Electronic Supplementary Information

Transformation between 2D covalent organic frameworks with distinct pore hierarchy via exchange of building blocks with different symmetries

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Section A. Instruments and Methods

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 ¹³C 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 8 kHz MAS spinning speed with a contact time of 1 ms. Recycle delay times are 2 s. The ¹³C 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)

Transmission electron microscopy was performed on a JEOL JEM-2100 instrument.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analyses were carried out on Waters TGA Q500 by heating the samples from 35 to 1000 $^{\circ}$ C under nitrogen atmosphere at a heating rate of 10 $^{\circ}$ 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/K α ($\lambda = 0.1542$ nm). The sample was 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 *Quantachrome autosorb iQ* automatic volumetric instrument. 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 $^{\circ}$ C for 3 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 (NLDFT) or the quenched solid state density functional theory (QSDFT), the pore size distributions were derived from the sorption curves.

Structural simulations 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. Before the simulation, the structure was firstly optimized in Gaussian 09 package by semiempirical calculations at PM3 level. 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. P3 space group was chosen for the primitive models in the initial simulations.

Section B. Synthesis and characterization of the monomers.

All reagents and solvents were purchased from commercial suppliers and used without further purification unless stated otherwise. The 3,5-bis(4-aminophenyl) benzamine (**BABA**) and 3,5-bis(4-formylphenyl) benzaldehyde (**BFBA**) were synthesized as previously reported in the literature.¹





1,3,5-tris(4-aminophenyl) benzene (TAPB)



1,3,5-tris(4-formylphenyl) benzene (TFPB)

Section C. The synthesis and characterization of COF-C_{2V}-NH₂.

1. Procedure for the preparation of $COF-C_{2V}-NH_2$.

BABA (13.6 mg, 0.050 mmol) and TFB (8.0 mg, 0.050 mmol) were dispersed in a mixture of dioxane-mesittylene (1/1, v/v) (2 mL) and acetic acid (aq., 6 M) (0.2 mL) 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 3 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in 1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 °C for 2 h to afford a pale yellow powder (16.8 mg, 89.4%). Anal. Calcd. For chemical formula C₂₇H₁₇N₃: C, 84.57; H, 4.47; N, 10.96. Found: C, 83.59; H, 5.49; N, 8.62.



2. Structural models and comparison of the experimental and simulated PXRD patterns.

Note: The condensation of BABA and TFB theoretically could give rise to two different types of 2D frameworks. One possesses uniform pore structure (single-pore COF), and the other holds two different kinds of pores (dual-pore COF).² For each of them, both eclipsed (AA) stacking and staggered (AB) stacking of the 2D layers were simulated, which were denoted as DP-AA and DP-AB, and SP-AA and SP-AB, respectively.



Fig S1. Structural illustrations for (a) DP-AA, (b) DP-AB, (c) SP-AA and (d) SP-AB.



Fig S2. (a) Experimental (black) and refined (red) PXRD patterns of $COF-C_{2V}-NH_2$, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) DP-AA, (d) DP-AB, (e) SP-AA and (f) SP-AB.

3. FT-IR spectra.





Fig S4. Solid-state ¹³C CP/MAS NMR spectrum of COF-C_{2V}-NH₂.

5. Thermogravimetric analysis profile.



Fig S5. TGA profile of $COF-C_{2V}-NH_2$.

6. Field-emission scanning electron microscopy and transmission electron microscopy.



Fig S6. FE-SEM (left) and TEM (right) images of COF-C_{2V}-NH₂.

7. N₂ adsorption-desorption isotherm and BET surface area plot.



Fig S7. N₂ adsorption-desorption isotherm (77 K) of COF-C_{2V}-NH₂.



Fig S8. BET surface area plot for $COF-C_{2V}-NH_2$ calculated from the isotherm.

8. Theoretical pore size distribution.



Fig S9. Theoretically simulated pore sizes of the two different kinds of pores in $COF-C_{2V}-NH_{2}$.

9. Fractional atomic coordinates.

Table S1. Fractional atomic coordinates for the unit cell of $COF-C_{2V}-NH_2$ with AA stacking.

