Supplementary Information

Organobase Modulated Synthesis of High-Quality β-Ketoenamine-Linked Covalent Organic Frameworks

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Section I Materials and Methods

1. Materials

1,3,5-Triformylphloroglucinol (Tp), 4,4'-biphenyldiamine (BD), 5,5′-diamino-2,2′-bipyridine (BPy), *p*-terphenyl-4,4"-diamine (TP), *p*-phenylenediamine (Pa), 3,3'-dimethoxybiphenyl-4,4'-diamine (BD(OMe)$_2$), 2,6-diamino-9,10-anthraquinone (DAAQ), *p*-azoaniline (Azo), 4,7-bis(4-aminophenyl)-2,1,3-benzothiadiazole (BT), and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAP) were purchased from Jilin Chinese Academy of Sciences-Yanshen technology Co. Ltd. Anhydrous *o*-dichlorobenzene (*o*-DCB), *n*-butanol (*n*-BuOH), 1,4-dioxane (Diox), 1,3,5-trimethylbenzene (Mes) and dimethylacetamide (DMAc) were obtained from Aladdin Industrial Corporation. Tetrahydrofuran and acetone were purchased from Shanghai Chemical Regents Company. All the chemicals used were from commercial suppliers without further purification.

2. Characterizations

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffraction spectrometer (Bruker D8 Advance, Germany) with Cu Kα radiation at λ = 0.154 nm operating at 40 kV and 40 mA. FT-IR spectra were recorded on a Nicolet 6700 (Thermofisher, USA) Fourier transformation infrared spectrometer. N$_2$ sorption isotherms were collected by a TriStar II 3020 volumetric adsorption analyzer (Micromeritics, USA) at 77K. The samples were degassed at 120°C for 12 h under vacuum condition before measurement. Solid-state CP/MAS ^{13}C NMR spectra were recorded on 400WB AVANCE III (Bruker, Switzerland) plus 400 MHz spectrophotometer at 298 K. ^{1}H NMR spectrum was recorded on a Varian Mercury plus 400 MHz spectrophotometer at 298 K.

3. Experimental Section

3.1 General Synthesis procedure of Tp-based COFs
0.08 mmol 1,3,5-triformylphloroglucinol (Tp) and amine-functionalized monomer (0.08 mmol triamines or 0.12 mmol diamines) were charged into a Pyrex tube (10 cm×1cm) and mixed with 1 mL given solvent. Then a certain volume of pyrrolidine (Py) (0.005, 0.02, 0.05 or 0.1 mL) or 0.1 mL 6M acetic acid (HOAc) aqueous solution

was added. After sonication for 10 minutes, the reaction solution was subjected to three freeze-pump-thaw cycles and the Pyrex tube was sealed off. The reaction proceeded at 120°C for 3 days. Afterwards, the product was filtered and washed with THF and acetone (10 mL×3 for each), respectively, followed by the Soxhlet extraction with THF for 3 days. The obtained solids were dried at 45°C in vacuum for 48 hours. If no specified, 1.96 vol% of pyrrolidine was used for synthesis of COFs.

Table S1. Reaction conditions and yields for all of the nine β-ketoenamine-linked 2D COFs, as displayed in **Scheme S1**.

Entry	COF	Amine monomer	Solvent (1 mL, v/v)	Yield (Py)	Yield (HOAc aq. 6M)
1	TpBD	BD	o-DCB:n-BuOH (9:1)	89%	85%
2	TpPa	Pa	Diox	84%	88%
3	TpTP	TP	o-DCB:n-BuOH (9:1)	88%	86%
4	TpAzo	Azo	Diox	84%	87%
5	TpBD(OMe)$_2$	BD(OMe)$_2$	o-DCB:n-BuOH (9:1)	83%	85%
6	TpTAP	TAP	o-DCB:n-BuOH (1:1)	85%	83%
7	TpDAAQ	DAAQ	DMAc:Mes (3:1,1.2mL)	80%	82%
8	TpBPy	BPy	Diox	76%	83%
9	TpBT	BT	o-DCB:n-BuOH(9:1)	80%	91%

3.2 Model reaction of Tp with Py

0.08 mmol Tp (16.8 mg) was dispersed in a 3 mL of ethanol. Once 0.02 mL (0.24 mmol) pyrrolidine was added into the mixture, all solids were dissolved to form the yellow and transparent solution. The reaction proceeded for 1 h at room temperature. Then the solvent was removed and the remaining solid was dried at 45°C in vacuum for 24 h. The pale-yellow powder was obtained in 92% isolated yield (32 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.24 (s, 1H), 3.71 (d, J = 60.2 Hz, 4H), and 1.96 (s, 4H).

3.3 Calculation of (100) domain size

The crystalline domain sizes of TpBD-COFs from different reaction time are calculated from Scherrer equation based on (100) diffraction peaks[S1]:

$$\sigma = \frac{K\gamma}{\beta \cos\theta}$$

σ: average domain size;

