Supplementary Information

Enhanced proton conductivity in azole-functionalized 3D single-crystalline COFs achieved via solvent-free melt-phase postsynthetic modification

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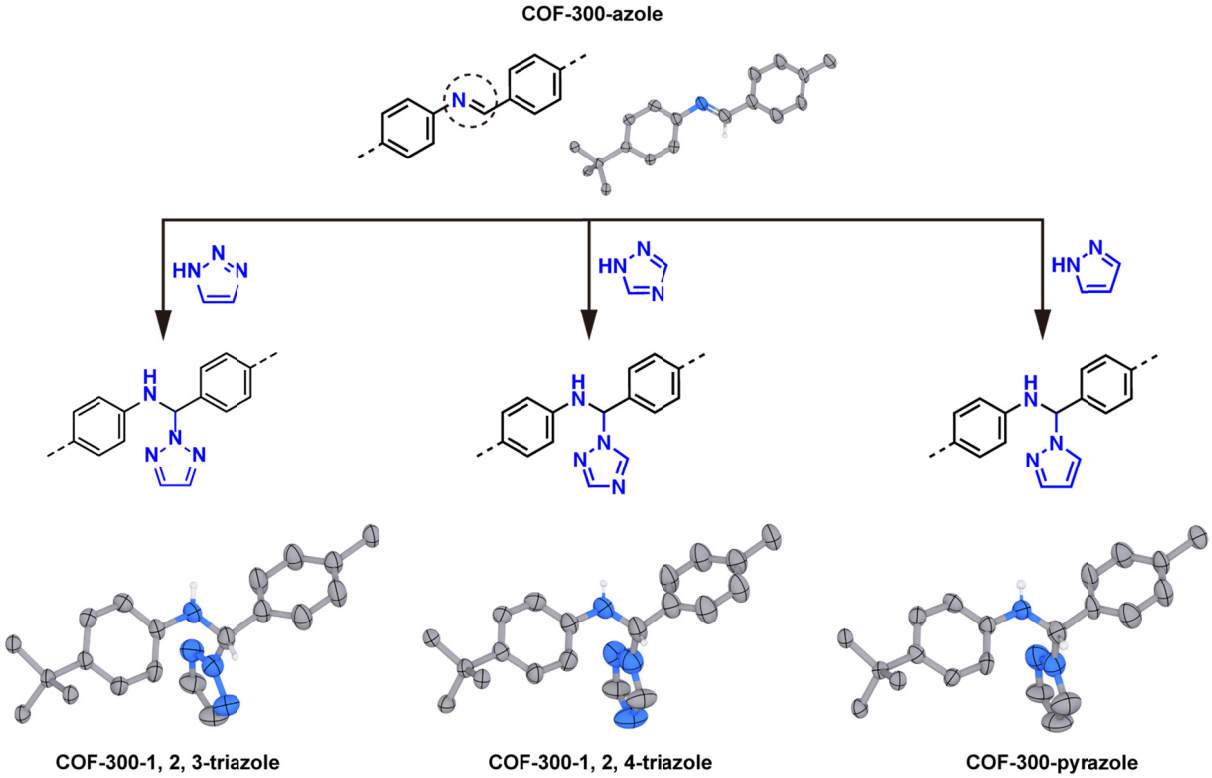
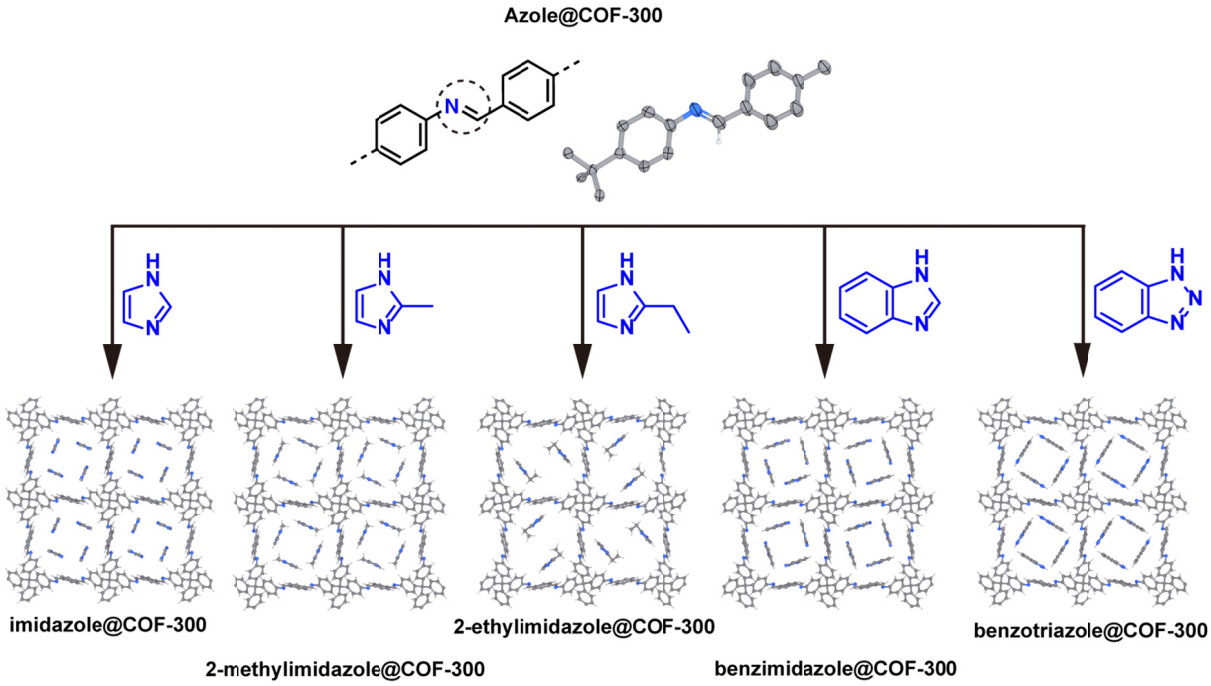
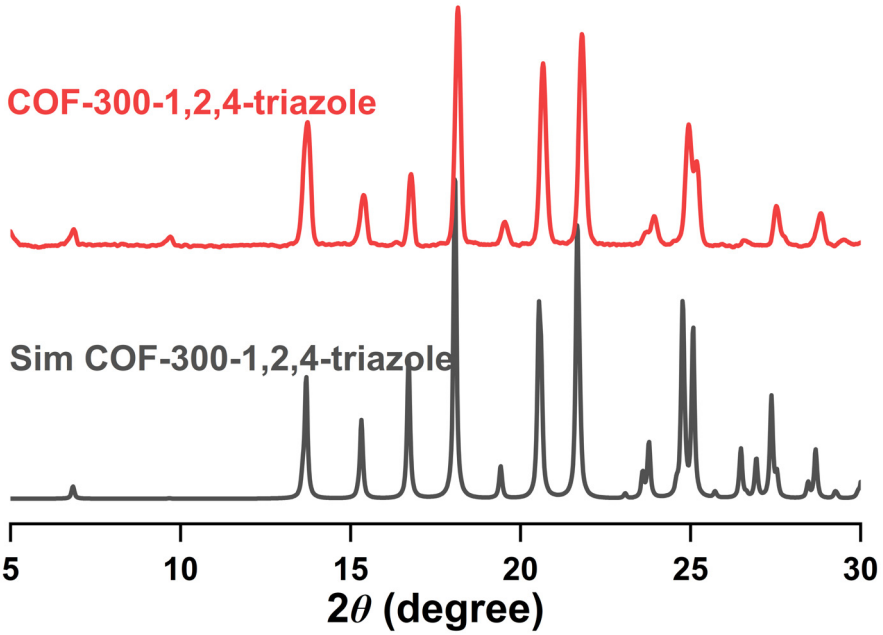