P3										
$a = b = 27.93$ Å, $c = 3.57$ Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma = 120^{\circ}$										
Element	Number	u	v	W	Element	Number	u	v	W	
С	1	2.89566	-0.73131	-0.68631	С	25	3.0986	-0.22524	-0.68605	
С	2	2.90562	-0.77562	-0.69766	С	26	3.14537	-0.17414	-0.66787	
С	3	2.96061	-0.76313	-0.70933	С	27	3.14489	-0.12616	-0.78098	
С	4	3.00494	-0.70889	-0.71193	С	28	3.09504	-0.13166	-0.91267	
С	5	2.99243	-0.66667	-0.69965	С	29	3.04776	-0.18236	-0.93418	
С	6	2.93818	-0.6763	-0.68872	Ν	30	3.81118	0.1555	-0.71277	
С	7	2.92483	-0.63248	-0.6835	Н	31	2.85279	-0.73997	-0.67796	
С	8	2.8622	-0.83293	-0.70142	Н	32	2.96925	-0.79736	-0.71952	
С	9	3.06216	-0.69519	-0.72885	Н	33	3.02671	-0.62355	-0.7025	
Ν	10	2.96476	-0.58171	-0.69294	Н	34	2.88084	-0.64447	-0.68058	

N	11	3.07344	-0.73464	-0.76337	Н	35	2.87502	-0.86428	-0.70775
С	12	2.96013	-0.5342	-0.72132	Н	36	3.09386	-0.65115	-0.71552
С	13	3.00556	-0.48292	-0.62283	Н	37	3.04359	-0.48097	-0.51991
С	14	3.00336	-0.43503	-0.64686	Н	38	3.03945	-0.39614	-0.55532
С	15	2.95454	-0.43573	-0.77561	Н	39	2.87055	-0.4911	-0.98633
С	16	2.90876	-0.48818	-0.8777	Н	40	2.87587	-0.57485	-0.9371
С	17	2.91186	-0.53559	-0.85019	Н	41	3.03919	-0.33176	-0.8717
С	18	2.9514	-0.38598	-0.79419	Н	42	2.94317	-0.25068	-0.76189
С	19	2.99917	-0.33388	-0.83422	Н	43	2.86219	-0.42705	-0.7221
С	20	2.99767	-0.28439	-0.81808	Н	44	3.10061	-0.26122	-0.58194
С	21	2.94506	-0.28886	-0.77973	Н	45	3.18328	-0.17142	-0.55609
С	22	2.89671	-0.33948	-0.75035	Н	46	3.09369	-0.09478	-1.00433
С	23	2.90029	-0.38712	-0.75715	Н	47	3.00996	-0.18456	-1.04448
С	24	3.0475	-0.23146	-0.81852					

Section D. The synthesis and characterization of COF-C₃-NH₂

1. Procedure for the synthesis of $COF-C_3-NH_2$ through COF-to-COF transformation from $COF-C_{2\nu}-NH_2$.

COF-C_{2V}-NH₂ (15.0 mg) and TAPB (82.0 mg, 0.232 mmol) were dispersed in a mixture of dioxane-mesittylene (1/1, v/v) (2 mL) and acetic acid (aq., 6 M) (0.2 mL) in a glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 10 min, warmed to the room temperature and then kept at 120 °C without disturbance for 3 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in 1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 °C for 2 h to afford a pale yellow powder (15.3 mg, 85.2%). For chemical formula $C_{33}H_{21}N_3$: C, 86.25; H, 4.61; N, 9.14. Found: C, 82.54; H, 5.52; N, 8.67.



2. Structural models and comparison of the experimental and simulated PXRD patterns.

The condensation of TAPB and TFB theoretically could give rise to only one type of 2D frameworks with uniform pore structure (single-pore COF). For the single-pore COF, both eclipsed (AA) stacking and staggered (AB) stacking of the 2D layers were simulated, which were denoted as SP-AA and SP-AB, respectively.



Fig S10. Structural illustrations for (a) SP-AA and (b) SP-AB.



Fig S11. (a) Experimental (black) and refined (red) PXRD patterns of $COF-C_3-NH_2$, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) SP-AA and (d) SP-AB.

3. The synthesis of COF-C₃-NH₂ by direct condensation of the monomers.

TAPB (35.2 mg, 0.10 mmol) and TFB (16.2 mg, 0.10 mmol) were dispersed in dioxane (1 mL) and acetic acid (aq., 6 M) (0.1 mL) 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 $^{\circ}$ C without disturbance for 3 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in 1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 $^{\circ}$ C for 2 h to afford a pale yellow powder (37.3 mg, 82.4%).



Fig S12. PXRD patterns of COF- C_3 -NH₂ synthesized by the COF-to-COF conversion (red) and direct condensation of the monomers (black).

4. FT-IR spectra.



Fig S13. FT-IR spectra of (a) COF- C_3 -NH₂, (b) COF- C_{2V} -NH₂ and (c) TAPB.

5. Solid-state¹³C CP/MAS NMR. $\frac{8}{9}$ $\frac{7}{9}$ $\frac{9}{1}$ \frac

Fig S14. Solid-state ¹³C CP/MAS NMR spectrum of COF-C₃-NH₂.

