

Supporting Information

Fabricating s-Collidine-Derived Vinylene-Linked Covalent Organic Frameworks for Photocatalysis

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1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on Vertex80+Hyperion 2000 spectrometer. The Solid-State Ultraviolet-Visible Spectroscopy were recorded on U-4100 spectrometer. Thermogravimetric analyses (TGA) were carried out under an N_2 atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ on a *TGA5500 thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Smart Lab 9kW. NMR experiments were carried out on a *JNM-ECZ400S spectrometer operating at resonance frequencies of 400 M Hz. The N_2 sorption isotherms were recorded at 77 K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurement, the samples were activated at 120 $^{\circ}\text{C}$ under vacuum ($< 10^{-3}$ torr) for 12h. SEM images were obtained with a REGULUS8230 scanning electron microscope. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were obtained with a JEM-2100 scanning electron microscope.

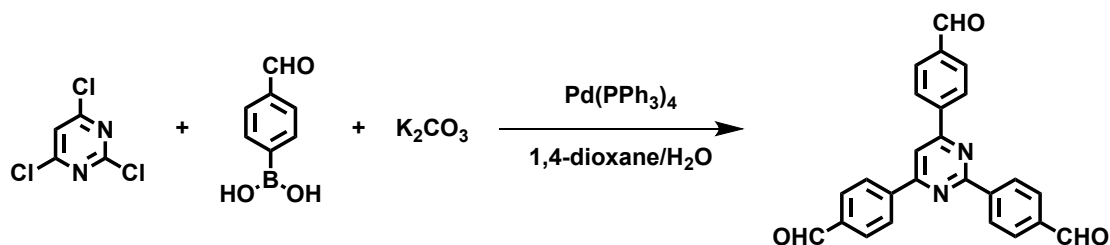
The Pawley refinement of the experimental PXRD was conducted by the Reflux module. The stimulated PXRD patterns were determined by the Reflex module. And the unit cell was optimized by Forcite module under molecular mechanics calculation using Universal as the forcefield to give the relative total energy.

2. Electrochemical Studies

Fluoride-tin oxide (FTO) glasses were firstly cleaned by sonication in ethanol for 30 min and dried under nitrogen flow. 5 mg of COF powder was mixed with 1 mL ethanol and ultra-sonicated for 2h to get slurry. 20 μL of the suspension was drop-casted on the FTO glass and dried in an oven at 60 $^{\circ}\text{C}$ for 30min. The photocurrent response was measured using a three-electrode setup with a working electrode (COF on FTO glass), counter electrode (Pt wire), and reference electrode (Ag/AgCl). The electrolyte was a 0.5 M Na_2SO_4 aqueous solution and was purged. The photocurrent responses were conducted with an Ivium workstation, with the working electrodes irradiated from the front side and the visible light was generated by LED. Electrochemical impedance spectroscopy (EIS) measurements were performed at Init E of 1.5 V with AC amplitude in the frequencies range of 1 Hz to 1×10^5 Hz. For Mott-Schottky experiments, the perturbation signal was 5 mV with the frequency of 1500, 2000 and 2500 Hz.

3. Synthesis

3.1 Synthesis of 4,4',4''-(pyrimidine-2,4,6-triyl)tribenzaldehyde (TFPM).

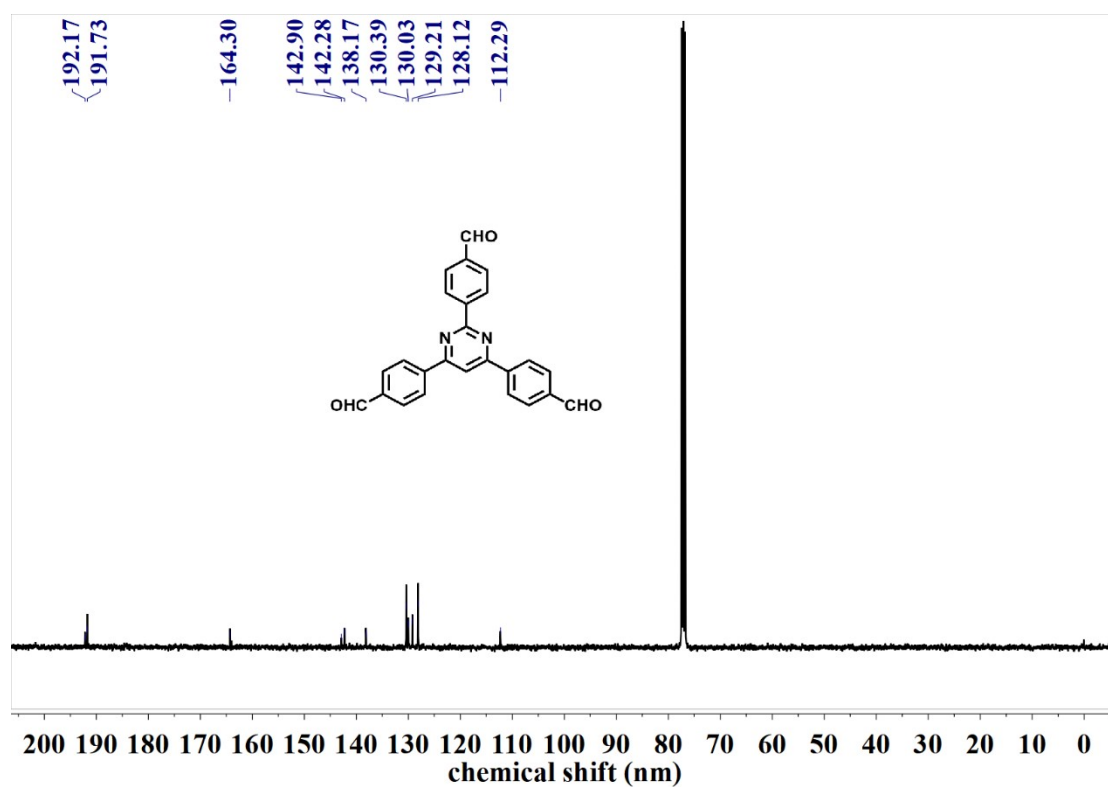
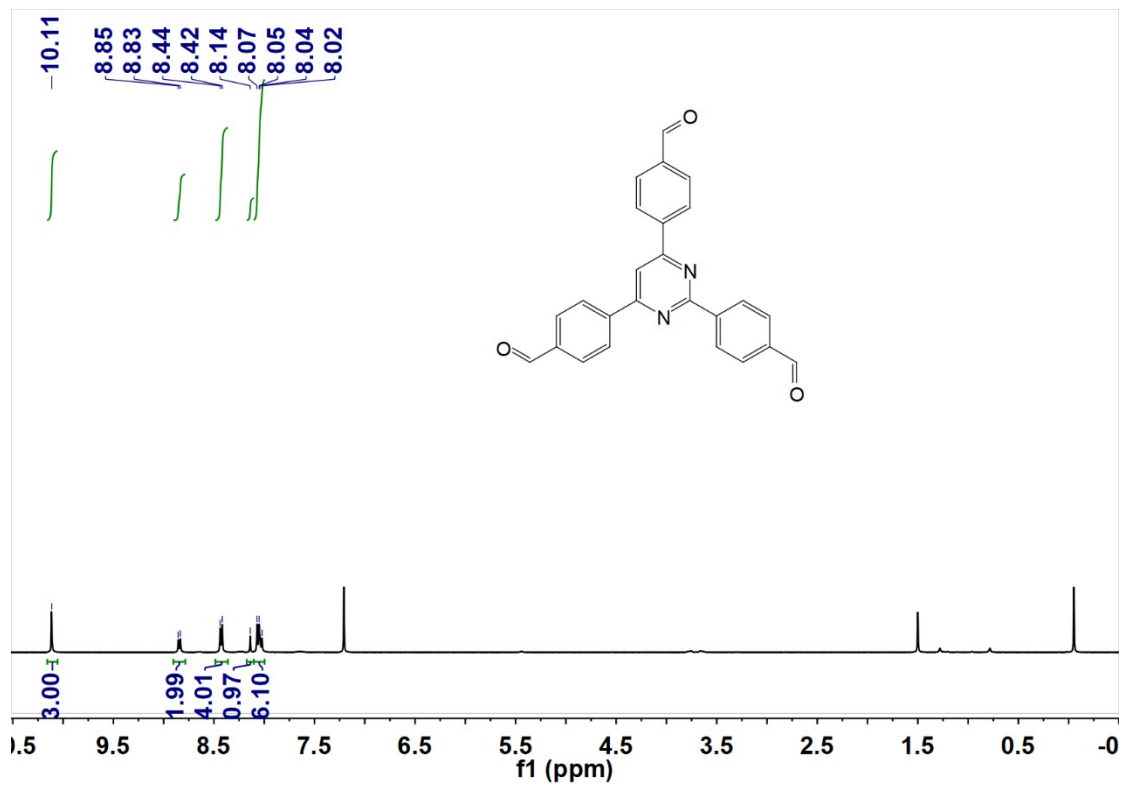


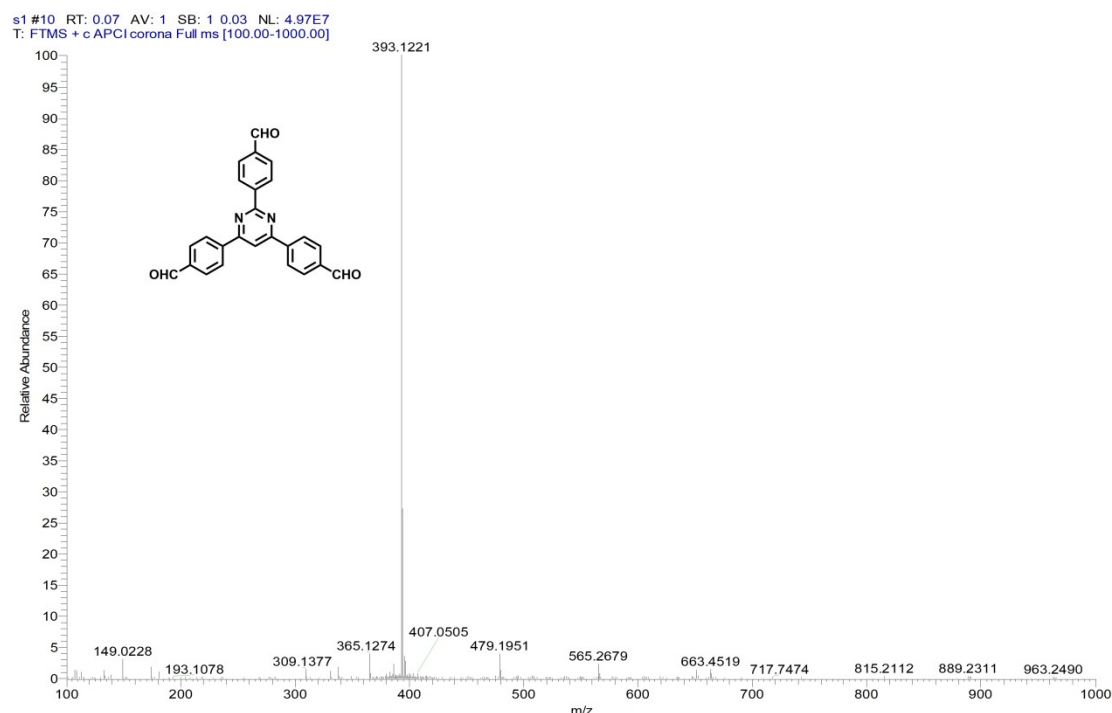
A solution of 2,4,6-trichloropyrimidine (0.92 g, 5.02 mmol), 2-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.38 g, 22.57 mmol), potassium carbonate (5.55 g, 40.13 mmol) in dioxane (30 mL) and H_2O (10 mL) was firstly prepared. Then $\text{Pd}(\text{PPh}_3)_4$ (150 mg) were added to this solution. The resulting mixture was stirred for 12 hours at 105 $^{\circ}\text{C}$ under nitrogen atmosphere. After that, the reaction cooled to room temperature, extracted with DCM, and purified by chromatography (DCM) on a silica gel column to give the product

TFPM. ^1H NMR (400 MHz, CDCl_3): δ 10.11 (s, 3H), 8.83 – 8.85 (m, 2H), 8.42 – 8.44 (m, 4H), 8.02 – 8.14 (m, 7H).

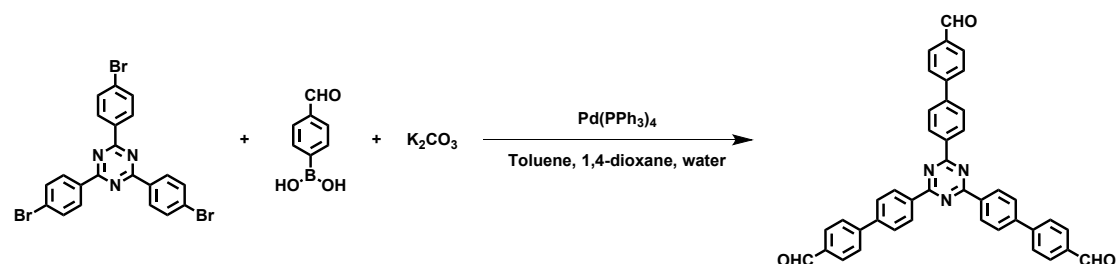
^{13}C NMR (400 MHz, CDCl_3): δ (p.p.m.) 192.17, 191.73, 164.30, 142.90, 142.28, 138.17, 130.39, 130.03, 129.21, 128.12, 112.29.

m/z calculated for TFPM ($\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_3$), 393.12 $[\text{M}+\text{H}]^+$; found, 393.1221.





