Supporting information

Facile Fabrication of Hollow Tubular Covalent Organic Frameworks Using Decomposable Monomer as Building Block

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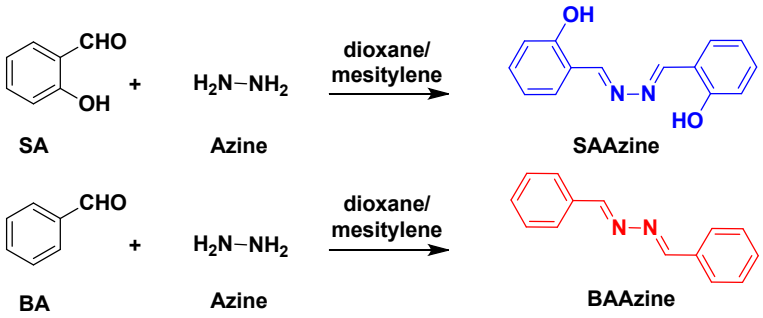
Materials

Hydrazine hydrate (Azine), acetic acid (HAc), 1,2-dichlorobenzene (*o*-DCB), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), chloroform-D ($CDCl_3$) and dimethyl sulfoxide-d6 (DMSO-d6) were from J&K Scientific Ltd. (Beijing, China). Benzaldehyde (BA), salicylaldehyde (SA), FH and TFB were obtained from Sigma (St Louis, USA). Tp was obtained from Huawei-Ruike (Beijing, China). 1,4-Dioxane, mesitylene and tetrahydrofuran (THF) were supplied by Tianjin Kermel Plant of Chemical Reagent (Tianjin, China). Water was purified with a Milli-Q system from Millipore (Milford, USA). Standard pH buffer solutions purchased from Beijing Solarbio Science & Technology were used to control the pH values as 4.01, 7.01 and 10.01. Standard HCl (0.1 M) and NaOH (0.1 M) solutions were prepared for pH=1 and pH=13, respectively.

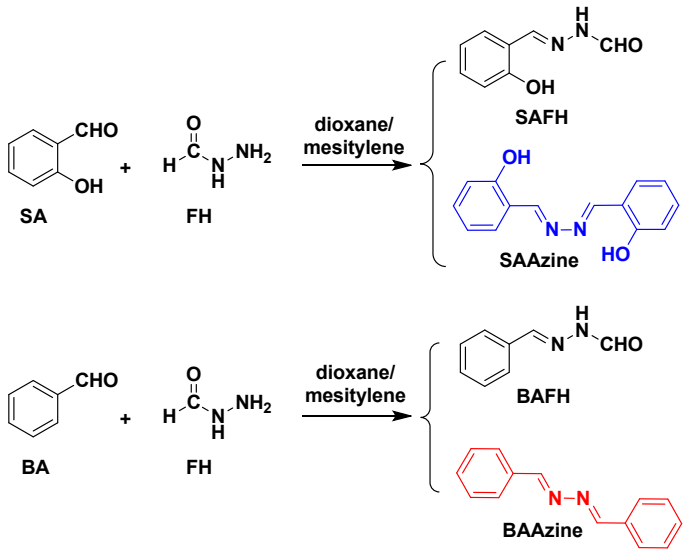
Synthesis of reference compounds

A model compound, *N*,*N*'-hydrazinebis(salicylideneimine) (SAAzine), was obtained by the reaction between SA and Azine. Solution of SA (1.3 mL, 12.5 μmol) was dissolved in dioxane/mesitylene (1:1, 2 mL) with vigorous stirring over 30 min. In addition, 1 mL Azine (373 μL, 6.25 μmol) was prepared, and then slowly added into SA solution. After sonication for 30 min, 0.3 mL of aqueous HAc (6 M) was added. The mixture solution was refluxed for 3 d. After cooling to room temperature, the product was isolated and dried under reduced pressure.

A reference compound, 1,2-di(benzylidene)hydrazine (BAAzine), was obtained by the reaction between BA and Azine. Solution of BA (1.25 mL, 12.5 μmol) was dissolved in 2 mL dioxane/mesitylene at 25 ^{o}C with ultrasonic dispersion over 30 min. In addition, 1 mL Azine dioxane/mesitylene solution (373 μL, 6.25 μmol) was prepared, and then slowly added into the solution of BA. The mixture solution was refluxed for 3 d. After cooling to room temperature, the product was isolated and dried under reduced pressure.



N'-(2-Hydroxybenzylidene)formohydrazide (SAFH) was synthesized with salicylaldehyde and formic hydrazide, while 2-(benzylidene)-1-methylhydrazide (BAFH) was synthesized with benzaldehyde and formic hydrazide using the same reaction conditions as the hydrazine-series COFs. SAFH was achieved with SA (130 μL, 1.25 μmol) and FH (0.035 g, 0.625 μmol). BAFH was achieved with BA (125 μL, 1.25 μmol) and FH (0.035 g, 0.625 μmol).



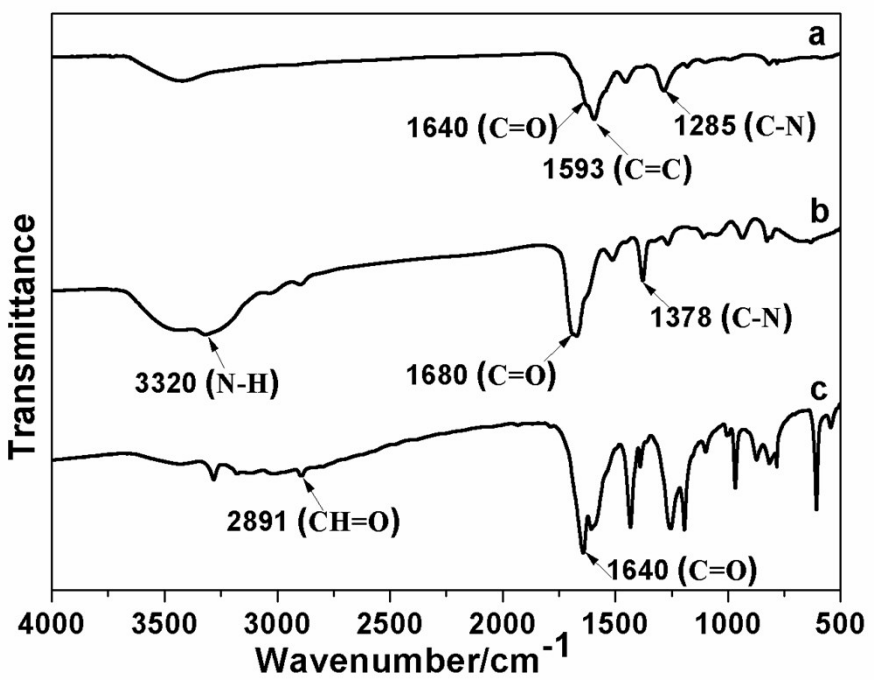


Fig. S1. FT-IR spectra of (a) COF, TpFH, and monomers of (b) FH and (c) Tp.

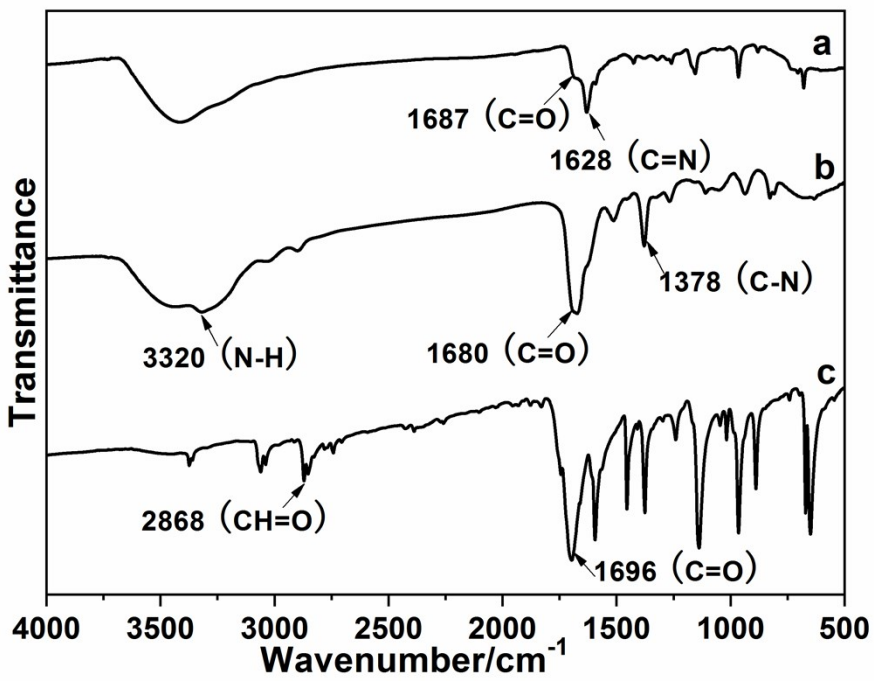


Fig. S2. FT-IR spectra of (a) COF, TFBFH, and monomers of (b) FH and (c) TFB.

