Supporting Information

Ultrasound-Induced Recrystallization of Covalent Organic Frameworks with Greatly Enhanced Crystallinity

Bo Chen[1,2], Xinghua Guo[1,2], Xu Han[1,2], Yingying Qian[1,2], Degao Wang*[,1,2,3]

[1]Qianwan Institute of CNITECH, Zhongchuang 1st Road, Zhongchuang Park, Qianwan New Area, Ningbo, Zhejiang, China

[2]Zhejiang Key Laboratory of Data-Driven High-Safety Energy Materials and Applications, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China

[3]Advanced Interdisciplinary Sciences Research (AIR) Center, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China

Correspondence: wangdegao@nimte.ac.cn

Table of contents

1. Instrumentation

Ultrasonic machine. Ultrasonic treatment was performed on a Scientz IID probe ultrasonicator from Ningbo Scientz Co. Ltd, equipped with a durable titanium probe. The probe was immersed approximately 1.5 cm below the liquid surface in before sonication. The applied ultrasonic power ranged from 150 to 350 W, and the total sonication duration was 240 min. A pulsed-sonication mode was employed, in which the ultrasound was applied for 1 s followed by a 1 s pause. If unstable monomer was used, such as the easily oxidized p-phenylenediamine under elevated temperature, an argon shielding gas was continuously introduced into the reaction vial until the reaction is over.

Powder X-ray diffraction (PXRD). PXRD measurements were performed on a Bruker D8 Advance, using in high throughput transmission mode with Kα focusing mirror and PIXCEL 1D detector with a Cu X-ray source. During the PXRD measurements, the X-ray generator was operated at a constant voltage of 40 kV and a current of 40 mA. A zero-background single-crystal silicon sample holder was used, onto which the finely ground COF powders were evenly spread prior to measurement. Data were collected over a 2θ range of 2–40°, with a step size of 0.02° and a counting time of 0.2 s per step, giving a total acquisition time of approximately 425.5 s. The intensity and FWHM for main diffraction peaks of COFs were obtained by Jade software.

Gas sorption analysis. The surface areas and nitrogen adsorption isotherms of COFs were obtained using a Micromeritics ASAP 2460 volumetric adsorption analyzer at 77.3 K. Before analysis, the samples were degassed at 120 °C overnight under vacuum. All measurements were carried out in the micropore analysis mode.

Fourier-transform infrared spectroscopy (FTIR). IR spectra were recorded on a Thermo Scientific Nicolet IS50 FTIR spectrometer. Pure KBr disc was used to record background, and the sample discs were tested as soon as they were prepared to prevent from oxidation or moisture.

Scanning electron microscopy (SEM). SEM images were collected on a Zeiss Sigma 300 emission

scanning electron microscope from Germany. Samples were sonicated in ethanol for 5 minutes. Then they were deposited on silicon plates and coating with gold before testing. Imaging was conducted at a working voltage of 5 kV and a working distance of 5.9 mm using a combination of upper and lower secondary electron detectors.

Transmission electron microscopy (TEM). TEM images were obtained on a JEOL JEM-F200 microscopy from Japan at an accelerating voltage of 200 kV. The samples were sonicated in ethanol for 10 minutes, and then dropped onto a copper grid before testing.

Elemental analysis (EA). Elemental data of C, H, N were obtained on a Elementar Unicube from Germany.

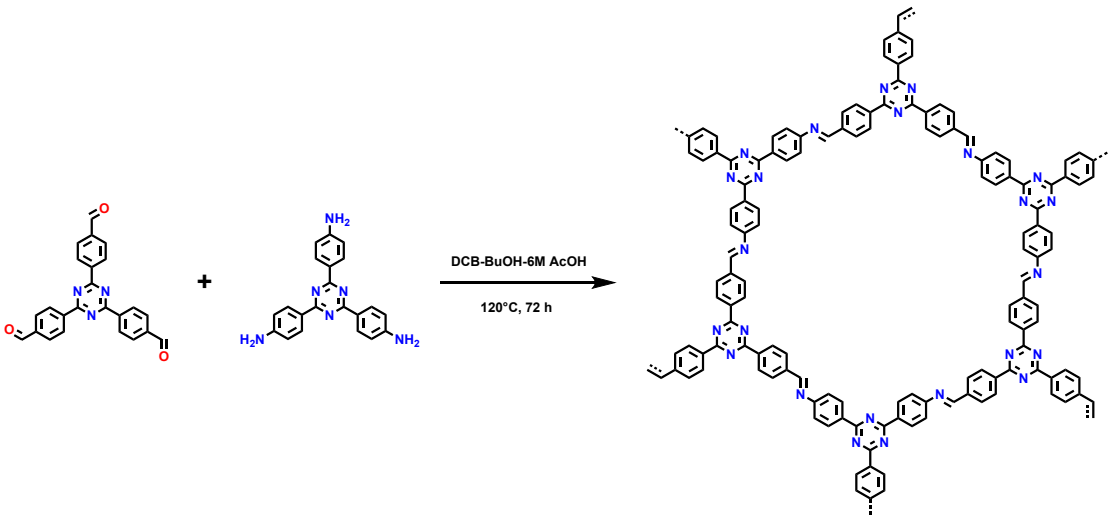
UV-Vis spectroscopy. Aqueous solution UV-Vis spectra were recorded on a Hitachi UH4150 spectrophotometer.

2. Synthetic procedures and methods

Materials: 1,2-dichlorobenzene (DCB), n-butanol (BuOH), N,N-dimethylformamide (DMF), ethanol, THF, ethyl acetate and acetic acid were purchased from Adamas or Greagent. 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TBT-CHO), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TBT-NH_2), 1,3,5-tris(4-aminophenyl)benzene (TBB-NH_2), 1,3,5-triformylbenzene (TFB), 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (THTA), p-phenylenediamine (PDA) and 2,2'-bipyridine-5,5'-diamine (BPY-NH_2) were purchased from Shanghai Kylpharm Co., Ltd. All commercial chemicals were used without further purification.

2.1 Solvothermal method

Solvothermal synthesis of COF-TBT-TBT



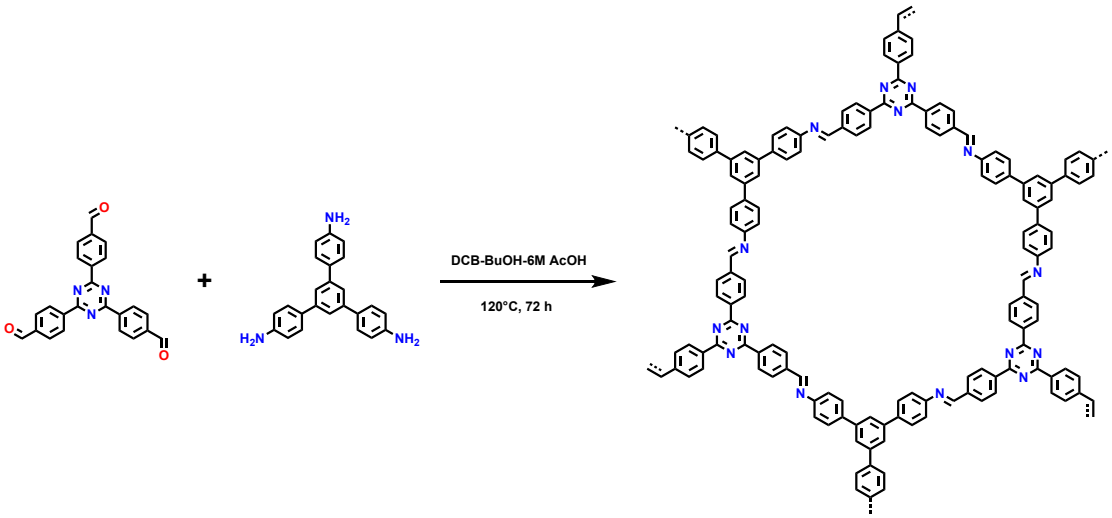
TBT-CHO (2,4,6-tris(4-formylphenyl)-1,3,5-triazine, 157.4 mg, 0.4 mmol) and TBT-NH_2 (2,4,6-tris(4-aminophenyl)-1,3,5-triazine, 141.8 mg, 0.4 mmol) were transferred into a 25 mL Pyrex tube. A mixed solution of o-DCB/n-BuOH (8 mL/ 4 mL) and 1.2 mL 6M AcOH solution were then added. The tube was sonicated for 5 min to get a fine dispersion. Then after cooled by liquid nitrogen, the tube was degassed and flame sealed. Then it was transferred into an oven to heat at 120 °C for 72 h yielding a yellow solid. After the reaction was complete, the resulting mixture was cooled to room temperature and the precipitate was collected by suction filtration, washed with ethanol (10 mL×3), THF (10 mL×3) and ethyl acetate (10 mL×3). The obtained sample was further dried under vacuum

at 80 °C overnight to afford COF-TBT-TBT.

Solvothermal synthesis of other COFs

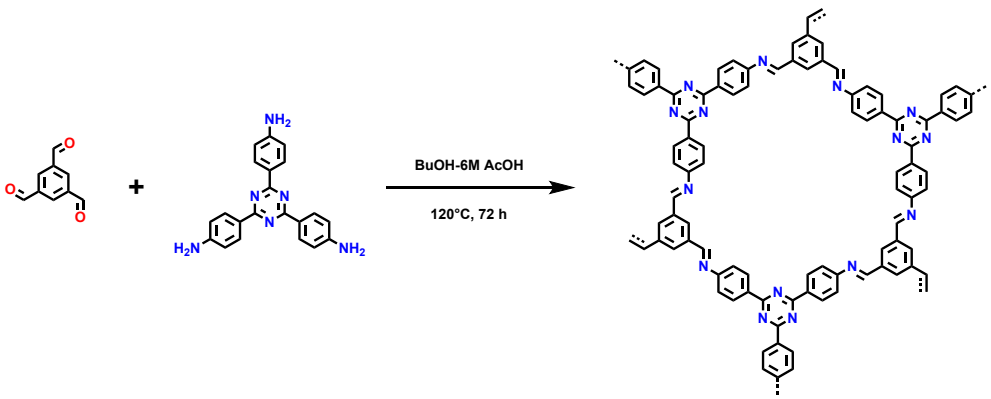
The solvothermal synthesis procedures for the other COFs were similar to that of COF-TBT-TBT, with the main differences being the compositions of the organic solvent and catalyst. When TsOH solution was used, additional $NaHCO_3$ solution washing was performed to neutralize and remove the acid. All other conditions, including reaction temperature and duration, were kept constant.

COF-TBT-TBB:



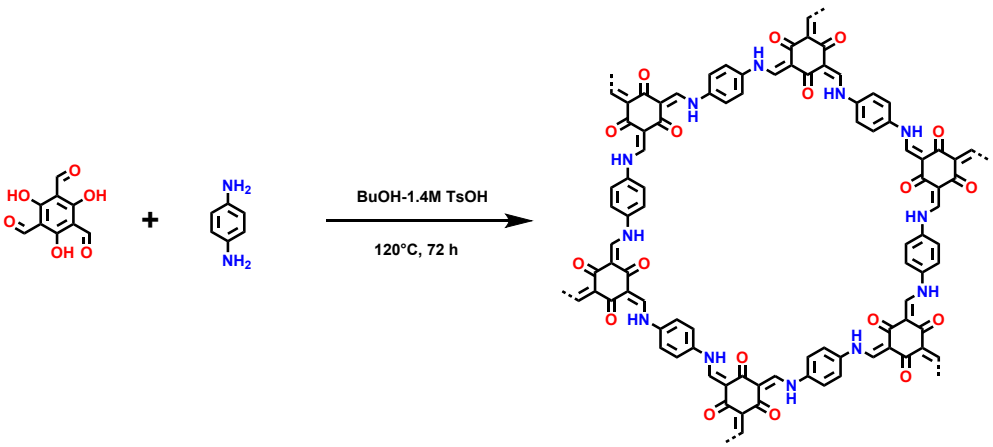
TBT-CHO (2,4,6-tris(4-formylphenyl)-1,3,5-triazine, 157.4 mg, 0.4 mmol) and TBB-NH_2 (1,3,5-tris(4-aminophenyl)benzene, 141.8 mg, 0.4 mmol) in o-DCB/n-BuOH/6M AcOH (8 mL/ 4mL/ 1.2 mL). Yellow powder.

