

Supporting Information

Facile Construction of Olefin-Linked Covalent Organic Frameworks for Enhanced Photocatalytic Organic Transformation via Wall Surface Engineering

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1. Materials and general procedures

All of the chemicals are commercially available, and used without further purification. 2,4,6-trimethyl-1,3,5-triazine (TMT) was purchased from Shanghai Tensus Bio-tech Co., Ltd. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on Vertex80+Hyperion 2000 spectrometer. The solid state nuclear magnetic analysis was recorded on AV(III)400. The UV spectra were recorded on U-4100 spectrometer. Thermogravimetric analyses (TGA) were carried out in 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 adsorption 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. Fluorescence emission spectrum was recorded on Horiba. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were obtained with JEM-2100 and JEM-F200 scanning electron microscope.

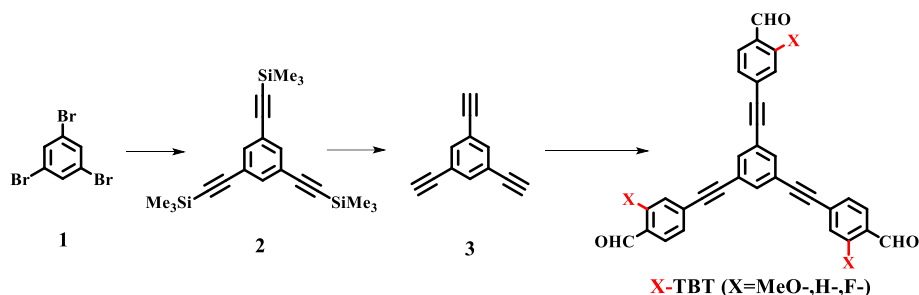
The Pawley refinement of the experimental PXRD was conducted by the Reflux module. The stimulated PXRD patterns were determined by the Reflex module. And the unit cell was optimized by Forcite module under molecular mechanics calculation using Universal as the forcefield to give the relative total energy.

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 COFs powder was mixed with 1 mL ethanol and ultra-sonicated for 2h to get slurry. 40 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 0.1 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 1000, 1500 and 2000 Hz.

3. Synthesis

3.1 Synthesis of X-TBT (X=MeO-, H-, F-)



2 1,3,5-tris((trimethylsilyl)ethynyl)benzene and **3** 1,3,5-triethynylbenzene were synthesized by the method of literatures [1].

Synthesis of **X-TBT** (X=MeO-, H-, F-):

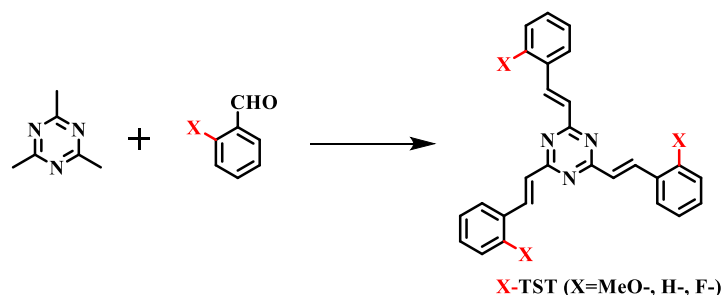
A mixture of CuI (101.45 mg, 0.532 mmol), PdCl₂(PPh₃)₂ (210.5 mg, 0.299 mmol), 1,3,5-triethynylbenzene (400 mg, 2.66 mmol), 4-bromo-2-methoxybenzaldehyde (2.41 g, 11.19 mmol), 4-bromobenzaldehyde (2.07 g, 11.19 mmol) and 4-bromo-2-fluorobenzaldehyde (2.27 g, 11.19 mmol) respectively in dried 20 mL THF and 4 mL Et₃N were stirred at 70°C overnight under nitrogen atmosphere. Upon cooling down, the mixture was extracted with DCM. The obtained organic layer was collected and dried with anhydrous sodium sulfate. After that, the solvent was removed at reduced pressure. The residue was chromatographed on silica gel to give MeO-TBT, H-TBT and F-TBT as powder. Yield: 50.3%, 55.6%, 47.7%, respectively.

MeO-TBT: ¹H NMR (400 MHz, CDCl₃): δ 10.44 (s, 3H), 7.83-7.81 (d, *J*=8 Hz, 3H), 7.72 (s, 3H), 7.19-7.17 (d, *J*=8 Hz, 3H), 7.13-7.12 (d, *J*=4 Hz, 3H), 3.96 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 189.03, 161.45, 134.87, 132.3, 129.94, 128.70, 128.83, 124.21, 123.73, 114.71, 90.87, 90.28.

H-TBT: ¹H NMR (400 MHz, CDCl₃): δ 10.36-10.35 (d, *J*=4 Hz, 3H), 7.89-7.88 (d, *J*=4 Hz, 6H), 7.73 (s, 3H), 7.69-7.67 (d, *J*=8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 191.3, 135.9, 134.9, 132.3, 129.7, 128.8, 123.8, 91.2, 90.0.

F-TBT: ¹H NMR (400 MHz, CDCl₃): δ 10.44 (s, 3H), 7.89-7.86 (m, 3H), 7.73 (s, 3H), 7.42-7.40 (m, 3H), 7.34-7.31 (m, 3H). we couldn't get the ¹³C NMR of F-TBT due to its low solubility.

3.2 Synthesis of model compound X-TST (X=MeO-, H-, F-)



A mixture of 2,4,6-Trimethyl-1,3,5-triazine (TMT) (50 mg, 0.406 mmol), KOH (79.72 mg, 1.42 mmol), 2-methoxybenzaldehyde (192.03 mg, 1.42 mmol), benzaldehyde (150.79 mg, 1.42 mmol) and 2-fluorobenzaldehyde (176.36 mg, 1.42 mmol) respectively in 15 mL CH₃OH were stirred at 80°C overnight under nitrogen atmosphere. After removal of solvent, the solid residue

was collected, then the residue was chromatographed on silica gel to give model compound (MeO-TST, H-TST, F-TST).

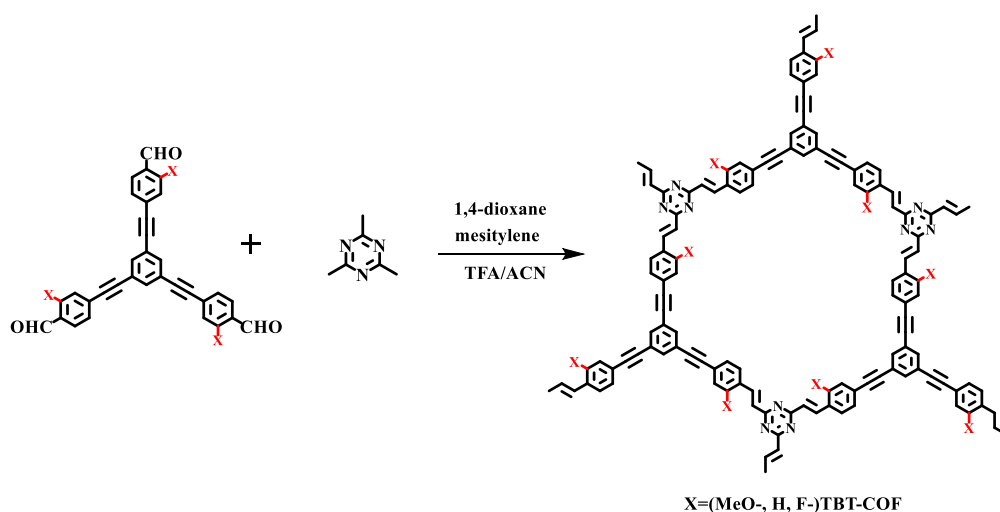
MeO-TST: ^1H NMR (400 MHz, CDCl_3): δ 8.19-8.15 (d, $J=16$ Hz, 3H), 7.60-7.58 (d, $J=8$ Hz, 6H), 6.98-6.91 (m, 9H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 175.87, 171.26, 161.20, 141.53, 129.82, 128.28, 123.67, 114.45, 55.47, 25.90.

H-TST: ^1H NMR (400 MHz, CDCl_3): δ 8.31-8.27 (d, $J=16$ Hz, 3H), 7.70-7.68 (d, $J=8$ Hz, 6H), 7.44-7.37 (m, 9H), 7.20-7.16 (d, $J=16$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.31, 141.82, 135.56, 129.96, 128.99, 128.25, 126.30.

F-TST: ^1H NMR (400 MHz, CDCl_3): δ 8.46-8.42 (d, $J=16$ Hz, 3H), 7.74-7.71 (t, $J=6$ Hz, 3H), 7.36-7.33 (m, 3H), 7.30-7.26 (d, $J=16$ Hz, 3H), 7.22-7.18 (t, $J=8$ Hz, 3H), 7.16-7.11 (t, $J=10$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.27, 161.46, 134.49, 131.35, 128.97, 128.53, 124.52, 123.59, 116.27.

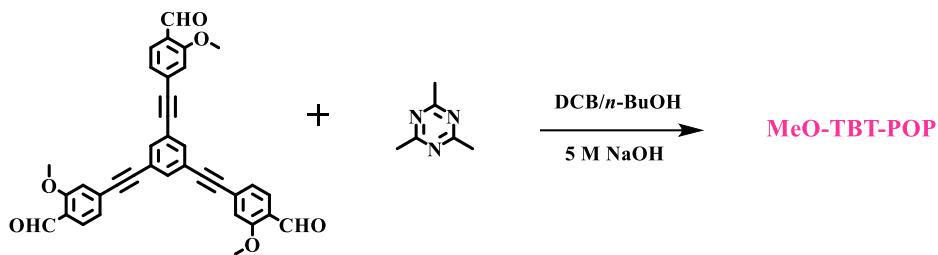
3.3 Synthesis of X-TBT-COF (X=MeO-, H-, F-)

TMT (6.91 mg, 0.056 mmol), 0.5 mL 1,4-dioxane, 0.5 mL mesitylene, 0.22 mL trifluoroacetic acid and 0.027 mL ACN were added individually various aldehydes such as MeO-TBT (31 mg, 0.056mmol), H-TBT (26 mg, 0.056mmol) or F-TBT (29 mg, 0.056mmol) in a Pyrex tube. This mixture was sonicated for 5 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 150 $^\circ\text{C}$ for 3 days. After the **MeO-TBT-COF**, **TBT-COF**, **F-TBT-COF** powders were filtered out, washed with NH_4OH solution (5mL \times 3) acetone (5mL \times 3), CH_2Cl_2 (5 mL \times 3), and dried under vacuum at 120 $^\circ\text{C}$ for 12 hours.



3.4 Synthesis of MeO-TBT-POP

The synthesis of **MeO-TBT-POP** was carried out by utilizing the protocol with a mixture of **MeO-TBT** (31 mg, 0.056 mmol) and **TMT** (6.91 mg, 0.056 mmol) in presence of 5 M NaOH (0.5 mL) using DCB (2 mL) and *n*-BuOH (2 mL) as solvent. This mixture was stirred and then heated at 80 $^\circ\text{C}$ for 1 days. After the reaction, the **MeO-TBT-POP** powders were filtered out, washed with ethanol, water and acetone. Then further purification of the resulted **MeO-TBT-POP** was carried out by Soxhlet extraction in THF for 48 h and dried under vacuum at 100 $^\circ\text{C}$ for 8 hours to give yellow powder.



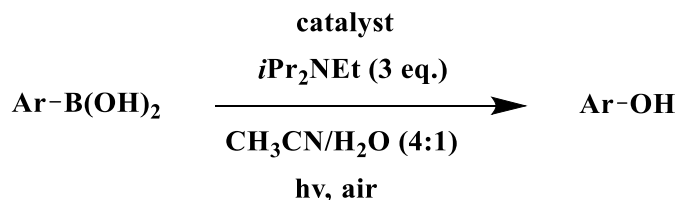
4. Experimental Procedure for Photocatalysis Reaction

4.1 A general procedure for C-3 thiocyanation of indoles.



Indoles and indole derivatives (0.24 mmol), COFs (0.016 mmol), NH_4SCN (0.48 mmol, 2.0 eq.) and THF (2.0 mL) were added to a 10 mL glass tube with a stir bar. The solution was stirred for 8 h at room temperature in O_2 atmosphere under irradiation with a 30W blue LED lamp (460 nm). 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.

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



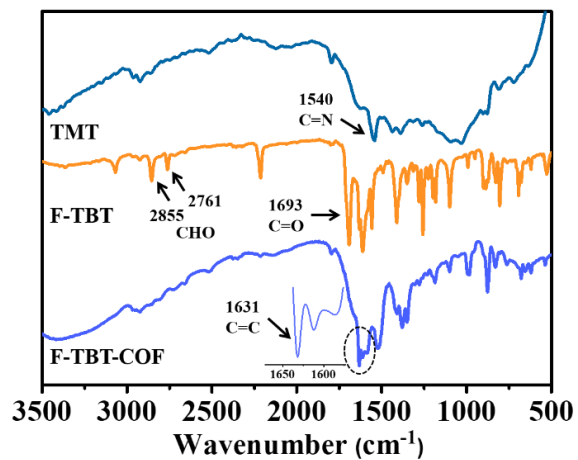
Arylboronic acid (0.20 mmol), COFs (0.015 mmol), $i\text{Pr}_2\text{NEt}$ (0.6 mmol, 3.0 eq.) and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v = 4/1, 2.0 mL) were added to a 10 mL glass tube with a stir bar. The solution was stirred for 12 h at room temperature under visible light irradiation in open 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.

4.3 Recycle experiments for the photocatalytic.

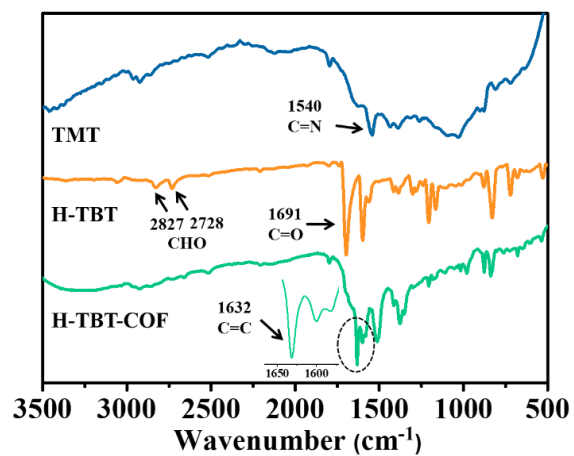
After the first run reaction was finished, the photocatalyst COFs was recovered by centrifugation, and then washed thoroughly with THF and CH_2Cl_2 . The recovered COFs was dried under vacuum at 100°C overnight. The used photocatalyst COFs was re-employed in next cycle under identical conditions.

5. Figures S 1. FT-IR

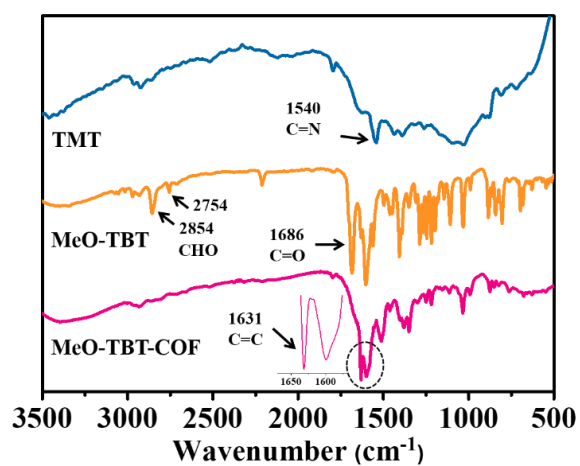
(a)



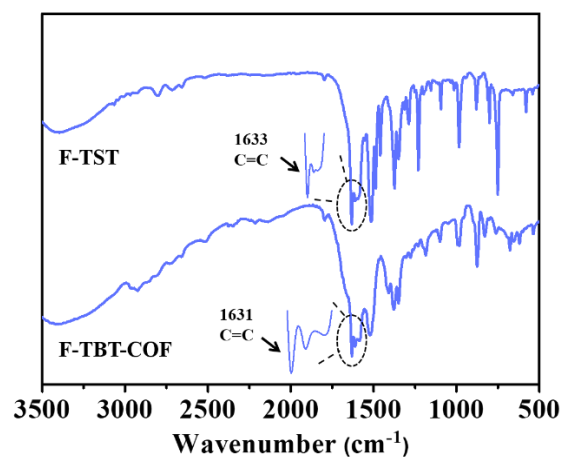
(b)



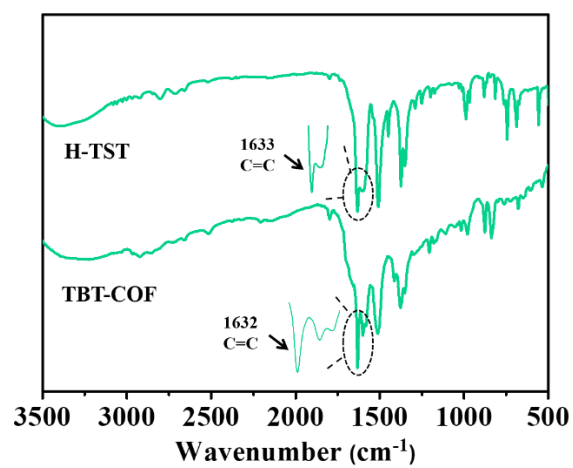
(c)



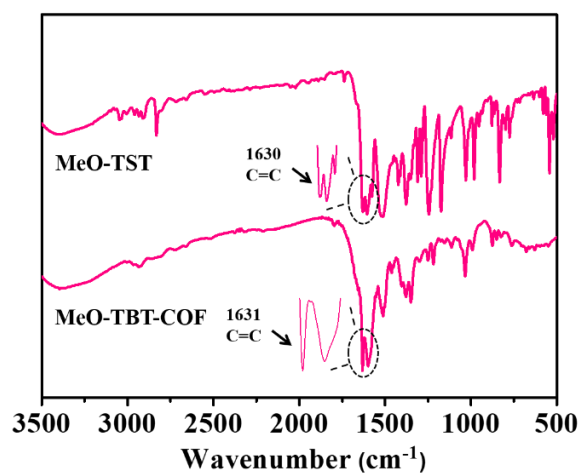
(d)



(e)



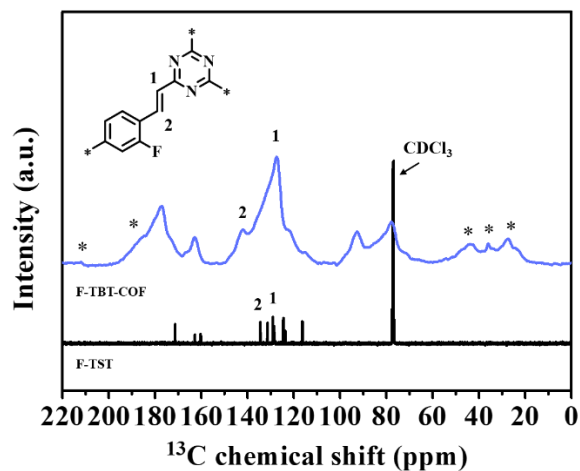
(f)



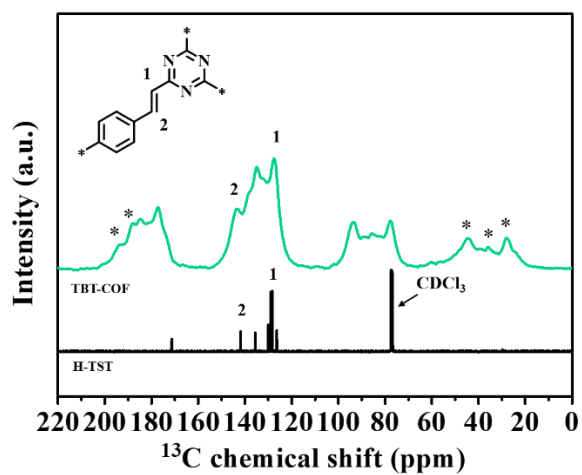
Figures S 1. IR spectrums of (a) F-TBT-COF (b) TBT-COF (c) MeO-TBT-COF, (d)-(f) IR spectrums comparison of model compounds with the three COFs.