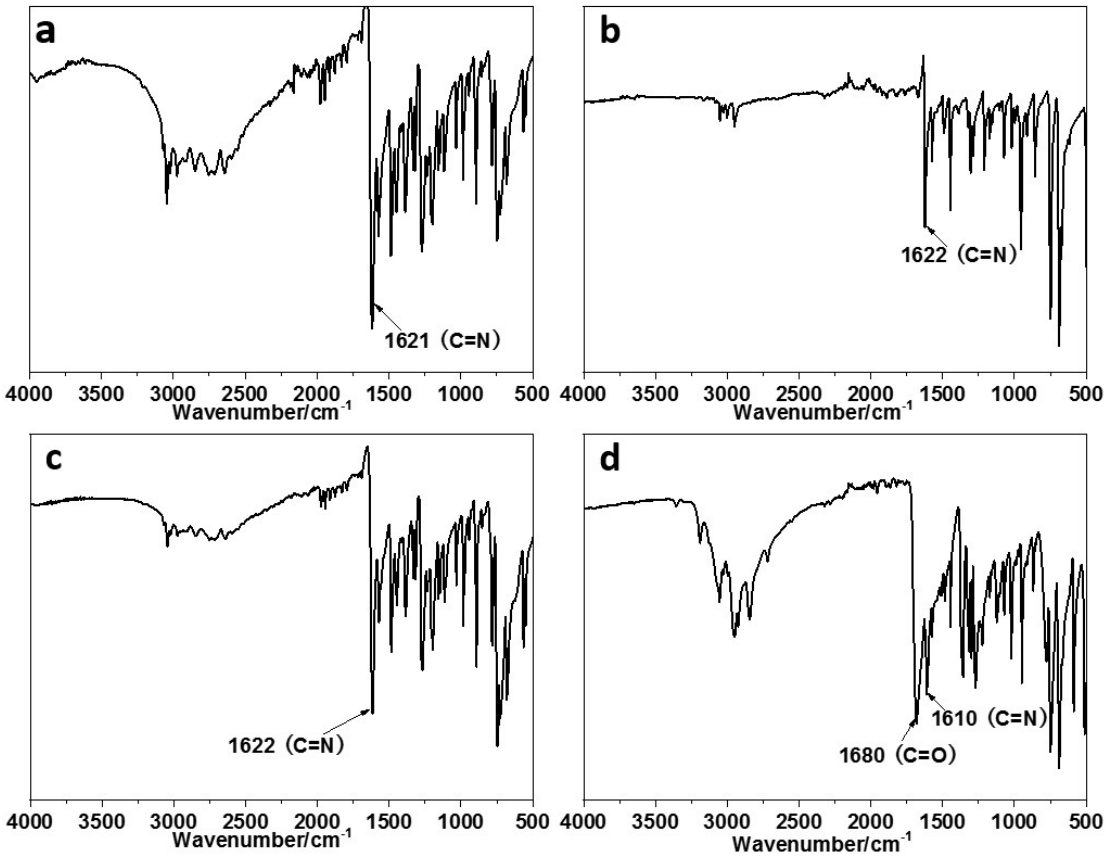


Fig. S3. FT-IR spectra of four kinds of products including (a) SA reacts with Azine, (b) BA reacts with Azine, (c) SA reacts with FH and (d) BA reacts with FH.

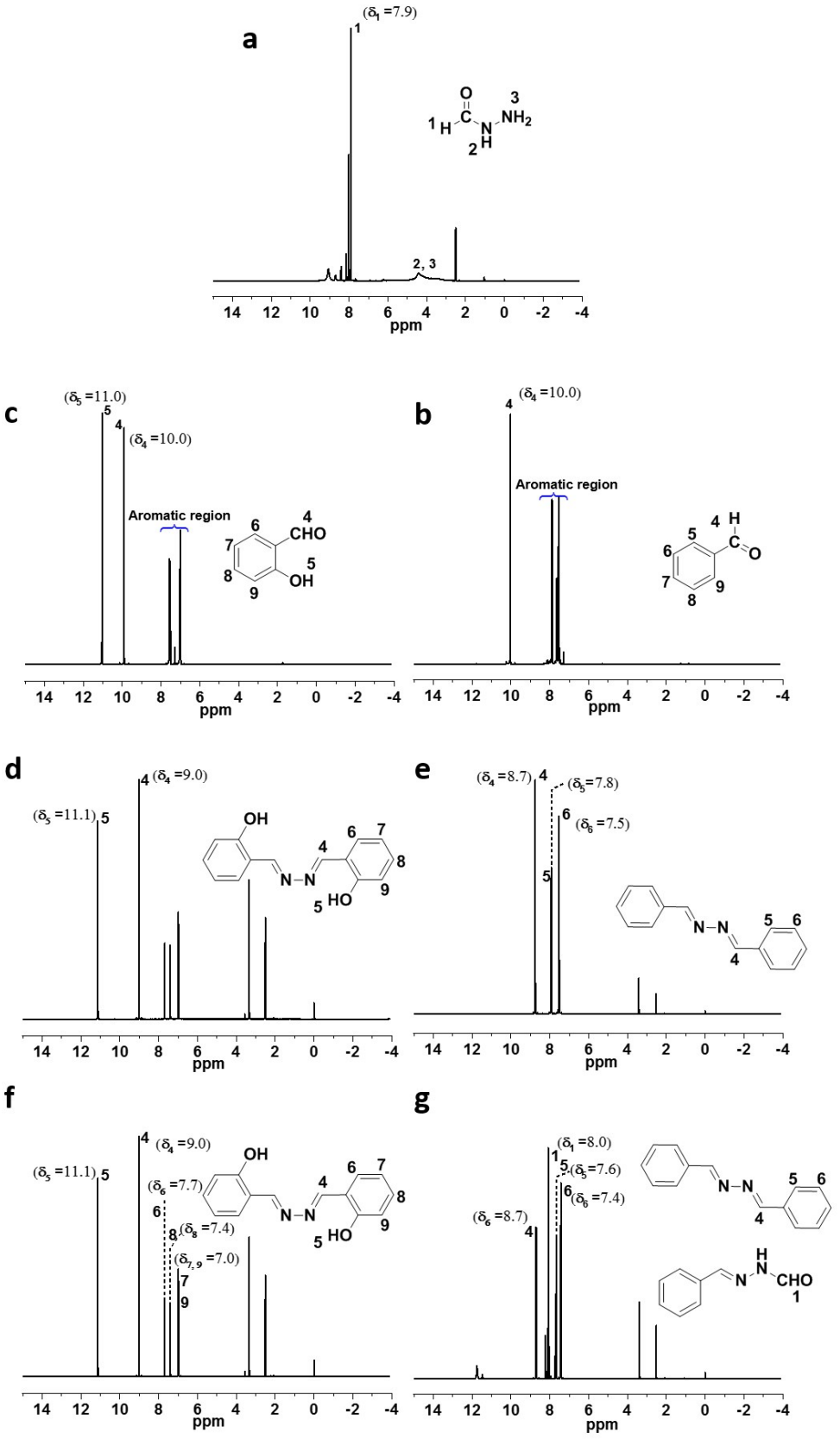


Fig. S4. ^{1}H NMR spectra of monomers (a) FH, (b) SA, (c) BA and the products of (d) SA reacts with Azine, (e) BA reacts with Azine, (f) SA reacts with FH and (g) BA reacts with FH.