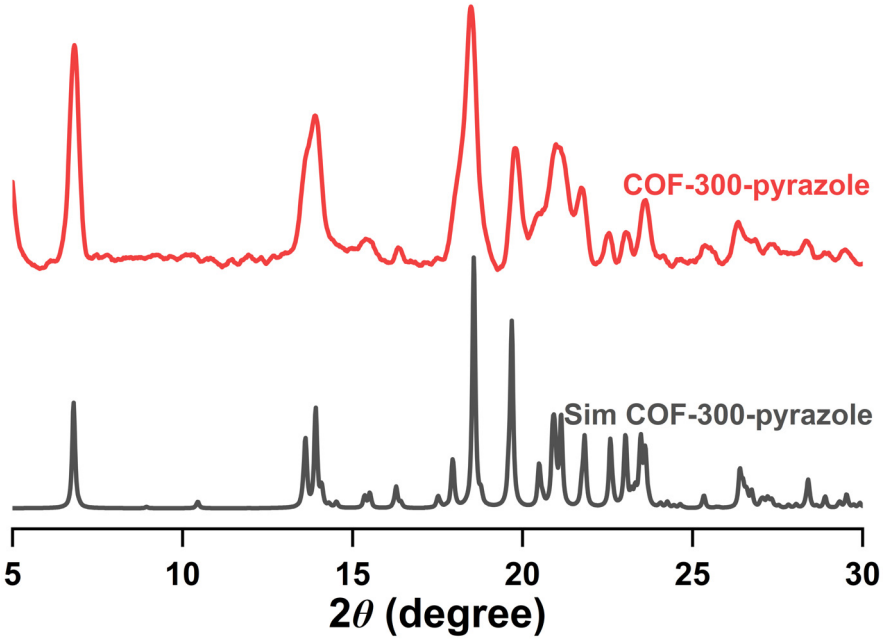
Supplementary Fig. 1. Crystal structures of COF-300-azole, including 1,2,3-triazole, 1,2,4-triazole, and pyrazole.



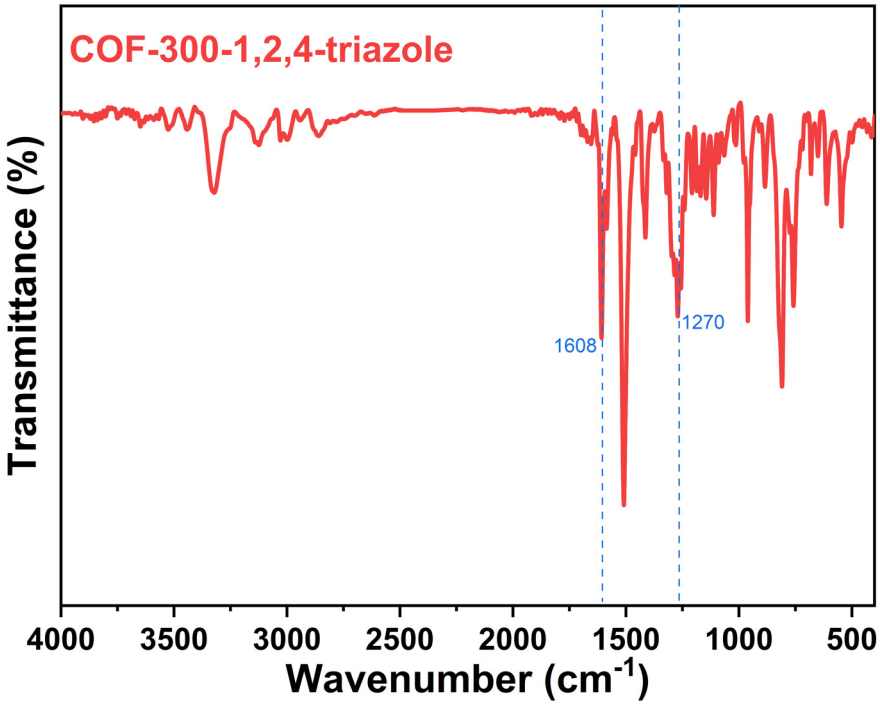
Supplementary Fig. 2. Crystal structures of azole@COF-300, including imidazole, 2-methylimidazole, 2-ethylimidazole, benzimidazole, and benzotriazole.