6. Figures S 2. Solid-state ^{13}C CP-MAS NMR and liquid ^{13}C NMR spectra

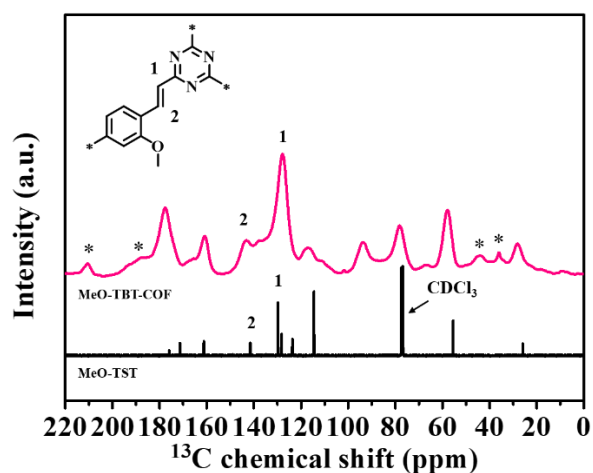
(a)



(b)

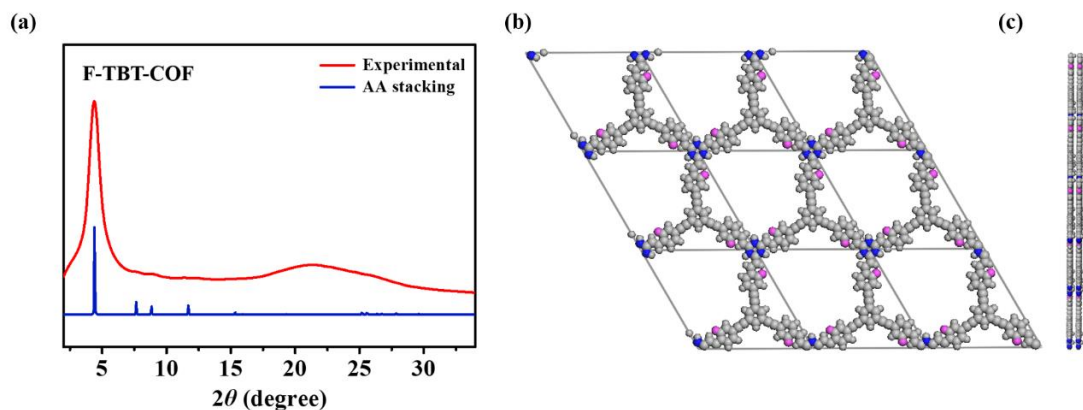


(c)

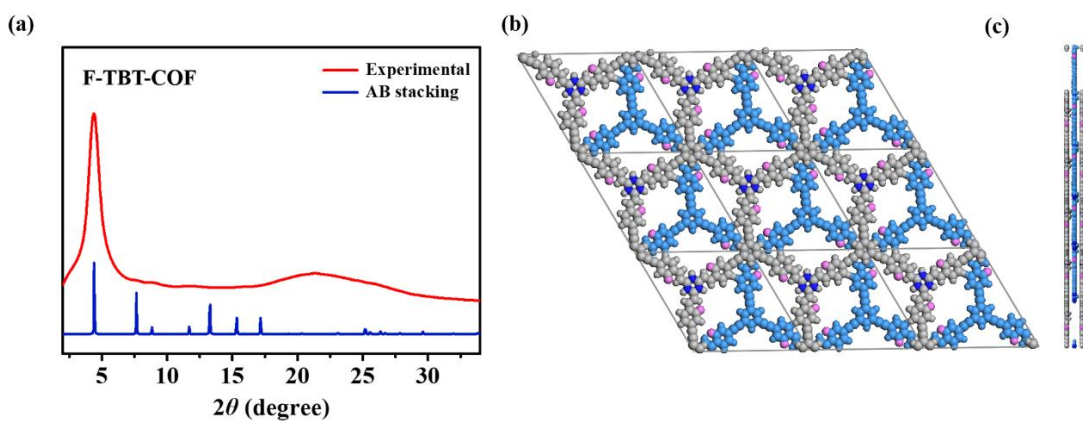


Figures S 2. Solid-state ^{13}C CP-MAS NMR spectra of F-TBT-COF, TBT-COF and MeO-TBT-COF, combined with liquid ^{13}C NMR spectra of F-TST, TST and MeO-TST (model compound) recorded. Asterisks denote spinning sidebands.

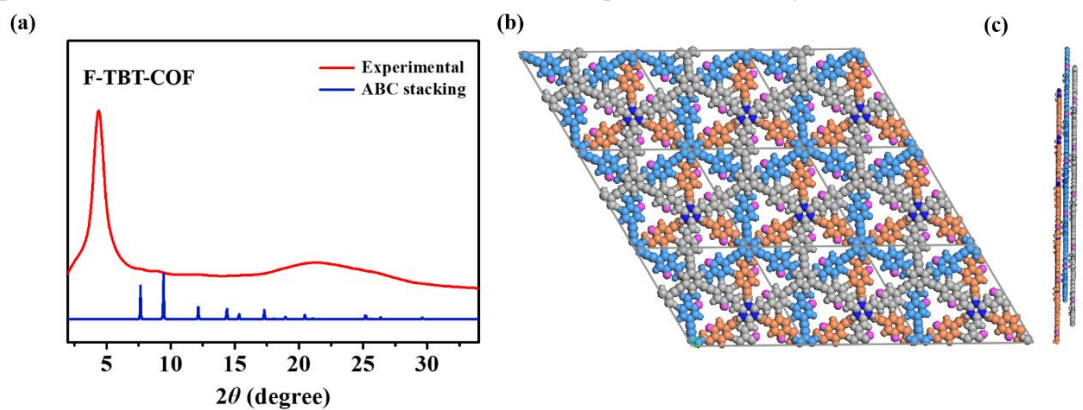
7. Figures S 3. Structural models of F-TBT-COF with three stacking modes and PXRD



Figures S 3-1. (a) Simulated PXRD patterns of AA (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AA-stacking.

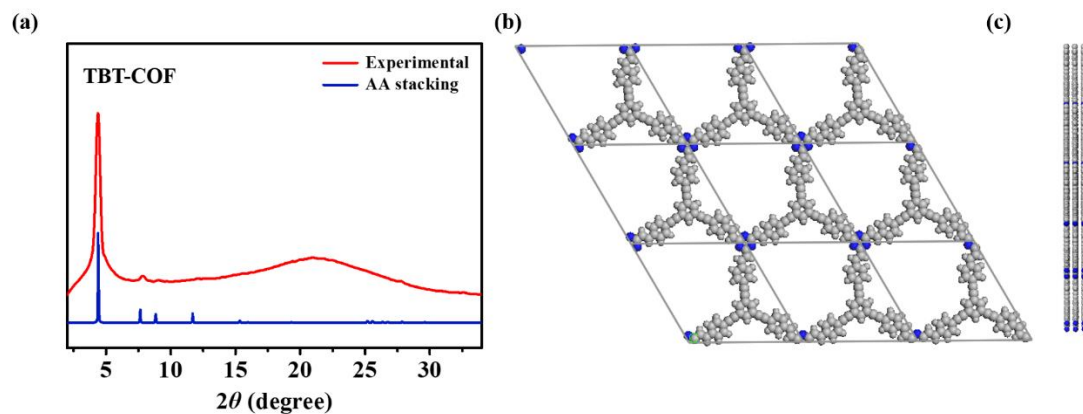


Figures S 3-2. (a) Simulated PXRD patterns of AB (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AB-stacking.

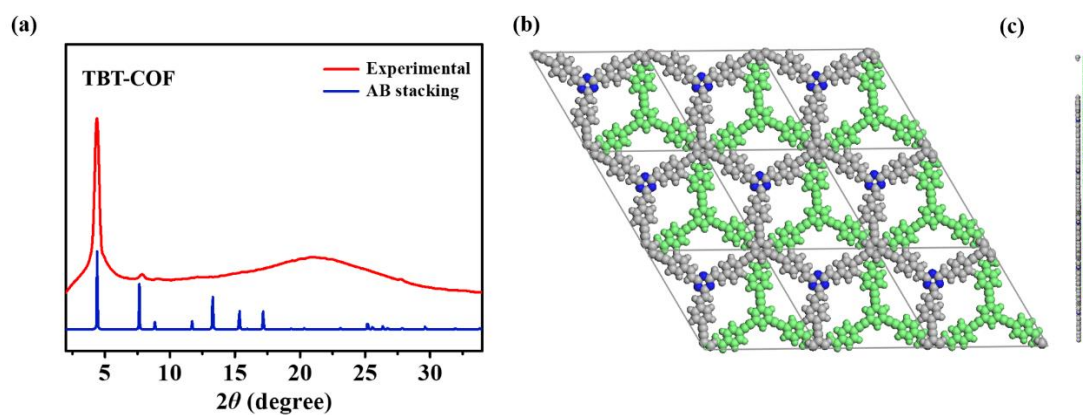


Figures S 3-3. (a) Simulated PXRD patterns of ABC (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed ABC-stacking.

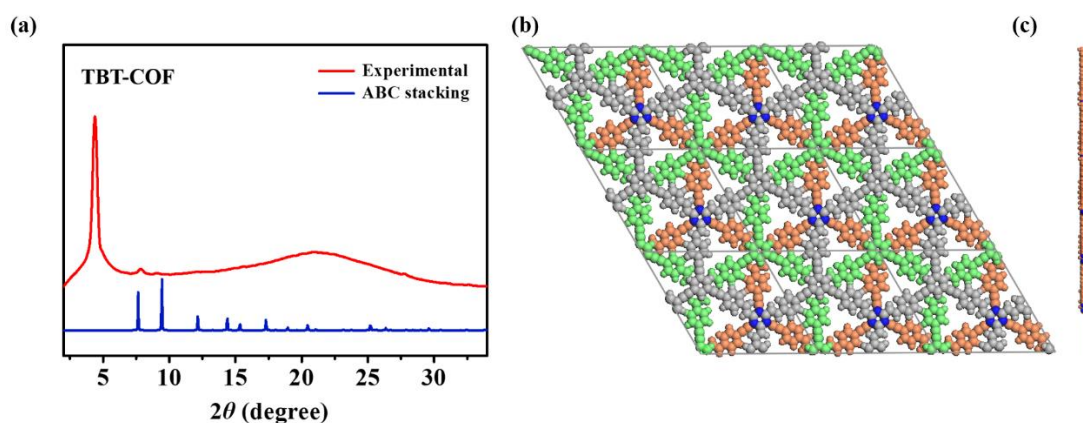
8. Figures S 4. Structural models of TBT-COF with three stacking modes and PXRD



Figures S 4-1. (a) Simulated PXRD patterns of AA (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AA-stacking.

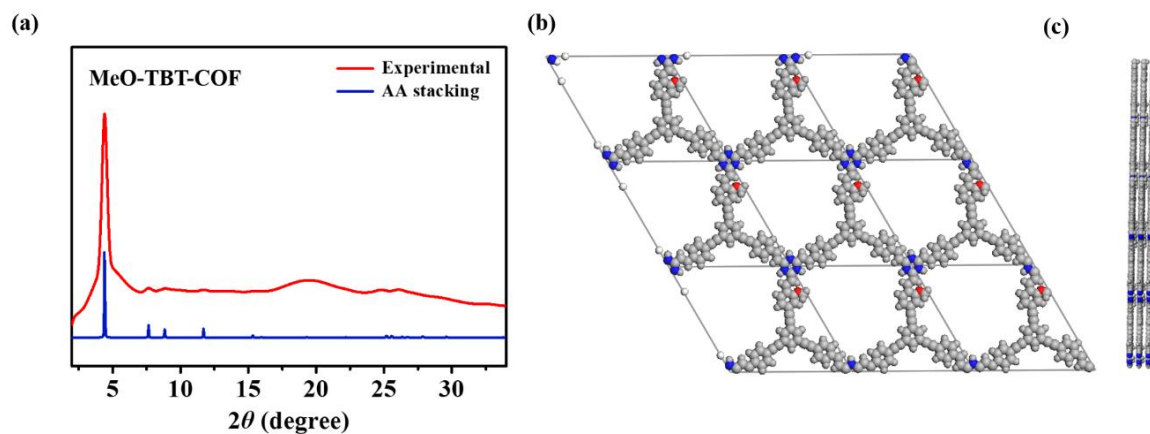


Figures S 4-2. (a) Simulated PXRD patterns of AB (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AB-stacking.

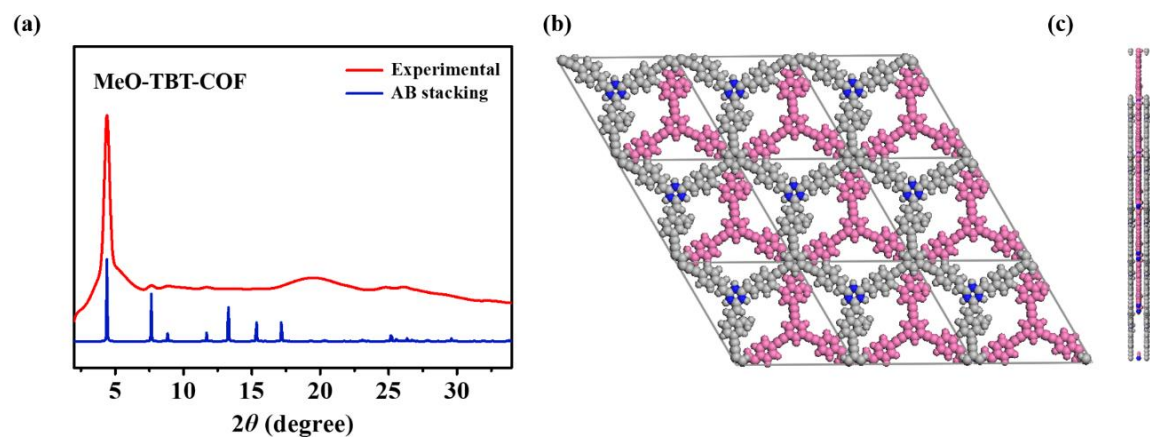


Figures S 4-3. (a) Simulated PXRD patterns of ABC (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed ABC-stacking.

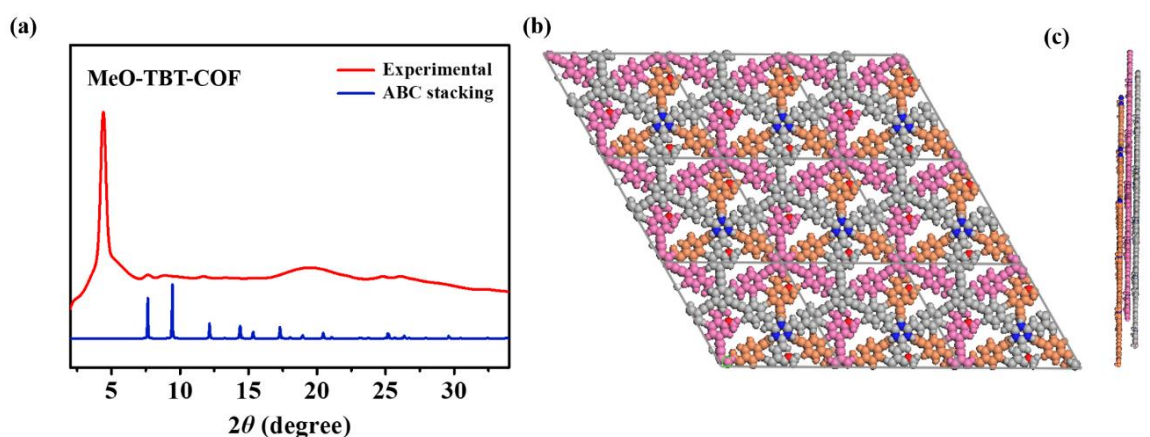
9. Figures S 5. Structural models of MeO-TBT-COF with three stacking modes and PXRD



Figures S 5-1. (a) Simulated PXRD patterns of AA (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AA-stacking.

