

Electronic Supplementary Information

Synthesis of Two and Three-Dimensional Covalent Organic Frameworks in Deep Eutectic Solvents

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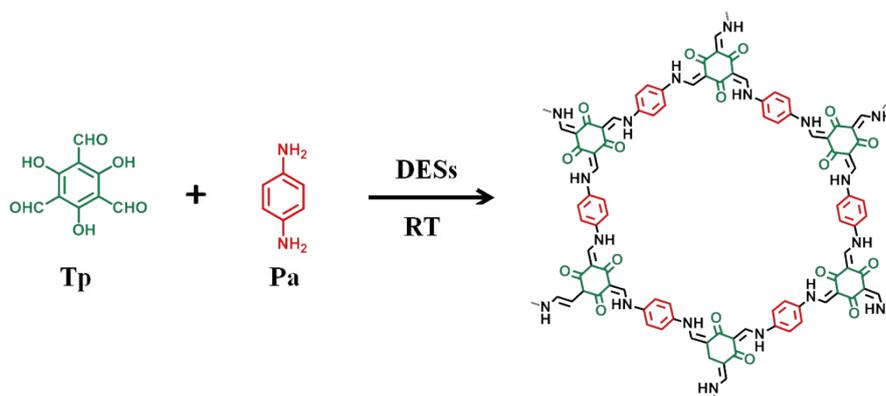
Section S1: Materials and Methods

All chemicals and reagents were commercially available and used without further purification. Deep eutectic solvents were synthesized according to the published procedures.¹ Power X-ray diffraction (PXRD) data were obtained with a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K α radiation from $2\theta = 2^\circ$ to 50° in 0.05° increment. Fourier transform infrared (FTIR) spectra of the samples were collected on a Spectrum 400 spectrometer (Perkin-Elmer). Thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA449C) over the temperature range from 25°C to 800°C under N_2 atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. Nitrogen adsorption and desorption isotherms were measured at 77 K using a ASiQwin Quantachrome instrument. The samples were treated at 120°C for 10 h before measurements. Specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Pore size distribution data were calculated based on the nonlocal density functional theory (NLDFT) model. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0kV.

General procedures for the synthesis of Deep Eutectic Solvents

Three kinds of DESs were prepared using choline chloride as hydrogen bond acceptor (HBA), while the hydrogen bond donors (HBD) were glycerol (Gly), ethylene glycol (EG) and urea (U). All the DESs were prepared by simply mixing HBA and HBD under stirring, and then reacted at 80°C for 0.5h until a uniform and stable liquid was formed. The molar ratio of HBA to HBD) was approximately 1:2. After the reaction was finished, the mixture was collected without further purification and then dried at 60°C under vacuum for 24 h to give a color-less liquid. The synthesized DESs were named ChCl/Gly, ChCl/EG and ChCl/U, respectively.

Synthesis of TpPa-Gly in ChCl-Gly



In a plastic centrifuge tube with the volume of 5.0 ml, 1,3,5-triformylphloroglucinol (Tp) (0.10 mmol, 21.0mg) and p-phenylenediamine (Pa) (0.15mmol, 16.2mg) were dissolved

in ChCl/Gly DES (7.6 eqv. 200uL) under vigorous stirring. The mixture was kept at room temperature for 2h. The precipitate was isolated by filtration and washed with ethanol (15mL×2). The collected powders were refluxed with DMF (10mL) for 8 h to remove any un-reacted residuals, then washed with ethanol (20mL×3) and acetone (20mL×3), and dried under vacuum at 100 °C for 12 h to give a red colored powder (yield of 91%). TpPa-EG and TpPa-U were synthesized in similar procedures.

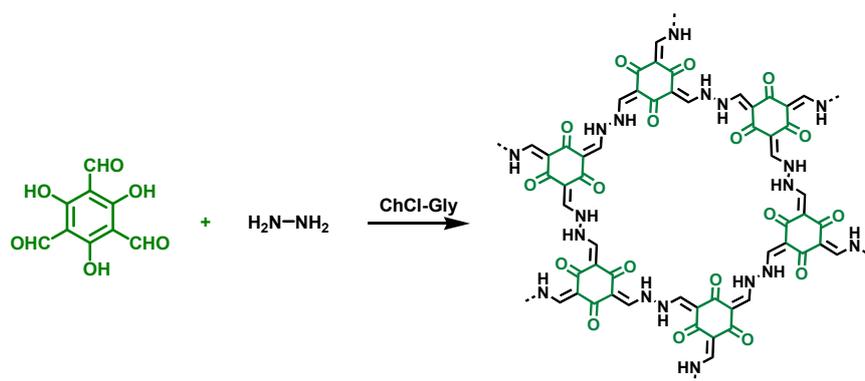
Bulky production of TpPa-Gly under ambient conditions

The procedure was almost the same as that mentioned above. Tp (5mmol, 1.05g) and Pa (7.5mmol, 0.81g) were weighed into a flask and suspended in ChCl/Gly (10 mL). After keeping for 24h at room temperature, the red solid was isolated by filtration and washed with ethanol (40mL×2). The collected powder was refluxed with DMF (20mL) for 8 h to remove unreacted residuals, then washed with ethanol (50mL×3) and acetone (50mL×3), evacuated in vacuum at 100 °C for 24 h to give a red colored powder. The weight of final purified TpPa-Gly was 1.6 g.

Synthesis of other 2D COFs in ChCl-Gly

Similar to the synthesis of TpPa-Gly, Tp (0.10 mmol, 21mg) and 4,4' -azodianiline (Azo) (0.15 mmol, 31.8mg) were used to produce TpAzo-Gly as deep red powders (yield of 85%); Tp (0.10 mmol, 21mg) and 2,2' -bipyridine-4,4' -diamine (Bpy) (0.15mmol, 27.9 mg) were used to yield TpBpy-Gly as yellow powders (yield of 83%); Tp (0.10 mmol, 21mg) and 2,5-dimethyl-1,4-phenylenediamine (Pa-CH₃) (0.15mmol, 20.4mg) were used to afford TpPa-CH₃-Gly as deep red powders (yield of 88%).

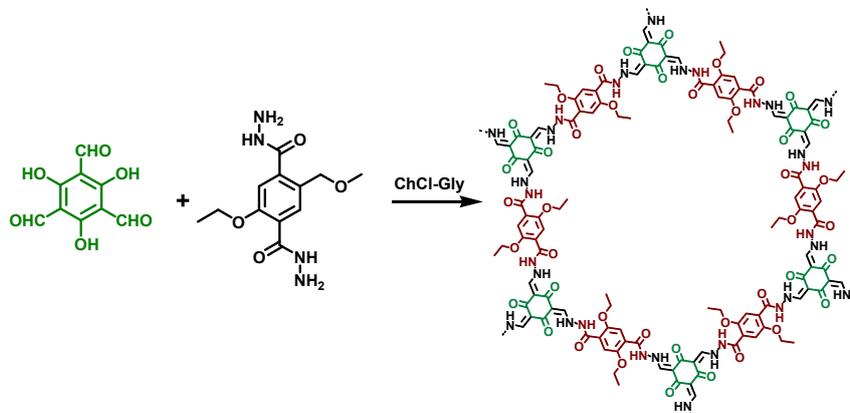
Synthesis of TpHa-Gly in ChCl-Gly



In a plastic centrifuge tube with the volume of 5.0 ml, Tp (0.10 mmol, 21.0 mg) and Ha (0.15mmol, 7.5mg) were dissolved in ChCl/Gly DES (7.6 eqv. 200 uL) under vigorous stirring. The mixture was kept at room temperature for 2h. The precipitate was isolated by filtration and washed with ethanol (15mL×2). The collected powders were refluxed

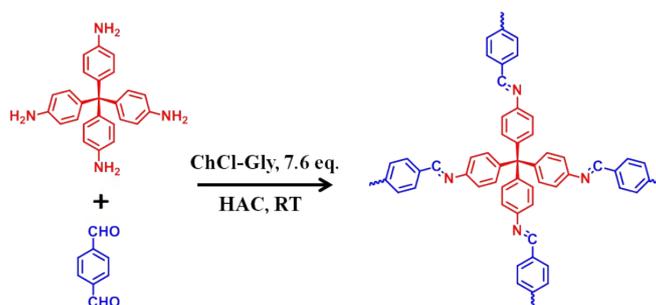
with DMF (10mL) for 8 h to remove any un-reacted residuals, then washed with ethanol (20mL×3) and acetone (20mL×3), and dried under vacuum at 100 °C for 12 h to give a red colored powder (yield of 90%).