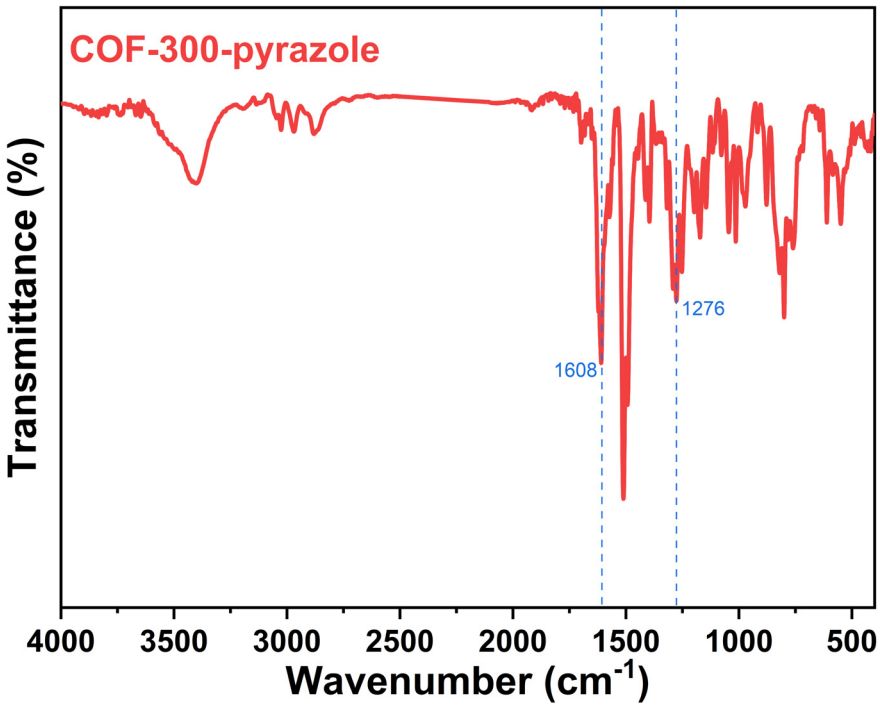
Supplementary Fig. 3. PXRD patterns for COF-300-1,2,4-triazole.



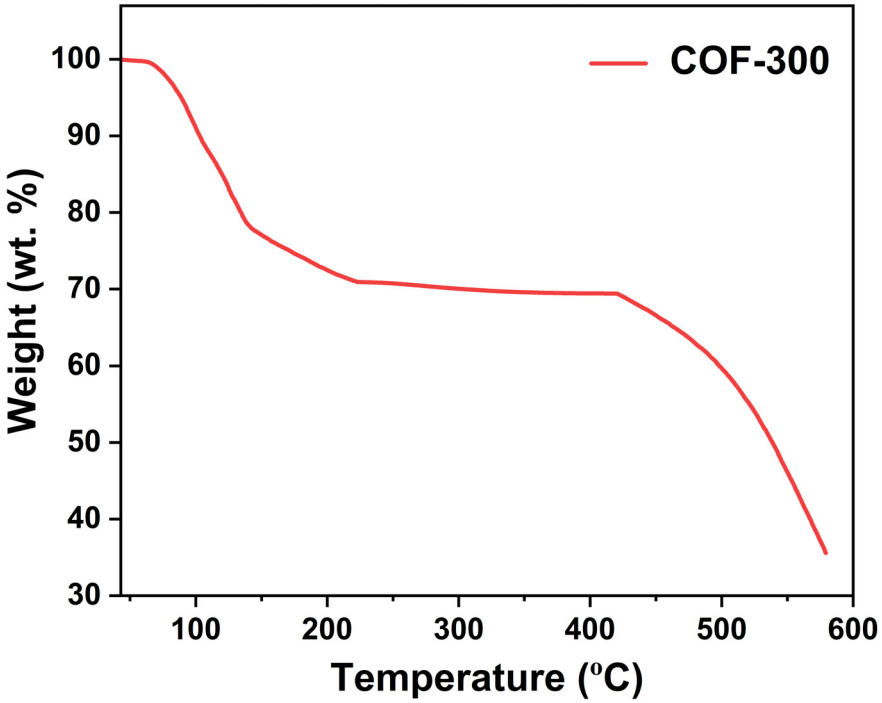
Supplementary Fig. 4. PXRD patterns for COF-300-pyrazole.



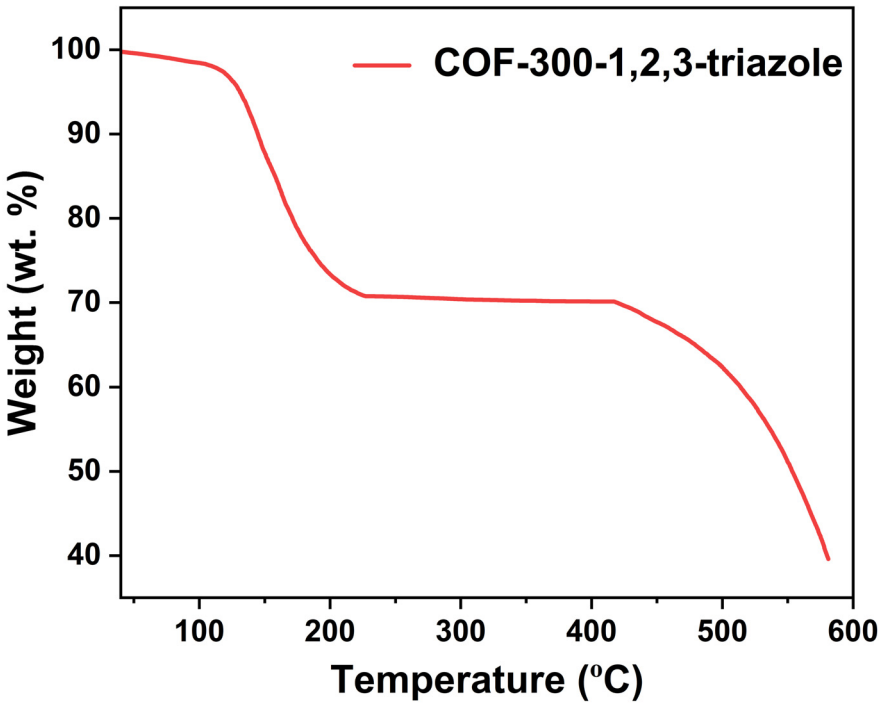
Supplementary Fig. 5. The FT-IR spectra of COF-300-1,2,4-triazole.