COF-TFB-TBT:



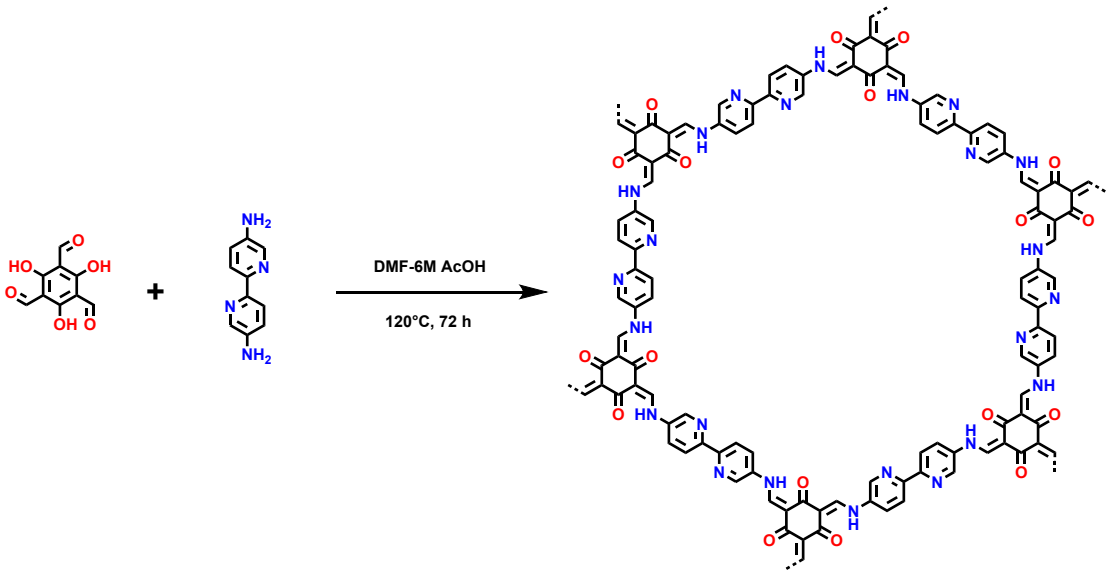
TFB (1,3,5-triformylbenzene, 97.3 mg, 0.6 mmol) and TBT-NH_2 (2,4,6-tris(4-aminophenyl)-1,3,5-triazine, 212.7 mg, 0.6 mmol) in n-BuOH/6M AcOH (12 mL/ 1.2 mL). Light yellow powder.

COF-THTA-PDA:



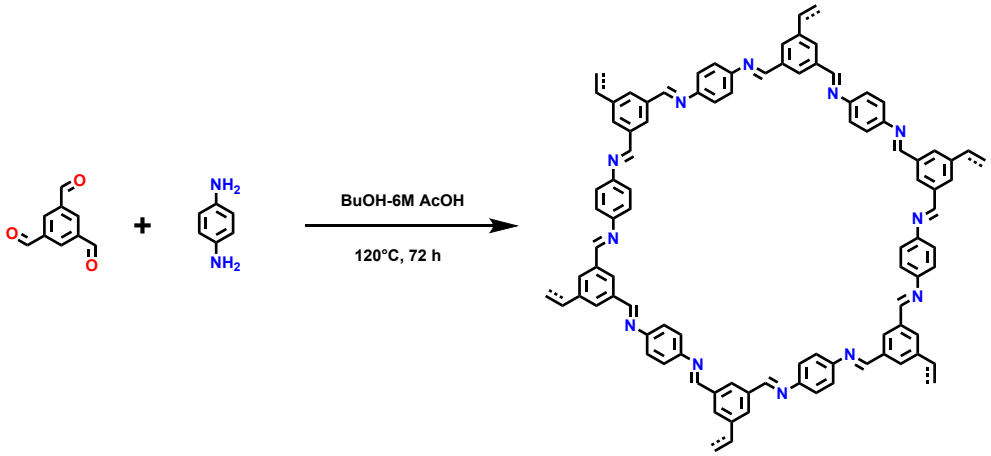
THAT (2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde, 126.0 mg, 0.6 mmol) and PDA (p-phenylenediamine, 97.4 mg, 0.9 mmol) in n-BuOH/1.4 M TsOH (12 mL/ 1.2 mL). Red powder.

COF-THTA-BPY:



THAT (2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde, 126.0 mg, 0.6 mmol) and BPY-NH_2 (2,2'-bipyridine-5,5'-diamine, 167.6 mg, 0.9 mmol) in DMF/6 M AcOH (12 mL/ 1.2 mL). Red powder.

COF-TFB-PDA:



TFB-CHO (1,3,5-triformylbenzene, 162.1 mg, 1 mmol) and PDA (p-phenylenediamine, 162.2 mg, 1.5 mmol) in n-BuOH/6 M AcOH (12 mL/ 1.2 mL). Yellow powder.

2.2 Sonication method

Sonication synthesis of COF-TBT-TBT

TBT-CHO (78.7 mg, 0.2 mmol) and TBT-NH_2 (70.9 mg, 0.2 mmol) were transferred into a 40 mL glass sample vial. A mixed solution of o-DCB/n-BuOH (12 mL/ 6 mL) and 1.8 mL 6M AcOH solution were then added. The tube was directly sonicated for 240 min to get COFs dispersion. Then after cooled to room temperature, the precipitate was collected by suction filtration, washed with ethanol (10 mL×3), THF (10 mL×3) and ethyl acetate (10 mL×3). The obtained sample was further dried under vacuum at 80 °C overnight to afford COF-TBT-TBT.

Sonication synthesis of other COFs

The sonication synthesis procedures for the other COFs were similar to that of COF-TBT-TBT, with the main differences being the compositions of the organic solvent and catalyst. When TsOH solution was used, additional $NaHCO_3$ solution washing was performed to neutralize and remove the acid. All other conditions were kept constant.

2.3 Ultrasonic recrystallization method

Ultrasonic conditions optimization

Different parameters of sonication power and sonication time were selected to get optimal ultrasonic conditions. For sonication power, 60, 100, 150, 250 and 350 W were used, with a 4 h sonication. For sonication time, the power was fixed at 250 W, and 0.5, 1, 2, 4 and 6 h were used. When the ultrasonic power exceeds 250 W or the ultrasonic duration exceeds 4 hours, the main PXRD diffraction peak of COF-TBT-TBT no longer increases significantly. Therefore, the optimal ultrasonic conditions are determined to be 250 W and 4 hours.

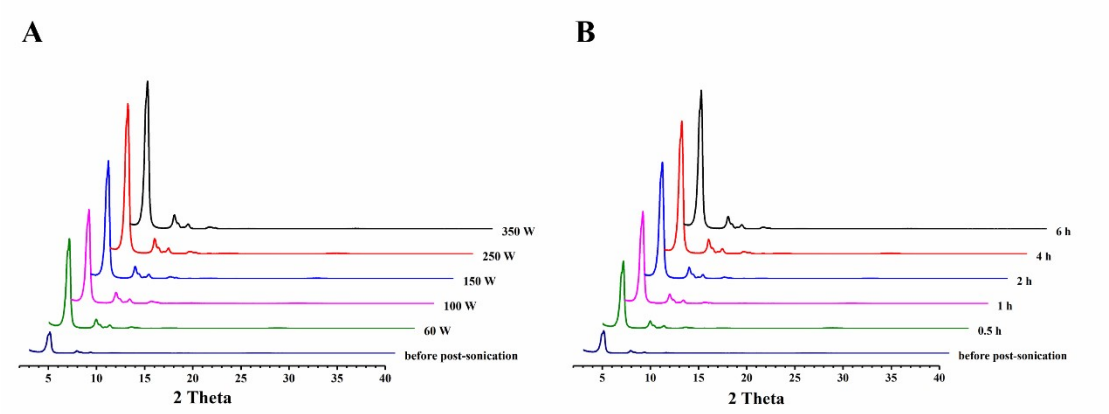


Figure S1. Condition optimization with different sonication power (A) and time (B).

In sonication process, the temperature is gradually rising in initial stage. When temperature is close to boiling point of solvent mixture, the temperature becomes steady, with solvent refluxing in the long bottle and cooled by air.

Ultrasonic recrystallization treatment of COF-TBT-TBT

COF-TBT-TBT (100 mg) obtained from solvothermal method was transferred into a 40 mL glass sample vial. A mixed solution of o-DCB/n-BuOH (12 mL/ 6 mL) and 1.8 mL 6M AcOH solution were then added. The tube was directly sonicated for 240 min to get COFs dispersion. Then after cooled to room temperature, the precipitate was collected by suction filtration, washed with ethanol (10 mL×3), THF (10 mL×3) and ethyl acetate (10 mL×3). The obtained sample was further dried under vacuum at 80 °C overnight to afford high crystalline COF-TBT-TBT, yield 92%.

Ultrasonic recrystallization treatment of other COFs

The recrystallization procedures for the other COFs were similar to that of COF-TBT-TBT, with the main differences being the compositions of the organic solvent and catalyst. The ratios of organic solvents and catalysts were the same as solvothermal and sonication synthesis. When TsOH solution was used, additional $NaHCO_3$ solution washing was performed to neutralize and remove the acid. All other conditions were kept constant. Yield: COF-TBT-TBB 84%, COF-TFB-TBT 91%, COF-THAT-PDA 83%, COF-THAT-BPY 95% and COF-TFB-PDA 82%.

2.4 Dye removal application

With 5 different standard solutions of Rhodamine B (0, 6.25, 12.5, 18.25 and 25 ppm) in water, a standard curve was obtained by fitting the UV-Vis absorbance at the maximum absorption wavelength (554 nm) to their concentrations. In adsorption experiments, 5 mg COFs of three methods were added into a 5 mL 50 ppm Rhodamine B solutions for adsorption experiment. After stirring for 24 h, the solutions were filtered and tested by UV-Vis spectroscopy. And the residual concentrations were calculated by the above standard curve.