K: shape factor (0.89);
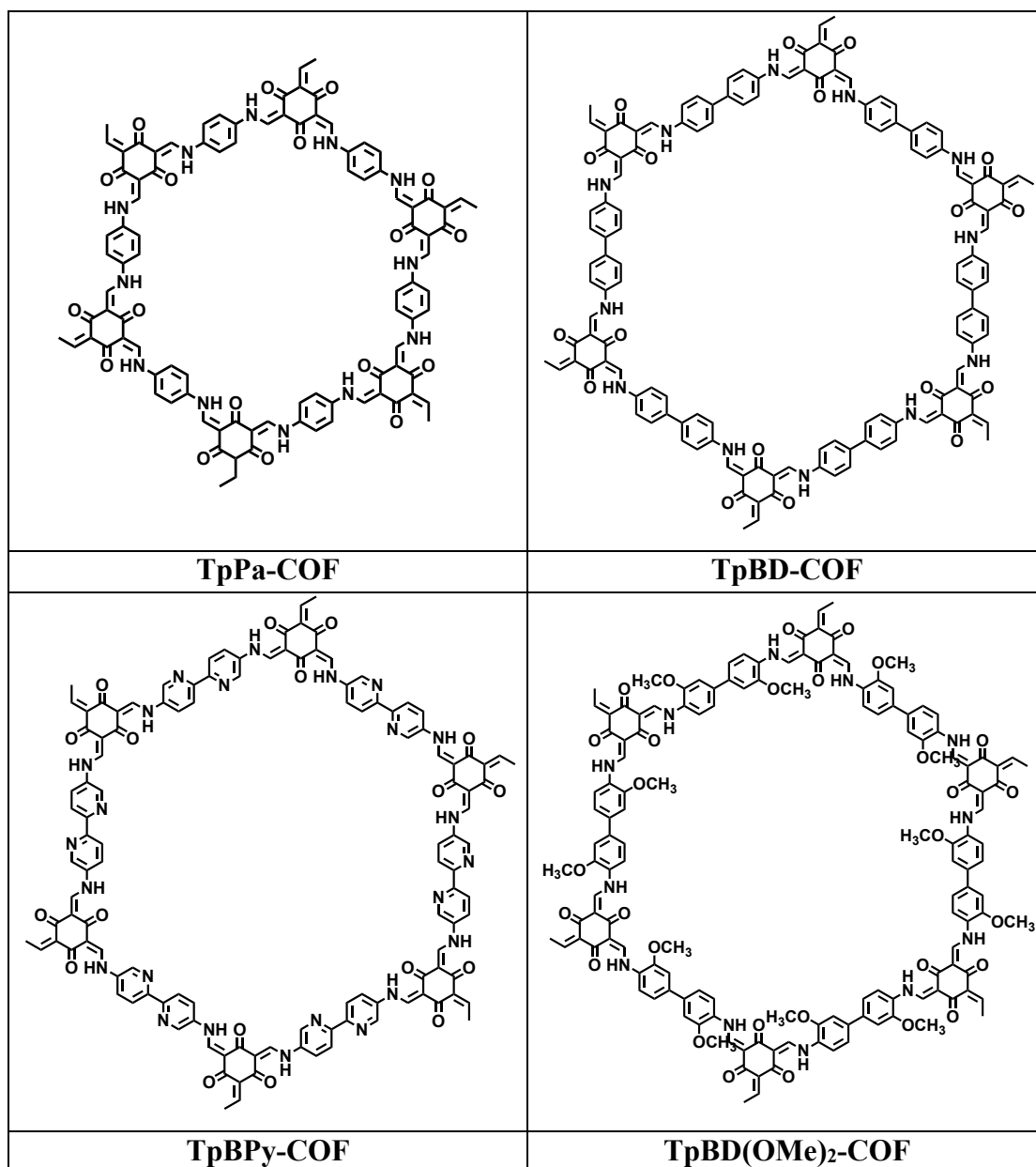
γ: X-ray diffraction wave length (1.54 Å);

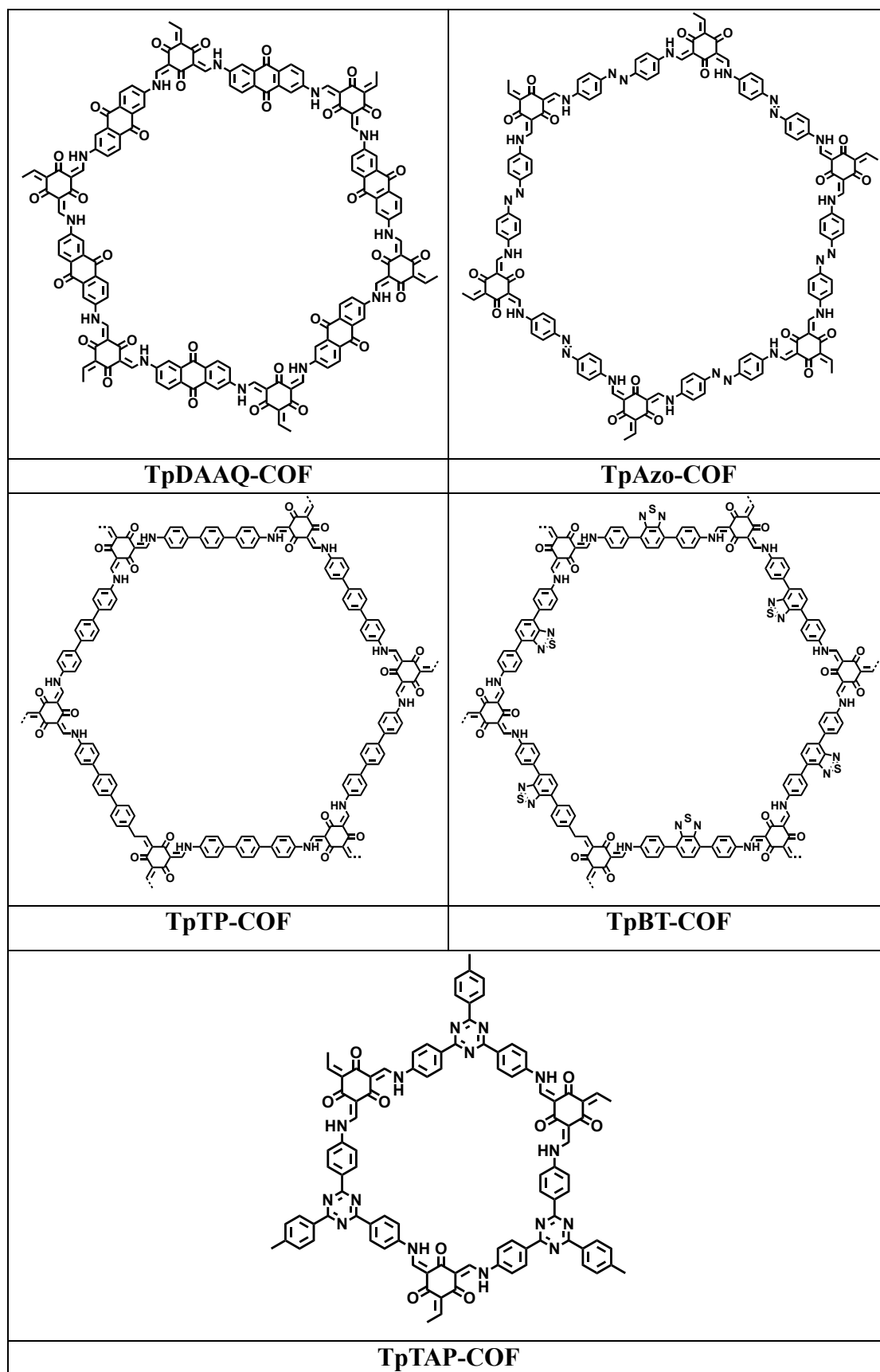β: full width at half maxima of (100) diffraction peak (radian system);