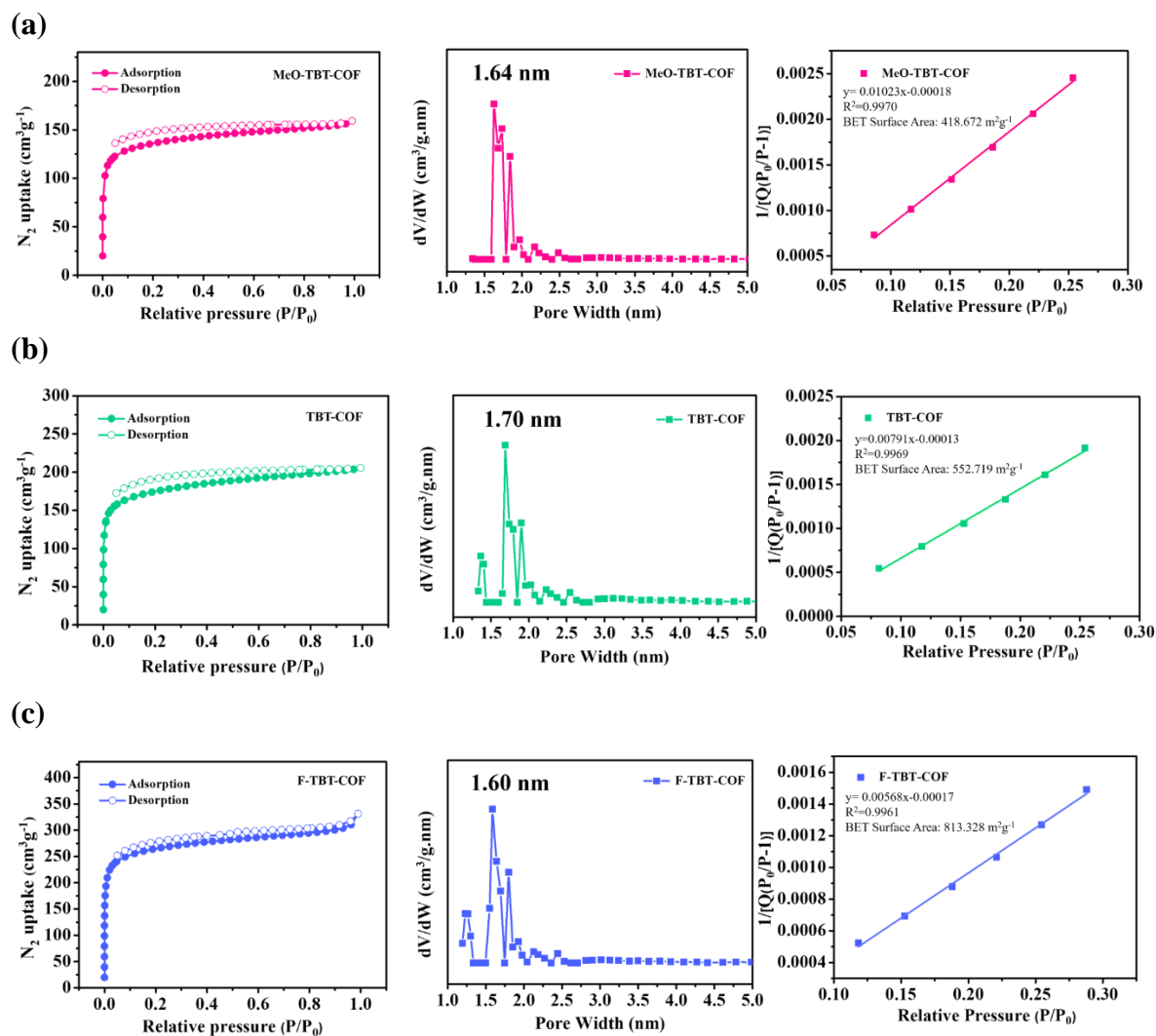


Figures S 5-2. (a) Simulated PXRD patterns of AB (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed AB-stacking.



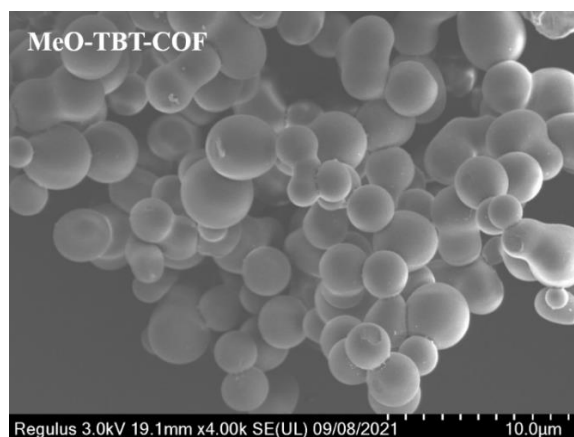
Figures S 5-3. (a) Simulated PXRD patterns of ABC (blue) stacking model compared to experimental pattern (red) (b) and (c) The view of the simulated eclipsed ABC-stacking.

10. Figure S 6. N₂ Sorption Studies

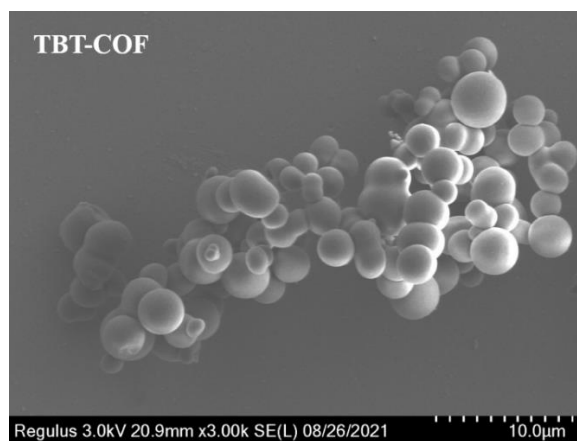


11. Figure S 7. Scanning Electron Microscopy (SEM)

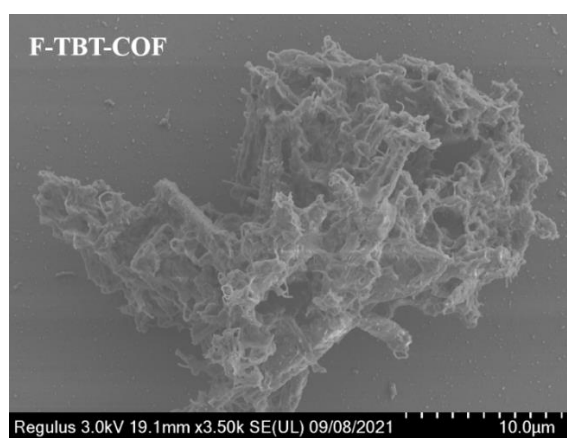
(a)



(b)

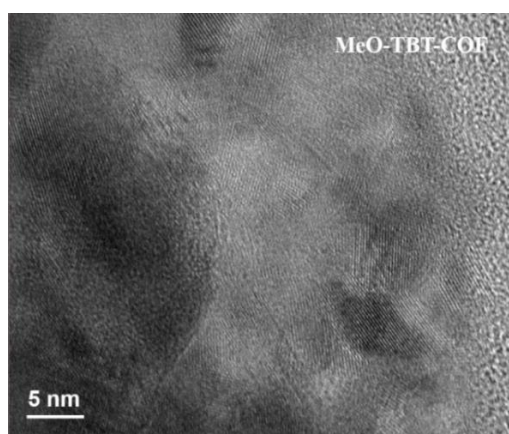


(c)

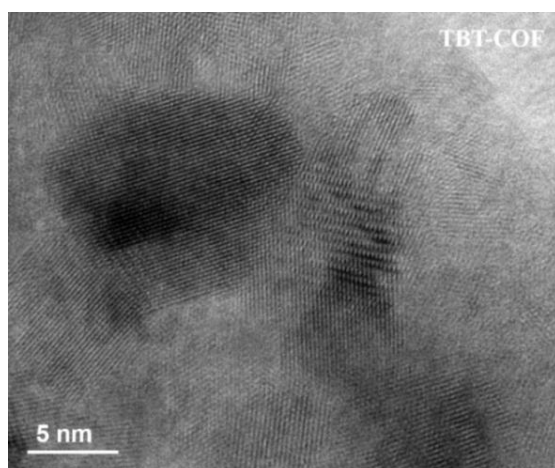


12. Figure S 8. Transmission electron microscopy (TEM)

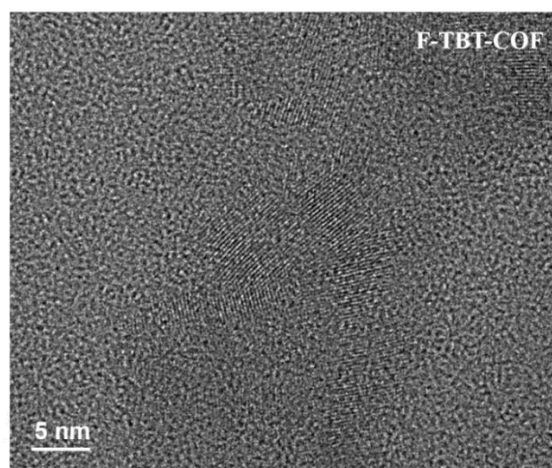
(a)



(b)

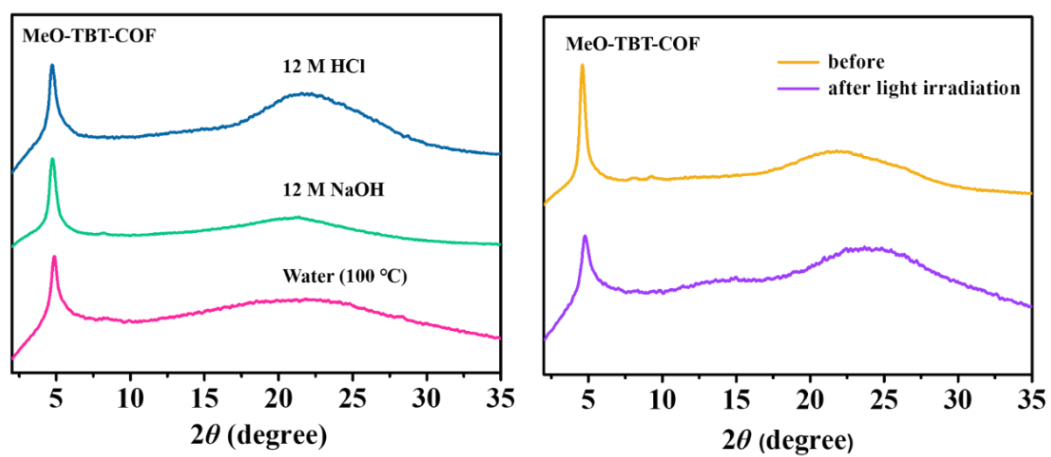


(c)



13. Figure S 9. IR, PXRD and BET of MeO-TBT-COF treated under different conditions

(a)



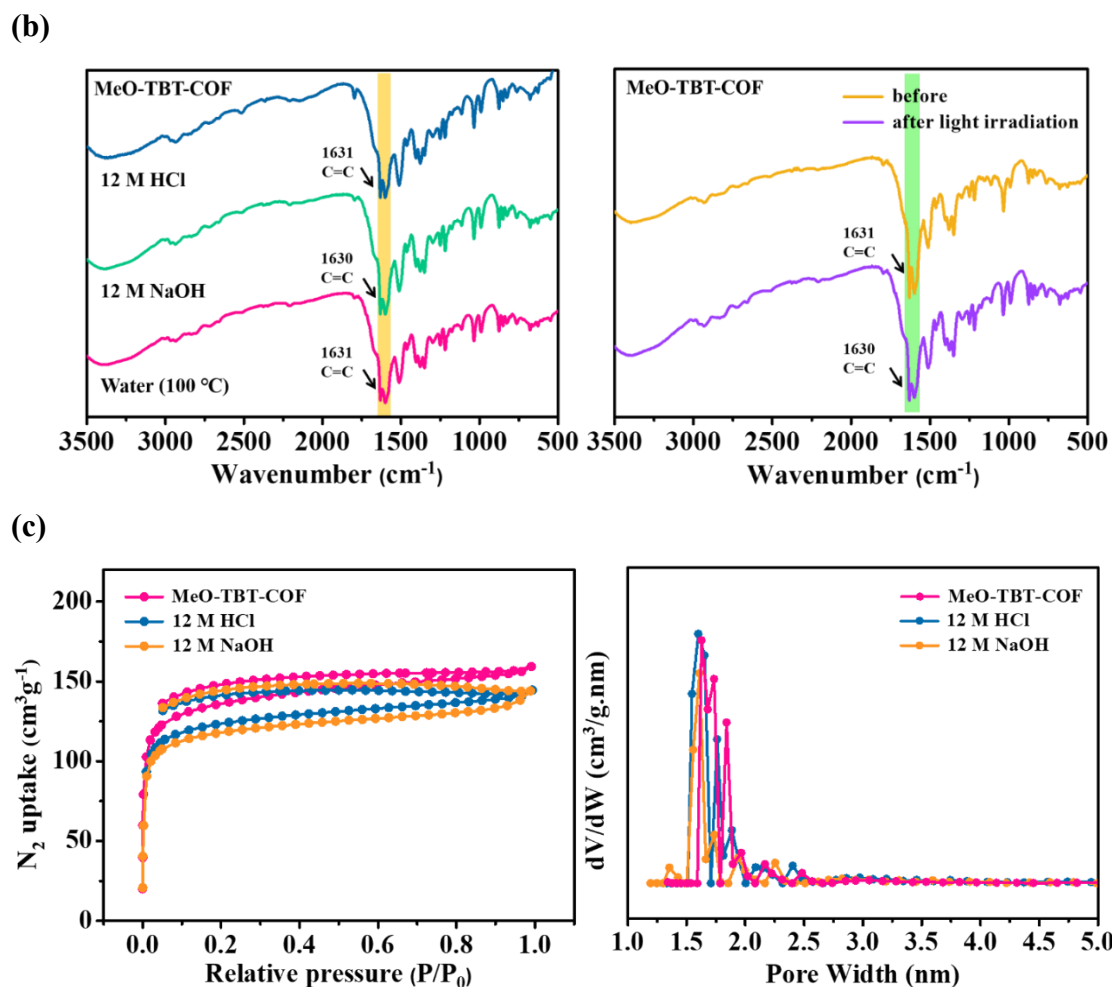
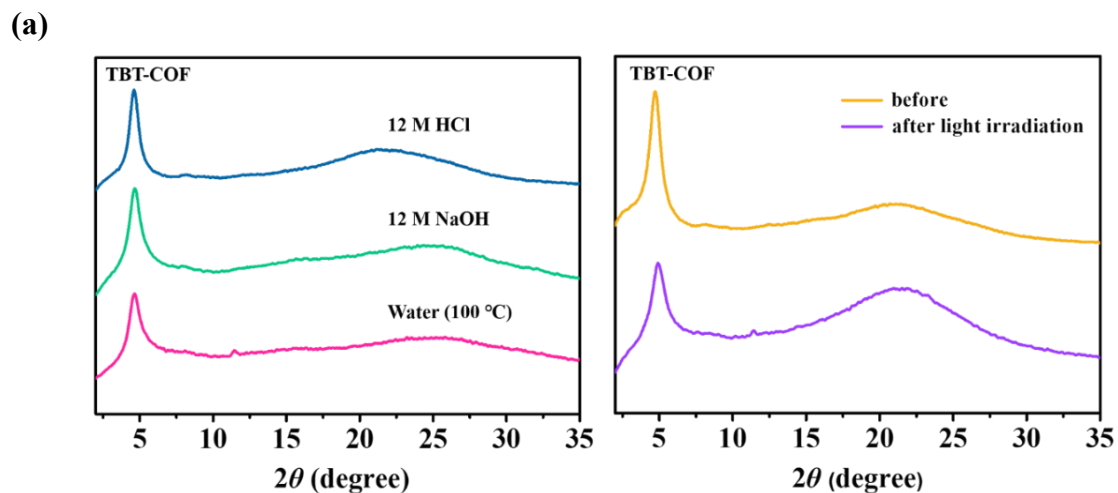


Figure S9. (a) PXRD and (b) IR of MeO-TBT-COF after immersed in different conditions for one week and light irradiation for 3 days; (c) N₂ sorption isotherm of MeO-TBT-COF after immersed in 12 M HCl and 12 M NaOH for one week.