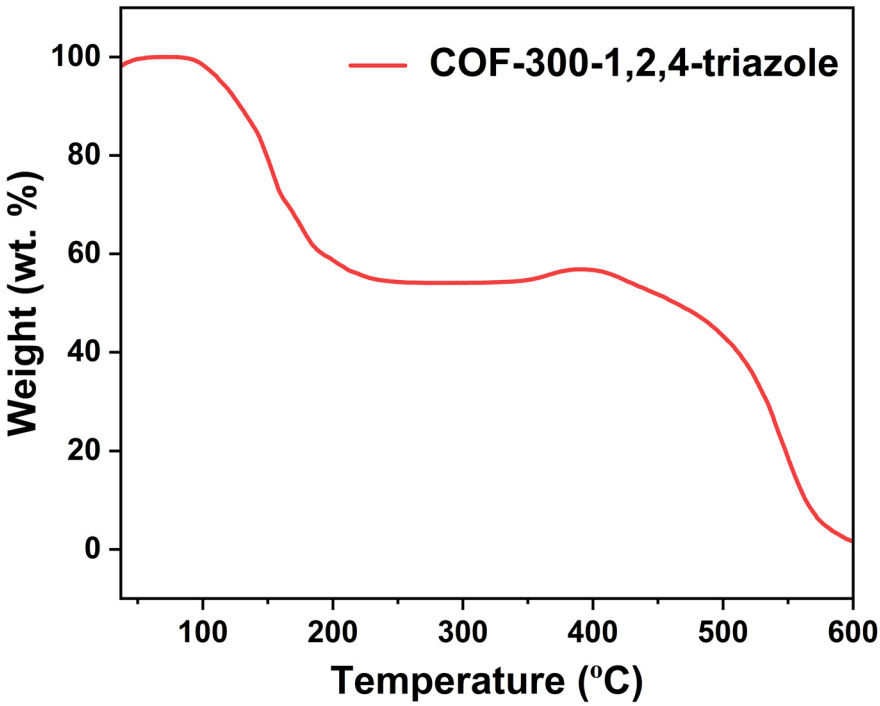
Supplementary Fig. 6. The FT-IR spectra of COF-300-pyrazole.



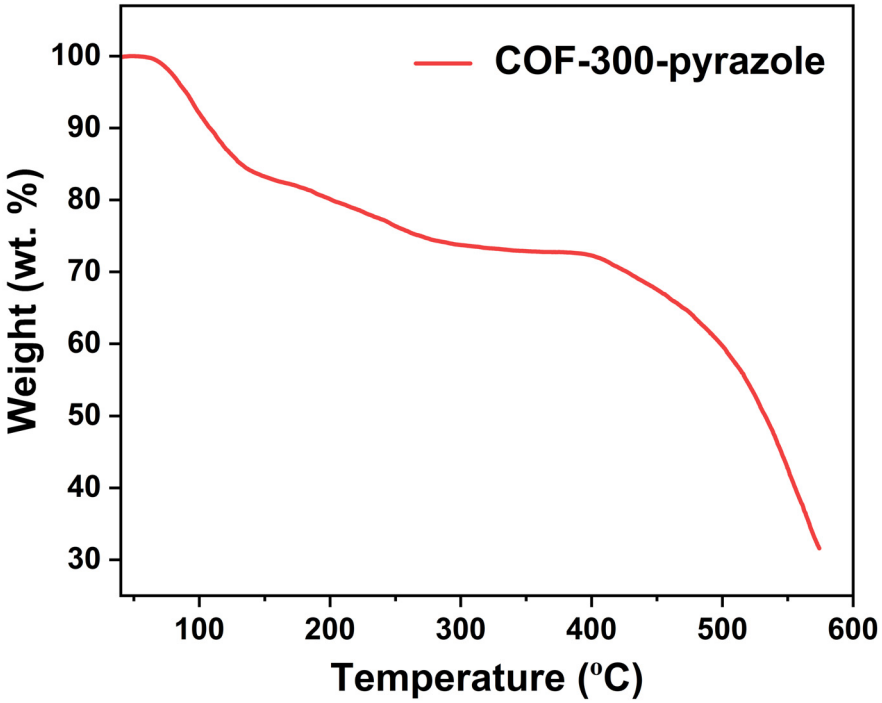
Supplementary Fig. 7. The TG curve of COF-300.



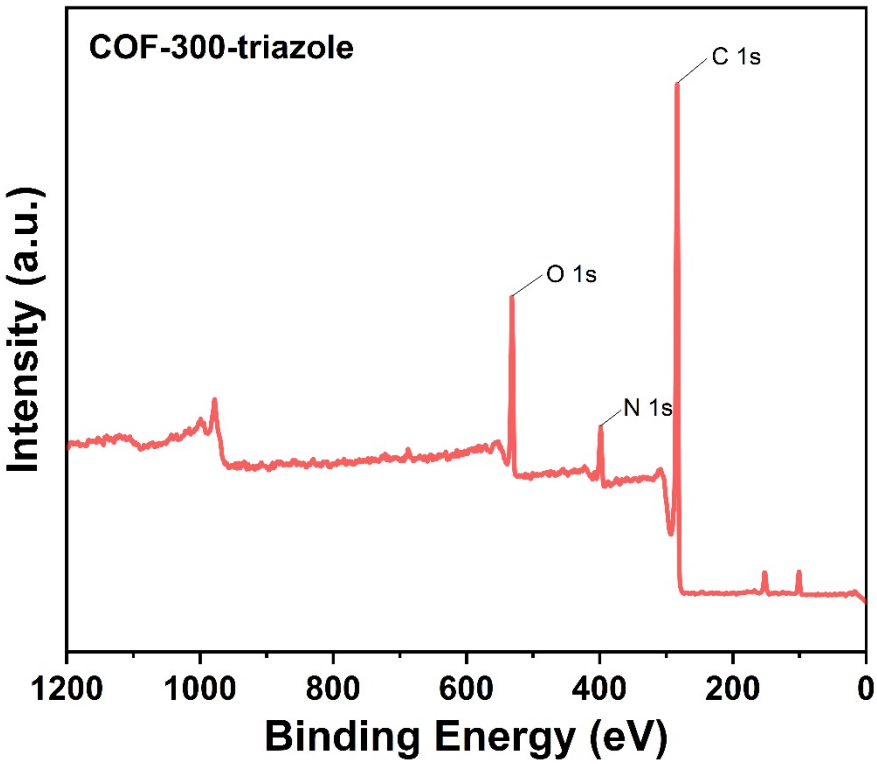
Supplementary Fig. 8. The TG curve of COF-300-1,2,3-triazole.