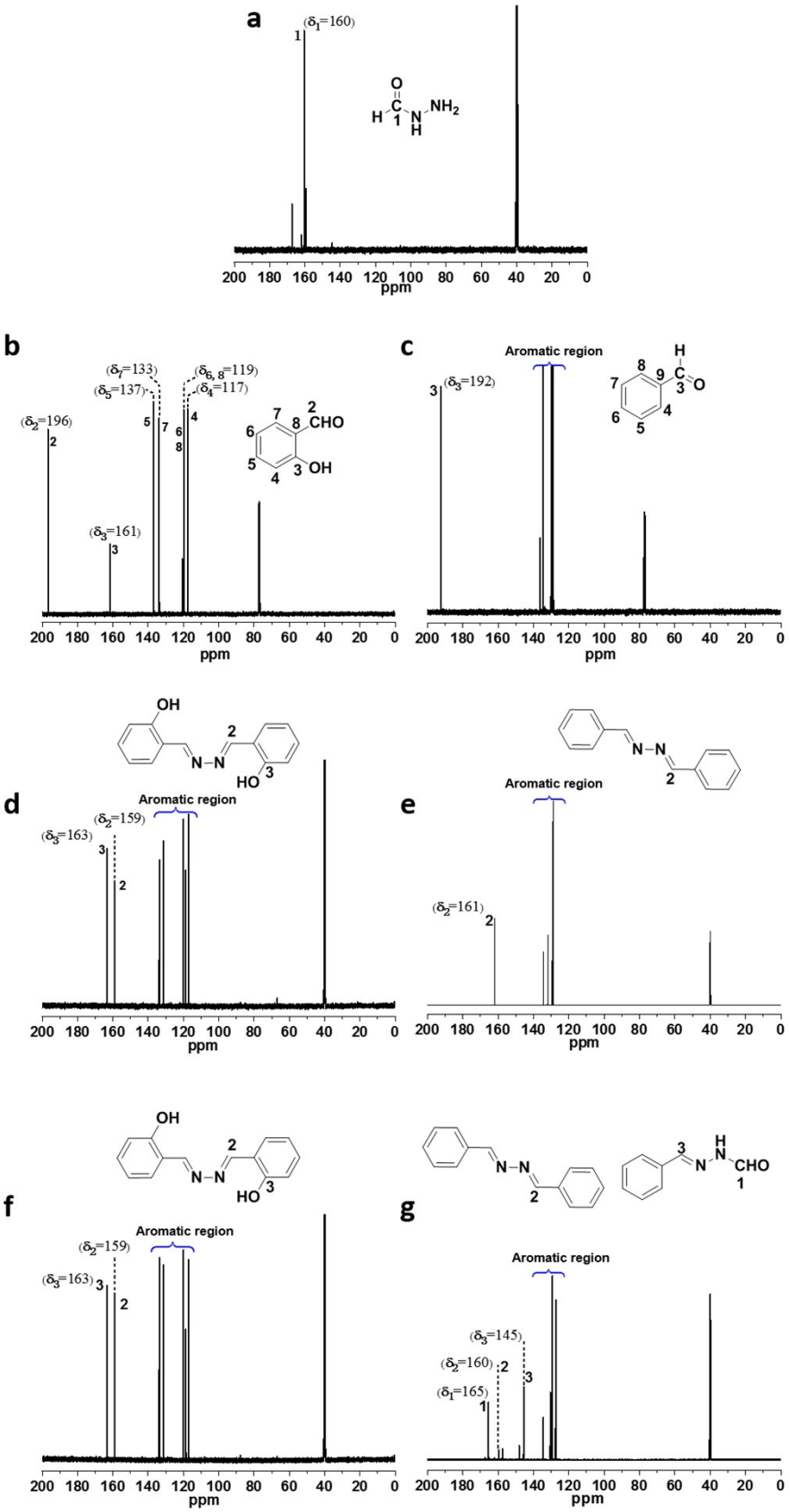


Fig. S5. ^{13}C NMR spectra of monomers (a) FH, (b) SA, (c) BA and the products of (d) SA reacts with Azine, (e) BA reacts with Azine, (f) SA reacts with FH and (g) BA reacts with FH.

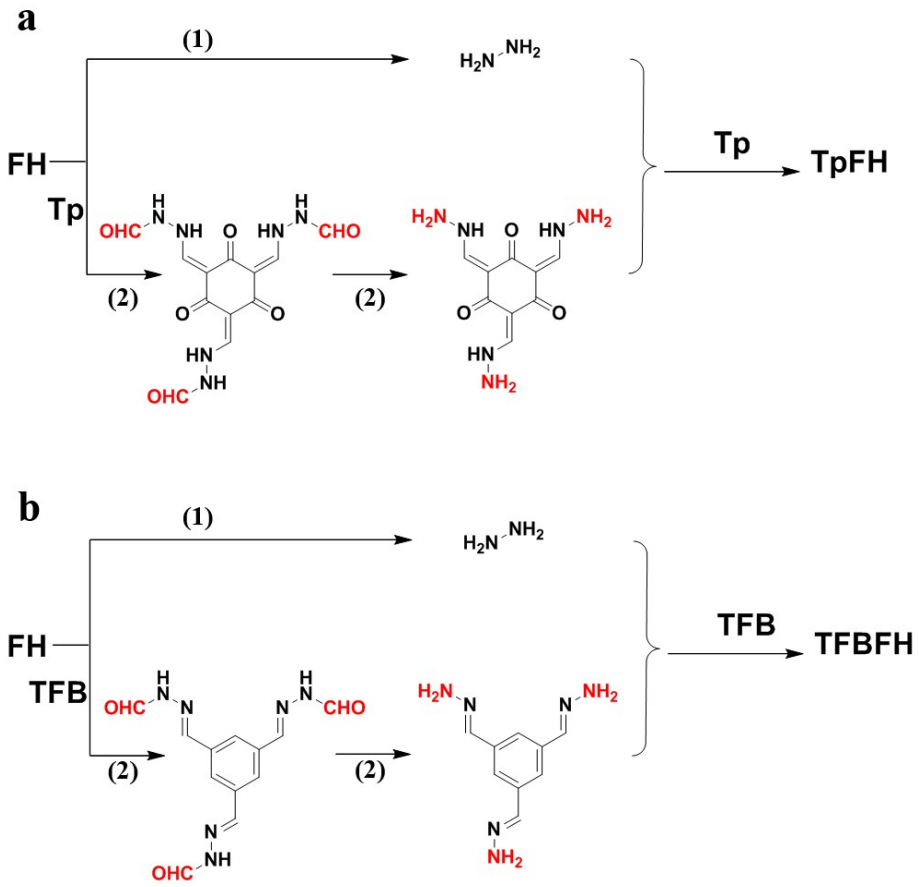


Fig. S6. The proposed reaction mechanism in formation of FH-based COFs.

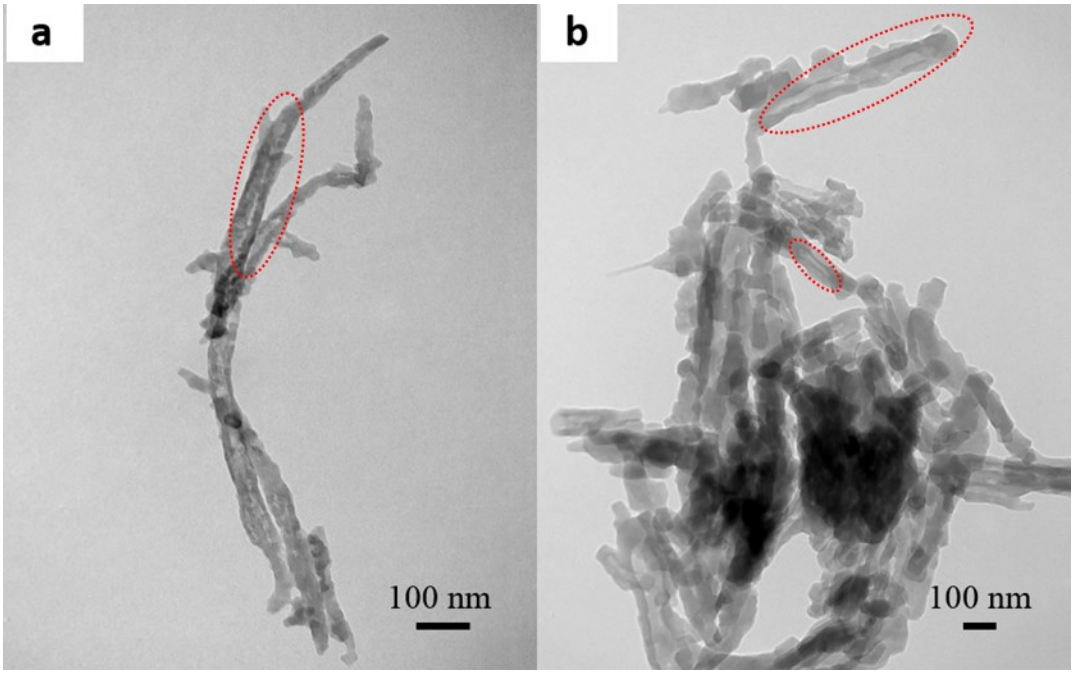


Fig. S7. TEM images of (a) TpFH and (b) TFBFH single microtube indicating the hollow nature of the tube.