14. Figure S 10. IR, PXRD and BET of TBT-COF treated under different conditions



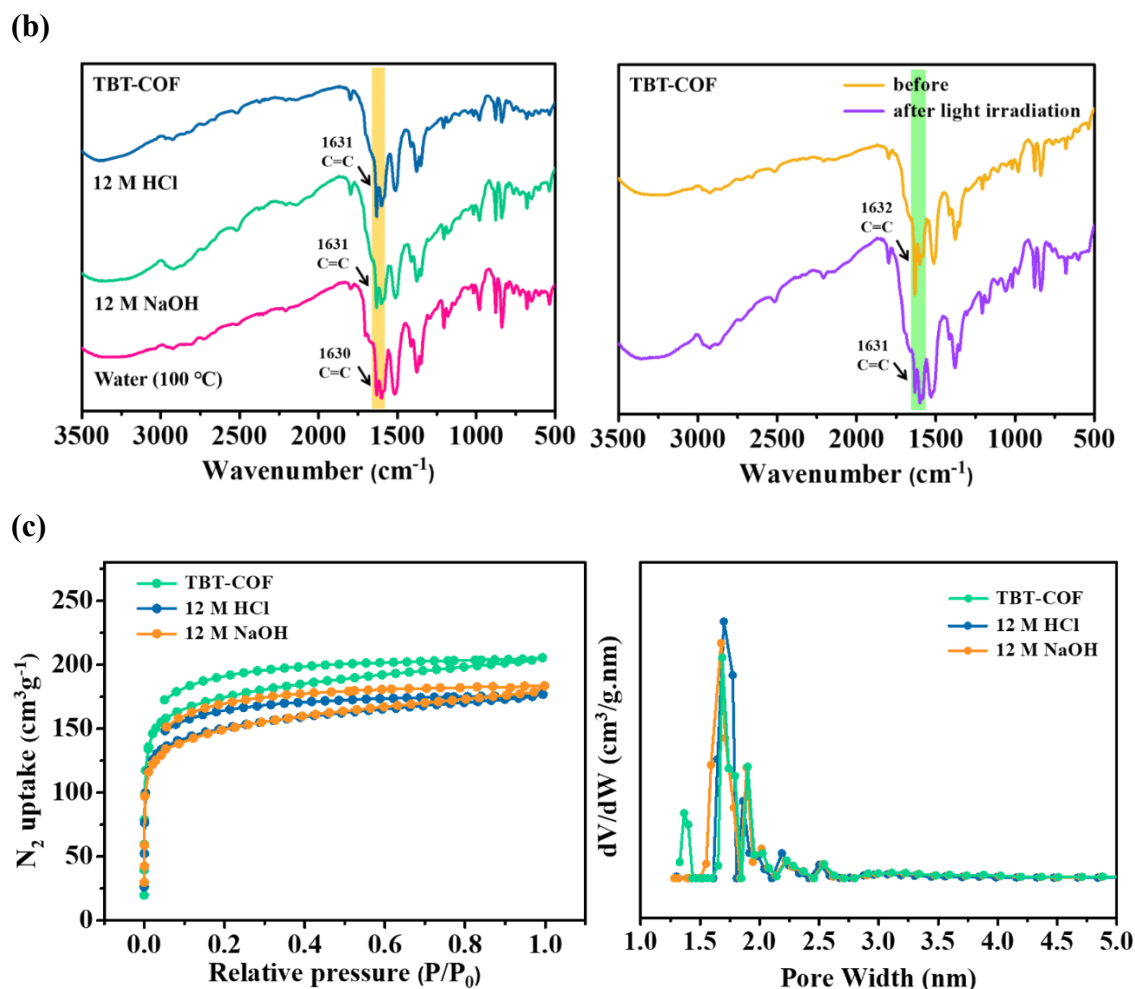
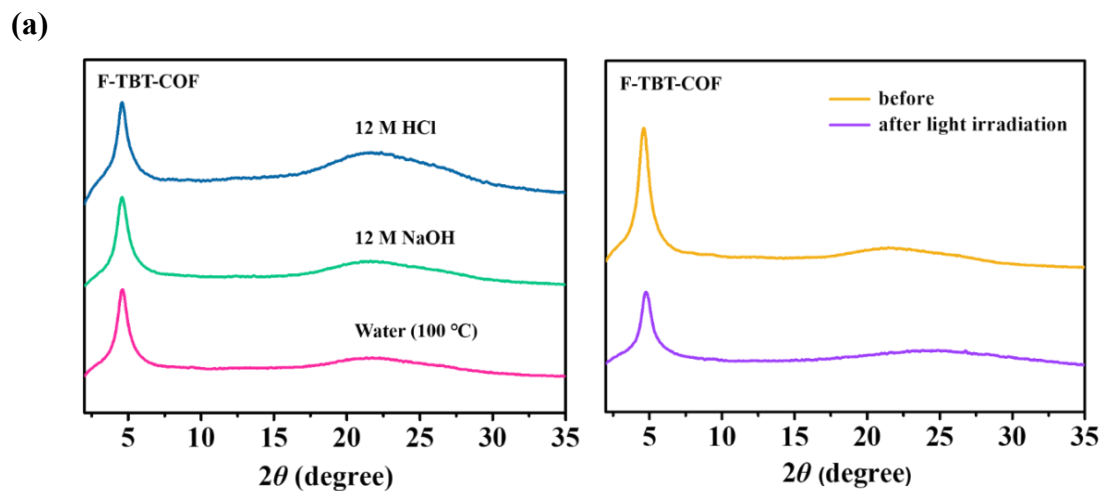


Figure S 10. (a) PXRD and (b) IR of TBT-COF after immersed in different conditions for one week and light irradiation for 3 days; (c) N_2 sorption isotherm of TBT-COF after immersed in 12 M HCl and 12 M NaOH for one week.

15. Figure S 11. IR, PXRD and BET of F-TBT-COF treated under different conditions



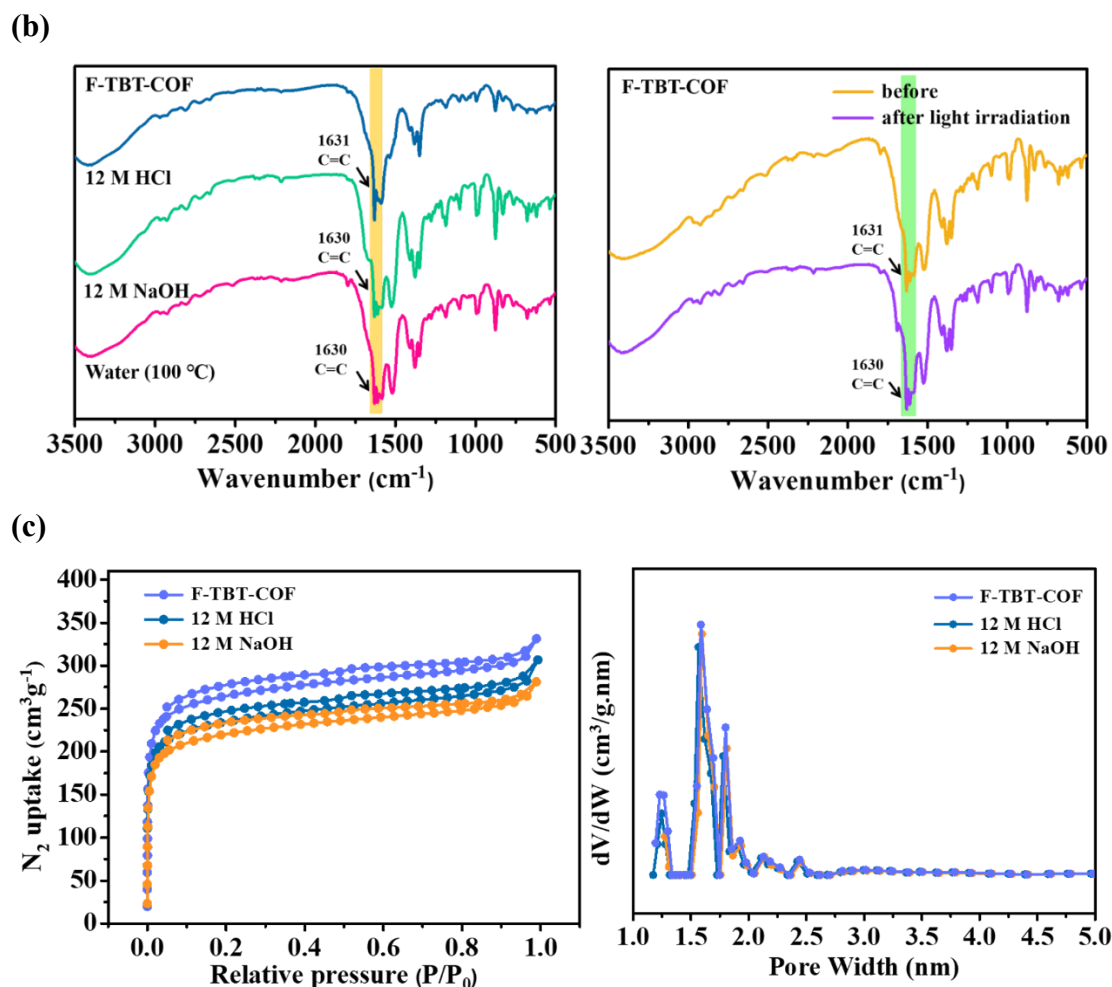


Figure S 11. (a) PXRD and (b) IR of F-TBT-COF after immersed in different conditions for one week and light irradiation for 3 days; (c) N_2 sorption isotherm of F-TBT-COF after immersed in 12 M HCl and 12 M NaOH for one week.

16. Figure S 12. Thermogravimetric analysis (TGA)

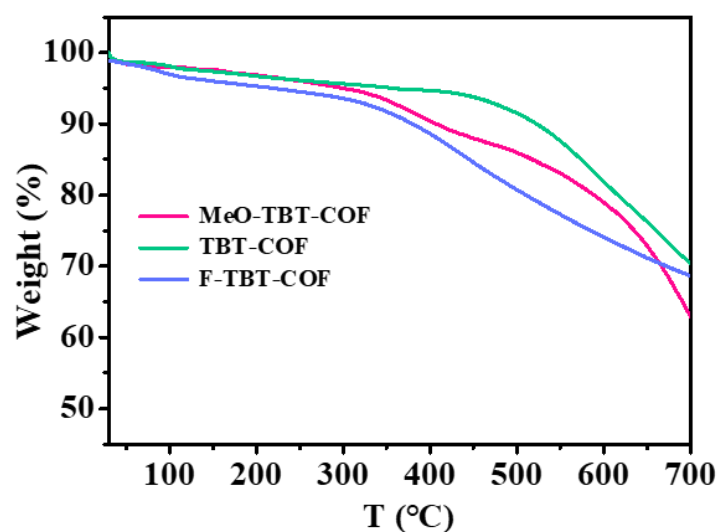
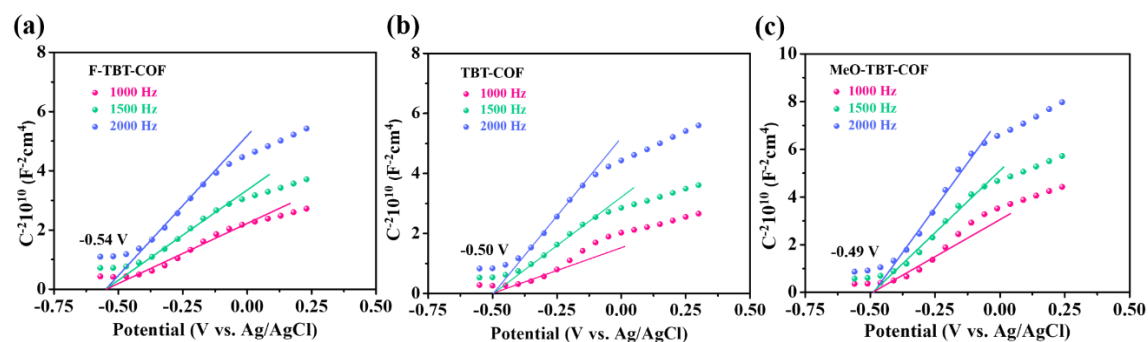


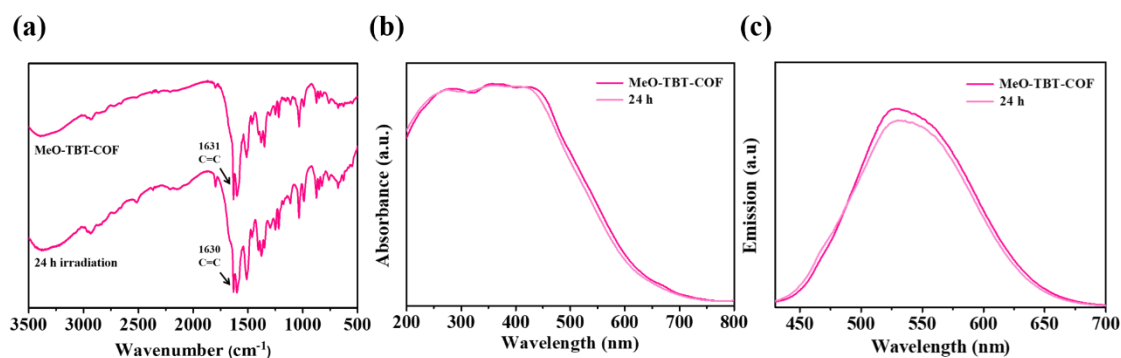
Figure S12. TGA analysis results of MeO-TBT-COF, TBT-COF and F-TBT-COF.

17. Figure S 13. Mott–Schottky plots of these three COFs



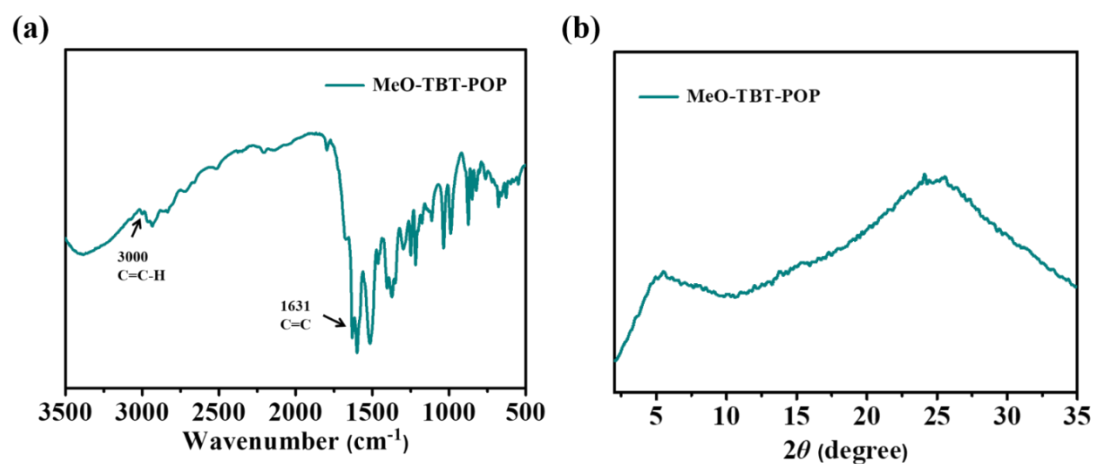
Figures S 13. Mott–Schottky plots of (a) the F-TBT-COF, (b) TBT-COF and (c) MeO-TBT-COF.

18. Figures S 14. Avoid photo addition reaction of MeO-TBT-COF



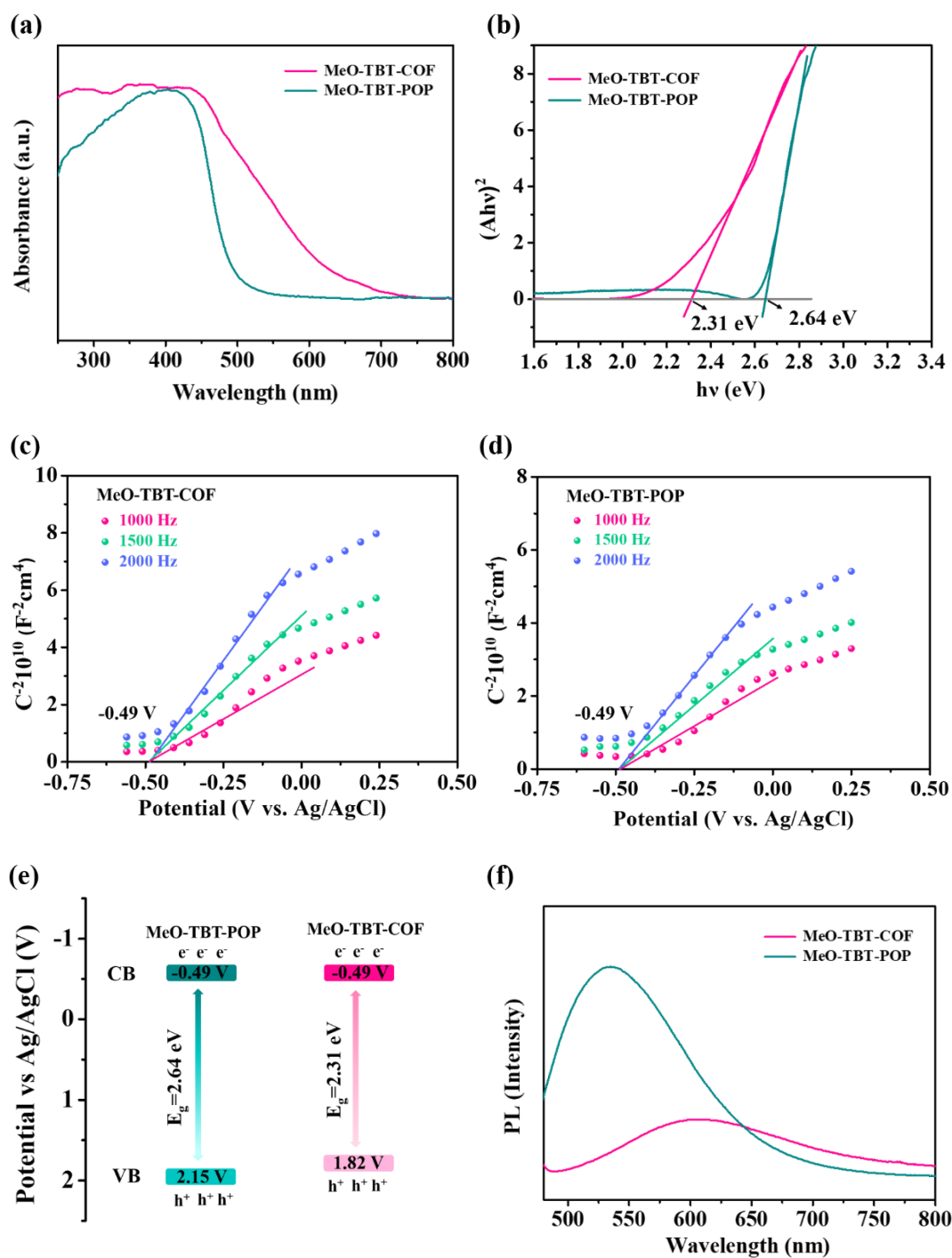
Figures S 14. After illumination for 24 h, (a) IR spectrums of MeO-TBT-COF; (b) UV–vis diffuse reflectance spectra and (c) fluorescence spectra of MeO-TBT-COF.