3. Characterization of COFs

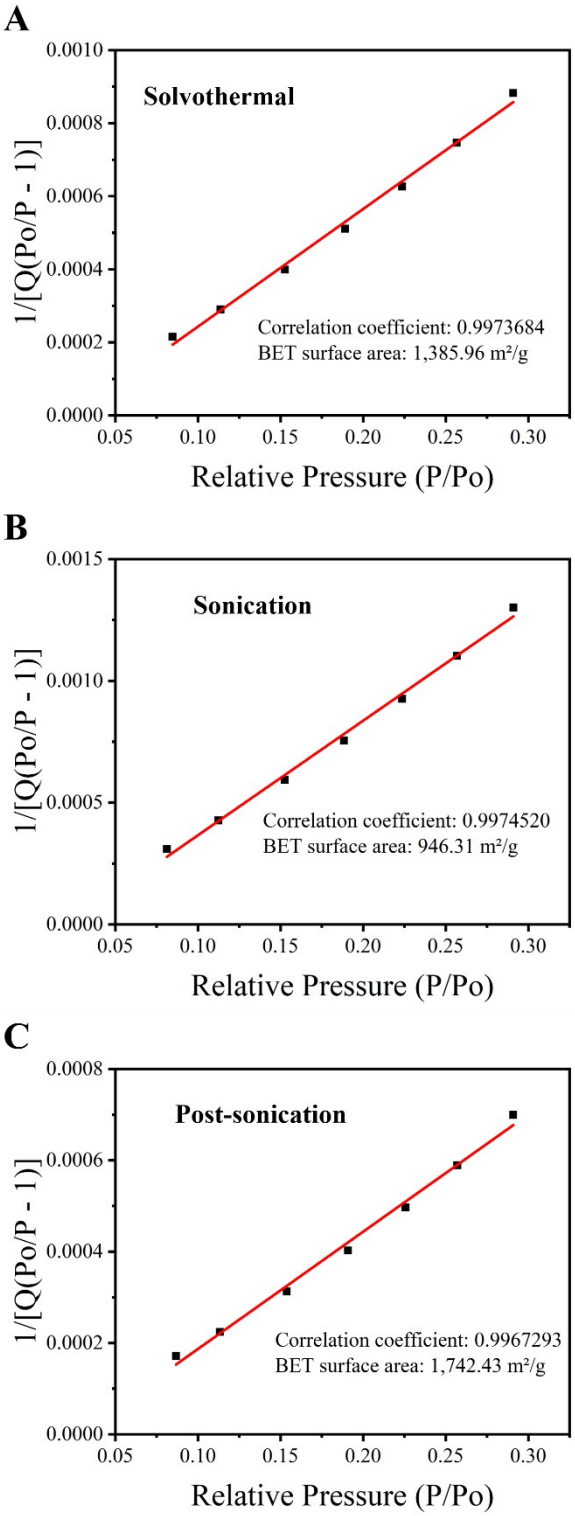


Figure S2. BET surface area fitting plot of COF-TBT-TBT by solvothermal (A), sonication (B) and post-sonication (C)

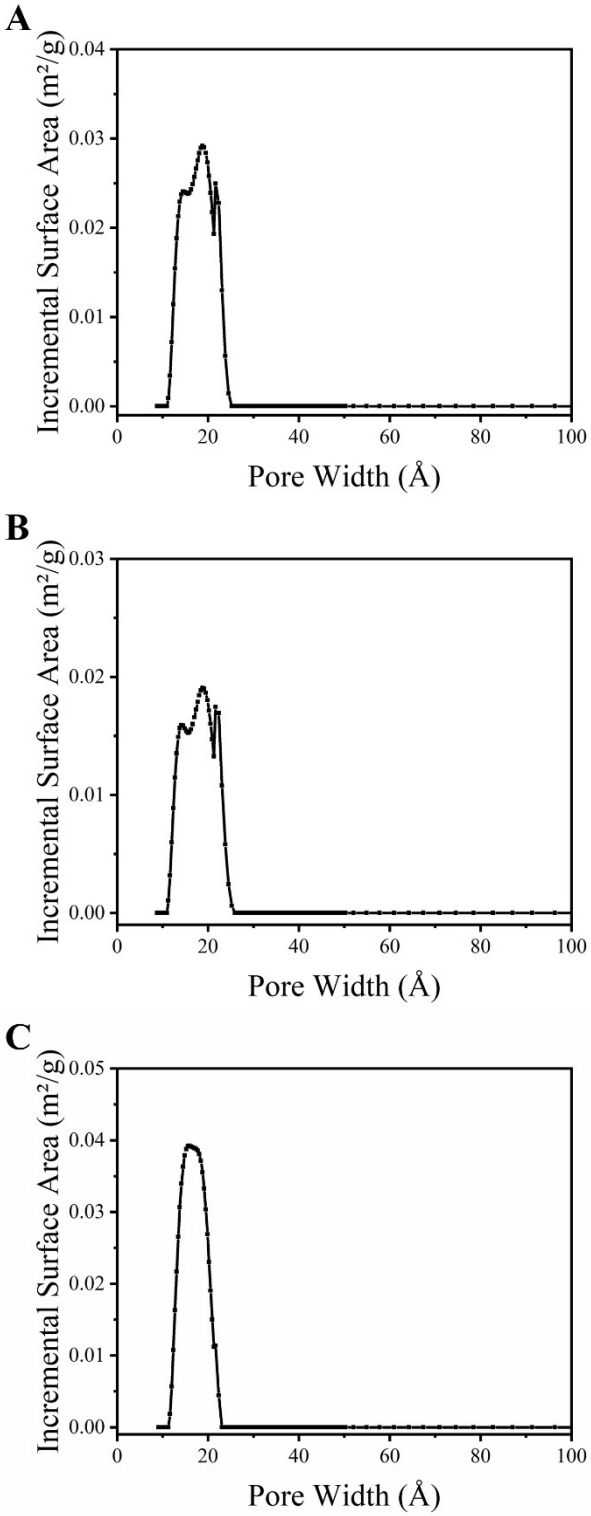


Figure S3. Pore size distribution of COF-TBT-TBT by solvothermal (A), sonication (B) and post-sonication (C)

Table S1. Organic elemental analysis (in weight %) for COF-TBT-TBT by three methods.

COF-TBT-TBT	N		C		H	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
Solvothermal	18.17	15.98	77.91	72.37	3.92	4.27
		16.07		72.63		4.29
Sonication	18.17	16.45	77.91	73.55	3.92	4.20
		16.51		73.86		4.20
Post-sonication	18.17	17.24	77.91	74.66	3.92	3.81
		17.35		75.04		3.75

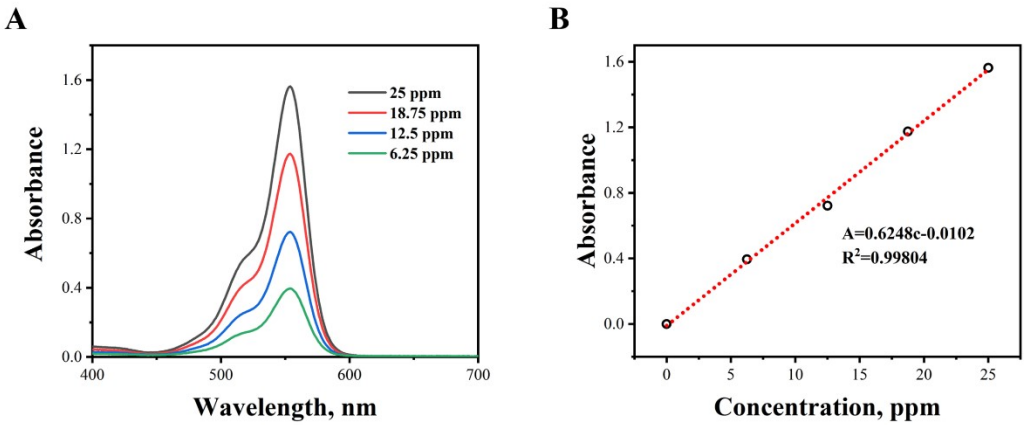


Figure S4. (A) UV-Vis absorption spectra of standard Rhodamine B solutions; (B) Standard curve with relation equation between Rhodamine B concentration and absorbance.

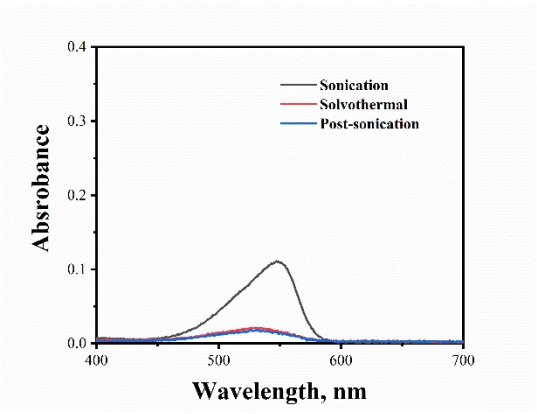


Figure S5. The UV-Vis spectra of Rhodamine B solutions after adsorption.

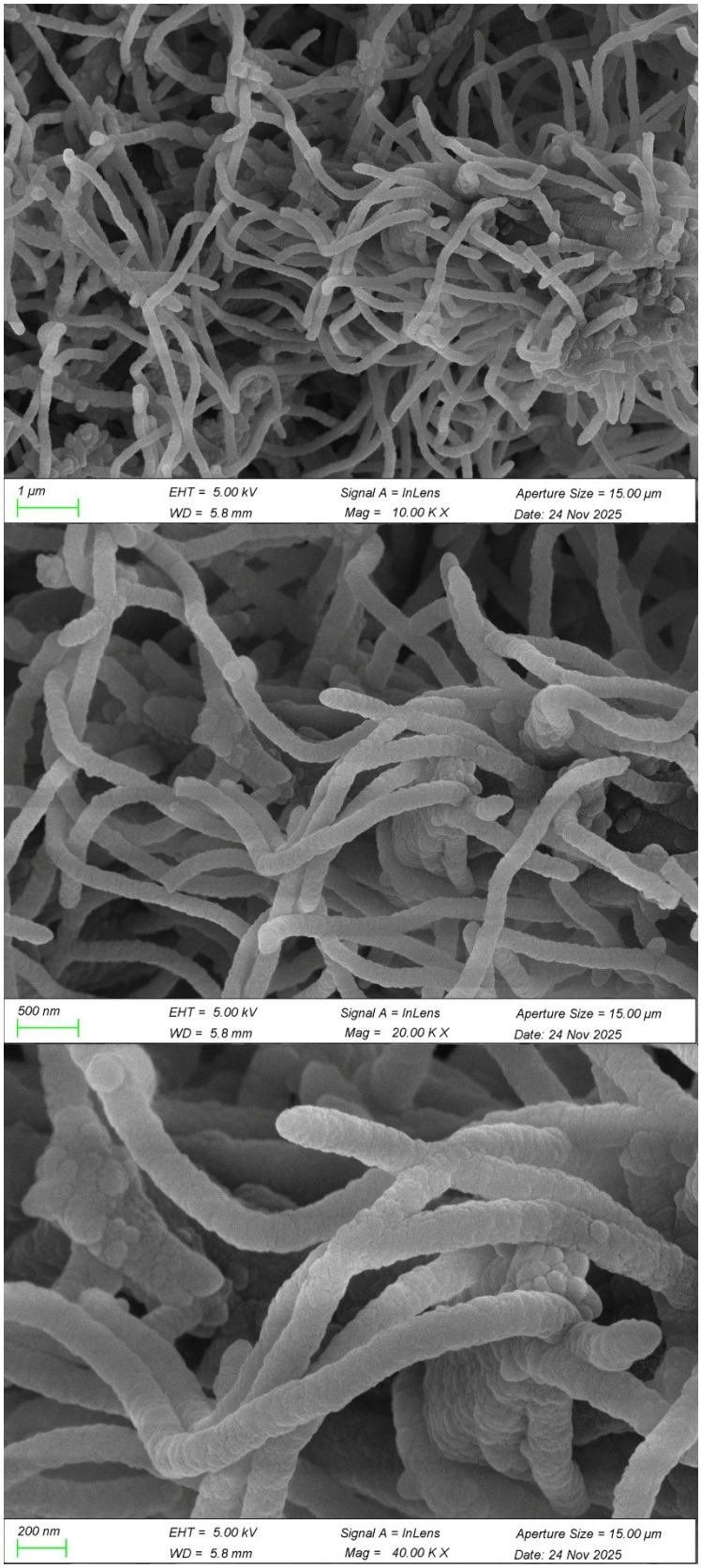


Figure S6. SEM images of COF-TBT-TBT by solvothermal method.