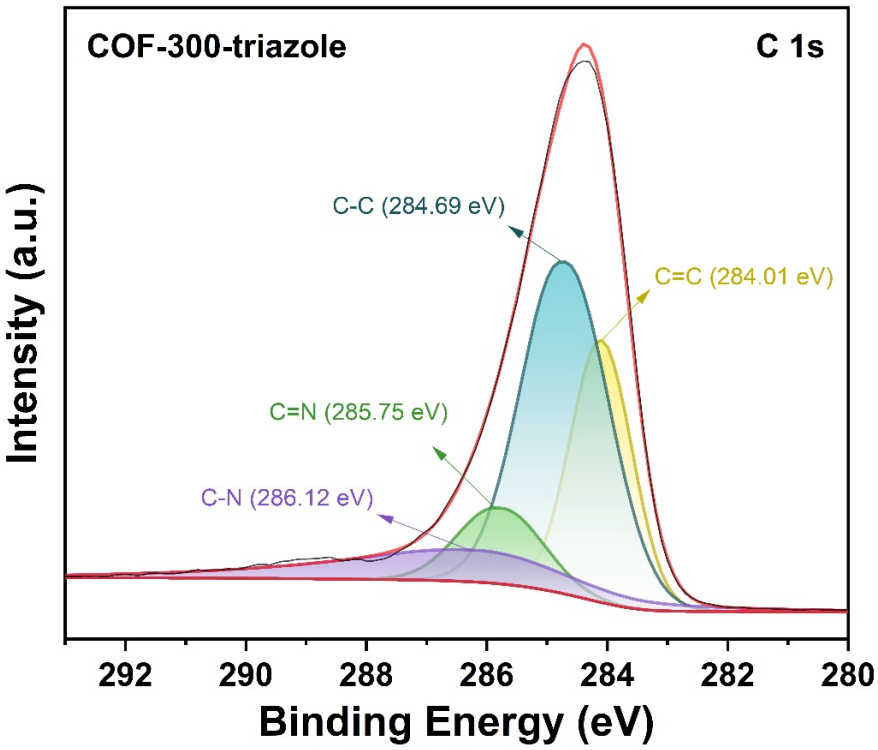
Supplementary Fig. 9. The TG curve of COF-300-1,2,4-triazole.



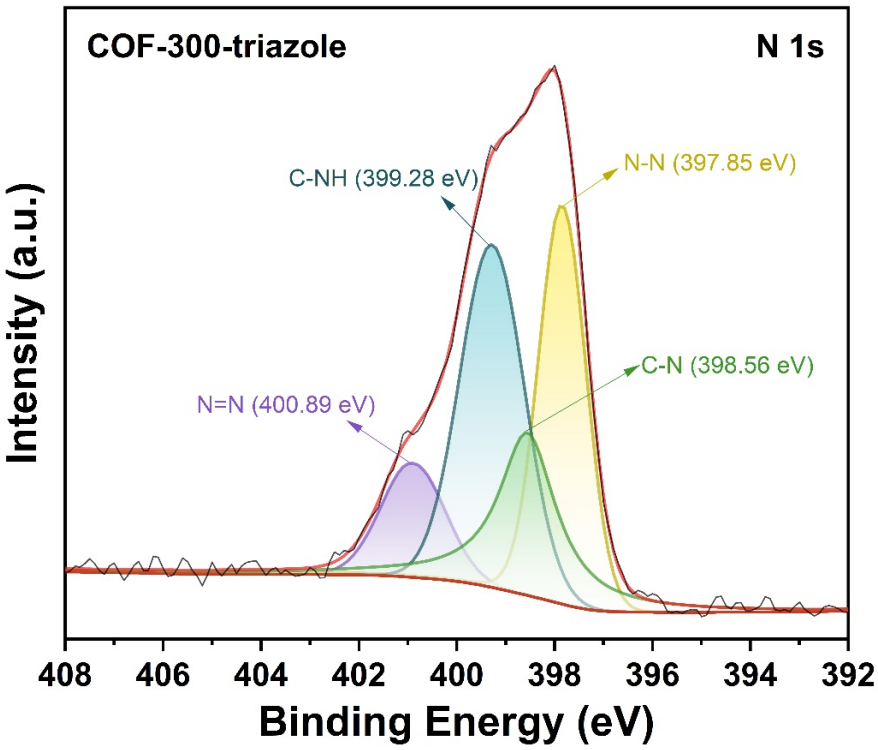
Supplementary Fig. 10. The TG curve of COF-300-pyrazole.



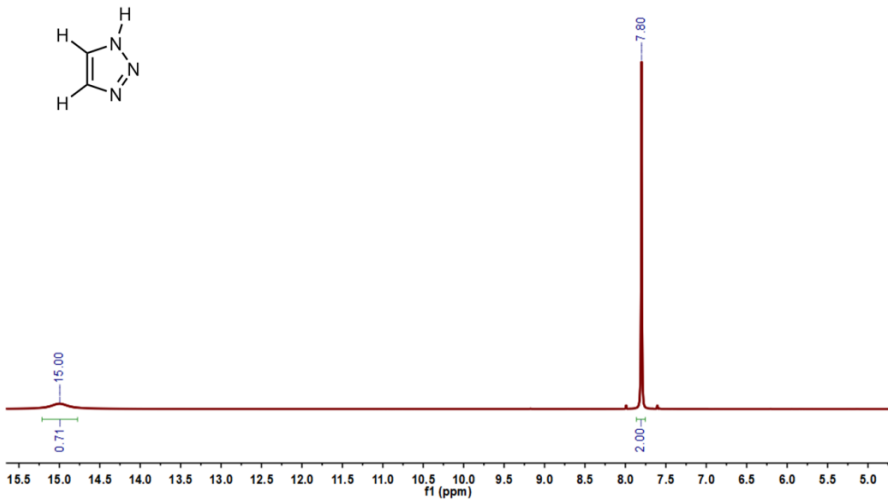
Supplementary Fig. 11. XPS spectra of COF-300-1,2,3-triazole.