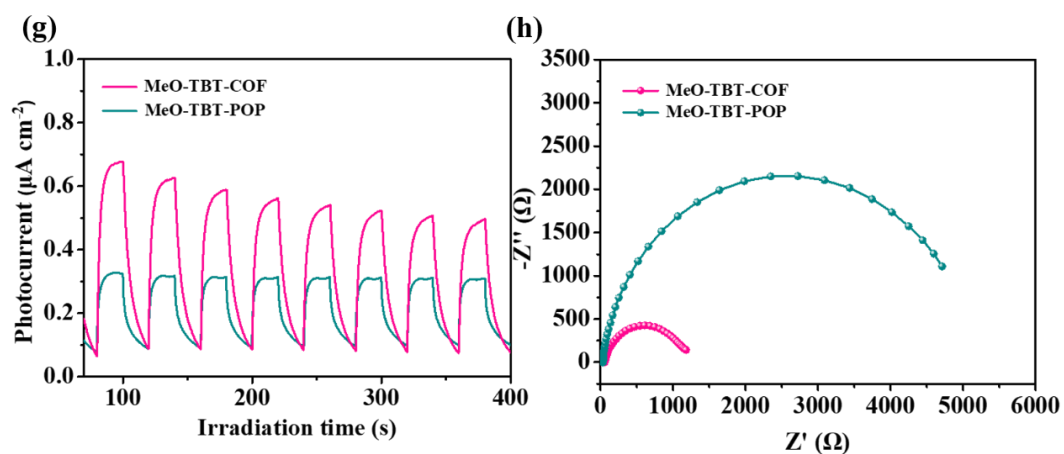
19. Figures S 15. FT-TR and PXRD of MeO-TBT-POP



Figures S 15. (a) FT-TR and (b) PXRD of MeO-TBT-POP.

20. Figures S 16. Optical and Electric Properties of MeO-TBT-POP

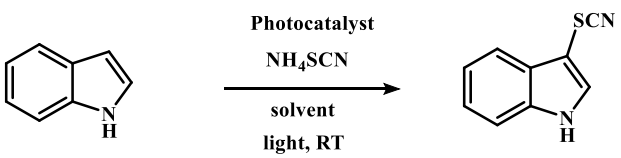




Figures S 16. (a) UV–vis diffuse reflectance spectra and (b) band gap energies of MeO-TBT-COF and MeO-TBT-POP; Mott–Schottky plots of (c) the MeO-TBT-COF and (d) MeO-TBT-POP; (e) Electronic band structure; (f) The PL spectra of MeO-TBT-COF and MeO-TBT-POP; (g) Photocurrent responses and (h) EIS curves of the MeO-TBT-COF and MeO-TBT-POP.

21. Table S1. Photocatalytic C-3 thiocyanation reaction of 1*H*-indole by these three COFs

Table S1. Control Experiments ^a

				
Entry	Visible light	Catalyst	Solvent (mL)	Yield (%) ^b
1	on	TBT-COF	DMF	30
2	on	F-TBT-COF	DMF	25
3	on	MeO-TBT-COF	DMF	49
4	on	MeO-TBT-COF	DCM	trace
5	on	MeO-TBT-COF	THF	95
6	on	MeO-TBT-COF	CH ₃ CN	70
7 ^c	on	MeO-TBT-COF	THF	46
8	off	MeO-TBT-COF	THF	0
9 ^d	on	MeO-TBT-COF	THF	25
10	on	~	THF	0
11	on	TBT-COF	THF	83
12	on	F-TBT-COF	THF	71
13	on	MeO-TBT-POP	THF	68

^aReaction conditions: photocatalyst (5 mg), 1*H*-indole (35 mg, 0.24mmol), NH₄SCN (36.69 mg, 0.48mmol), solvent (2 mL), O₂, 30 W blue LED lamp with 460 nm, 25 °C, 8h. ^bIsolated yield. ^c2.0 equiv of KSCN was used. ^dIn N₂.

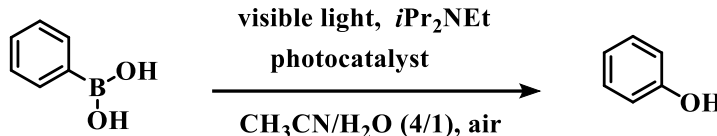
22. Table S2. Comparison with different heterogeneous catalysts of photocatalytic C-3 thiocyanation reaction of 2-methyl-1*H*-indole

Entry	Catalyst	Time (h)	Yield (%)
1	MeO-TBT-COF (this work)	8	98
2	COF-JLU24 ^a	7	97
3	CMP-CSU6 ^b	10	97
4	Ag/ TNT ^c	18	98
5	ARS-TiO ₂ ^d	20	96
6	TiO ₂ / MoS ₂ ^e	16	90
7	NCS/ thiourea ^f	0.5	87
8	Mn (OAc) ₃ ^g	~	60

(a) L. Zhang, Z. P Li, S. J. Han, C. Z Li, P. P. Shao, H. Xia, H. Li, X. Chen, X. Feng and X. M. Liu, *J. Mater. Chem. A.*, 2020, 8, 8706. (b) W. J. Zhang, J. T. Tang, W. G. Yu, Q. Huang, Y. Fu, G. C. Kuang, C. Y. Pan and G. P. Yu, *ACS Catal.*, 2018, 8, 8084–8091. (c) M. Hosseini-Sarvari, Z. Hosseinpour and M. Koohgard, *New J. Chem.*, 2018, 42, 19237. (d) M. Koohgard, Z. Hosseinpour, A. M. Sarvestani and M. Hosseini-Sarvari, *Catal. Sci. Technol.*, 2020, 10, 1401. (e) L. Wang, C. C Wang, W. J. Liu, Q. Chen, and M. Y. He, *Tetrahedron Letters.*, 2016, 1771-1774. (f) C. C Wang, Z. H. Wang, L. Wang, Q. Chen and M. Y. He, *Chin. J. Chem.*, 2016, 34, 1081-1085. (g) X. Q. Pan, M. Y. Lei, J. P. Zou, W. Zhang, *Tetrahedron Letters.*, 50 (2009), 347–349.

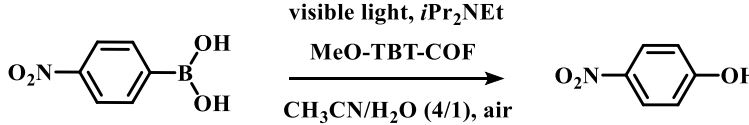
23. Table S3. Photocatalytic oxidativ of phenylboronic acid to phenols by these three COFs

Table S3. Control Experiments ^a

				
Entry	Visible light	Catalyst	air	Yield (%) ^b
1	on	MeO-TBT-COF	+	92
2	on	TBT-COF	+	87
3	on	F-TBT-COF	+	79
4	off	MeO-TBT-COF	+	N.D.
5	on	~	+	trace
6	on	MeO-TBT-COF	-	trace
7	on	MeO-TBT-POP ^c	+	70

^aReaction conditions: Phenylboronic Acid (1.0 mmol), MeO-TBT-COF (5 mg), CH₃CN (2 mL), H₂O (0.5 mL), *i*Pr₂NEt (3.0 mmol, 3.0 equiv.), irradiation with 20 W white LEDs, 12 h. ^bIsolated yield. ^cMeO-TBT-POP is amorphous MeO-TBT-COF.

24. Table S4. Comparison with different heterogeneous catalysts of photocatalytic oxidativ of phenylboronic acid to phenols

			
Entry	Catalyst	Time (h)	Yield (%)
1	MeO-TBT-COF (this work)	12	99
2	JLU-190 ^a	30	99
3	COF-p-3Ph ^b	4	99
4	COF-JLU25 ^c	24	90
5	Rh ₂ (bpy) ₂ (OAc) ₄ ^d	~	90
6	PCP-MF ^e	19	95

(a) *J. Am. Chem. Soc.* **2018**, *140*, 4623–4631. (b) *J. Am. Chem. Soc.* **2020**, *142*, 11893–11900. (c) *Eur. J. Org. Chem.* **2021**, 3986–3991. (d) *J. Org. Chem.* **2020**, *85*, 2040–2047 (e) *Polymer* **2017** *126* (2017), 291-295

25. Figures S 17. Water contact angle measurements of the three materials

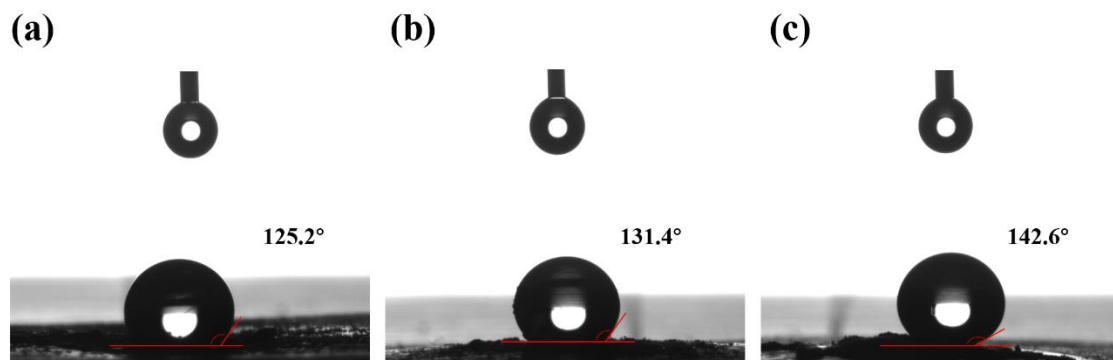


Figure 17. Water contact angle measurements of (a) MeO-TBT-COF, (b) TBT-COF and (c) F-TBT-COF at room temperature in air.

26. Figures S 18. BET of MeO-TBT-COF after five cycles

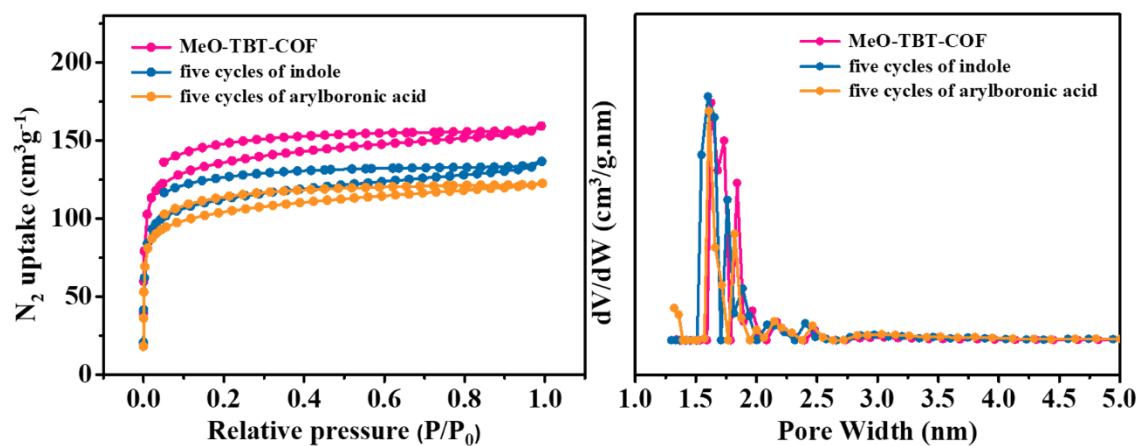
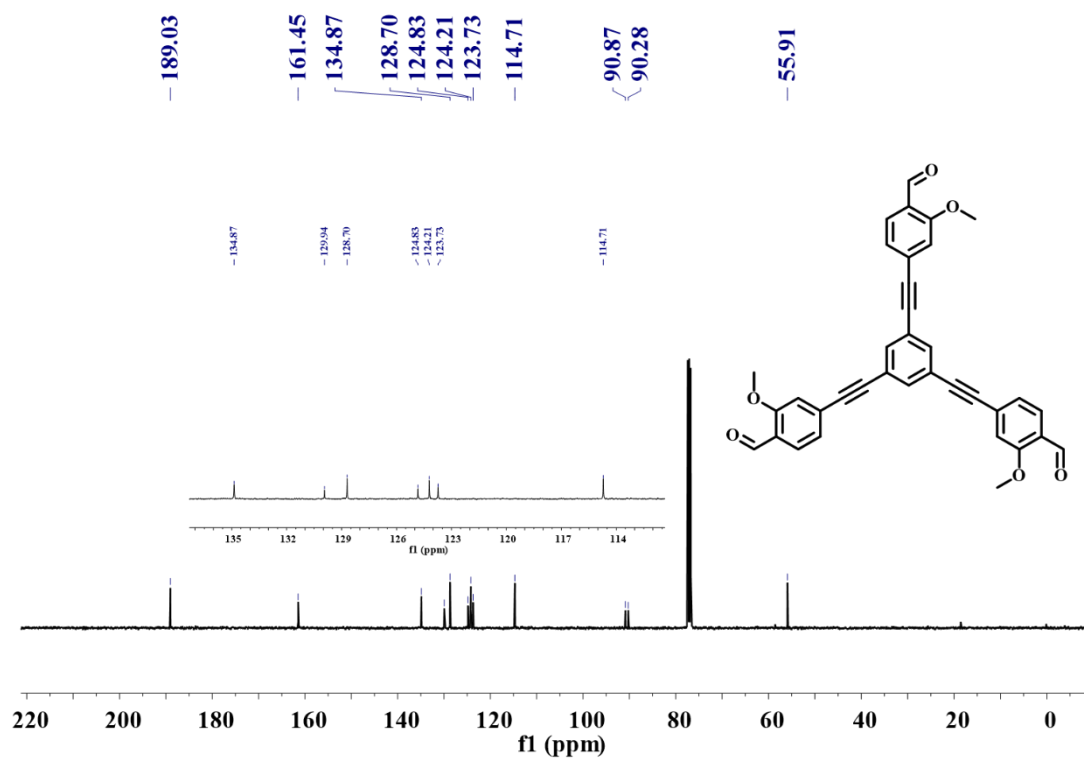
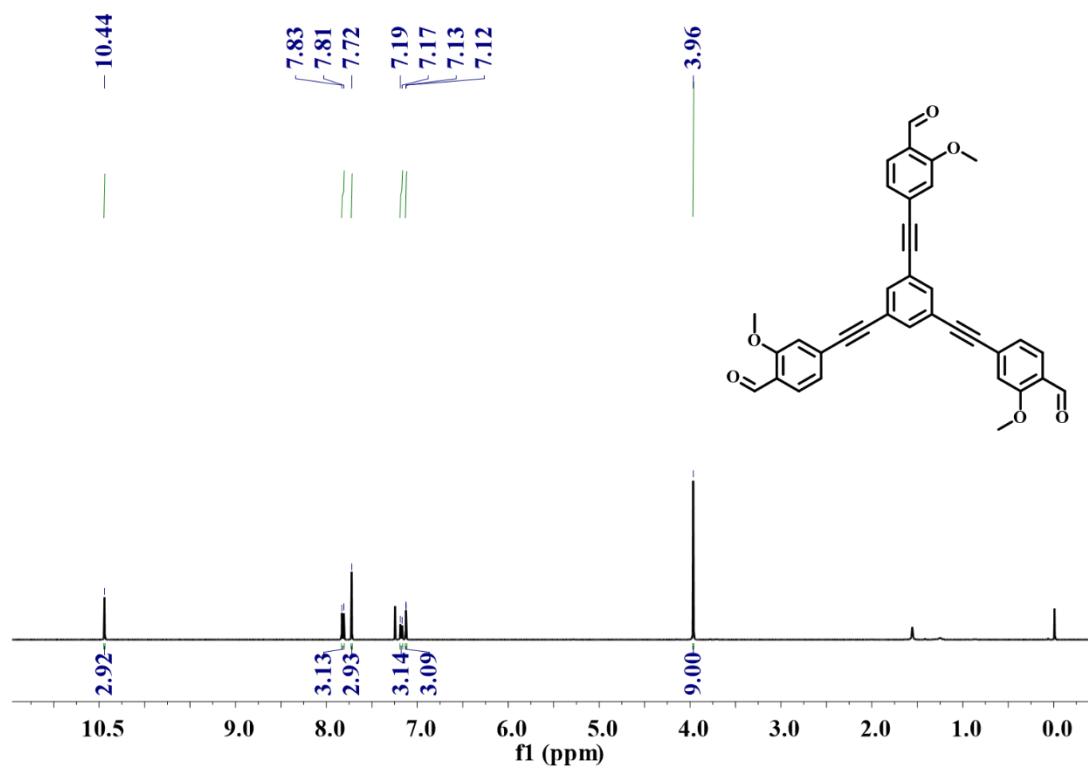
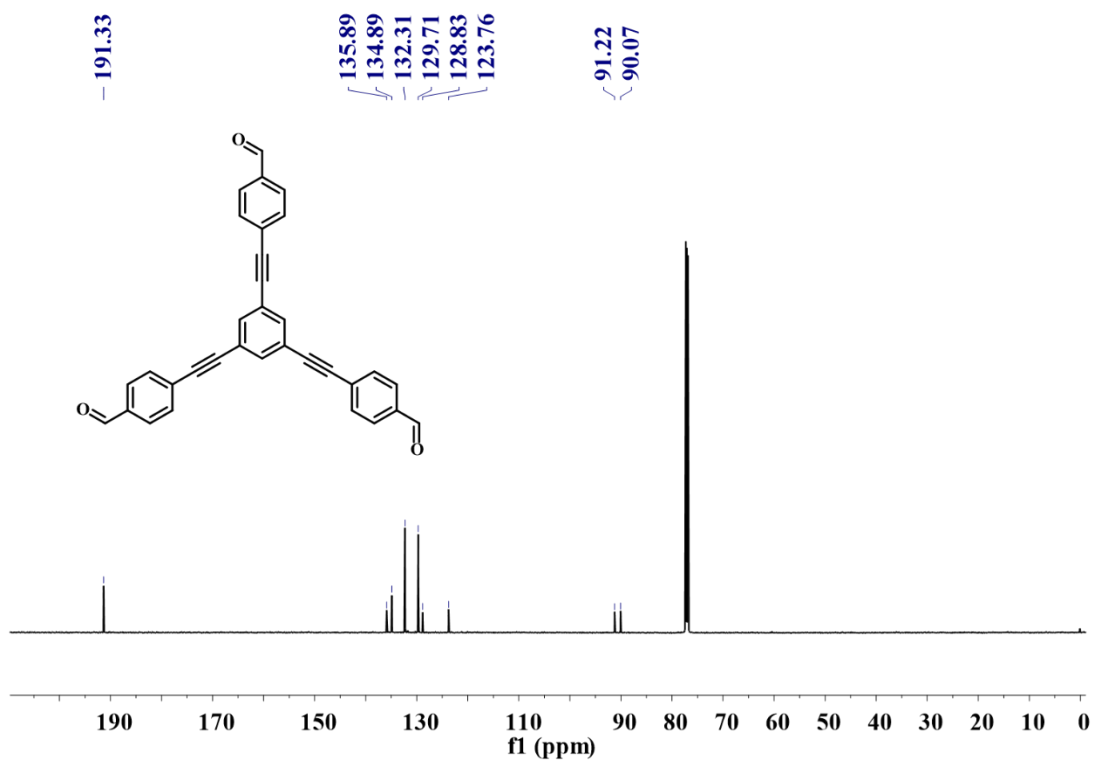
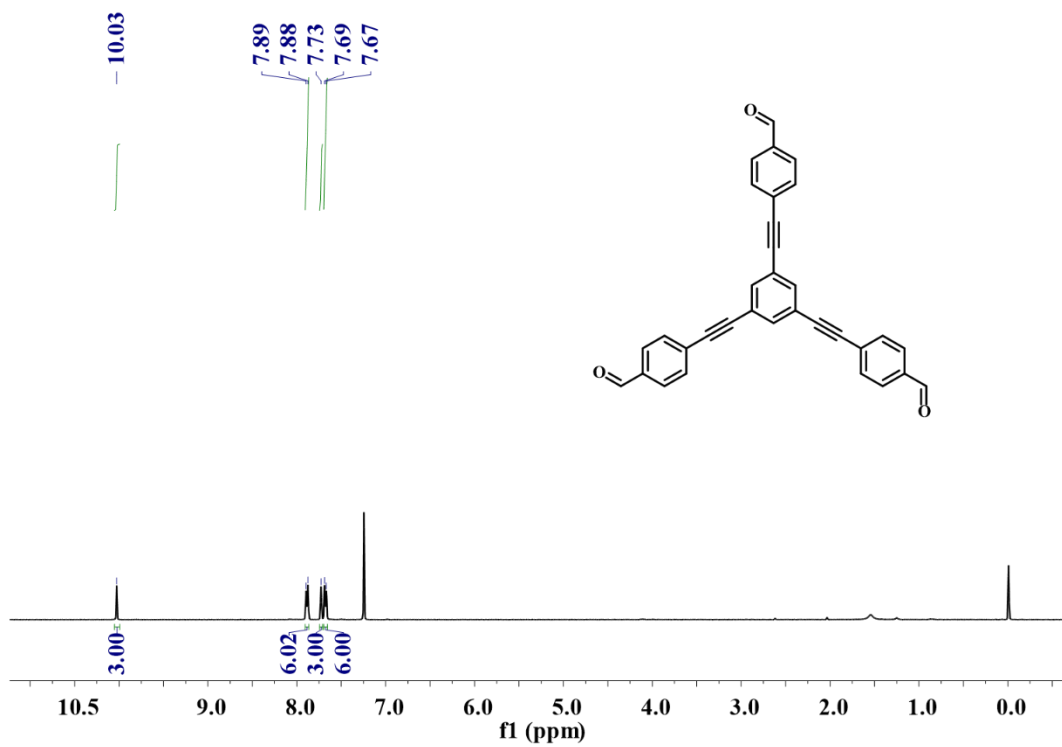
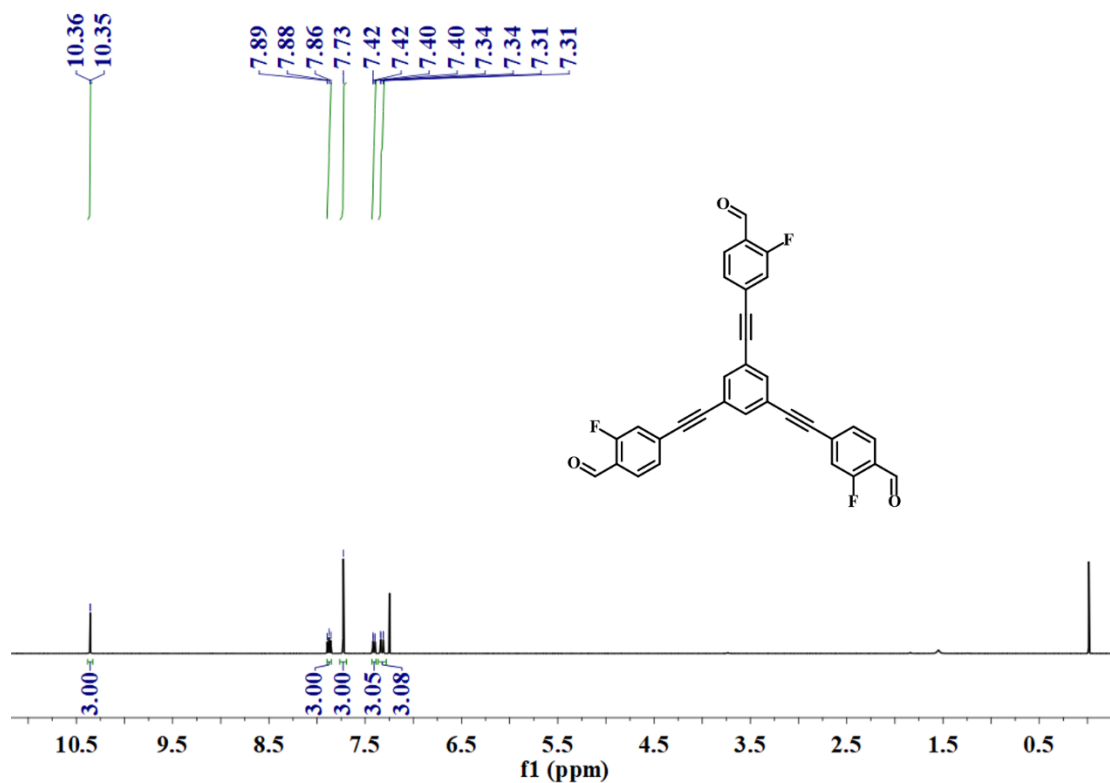