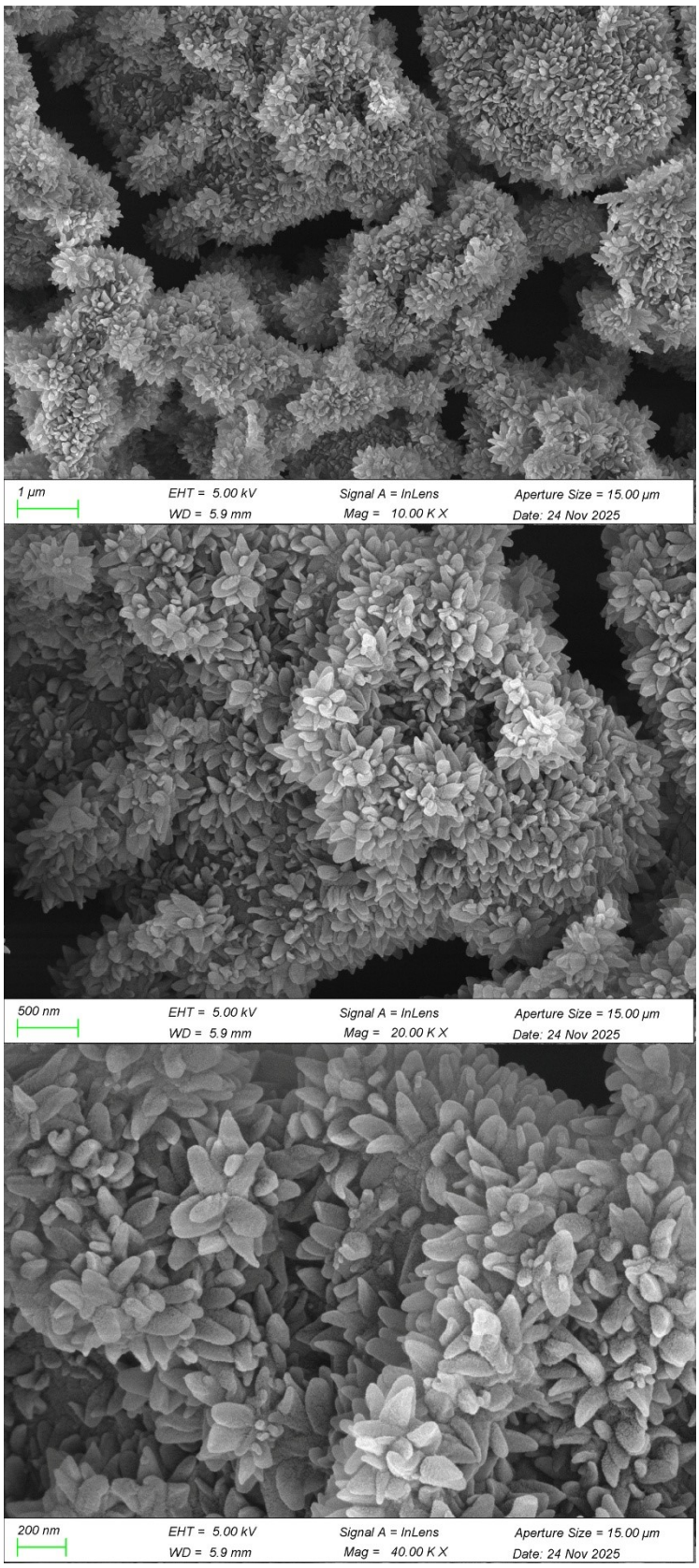


Figure S7. SEM images of COF-TBT-TBT by sonication method.

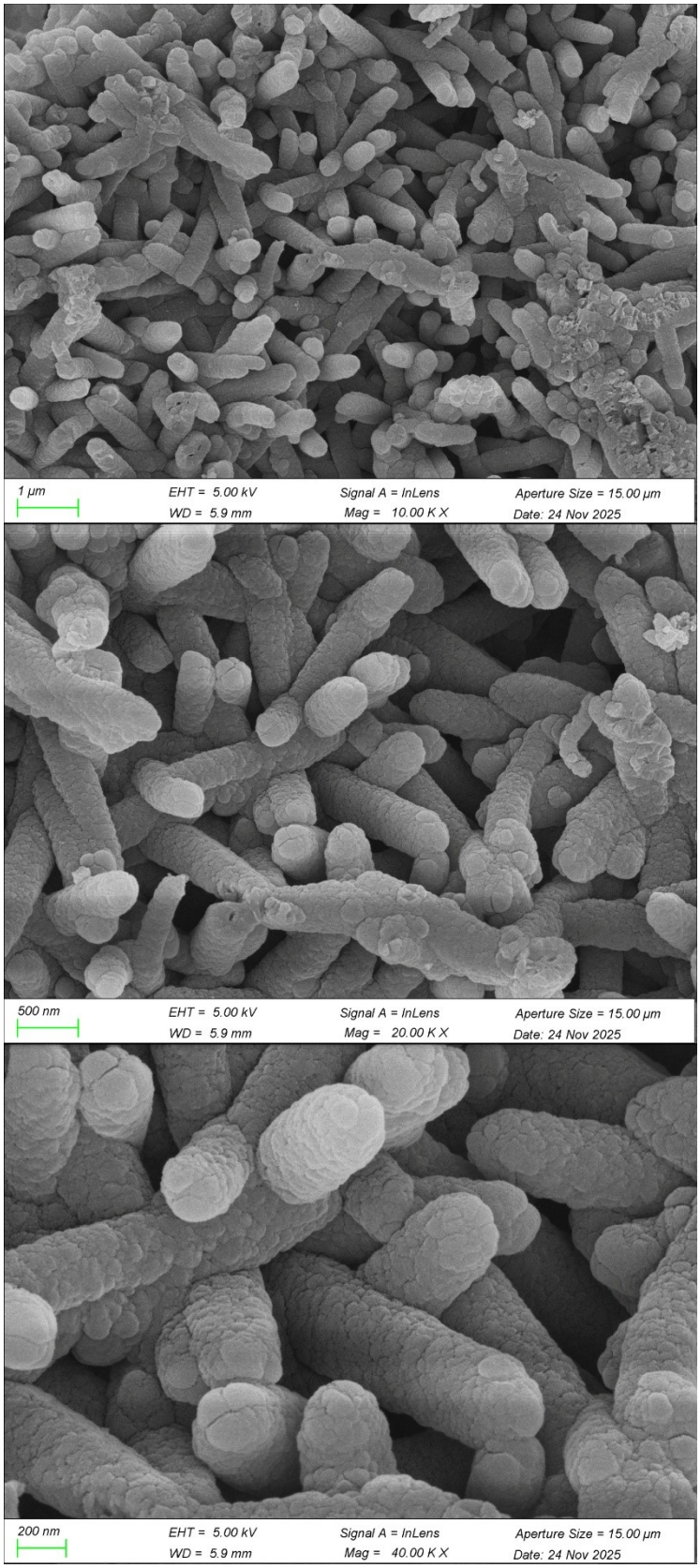


Figure S8. SEM images of COF-TBT-TBT by post-sonication method.

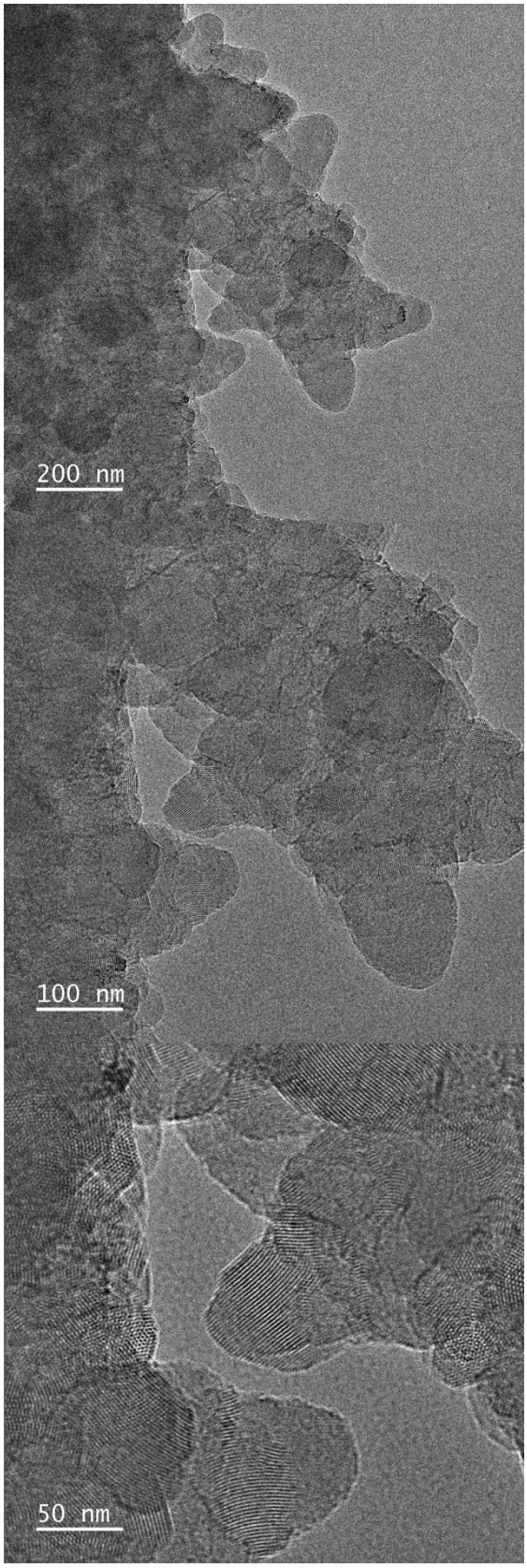


Figure S9. TEM images of COF-TBT-TBT by solvothermal method.

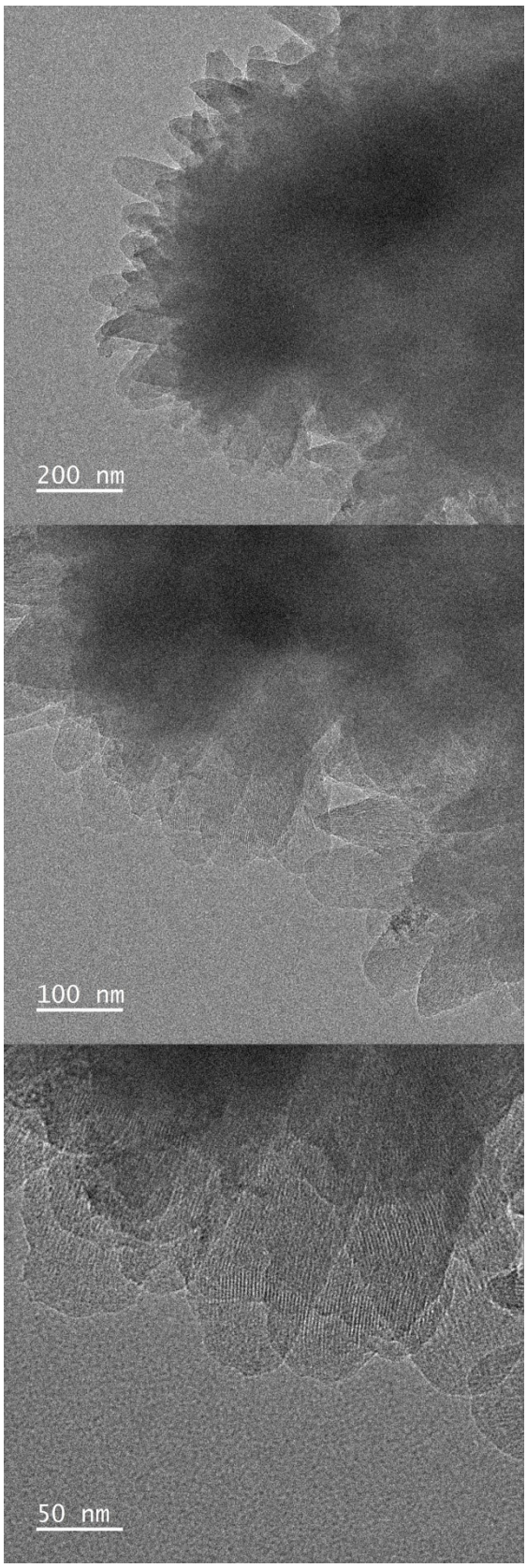


Figure S10. TEM images of COF-TBT-TBT by sonication method.