θ: Bragg angle of the (100) diffraction peak.

4. Reference

[S1] N. C. Flanders, M. S. Kirschner, P. Kim, T. J. Fauvell, A. M. Evans, W. Helweh, A. P. Spencer, R. D. Schaller, W. R. Dichtel and L. X. Chen, *J. Am, Chem. Soc,* 2020, **142**, 14957-14965.

Section II Figures and Tables

TpPa-COF

TpBD-COF

TpBPy-COF

TpBD(OMe)₂-COF

TpDAAQ-COF	**TpAzo-COF**
TpTP-COF	**TpBT-COF**
TpTAP-COF	

Scheme S1. Structures of Tp-based β-ketoenamine-linked 2D COFs.
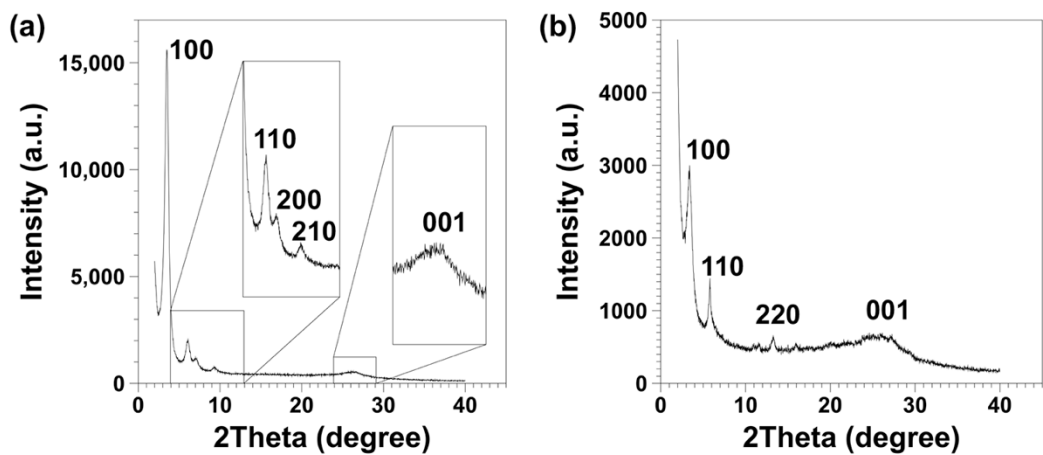
Fig. S1 PXRD patterns of TpBD-COFs synthesized using pyrrolidine (0.02 mL, 1.96 vol%) and acetic acid aqueous solution (6M, 0.1 mL), respectively. The reaction conditions: o-DCB/n-BuOH = 9/1 (1 mL, v/v), 120ºC and 3 days.