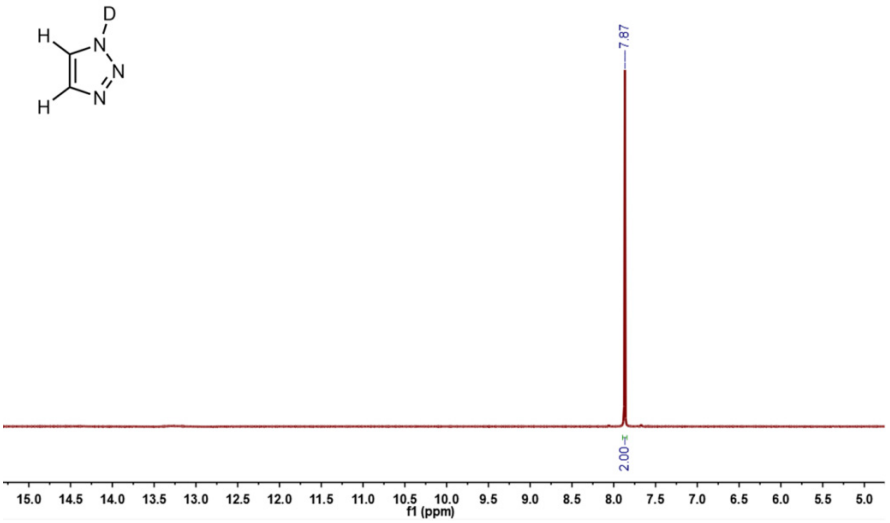
Supplementary Fig. 12. High-resolution XPS spectra of COF-300-1,2,3-triazole C 1s.



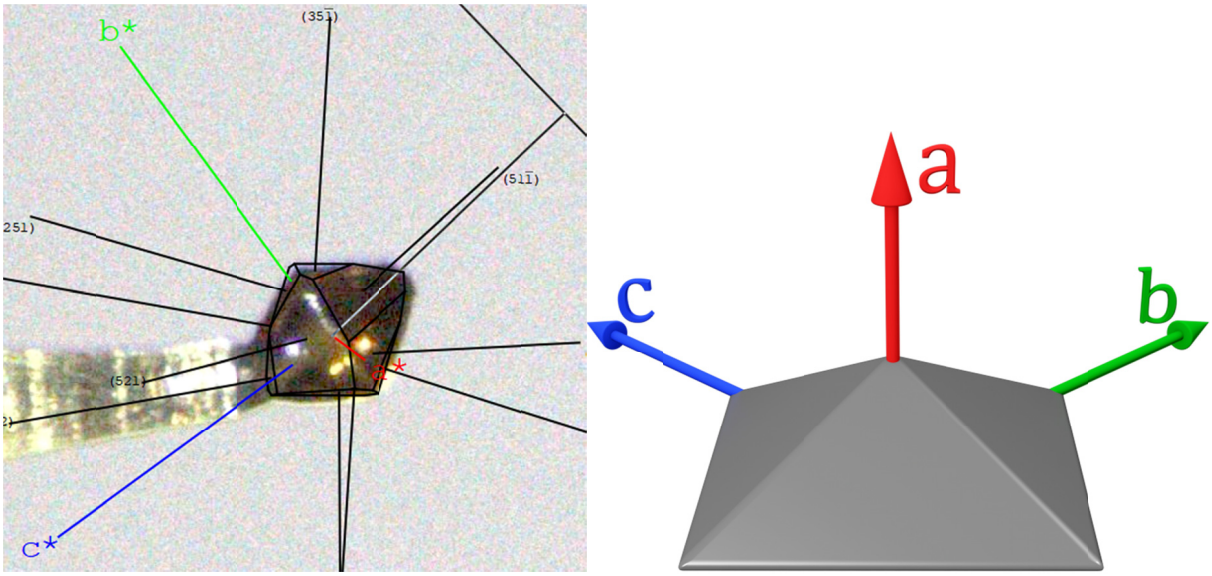
Supplementary Fig. 13. High-resolution XPS spectra of COF-300-1,2,3-triazole N 1s.



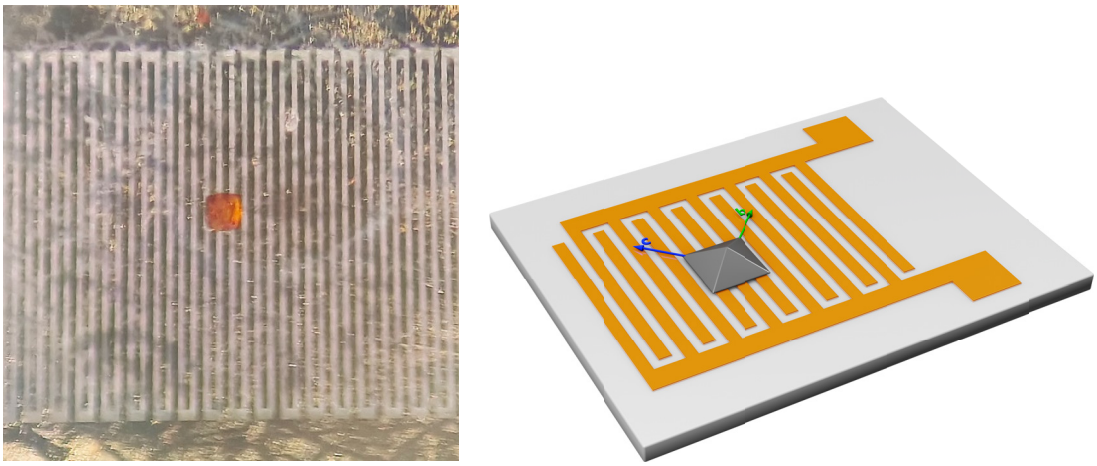
Supplementary Fig. 14. ^{1}H NMR spectrum (500 MHz, DMSO-d6) of 1H-1,2,3-triazole.