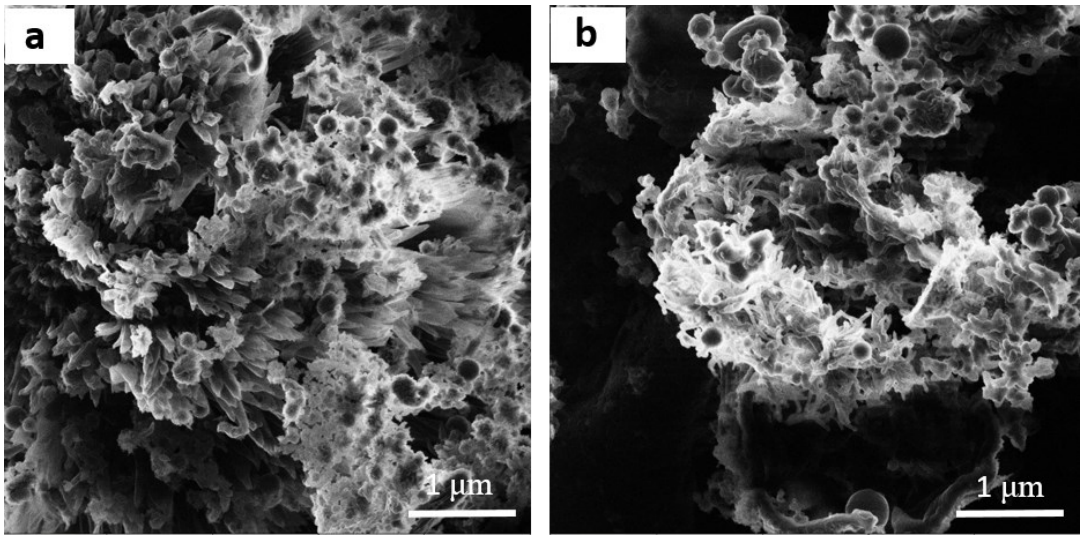


Fig. S8. HIM images of (a) TpAzine and (b) TFBAzine showing flower like morphology.

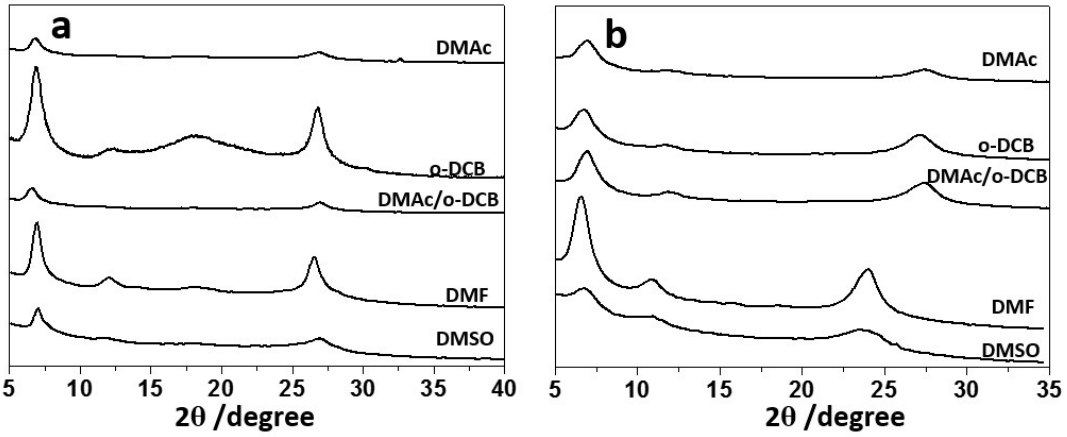


Fig. S9. PXRD patterns of (a) TpFH and (b) TFBFH fabricated with different solvents.

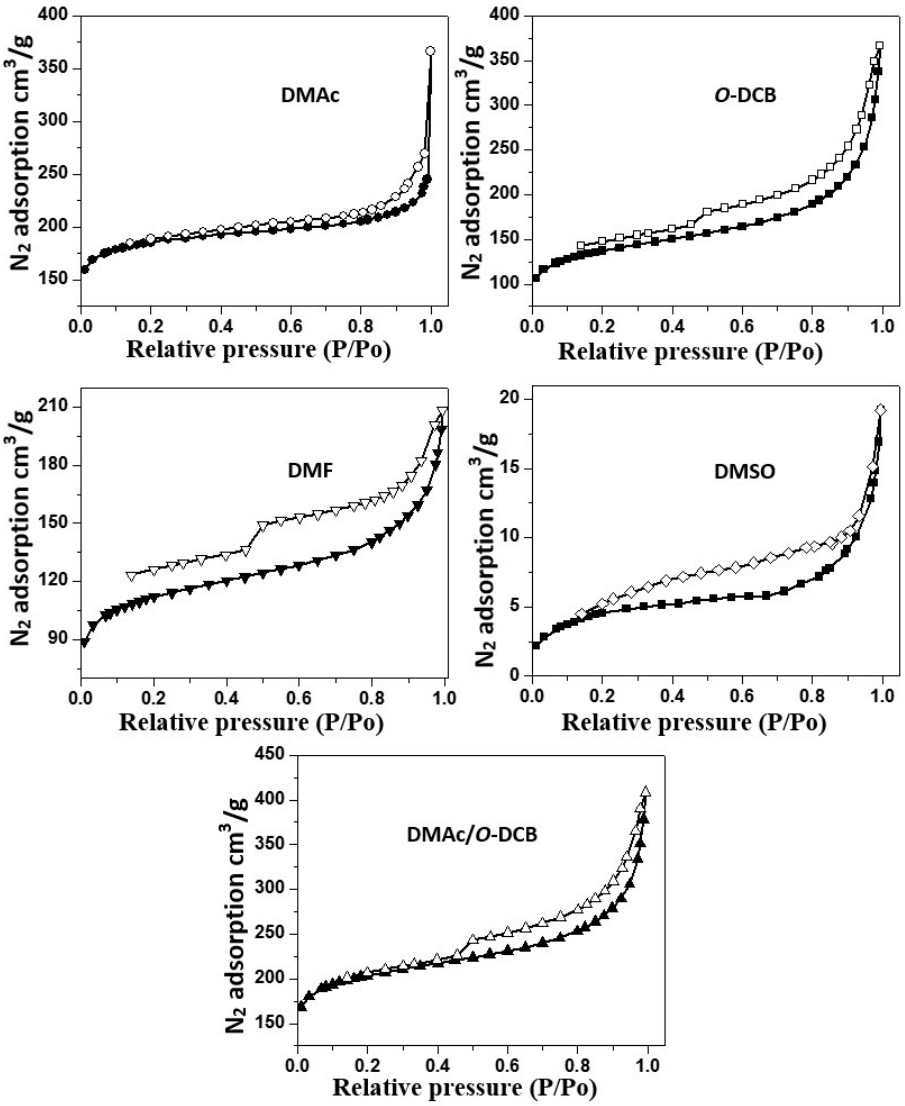


Fig. S10. N_2 adsorption isotherm of TpFH fabricated with different solvents.