Synthesis of TpDTPH-Gly in ChCl-Gly



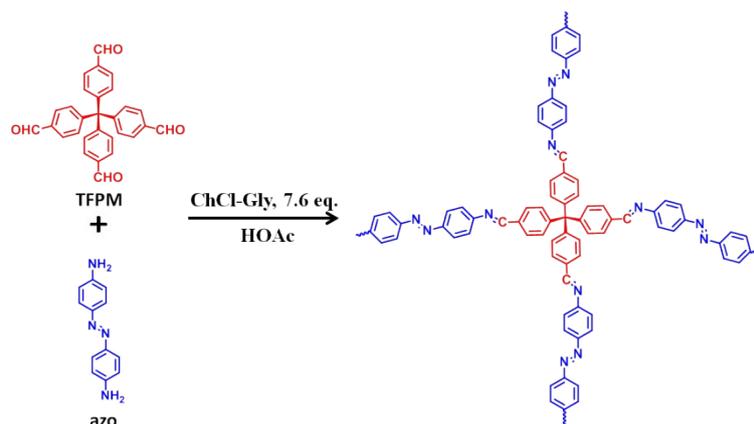
In a plastic centrifuge tube with the volume of 5.0 ml, Tp (0.10 mmol, 21.0 mg) and DTPH (0.15mmol, 42.3mg) were dissolved in ChCl/Gly DES (7.6 eqv. 200 uL) under vigorous stirring. The mixture was kept at 50 °C for 12h. The precipitate was isolated by filtration and washed with ethanol (15mL×2). The collected powders were refluxed with DMF (10mL) for 8 h to remove any un-reacted residuals, then washed with ethanol (20mL×3) and acetone (20mL×3), and dried under vacuum at 100 °C for 12 h to give a light yellow colored powder (yield of 80%).

Synthesis of 3D-COF-1 in ChCl-Gly



A centrifuge tube (5 mL) was charged with tetrakis(4-formylphenyl)-methane (TFPM) (21.6 mg, 0.05 mmol) and p-phenylenediamine (Pa) (10.8 mg, 0.1 mmol) in ChCl/gly (7.6 eq., 200uL) with acetic acid (6M, 8uL) as the catalyst, followed by keeping at room temperature for 2 hours to produce crystalline solids. The obtained light yellow precipitate was isolated by filtration and washed with acetone (20mL×3) and ethanol (20mL×3). The 3D-COF-10 was obtained after drying at 100°C under vacuum for 10 h (yield of 73%).

Synthesis of 3D-COF-HNU10 in ChCl-Gly



The procedure was almost the same as that mentioned above for 3D-COF-1 synthesis. A centrifuge tube (5 mL) was charged with tetrakis(4-formylphenyl)-methane (TFPM) (21.6 mg, 0.05 mmol) and 4,4'-azodianiline (Azo) (21.2 mg, 0.1 mmol) in ChCl/gly (200uL) with acetic acid (6M, 8uL) as the catalyst, followed by keeping at 50°C for 24 hours to produce crystalline solids. The obtained yellow precipitate was isolated by filtration and washed with acetone (20mL×3) and ethanol (20mL×3). The 3D-COF-HNU10 was obtained after drying at 100°C under vacuum for 10 h (yield of 69%).

Section S2: Figures

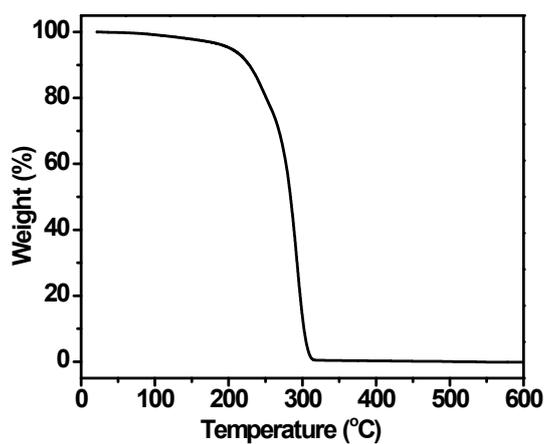


Figure S1. TGA curve of ChCl-Gly (1:2).

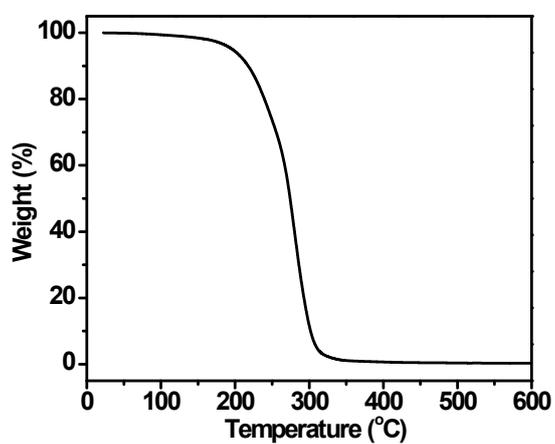


Figure S2. TGA curve of ChCl-U (1:2).

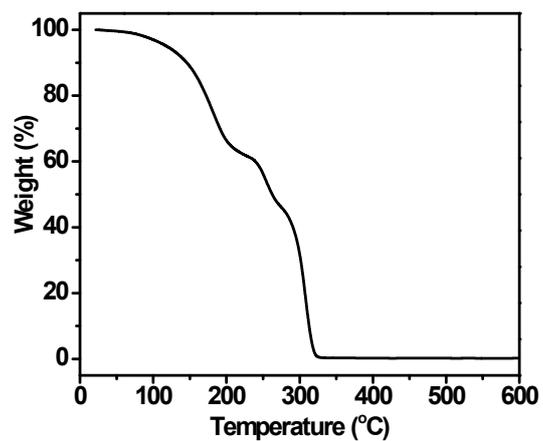


Figure S3. TGA curve of ChCl-EG (1:2).

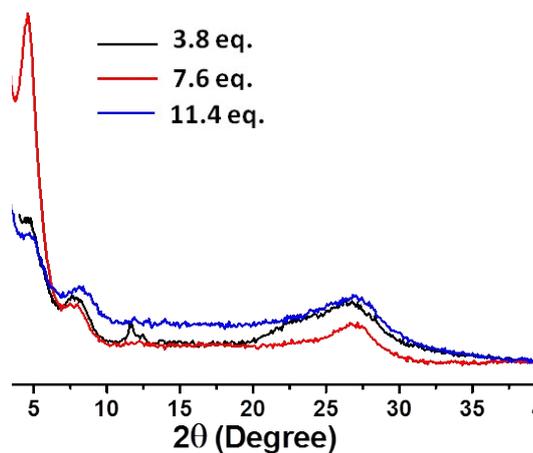


Figure S4. XRD patterns of the TpPa-Gly synthesized in ChCl/Gly with different equivalents with respect to Tp.

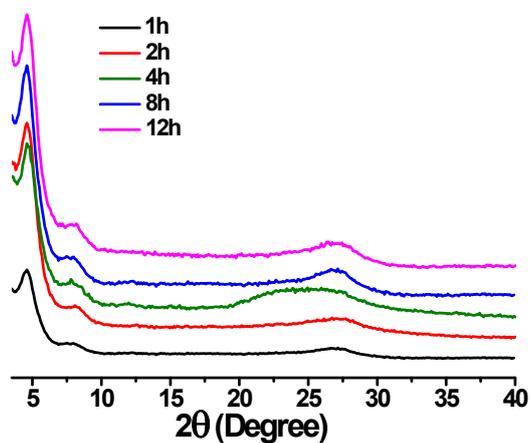


Figure S5. PXRD patterns of TpPa-Gly prepared in ChCl/Gly with different reaction time.

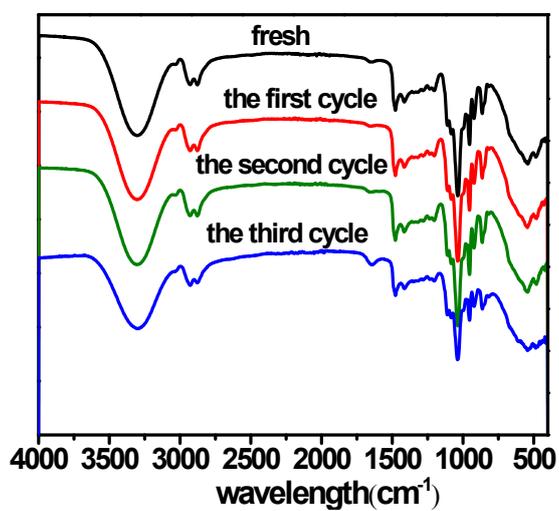


Figure S6. FT-IR spectra of ChCl-Gly (1:2) before and after each cycle.

