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Electronic Supplementary Information

Large-scale synthesize of azine-linked covalent organic frameworks in water and promoted by water

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Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) spectra were collected on Agilent DD2 600 Solid system, equipped with a 3.2 mm HFXY MAS probe. The Hartmann-Hahn conditions of the CP experiment were obtained at a 15 kHz MAS spinning speed with a contact time of 2.0 ms. Recycle delay times are 5 s. The ^{13}C chemical shifts were externally referenced to tetramethylsilane ($\delta = 0.0$ ppm).

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a XL30 FEG scanning electron microscope. The samples were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter 9 coater (ambient temperature, 85 torr pressure in a nitrogen atmosphere, sputtered for 80 s from a solid gold target at a current of 20 mA) before being submitted to SEM characterization.

Transmission electron microscopy (TEM)

TEM was performed on a Philips CM 200/FEG transmission electron microscope. The samples were prepared by carefully dropping suspending solutions of the COFs in anhydrous EtOH onto the carbon coated copper grid followed by removal of the solvent under vacuum.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analyses were carried out on Waters TGA Q500 by heating the samples from 35 to 900 ^{o}C under nitrogen atmosphere at a heating rate of 10 ^{o}C /min.

Powder X-ray diffraction experiment (PXRD)

Powder X-ray diffraction measurements were carried out with an X'Pert PROX system using monochromated Cu/Kα ($\lambda = 0.1542$ nm). The samples were spread on the square recess of XRD sample holder as a thin layer.

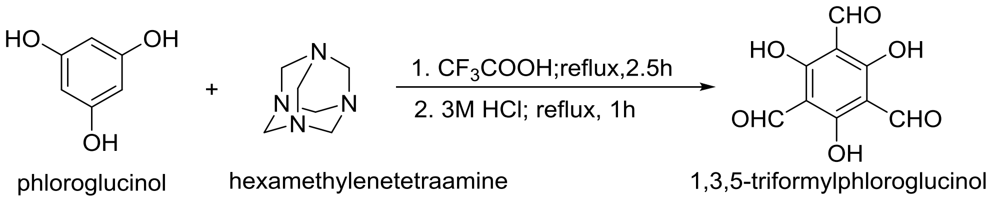
Nitrogen adsorption-desorption isotherm measurements

The measurements were carried out using a Micromeritics ASAP 2020 HD88 analyzer. Before gas adsorption measurements, the as-prepared samples (~50 mg) were activated by being immersed in anhydrous dioxane for 12 h. The solvent was decanted and the samples were dried under dynamic vacuum at 160^{o}C for 8 h. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory model, the pore size distributions were derived from the sorption curves.

Structural simulation and powder X-ray diffraction analysis

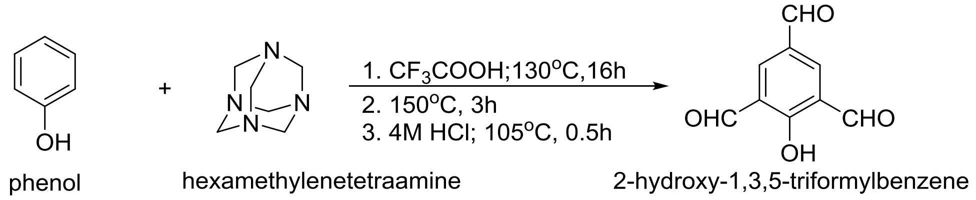
The Pawley refinement of the experimental PXRD was conducted by the Reflux module in the Materials Studio 7.0. The simulations of the possible structures were carried out in Accelrys Materials Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. P6 space group was chosen for the primitive models in the initial simulations.

Synthesis of 1,3,5-triformylphloroglucinol



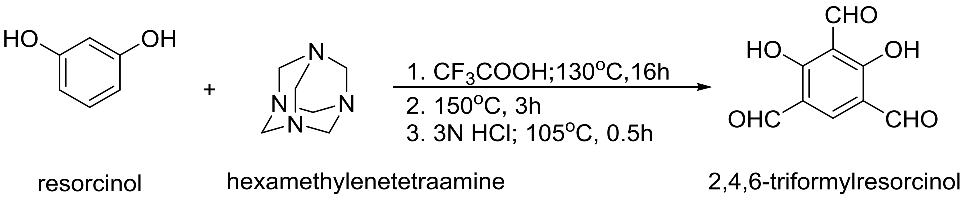
A mixture of hexamethylenetetramine (22.3 g, 158.6 mmol) and phloroglucinol (10.0 g, 79.3 mmol) were dissolved in trifluoroacetic acid (60 mL) under an argon atmosphere. The reaction mixture was heated at 100 ^{o}C for 2.5 h, then added HCl (3 M, 200 mL) and heated at 100 ^{o}C for another 1 h. After being cooled to room temperature, the solution was filtered through Celite, extracted with dichloromethane (3×150 mL), dried over sodium sulfate, and filtered. Rotary evaporation of the solution afforded an organic powder (3.33g, 20%).The characterizations are consistent with the literature reported.[1] ^{1}H NMR (500 MHz, CDCl$_3$) δ 14.11 (s, 3H), 10.15 (s, 3H).

Synthesis of 2-hydroxy-1,3,5-triformylbenzene



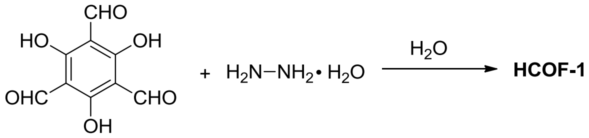
A mixture of phenol (7.27 g, 77 mmol) and hexamethylenetetramine (HMTA) (23.52 g, 167 mmol) were dissolved in 70 mL trifluoroacetic acid (TFA) under an argon atmosphere. The mixture was stirred at 130℃ for 16h, then heated to 150℃ for 3h. The mixture was treated with 100 mL of 4M HCl after cooled to 120℃, then heated at 105℃ for 30min and cooled to room temperature overnight. The crude products were filtered off, washed with water, ethol. Then powders were recrystallized from DMF. Yield: 6.14g (44.6%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 2H), 10.00 (s, 1H), 8.53 (s, 2H).

Synthesis of 2,4,6-triformylresorcinol



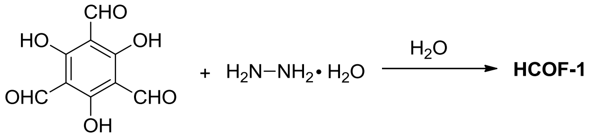
A mixture of resorcinol (7.16g, 65 mmol) and hexamethylenetetramine (HMTA) (20 g, 143 mmol) were dissolved in 70 mL trifluoroacetic acid (TFA) under an argon atmosphere. The mixture was stirred at 120℃ for 24h, then heated to 150℃ for 3h. The mixture was treated with 110 mL of 3N HCl after cooled to 120℃, then heated at 105℃ for 30min and cooled to room temperature overnight. The crude products were filtered off, washed with water, ethol. Then powders were recrystallized from DMF. Yield: 3.41g (27%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 10.09 (s, 2H), 8.39 (s, 1H).

General procedure for the preparation of HCOF-1 under hydrothermal condition

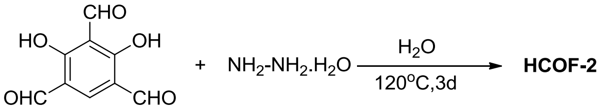


1,3,5-triformylphloroglucinol (21.0 mg, 0.1 mmol) and hydrazine hydrate (0.01 mL 80% weight in water, 0.15 mmol) were dissolved in deionized water(1mL) in a glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 10 min, warmed to room temperature and then kept at 120°C without disturbance for different times to yield a red solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 °C for 2 h to afford a red powder , which was insoluble in common organic solvents such as acetone, ethanol, and N, N-dimethylformamide. Anal. Calcd. For chemical formula C_3H_2NO: C, 52.95; H, 2.96; N, 20.58. Found: C, 52.88; H, 4.26; N, 19.27.

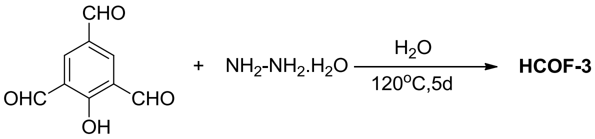
Representative procedure for the scale-up preparation of the COFs



To a 500 mL sealed glass tube, 1,3,5-triformylphloroglucinol (10.5 g, 0.05 mol), deionized water (350 mL) and hydrazine hydrate (4.6 mL 80% weight in water, 0.076 mol) were added. The whole mixture was sealed after being degassed in a liquid nitrogen bath for 30 min, warmed to room temperature and then kept at 120 °C without disturbance for 12 h to yield a red solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 °C for 2 h to afford a red powder (9.9 g, 97%).