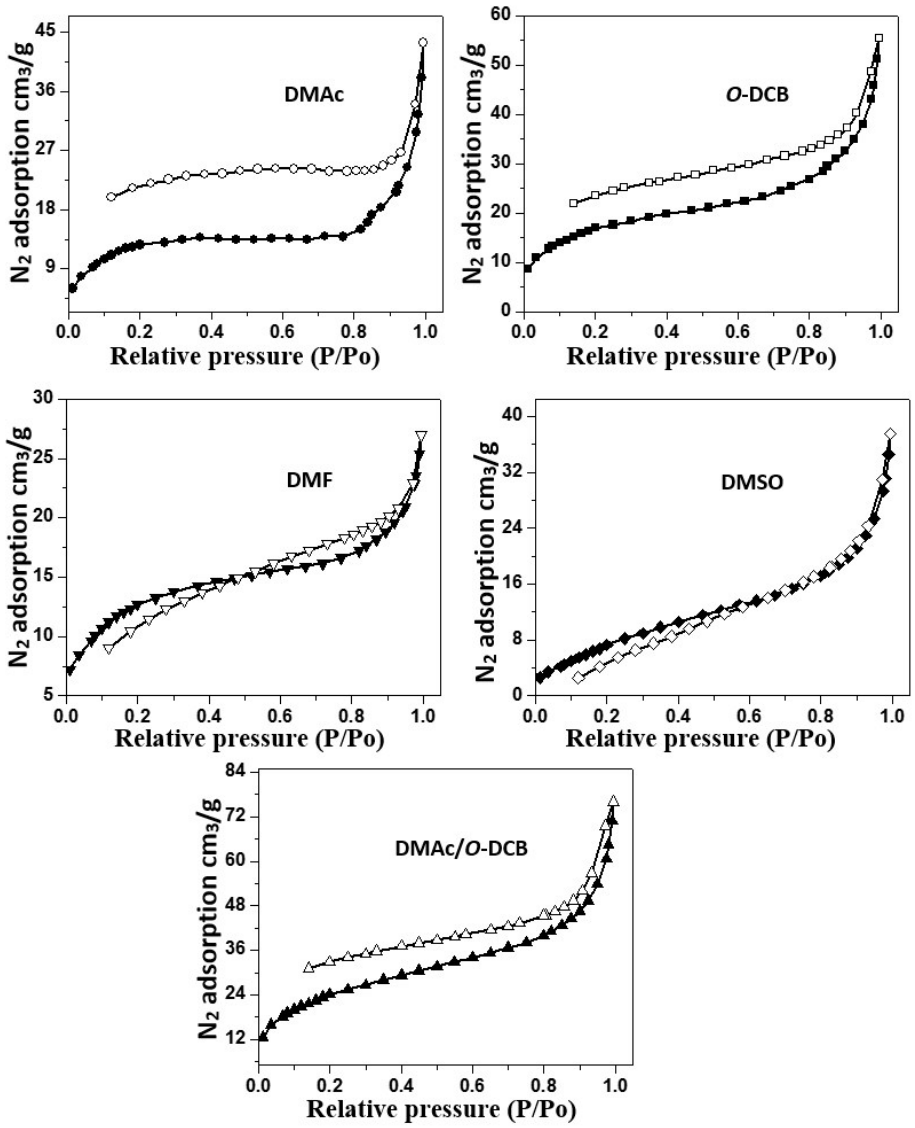


Fig. S11. N_2 adsorption isotherm of TFBFH fabricated with different solvents.

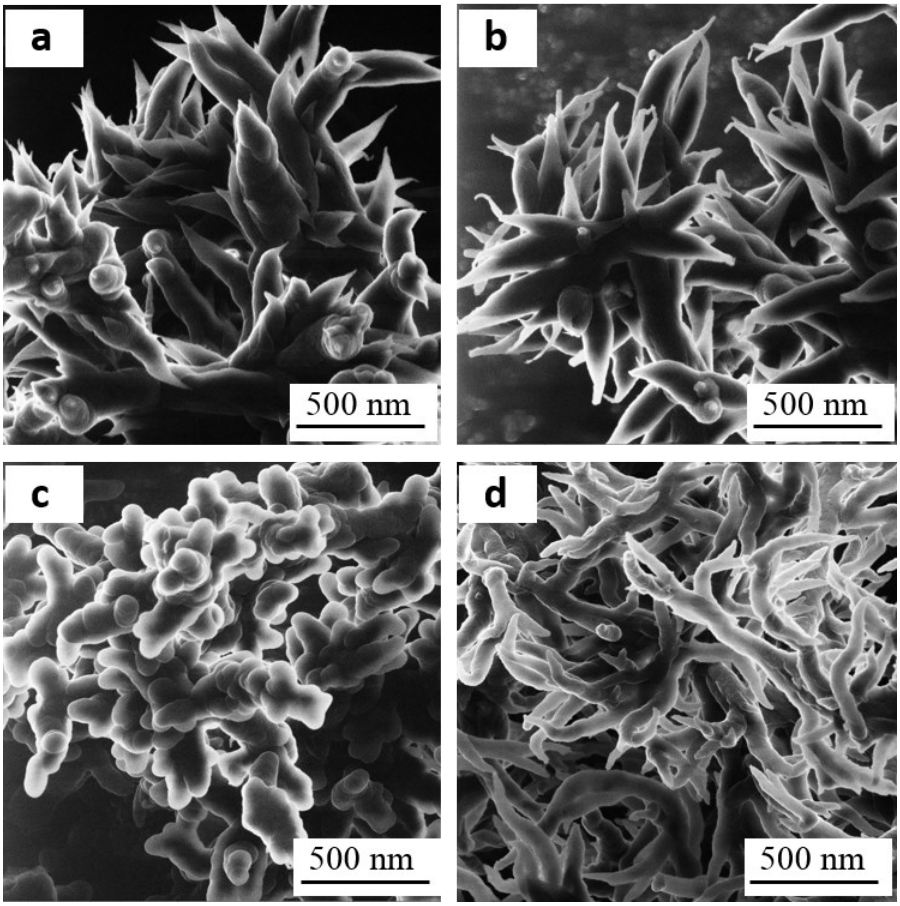


Fig. S12. HIM micrographs of (a, b) TpFH and (c, d) TFBFH fabricated with (a, c) DMF and (b, d) DMSO.