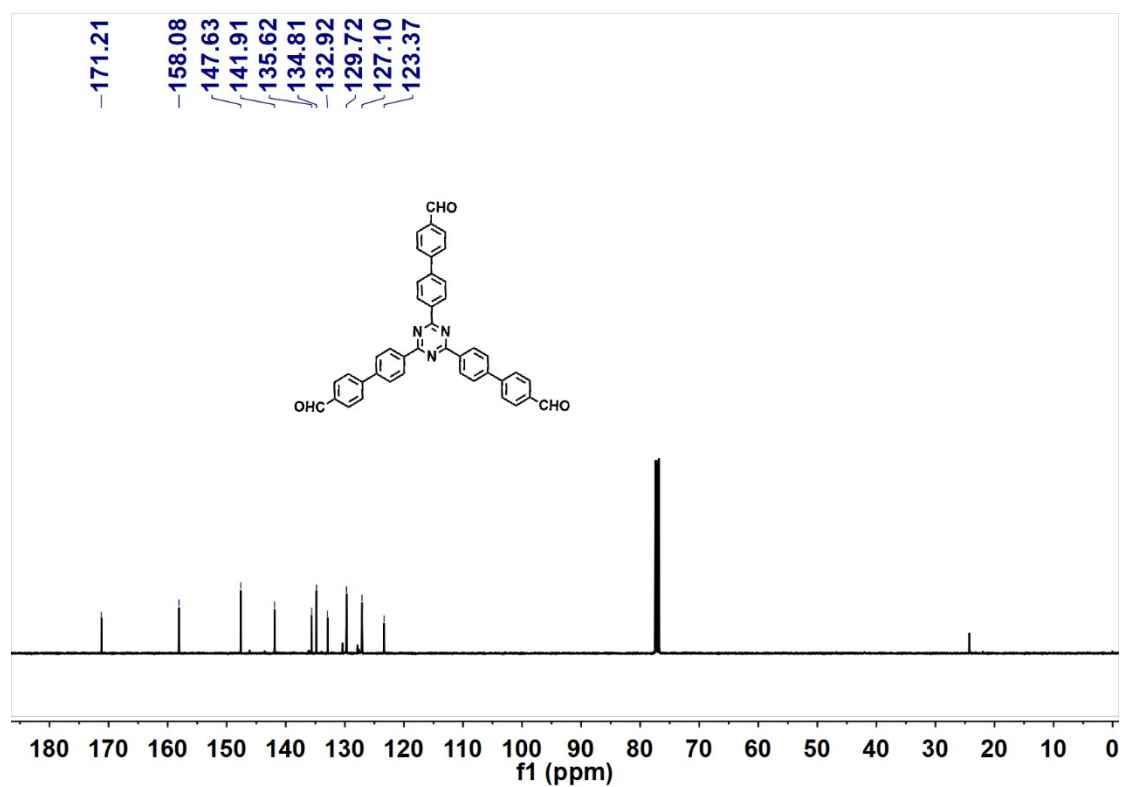
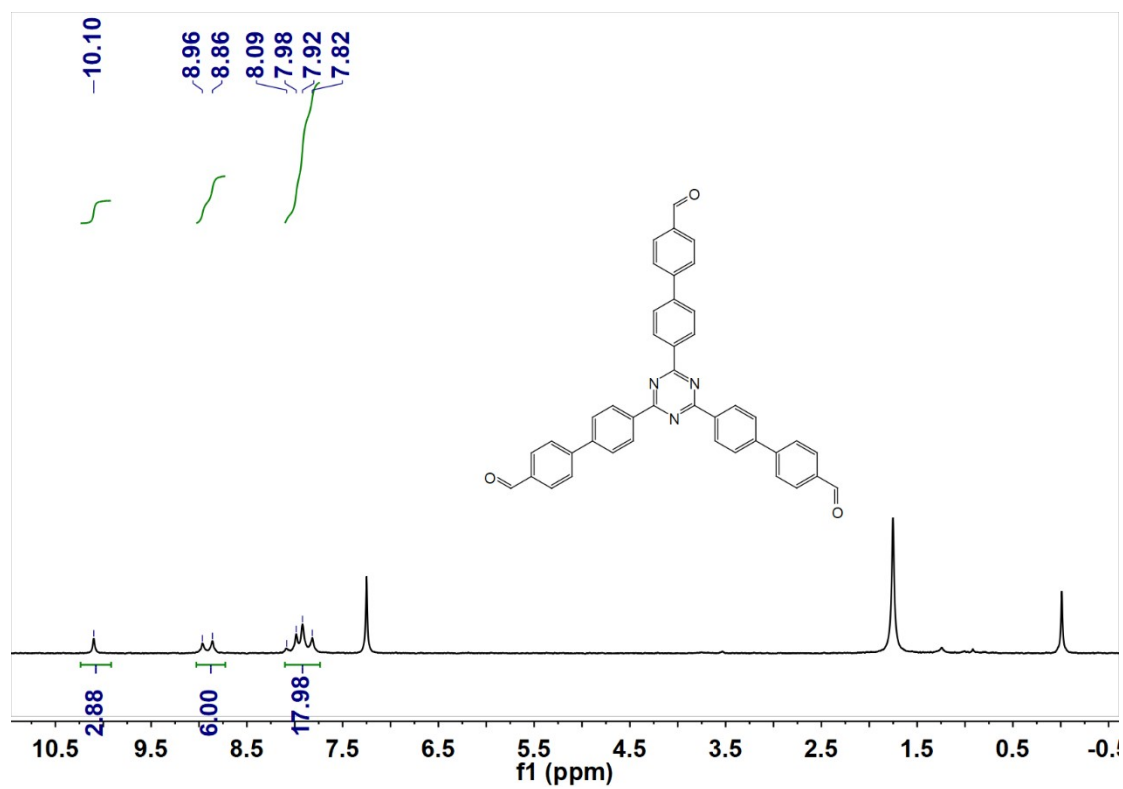
3.2 Synthesis of 1,3,5-tris-(4'-formyl-biphenyl-4-yl)triazine (TFBT)



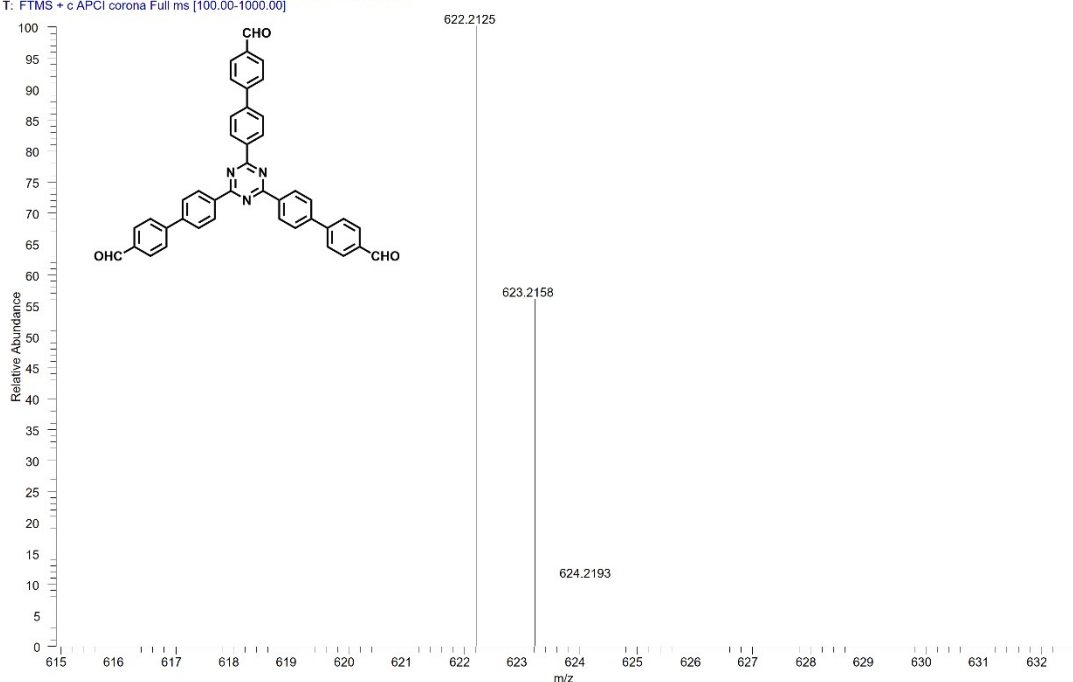
To an oven-dried Schlenk flask equipped with stirrer bar was added 1,3,5-tribromobenzene (2.73 g, 5.0 mmol), 4-formylphenylboronic acid (2.40 g, 16.0 mmol) and K_2CO_3 (5.53 g, 40 mmol) before the flask was evacuated and refilled with N_2 three times. Toluene, water and 1,4-dioxane were added and the mixture was degassed (N_2) for 30 min prior to addition of $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol). The resulting suspension was heated at 90 °C and reflux for 3 d. After being cooled to room temperature, the solvent was removed by filtration under reduced pressure. The precipitate was filtered and washed with acetone, water and methanol. The resulting solid was collected and dried in vacuo oven to afford the desired product as off-white solid. (1.77 g, 57 %). 1H NMR ($CDCl_3$, 400 MHz): δ 10.10 (s, 3H), 8.86-8.96 (m, 6H), 7.82-8.09 (m, 18H).

^{13}C NMR (400 MHz, $CDCl_3$): δ (p.p.m.) 171.21, 158.08, 147.63, 141.91, 135.62, 134.81, 132.92, 129.72, 127.10, 123.37.

m/z calculated for TFBT ($C_{42}H_{27}N_3O_3$), 622.21 $[M+H]^+$; found, 622.2125.

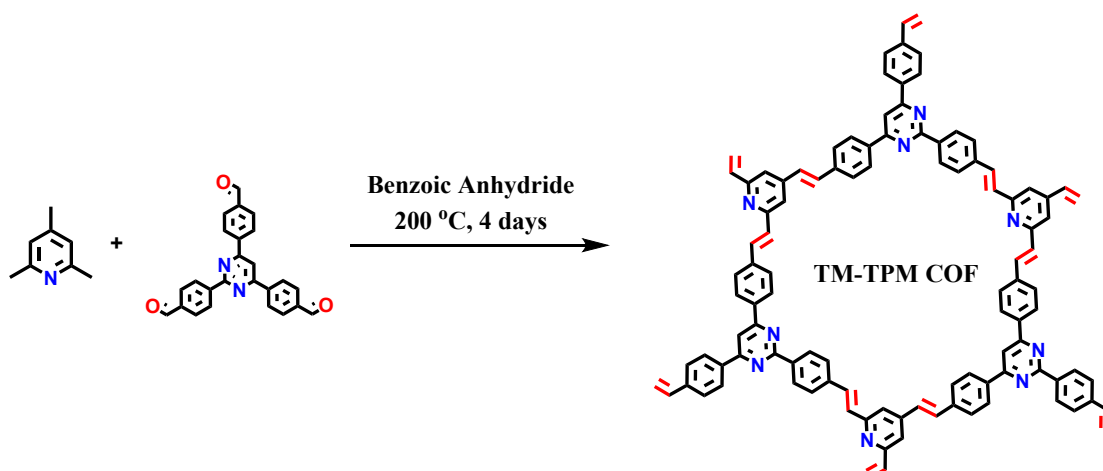


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T: FTMS + c APCI corona Full ms [100.00-1000.00]



3.3 General Synthesis of COFs and POPs

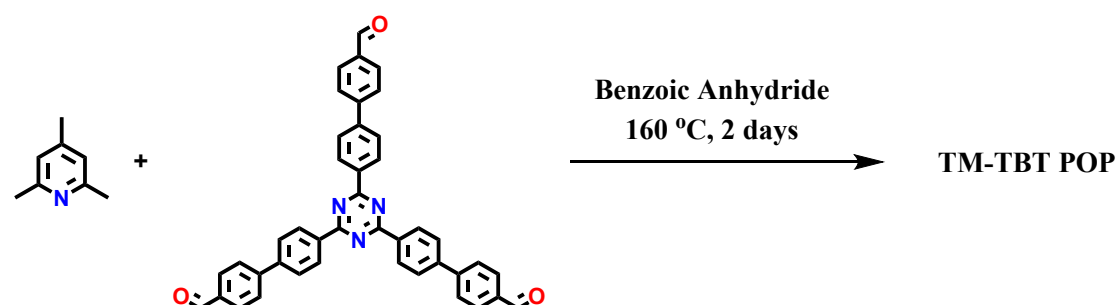
Synthesis of T M-TPM-COF



A Pyrex tube was charged with 2,4,6-Trimethylpyridine (**TMP**) (24.20 mg, 199.70 μmol), 4,4',4''-(pyrimidine-2,4,6-triyl)tribenzaldehyde (**TFPM**) (78.36 mg, 199.70 μmol) and benzoic anhydride (135.53 mg, 0.599 mmol). The tube was evacuated under dynamic vacuum and flame sealed. Following this, the tube was heated to 200 °C and kept at this temperature for 4 days. After the reaction, the yellow solid was washed with tetrahydrofuran, acetone and methanol. Finally, the material was dried at 120 °C under vacuum condition to yield the **TM-TP-COF** powders.

Chemical reaction scheme showing the synthesis of TM-TBT COF. The reaction involves 2,4,6-trimethylpyridine (NMP) and a triformyl derivative of 1,3,5-trisubstituted benzene (TBT-CHO) reacting in the presence of benzoic anhydride at 200 °C for 4 days to form the TM-TBT COF. The product is a 2D hexagonal lattice structure with NMP and TBT units linked by imine bonds.

Synthesis of TM-TBT-POP



S-7

4. FT-IR of COFs

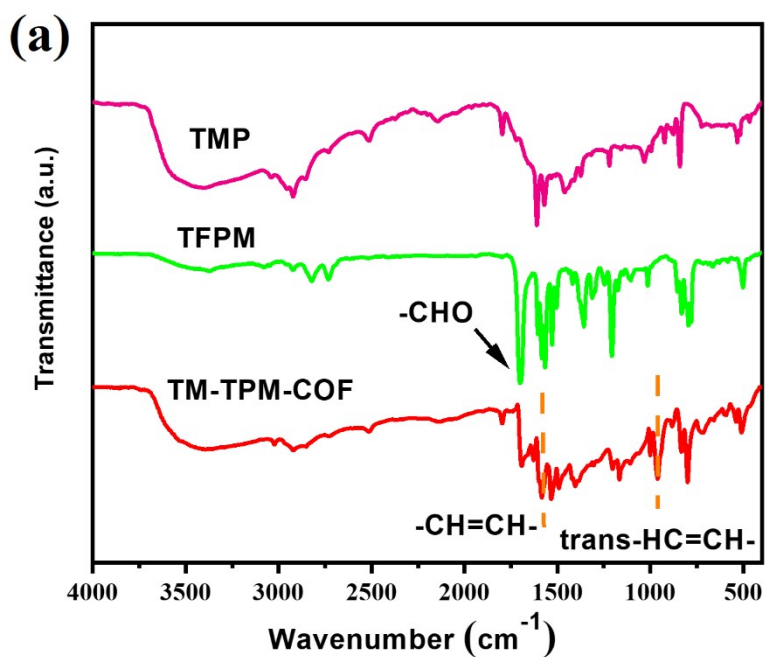


Figure S1. FT-IR spectra of TFPM, TMP, and TM-TPM COF.