To a 100 mL sealed glass tube, 2,4,6-triformylresorcinol (1 g, 0.00515 mol), deionized water (50 mL) and hydrazine hydrate (0.44 mL 85% weight in water, 0.00773 mol) were added. The whole mixture was sealed after being degassed in a liquid nitrogen bath for 30 min, warmed to room temperature and then kept at 120 ^{o}C without disturbance for 12 h or 3d to yield a yellow solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with THF for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford a red powder (0.98 g, 88% for an experiment of 3d). Anal. Calcd. For chemical formula $C_{18}H_{12}N_6O_4$: C, 57.45; H, 3.21; N, 22.33. Found: C, 56.91; H, 4.34; N, 21.44.



To a 500 mL sealed glass tube, 2-hydroxy-1,3,5-triformylbenzene (3.56 g, 0.02 mol), deionized water (300 mL) and hydrazine hydrate (1.71 mL 85% weight in water, 0.03 mol) were added. The whole mixture was sealed after being degassed in a liquid nitrogen bath for 30 min, warmed to room temperature and then kept at 120 ^{o}C without disturbance for 5d to yield a yellow solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with THF for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford a yellow powder (3.6 g, 90%). Anal. Calcd. For chemical formula $C_{18}H_{12}N_6O_2$: C, 62.79; H, 3.49; N, 24.42. Found: C, 60.81; H, 3.99; N, 23.05.

General Procedure for the screening of condensation conditions for the hydrothermal synthesis of HCOF-1

1,3,5-triformylphloroglucinol (21.0 mg, 0.1 mmol) and hydrazine hydrate (0.01 mL 80% weight in water, 0.15 mmol) were dissolved in deionized water (1mL) and acetic acid (aq., 0.1 mL, 0, 3 or 6 M) in a glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 10 min, warmed to room temperature and then kept at 80, 120 or 150 ^{o}C without disturbance for different times to yield a red solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford a red powder.

Table S1. Synthesis of **HCOF-1** under different hydrothermal conditions.

Entry	**Solvent(1 mL)**	**Catalyst (0.1 mL)**	**Time (h)**	**Temperature (℃)**
1	Water	6.0 mol L^{-1} AcOH	72	80
2				120
3				150

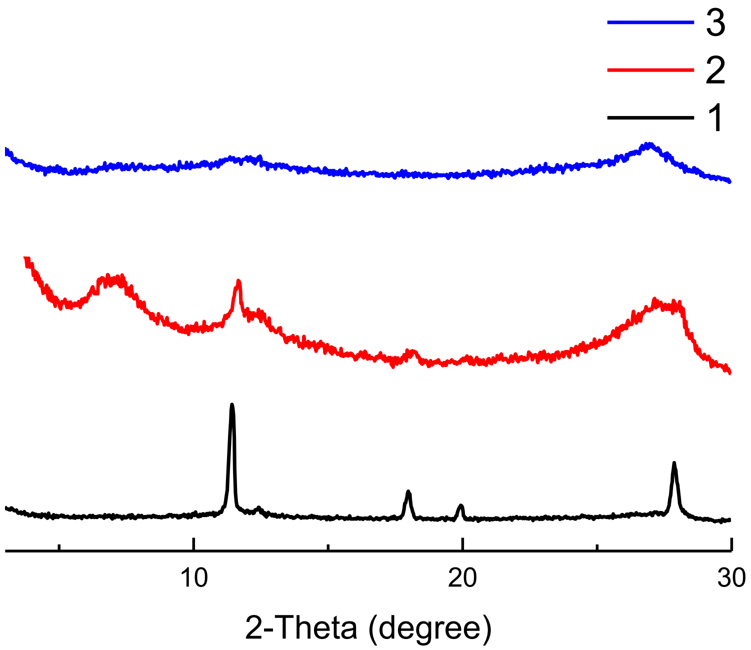


Figure S1. PXRD profiles of **HCOF-1** synthesized under different temperatures.

Table S2. Synthesis of **HCOF-1** under different hydrothermal conditions.

Entry	**Solvent (1 mL)**	**Catalyst (0.1 mL)**	**Time (h)**	**Temperature (℃)**
1	Water	0 M AcOH	72	120
2		3.0 M AcOH		
3		6.0 M AcOH		

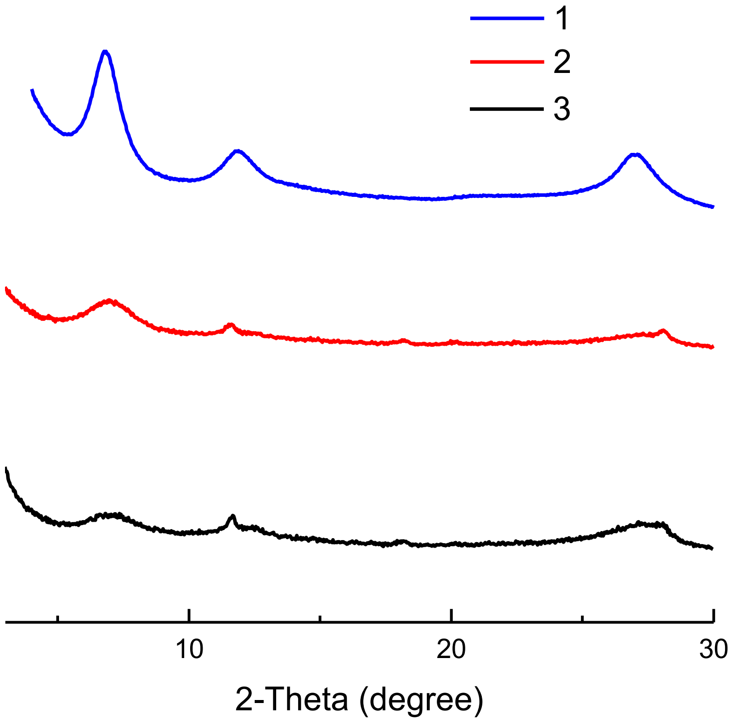


Figure S2. PXRD profiles of **HCOF-1** synthesized under different concentrations of AcOH.

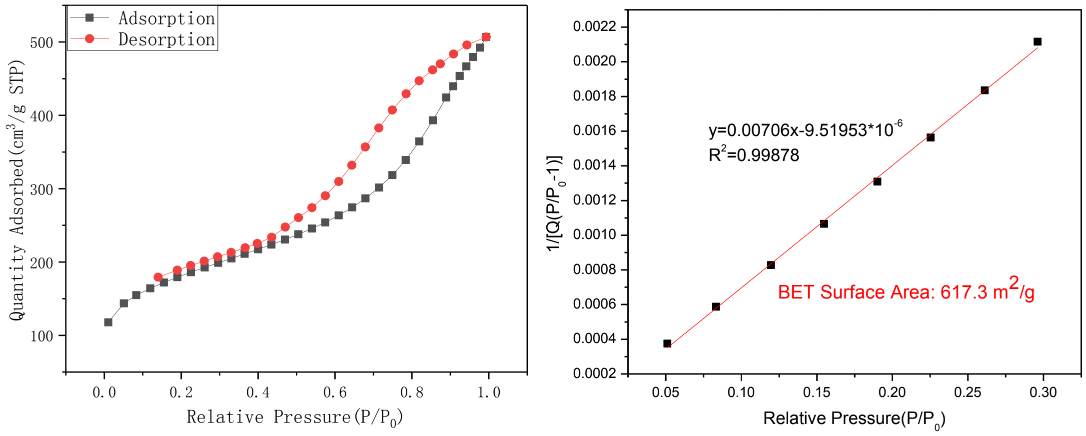


Figure S3. N_2 adsorption−desorption isotherms (77 K) (left) and BET surface area plot (right) of **HCOF-1** (1g-scale-synthesis).