6. Thermogravimetric analysis profile.



Fig S15. TGA profile of COF-C₃-NH₂.

7. Field-emission scanning electron microscopy and transmission electron microscopy.





Fig S16. FE-SEM (left) and TEM (right) images of COF-C₃-NH₂.

8. N₂ adsorption-desorption isotherm and BET surface area plot.



Fig S17. N₂ adsorption-desorption isotherm (77 K) of COF-C₃-NH₂.



Fig S18. BET surface area plot for COF-C₃-NH₂ calculated from the isotherm.

9. Theoretical pore size distribution.



Fig S19. Theoretically simulated pore size of the pore in $COF-C_3-NH_2$.

10. Fractional atomic coordinates.

Table S2. Fractional atomic coordinates for the unit cell of $COF-C_3-NH_2$ with AA
stacking.
P3

P3										
$a = b = 18.56$ Å, $c = 3.57$ Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma = 120^{\circ}$										
Element	Number	u	v	w	Element	Number	u	v	w	
N	1	1.52691	1.42074	0.93637	С	11	1.72062	2.41798	0.91137	
С	2	1.48973	1.46988	0.98032	С	12	1.75356	2.36477	0.91257	
С	3	1.40658	1.43804	0.8725	Н	13	1.37192	1.37538	0.75063	
С	4	1.36777	1.48415	0.90839	Н	14	1.30363	1.45734	0.80588	
С	5	1.41064	1.56646	1.06005	Н	15	1.53049	1.65911	1.3038	
С	6	1.49478	1.59734	1.17474	Н	16	1.59706	1.57667	1.22985	
С	7	1.53254	1.55038	1.13356	Н	17	1.24645	1.51274	1.08505	
С	8	1.37175	1.6167	1.0881	Н	18	1.65343	1.5144	0.92041	
С	9	1.28478	1.5807	1.09338	Н	19	1.76341	2.4854	0.91357	
С	10	1.60607	1.44793	0.91946						

Section E. The synthesis and characterization of COF-C_{2V}-CHO

1. Procedure for the preparation of COF-C_{2V}-CHO.

BFBA (17.9 mg, 0.057 mmol) and TAPB (20.0 mg, 0.057mmol) were dispersed in a mixture of 1,2-dichlorobenzene -(n-butanol) (1/3, v/v) (2 mL) and acetic acid (aq., 6 M) (0.2 mL) 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 4 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in the1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 °C for 2 h to afford a pale yellow powder (31.3 mg, 89.4%). Anal. Calcd. For chemical formula C45H29N3: C, 88.35; H, 4.78; N, 6.87. Found: C, 86.55; H, 4.93; N, 6.27.



2. Structural models and comparison of the experimental and simulated PXRD patterns.

Note: The condensation of TAPB and BFBA theoretically could give rise to two different types of 2D frameworks. One possesses uniform pore structure (single-pore COF), and the other holds two different kinds of pores (dual-pore COF).² For each of them, both eclipsed (AA) stacking and staggered (AB) stacking of the 2D layers were simulated, which were denoted as DP-AA and DP-AB, and SP-AA and SP-AB, respectively.



Fig S20. Structural illustrations for (a) DP-AA, (b) DP-AB, (c) SP-AA and (d) SP-AB.



Fig S21. (a) Experimental (black) and refined (red) PXRD patterns of $COF-C_{2V}$ -CHO, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) DP-AA, (d) DP-AB, (e) SP-AA and (f) SP-AB.

3. FT-IR spectra.



Fig S22. FT-IR spectra of (a) COF-C_{2V}-CHO, (b) BFBA and (c) TAPB.

4. Solid-state¹³C CP/MAS NMR.



Fig S23. Solid-state ¹³C CP/MAS NMR spectrum of COF-C_{2V}-CHO.

5. Thermogravimetric analysis profile.



Fig S24. TGA profile of COF-C_{2V}-CHO.

6. Field-emission scanning electron microscopy and transmission electron microscopy.



Fig S25. FE-SEM (left) and TEM (right) images of COF-C_{2V}-CHO.

7. N₂ adsorption-desorption isotherm and BET surface area plot.



Fig S26. N₂ adsorption-desorption isotherm (77 K) of COF-C_{2V}-CHO.



Fig S27. BET surface area plot for COF- C_{2V} -CHO calculated from the isotherm.

8. Theoretical pore size distributions.



Fig S28. Theoretically simulated pore sizes of the two different kinds of pores in $COF-C_{2V}$ -CHO.