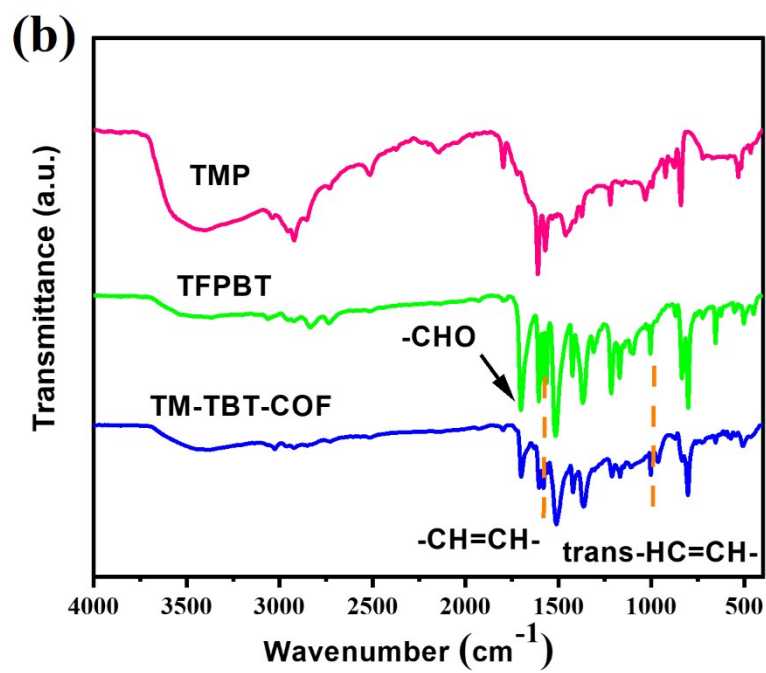
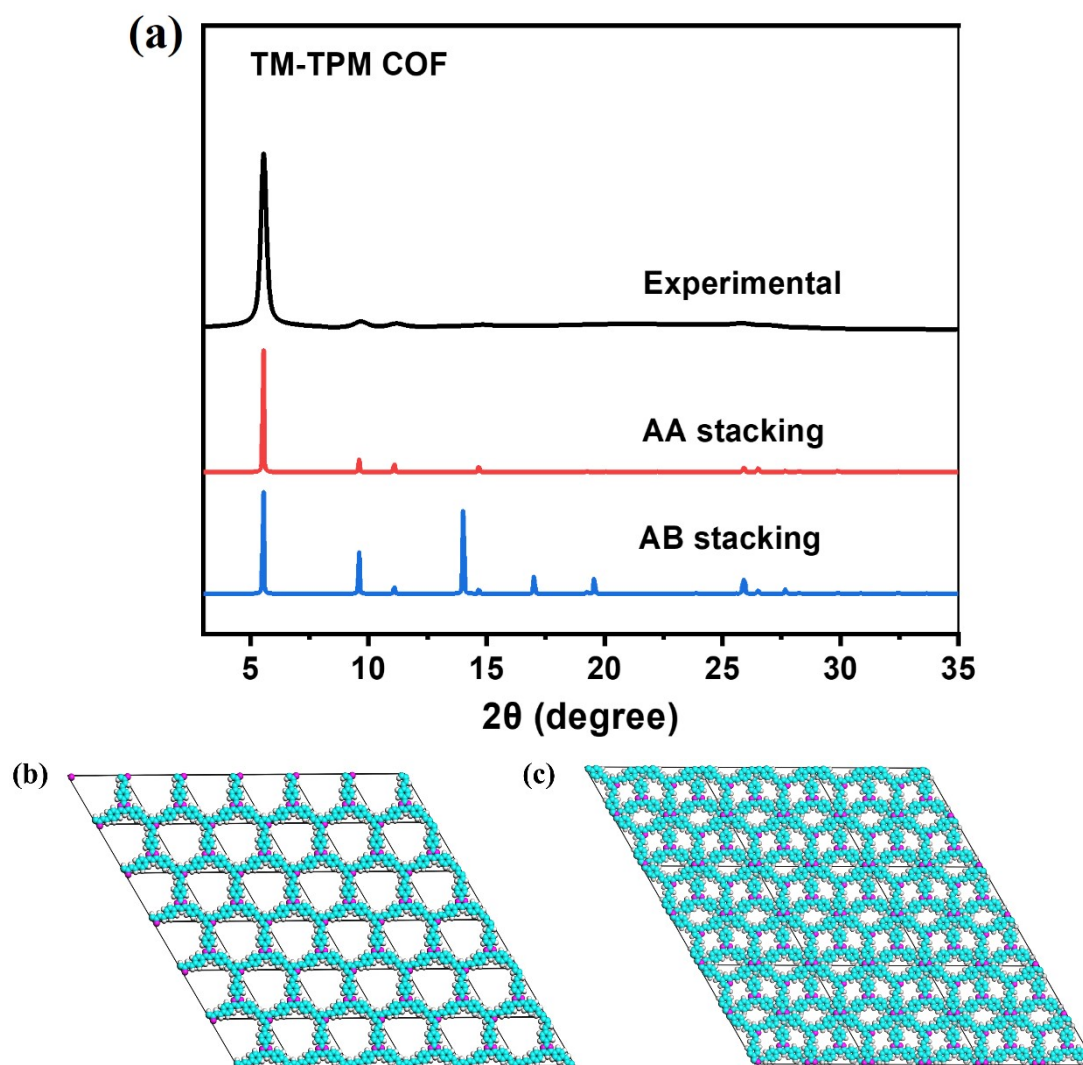
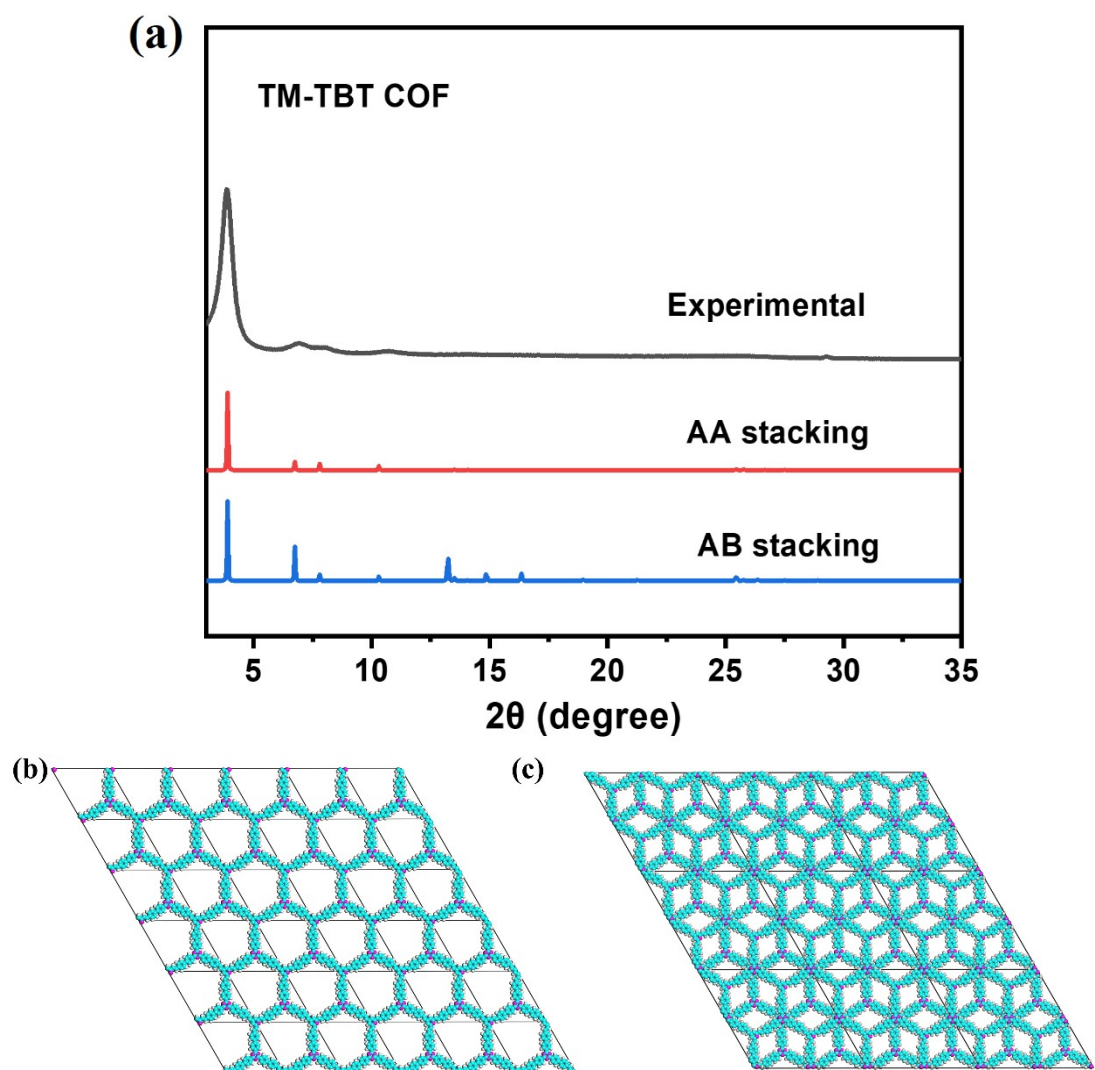


Figure S2. FT-IR spectra of TFPBT, TMP, and TM-TBT COF.

5. Structure Simulation and PXRD of TM-TPM COF and TM-TBT COF



Figures S3 PXRD of TM-TPM COF and the scheme of simulated AA stacking, AB stacking for TM-TPM COF.



Figures S4 PXRD of TM-TBT COF and the scheme of simulated AA stacking, AB stacking for TM-TBT COF.

6. BET

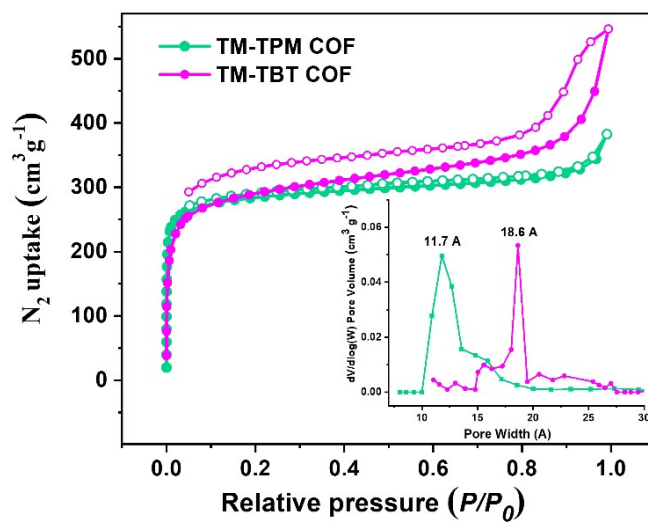


Figure S5 Nitrogen adsorption /desorption isotherms at 77K, inset: the pore size distribution maps of TM-TPM-COF (green) and TM-TBT-COF (pink)

7. Scanning Electron Microscopy (SEM)

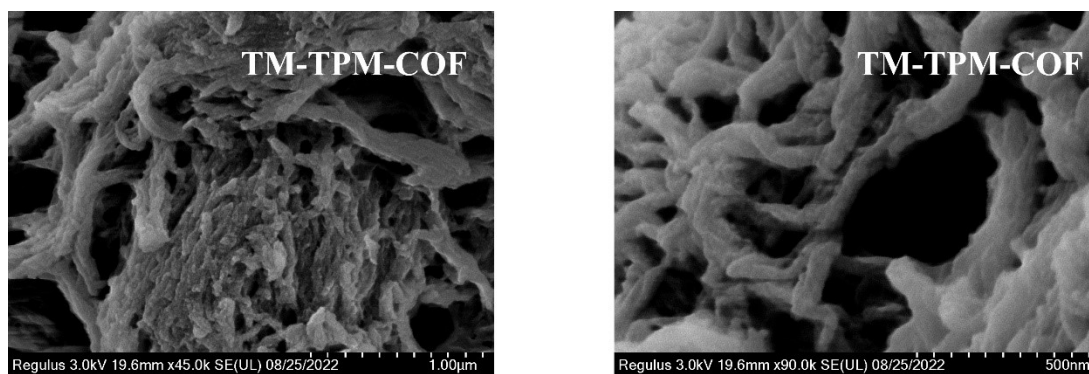


Figure S6. SEM images of TM-TPM COF

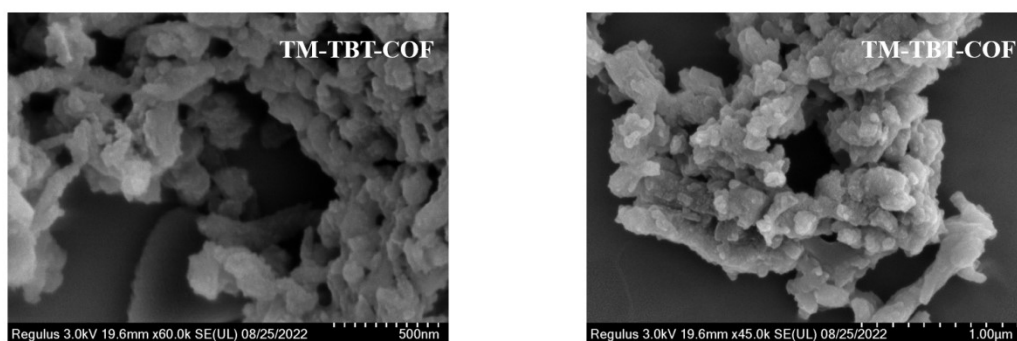


Figure S7. SEM images of TM-TBT COF

8. Transmission electron microscopy (TEM)

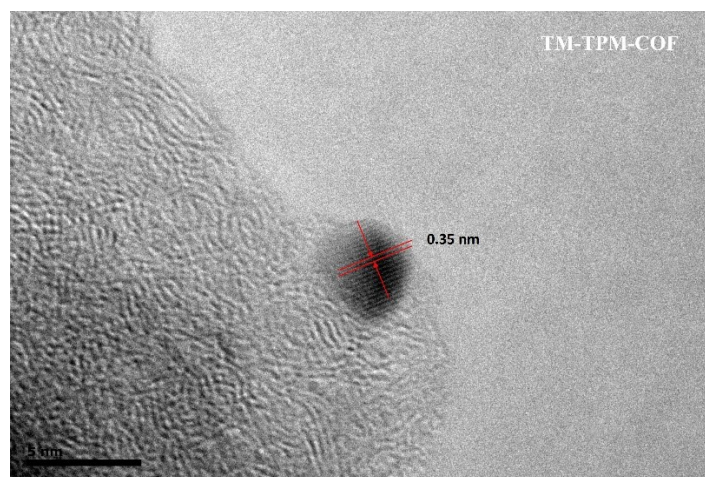


Figure S8. TEM images of TM-TPM COF

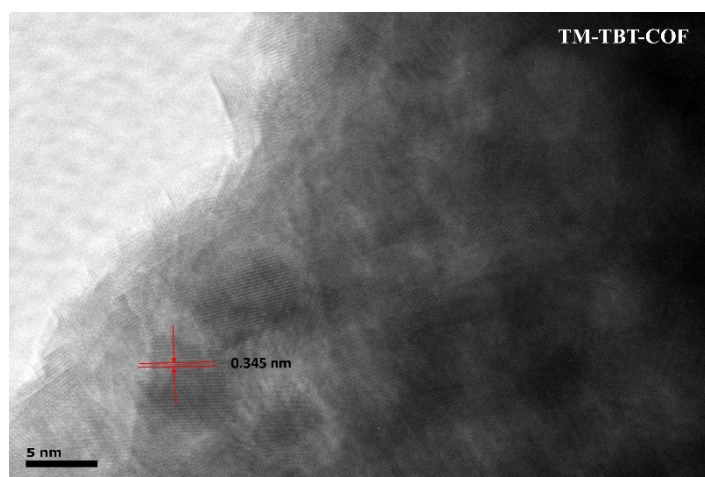


Figure S9. TEM images of TM-TBT COF

9. Thermogravimetric analysis (TGA)

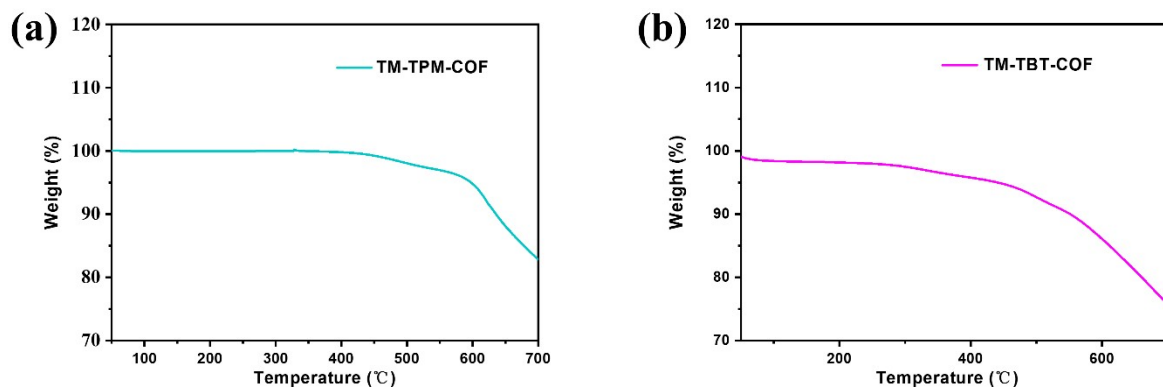


Figure S10. TGA curves of TM-TPM COF and TM-TBT COF

10. Chemical stability of COFs

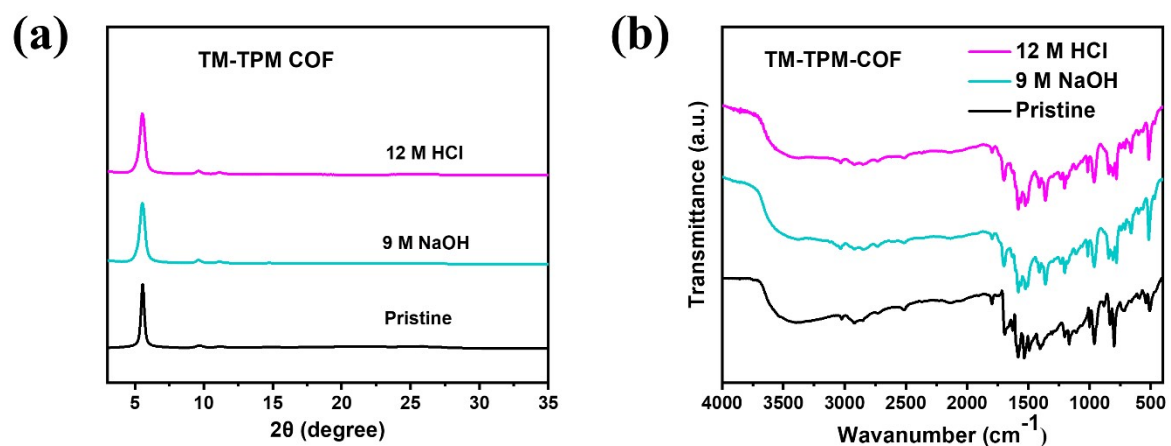


Figure S11. PXRD patterns (a) and FT-IR spectra (b) of TM-TPM COF after soaking in aqueous solution of NaOH (9 M) and HCl (12 M) for one week.