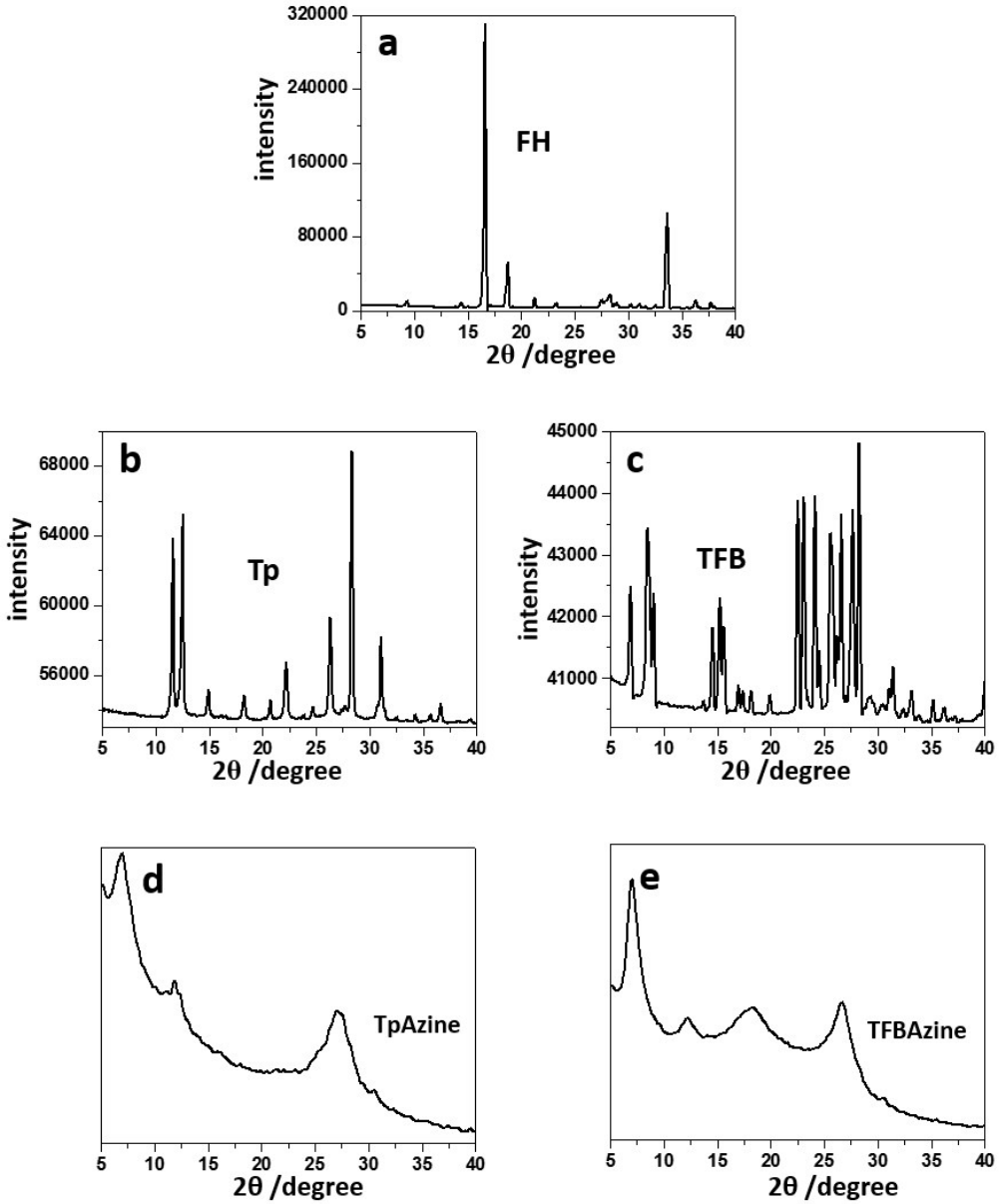


Fig. S13. PXRD patterns of (a) FH, (b) Tp, (c) TFB, (d) TpAzine and (e) TFBAzine.

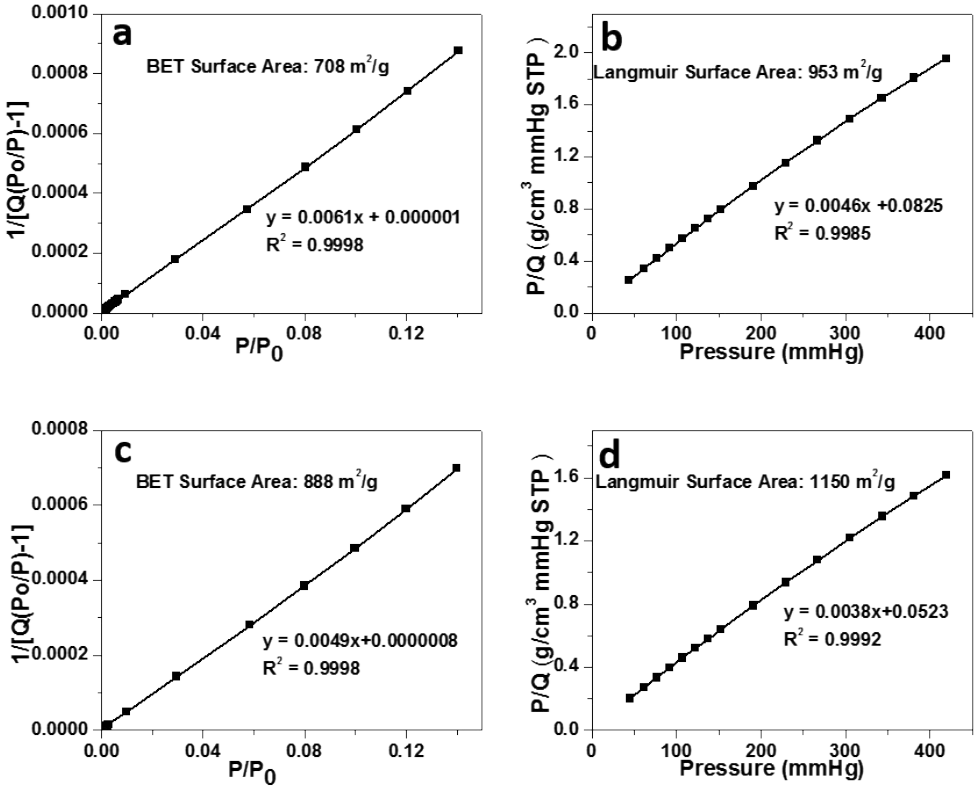


Fig. S14. (a, c) BET, (b, d) Langmuir surface area plots of (a, b) TpFH and (c, d) TFBFH.

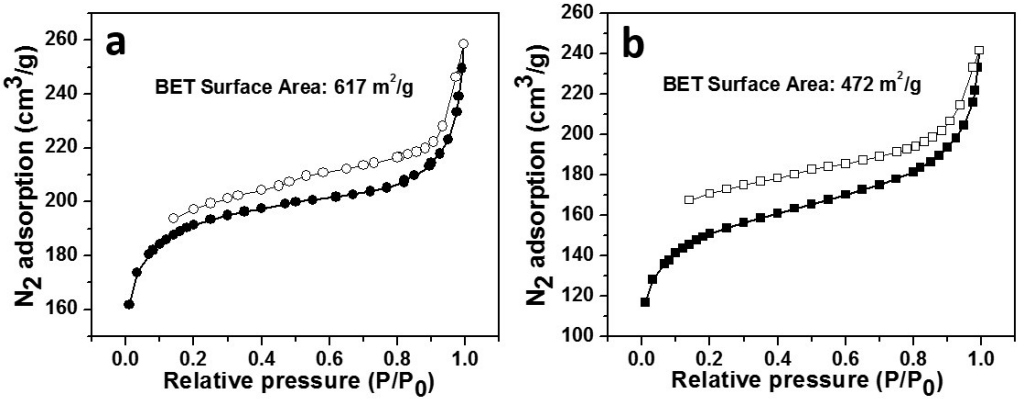


Fig. S15. N_2 adsorption isotherm (77 K) of (a) TpAzine and (b) TFBAzine.

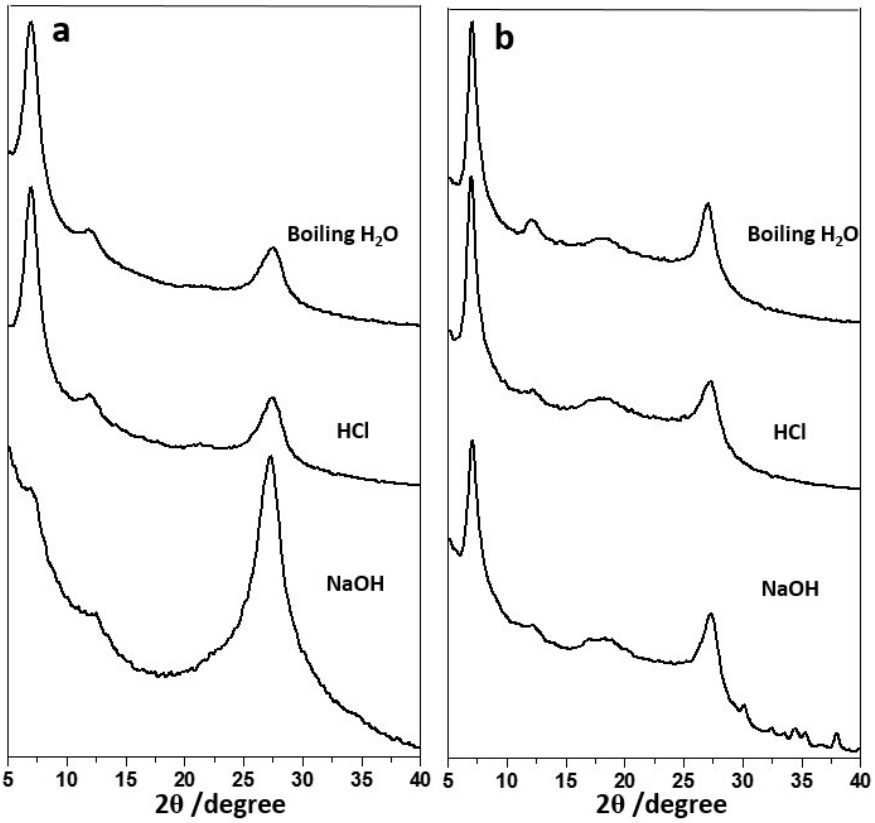


Fig. S16. PXRD patterns after treatment in different systems of (a) TpFH and (b) TFBFH.