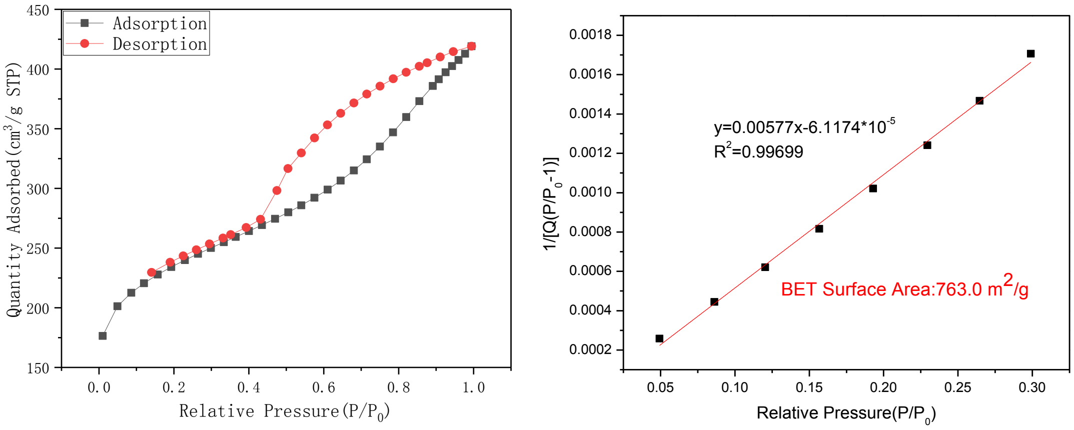


Figure S4. N_2 adsorption−desorption isotherms (77 K) (left) and BET surface area plot (right) of **HCOF-1** (10g-scale-synthesis).

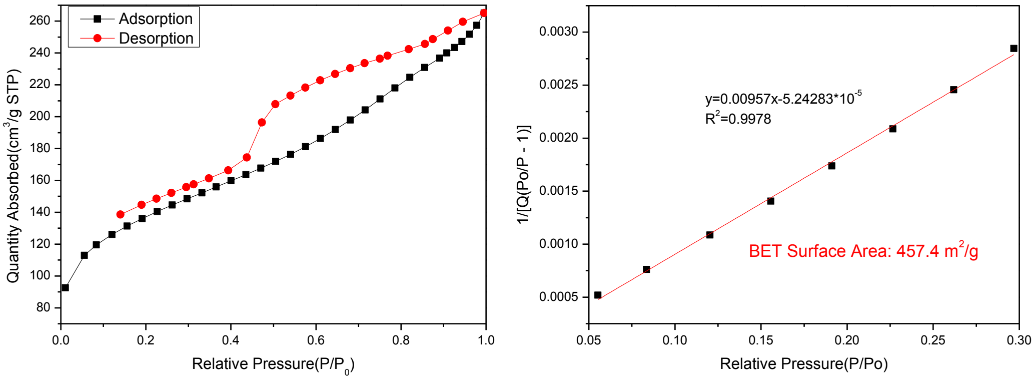


Figure S5. N_2 adsorption−desorption isotherms (77 K) (left) and BET surface area plot (right) of **HCOF -1** (synthesized by running the hydrothermal reaction for 2 h).

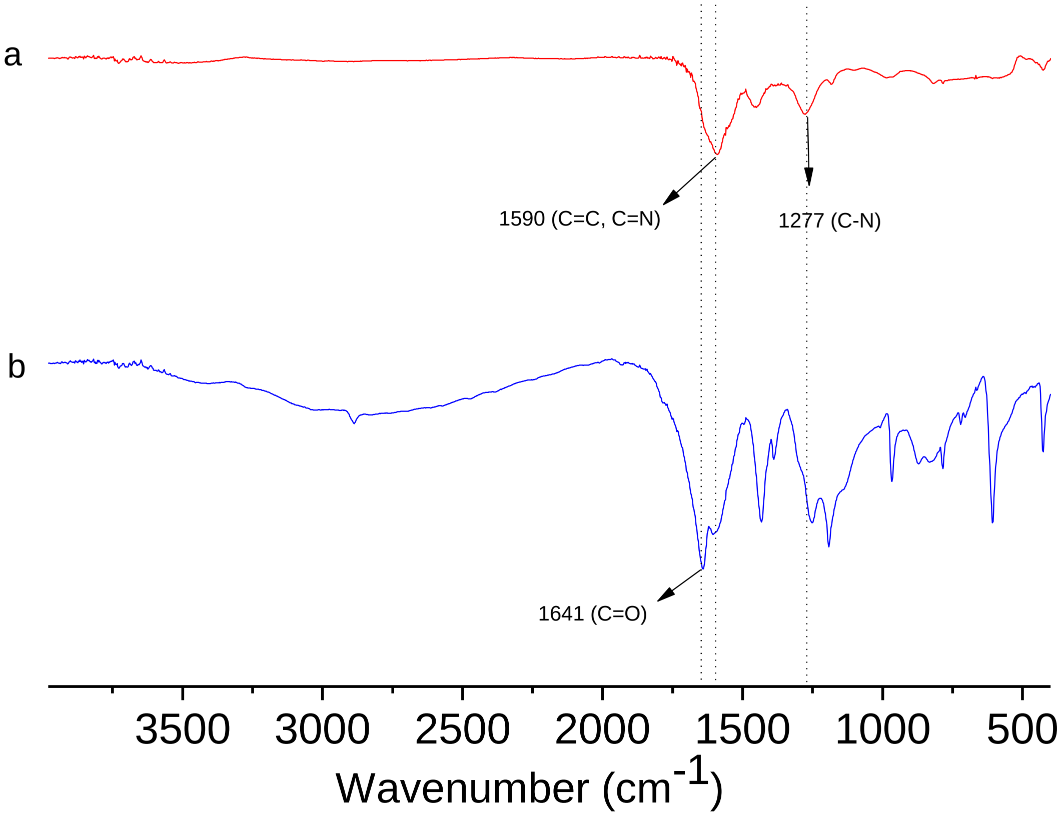


Figure S6. FT-IR spectra of (a) **HCOF-1** and (b) 1,3,5-triformylphloroglucinol.

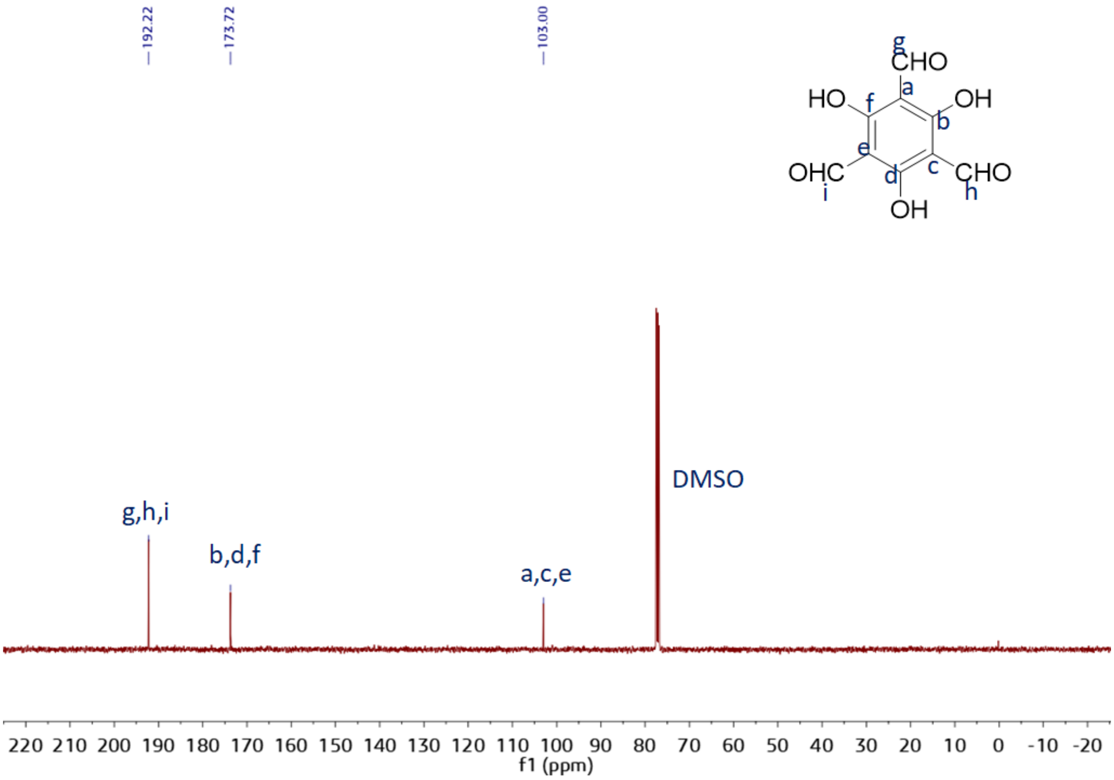


Figure S7. ^{13}C NMR spectrum of 1,3,5-triformylphloroglucinol.