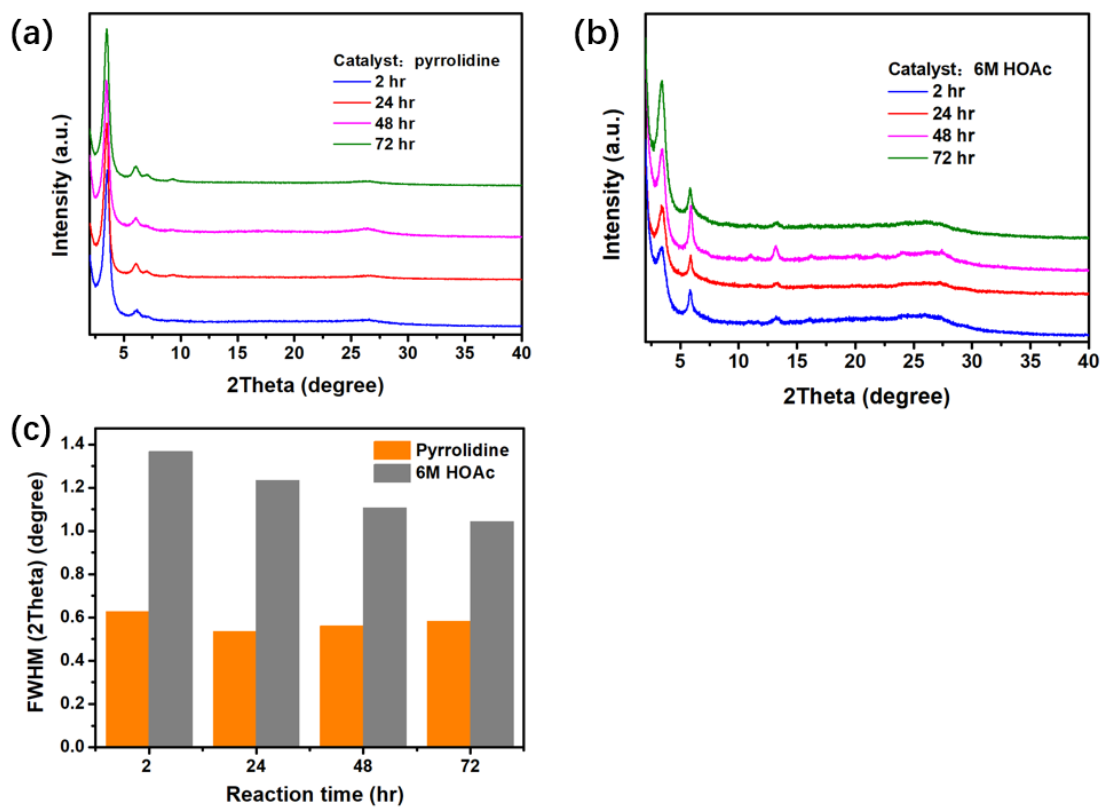
Fig. S2 PXRD patterns of TpBD-COFs synthesized for 2h, 24h, 48h and 72h using Py (a) and 6M HOAc aq. (b), respectively. (c) Estimation of full widths at half maximum (FWHM) for the predominated peak at 3.5º in (a) and (b), which is corresponding to the (100) lattice plane. Average domain sizes are calculated with Scherrer equation based on the FWHM of (100) diffraction peaks.
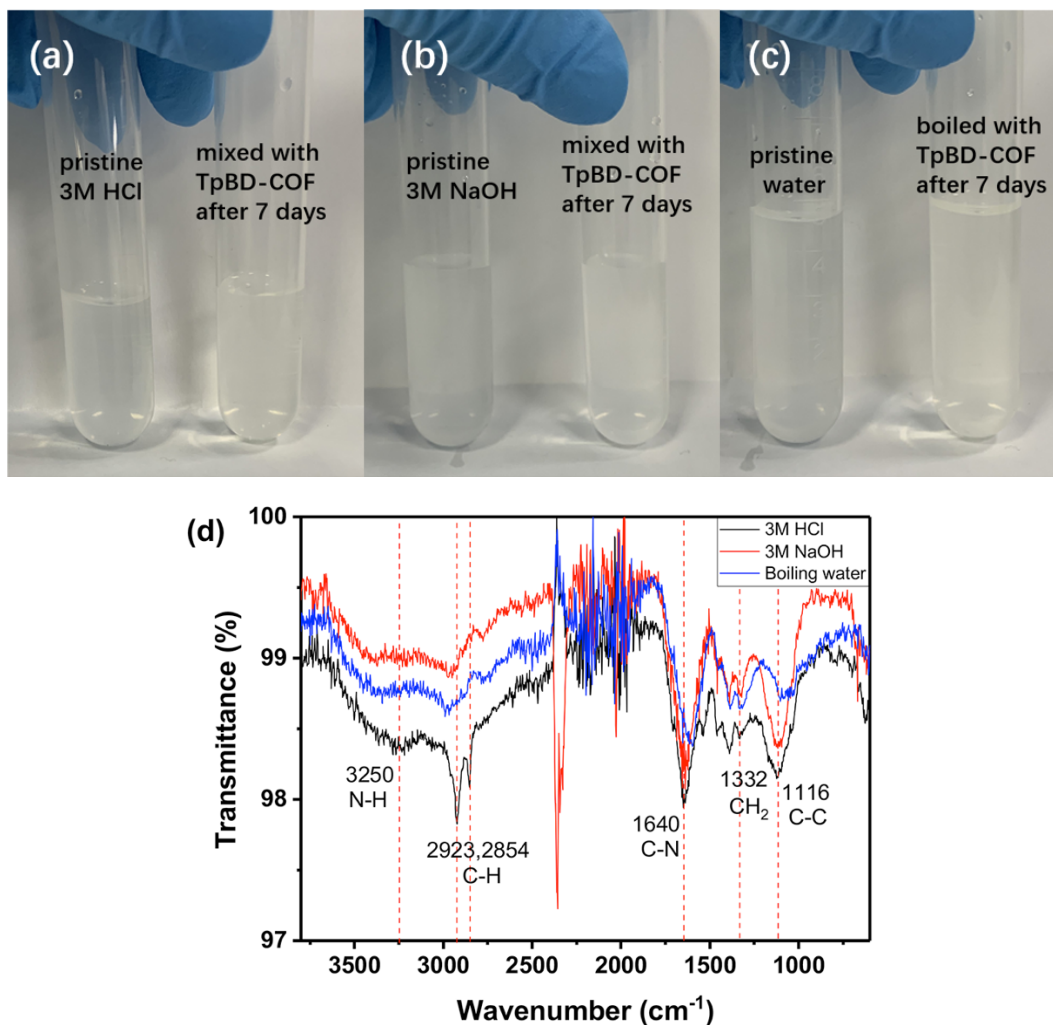
Fig.S3 (a-c) Photographs of the solutions of 3M HCl aq., 3M NaOH aq., and boiling water before and after the treatment for the TpBD-COF(Py). The obtained COF solids remained the relative weights of 99wt.