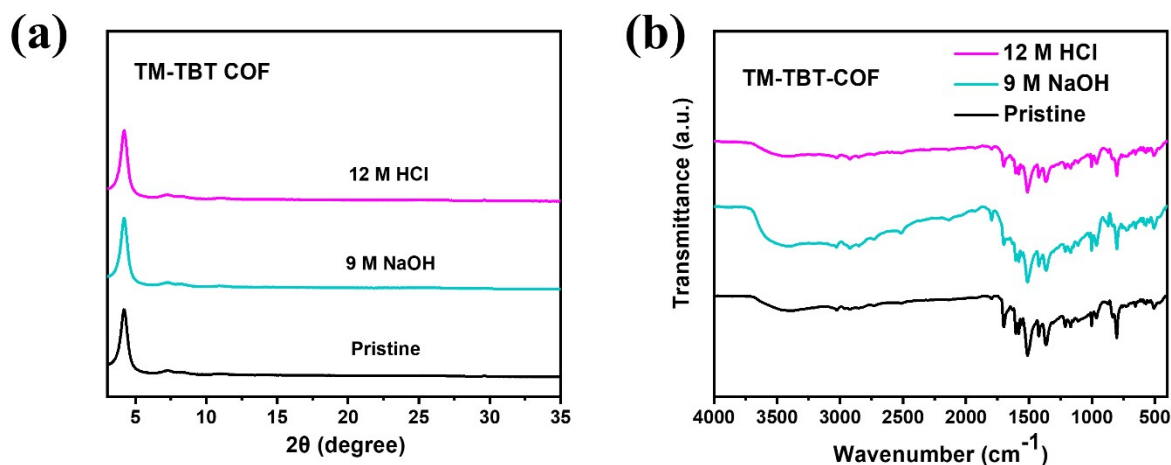


Figure S12. PXRD patterns (a) and FT-IR spectra (b) of TM-TBT COF after soaking in aqueous solution of NaOH (9 M) and HCl (12 M) for one week.

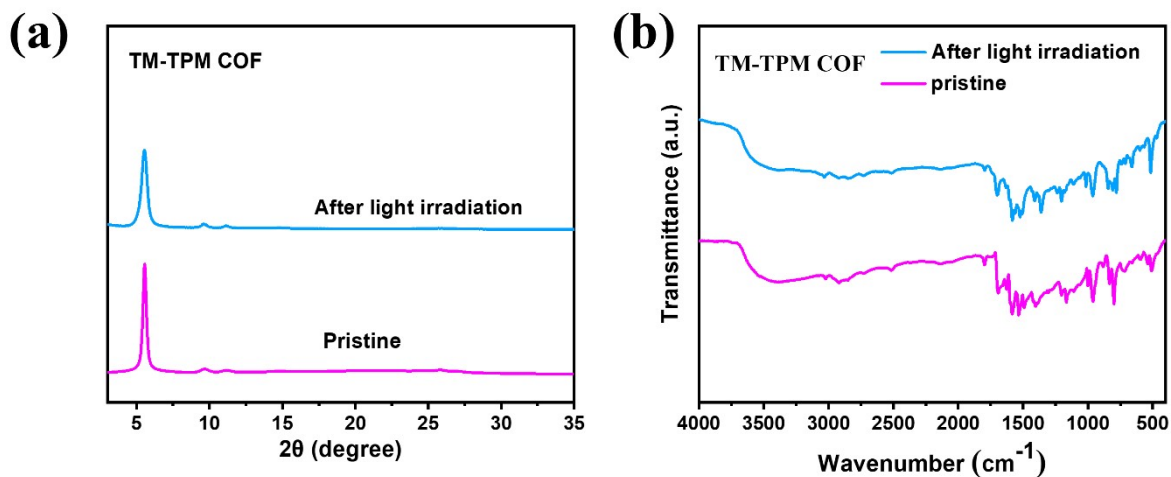


Figure S13. PXRD patterns (a) and FT-IR spectra (b) of TM-TPM COF before and after light irradiation for 3 days.

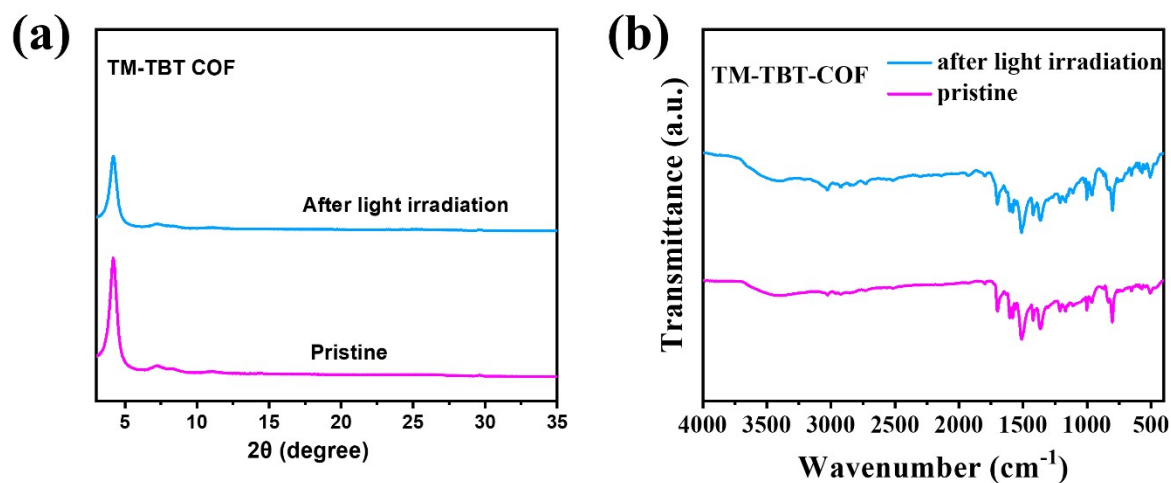
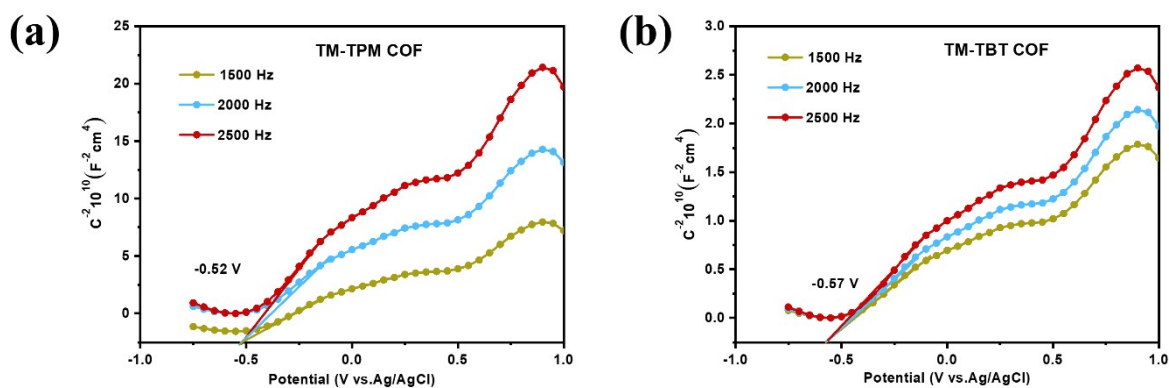


Figure S14. PXRD patterns (a) and FT-IR spectra (b) of TM-TBT COF before and after light irradiation for 3 days.

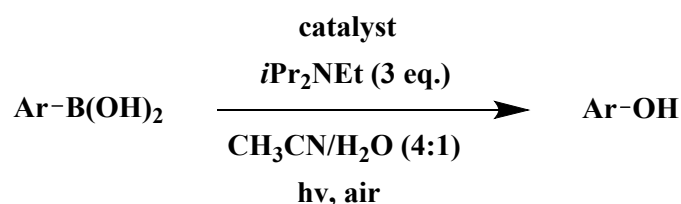
11. Mott-Schottky plots



Figures S15. Mott-Schottky plots of (a) TM-TPM COF and (b) TM-TBT COF.

12. Experimental Procedure for Photocatalysis Reaction

General procedure for photocatalytic oxidative hydroxylation of arylboronic acids to phenols.



Arylboronic acid (0.20 mmol), COFs (0.015 mmol), $i\text{Pr}_2\text{NEt}$ (0.60 mmol, 3.0 eq.) and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v = 4/1, 2.0 mL) were added to a 10 mL glass tube with a stir bar. The solution was stirred for 6 h at room temperature under visible light irradiation in open to air. After the reaction was quenched, the catalyst was isolated by centrifugation and thoroughly washed with acetone for three times. The combined organic phases were evaporated under vacuum to give the crude product. The residue was purified by silica gel column chromatography to afford the desired product.

Table S1. Control experiments of photocatalytic oxidative hydroxylation of arylboronic acids to phenols reaction^a

$\text{C}_6\text{H}_5\text{B(OH)}_2 \xrightarrow[\text{CH}_3\text{CN/H}_2\text{O (4/1), air}]{\text{visible light, catalysts, } i\text{Pr}_2\text{NEt (3 eq.)}} \text{C}_6\text{H}_5\text{OH}$				
Entry	visible Light	catalyst	air	yield (%) ^b
1	on	TM-TP-COF	+	75
2	on	TM-TBT-COF	+	93
3	off	TM-TBT-COF	+	trace
4	on	TM-TBT-COF	-	trace
5	on	no	+	trace
^c 6	on	TM-TBT-COF	+	trace
^d 7	on	TM-TBT-COF	+	72

^a Reaction conditions: Phenylboronic Acid (1.0 mmol), COF catalyst (5 mg), CH_3CN (2 mL), H_2O (0.5 mL), $i\text{Pr}_2\text{NET}$ (3.0 mmol, 3.0 equiv.), irradiation with 20 W white LEDs, 12 h. ^b Isolated yield. ^c p-benzoquinone as the superoxide radical scavenger. ^d TM-TBT-POP is amorphous TM-TBT-COF

13. Characterization of TM-TBT POP

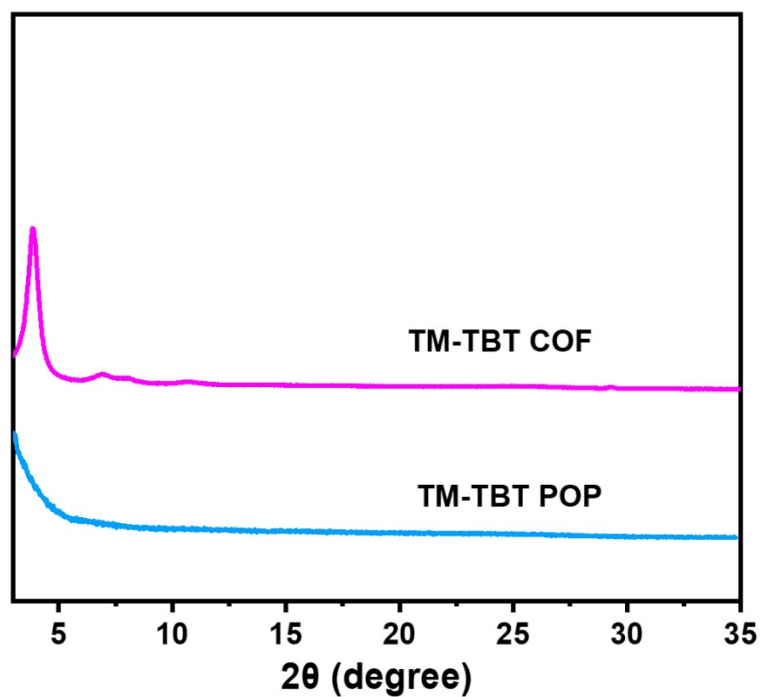


Figure S16. PXRD of TM-TBT COF and TM-TBT POP

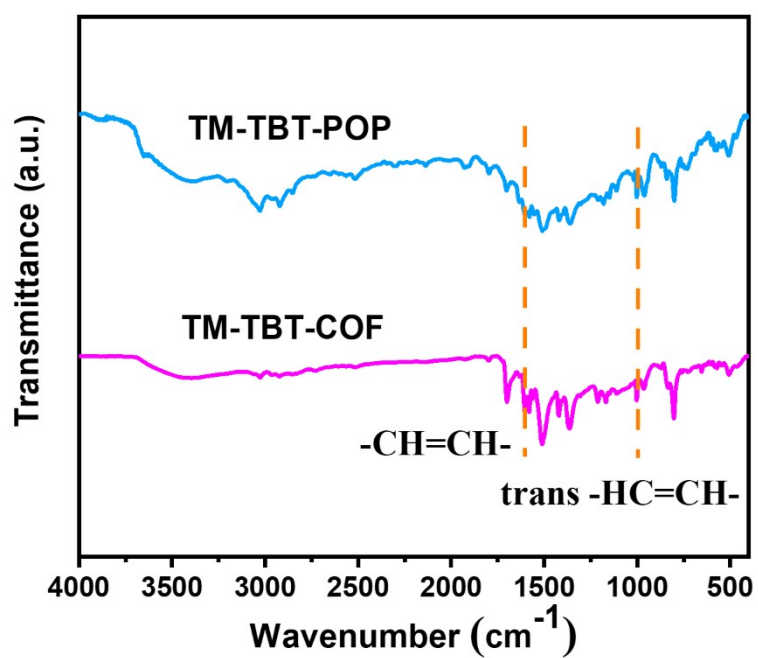


Figure S17. FT-IR spectra of TM-TBT COF and TM-TBT POP.

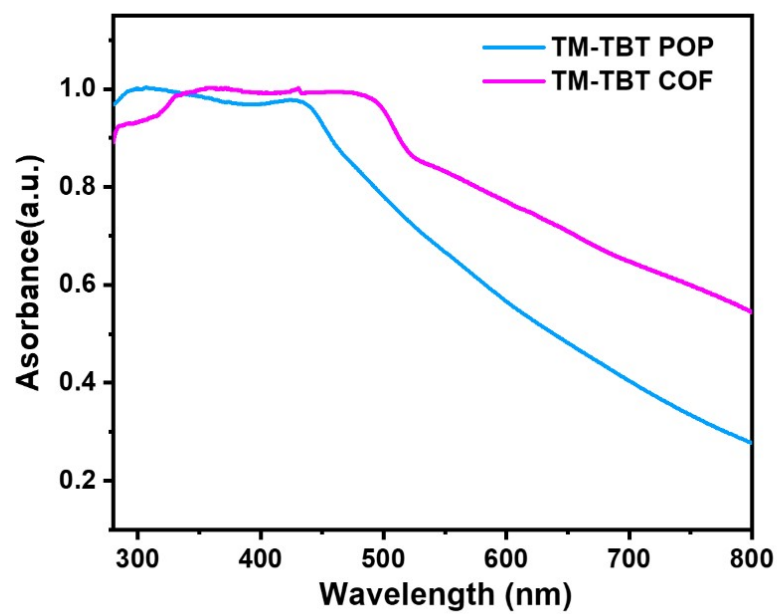


Figure S18. (a,b) UV-vis diffuse reflectance spectra of TM-TBT COF and TM-TBT POP

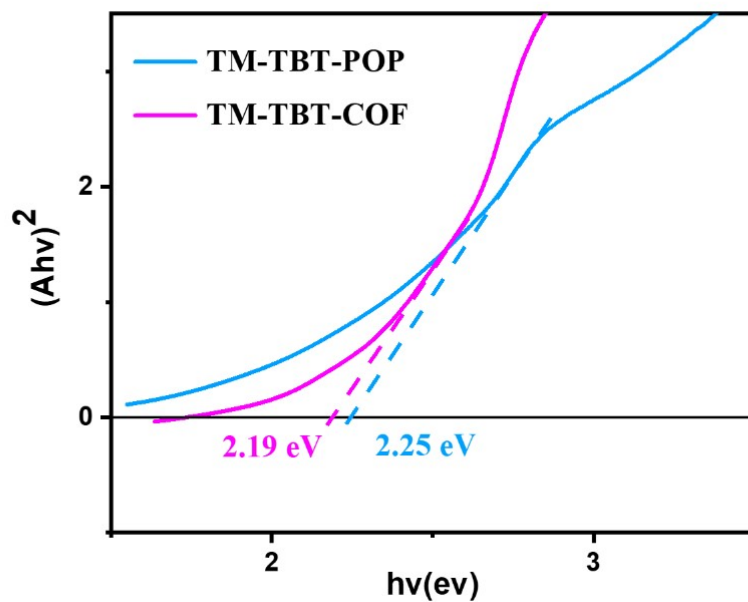


Figure S19. Tauc plots of TM-TBT COF and TM-TBT POP

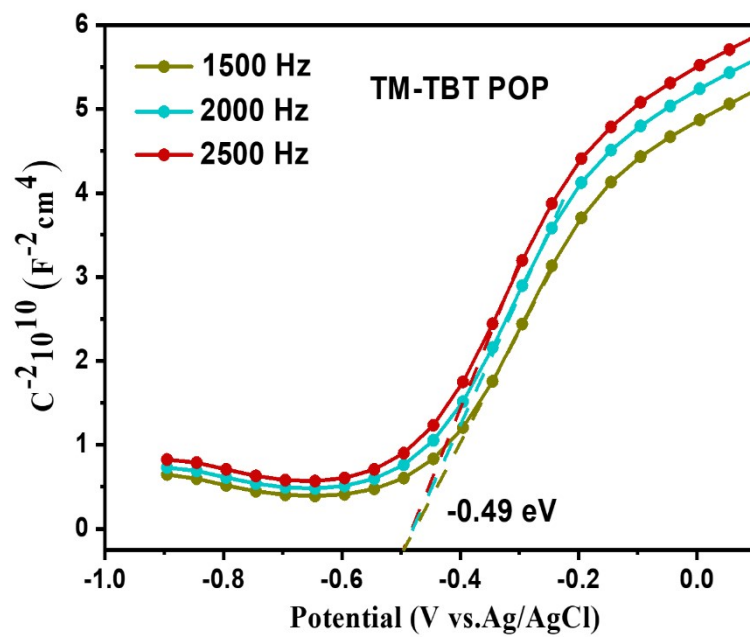


Figure S20. Mott-Schottky plots of TM-TBT POP.