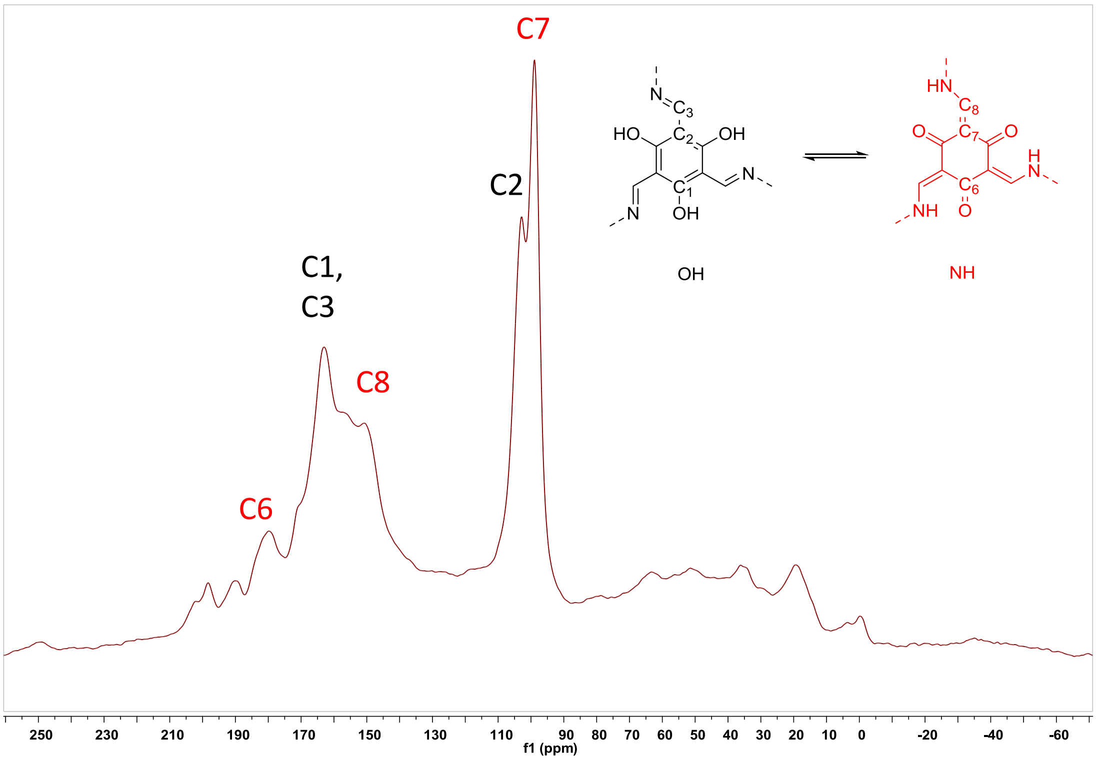


Figure S8. Solid-state ^{13}C CP/MAS NMR spectrum of **HCOF-1**.

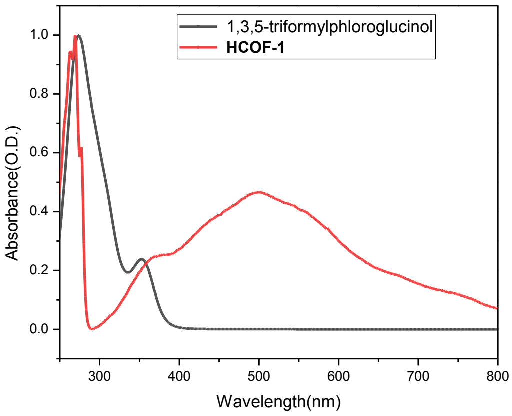


Figure S9. UV-vis spectra of (a) **HCOF-1** and (b) 1,3,5-triformylphloroglucinol.

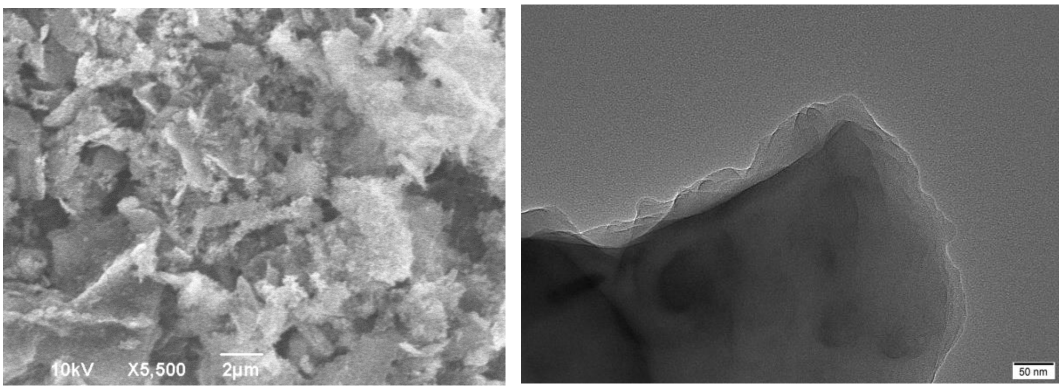


Figure S10. SEM image (left) and TEM image (right) of **HCOF-1**.

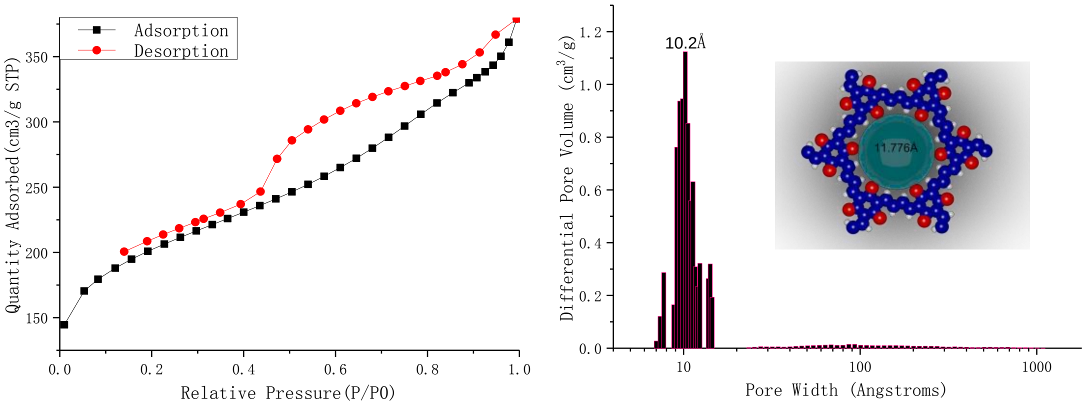


Figure S11. N_2 adsorption−desorption isotherms (77 K) of **HCOF-1** (left), and pore size distribution profile of **HCOF-1** (right) (the inserted photograph shows the theoretical pore size).

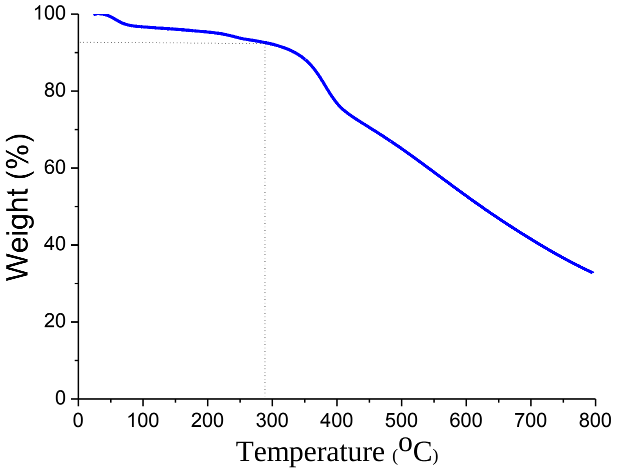


Figure S12. TGA profile of **HCOF-1** under nitrogen atmosphere.