%, 98wt.% and 99wt.% to the original one, respectively. (d) FT IR spectra of the material obtained in the solutions after treatment. As its content is very low, it is roughly estimated that the material is pyrrolidine.
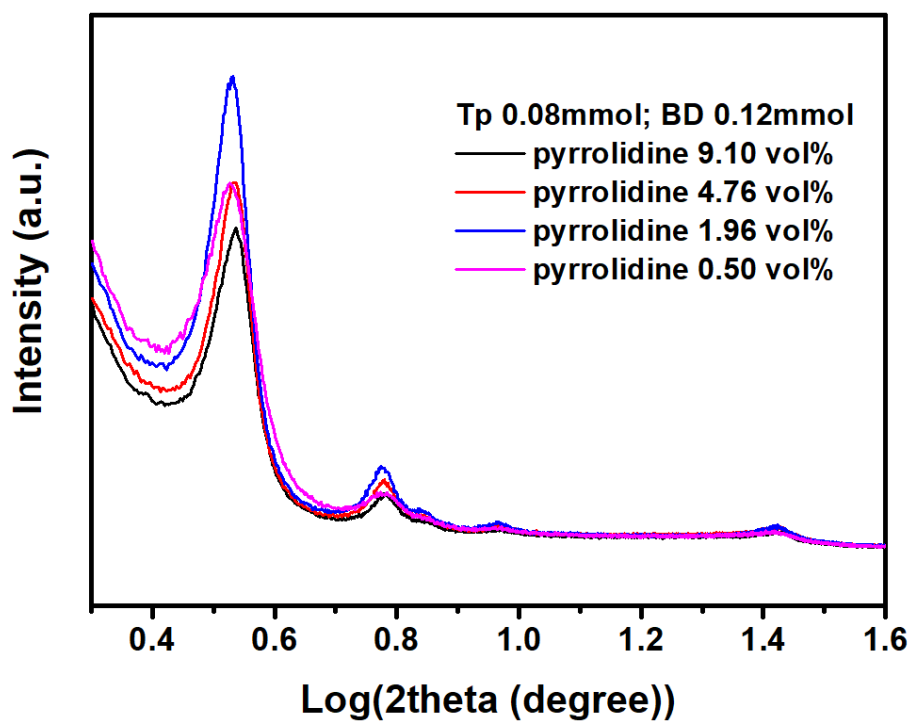
Fig. S4 PXRD patterns of TpBD-COFs synthesized by using the various concentrations of Py in a mixture of o-DCB and n-BuOH (9/1, v/v) at 120°C for 3 days.
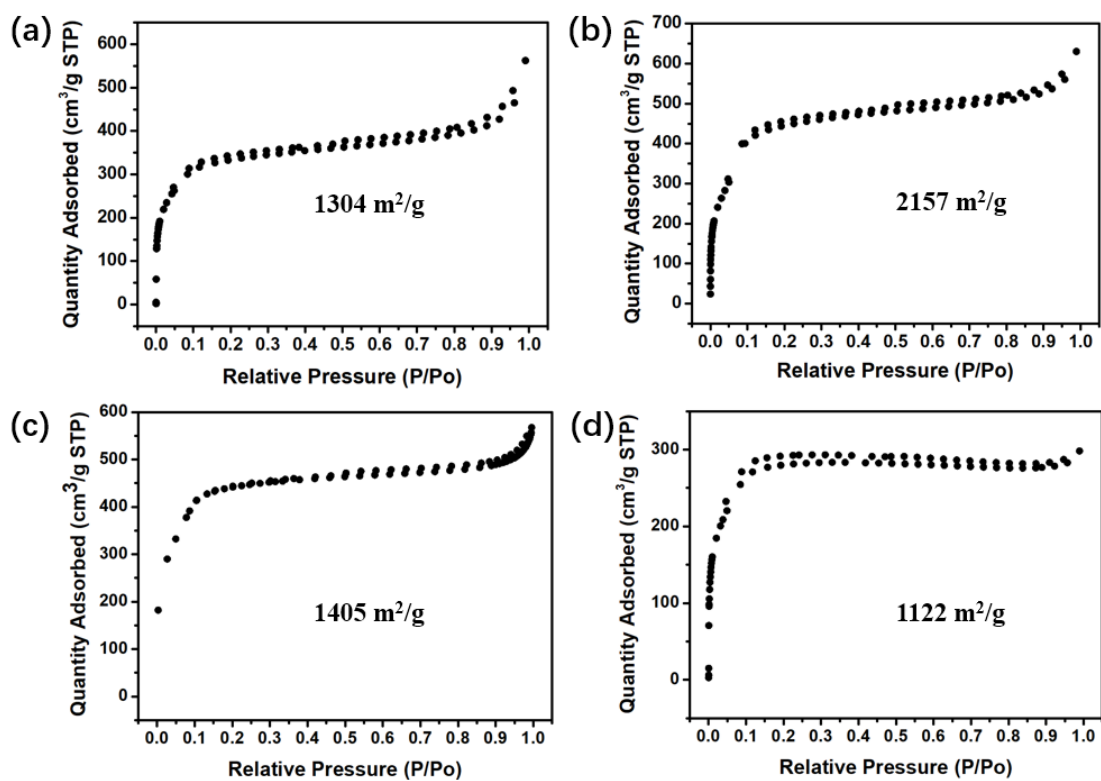
Fig. S5 N$_2$ sorption isotherms of TpBD-COF with (a) 0.5 vol.%, (b) 1.96 vol.%, (c) 4.76 vol.% and (d) 9.10 vol.% Py, and their corresponding yields are 91%, 89%, 81% and 70%, respectively.

