-5.66732	-0.52032	C73	6.96726	-5.12326	0.00000
H50	6.62535	-5.69853	0.14376	C74	7.00296	-5.13524	0.00000
H51	6.61677	-5.65540	0.37656	C75	7.01486	-5.11138	0.00000
H52	6.46679	-5.07048	0.24141	C76	6.99106	-5.07576	0.00000
H53	6.48631	-5.06553	-0.53651	C77	6.95536	-5.06378	0.00000
H54	6.50227	-5.06149	0.29509	C78	7.06247	-5.18284	0.00000
H55	7.03086	-5.21635	0.35897	C79	7.07412	-5.15885	0.00000

H56	7.01703	-5.20527	-0.52583	C80	7.08627	-5.21868	0.00000
H57	6.98727	-5.18144	0.16686	C81	7.12173	-5.23032	0.00000
C1	6.39674	-5.34911	0.00000	C82	7.13363	-5.20667	0.00000
C2	6.38484	-5.28963	0.00000	C83	7.10982	-5.17083	0.00000
C3	6.33723	-5.30151	0.00000	C84	7.19313	-5.25428	0.00000
C4	6.30153	-5.28953	0.00000	C85	6.61097	-5.67058	0.00000
C5	6.42054	-5.38473	0.00000	C86	6.49145	-5.07529	0.00000
C6	6.39649	-5.26564	0.00000	C87	7.01486	-5.19472	0.00000
C7	6.43219	-5.27762	0.00000	N1	6.36103	-5.33713	0.00000
C8	6.44409	-5.25376	0.00000	N2	6.40864	-5.32525	0.00000
C9	6.42029	-5.21814	0.00000	N3	6.34913	-5.27765	0.00000
C10	6.38458	-5.20616	0.00000	N4	6.46790	-5.20626	0.00000
C11	6.37268	-5.23002	0.00000	N5	6.51550	-5.11126	0.00000
C12	6.40864	-5.40859	0.00000	N6	6.48005	-5.51568	0.00000
C13	6.43244	-5.44421	0.00000	N7	6.57526	-5.65860	0.00000
C14	6.46815	-5.45619	0.00000	N8	6.61046	-5.08737	0.00000
C15	6.48005	-5.43233	0.00000	N9	6.72922	-5.01598	0.00000
C16	6.45625	-5.39671	0.00000	N10	6.71732	-4.95650	0.00000
C17	6.27772	-5.25369	0.00000	N11	6.66972	-4.96838	0.00000
C18	6.24202	-5.24193	0.00000	N12	6.90775	-5.07566	0.00000
C19	6.23012	-5.26557	0.00000	N13	7.02677	-5.17086	0.00000
C20	6.25392	-5.30141	0.00000	N14	7.16933	-5.21843	0.00000
C21	6.28962	-5.31339	0.00000	N15	6.59907	-5.77756	0.00000
C22	6.43219	-5.19428	0.00000	O1	6.56311	-5.18250	0.00000
C23	6.49195	-5.49203	0.00000	O2	6.50385	-5.63464	0.00000
C24	6.47980	-5.18240	0.00000	O3	7.05032	-5.12323	0.00000

Table S3. Fractional atomic coordinates for the unit cell of TFPB-DAPO-COF with AA stacking.