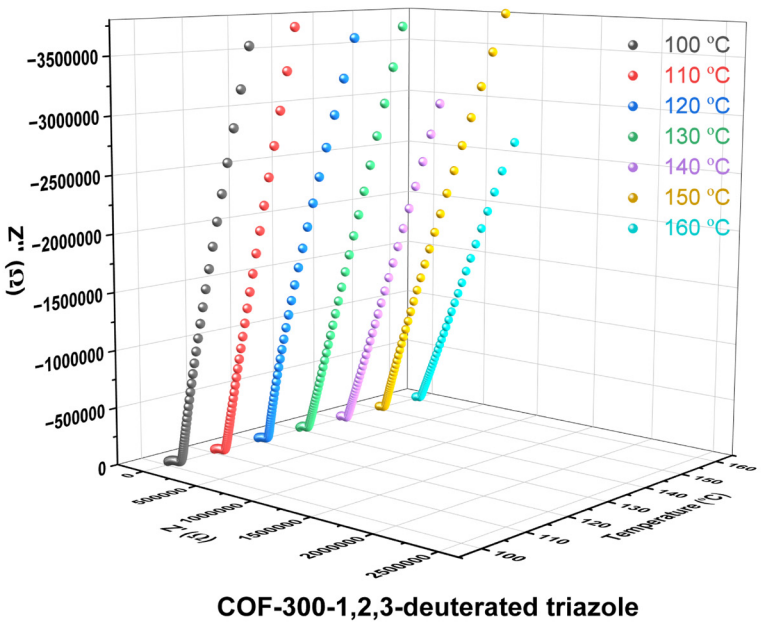
Supplementary Fig. 15. ^{1}H NMR spectrum (500 MHz, DMSO-d6) of 1D-1,2,3- deuterated triazole.



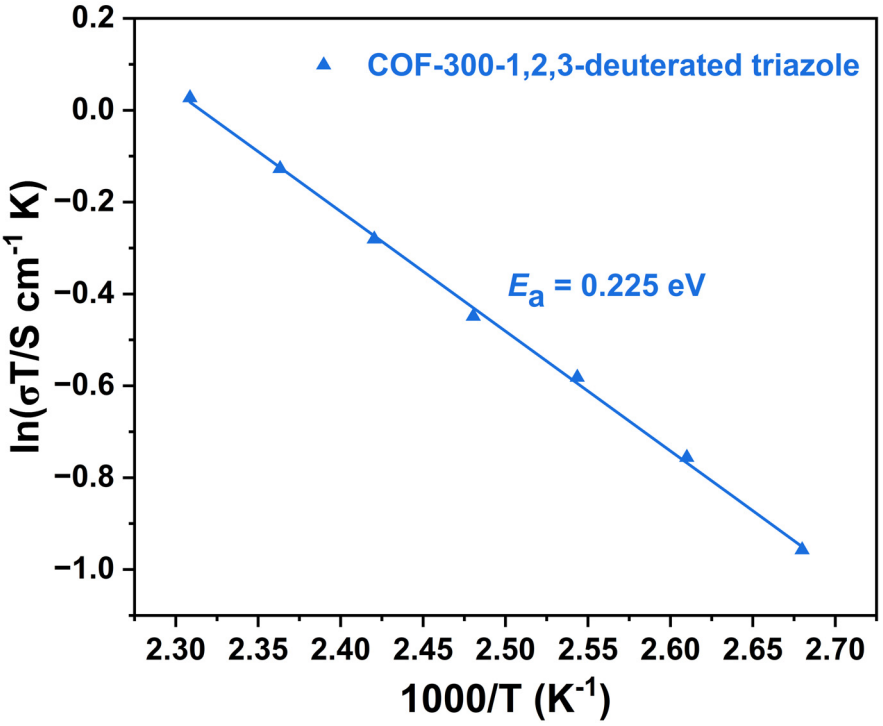
Supplementary Fig. 16. The indexed crystal faces of COF-300-1,2,3-triazole.



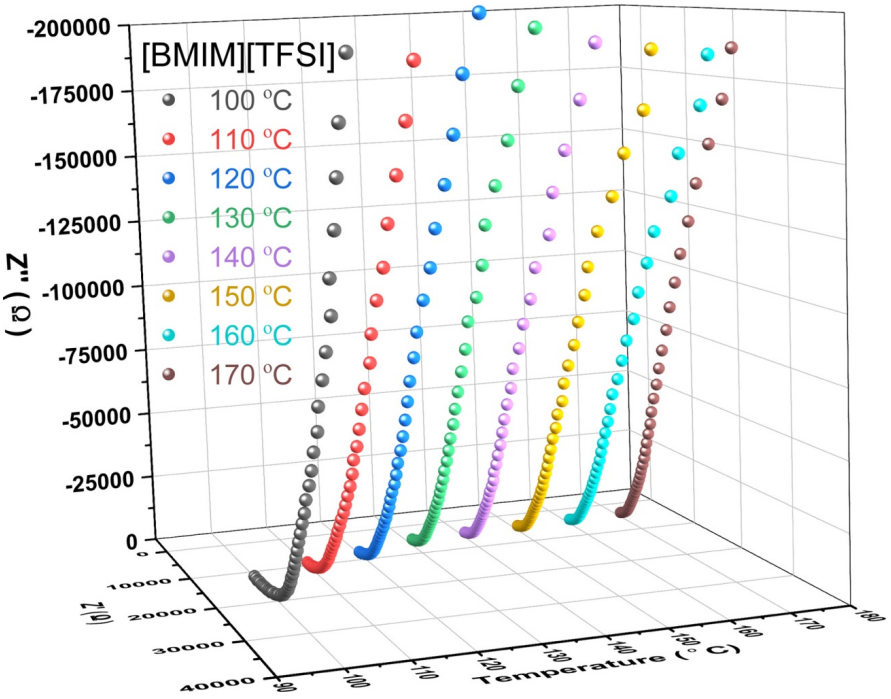
Supplementary Fig. 17. The photograph and illustration of single crystal placement on interdigital electrode.