Table S1. BET surface areas of TpBD-COFs synthesized using the different organobases (1.96 vol%).

Organobases	BET surface area (m^2/g)
Pyrrolidine	2157
1-Methyl pyrrolidine	298
2-Methyl pyrrolidine	1050
Piperazine	1029
Piperidine	634
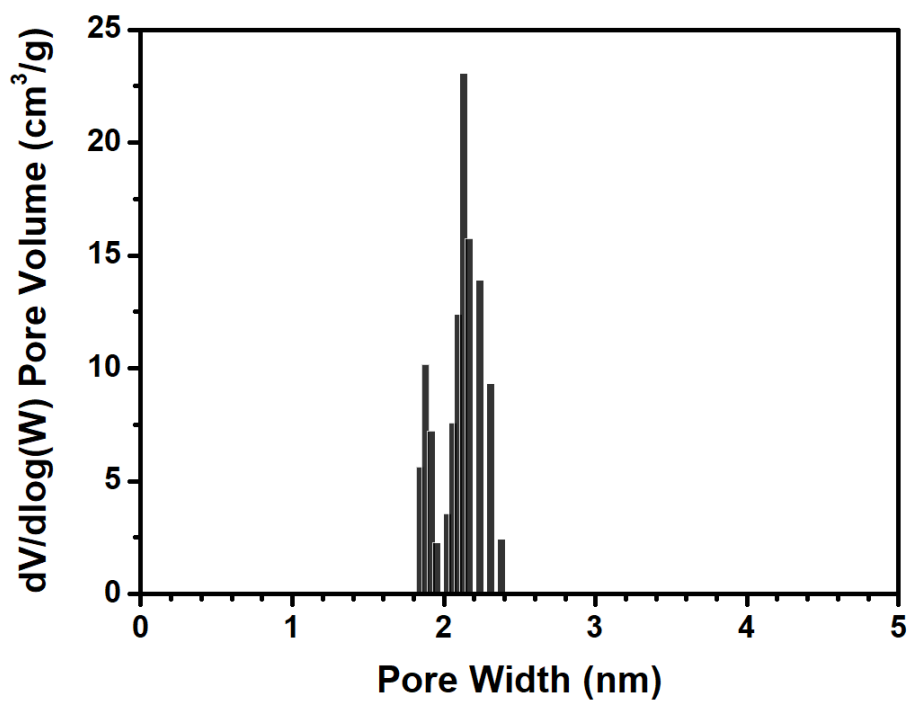
Fig. S6 Pore-size distribution of PyBD-COF synthesized using 1.96 *vol.*% of pyrrolidine. The simulated pore size is 2.3 nm according to the early report (R. Banerjee et al. J. Am. Chem. Soc. 2013, 135, 5328).