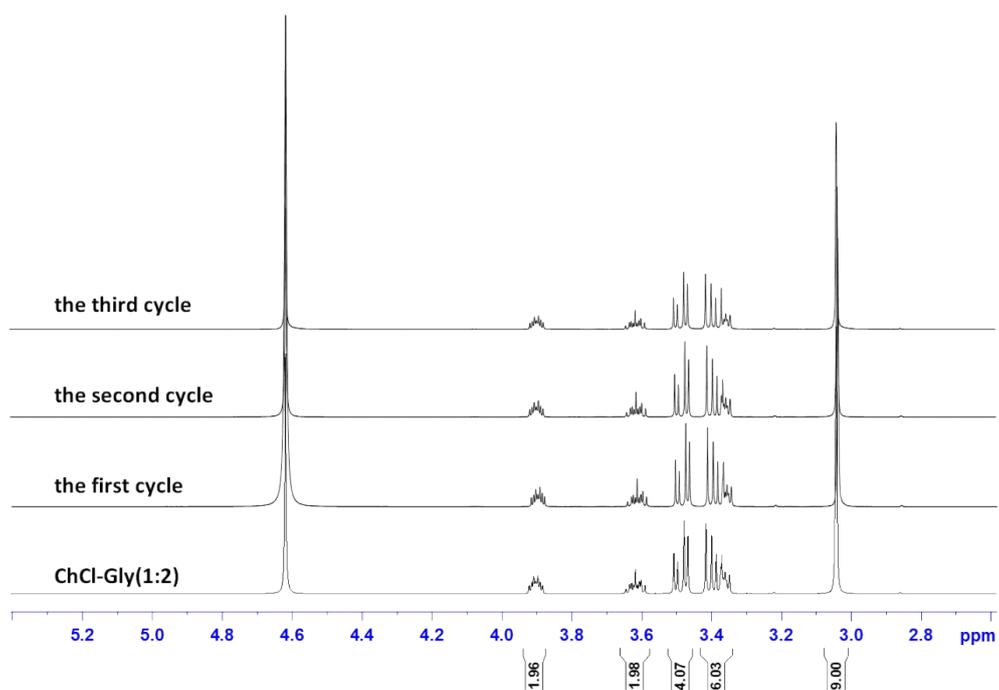


Figure S7. ^1H NMR spectra of ChCl-Gly (1:2) before and after each cycle.

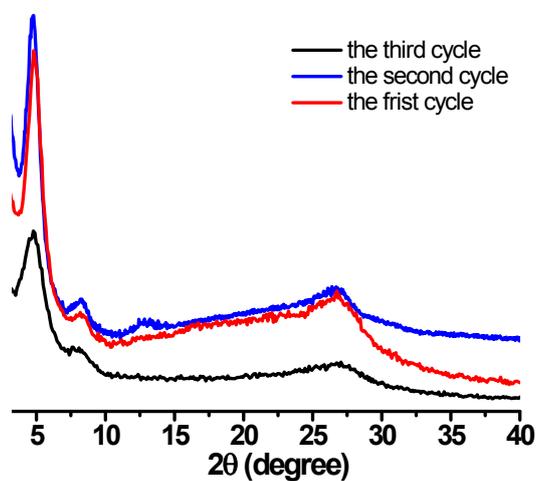


Figure S8. PXRD patterns of the recovered TpPa-Gly.

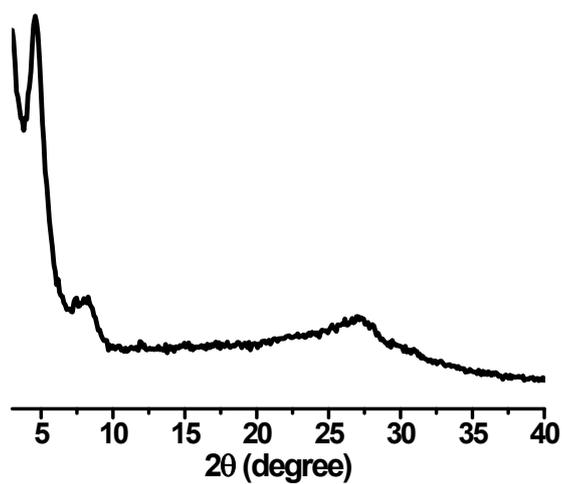


Figure S9. PXRD pattern of TpPa-Gly based on scale-up (1.6 g) synthesis by enlarging the amounts of reactants and solvents.

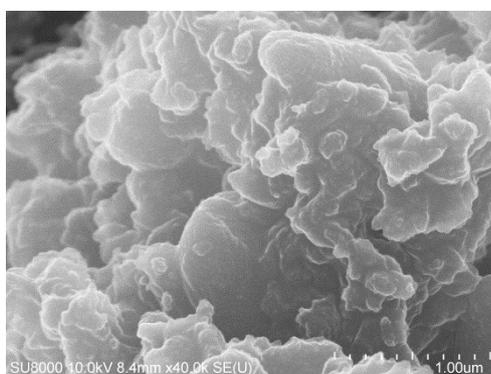


Figure S10. SEM images of the TpPa-Gly.

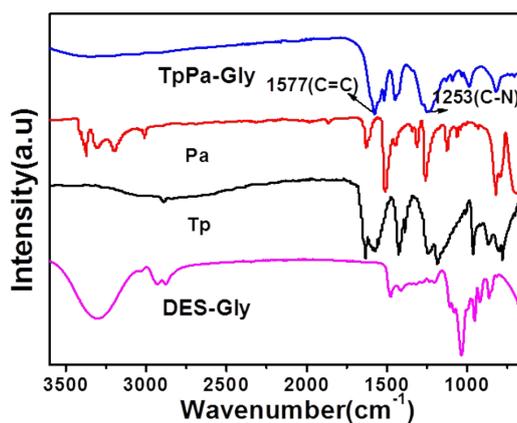


Figure S11. Comparison of the FT-IR spectra of TpPa-Gly with the precursor compounds Tp and Pa, and ChCl-Gly.

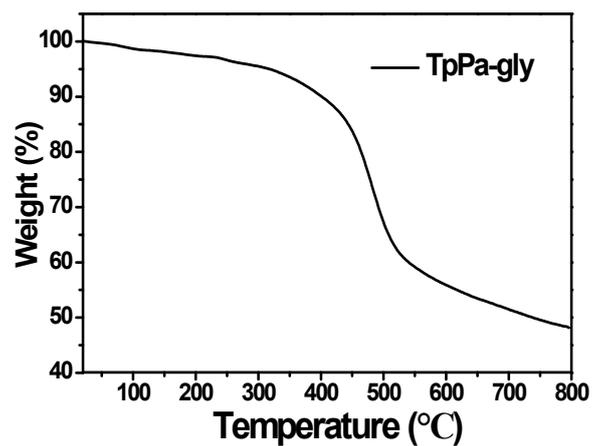


Figure S12. TGA curve of TpPa-Gly.

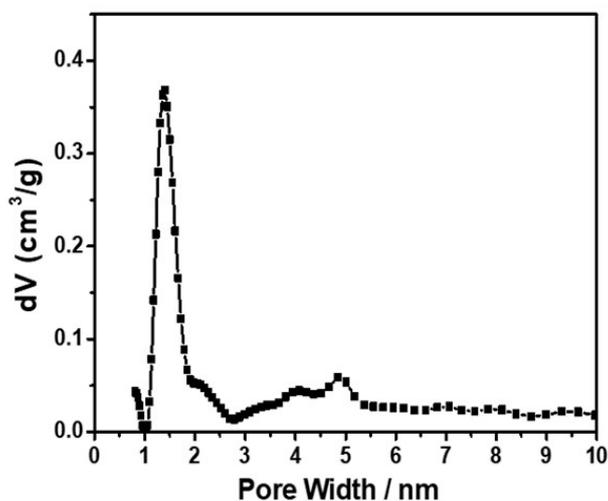


Figure S13. The pore-size distribution of TpPa-Gly estimated by NLDFT.

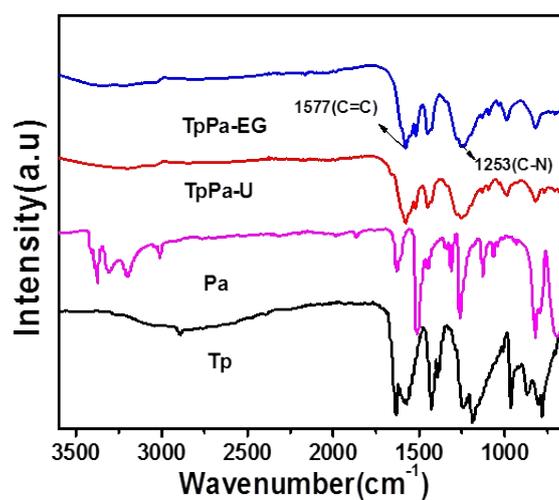


Figure S14. FT-IR spectra of the TpPa-EG (blue) and TpPa-U (red).