Figure S18. N_2 sorption isotherm of 1*H*-indole and phenylboronic acid photocatalyzed by MeO-TBT-COF.

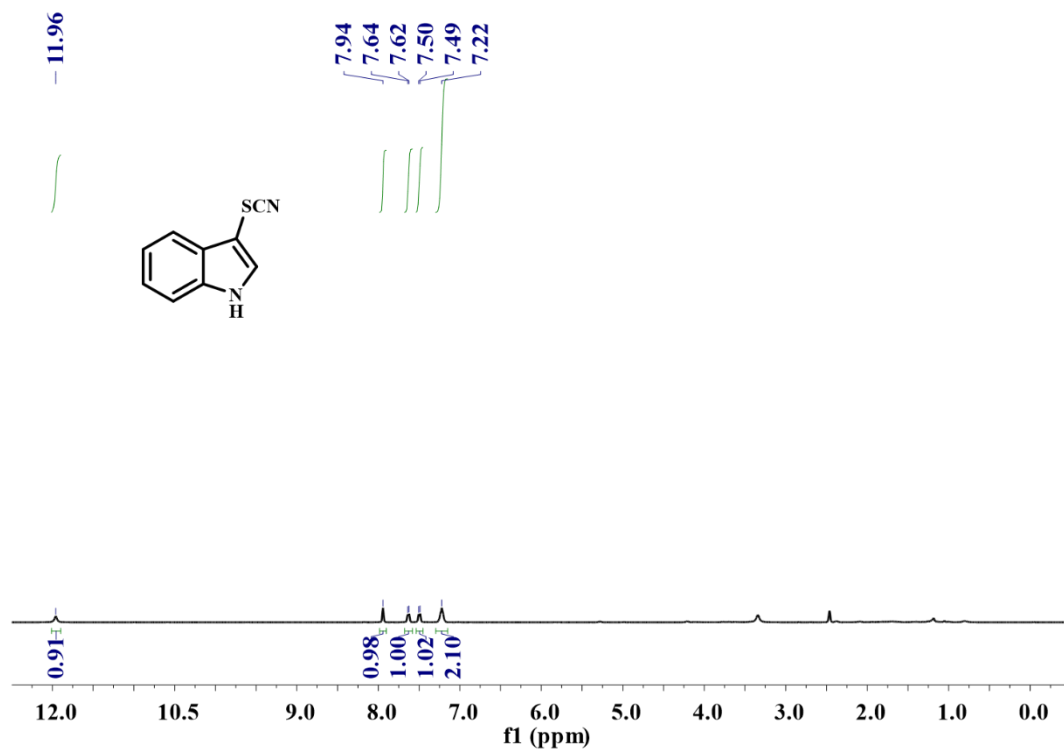
27. Liquid NMR Spectra



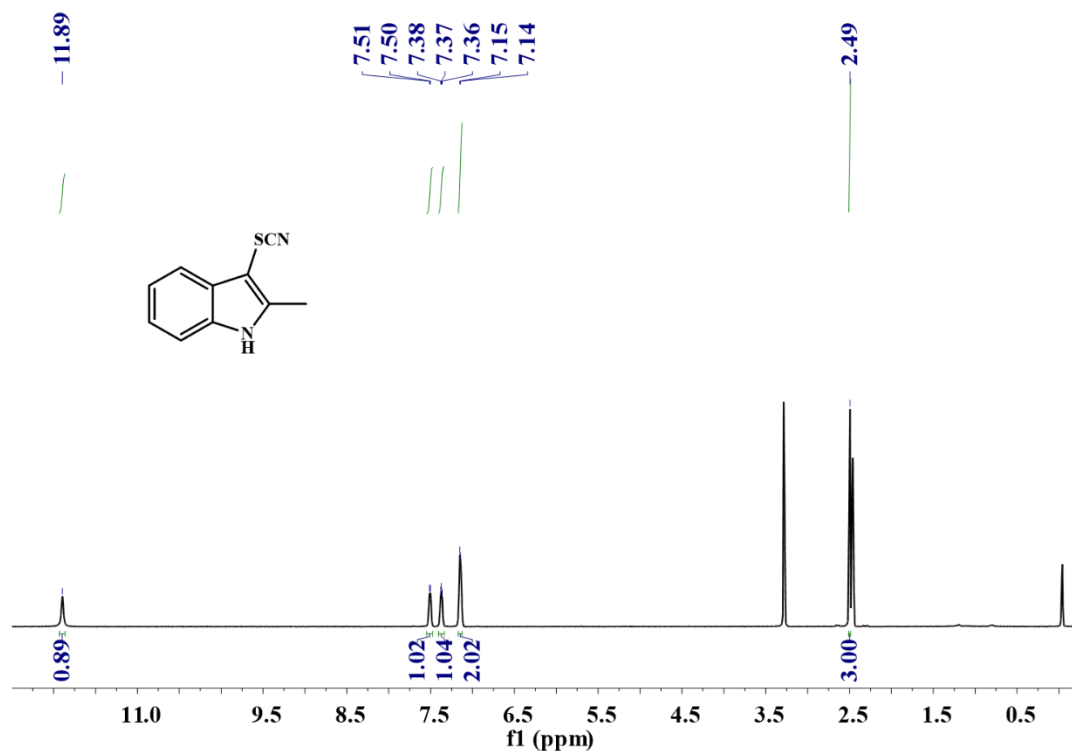




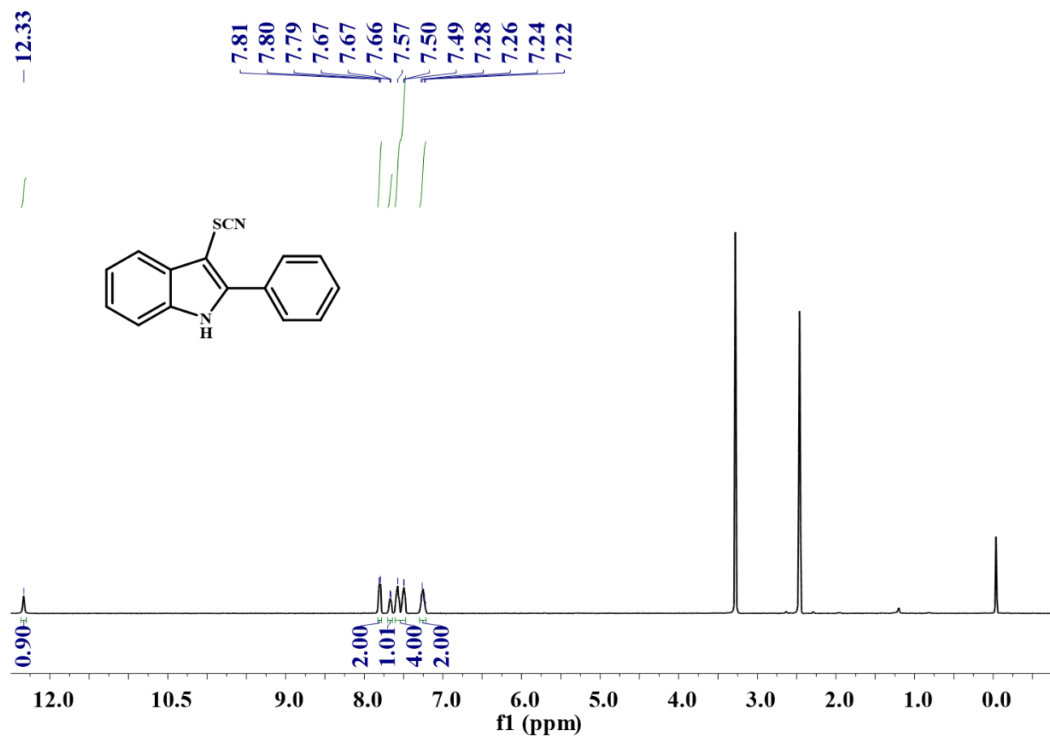
3-Thiocyanato-1H-indole: $^1\text{H NMR}$ (DMSO, 400 MHz): δ 11.96 (s, 1H), 7.94 (s, 1H), 7.64-7.62 (d, $J = 8$ Hz, 1H), 7.50-7.49 (d, $J = 4$ Hz, 1H), 7.22 (s, 2H) ppm.



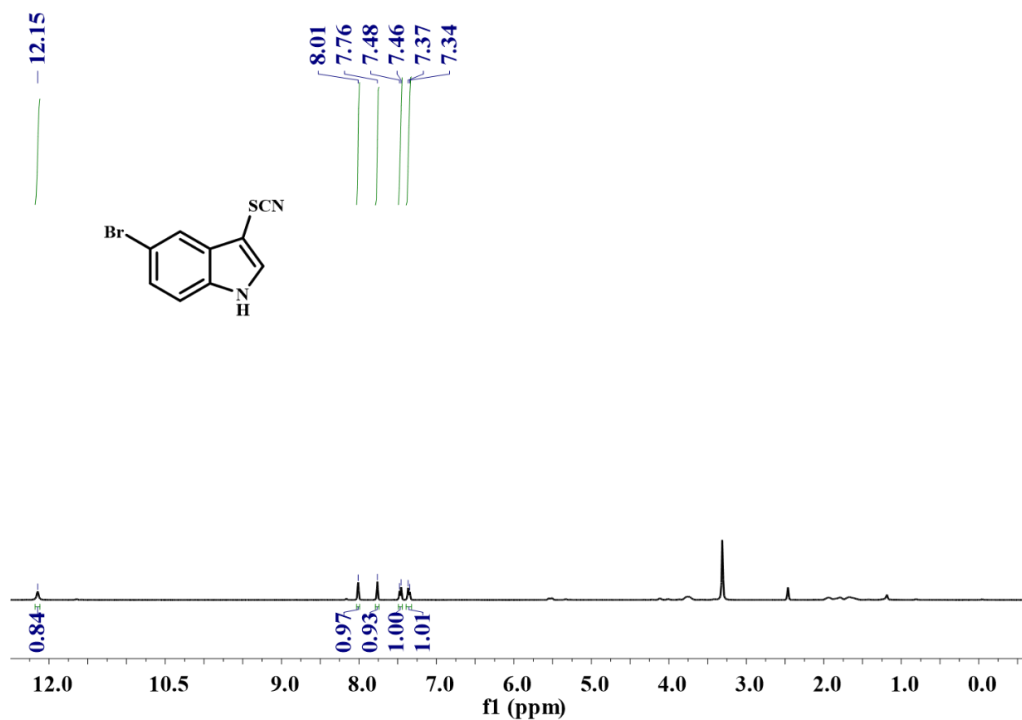
2-Methyl-3-thiocyanato-1H-indole: ^1H NMR (DMSO, 400 MHz): δ 11.89 (s, 1H), 7.51-7.50 (d, $J = 4$ Hz, 1H), 7.38-7.36 (m, 1H), 7.15-7.14 (d, $J = 4$ Hz, 2H), 2.49 (s, 3H) ppm.