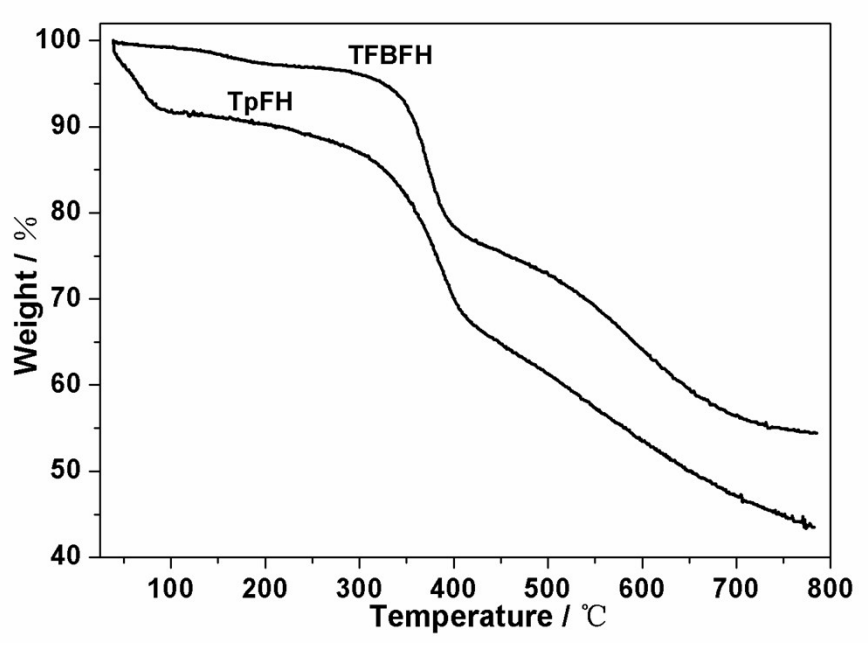


Fig. S17. TGA analysis result of as-synthesized COFs under N_2 atmosphere.

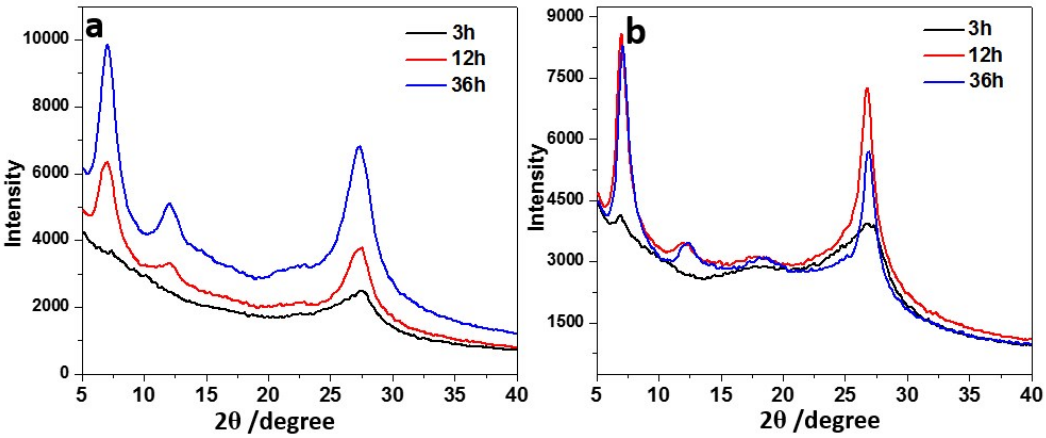


Fig. S18. PXRD patterns of COFs (a) TpFH and (b) TFBFH with different time intervals.

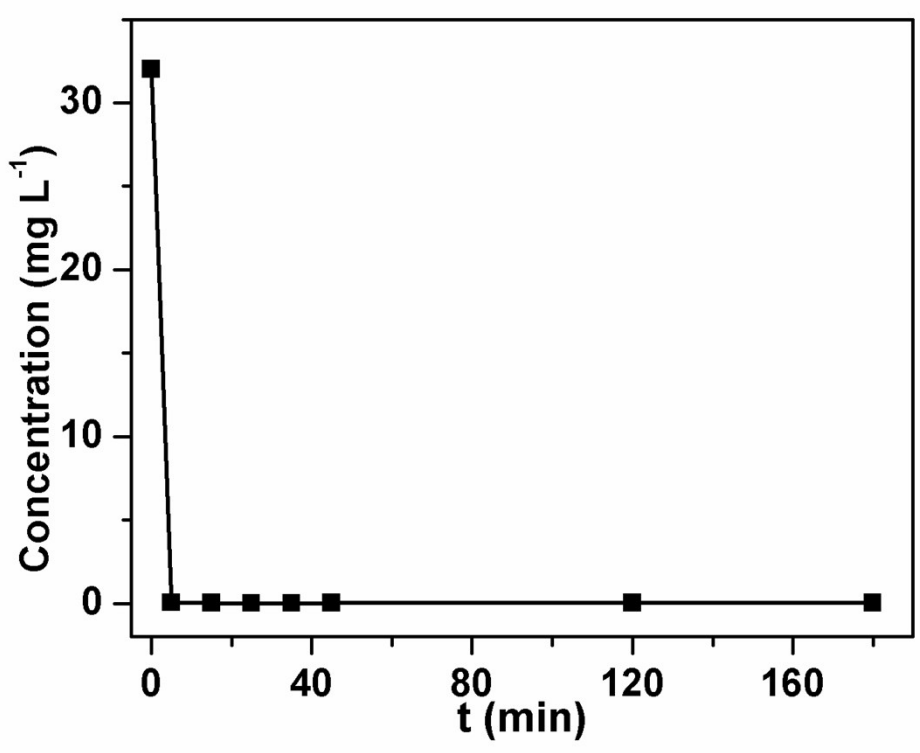


Fig. S19. Cu(II) sorption kinetics under the initial Cu(II) concentration of 32 mg L^{-1}.

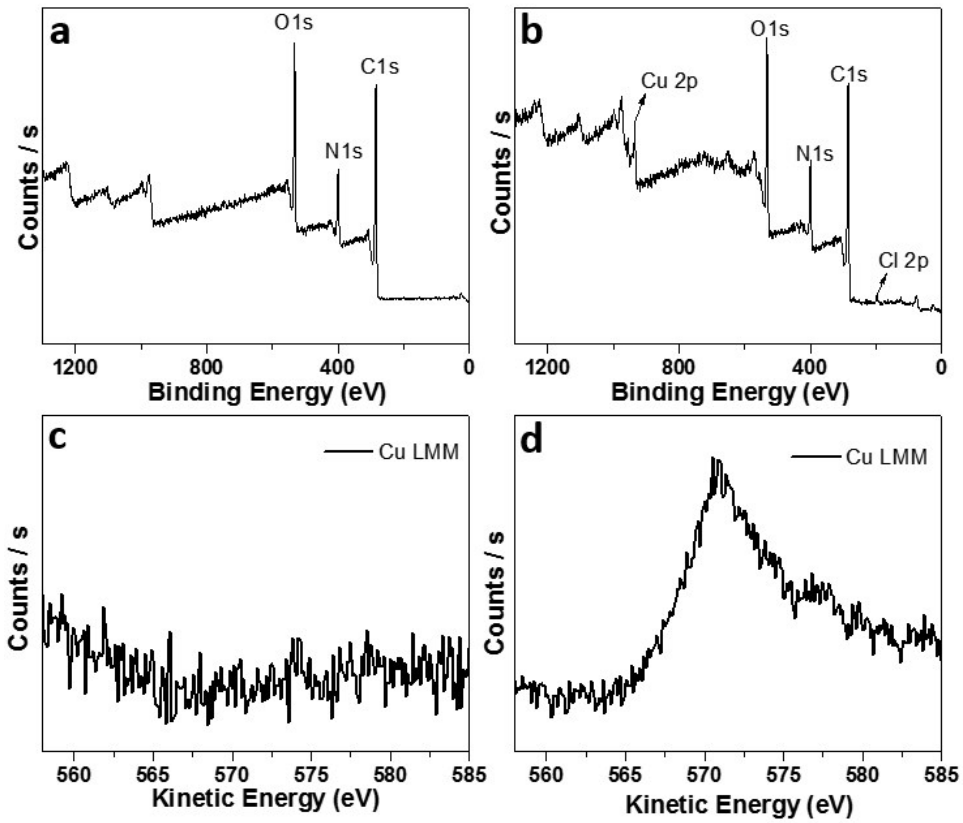


Fig. S20. (a, b) Low-resolution XPS survey wide scans spectra and (c, d) Cu LMM spectra of Cu(II) of (a, c) TpFH and (b, d) TpFH-Cu.