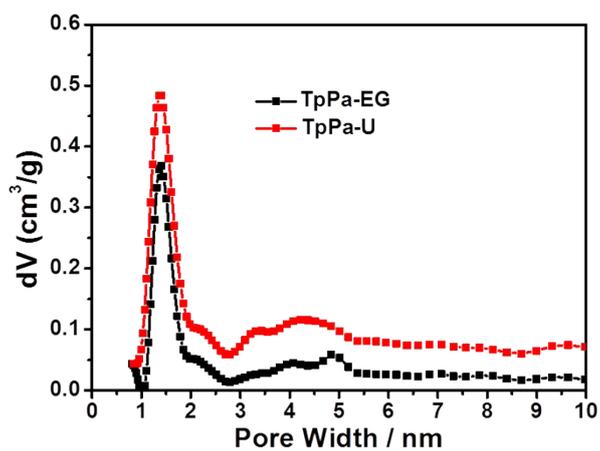


Figure S15. DFT pore size distribution for TpPa-EG and TpPa-U.

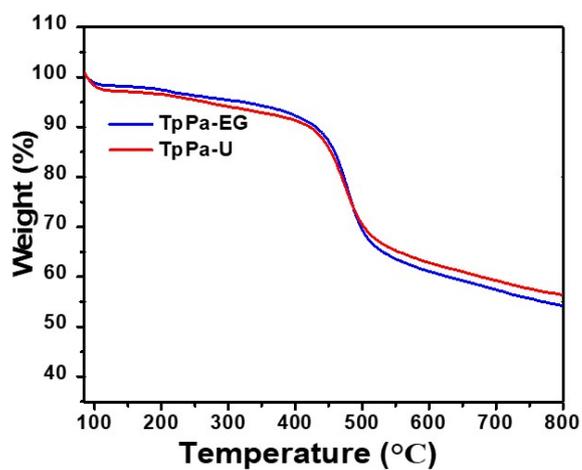


Figure S16. TGA curve for TpPa-EG (blue) and TpPa-U (red) under N₂ atmosphere to show the high thermal stability.

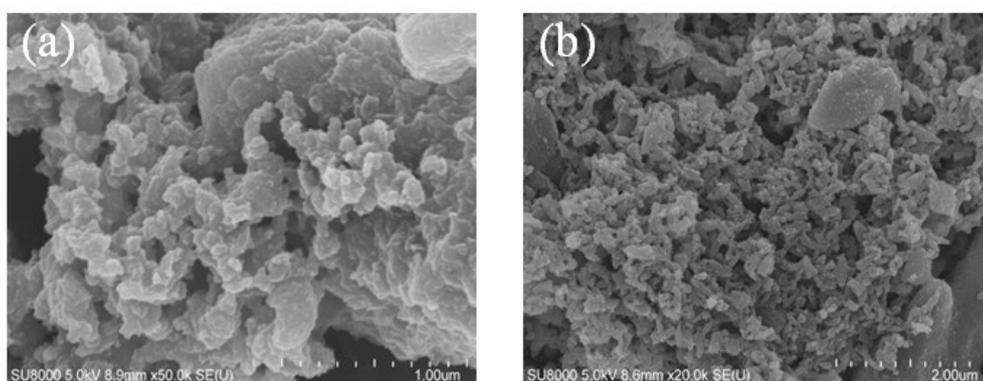


Figure S17. SEM images of the TpPa-EG (a) and TpPa-U (b).

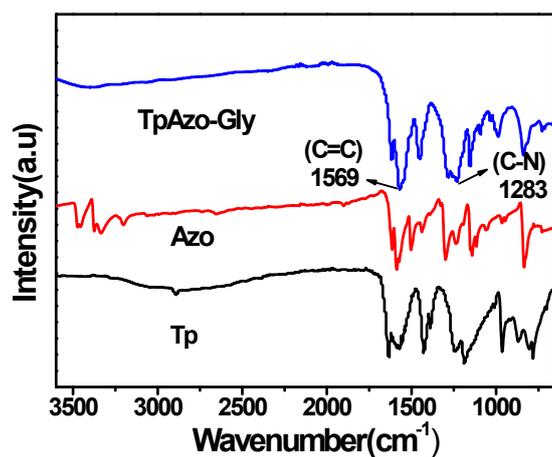


Figure S18. FT-IR spectra of TpAzo-Gly (blue).

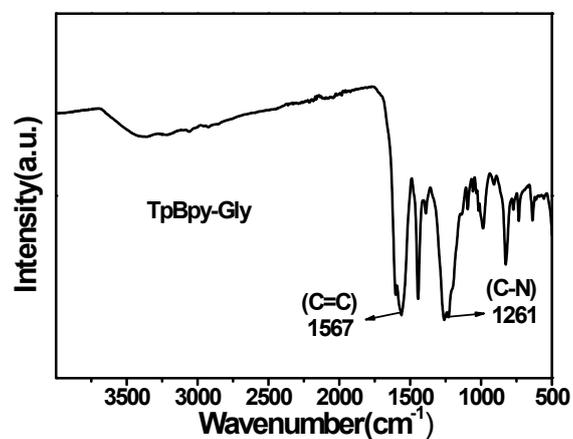


Figure S19. FT-IR spectra of TpBpy-Gly.

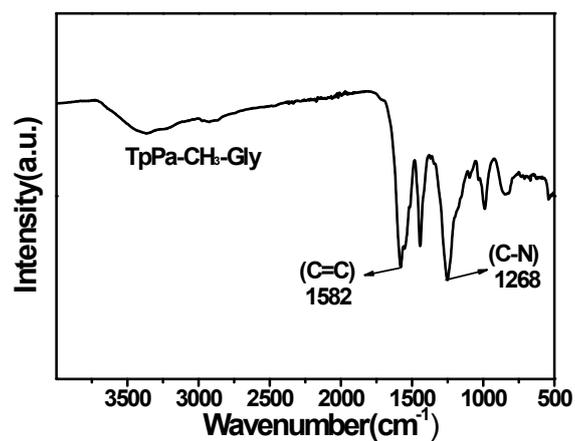


Figure S20. FT-IR spectra of TpPa-CH₃-Gly.

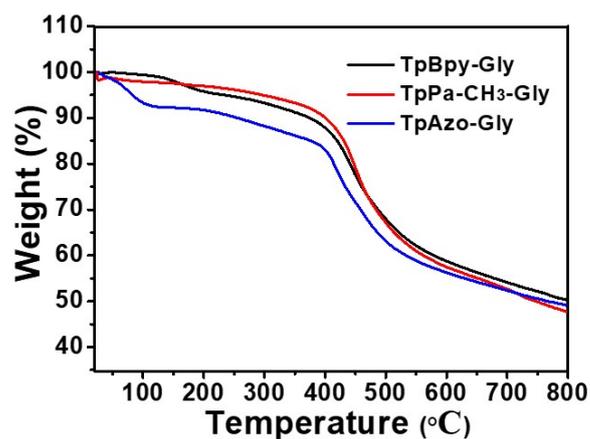


Figure S21. TGA curves of TpAzo-Gly (blue), TpBpy-Gly (black) and TpPa-CH₃-Gly (red) under N₂ atmosphere to show the high thermal stability.

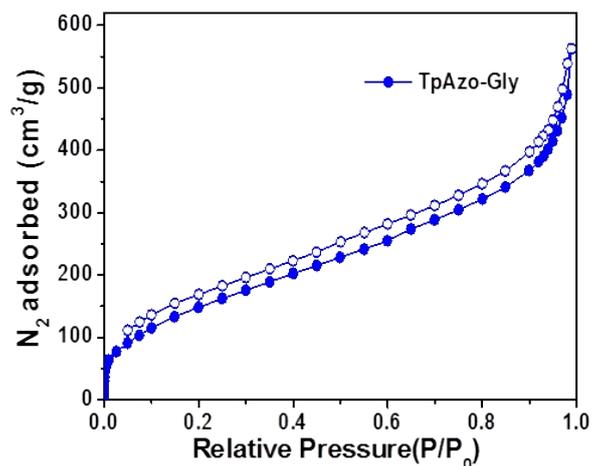


Figure S22. N₂ adsorption-desorption isotherms of TpAzo-Gly.

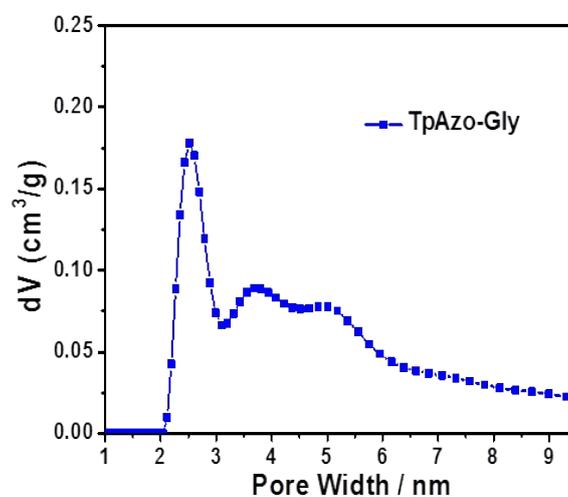


Figure S23. Pore-size distribution of TpAzo-Gly.