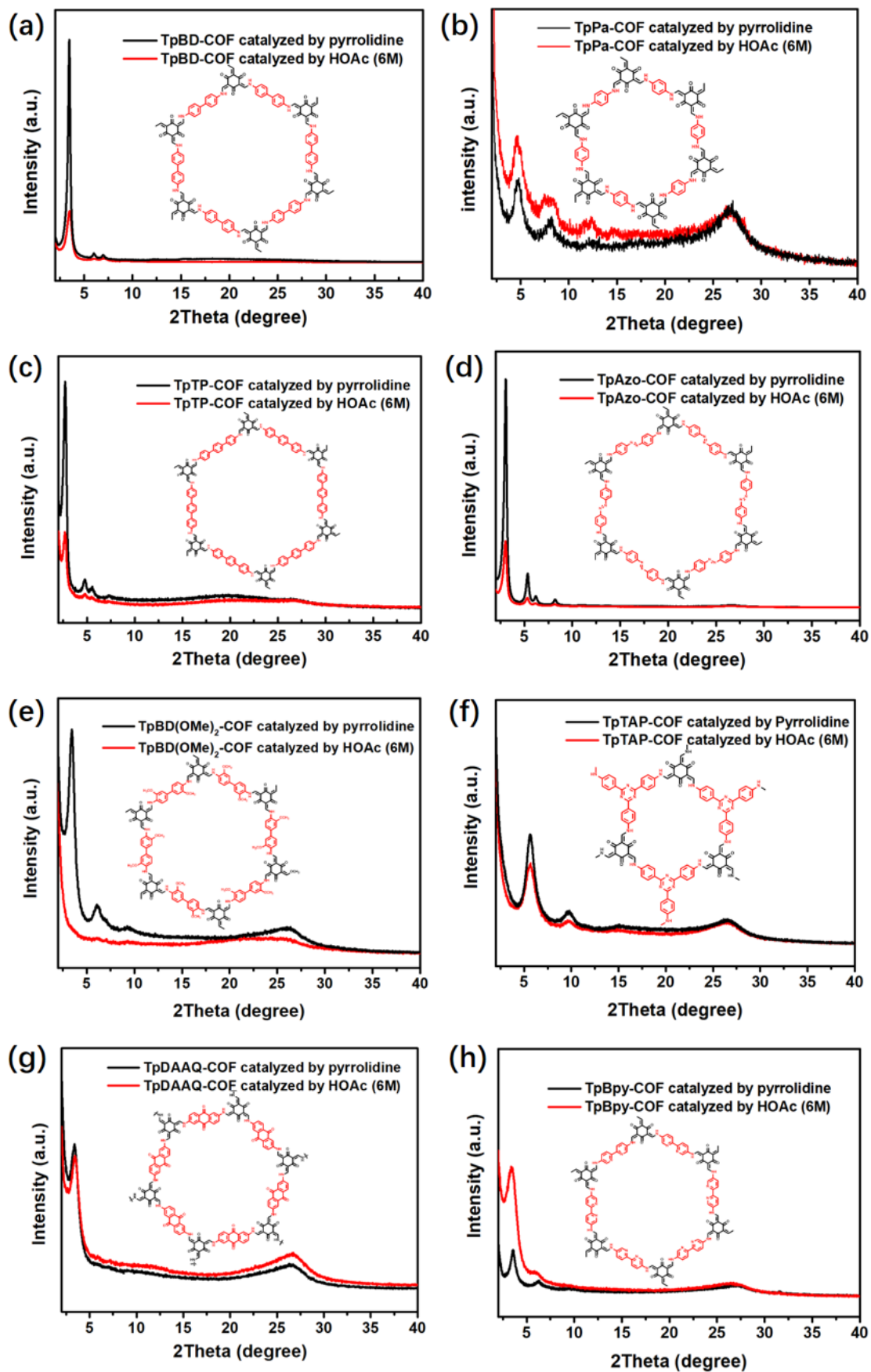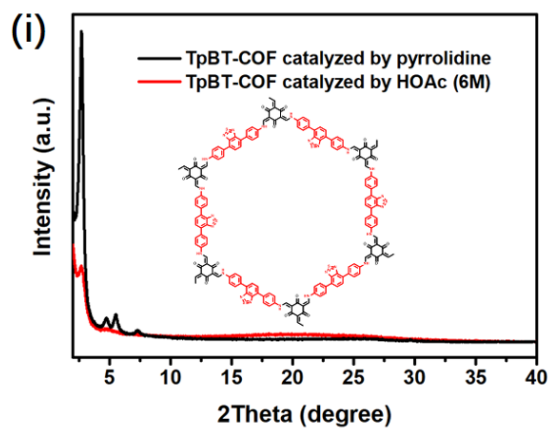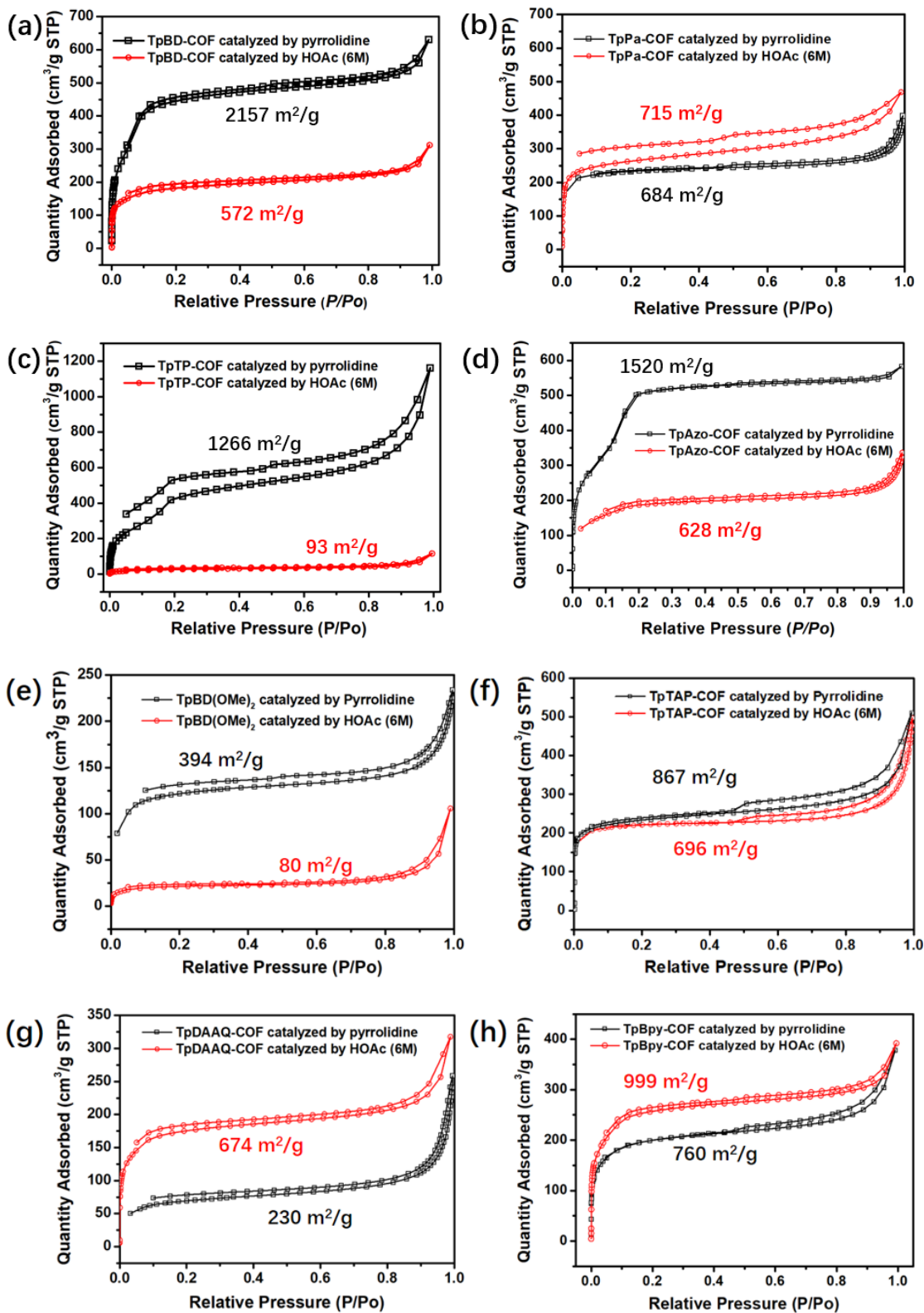
Fig. S7 PXRD patterns of (a) TpBD-COF, (b) TpPa-COF, (c) TpTP-COF, (d) TpAzo-COF, (e) TpBD(OMe)$_2$-COF, (f) TpTAP-COF, (g) TpDAAQ-COF, (h) TpBpy-COF and (i) TpBT-COF.
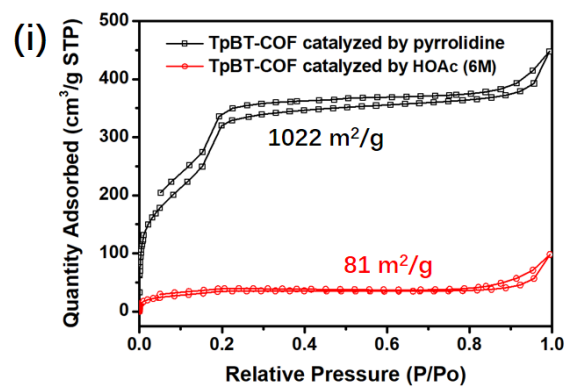