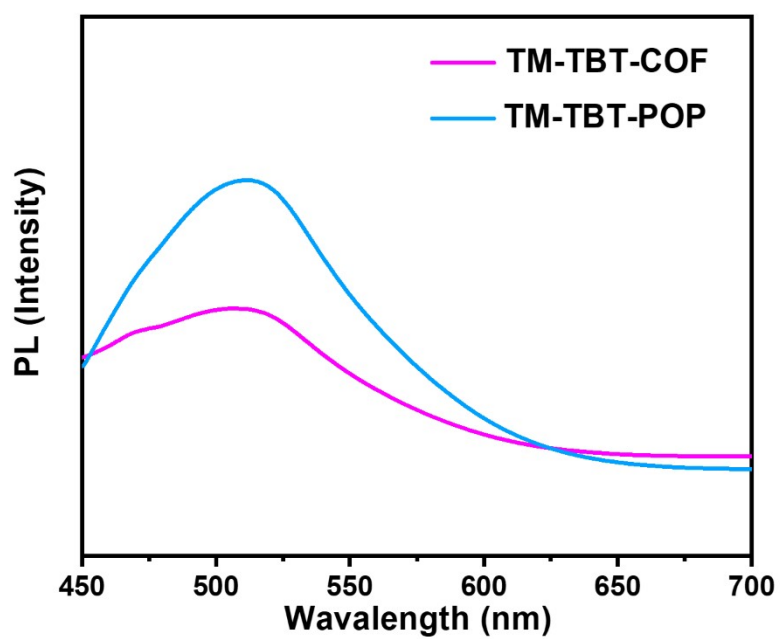
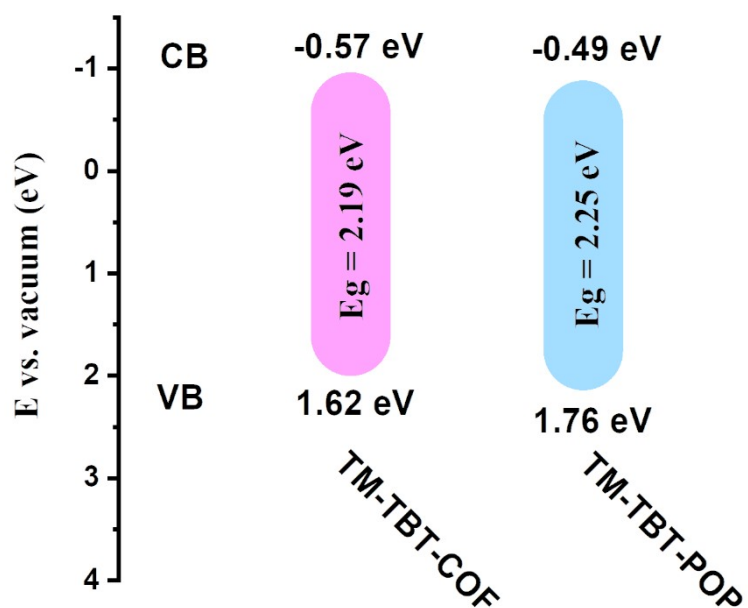
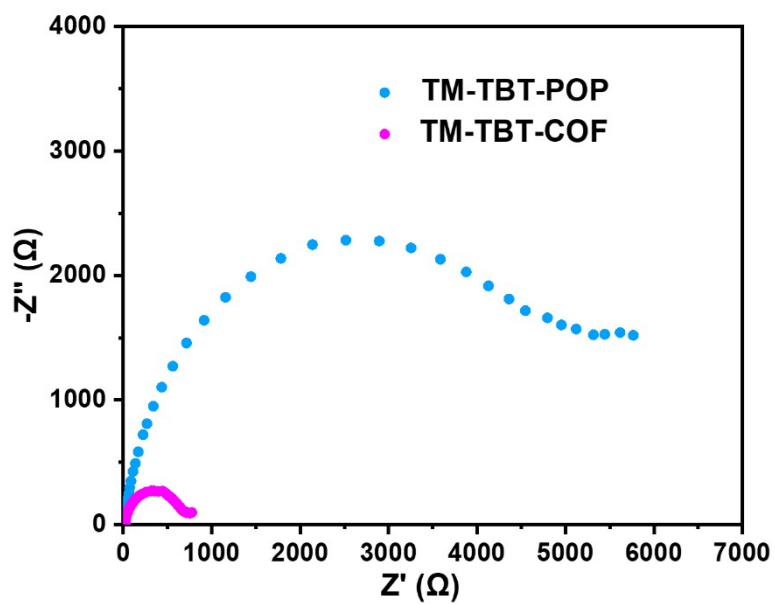


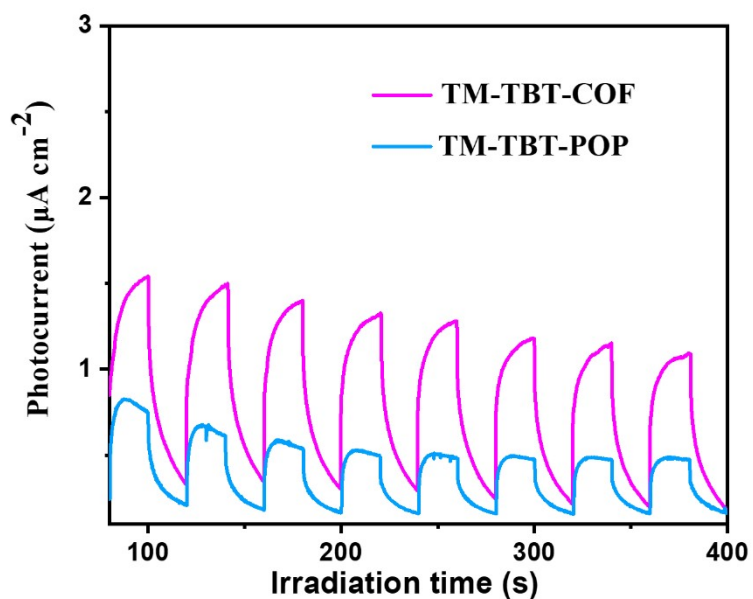
Figure S21. Fluorescence spectra of TM-TBT COF and TM-TBT POP



Figures S22. Band gap energy and band edge positions of TM-TBT COF and TM-TBT POP

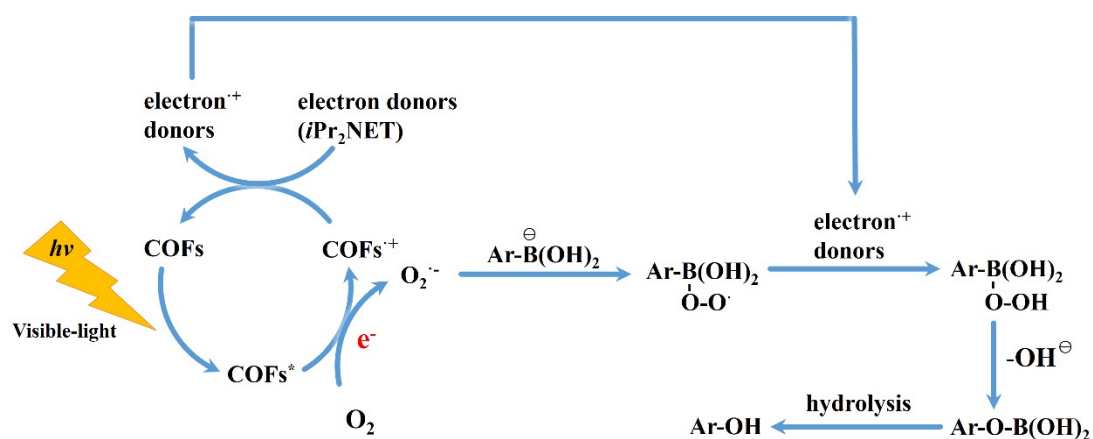


Figures S23. Electrochemical impedance spectroscopy (EIS) Nyquist plots of TM-TBT COF and TM-TBT POP



Figures S24. photocurrent–time plots of TM-TBT COF and TM-TBT POP

14. Proposed mechanism for the photocatalytic oxidative hydroxylation of arylboronic acids to phenols.



Figures S25. Proposed mechanism for photocatalytic oxidative hydroxylation of arylboronic acids to phenols by COFs.

15. Electron Paramagnetic Resonance (EPR) and catalytic yield and stability

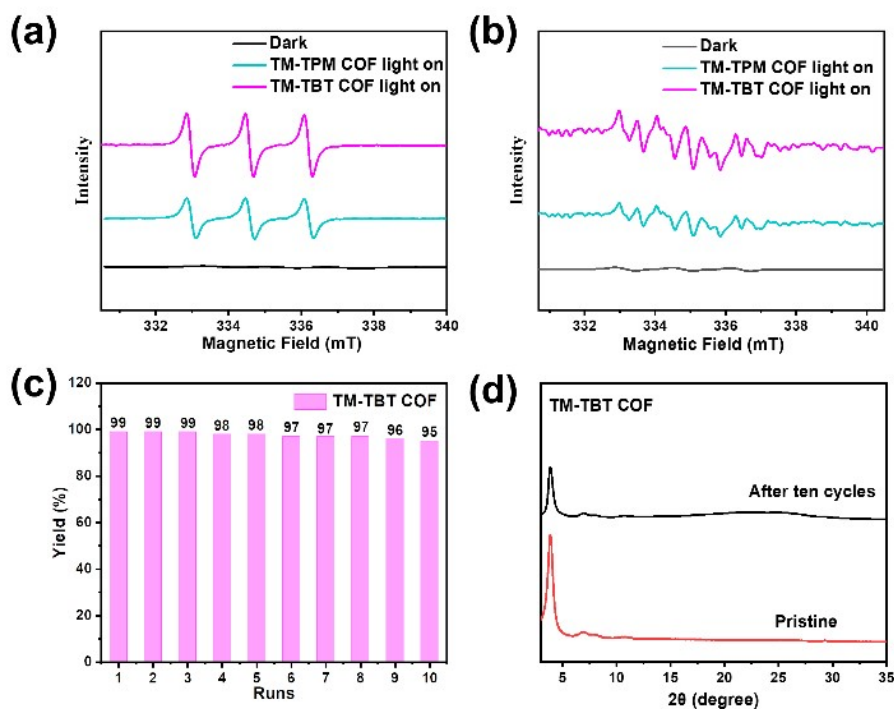
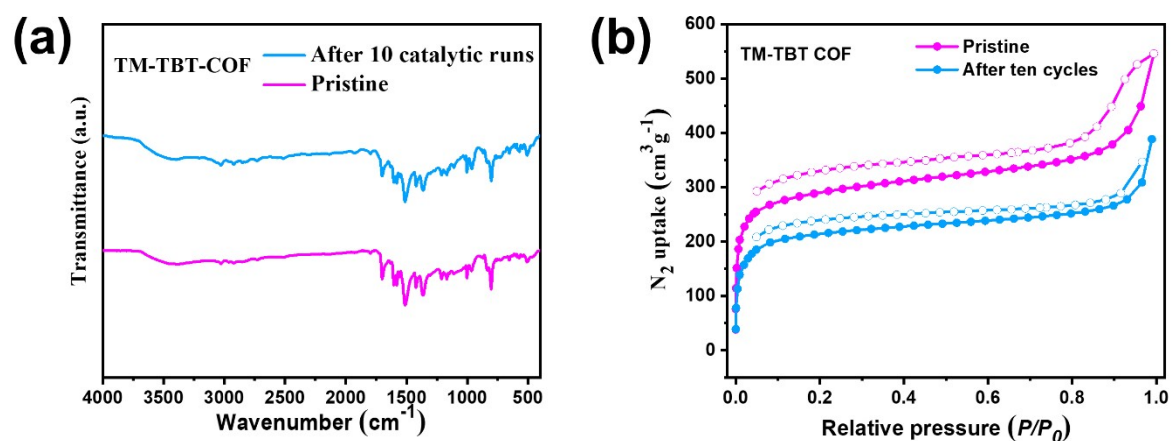


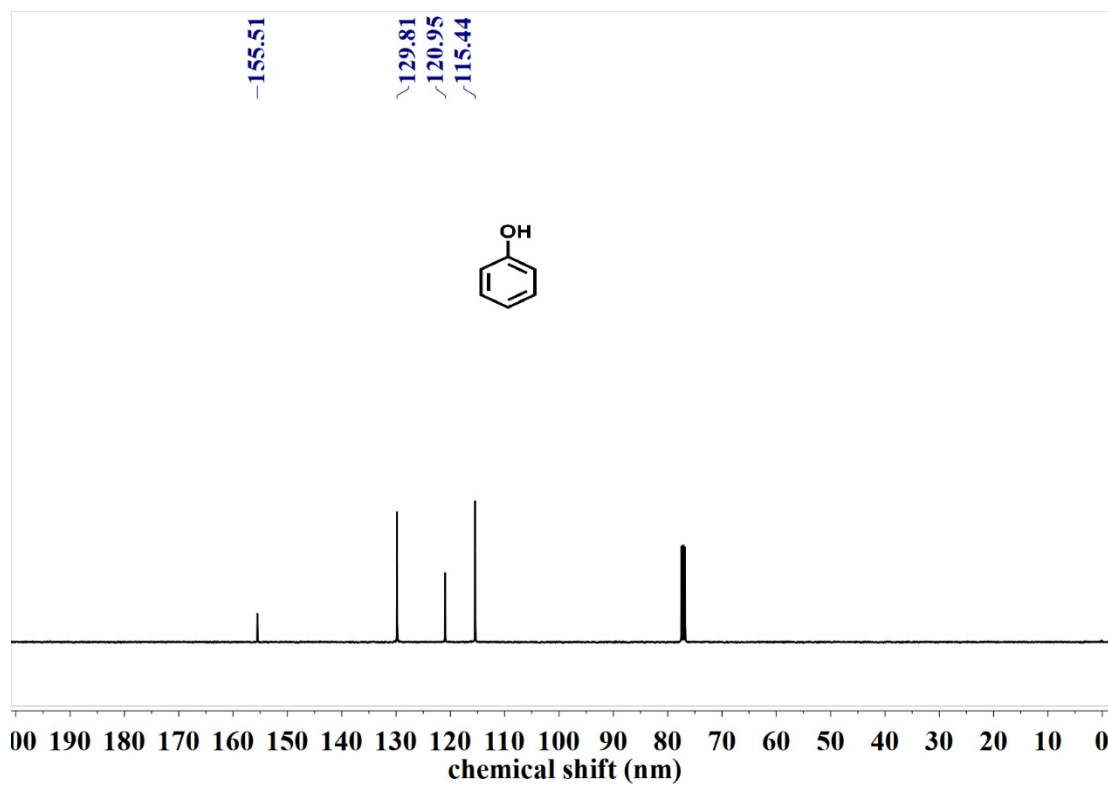
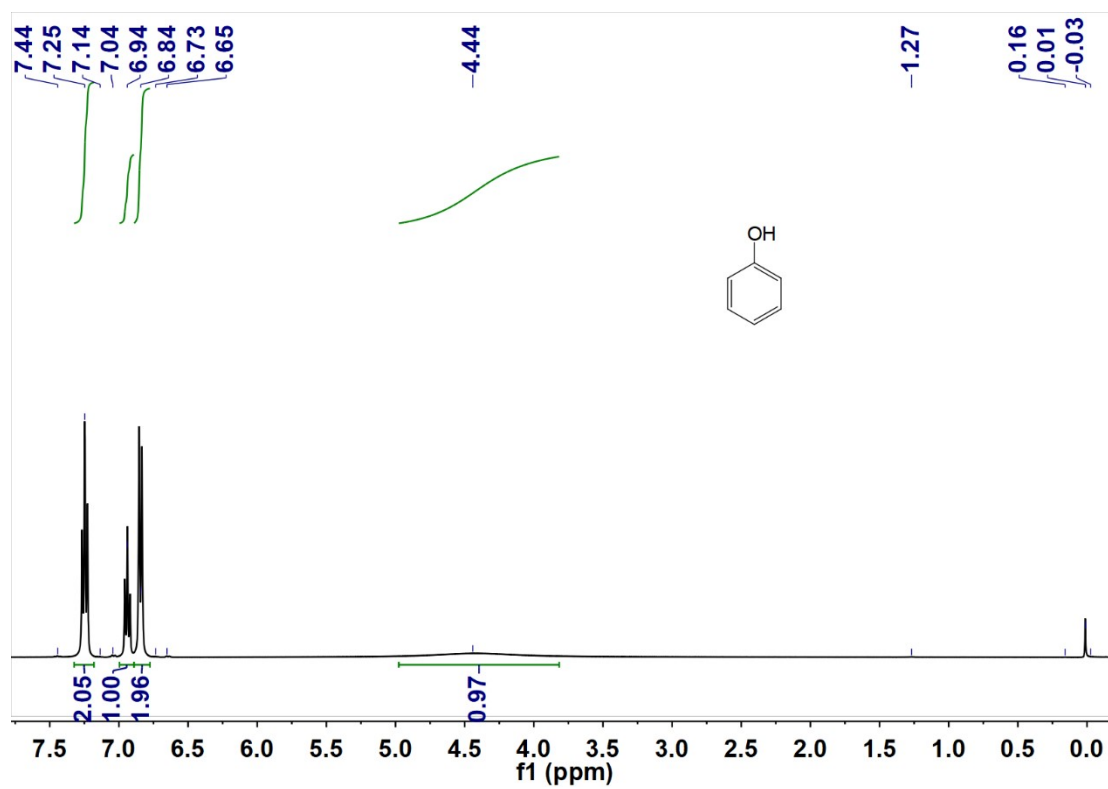
Figure S26. EPR spectra of TM-TPM-COF and TM-TBT-COF in the presence of (a) TEMP and (b) DMPO. (c) The recyclability study of TM-TBT-COF. (d) PXRD patterns of the pristine TM-TBT-COF and the samples after 10 runs of catalysis.