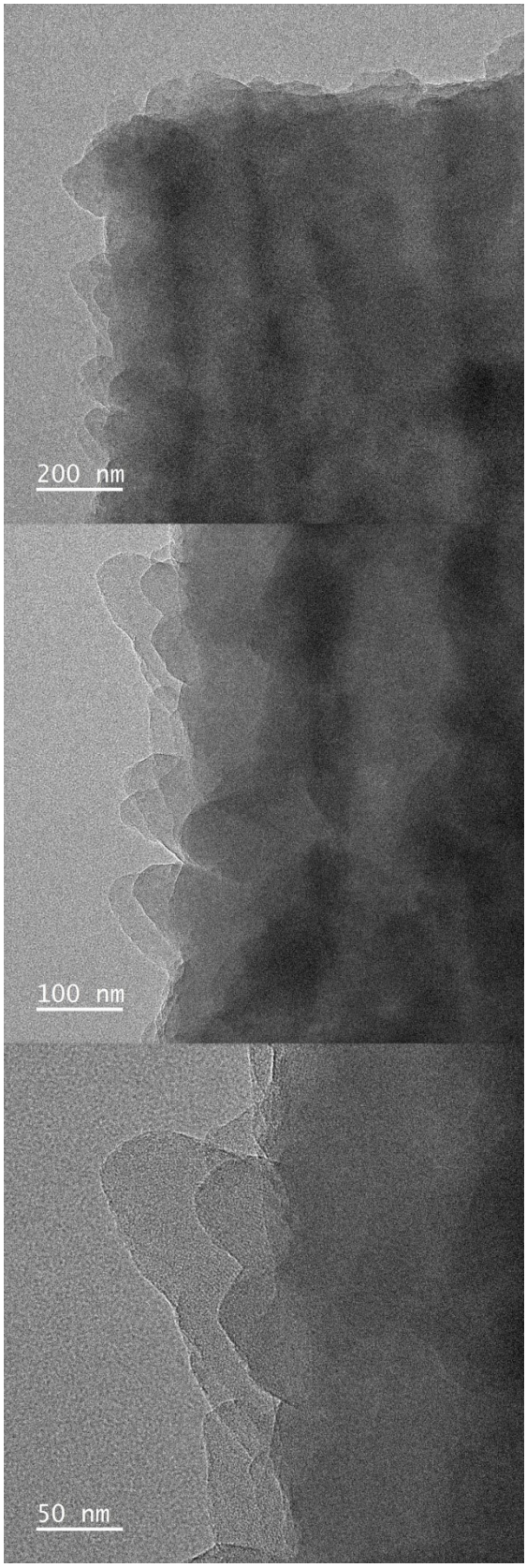


Figure S11. TEM images of COF-TBT-TBT by post-sonication method.

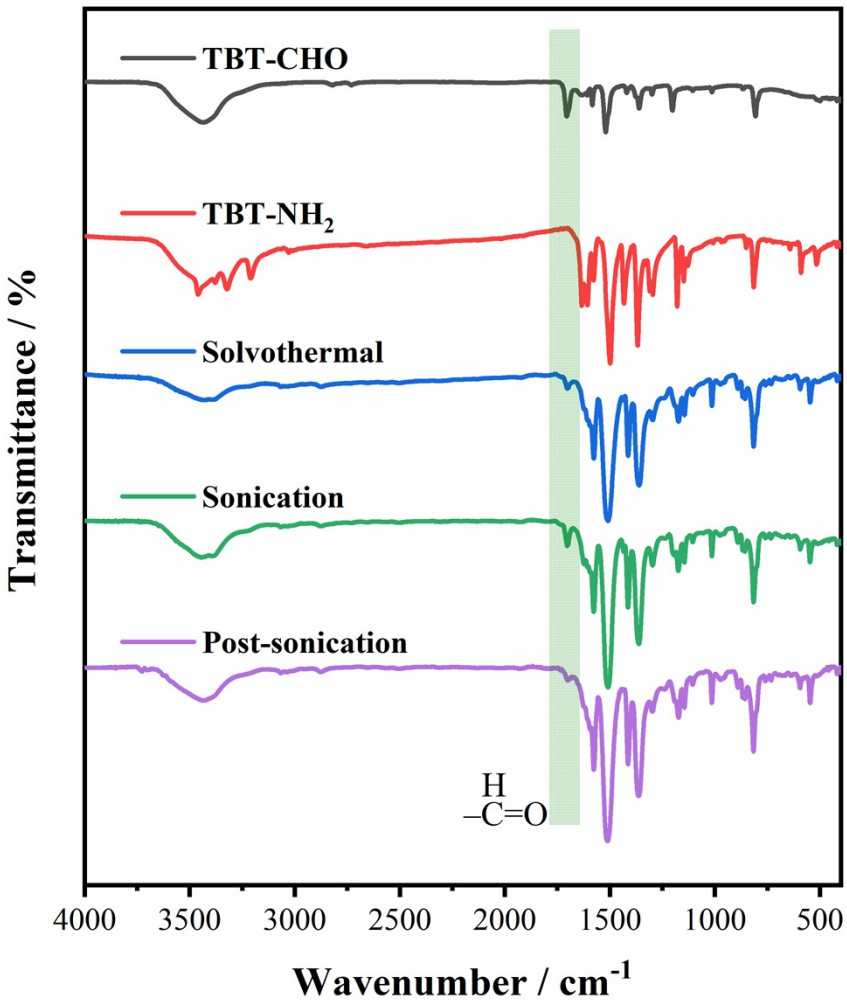


Figure S12. Infrared spectrums of COF-TBT-TBT and their monomers.

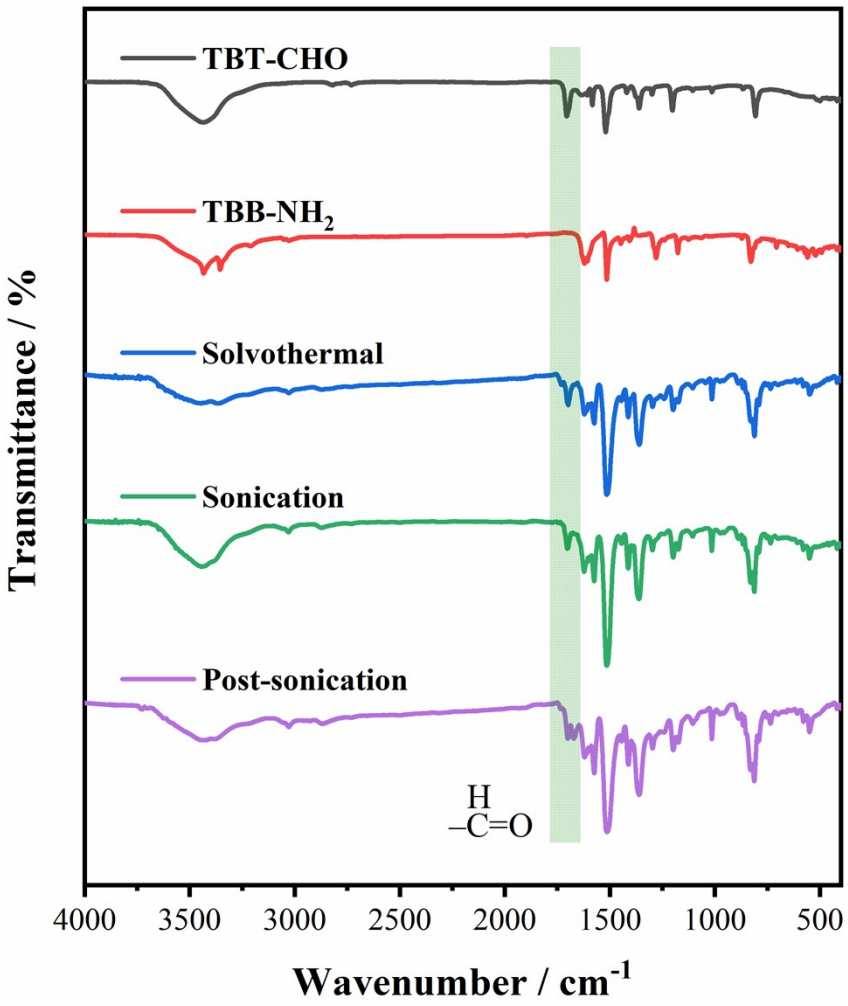


Figure S13. Infrared spectrums of COF-TBT-TBB and their monomers.

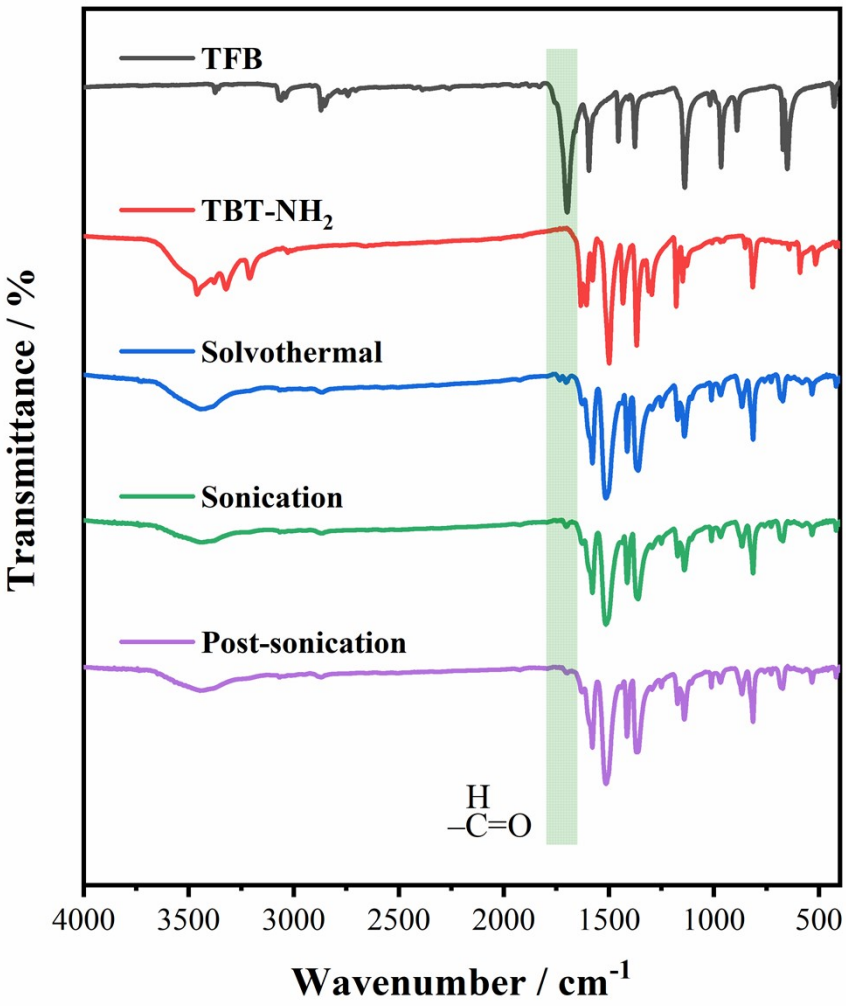


Figure S14. Infrared spectrums of COF-TFB-TBT and their monomers.