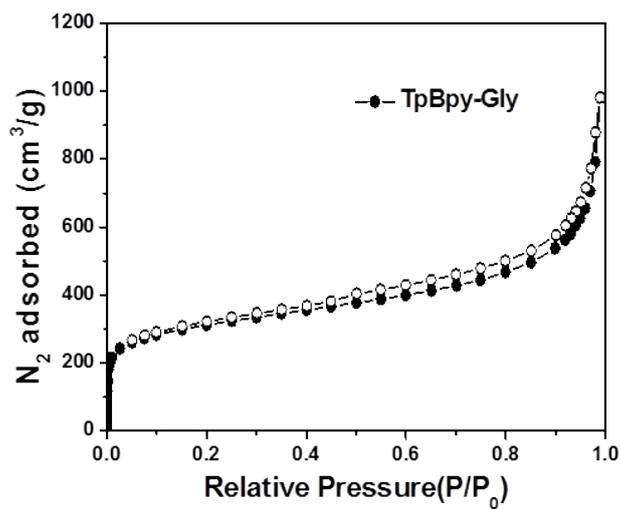


Figure S24. N₂ adsorption-desorption isotherms of TpBpy-Gly.

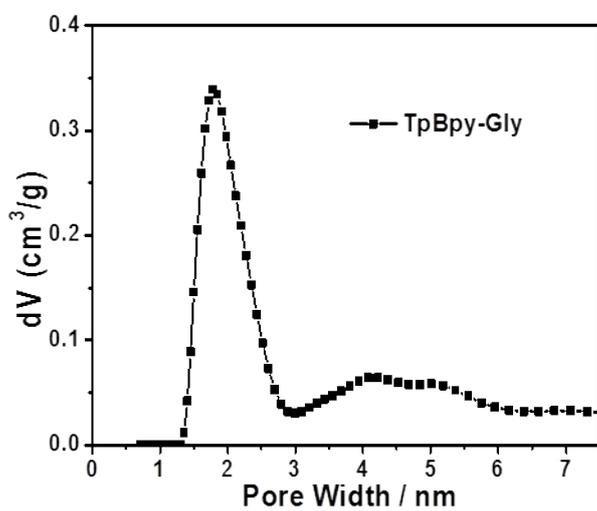


Figure S25. Pore-size distribution of TpBpy-Gly.

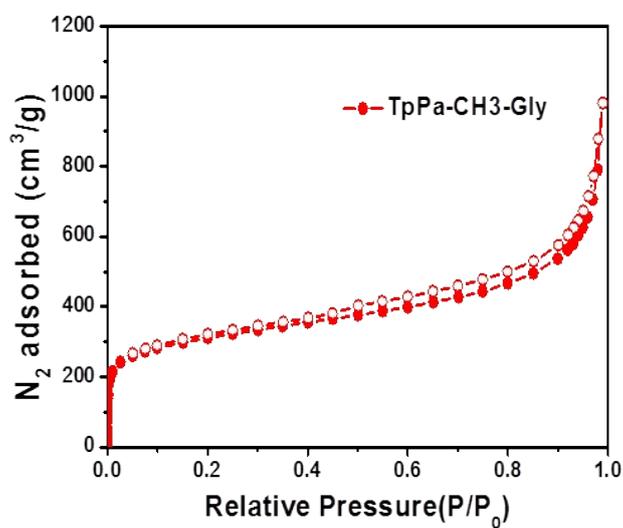


Figure S26. N₂ adsorption-desorption isotherms of TpPa-CH₃-Gly.

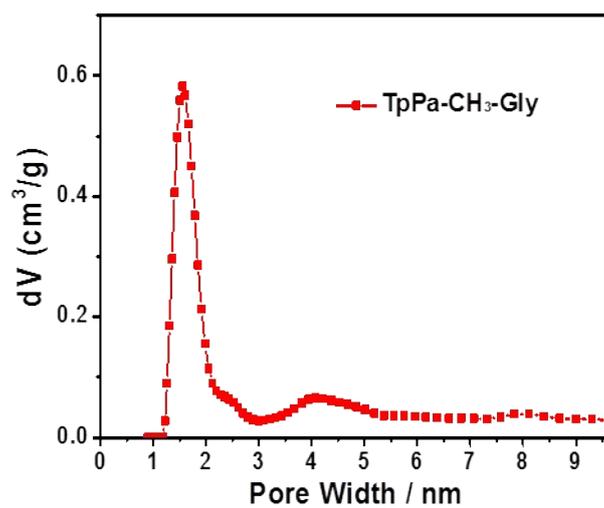


Figure S27. Pore-size distribution of TpPa-CH₃-Gly.

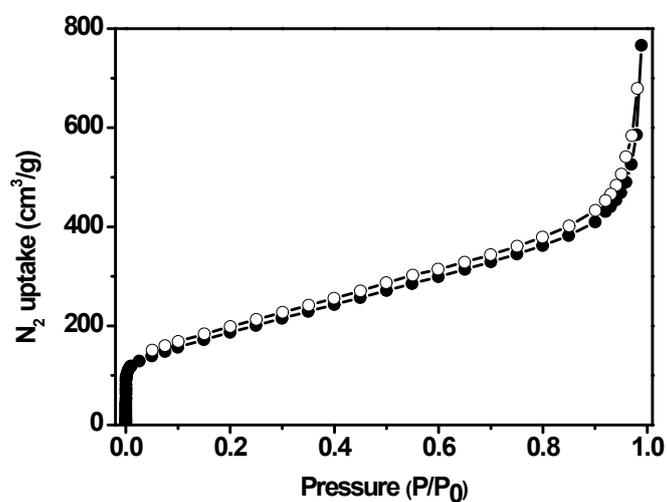


Figure S28. N₂ adsorption and desorption isotherms of TpHa-Gly.

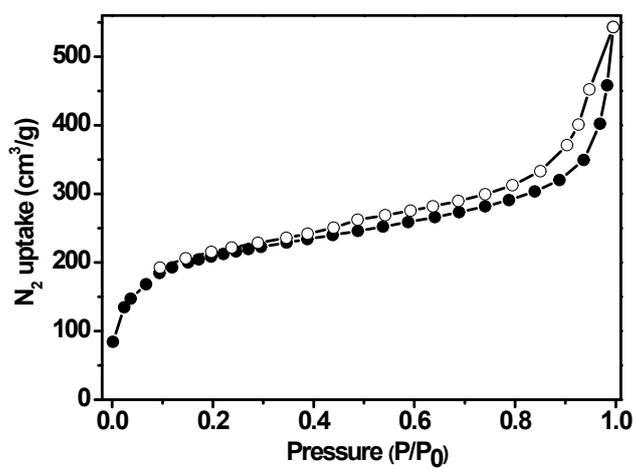


Figure S29. N₂ adsorption and desorption isotherms of TpDTPH-Gly.

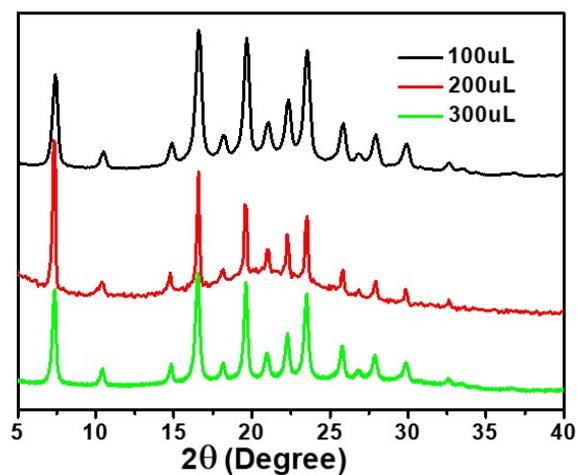


Figure S30. PXRD patterns of 3D-COF-1 prepared by using different amounts of ChCl/Gly.

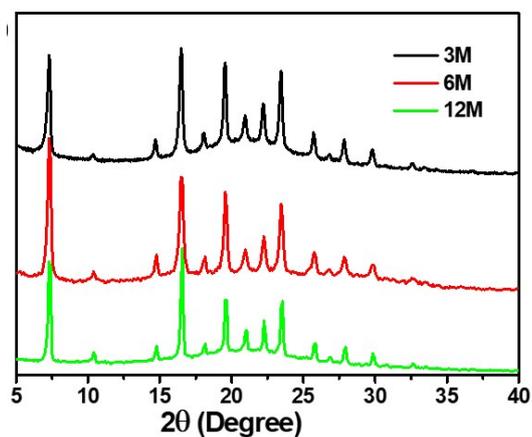


Figure S31. PXRD patterns of 3D-COF-1 prepared in the presence of aqueous 3M HOAc (black), 6 M HOAc (red), and 12 M HOAc (green) under ambient conditions.