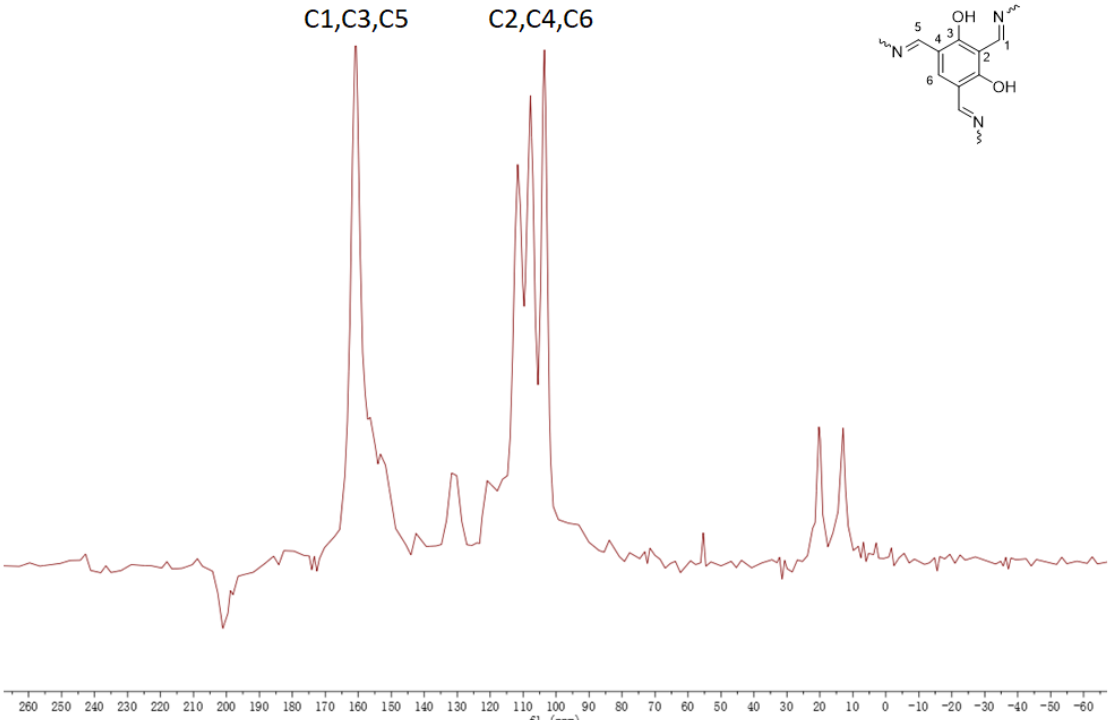


Figure S13. Solid-state ^{13}C CP/MAS NMR spectrum of **HCOF-2**.

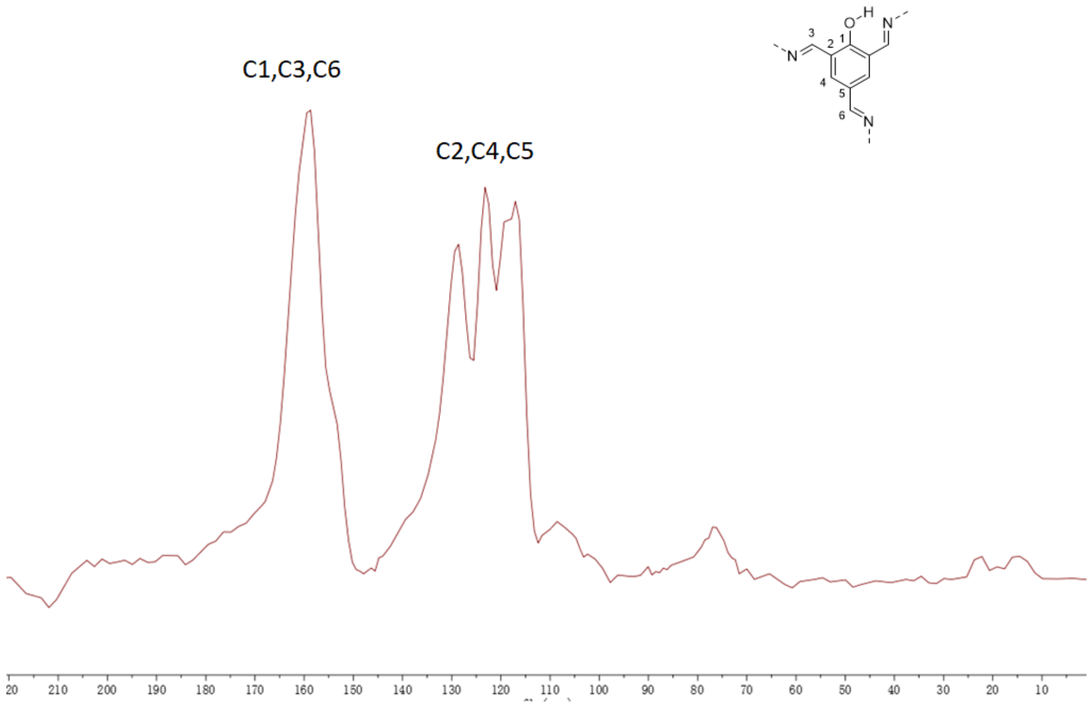


Figure S14. Solid-state ^{13}C CP/MAS NMR spectrum of **HCOF-3**.

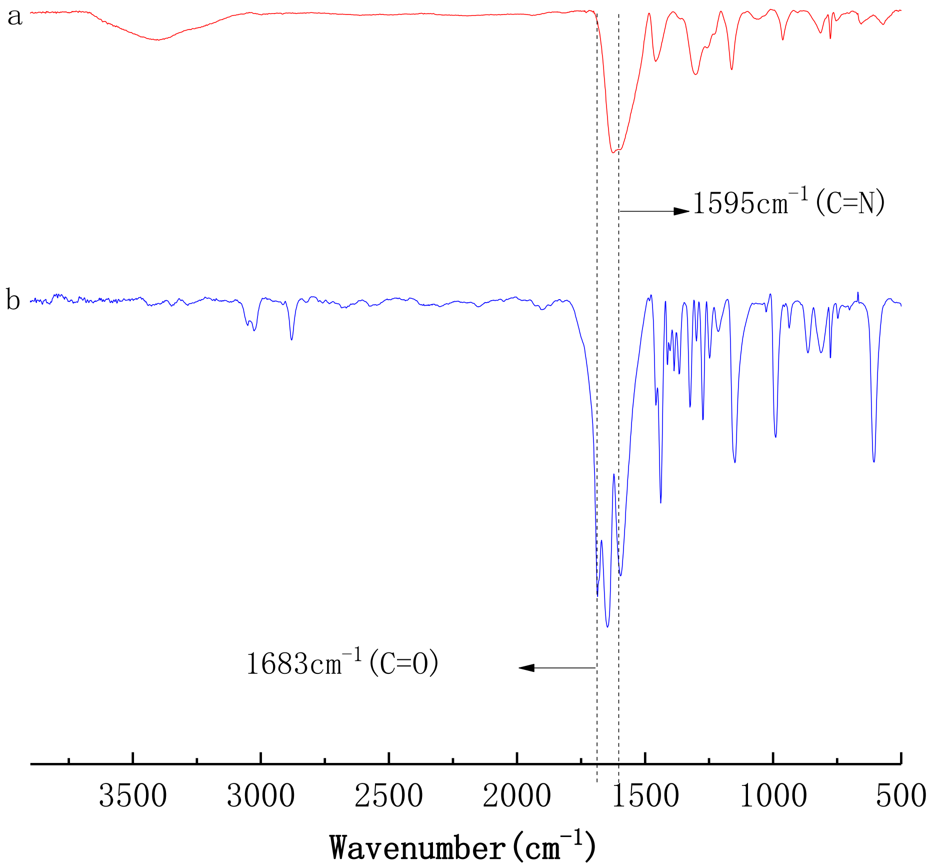


Figure S15. FT-IR spectra of (a) **HCOF-2** and (b) 2,4,6-triformylresorcinol.