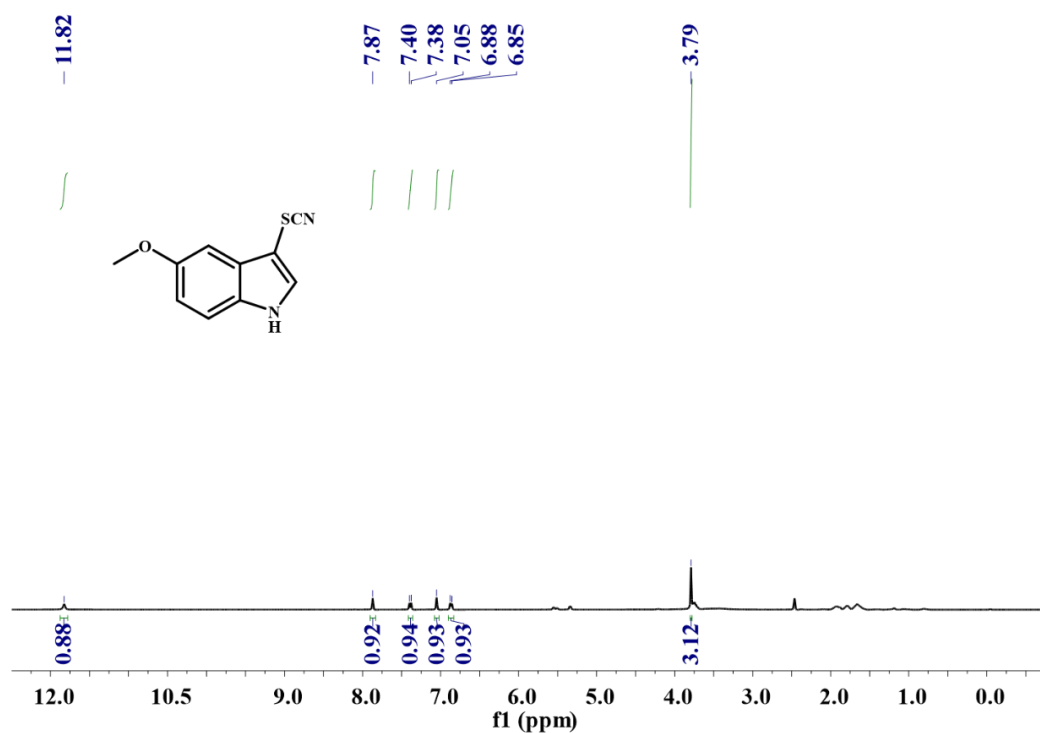
2-Phenyl-3-thiocyanato-1H-indole: ^1H NMR (DMSO, 400 MHz): δ 12.33 (s, 1H), 7.81-7.79 (m, 2H), 7.67-7.66 (m, 1H), 7.57-7.49 (m, 4H), 7.28-7.22 (m, 2H) ppm.



5-Bromo-3-thiocyanato-1H-indole: ^1H NMR (DMSO, 400 MHz): δ 12.15 (s, 1H), 8.01 (s, 1H), 7.76 (s, 1H), 7.48-7.46 (d, $J = 8$ Hz, 1H), 7.37-7.34 (d, $J = 12$ Hz, 1H) ppm.

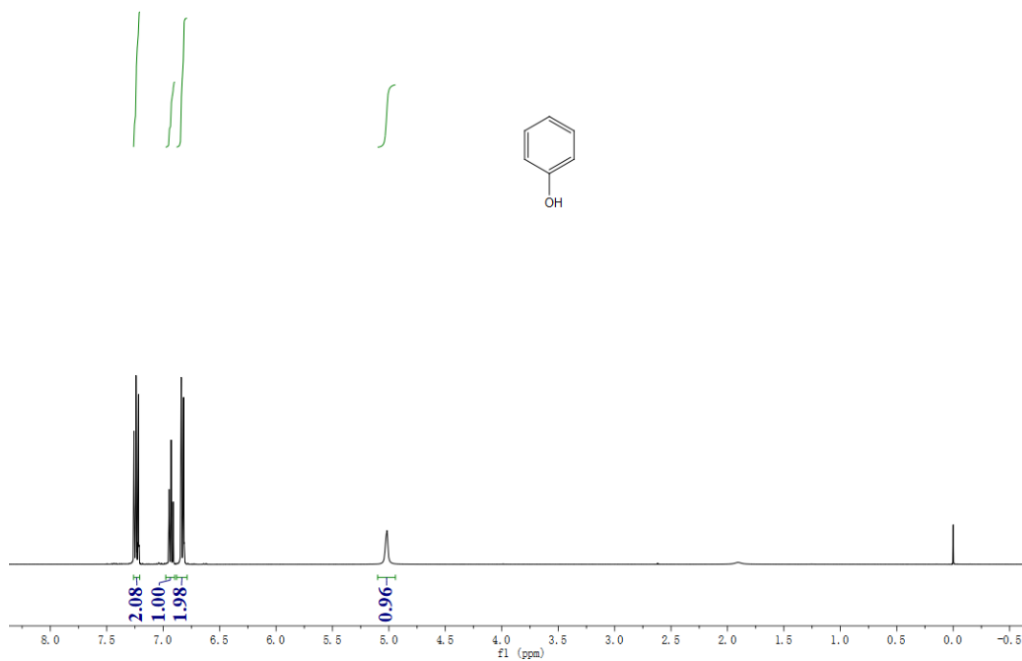
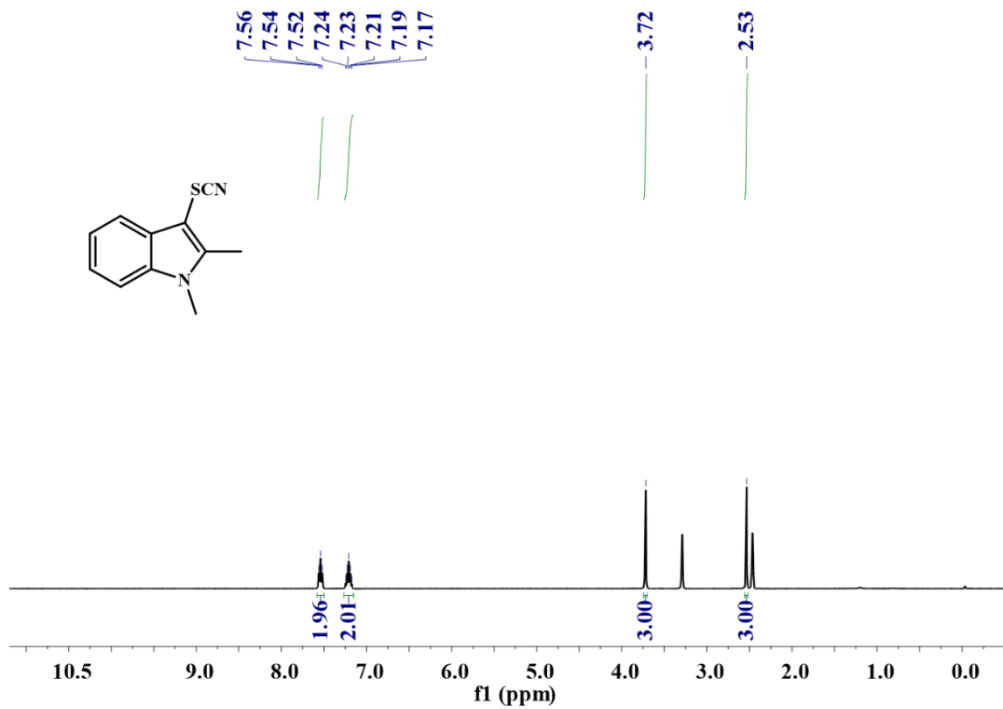


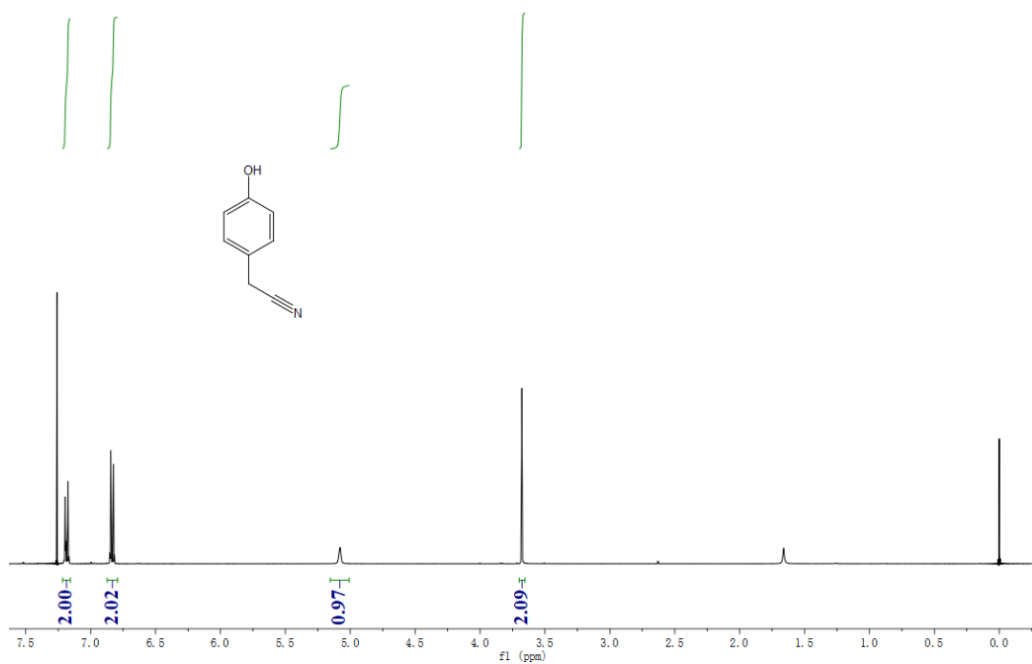
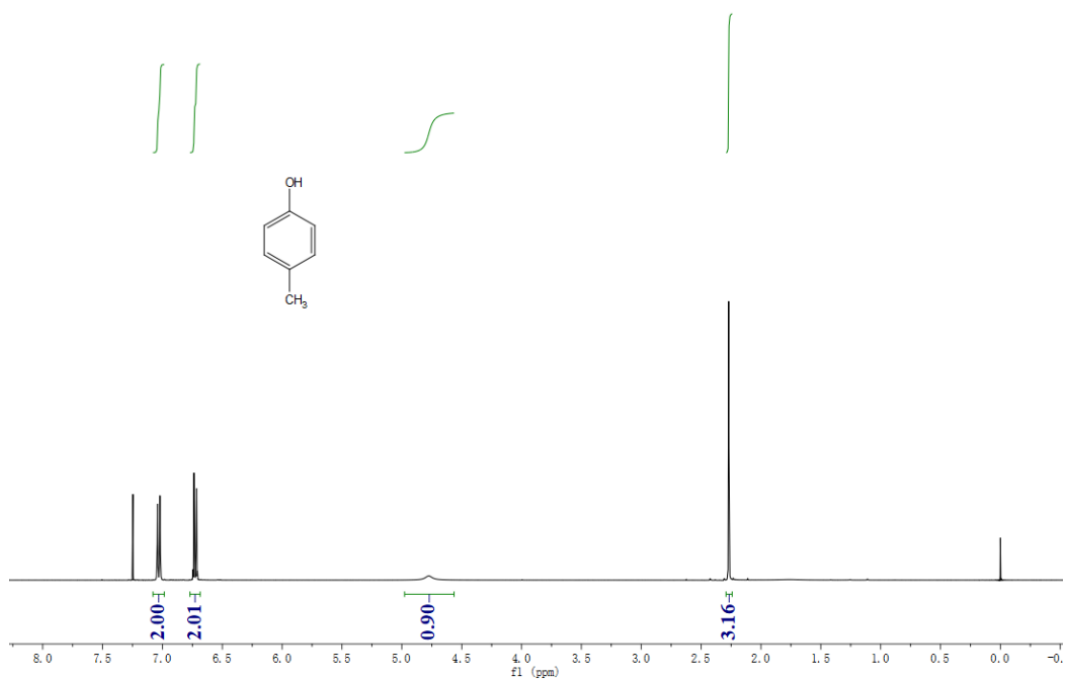
5-Methoxy-3-thiocyanato-1H-indole: ^1H NMR (DMSO, 400 MHz): δ 11.82 (s, 1H), 7.87 (s, 1H), 7.40-7.38 (d, $J = 8$ Hz, 1H), 7.05 (s, 1H), 6.88-6.85 (m, 1H), 3.79 (s, 3H) ppm.

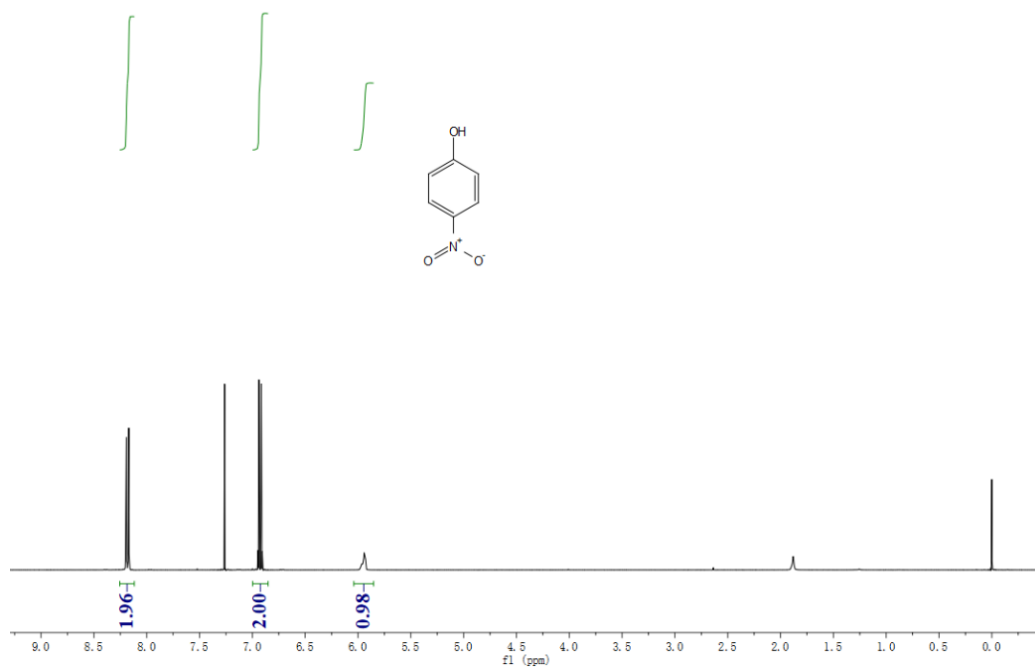
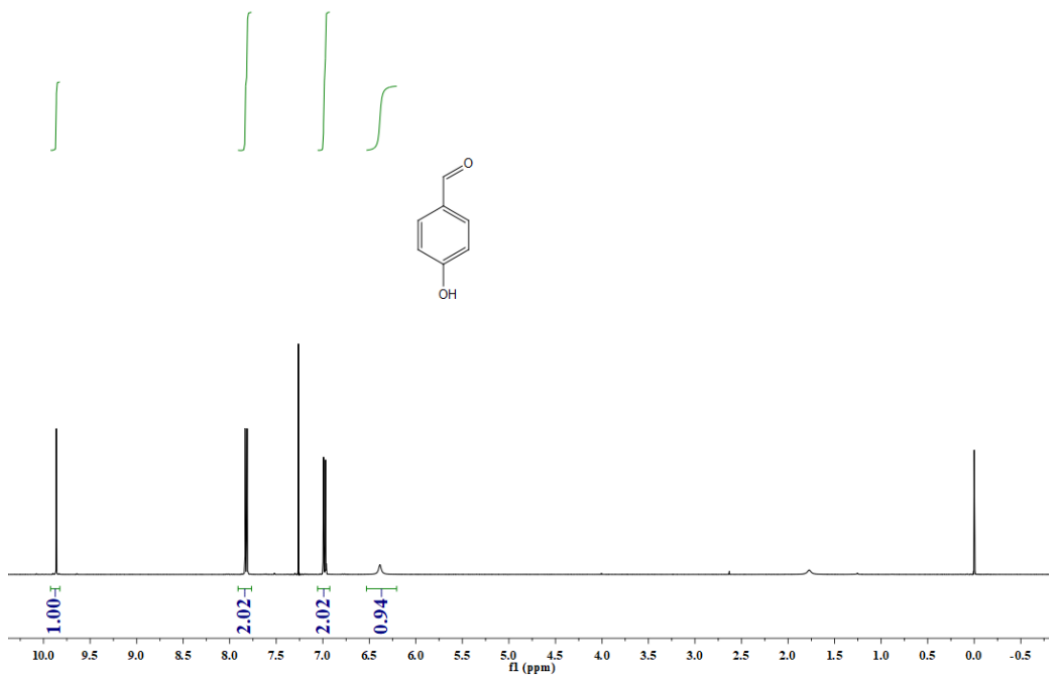