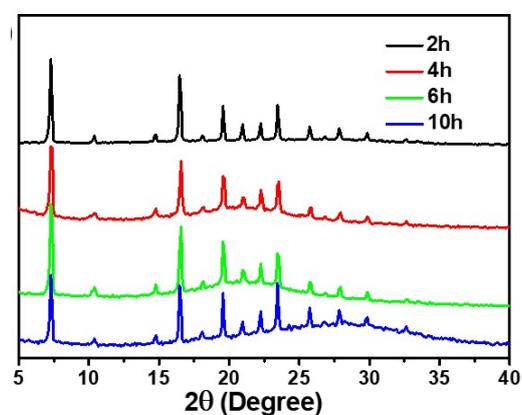


Figure S32. PXRD patterns of 3D-COF-1 prepared in ChCl/Gly with different reaction time.

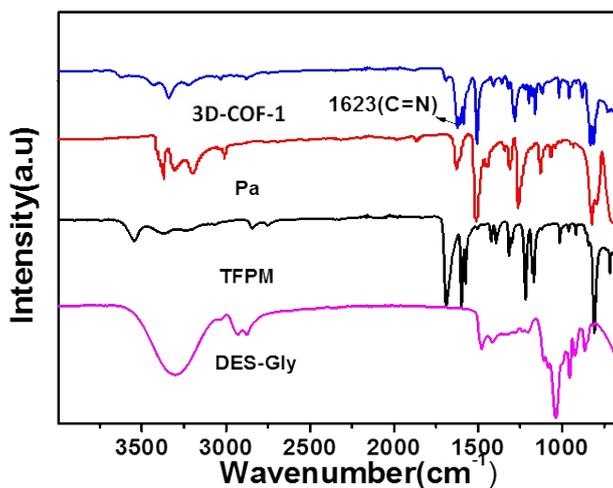


Figure S33. Comparison of the FT-IR spectra of 3D-COF-1 with the precursor compounds Pa and TFPM.

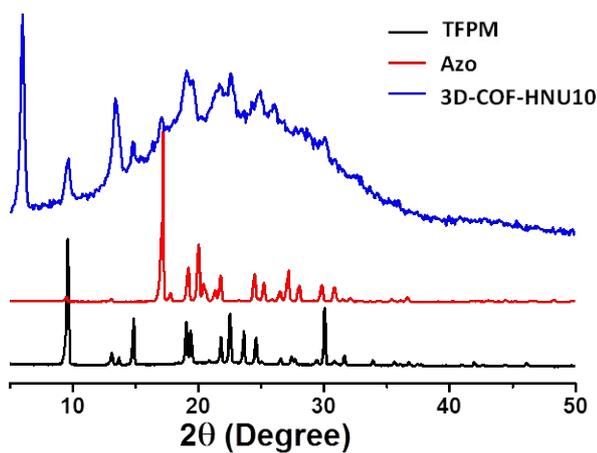


Figure S34. Comparison of the PXRD of 3D-COF-HNU10 with the precursor compounds Azo and TFPM.

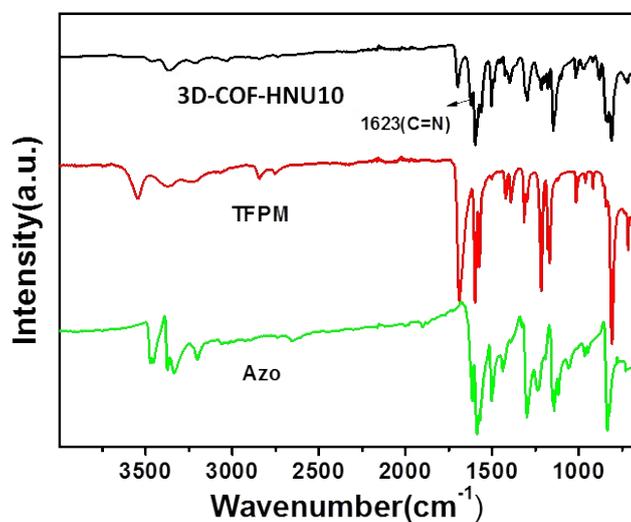


Figure S35. Comparison of the FT-IR spectra of 3D-COF-HNU10 with the precursor compounds Azo and TFPM.

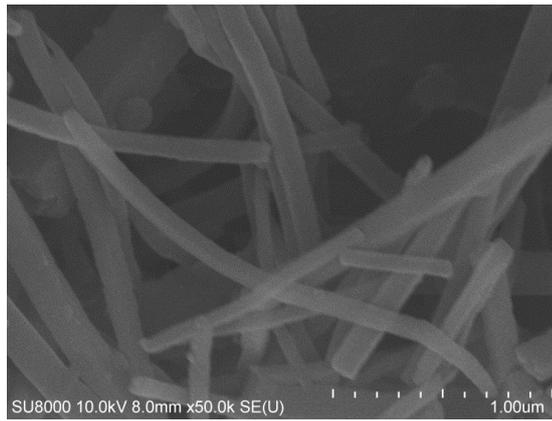


Figure S36. SEM images of 3D-COF-HNU10.

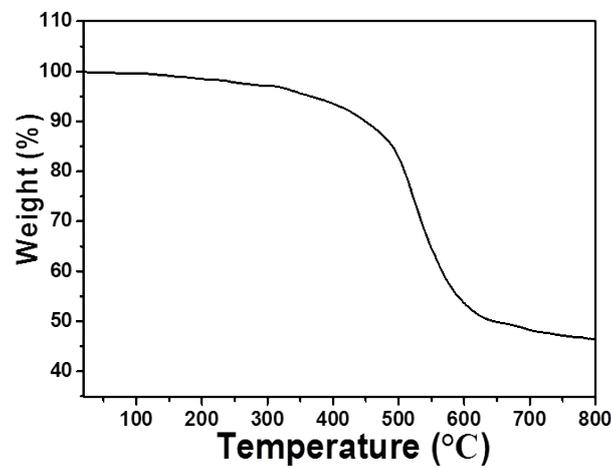


Figure S37. TGA curve of 3D-COF-HNU10 under N₂ atmosphere to show the high thermal stability.

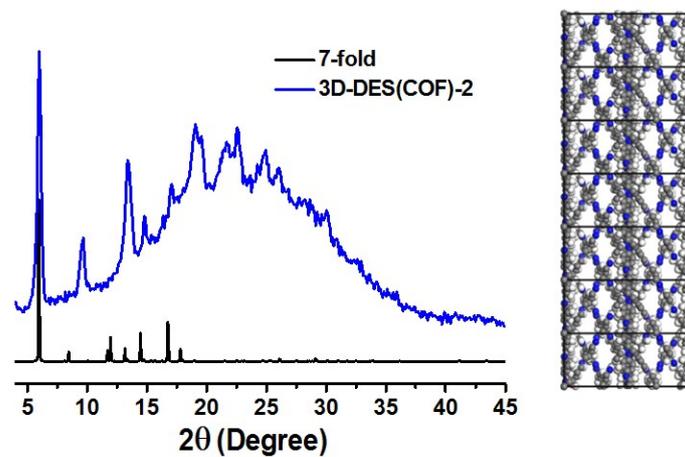


Figure S38. The calculated PXRD pattern of 3D-COF-HNU10 based on the 7-fold interpenetrated diamond net. 118P-4N₂, $a=b=29.635241\text{\AA}$, $c=11.74474\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

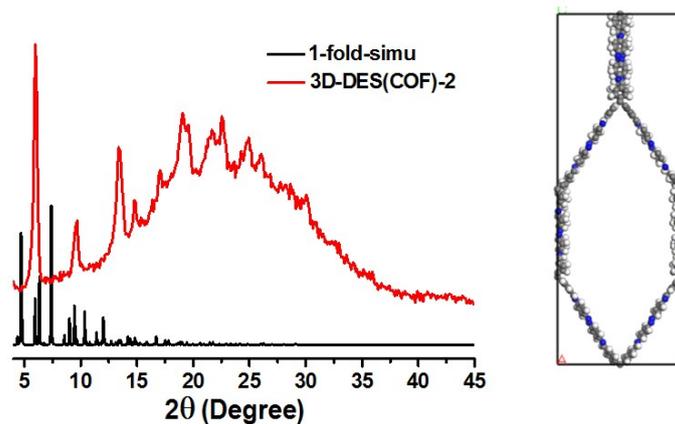


Figure S39. The calculated PXRD pattern of 3D-COF-HNU10 based on the 1-fold interpenetrated diamond net. 118P-4N2, $a=b=29.677974\text{\AA}$, $c=82.698616\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

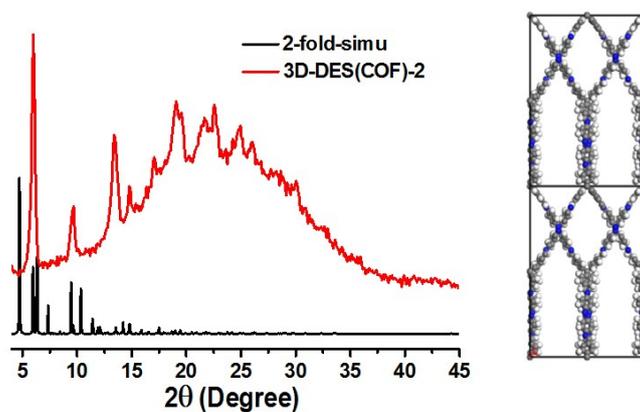


Figure S40. The calculated PXRD pattern of 3D-COF-HNU10 based on the 2-fold interpenetrated diamond net. 117P-4B2, $a=b=29.716863\text{\AA}$, $c=41.16785$, $\alpha=\beta=\gamma=90^\circ$.