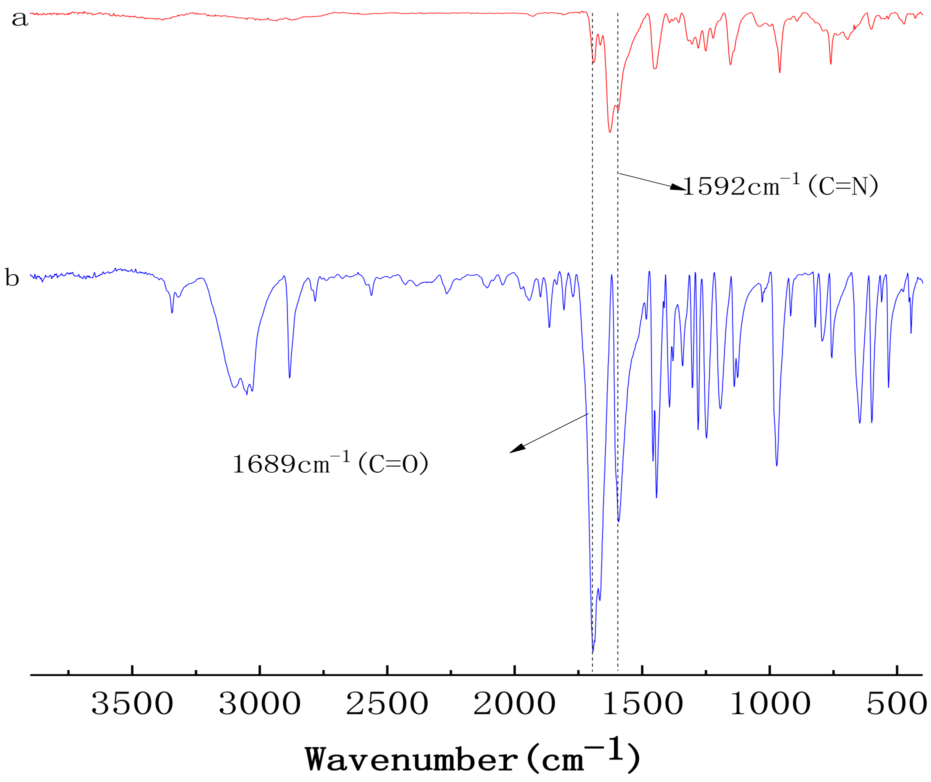


Figure S16. FT-IR spectra of (a) **HCOF-3** and (b) 2-hydroxy-1,3,5-triformylbenzene.

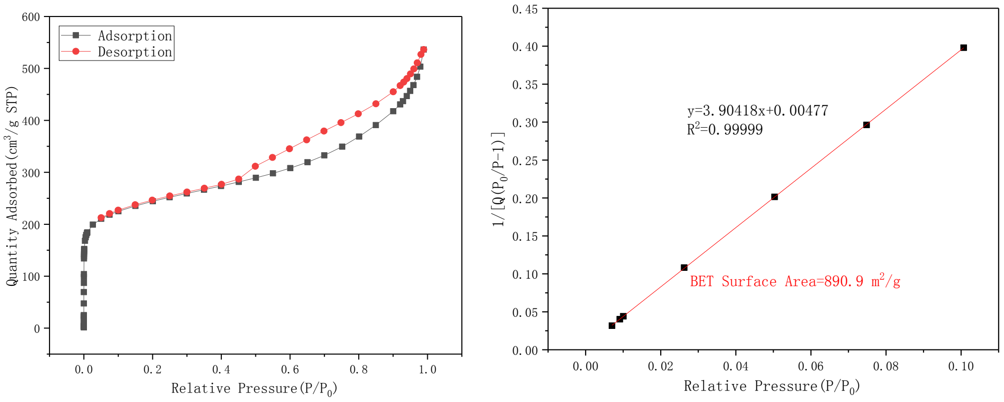


Figure S17. N_2 adsorption−desorption isotherms (77 K) (left) and BET surface area plot (right) of **HCOF-2** (1g-scale-synthesis).

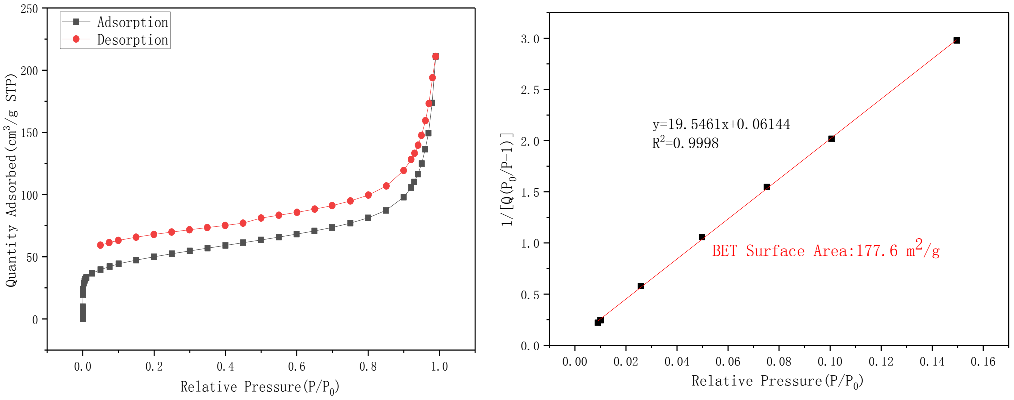


Figure S18. N_2 adsorption−desorption isotherms (77 K) (left) and BET surface area plot (right) of **HCOF-3** (3g-scale-synthesis).

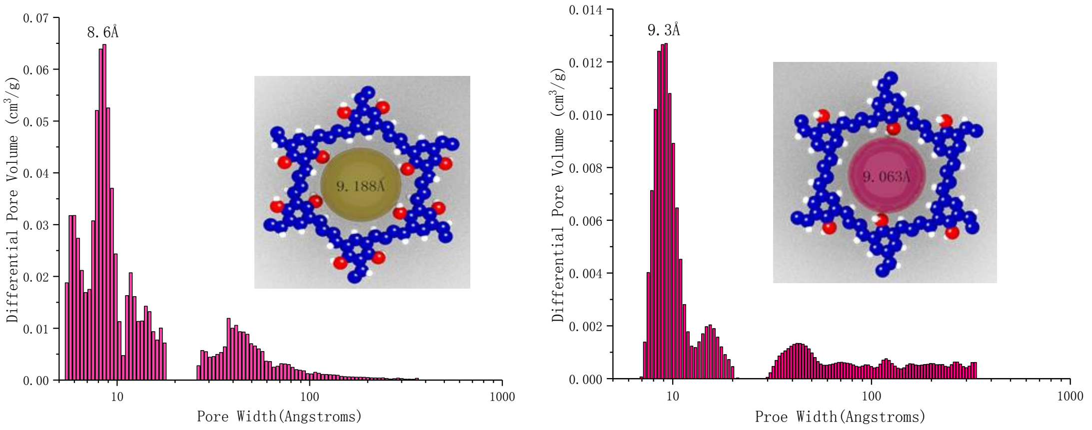


Figure S19. Pore size distribution profile of **HCOF-2** (left) and **HCOF-3**(right) (the inserted photograph shows the theoretical pore size).

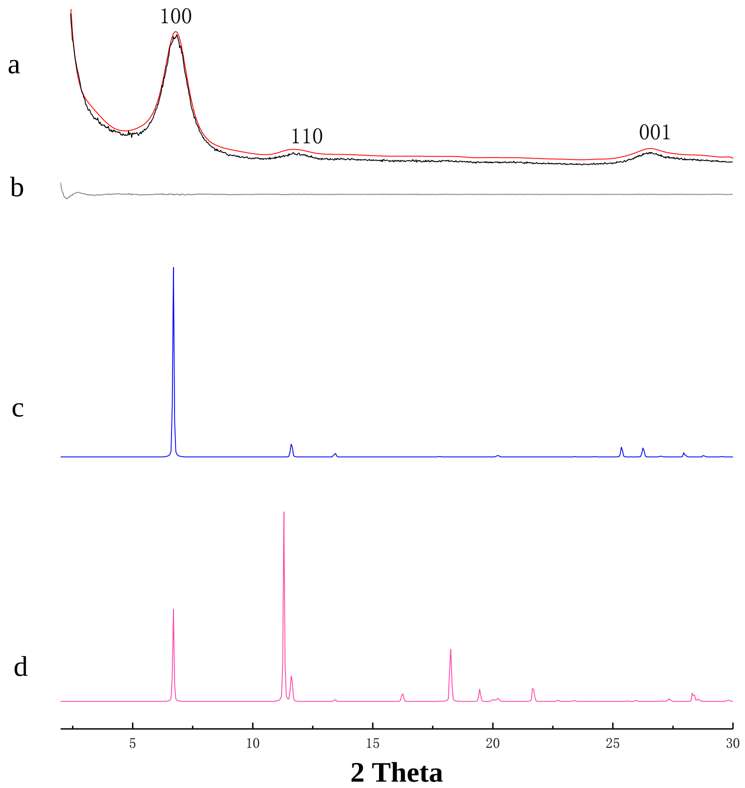


Figure S20. (a) Experimental (black) and refined (red) PXRD patterns of **HCOF-2**, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) **HCOF-2** with AA stacking, (d) **HCOF-2** with AB stacking.