Fig. S8 N$_2$ sorption isotherms of (a) TpBD-COF, (b) TpPa-COF, (c) TpTP-COF, (d) TpAzo-COF, (e) TpBD(OMe)$_2$-COF, (f) TpTAP-COF, (g) TpDAAQ-COF, (h) TpBpy-COF and (i) TpBT-COF.
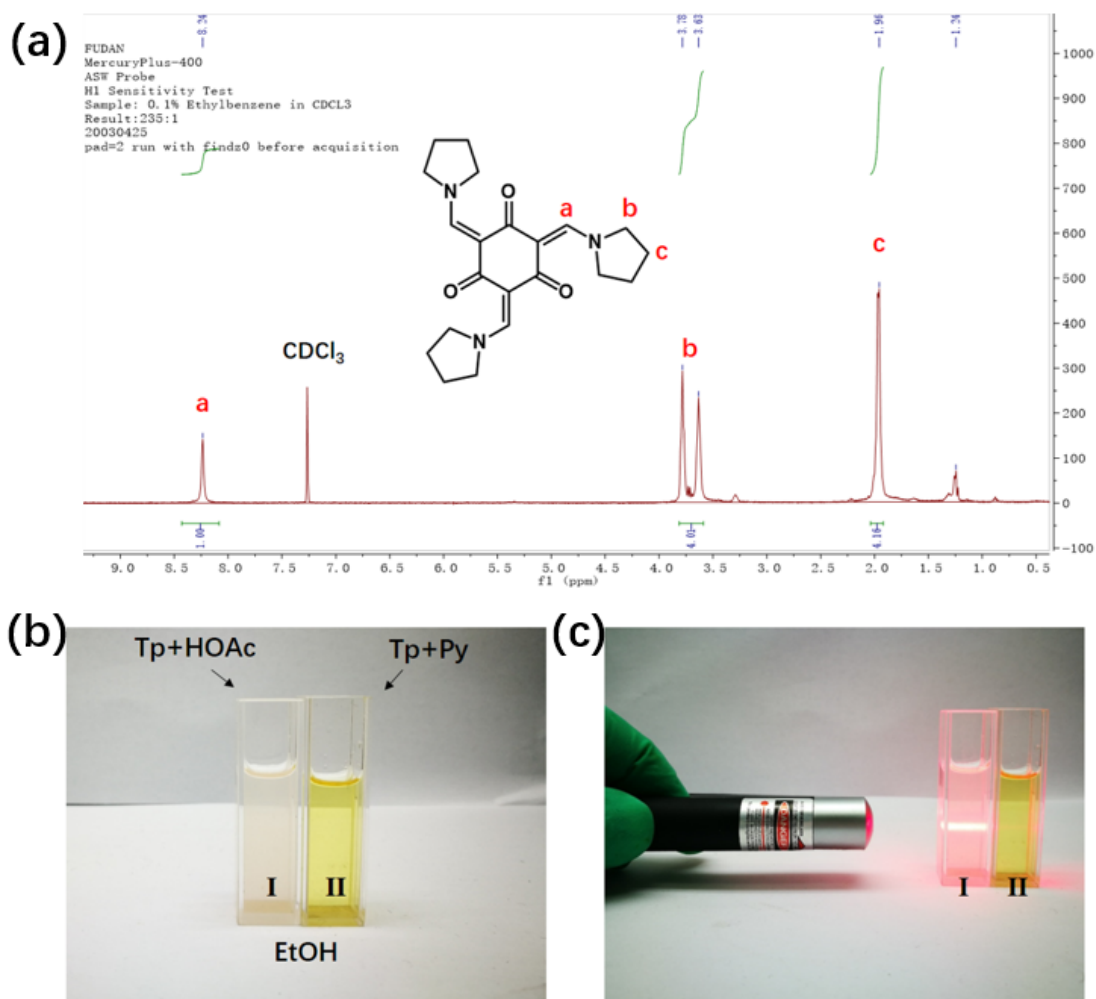
Fig. S9 (a) ^{1}H NMR spectrum of the product obtained from a mixture of Tp and Py in ethanol. With addition of Py, Tp was completely dissolved in EtOH, as shown in (b). In contrast, HOAc didn't work for the Tp dissolution. Also, it could be proved by the Tyndall effect in (c).