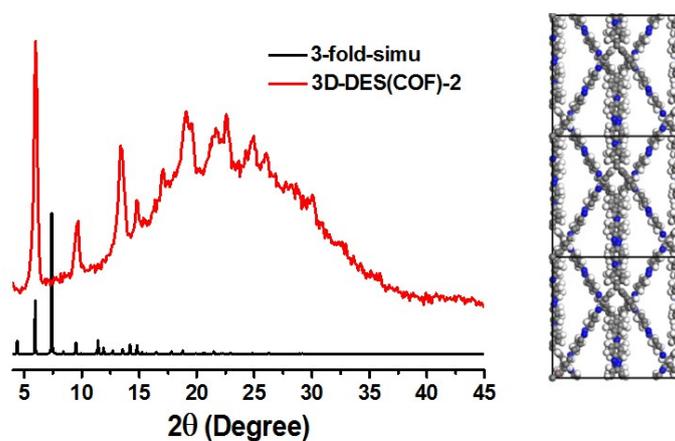


Figure S41. The calculated PXRD pattern of 3D-COF-HNU10 based on the 3-fold interpenetrated diamond net. 118P-4N2, $a=b=29.755285\text{\AA}$, $c=27.40066\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

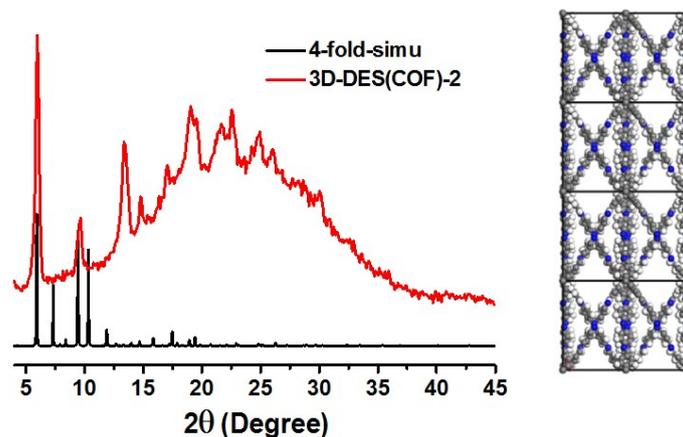


Figure S42. The calculated PXRD pattern of 3D-COF-HNU10 based on the 4-fold interpenetrated diamond net. 117P-4B2, $a=b=29.770039\text{\AA}$, $c=20.53345\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

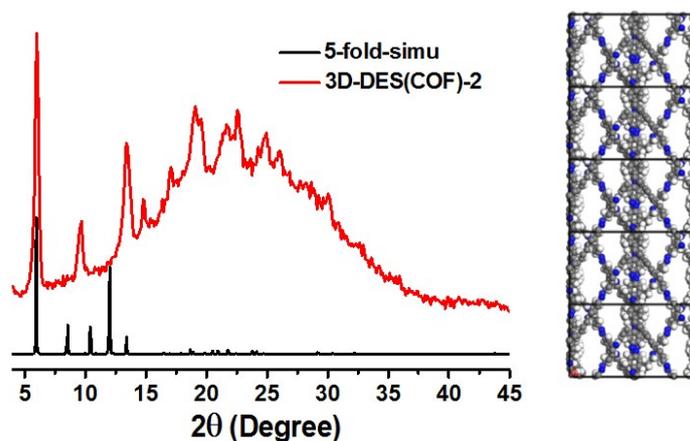


Figure S43. The calculated PXRD pattern of 3D-COF-HNU10 based on the 5-fold interpenetrated diamond net. 118P-4N2, $a=b=29.761953\text{\AA}$, $c=16.42007\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

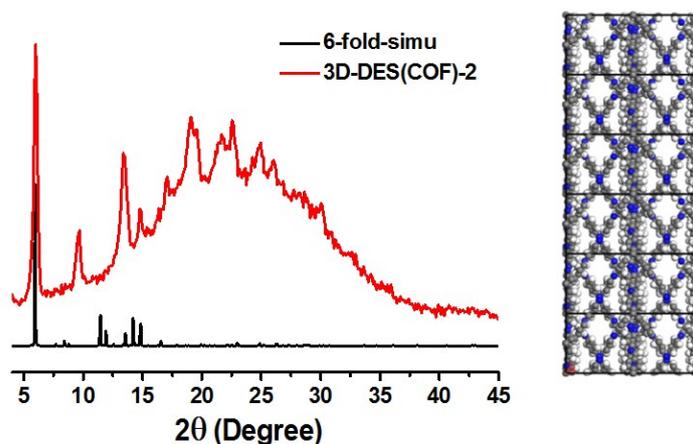


Figure S44. The calculated PXRD pattern of 3D-COF-HNU10 based on the 6-fold interpenetrated diamond net. 117P-4B2, $a=b=29.714523\text{\AA}$, $c=13.69055\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

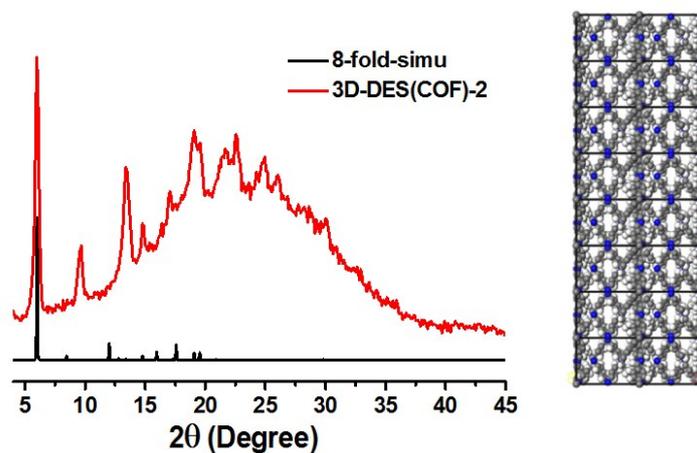


Figure S45. The calculated PXRD pattern of 3D-COF-HNU10 based on the 8-fold interpenetrated diamond net. 117P-4B2, $a=b=29.531112\text{\AA}$, $c=10.28493\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

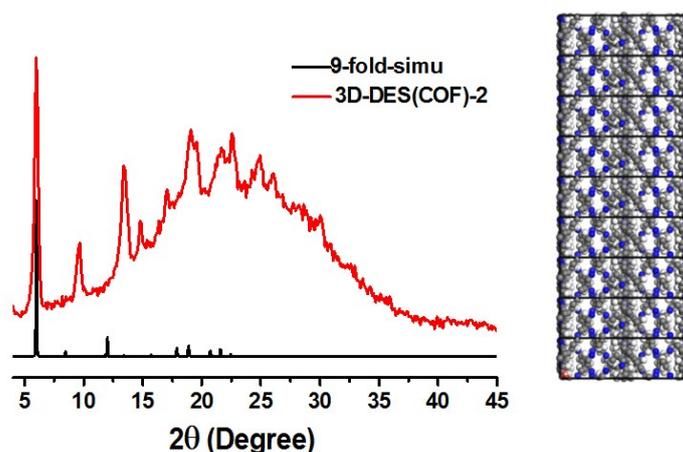


Figure S46. The calculated PXRD pattern of 3D-COF-HNU10 based on the 9-fold interpenetrated diamond net. 118P-4N2, $a=b=29.532956\text{\AA}$, $c=9.144992\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$.

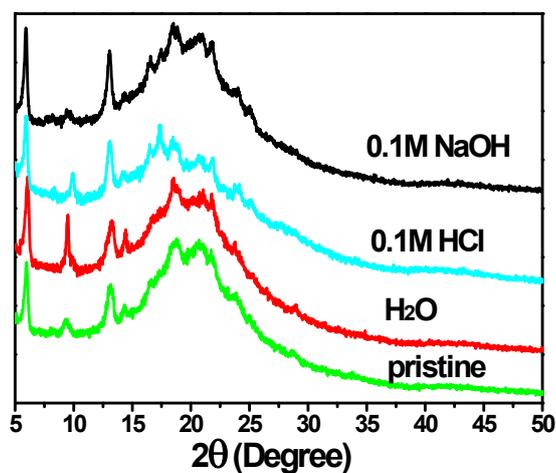


Figure S47. PXRD patterns of 3D-COF-HNU10 immersed in hot water, 0.1M HCl or 0.1M NaOH for 72 h.