9.Fractional atomic coordinates

Table S3. Fractional atomic coordinates for the unit cell of COF- $C_{2\nu}$ -CHO with AA stacking.

P3										
$a = b = 40.37$ Å, $c = 3.66$ Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma = 120^{\circ}$										
Element	Number	u	v	w	Element	Number	u	v	w	
С	1	1.88165	1.68753	1.31316	С	40	2.23272	1.85637	0.96293	
С	2	1.88941	1.65992	1.4595	С	41	2.3747	1.93004	1.0312	
С	3	1.92574	1.66518	1.465	С	42	2.40878	1.93104	1.08963	
С	4	1.95738	1.69862	1.3143	С	43	2.444	1.96387	1.00987	
С	5	1.94926	1.72667	1.17115	С	44	2.44342	1.99587	0.86766	
С	6	1.91283	1.72109	1.17224	С	45	2.40971	1.99562	0.80794	
С	7	1.99506	1.70295	1.28854	Ν	46	2.12978	1.78635	1.04599	
С	8	2.03668	1.67464	1.25725	Ν	47	2.47938	1.96583	1.06525	
С	9	2.00054	1.67124	1.3057	С	48	2.48581	1.94	1.20275	
С	10	2.06809	1.71183	1.19224	Н	49	1.86621	1.63347	1.57842	
С	11	2.06421	1.74408	1.1721	Н	50	1.92998	1.6428	1.58899	
С	12	2.02798	1.73912	1.22598	Н	51	1.9718	1.75262	1.03943	
С	13	2.09604	1.78195	1.09624	Н	52	1.90839	1.74341	1.04929	
С	14	2.72996	1.70052	0.98738	Н	53	1.97595	1.64256	1.34942	
С	15	2.73543	1.66857	0.92894	Н	54	2.09616	1.71449	1.14484	

	1								
С	16	2.76985	1.67082	1.00273	Н	55	2.02457	1.76439	1.21462
С	17	2.80105	1.70458	1.13881	Н	56	2.09001	1.80566	1.08333
С	18	2.79607	1.73611	1.20048	Н	57	2.71241	1.64201	0.80985
С	19	2.76179	1.73435	1.13234	Н	58	2.77298	1.64582	0.94524
N	20	2.83676	1.70781	1.20499	Н	59	2.81997	1.76278	1.30843
С	21	2.84282	1.68062	1.30875	Н	60	2.75933	1.75969	1.19239
С	22	2.52472	1.9472	1.22003	Н	61	2.81973	1.65187	1.38469
С	23	2.53162	1.91878	1.36013	Н	62	2.50779	1.89166	1.46066
С	24	2.56783	1.92384	1.37853	Н	63	2.57192	1.90098	1.4934
С	25	2.60027	1.95848	1.25576	Н	64	2.61682	2.01426	1.01176
С	26	2.59307	1.98745	1.11894	Н	65	2.55267	2.00453	0.98543
С	27	2.55656	1.98158	1.10103	Н	66	2.24004	1.95915	0.84863
С	28	2.26772	1.9603	0.83271	Н	67	2.30487	1.90162	0.74024
С	29	2.26792	1.92572	0.79145	Н	68	2.3625	2.02238	0.95732
С	30	2.30378	1.92804	0.77668	Н	69	2.19511	1.90946	0.60849
С	31	2.33826	1.9623	0.84066	Н	70	2.1361	1.85072	0.73592
С	32	2.33613	1.99581	0.88895	Н	71	2.19984	1.79902	1.15672
С	33	2.30114	1.99555	0.89669	Н	72	2.25957	1.85778	1.04495
С	34	2.23306	1.88936	0.81516	Н	73	2.34796	1.90414	1.10725
С	35	2.3737	1.96252	0.88842	Н	74	2.40785	1.90543	1.20327
С	36	2.19676	1.88541	0.72949	Н	75	2.47052	2.02176	0.79971
С	37	2.16329	1.85219	0.80432	Н	76	2.41066	2.02119	0.6919
С	38	2.16345	1.82045	0.9606	Н	77	2.46312	1.91222	1.30491
С	39	2.19893	1.82337	1.03339					

Section F. The synthesis and characterization of COF-C₃-CHO

1. Procedure for the synthesis of $COF-C_3$ -CHO through COF-to-COF transformation from $COF-C_{2V}$ -CHO.

COF-C_{2V}-CHO (15.0 mg) and TFPB (95.0 mg, 0.244 mmol) were dispersed in a mixture of 1,2-dichlorobenzene -(n-butanol) (1/3, v/v) (2 mL) and acetic acid (aq., 6 M) (0.2 mL) 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 6 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in 1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 °C for 2 h to afford a pale yellow powder (12.1 mg, 71.3%). C₅₁H₃₃N₃: C, 89.05; H, 4.84; N, 6.11. Found: C, 83.1; H, 5.63; N, 5.00.