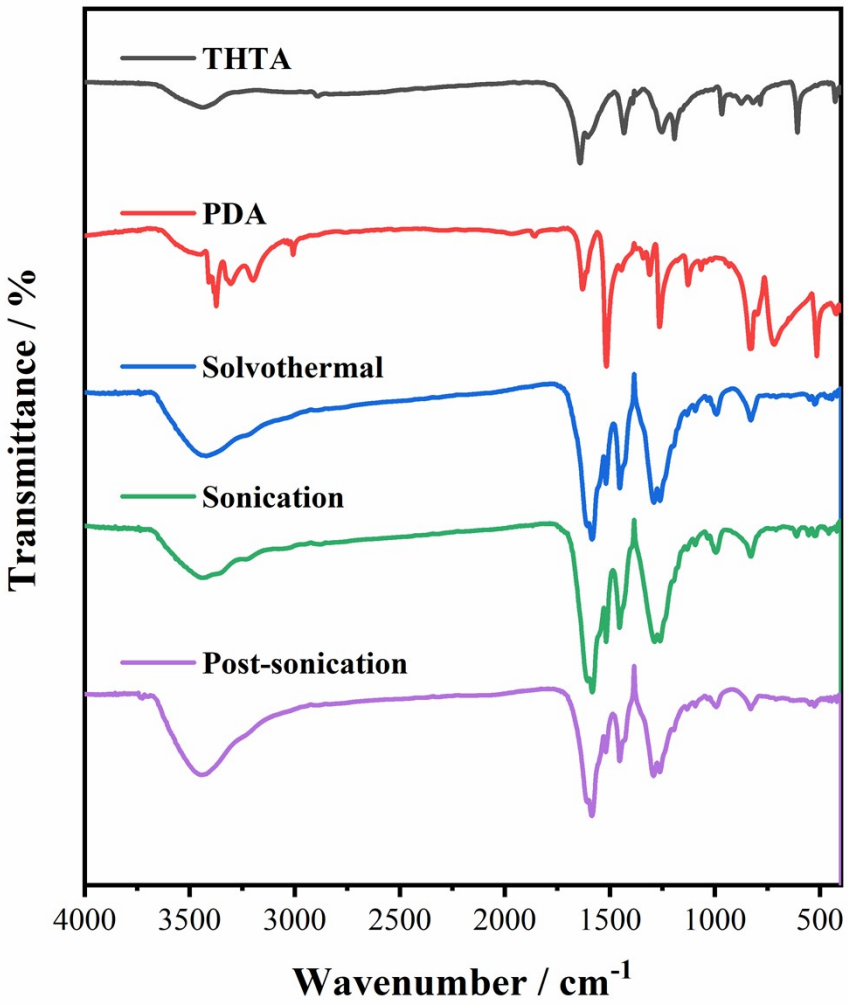


Figure S15. Infrared spectrums of COF-THTA-PDA and their monomers.

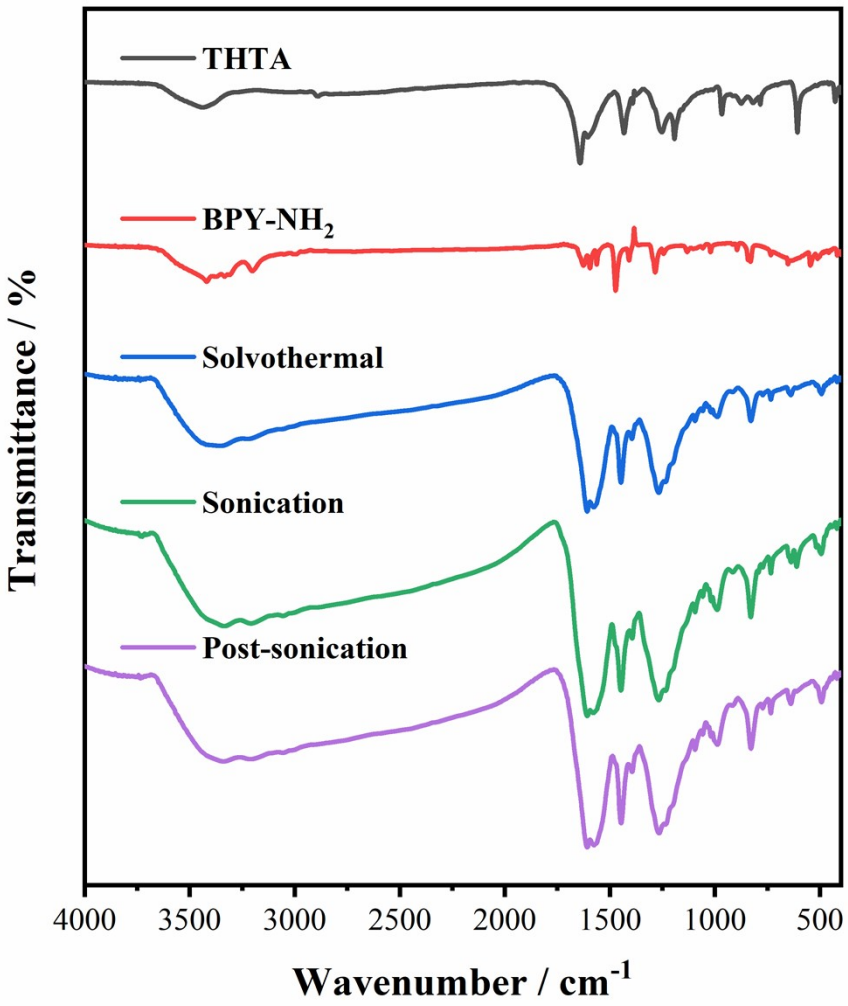


Figure S16. Infrared spectrums of COF-THTA-BPY and their monomers.

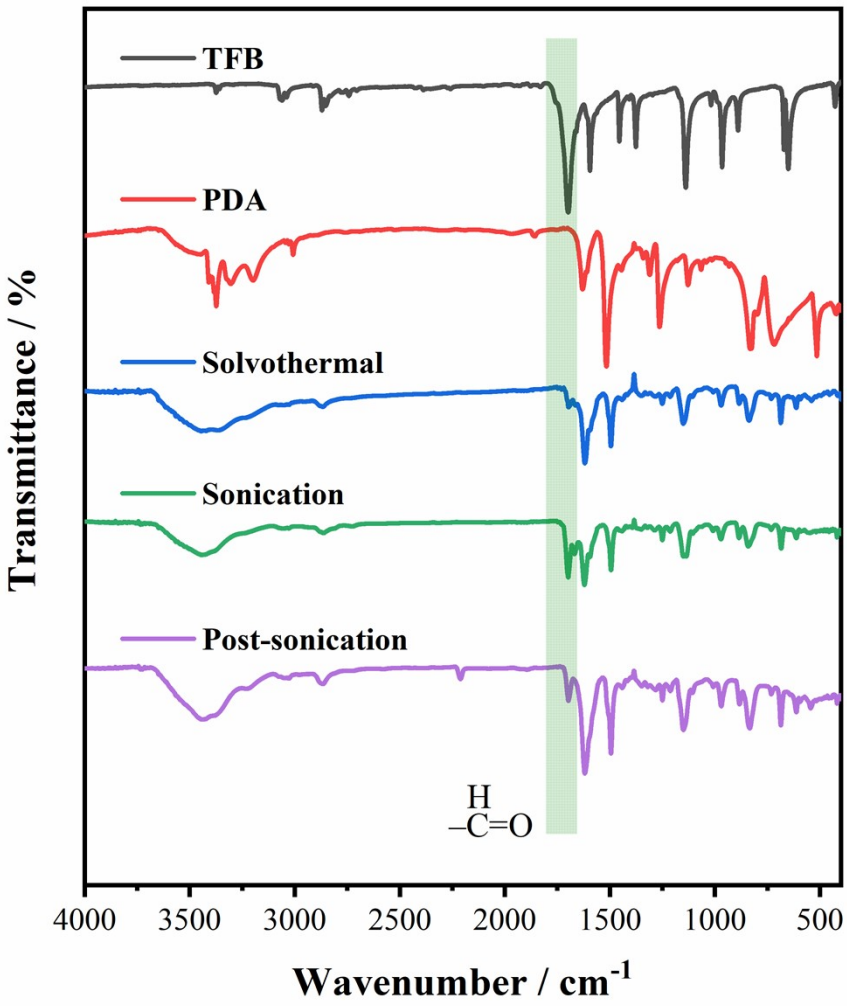


Figure S17. Infrared spectrums of COF-TFB-PDA and their monomers.

4. Structural refinements with PXRD data

Structural modelling of COFs. Structural atomistic simulations of the possible framework structures were carried out using Material Studio software. Firstly, the structural frameworks of 2D COFs were constructed followed the theoretical topology, and each atom was assigned the correct valence and bonding pattern. A preliminary 2D layered framework was generated in space group P1. Secondly, a geometry optimization is performed using the Forcite Calculation to remove steric clashes and obtain a chemically reasonable starting model. Lastly, the experimental PXRD data was loaded for the structural refinement. During the refinement process, multiple parameters were adjusted to minimize Rp and Rwp (ideally below 10%) while ensuring the structural correctness of the model.

4.1 COF-TBT-TBT

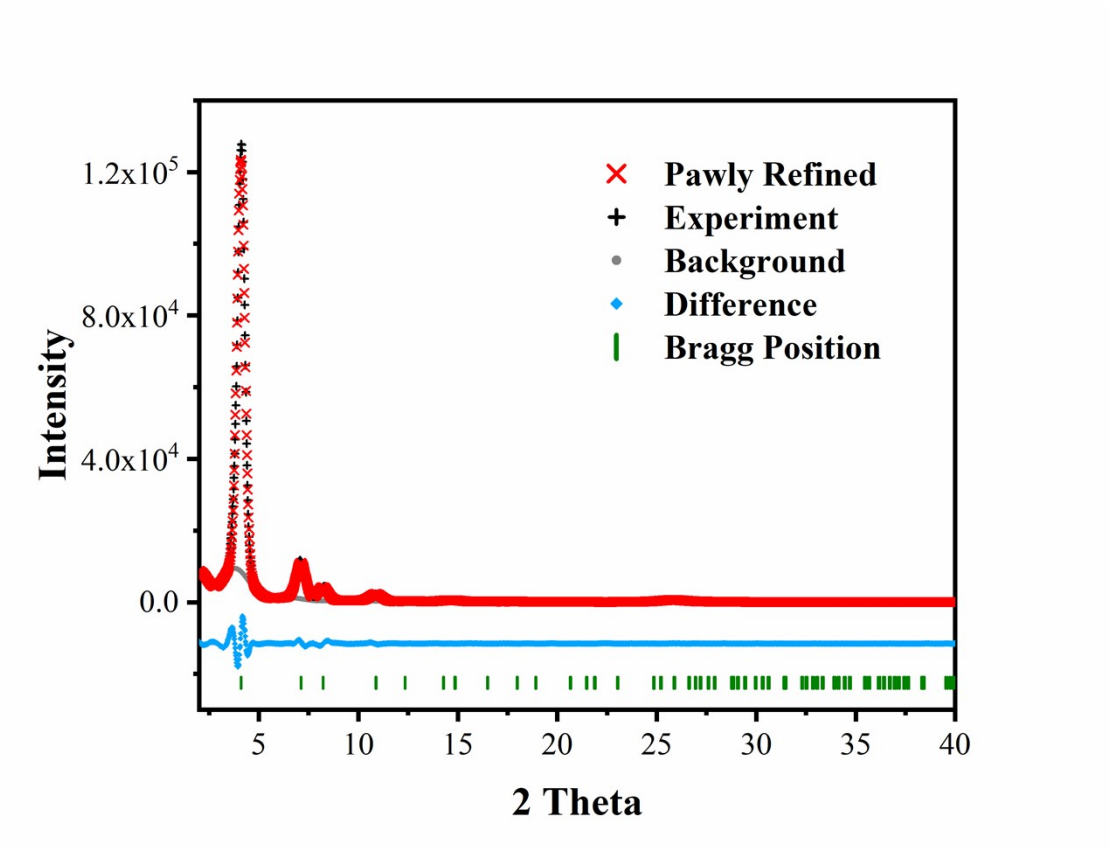


Figure S18. Pawley refinements against the PXRD patterns of COF-TBT-TBT.