P6/m							
a = 45.630 Å, b = 45.598 Å, c = 2.00 Å, α = β = 90°, γ = 59.926°							
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
H1	7.24546	-6.78679	0.00000	C22	7.12407	-6.69633	0.00000
H2	7.33072	-6.76544	0.00000	C23	7.14788	-6.73195	0.00000
H3	7.22382	-6.67996	0.00000	C24	7.18359	-6.74394	0.00000
H4	7.34519	-6.73654	0.00000	C25	7.32616	-6.62508	0.00000
H5	7.36643	-6.69409	0.00000	C26	7.38568	-6.92248	0.00000
H6	7.25953	-6.60860	0.00000	C27	7.37352	-6.61308	0.00000
H7	7.23829	-6.65105	0.00000	C28	7.40923	-6.62506	0.00000
H8	7.27400	-6.82949	0.00000	C29	7.42113	-6.60120	0.00000
H9	7.31666	-6.89371	0.00000	C30	7.39733	-6.56558	0.00000
H10	7.40212	-6.87247	0.00000	C31	7.36162	-6.55360	0.00000
H11	7.35935	-6.80843	0.00000	C32	7.34972	-6.57745	0.00000
H12	7.18081	-6.66539	0.00000	C33	7.46874	-6.58933	0.00000
H13	7.11684	-6.64396	0.00000	C34	7.44494	-6.55371	0.00000
H14	7.13850	-6.75089	0.00000	C35	7.39758	-6.98196	0.00000
H15	7.20247	-6.77232	0.00000	C36	7.38593	-7.00594	0.00000
H16	7.30730	-6.59669	0.00000	C37	7.40974	-7.04156	0.00000
H17	7.41401	-6.93190	0.00000	C38	7.44519	-7.05342	0.00000
H18	7.42811	-6.65344	0.00000	C39	7.45709	-7.02956	0.00000
H19	7.34274	-6.52522	0.00000	C40	7.43329	-6.99394	0.00000
H20	7.32137	-6.56798	0.00000	C41	7.42164	-7.10104	0.00000
H21	7.35762	-6.99665	0.00000	C42	7.45735	-7.11303	0.00000
H22	7.48544	-7.03903	0.00000	C43	7.40974	-7.12490	0.00000
H23	7.44267	-6.97500	0.00000	C44	7.43354	-7.16052	0.00000
H24	7.38139	-7.11543	0.00000	C45	7.46925	-7.17251	0.00000
H25	7.42416	-7.17946	0.00000	C46	7.48115	-7.14865	0.00000

H26	7.50950	-7.15812	0.00000	C47	7.50445	-6.60132	0.00000
H27	7.52333	-6.62970	0.00000	C48	7.51635	-6.57746	0.00000
H28	7.54470	-6.58693	0.00000	C49	7.49255	-6.54184	0.00000
H29	7.43796	-6.50147	0.00000	C50	7.45684	-6.52985	0.00000
H30	7.55881	-6.55821	0.00000	C51	7.53990	-6.52984	0.00000
H31	7.60654	-6.54631	0.00000	C52	7.55181	-6.50620	0.00000
H32	7.62778	-6.50386	0.00000	C53	7.58751	-6.51797	0.00000
H33	7.52088	-6.41838	0.00000	C54	7.59942	-6.49433	0.00000
H34	7.49964	-6.46082	0.00000	C55	7.57561	-6.45849	0.00000
H35	7.64210	-6.47522	0.00000	C56	7.53990	-6.44672	0.00000
H36	7.62083	-6.36830	0.00000	C57	7.52800	-6.47036	0.00000
H37	7.53535	-6.38947	0.00000	C58	7.58751	-6.43485	0.00000
H38	7.59207	-6.32542	0.00000	C59	7.62322	-6.44683	0.00000
H39	7.54941	-6.26121	0.00000	C60	7.63512	-6.42298	0.00000
H40	7.46395	-6.28245	0.00000	C61	7.61132	-6.38713	0.00000
H41	7.50672	-6.34648	0.00000	C62	7.57561	-6.37537	0.00000
H42	7.45205	-6.22302	0.00000	C63	7.56371	-6.39901	0.00000
H43	7.68526	-6.48952	0.00000	C64	7.55181	-6.33953	0.00000
H44	7.74923	-6.51095	0.00000	C65	7.56371	-6.31589	0.00000
H45	7.72757	-6.40402	0.00000	C66	7.53990	-6.28005	0.00000
H46	7.66383	-6.38273	0.00000	C67	7.50420	-6.26806	0.00000
H47	7.78718	-6.45171	0.00000	C68	7.49229	-6.29192	0.00000
H48	7.85151	-6.57286	0.00000	C69	7.51610	-6.32754	0.00000
H49	7.89433	-6.48747	0.00000	C70	7.48039	-6.23244	0.00000
H50	7.83009	-6.46620	0.00000	C71	7.67083	-6.43496	0.00000
H51	7.97066	-6.66818	0.00000	C72	7.69464	-6.47058	0.00000
H52	8.03463	-6.68960	0.00000	C73	7.73035	-6.48257	0.00000
H53	8.01323	-6.58280	0.00000	C74	7.74199	-6.45859	0.00000
H54	8.07779	-6.70391	0.00000	C75	7.71819	-6.42296	0.00000
H55	7.51287	-7.09777	-0.52032	C76	7.68274	-6.41110	0.00000