Fig. S29. PXRD patterns of (a) COF-C_{2V}-CHO and (b–g) the samples prepared by heating the mixtures of COF-C_{2V}-CHO and different equivalents of TFPB for 96 h at 120 $^{\circ}$ C.

2. Structural models and comparison of the experimental and simulated PXRD patterns.

The condensation of TAPB and TFPB theoretically could give rise to only one types of 2D frameworks with uniform pore structure (single-pore COF). For the single-pore COF, both eclipsed (AA) stacking and staggered (AB) stacking of the 2D layers were simulated, which were denoted as SP-AA and SP-AB, respectively.



Fig S30. Structural illustrations for (a) SP-AA and (b) SP-A. Note: $COF-C_3$ -CHO with AA or AB stacking is named SP-AA and SP-AB, respectively.



Fig S31. (a) Experimental (black) and refined (red) PXRD patterns of COF-C₃-CHO, (b) difference plot between the experimental and refined PXRD patterns, and simulated PXRD patterns of (c) SP-AA and (d) SP-AB.

3. The synthesis of COF-C₃-CHO by direct condensation of the monomers

TAPB (20.0 mg, 0.057 mmol) and TFPB (22.0 mg, 0.057 mmol) were dispersed in mesitylene/1,4-dioxane (0.9 mL/0.1 mL) and acetic acid (aq., 6 M) (0.1 mL) 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 3 days to yield a pale yellow solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dichloromethane and acetone for 3 times, and immersed in 1,4-dioxane for 1 days. Finally, the solid was dried under dynamic vacuum at 120 °C for 2 h to afford a pale yellow powder (34.5 mg, 87.6%).



Fig S32. PXRD patterns of COF- C_3 -NH₂ synthesized by the COF-to-COF conversion (red) and direct condensation of the monomers (black).

4. FT-IR spectra.



Fig S33. FT-IR spectra of (a) COF-C₃-CHO, (b) COF-C_{2V}-CHO and (c) TFPB.



Fig S34. Solid-state ¹³C CP/MAS NMR spectrum of COF-*C*₃-CHO.

6. Thermogravimetric analysis profile.





7. Field-emission scanning electron microscopy and transmission electron microscopy.



Fig S36. FE-SEM (left) and TEM (right) images of COF-C₃-CHO.

8. N₂ adsorption-desorption isotherm and BET surface area plot.



Fig S37. N₂ adsorption-desorption isotherm (77 K) of COF-C₃-CHO.



Fig S38. BET surface area plot for COF- C_3 -CHO calculated from the isotherm.

9. Theoretical pore size distributions.



Fig S39. Theoretically simulated pore size of the pores in COF-C₃-CHO.

10. Fractional atomic coordinates.

Table S4. Fractional atomic coordinates for the unit cell of $\text{COF-}C_3$ -CHO with AA stacking.

P3										
$a = b = 25.84$ Å, $c = 3.84$ Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma = 120^{\circ}$										
Element	Number	u	v	w	Element	Number	u	v	W	
С	1	2.06155	2.0377	1.11428	С	16	2.17803	2.44941	0.93553	
С	2	2.02453	2.06325	1.11051	С	17	2.39705	2.69637	0.67057	
С	3	2.04914	2.12684	1.09045	С	18	2.36637	2.72864	0.66314	
С	4	2.10486	2.16471	0.92137	Н	19	2.11019	2.06747	1.10797	
С	5	2.12756	2.2253	0.89942	Н	20	2.12944	2.14519	0.79645	
С	6	2.09748	2.25316	1.04288	Н	21	2.17015	2.25185	0.76113	
С	7	2.04265	2.21623	1.21038	Н	22	2.01775	2.23582	1.33054	
С	8	2.01889	2.15549	1.23441	Н	23	1.97659	2.1289	1.37526	
С	9	2.12033	2.31703	1.02423	Н	24	2.09345	2.33419	1.1473	
Ν	10	2.17063	2.35075	0.86688	Н	25	2.2743	2.4133	0.54567	
С	11	2.20062	2.413	0.81759	Н	26	2.33001	2.52067	0.44793	
С	12	2.25583	2.4407	0.64391	Н	27	2.19017	2.53685	0.99211	
С	13	2.28742	2.50136	0.59011	Н	28	2.13528	2.42985	1.07543	
С	14	2.26536	2.53905	0.71073	Н	29	2.39248	2.77761	0.67546	
С	15	2.20881	2.51018	0.88463						

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