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

COF-TBT-TBT: Space group P6			
a= 25.6868 Å, b= 25.6868 Å, c= 3.4653 Å α=β=90°, γ=120°			
Rwp=8.05%, Rp=6.33%			
C1	0.08225	-0.47411	0.00000
C2	0.11679	-0.50227	0.00000
C3	0.17949	-0.46809	0.00000
C4	0.20857	-0.40516	0.00000
C5	0.17393	-0.37692	0.00000
C6	0.11123	-0.41107	0.00000
C7	0.27475	-0.36915	0.00000
N8	0.30817	-0.39669	0.00000
N9	0.51044	-0.47915	0.00000
C10	0.48819	-0.53690	0.00000
C11	0.52693	-0.56369	0.00000
C12	0.50046	-0.62623	0.00000
C13	0.53630	-0.65296	0.00000
C14	0.59912	-0.61740	0.00000
C15	0.62554	-0.55466	0.00000
C16	0.58969	-0.52792	0.00000
C17	0.63689	-0.64566	0.00000
N18	0.61112	-0.70648	0.00000
H19	0.09382	-0.55340	0.00000
H20	0.20737	-0.49136	0.00000
H21	0.19690	-0.32579	0.00000
H22	0.08337	-0.38778	0.00000
H23	0.43731	-0.56737	0.00000

H24	0.44944	-0.65566	0.00000
H25	0.51450	-0.70400	0.00000
H26	0.67654	-0.52512	0.00000
H27	0.61150	-0.47688	0.00000

4.2 COF-TBT-TBB

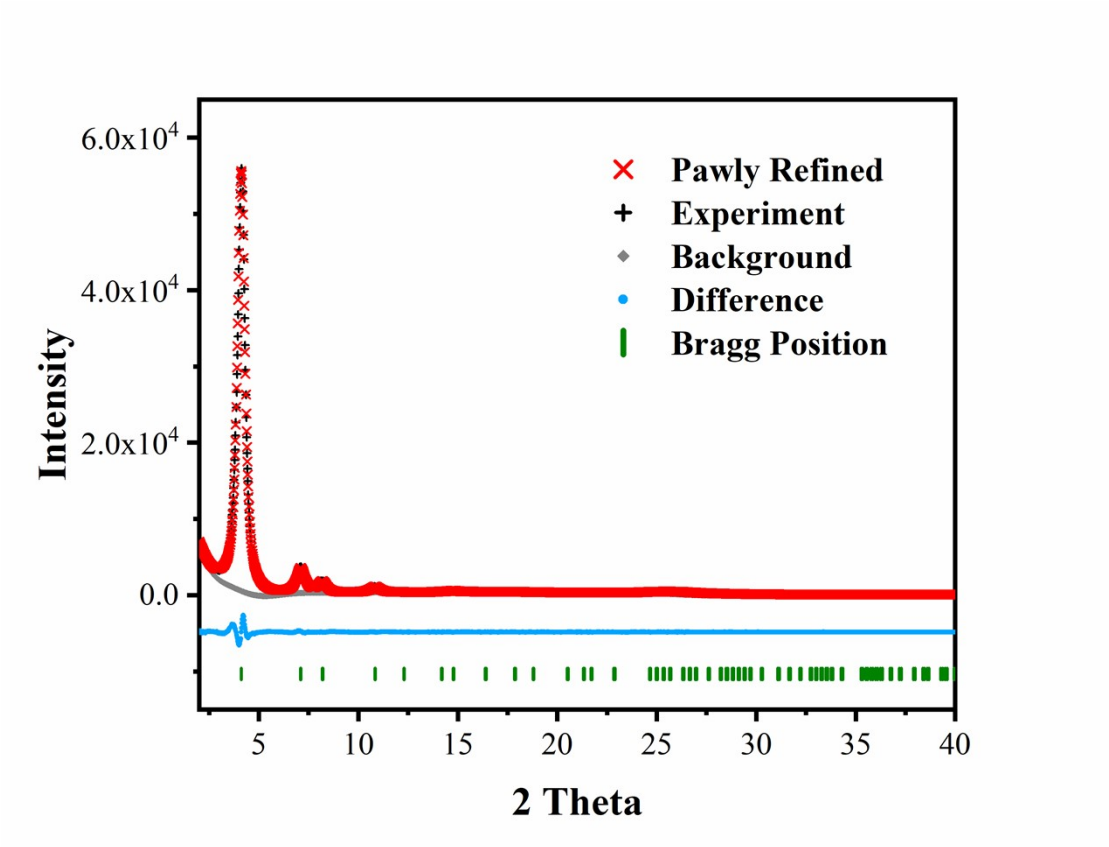


Figure S19. Pawley refinements against the PXRD patterns of COF-TBT-TBB.

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

COF-TBT-TBB: Space group P6			
a= 26.1347 Å, b= 26.1347 Å, c= 3.6713 Å α = β = 90°, γ = 120°			
Rwp = 5.43 %, Rp = 4.46 %			
C1	1.91731	0.47090	0.00000

C2	1.88309	0.49835	0.00000
C3	1.82135	0.46460	0.00000
C4	1.79249	0.40258	0.00000
C5	1.82701	0.37515	0.00000
C6	1.88879	0.40889	0.00000
C7	1.72685	0.36684	0.00000
C8	1.69251	0.39444	0.00000
N9	1.49044	0.47499	0.00000
C10	1.51189	0.53179	0.00000
C11	1.47358	0.55817	0.00000
C12	1.49963	0.61972	0.00000
C13	1.46450	0.64622	0.00000
C14	1.40267	0.61153	0.00000
C15	1.37663	0.54975	0.00000
C16	1.41179	0.52322	0.00000
C17	1.36566	0.63974	0.00000
N18	1.39129	0.69965	0.00000
H19	1.90547	0.54861	0.00000
H20	1.79386	0.48740	0.00000
H21	1.80476	0.32489	0.00000
H22	1.91626	0.38605	0.00000
H23	1.71491	0.44471	0.00000
H24	1.56190	0.56190	0.00000
H25	1.54980	0.64867	0.00000
H26	1.48608	0.69643	0.00000
H27	1.32646	0.52073	0.00000
H28	1.39020	0.47301	0.00000

4.3 COF-TFB-TBT

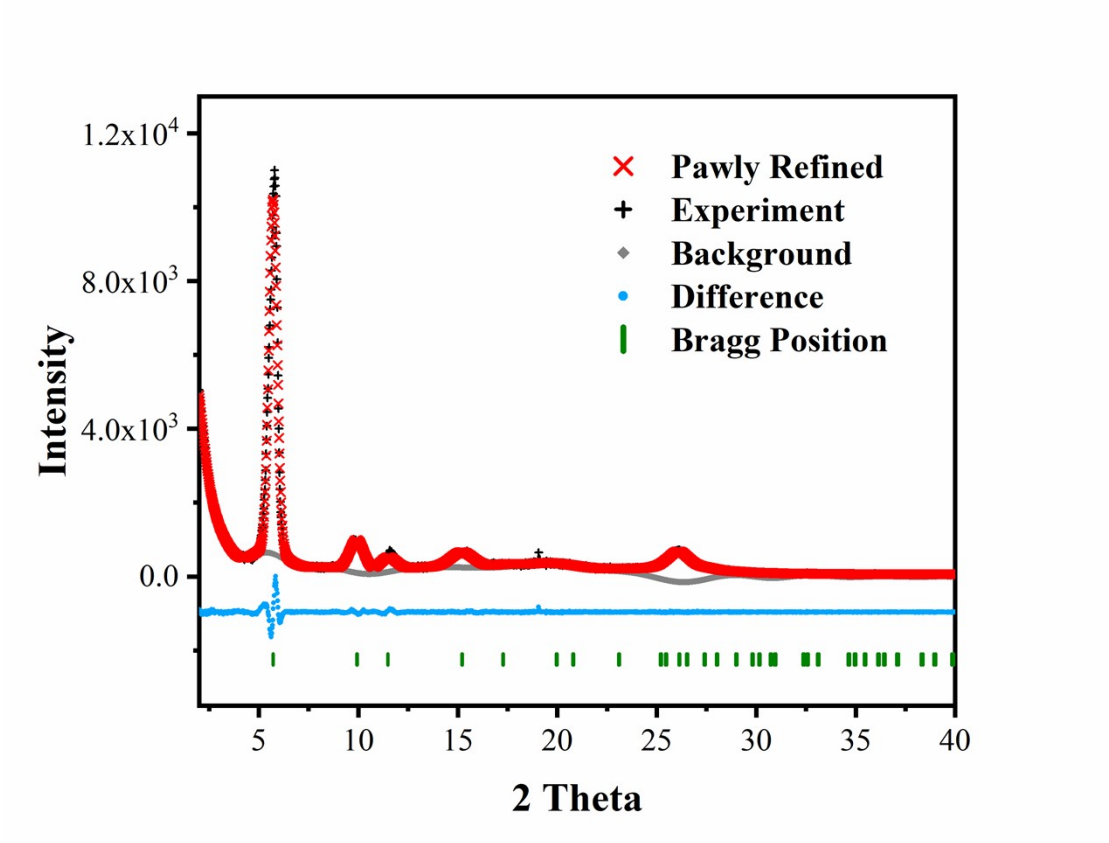


Figure S20. Pawley refinements against the PXRD patterns of COF-TFB-TBT.

Table S4. Fractional atomic coordinates for the unit cell of COF-TFB-TBT.

COF-TFB-TBT: Space group P6			
a= 17.9251 Å, b= 17.9251 Å, c= 3.5257 Å α = β = 90°, γ = 120°			
Rwp = 9.58%, Rp = 7.22%			
N1	0.37187	0.75007	0.00000
C2	0.28812	0.70551	0.00000
C3	0.50873	0.76101	0.00000
C4	0.27821	0.83433	0.00000
C5	0.23194	0.87422	0.00000
C6	0.14506	0.82799	0.00000

C7	0.10613	0.74180	0.00000
C8	0.15231	0.70188	0.00000
N9	0.09375	0.86504	0.00000
C10	0.11779	0.94332	0.00000
C11	0.05694	0.97161	0.00000
C12	0.08478	0.05647	0.00000
H13	0.34487	0.87157	0.00000
H14	0.26506	0.94078	0.00000
H15	0.03941	0.70531	0.00000
H16	0.11995	0.63509	0.00000
H17	0.18249	0.98942	0.00000
H18	0.15050	0.09994	0.00000

4.4 COF-THTA-PDA

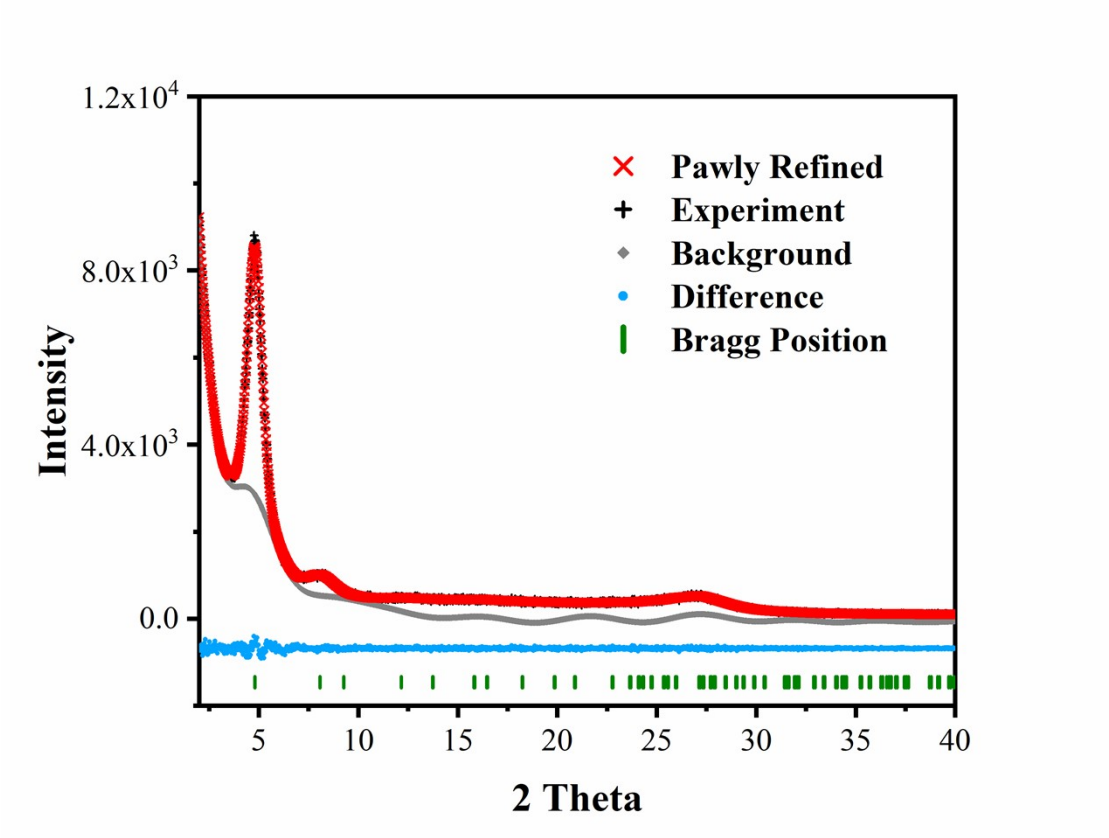


Figure S21. Pawley refinements against the PXRD patterns of COF-THAT-PDA.