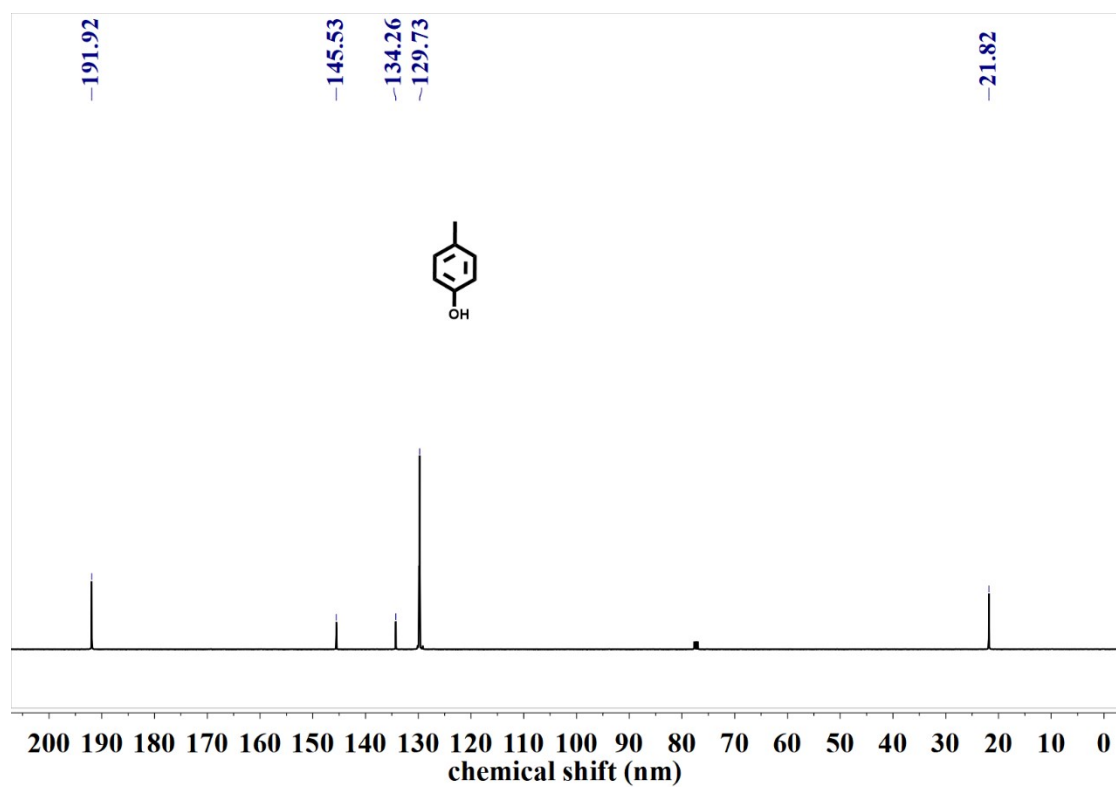
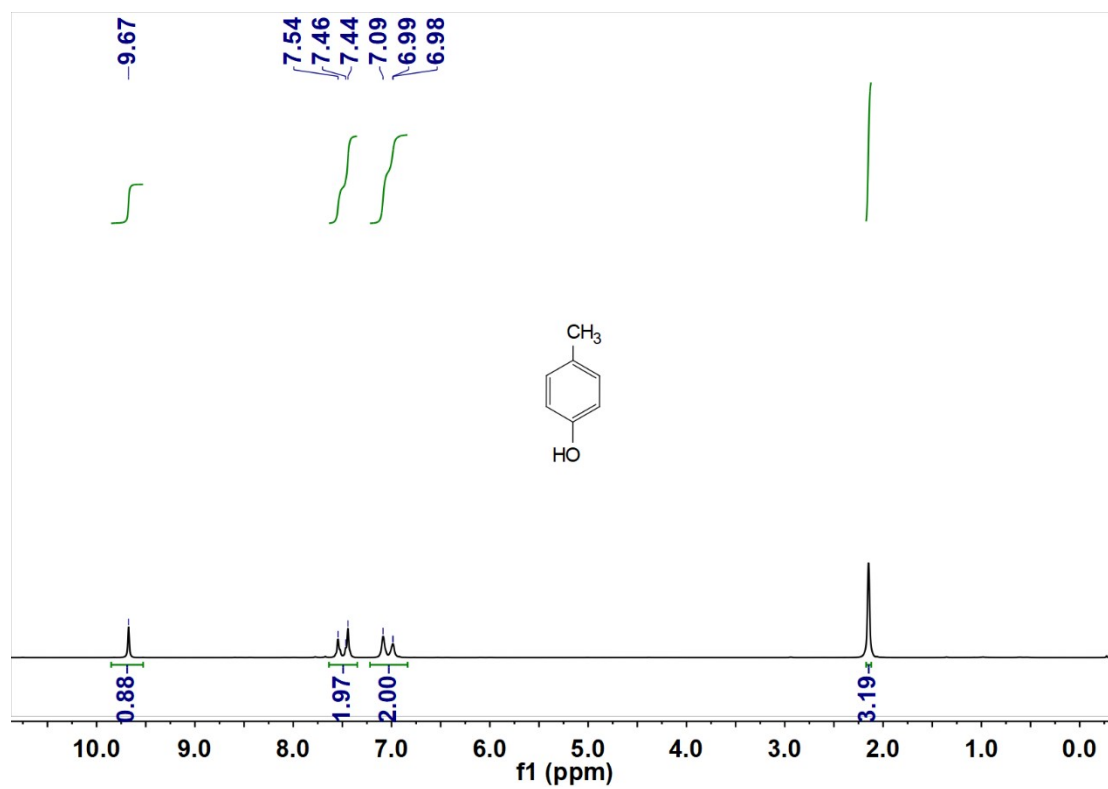
16. Recycle experiments for the photocatalytic oxidative hydroxylation of arylboronic acids to phenols.

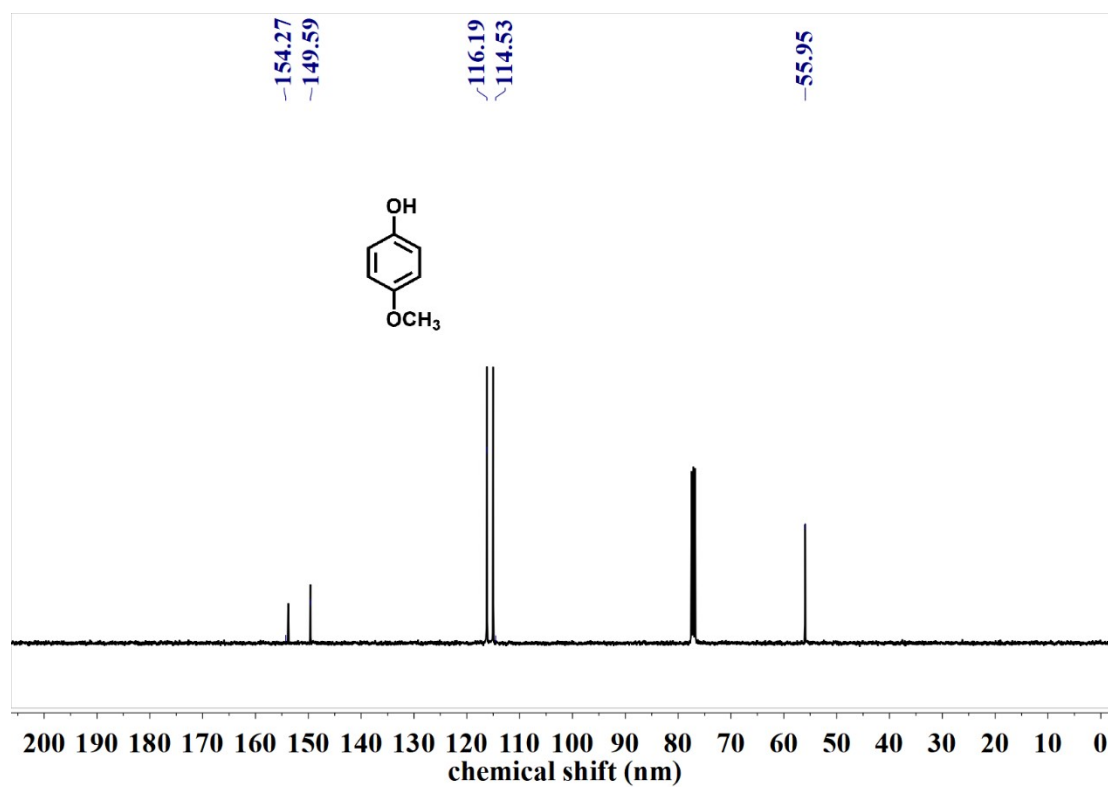
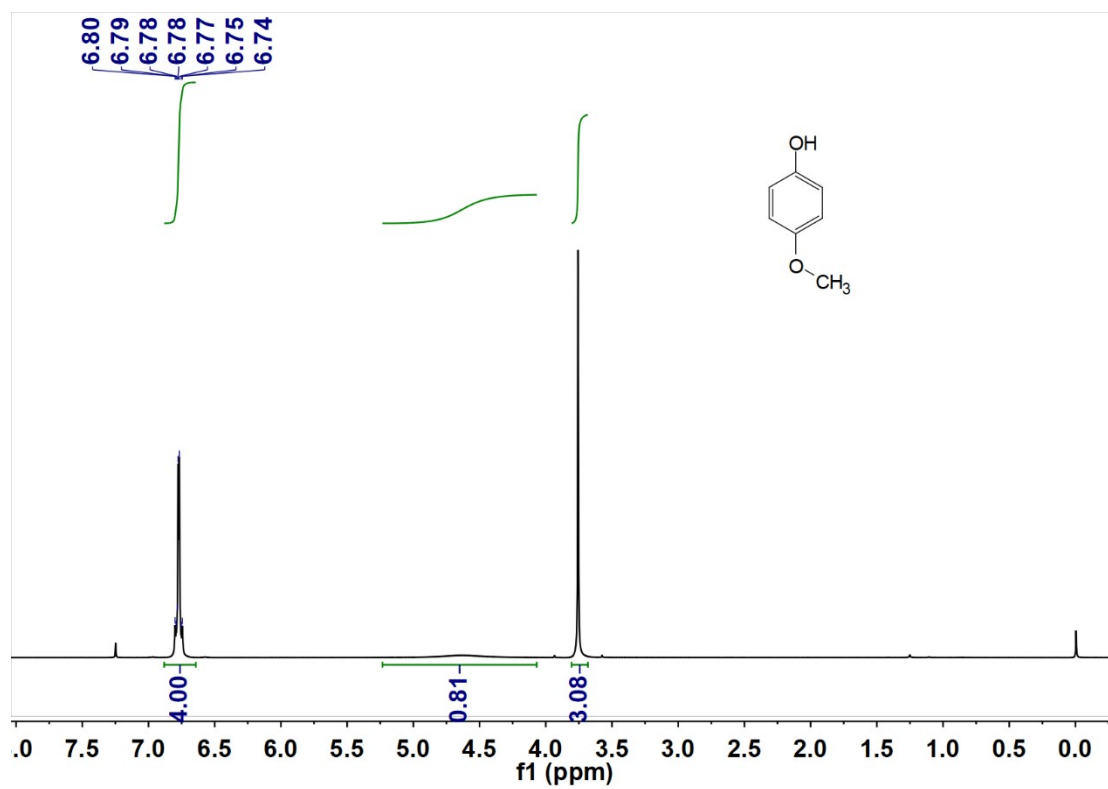