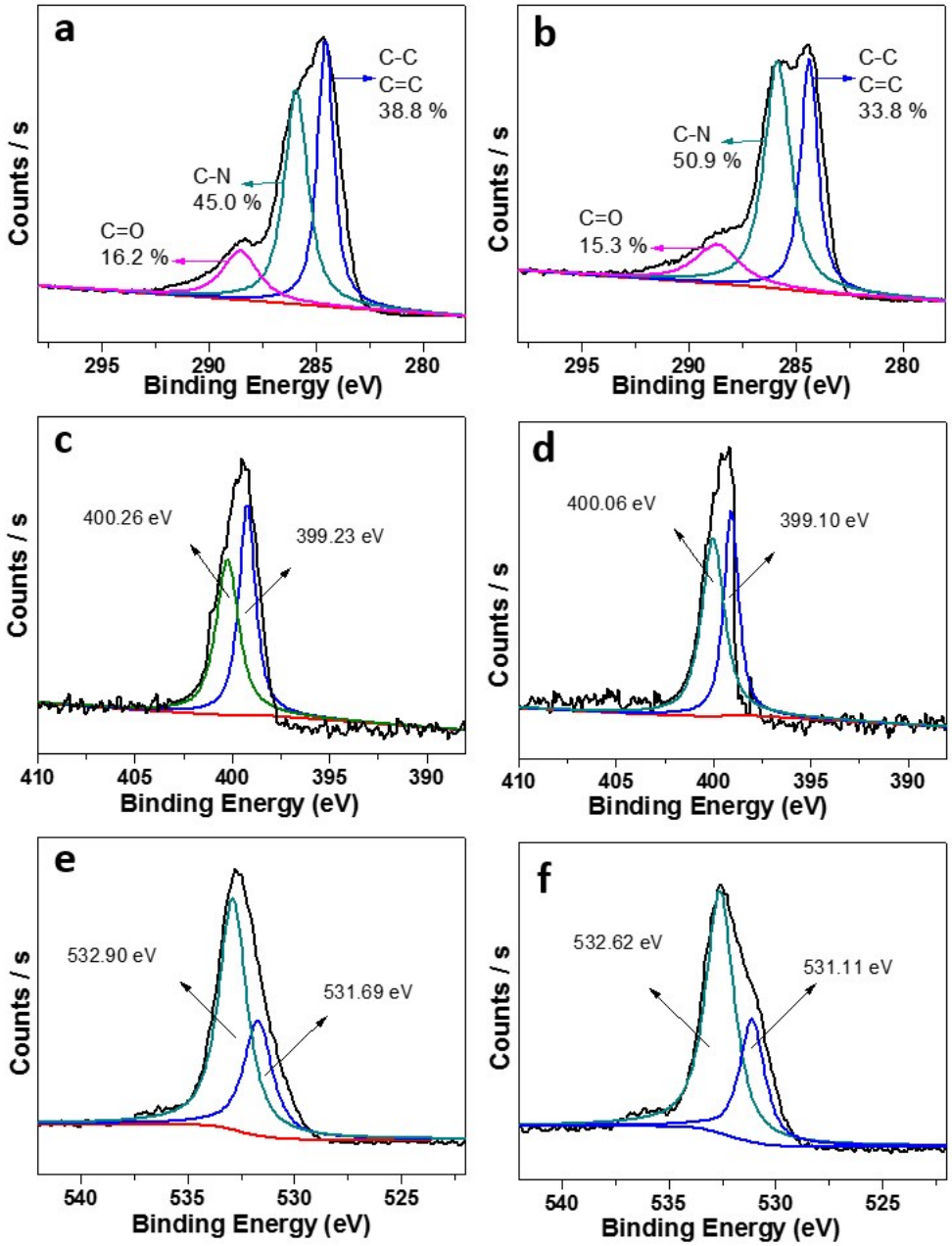


Fig. S21. High-resolution XPS (a, b) C1s, (c, d) N1s, (e, f) O1s, spectra of (a, c, e) TpFH and (b, d, f) TpFH-Cu.

Table S1 Fractional atomic coordinates for the unit cell of TpFH.

TpFH in eclipsed (AA) model, (Space group-*P*1) a=15.39 Å, b=3.28Å, c=14.48 Å; α=90°, β=120°, γ=90°			
Atom	**x/a**	**y/b**	**z/c**
N1	0.48134	0.51644	0.45564
C2	0.19877	0.51644	0.62360
C3	0.38328	0.51644	0.75967
C4	0.33184	0.51644	0.57101
C5	0.46218	0.51644	0.86826
H6	0.54377	0.51644	0.88800
C7	0.09257	0.51644	0.59569
H8	0.07227	0.51644	0.66138
N9	0.02392	0.51644	0.50035
C10	0.57458	0.51644	0.48078
H11	0.63598	0.51644	0.56822
N12	0.49612	0.51644	0.03264
C13	0.65645	0.51644	0.23880
O14	0.67606	0.51644	0.18086
C15	0.70818	0.51644	0.42853
C16	0.52263	0.51644	0.29170
O17	0.44635	0.51644	0.27165
O18	0.16887	0.51644	0.46457
N19	0.45238	0.51644	0.51547
C20	0.73495	0.51644	0.34750
C21	0.55044	0.51644	0.21144
C22	0.60188	0.51644	0.40010
C23	0.47154	0.51644	0.10284
H24	0.38995	0.51644	0.08310
C25	0.84115	0.51644	0.37541
H26	0.86145	0.51644	0.30972
N27	0.90980	0.51644	0.47075
C28	0.35914	0.51644	0.49033
H29	0.29774	0.51644	0.40288
N30	0.43760	0.51644	0.93846
C31	0.27727	0.51644	0.73230
O32	0.25766	0.51644	0.79025
C33	0.22554	0.51644	0.54257
C34	0.41109	0.51644	0.67941
O35	0.48737	0.51644	0.69945
O36	0.76485	0.51644	0.50653
H37	0.49003	0.75804	0.56813
H38	0.38575	0.74689	0.92565

H39	1.01663	0.72331	1.45691
H40	0.44369	0.75804	0.40297
H41	0.54797	0.74689	0.04545
H42	0.90059	0.30957	0.51984

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390 **Table S2** Fractional atomic coordinates for the unit cell of TFBFH.

TFBFH in eclipsed (AA) model, (Space group-*P*1) a=15.27 Å, b=3.35Å, c=14.18 Å; α=90°, β=120°, γ=90°			
Atom	**x/a**	**y/b**	**z/c**
N1	0.50332	0.47986	0.48335
C2	0.21751	0.47986	0.65799
C3	0.40413	0.47986	0.79946
C4	0.35211	0.47986	0.60331
C5	0.48395	0.47986	0.91237
H6	0.56649	0.47986	0.93361
C7	0.11008	0.47986	0.62897
H8	0.08929	0.47986	0.69578
N9	0.04064	0.47986	0.52984
C10	0.59763	0.47986	0.50949
N11	0.51827	0.47986	0.04355
C12	0.68045	0.47986	0.25790
H13	0.70060	0.47986	0.19060
C14	0.73277	0.47986	0.45517
C15	0.54509	0.47986	0.31290
H16	0.46267	0.47986	0.29211
H17	0.18281	0.47986	0.48442
N18	0.47403	0.47986	0.54556
C19	0.75985	0.47986	0.37092
C20	0.57322	0.47986	0.22945
C21	0.62525	0.47986	0.42560
C22	0.49341	0.47986	0.11654
C23	0.86727	0.47986	0.39994
N24	0.93671	0.47986	0.49907
C25	0.37972	0.47986	0.51942
H26	0.31808	0.47986	0.43005
N27	0.45908	0.47986	0.98536
C28	0.29690	0.47986	0.77101
H29	0.27676	0.47986	0.83831
C30	0.24458	0.47986	0.57374
C31	0.43226	0.47986	0.71601
H32	0.51468	0.47986	0.73680
H33	0.79455	0.47986	0.54449
H34	0.88659	0.47986	0.33609
H35	0.65655	0.47985	0.59446
H36	0.41456	0.47986	0.09653

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393 **Table S3** Elemental composition of the TpFH and TpFH-Cu sample based upon
394 analysis of the survey spectra.

Peak	Peak BE/eV	At. % (TpFH)	At. % (TpFH-Cu)
O 1S	532.51	21.38	20.56
C 1S	285.18	64.53	60.4
N 1S	399.81	14.09	15.71
Cu 2p3	934.26	0	2.14
Cl 2P3	198.05	0	1.18

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