Table S5. Fractional atomic coordinates for the unit cell of COF-THAT-PDA.

COF-THTA-PDA: Space group P6/M			
a= 22.8893 Å, b= 22.8893 Å, c= 3.7133 Å α = β = 90°, γ = 120°			
Rwp = 3.56%, Rp = 2.42%			
C1	0.69359	0.40706	0.00000
C2	0.61942	0.36022	0.00000
O3	0.71627	0.46801	0.00000
C4	0.80723	0.42530	0.00000
N5	0.59357	0.45160	0.00000
C6	0.54549	0.47405	0.00000
C7	0.56970	0.54317	0.00000
C8	0.52498	0.57376	0.00000
H9	0.82566	0.48169	0.00000
H10	0.64770	0.49107	0.00000
H11	0.62637	0.57998	0.00000
H12	0.54821	0.63094	0.00000

4.5 COF-THTA-BPY

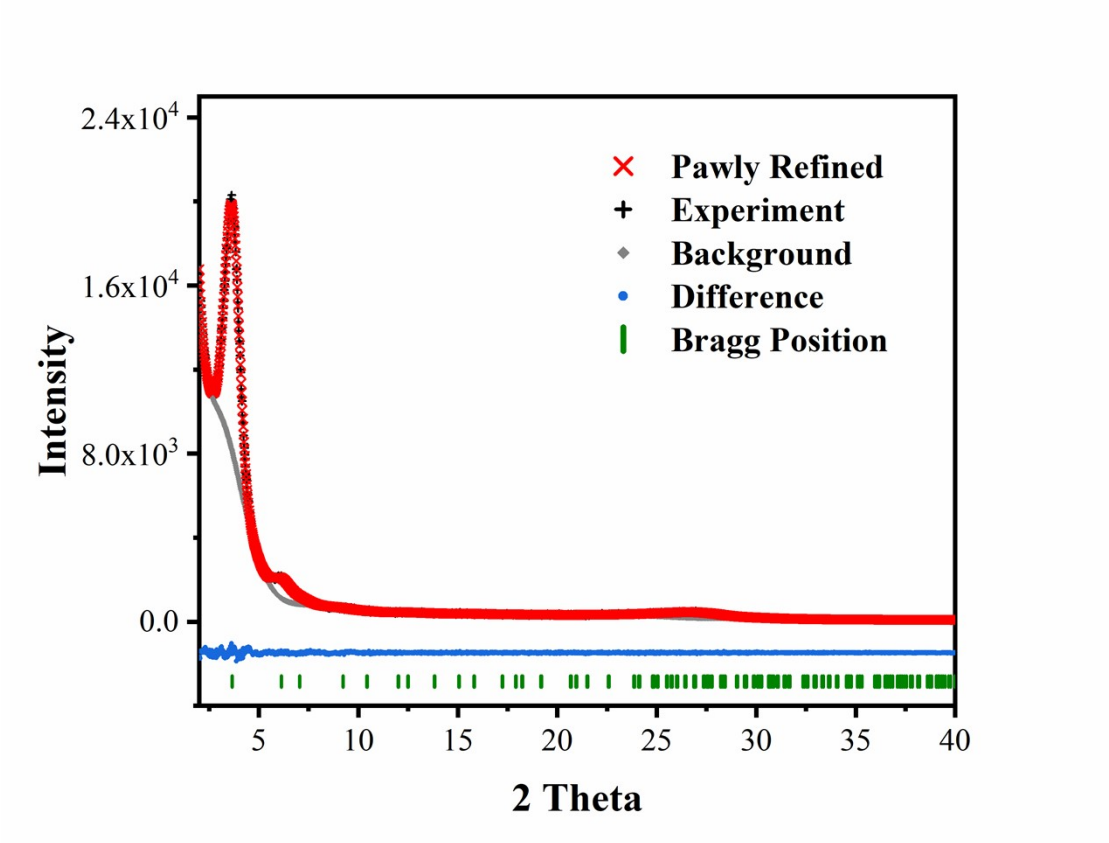


Figure S22. Pawley refinements against the PXRD patterns of COF-THAT-BPY.

Table S6. Fractional atomic coordinates for the unit cell of COF-THAT-BPY.

COF-THTA-BPY: Space group P6			
a= 30.1366 Å, b= 30.1366 Å, c= 3.6259 Å α = β = 90°, γ = 120°			
Rwp = 2.93%, Rp = 1.83%			
C1	0.29806	0.68815	0.00000
C2	0.27689	0.63173	0.00000
O3	0.37293	0.76975	0.00000
C4	0.29440	0.55902	0.00000
N5	0.27997	0.75903	0.00000
C6	0.24387	0.77692	0.00000

C7	0.26178	0.82975	0.00000
N8	0.22790	0.84739	0.00000
C9	0.17599	0.81486	0.00000
C10	0.15661	0.76153	0.00000
C11	0.19071	0.74266	0.00000
C12	0.14105	0.83617	0.00000
N13	0.16105	0.88817	0.00000
C14	0.13053	0.90975	0.00000
C15	0.07685	0.87844	0.00000
C16	0.05547	0.82509	0.00000
C17	0.08746	0.80371	0.00000
N18	0.04370	0.89989	0.00000
C19	0.06268	0.95411	0.00000
C20	0.03206	0.97489	0.00000
C21	0.05684	0.03173	0.00000
O22	0.95383	0.89621	0.00000
H23	0.32263	0.54429	0.00000
H24	0.32127	0.78846	0.00000
H25	0.30471	0.85812	0.00000
H26	0.11347	0.73407	0.00000
H27	0.17536	0.69958	0.00000
H28	0.14852	0.95320	0.00000
H29	0.01209	0.79908	0.00000
H30	0.07007	0.76032	0.00000
H31	0.00151	0.87427	0.00000
H32	0.10571	0.98207	0.00000

4.6 COF-TFB-PDA

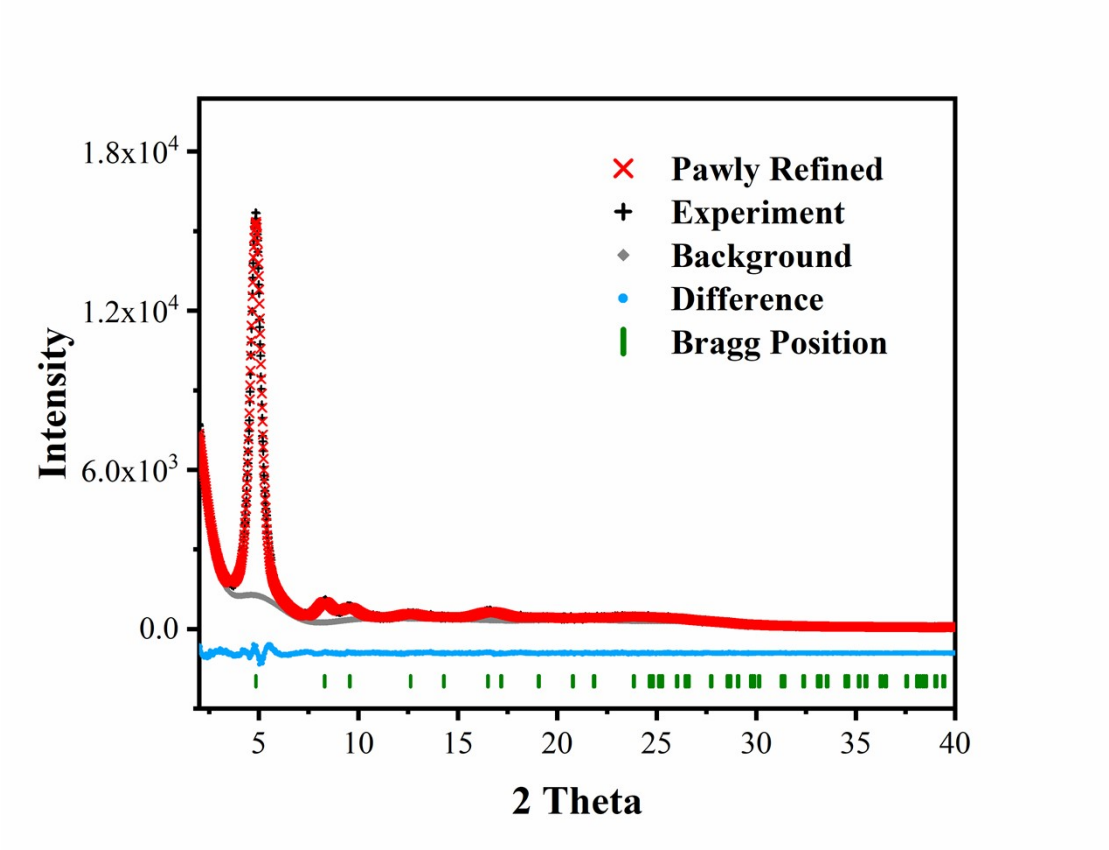


Figure S23. Pawley refinements against the PXRD patterns of COF-TFB-PDA.

Table S7. Fractional atomic coordinates for the unit cell of COF-TFB-PDA.

COF-TFB-PDA: Space group P6/M			
a= 21.7742 Å, b= 21.7742 Å, c= 3.6497 Å α = β = 90°, γ = 120°			
Rwp = 5.07%, Rp = 3.75%			
C1	1.28736	-0.30871	0.00000
C2	1.26250	-0.37957	0.00000
C3	1.38232	-0.18873	0.00000
N4	1.44726	-0.14386	0.00000
C5	1.47314	-0.07140	0.00000

C6	1.42897	-0.54410	0.00000
C7	1.47311	-0.57095	0.00000
H8	1.24975	-0.28872	0.00000
H9	1.34390	-0.16975	0.00000
H10	1.37106	-0.58020	0.00000
H11	1.45111	-0.62888	0.00000

Table S8. Differences of four post-synthetic treatment method.

Method	Purpose	Difference
Solvent annealing[1]	Increasing crystallinity	Similar to the solvothermal method, usually need a long-time period (several days) and a limited improvement on crystallinity. Applicable for almost all COFs.
Steam treatment[2]	Reorient COF pore channels	Usually used in COFs film for ions separation. No big change in COFs crystallinity.
Mechanical grinding[3]	Producing COFs nanomaterials	Often used to get COFs nanosheet. Reduced crystallinity caused by decreased number of stacked layers.
Post-sonication	Increasing crystallinity	Fast processing time (several hours) and significant crystalline improvement.

References

1. X.-H. Han, J.-Q. Chu, W.-Z. Wang, Q.-Y. Qi and X. Zhao, *Chin. Chem. Lett.*, 2022, **33**, 2464-2468.
2. C. Yin, M. Liu, Z. Zhang, M. Wei, X. Shi, Y. Zhang, J. Wang and Y. Wang, *J. Am. Chem. Soc.*, 2023, **145**, 11431-11439.
3. Z. Wang, X. Yan, Q. Hou, Y. Liu, X. Zeng, Y. Kang, W. Zhao, X. Li, S. Yuan, R. Qiu, M. H. Uddin, R. Wang, Y. Xia, M. Jian, Y. Kang, L. Gao, S. Liang, J. Z. Liu, H. Wang and X. Zhang, *Nat. Comm.*, 2023, **14**, 236.