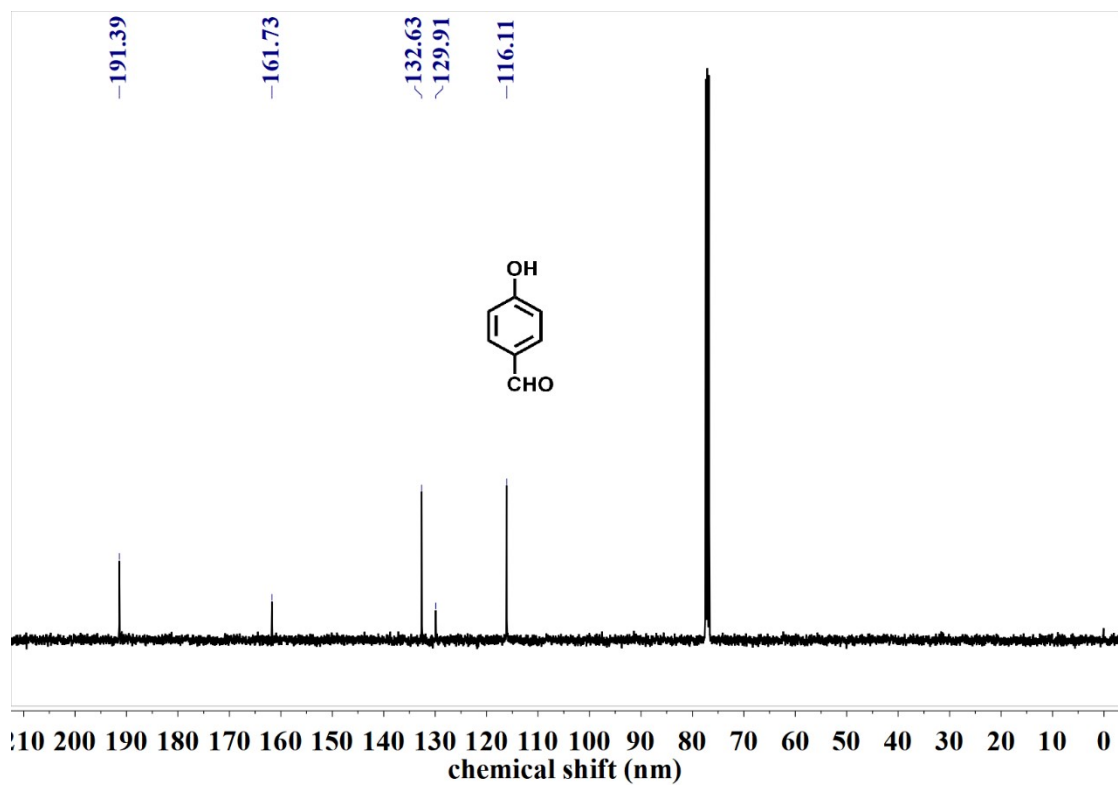
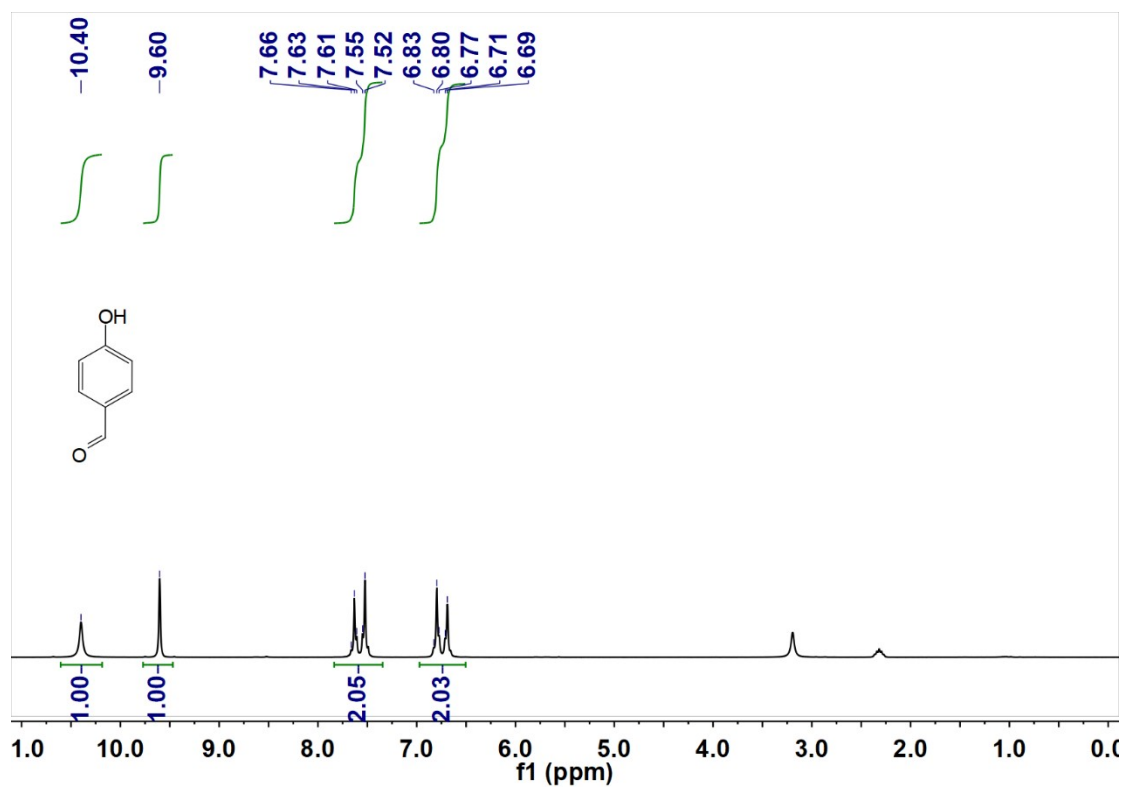
Figures S27. FT-IR spectra (a) and N₂ sorption isotherms (b) of the pristine TM-TBT COF and the samples after 10 runs of catalysis.

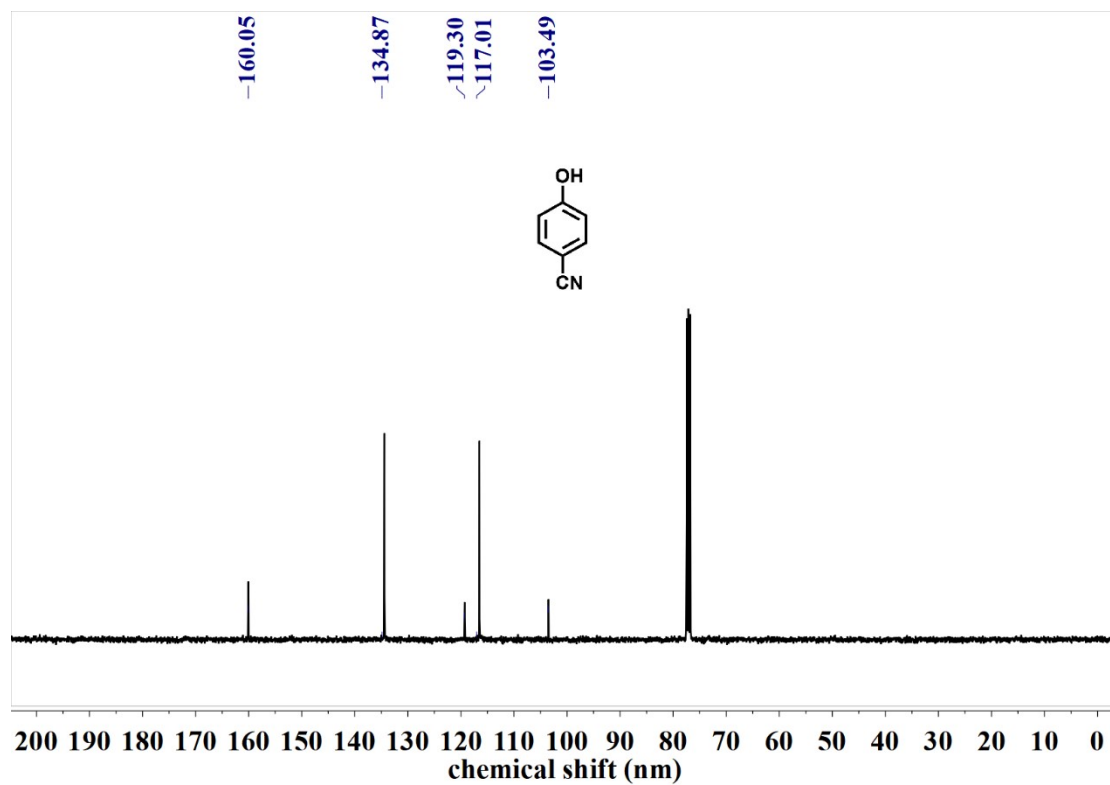
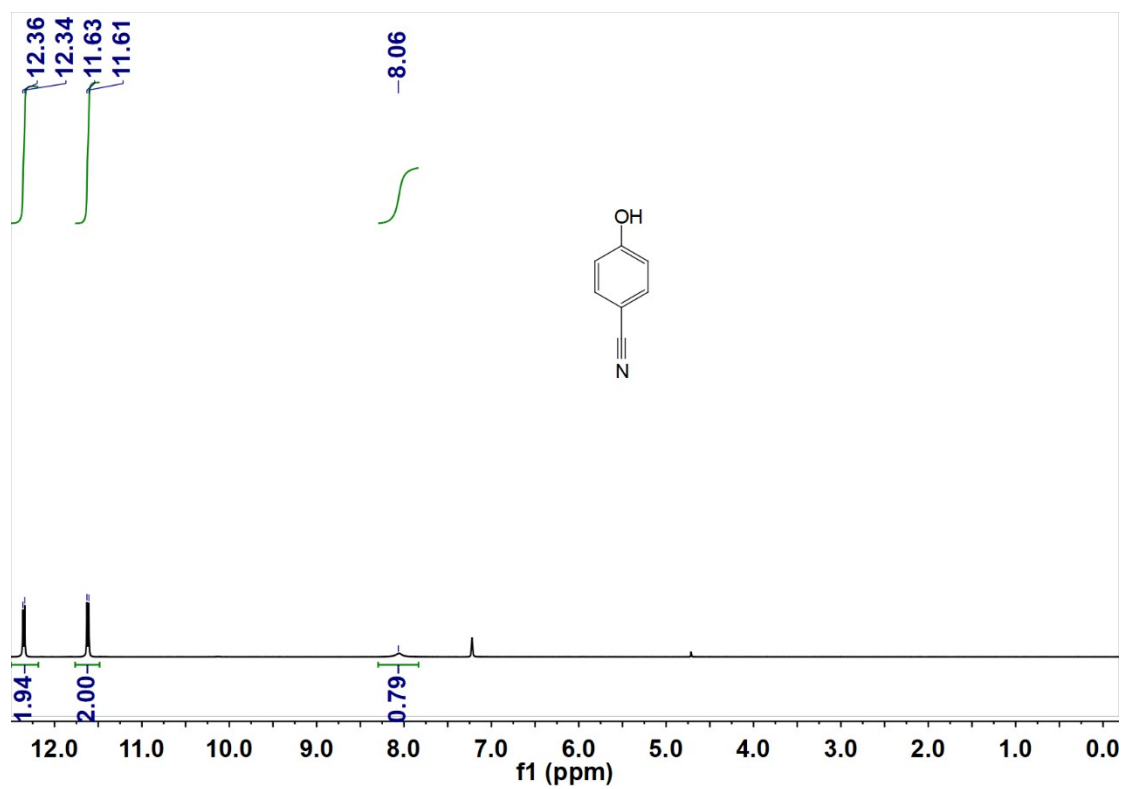
17. Liquid NMR Spectra

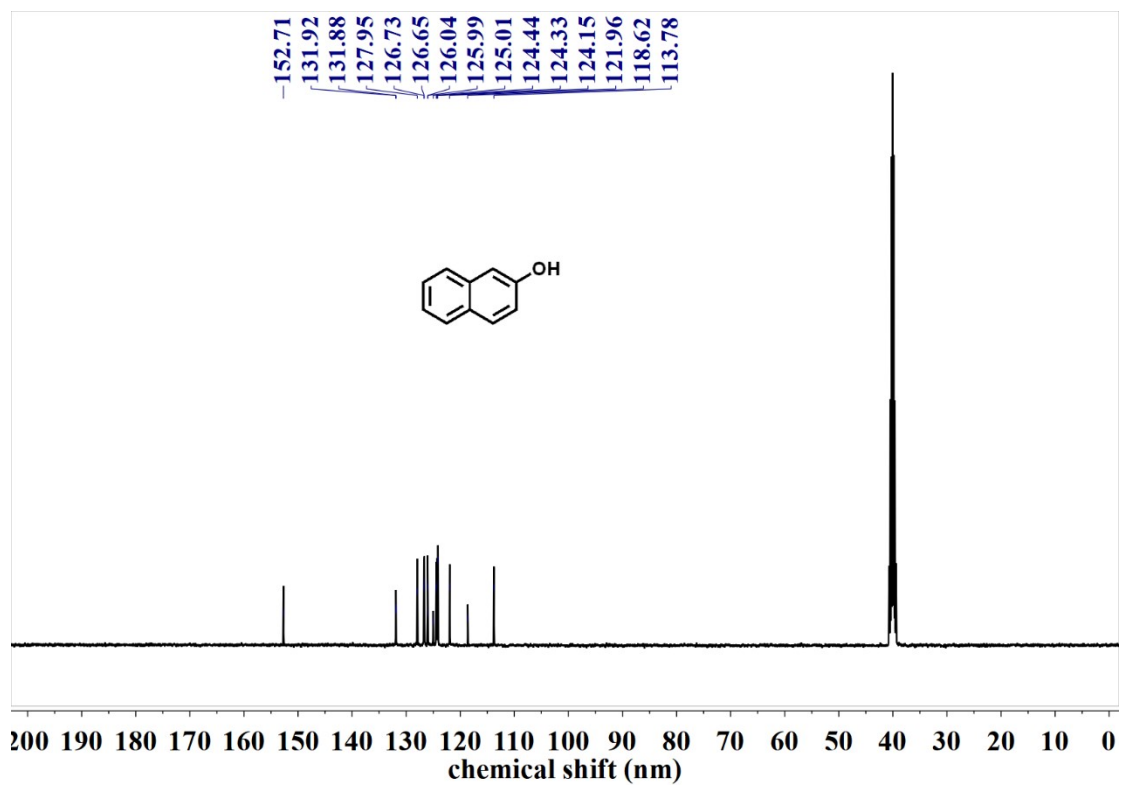
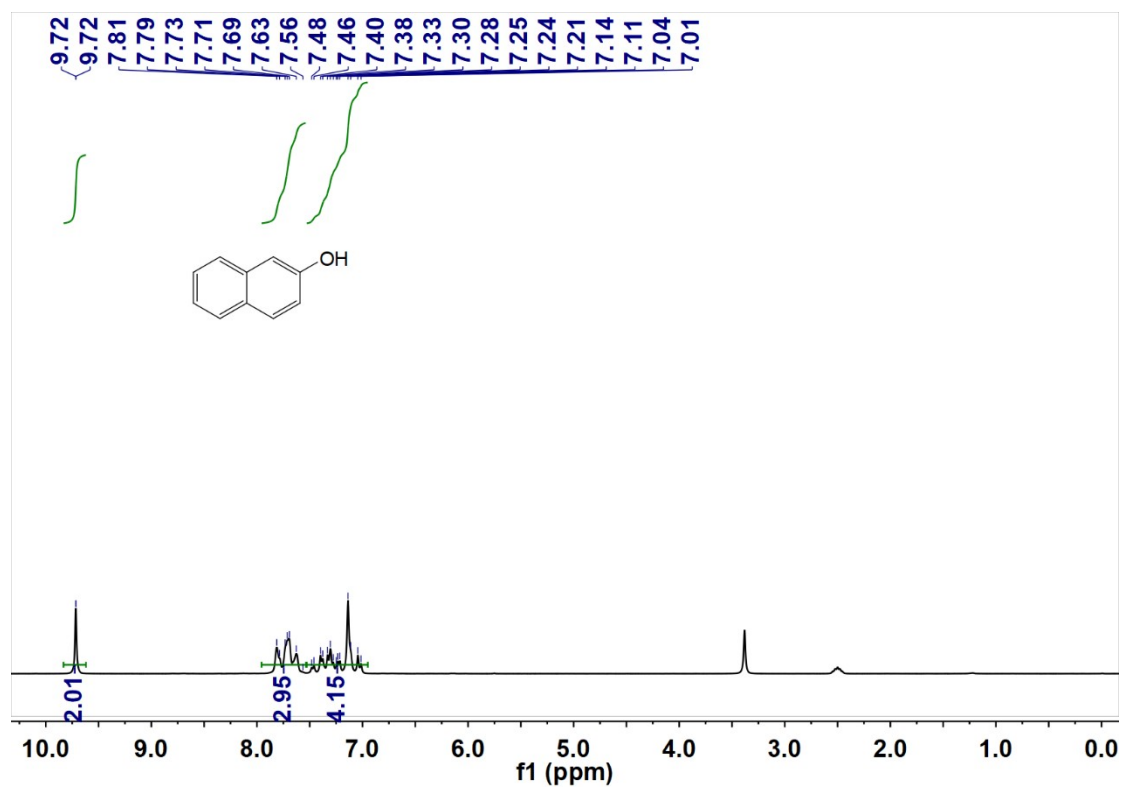