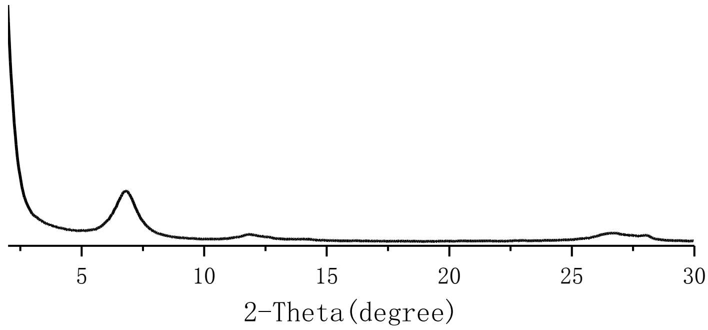


Figure S21. Experimental PXRD patterns of **HCOF-2** (synthesized by running the hydrothermal reaction for 12 h).

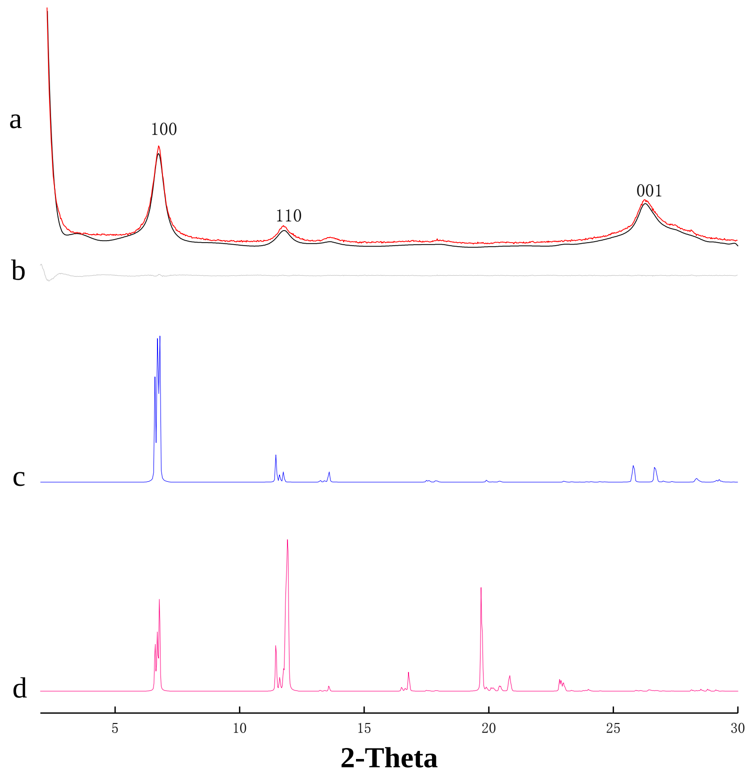


Figure S22. (a) Experimental (black) and refined (red) PXRD patterns of **HCOF-3**, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) **HCOF-3** with AA stacking, (d) **HCOF-3** with AB stacking.

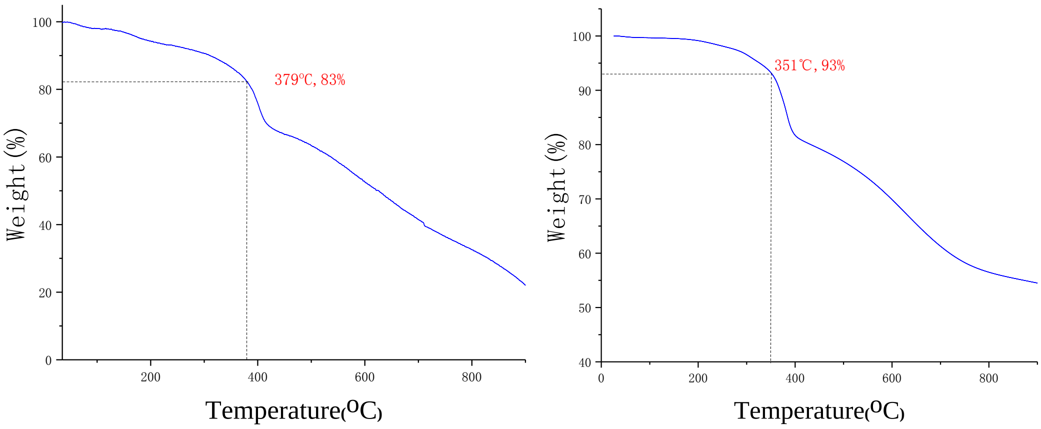


Figure S23. TGA profile of **HCOF-2** (left) and **HCOF-3** (right) under nitrogen atmosphere.

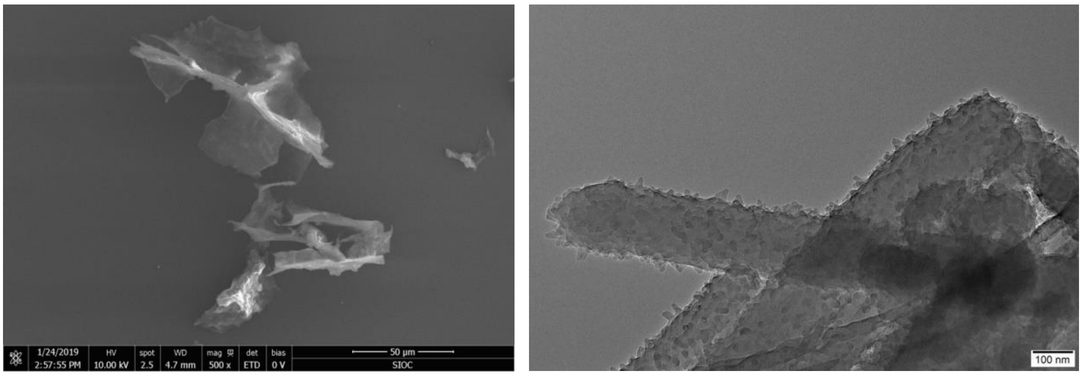


Figure S24. SEM image (left) and TEM image (right) of **HCOF-2**.

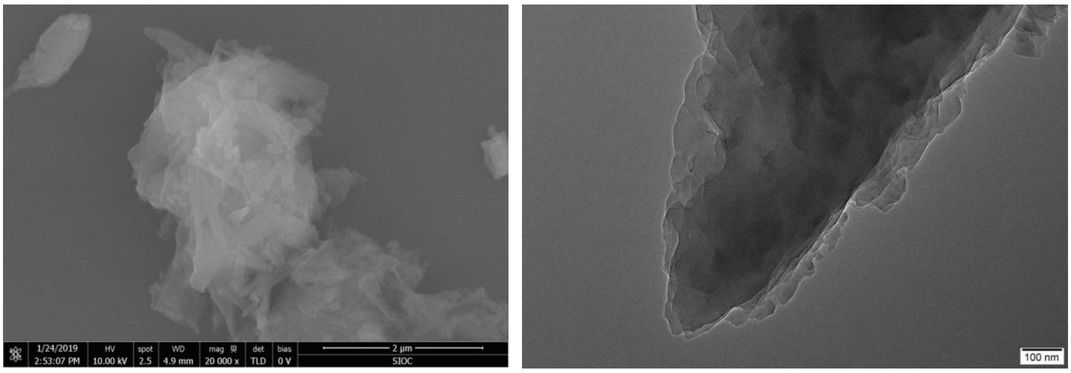


Figure S25. SEM image (left) and TEM image (right) of **HCOF-3**.