H56	7.51909	-7.12898	0.14376	C77	7.77770	-6.47057	0.00000
H57	7.51050	-7.08585	0.37656	C78	7.83722	-6.51818	0.00000
H58	7.36077	-6.50127	0.24158	C79	7.86102	-6.55402	0.00000
H59	7.38028	-6.49635	-0.53652	C80	7.89673	-6.56579	0.00000
H60	7.39627	-6.49232	0.29493	C81	7.90863	-6.54215	0.00000
H61	7.92463	-6.64694	0.35819	C82	7.88483	-6.50631	0.00000
H62	7.91072	-6.63577	-0.52605	C83	7.84912	-6.49454	0.00000
H63	7.88105	-6.61194	0.16785	C84	7.95624	-6.61361	0.00000
C1	7.25475	-6.76778	0.00000	C85	7.96814	-6.58976	0.00000
C2	7.29046	-6.77955	0.00000	C86	7.98005	-6.64924	0.00000
C3	7.30236	-6.75591	0.00000	C87	8.01575	-6.66122	0.00000
C4	7.27855	-6.72007	0.00000	C88	8.02766	-6.63736	0.00000
C5	7.24285	-6.70830	0.00000	C89	8.00385	-6.60174	0.00000
C6	7.23094	-6.73194	0.00000	C90	8.08717	-6.68497	0.00000
C7	7.19524	-6.71995	0.00000	C91	7.50470	-7.10103	0.00000
C8	7.31426	-6.81539	0.00000	C92	7.38542	-6.50610	0.00000
C9	7.29046	-6.69643	0.00000	C93	7.90863	-6.62527	0.00000
C10	7.32616	-6.70819	0.00000	N1	7.36162	-6.63693	0.00000
C11	7.33807	-6.68456	0.00000	N2	7.40923	-6.54172	0.00000
C12	7.31426	-6.64871	0.00000	N3	7.37377	-6.94633	0.00000
C13	7.27855	-6.63695	0.00000	N4	7.46900	-7.08904	0.00000
C14	7.26665	-6.66059	0.00000	N5	7.50445	-6.51798	0.00000
C15	7.30236	-6.83903	0.00000	N6	7.80151	-6.50619	0.00000
C16	7.32616	-6.87487	0.00000	N7	7.92053	-6.60163	0.00000
C17	7.36187	-6.88685	0.00000	N8	8.06336	-6.64935	0.00000
C18	7.37377	-6.86300	0.00000	N9	7.49305	-7.20813	0.00000
C19	7.34997	-6.82737	0.00000	O1	7.45684	-6.61319	0.00000
C20	7.17143	-6.68433	0.00000	O2	7.39783	-7.06542	0.00000
C21	7.13572	-6.67234	0.00000	O3	7.94434	-6.55413	0.00000

Table S4. Elemental analysis of the TFPT-DAPO-COF and TFPB-DAPO-COF.

Sample	Expected C%	Expected H%	Expected N%	Found C%	Found H%	Found N%
TFPB-DAPO-COF	82.34	4.83	9.29	77.40	6.52	5.42
TFPT-DAPO-COF	76.69	4.63	15.42	77.36	7.74	8.88

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