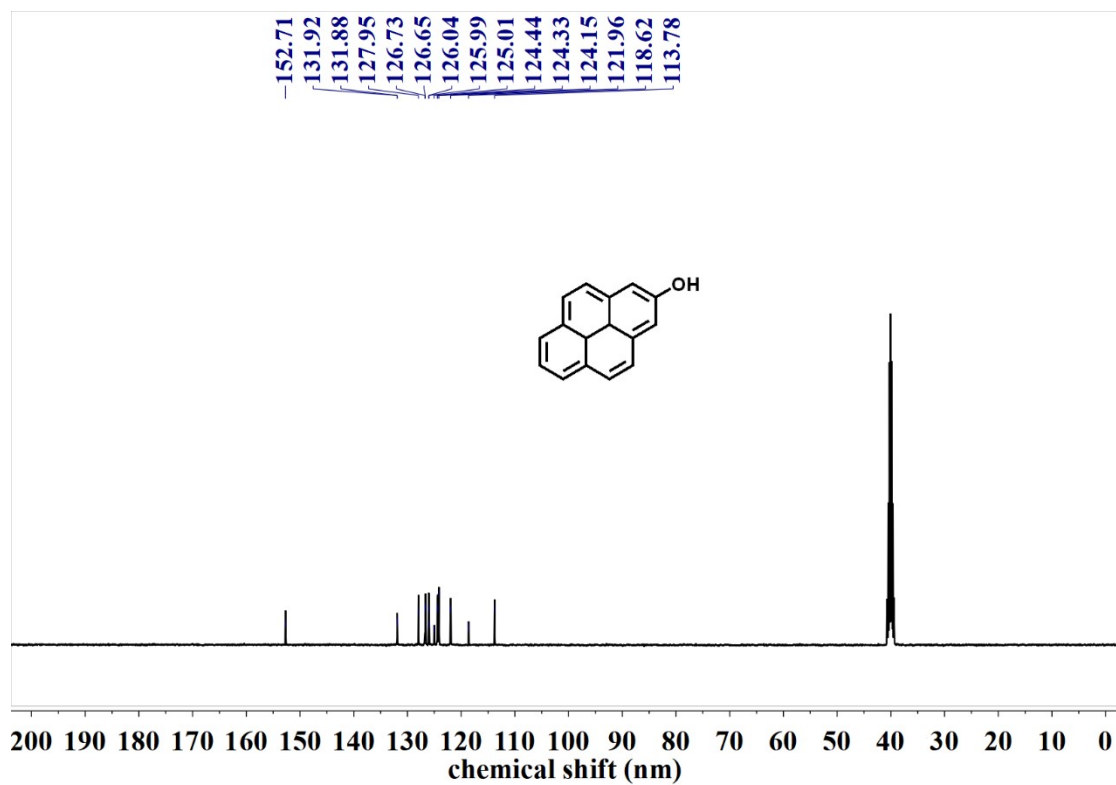
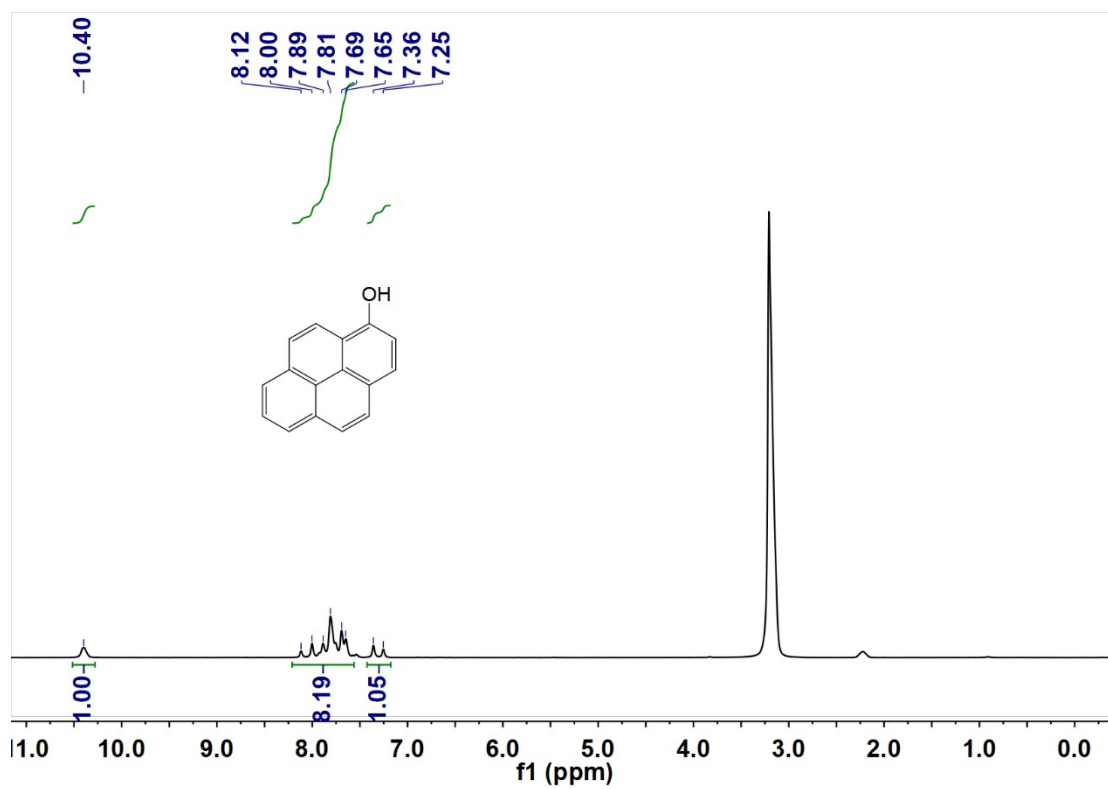


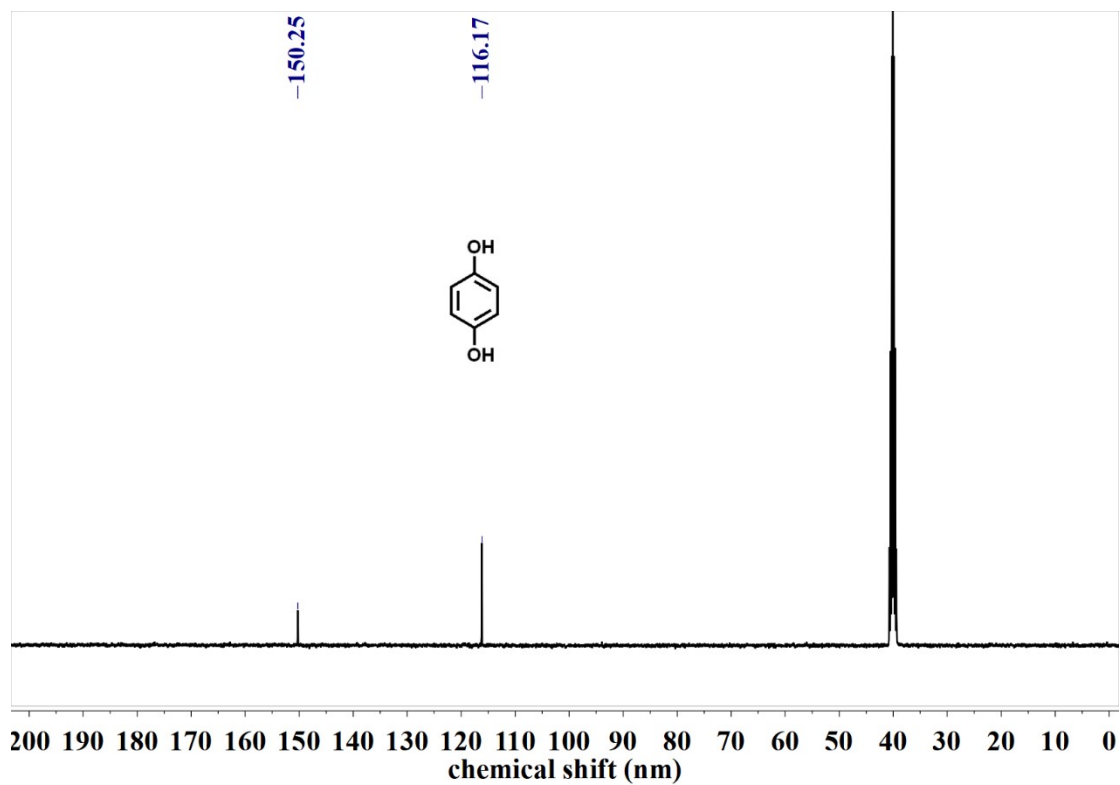
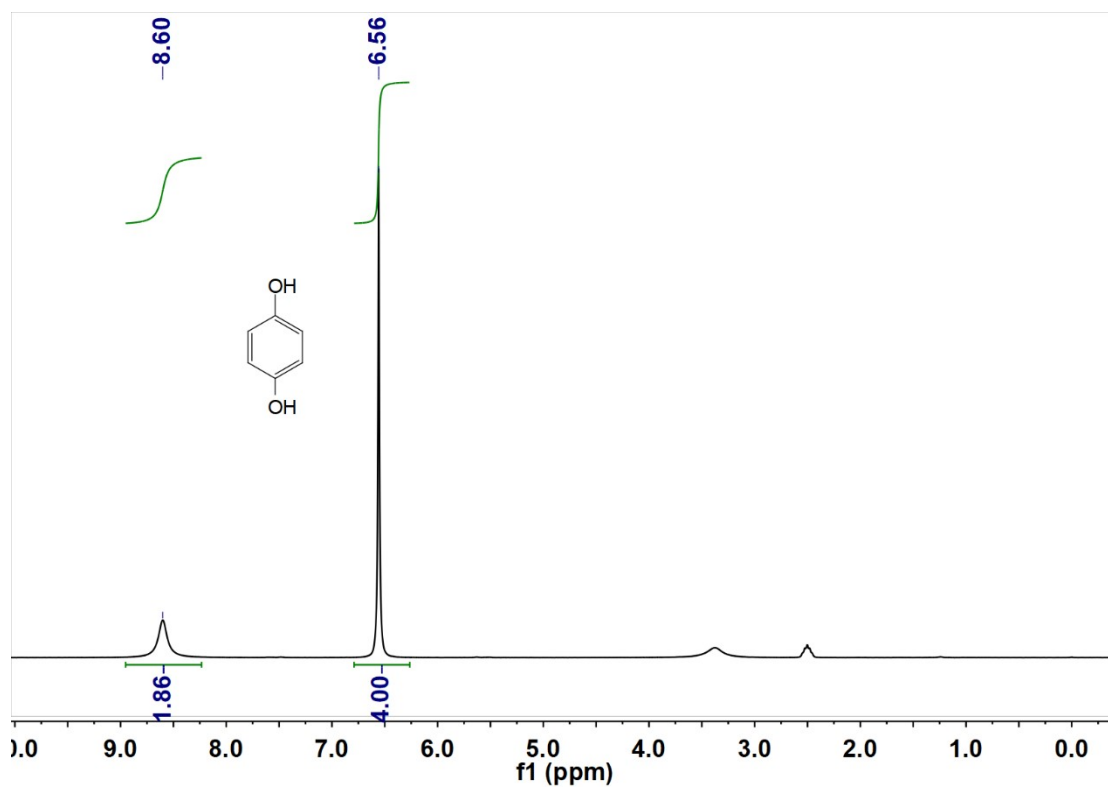












18. Tables S2–S3 Fractional atomic coordinates and unit cell parameters

Table S2 Fractional atomic coordinates for the unit cell of TM-TPM COF.

TM-TPM COF			
a = b = 18.44 Å, c = 3.49 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$			
C1	0.08373	0.05002	0
C2	0.03292	0.08378	0
C3	0.17331	0.10581	0
C4	0.22838	0.08156	0
C5	0.31816	0.13683	0
C6	0.36808	0.10236	0
C7	0.45283	0.15106	0
C8	0.49084	0.23616	0
C9	0.44075	0.27098	0.00001
C10	0.35541	0.22197	0.00001
C11	0.58181	0.28694	0
N12	0.62034	0.36983	0
C13	0.94822	0.03351	0
C14	0.91586	0.94902	0
C15	0.89238	0.06731	0
C16	0.91753	0.147	0
C17	0.86348	0.18278	0
C18	0.89859	0.26741	0
C19	0.85038	0.30419	0
C20	0.76542	0.25727	0
C21	0.73027	0.17224	0
C22	0.77854	0.13539	0
C23	0.71412	0.29672	0
C24	0.62928	0.24944	0
C25	0.96756	0.91585	0
N26	0.04978	0.96738	0
C27	0.93473	0.82609	0
C28	0.85518	0.77058	0
C29	0.81937	0.6805	0
C30	0.73469	0.63128	0
C31	0.69738	0.54624	0
C32	0.74366	0.50751	0
C33	0.82875	0.55686	0
C34	0.86623	0.64226	0
C35	0.70325	0.41659	0
N36	0.7488	0.37929	0
H37	0.06031	0.15238	0

H38	0.1991	0.17419	0
H39	0.20778	0.01417	0
H40	0.33881	0.03355	-0.00001
H41	0.49237	0.12179	-0.00001
H42	0.46892	0.33968	0.00001
H43	0.31588	0.25126	0.00001
H44	0.84742	0.90678	0
H45	0.824	0.02471	0
H46	0.98507	0.19324	0
H47	0.96744	0.30647	0
H48	0.88018	0.37305	0
H49	0.66155	0.13193	0
H50	0.74873	0.06653	0
H51	0.59877	0.18052	0
H52	0.97802	0.80113	0
H53	0.80819	0.79092	0
H54	0.69603	0.66151	-0.00001
H55	0.62849	0.50757	-0.00001
H56	0.86863	0.52797	0
H57	0.93512	0.68092	0

Table S3 Fractional atomic coordinates for the unit cell of TM-TBT COF.

TM-TBT COF			
a = b = 26.20 Å, c = 3.49 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$			
C1	0.06113	0.035	0
C2	0.02626	0.06154	0
C3	0.12565	0.07278	0
C4	0.16223	0.05125	0
C5	0.22691	0.08913	0
C6	0.26181	0.06261	0
C7	0.32333	0.09713	0
C8	0.35121	0.15895	0
C9	0.31594	0.1854	0
C10	0.25438	0.15087	0
C11	0.41661	0.19545	0
C12	0.44478	0.25729	0
C13	0.50637	0.2915	0
C14	0.54111	0.2646	0
C15	0.51312	0.2029	0
C16	0.4516	0.16873	0
C17	0.60621	0.30052	0
N18	0.63351	0.36041	0

C19	0.96471	0.02641	0
C20	0.93921	0.96513	0
C21	0.92609	0.05234	0
C22	0.947	0.11039	0
C23	0.90912	0.1371	0
C24	0.93583	0.19853	0
C25	0.90152	0.22571	0
C26	0.83972	0.19194	0
C27	0.81305	0.13019	0
C28	0.84739	0.10294	0
C29	0.80351	0.22112	0
C30	0.74168	0.18771	0
C31	0.70776	0.21537	0
C32	0.73495	0.27704	0
C33	0.79665	0.31051	0
C34	0.83053	0.28287	0
C35	0.69921	0.30638	0
N36	0.63936	0.27384	0
C37	0.97523	0.93956	0
N38	0.03496	0.97501	0
C39	0.94972	0.875	0
C40	0.89167	0.83769	0
C41	0.86473	0.77305	0
C42	0.80327	0.73861	0
C43	0.77573	0.6771	0
C44	0.80915	0.6487	0
C45	0.87096	0.68351	0
C46	0.89857	0.74515	0
C47	0.77956	0.58325	0
C48	0.81264	0.55449	0
C49	0.78463	0.49288	0
C50	0.72293	0.45867	0
C51	0.68977	0.48722	0
C52	0.71777	0.5488	0
C53	0.69338	0.39354	0
N54	0.72591	0.3662	0
H55	0.04791	0.11163	0
H56	0.14638	0.12277	0
H57	0.14382	0.00156	0
H58	0.23982	0.01249	0
H59	0.35145	0.07513	0
H60	0.33739	0.23547	0
H61	0.22627	0.17288	0

H62	0.41693	0.27958	0
H63	0.52866	0.34164	0
H64	0.54053	0.18014	0
H65	0.42931	0.11859	0
H66	0.8892	0.93593	0
H67	0.87616	0.02247	0
H68	0.9966	0.14212	0
H69	0.98596	0.22649	0
H70	0.92369	0.27584	0
H71	0.76296	0.10173	0
H72	0.82522	0.05281	0
H73	0.71915	0.13755	0
H74	0.6576	0.18774	0
H75	0.8196	0.3607	0
H76	0.88069	0.31049	0
H77	0.97989	0.85529	0
H78	0.85981	0.85541	0
H79	0.77557	0.76107	0
H80	0.72558	0.6494	0
H81	0.89918	0.66161	0
H82	0.94872	0.77284	0
H83	0.86281	0.58185	0
H84	0.812	0.47007	0
H85	0.63957	0.46024	0
H86	0.69041	0.57162	0