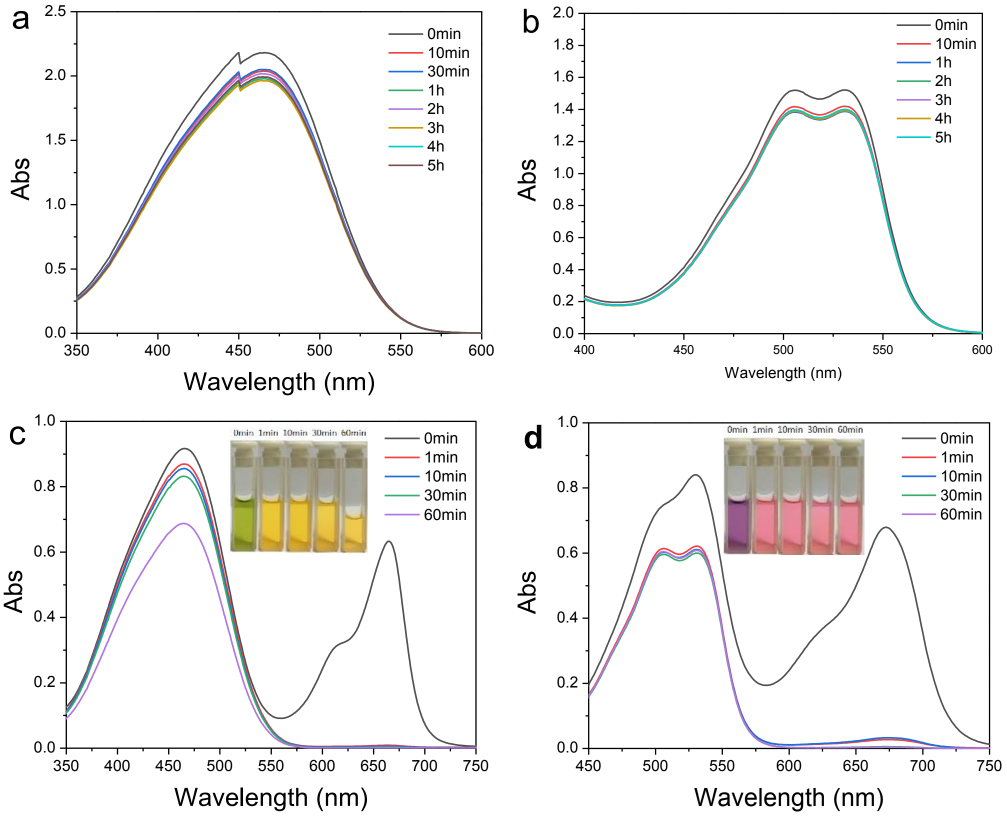


Figure S26. Time-dependent UV-vis absorption spectra of (a) MO, (b) AR1, (c) MB/MO, and (d) MB/AR1 in the presence of **HCOF-1**. The inserted photographs show the color change during the processes of dyes uptakes.

Table S3. The space groups and cell parameters of the **HCOF-1** structures.

Structure	Space Group	Cell Parameters
AA	P6	a = b = 15.41Å, c = 3.34 Å, α = β = 90.00° and γ = 120.00 °
AB	P3	a = b = 15.41 Å, c = 6.68 Å, α = β = 90.00° and γ = 120.00 °

Table S4. Fractional atomic coordinates for the unit cell of **HCOF-1** with AA stacking.

P6				
A = b = 15.41 Å, c = 3.34 Å, α = β = 90.00° and γ = 120.00 °				
Element	Number	u	v	w
N	1	0.04958	0.53953	-0.01066
C	2	0.12955	0.51955	0.05933
C	3	0.2252	0.59061	0.13572
C	4	0.25848	0.69842	0.18496
O	5	0.1995	0.72455	0.29095
H	6	0.06292	0.61119	-0.07383
H	7	0.11114	0.44213	0.04468

Table S5. The space groups and cell parameters of the **HCOF-2** structures.

Structure	Space Group	Cell Parameters
AA	P1	a =14.70Å b = 15.44Å, c = 3.20Å, α = β = 90.00° and γ = 120.00 °
AB	P1	a =14.70Å b = 15.44 Å, c = 6.40Å, α = β = 90.00° and γ = 120.00 °

Table S6. Fractional atomic coordinates for the unit cell of **HCOF-2** with AA stacking.

P1				
a =15.45 b = 15.05 Å, c = 3.45 Å, α = β = 90.00° and γ = 120.00 °				
Element	Number	u	v	w
H	1	4.686746	-3.957565	0.295478
H	2	4.757805	-4.302301	-0.035101
H	3	4.481584	-4.413417	0.239185
H	4	4.933108	-4.170492	-0.153755
H	5	4.488538	-4.193731	0.420488
H	6	4.816885	-3.92317	-0.077581
H	7	4.589001	-4.604203	-0.280924
H	8	4.315891	-4.716394	-0.020075
H	9	4.140912	-4.847964	0.125036
H	10	4.383296	-5.066227	-0.203277
H	11	4.630279	-4.710655	-0.072775
H	12	4.181107	-5.062432	0.253967
C	13	4.638016	-4.028948	0.154812
C	14	4.671135	-4.104324	0.11628
C	15	4.600647	-4.208947	0.158832
C	16	4.631123	-4.280389	0.087334
C	17	4.733498	-4.2473	0.006086
C	18	4.805679	-4.143947	-0.01144
C	19	4.773945	-4.071996	0.028253
C	20	4.555326	-4.389662	0.113955
C	21	4.913851	-4.113533	-0.074261
C	22	4.518437	-4.628625	-0.129726
C	23	4.444923	-4.737995	-0.083191
C	24	4.341192	-4.771281	-0.029365
C	25	4.268973	-4.874561	-0.000451
C	26	4.302044	-4.946214	-0.012688
C	27	4.404986	-4.914107	-0.078234
C	28	4.477021	-4.810224	-0.107225
C	29	4.160293	-4.903978	0.033004

C	30	4.436447	-4.991156	-0.098965
N	31	4.553521	-4.045262	0.004731
N	32	4.574103	-4.457866	-0.016227
N	33	4.501123	-4.560641	0.013351
N	34	4.088278	-4.994125	-0.053886
N	35	4.524561	-4.971845	0.023051
N	36	4.986017	-4.021602	-0.013126
O	37	4.500314	-4.244393	0.277762
O	38	4.84511	-3.969914	-0.038194
O	39	4.579526	-4.781657	-0.155618
O	40	4.236399	-5.048877	0.063539

Table S7. The space groups and cell parameters of the **HCOF-3** structures.

Structure	Space Group	Cell Parameters
AA	P1	a =15.42Å b = 14.96Å, c = 3.51Å, α = β = 90.00° and γ = 120.00 °
AB	P1	a =15.42Å b = 14.96 Å, c = 7.02Å, α = β = 90.00° and γ = 120.00 °

Table S8. Fractional atomic coordinates for the unit cell of **HCOF-3** with AA stacking.

P1				
a =15.45 b = 15.05 Å, c = 3.45 Å, α = β = 90.00° and γ = 120.00 °				
Element	Number	u	v	w
H	1	4.873489	-3.193579	0.060414
H	2	4.593068	-3.295044	-0.044866
H	3	4.824309	-3.372184	0.056277
H	4	4.417847	-3.425892	-0.150001
H	5	4.651418	-3.659135	0.015615
H	6	4.450274	-3.647463	-0.333061
H	7	4.212639	-3.752867	0.133706
H	8	3.806521	-3.801985	0.00119
H	9	4.036204	-3.882272	0.042685
H	10	3.978709	-3.516588	-0.023039
H	11	3.755762	-3.981151	-0.024713
H	12	4.108303	-3.497802	0.276335
C	13	4.79637	-3.212478	0.024259
C	14	4.717653	-3.321541	-0.0027
C	15	4.615945	-3.352361	-0.042538
C	16	4.543101	-3.45692	-0.071587
C	17	4.573925	-3.531403	-0.077019

C	18	4.675187	-3.500712	-0.017858
C	19	4.746062	-3.396123	0.016222
C	20	4.436522	-3.484518	-0.079367
C	21	4.706977	-3.578288	0.003484
C	22	4.194348	-3.693042	0.082879
C	23	4.087916	-3.720221	0.072659
C	24	4.059213	-3.644613	0.090406
C	25	3.956982	-3.673923	0.053417
C	26	3.884987	-3.778567	0.027421
C	27	3.912427	-3.853999	0.029988
C	28	4.014123	-3.82436	0.04912
C	29	3.924626	-3.596673	0.024017
C	30	3.832851	-3.962801	0.005742
N	31	4.77597	-3.139086	0.001845
N	32	4.365809	-3.575495	0.015366
N	33	4.265561	-3.600267	0.014052
N	34	3.830894	-3.624018	0.039577
N	35	3.852825	-4.036547	0.023746
N	36	4.800774	-3.550826	0.010298
O	37	4.50735	-3.635052	-0.155792
O	38	4.132957	-3.54246	0.157726

Reference

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