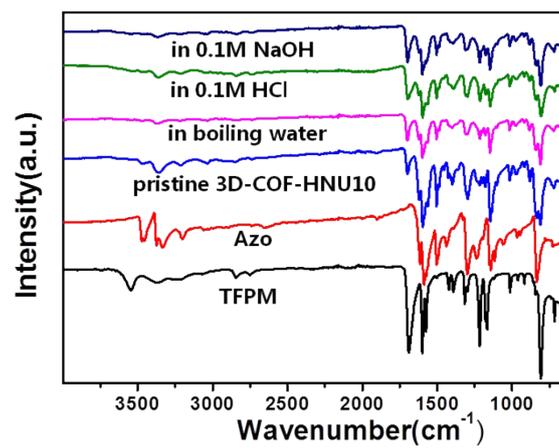


Figure S48. FTIR spectra of 3D-COF-HNU10 before and after 3-day immersed in boiling water, 0.1 M HCl, and 0.1 M NaOH, respectively.

Section S3: Tables

Table S1. The viscosity and thermal decomposition temperature of the DESs used in this work.

Entry	DES	Viscosity/mPa.s	Decomposition temperature/ °C
1	ChCl-Gly (1:2)	259 (25°C) ^[2]	210
2	ChCl-U (1:2)	750 (25°C) ^[2]	200
3	ChCl-EG (1:2)	37 (25°C) ^[2]	140

Table S2. The yield and material properties of the synthesized 2D and 3D COFs prepared by the conventional solvothermal method and present method

Entry	COF	Yield /%	BET surface area/ m ² /g	Pore size /nm	Ref.
1	TpPa	91	747	1.4	This work
		80	535	1.25	<i>J. Am. Chem. Soc.</i> 2012, 134, 19524
2	TpPa-CH ₃	88	1330	1.5	This work
		82	339	1.35	<i>J. Am. Chem. Soc.</i> 2012, 134, 19524
3	TpAzo	85	573	2.3	This work
		75	1328	2.5	<i>J. Am. Chem. Soc.</i> 2014, 136, 6570
4	TpBpy	83	955	1.9	This work
		---	1660	2.1	<i>Chem. Mater.</i> 2016, 28, 4375
5	TpHa	90	671	0.6	This work
		--	415	0.9	<i>Chem. Mater.</i> 2016, 28, 1277
6	TpDTPH	80	796	0.7-1.5	This work
		--	757	2.1	<i>Chem. Mater.</i> 2016, 28, 1277
7	3D-COF-1	73	511	1.7, 5	This work
		80	596	--	<i>J. Am. Chem. Soc.</i> 2018, 140, 4494
8	3D-COF-HNU10	69	309	1.7, 5	This work
		--	--	--	solvothermal method

Table S3. Unit cell parameters and fractional atomic coordinates for 3D-COF-1 based on the 5-interpenetrated diamond net³

Space group		<i>I</i> 4 ₁ /a	
Calculated unit cell		$a = b = 23.6865 \text{ \AA}, c = 13.3002 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$	
atoms	x	y	Z
C1	0.4499	0.7218	0.6044
C2	0.4936	0.714	1.53114
N3	0.484	0.67849	1.43836
C4	0.5441	0.7442	1.5553
C5	0.5195	0.6658	1.3615
C6	0.5096	0.6273	1.2650
C7	0.5547	0.6176	1.1960
C8	0.5508	0.5816	1.108
C9	0.500	0.55273	1.0798
C10	0.4550	0.5628	1.1490
C11	0.459	0.5988	1.2372
H12	0.4081	0.7005	0.5937
H13	0.5815	0.7419	1.5035
H14	0.5633	0.6837	1.3595
H15	0.5966	0.6385	1.20811
H16	0.5886	0.5752	1.0589
H17	0.4129	0.5422	1.1365
H18	0.42	0.60371	1.28432
C19	0	0.5	0.75

Table S4. Unit cell parameters and fractional atomic coordinates for 3D-COF-10 based on the 7-interpenetrated diamond net

Space group	P-4N2		
Calculated unit cell	a=b=29.635241Å c=11.744742 Å, $\alpha = \beta = \gamma = 90^\circ$		
atoms	x	y	z
C1	0.94137	0.46325	3.88606
C2	0.19364	0.46745	4.30777
C3	0.12797	0.48210	4.12331
C4	0.09972	0.48955	4.02161
C5	0.08227	0.45132	3.96824
C6	0.05243	0.45542	3.87822
C7	0.04035	0.49801	3.83327
H8	0.19457	0.44066	4.24560
H9	0.13387	0.44737	4.14721
H10	0.09018	0.41783	3.99954
H11	0.03732	0.42467	3.84627
C12	0.21832	0.46159	4.40806
C13	0.22023	0.49588	4.48921
H14	0.23666	0.43052	4.42242
C15	0.17152	0.54215	4.36963
C16	0.16941	0.50775	4.28818
N17	0.14273	0.51475	4.18714
C18	0.08811	0.53252	3.97973
H19	0.15329	0.57328	4.35524
H20	0.04835	0.57008	3.85879
H21	0.10074	0.56251	4.02169
C22	0.19671	0.53636	4.46972
H23	0.19809	0.56325	4.53192
C24	0.47291	0.36547	-1.14323
C25	0.48166	0.39645	-1.23897
C26	0.44661	0.40594	-1.31528
C27	0.45248	0.43736	-1.40253
C28	0.49424	0.45948	-1.41801
H29	0.44090	0.34818	-1.14305
H30	0.41388	0.39022	-1.30463
H31	0.42331	0.44559	-1.45360
N32	0.24707	0.48904	4.58909
C33	0.44889	0.47037	5.34161
C34	0.41786	0.47657	5.25329
H35	0.46624	0.43828	5.34811
H36	0.41136	0.44917	5.19443
N37	0.50176	0.36030	-1.06064

C38	0.45498	0.30951	-0.93789
H39	0.42610	0.31169	-0.99323
C40	0.45077	0.28308	-0.83998
C41	0.48652	0.27918	-0.76347
N42	0.48034	0.25199	-0.66400
H43	0.41946	0.26557	-0.82281
C44	0.53138	0.32880	-0.88370
C45	0.49563	0.33249	-0.96127
H46	0.56260	0.34663	-0.90011
C47	0.52701	0.30229	-0.78532
H48	0.55490	0.29970	-0.72620
C49	0.50000	0.00000	0.25000
C50	0.50000	0.50000	-1.50000

Table S5 Synthesis of 3D-COF-HNU10 by the polymerization of TFPM (0.1 mmol, 1 equiv) and Azo (0.2 mmol, 2 equiv) at different reaction conditions^a.

Solvents	AcOH	Product	PXRD
Dioxane : mesitylene (1mL : 1mL)	0.2mL/ 6M	yellow solid	No peaks
Dioxane : mesitylene (0.5 mL:0.5 mL)	0.1mL/ 3M	yellow solid	No peaks
Dioxane : mesitylene (1.5 mL: 0.5 mL)	0.1mL/ 6M	yellow solid	No peaks
Dioxane (2 mL)	0.1mL/ 6M	No product	—
Dioxane (1 mL)	0.1mL/ 3M	No product	—
DMAC : o-DCB (1 mL: 1 mL)	0.1mL/ 6M	No product	—
DMAC : o-DCB (1.5 mL: 0.5 mL)	0.2mL/ 6M	No product	—
BmimTf ₂ N (100uL) ^b	0	No product	—
BmimTf ₂ N (100uL) ^b	8uL AcOH	yellow solid	No peaks

Reaction conditions: a, 120°C, 3days in sealed tubes. b, 25°C, 12 h in an open system.

Section S4: References

- [1] Abbott A. P., Boothby D., Capper G., et al. Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *J. Am. Chem. Soc.*, **2004**, 126, 9142-9147.
- [2] C. D'Agostino, R. C. Harris, A. P. Abbott, L. F. Gladdena, M. D. Mantle, *Phys. Chem. Chem. Phys.*, **2011**, 13, 21383-21391.
- [3] Guan X., Ma Y., Li H., Yusran Y., Xue M., Fang Q., Yan, Y., Valtchev V., Qiu S., Fast, Ambient Temperature and Pressure Ionothermal Synthesis of Three-Dimensional Covalent Organic Frameworks. *J. Am. Chem. Soc.*, **2018**, 140, 4494-4498.