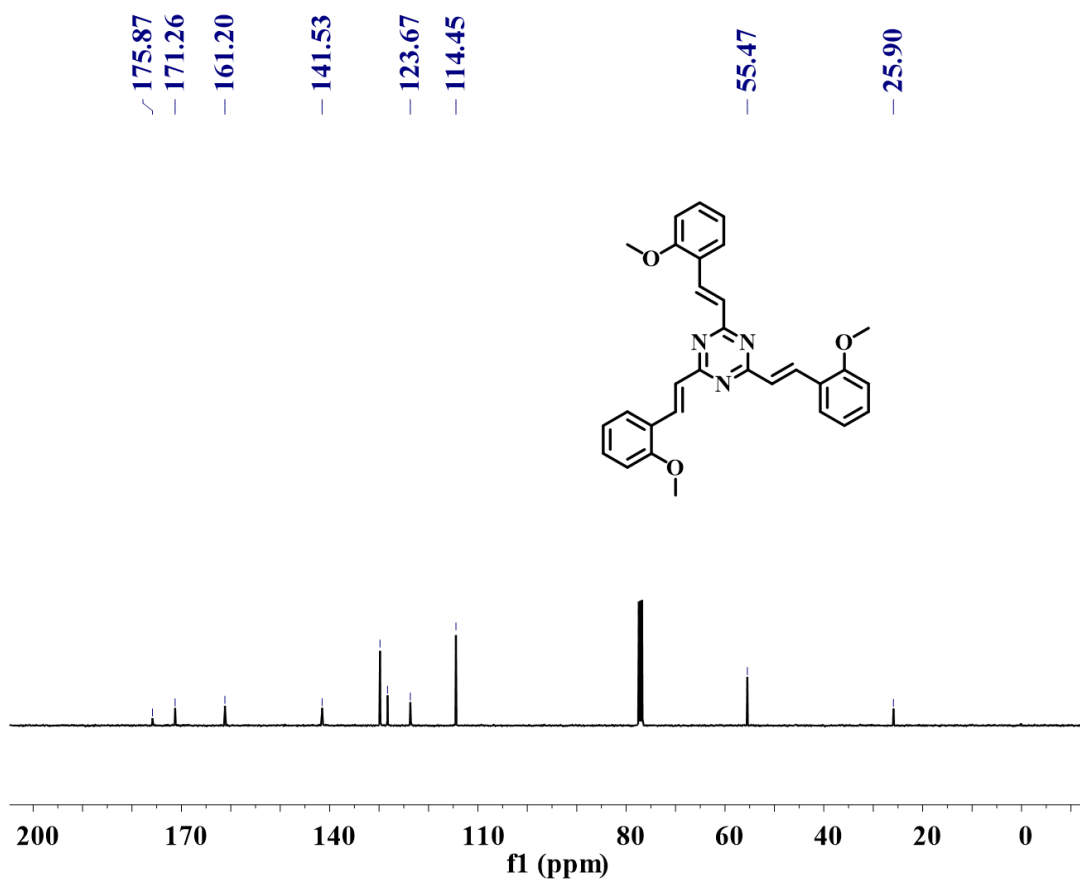
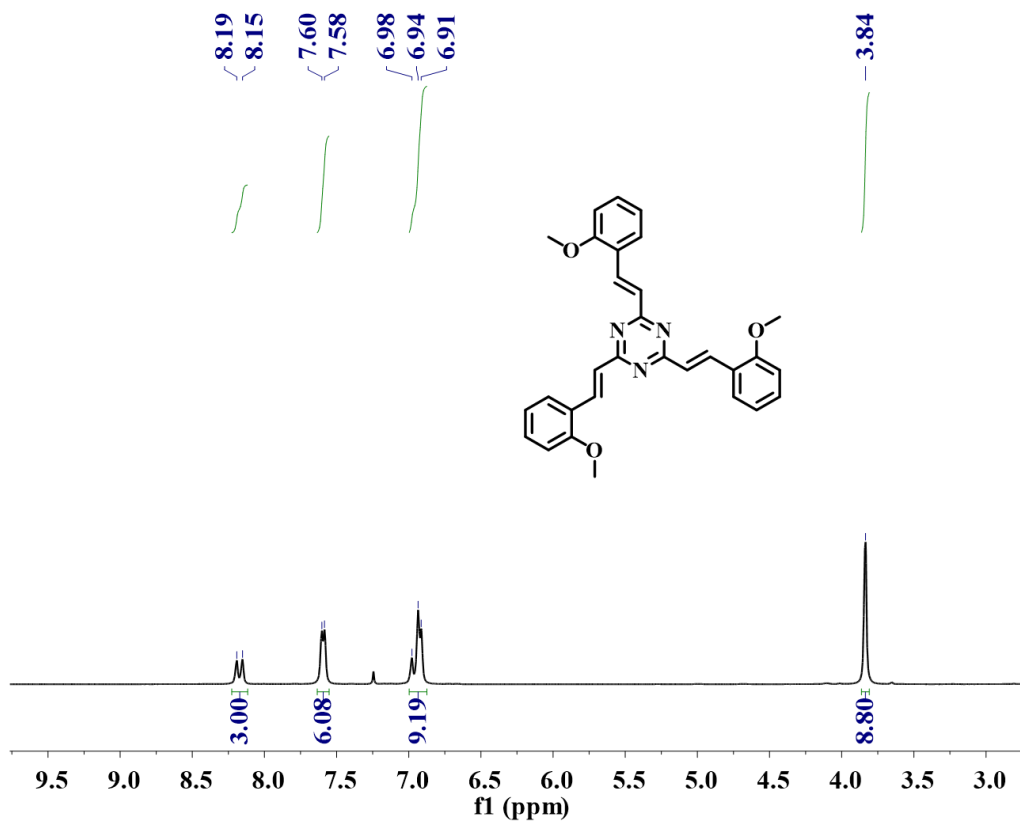
1, 2-Dimethyl-3-thiocyanato-1H-indole: $^1\text{H NMR}$ (DMSO, 400 MHz): δ 7.56-7.52

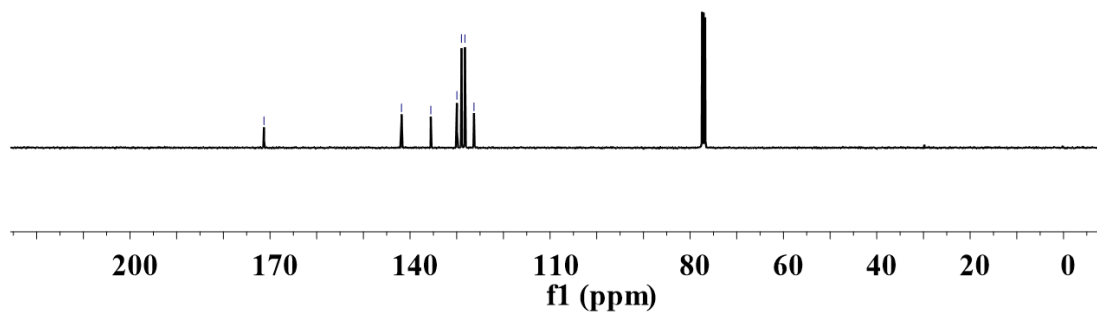
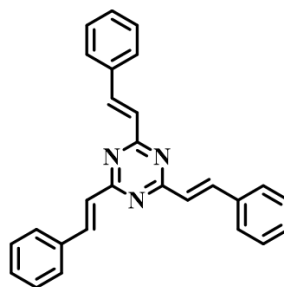
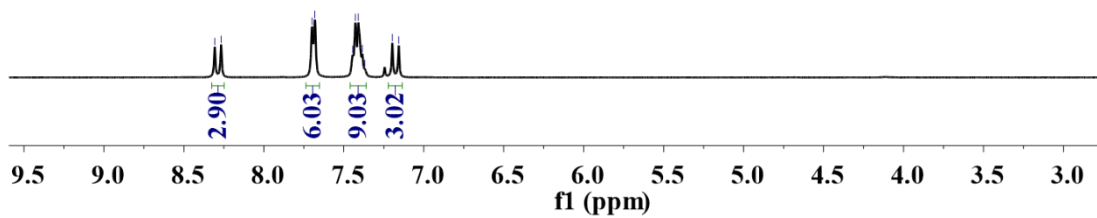
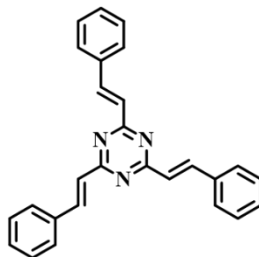
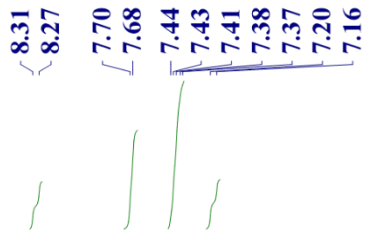
(m, 2H), 7.24-7.17 (m, 2H), 3.72 (s, 3H), 2.53 (s, 3H) ppm.

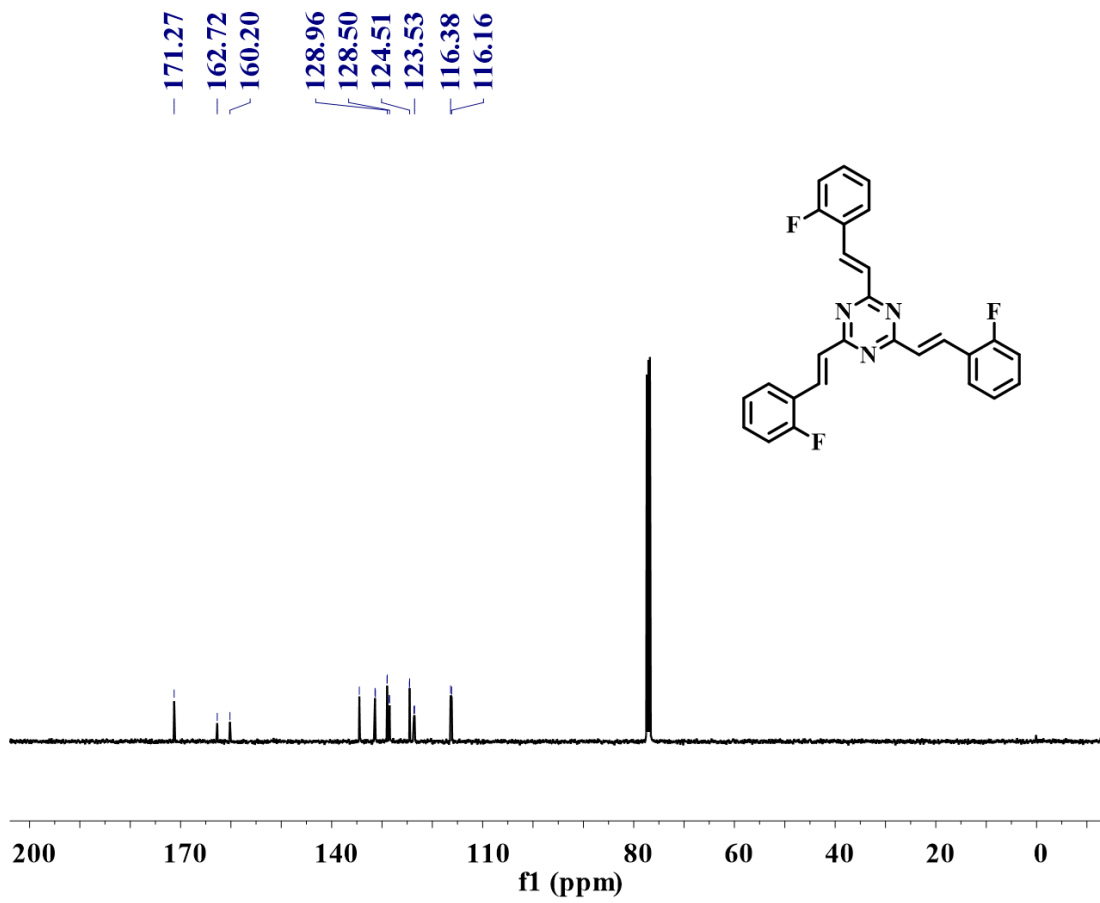
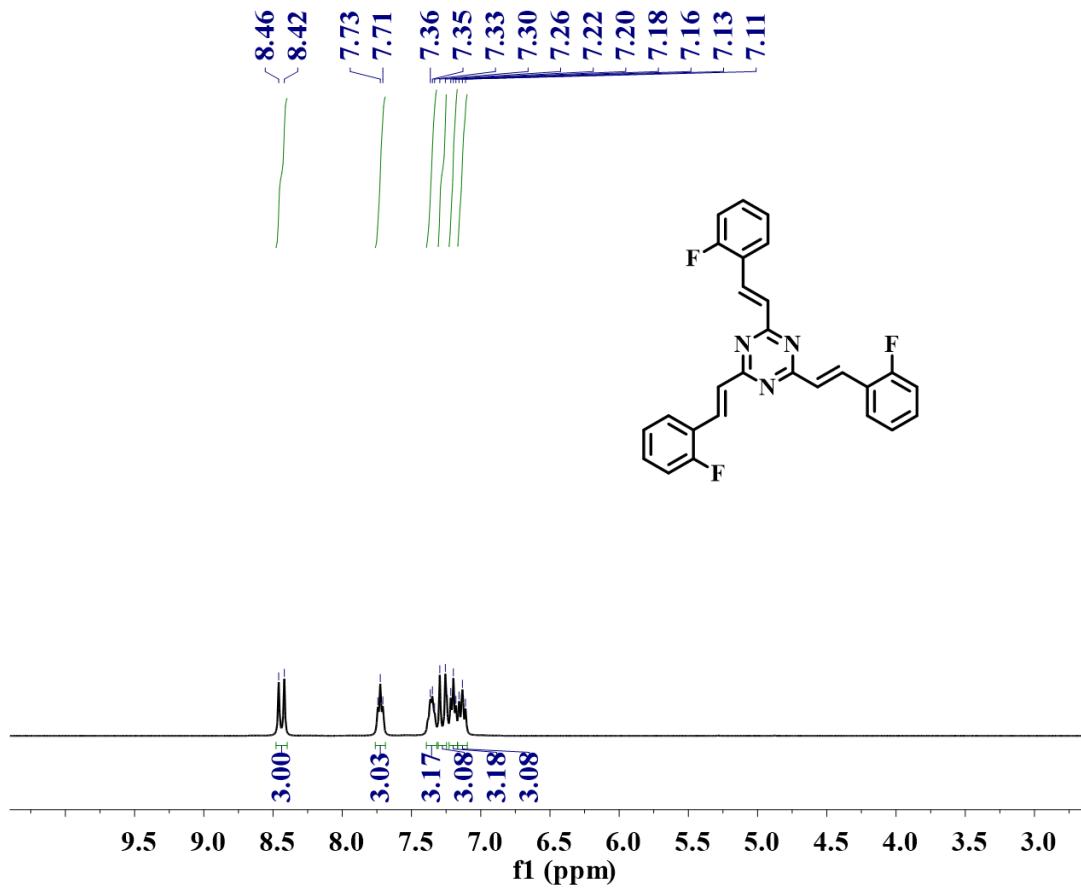












28. Tables S5 Fractional atomic coordinates and unit cell parameters

Fractional atomic coordinates for the unit cell of F-TBT-COF

Space group: P3 a = b = 23.283 Å, c = 3.437 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$			
N1	0.0413	0.06666	-0.19211
C2	0.06689	0.02538	-0.19211
C3	0.13899	0.05185	-0.19211
C4	0.1824	0.11671	-0.19211
C5	0.25522	0.14571	-0.19211
C6	0.29409	0.21497	-0.19211
C7	0.36334	0.24617	-0.19211
C8	0.39465	0.20832	-0.19211
C9	0.35644	0.13912	-0.19211
C10	0.28705	0.10756	-0.19211
C11	0.46597	0.24062	-0.19211
C12	0.52586	0.2681	-0.19211
C13	0.59722	0.30114	-0.19211
C14	0.63453	0.37052	-0.19211
F15	0.78851	1.74816	0.80789
H16	0.1595	0.01648	-0.19211
H17	0.16405	0.15385	-0.19211
H18	0.26866	0.24599	-0.19211
H19	0.39435	0.30262	-0.19211
H20	0.38171	0.10796	-0.19211
H21	0.60843	0.4009	-0.19211

Fractional atomic coordinates for the unit cell of TBT-COF

Space group: P3 a = b = 23.282 Å, c = 3.435 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$			
N1	0.04008	0.06688	-0.19212
C2	0.06717	0.02685	-0.19212
C3	0.13969	0.05495	-0.19212
C4	0.18208	0.12017	-0.19212
C5	0.25487	0.14968	-0.19212
C6	0.29459	0.21887	-0.19212
C7	0.36384	0.24895	-0.19212
C8	0.39419	0.21011	-0.19212
C9	0.35481	0.14087	-0.19212
C10	0.28544	0.11073	-0.19212
C11	0.46563	0.24154	-0.19212
C12	0.5256	0.26859	-0.19212

C13	0.59712	0.30137	-0.19212
C14	0.63481	0.37081	-0.19212
H15	0.16141	0.02061	-0.19212
H16	0.16259	0.15638	-0.19212
H17	0.27009	0.25075	-0.19212
H18	0.39572	0.30533	-0.19212
H19	0.37912	0.10881	-0.19212
H20	0.25356	0.05435	-0.19212
H21	0.60899	0.40147	-0.19212

Fractional atomic coordinates for the unit cell of MeO-TBT-COF

Space group: P3			
a = b = 23.284 Å, c = 3.442 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$			
N1	0.0421	0.06649	-0.19211
C2	0.0667	0.02441	-0.19211
C3	0.13853	0.0498	-0.19211
C4	0.18263	0.11442	-0.19211
C5	0.25542	0.14293	-0.19211
C6	0.2938	0.21223	-0.19211
C7	0.36296	0.24414	-0.19211
C8	0.39487	0.207	-0.19211
C9	0.35739	0.13786	-0.19211
C10	0.28739	0.10467	-0.19211
C11	0.46613	0.23986	-0.19211
C12	0.52598	0.26765	-0.19211
C13	0.59726	0.30092	-0.19211
C14	0.63429	0.37028	-0.19211
O15	0.7859	1.75092	0.80789
C16	0.71529	1.71491	0.80789
H17	0.15823	0.01376	-0.19211
H18	0.16507	0.15218	-0.19211
H19	0.26774	0.24264	-0.19211
H20	0.39338	0.30062	-0.19211
H21	0.38325	0.10725	-0.19211
H22	0.60796	0.40044	-0.19211
H23	0.69704	1.66101	0.88872
H24	0.69628	1.71716	0.50625
H25	0.696	1.73772	1.02869

[1] Yi-Qi Zhang.; Nenad Kepećija.; Mario Ruben.; Johannes V. Barth., Homo-coupling of terminal alkynes on a noble metal surface. *Nat. Commun.* 2012, 3, 1286.