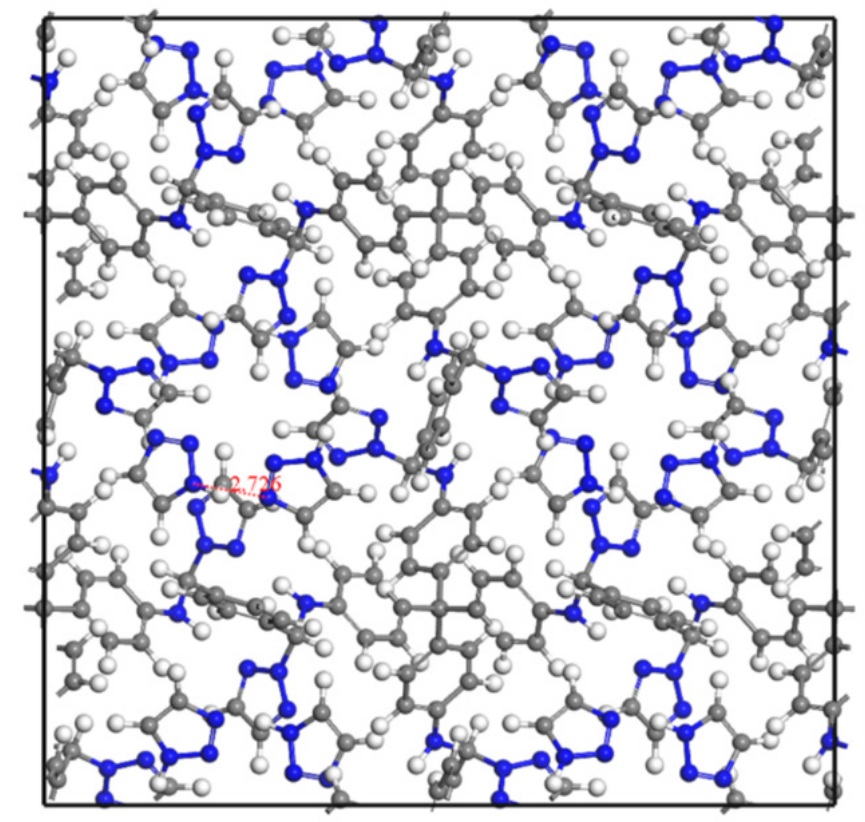
Supplementary Fig. 18. The proton conduction curve of COF-300-1,2,3-deuterated triazole at 100–160 °C.



Supplementary Fig. 19. The E_a of COF-300-1,2,3-deuterated triazole at 100–160 °C.



Supplementary Fig. 20. The proton conduction curve of [BMIM][TFSI] at 100–170 °C.



Supplementary Fig. 21. Top view of the optimized geometric structure of COF-300-1,2,3-triazole. The optimized N–H···N H-bond length in COF-300-triazole is inserted. The optimized lattice constants is also presented.

Supplementary Table 1. Anhydrous single crystal proton conductivity of COF-300-1,2,3-triazole at 100–170 ˚C.

Material	Temperature (ºC)	Proton conductivities (S cm^{-1})
COF-300-1,2,3-triazole	100	0.002189597
	110	0.002728048
	120	0.003042542
	130	0.003232167
	140	0.003277614
	150	0.003610336
	160	0.003880594
	170	0.004231058

Supplementary Table 2. Anhydrous single crystal proton conductivity of COF-300-1,2,4-triazole at 100–170 ˚C.

Material	Temperature (ºC)	Proton conductivities (S cm^{-1})
COF-1,2,4-300-triazole	100	0.002026712
	110	0.002269504
	120	0.002489792
	130	0.003286258
	140	0.003425127
	150	0.003625257
	160	0.003874167
	170	0.004146453

Supplementary Table 3. Anhydrous single crystal proton conductivity of COF-300-pyrazole at 100–170 ˚C.

Material	Temperature (ºC)	Proton conductivities (S cm^{-1})
COF-300- pyrazole	100	0.002414759
	110	0.002778357
	120	0.00308043
	130	0.00321231
	140	0.00358915
	150	0.003882289
	160	0.004236705
	170	0.004349906

Supplementary Table 4. Anhydrous single crystal proton conductivity of COF-300-1,2,3-deuterated triazole at 100–160 ˚C.

Material	Temperature (ºC)	Proton conductivities (S cm^{-1})
COF-300- deuterated triazole	100	0.001028807
	110	0.001225716
	120	0.001422131
	130	0.001583832
	140	0.001828488
	150	0.002081512
	160	0.002371593

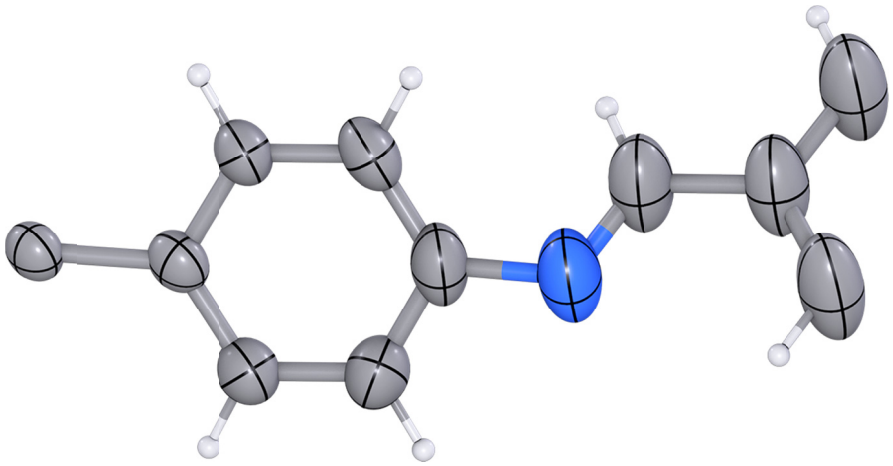
Supplementary Table 5. Anhydrous proton conductivity of [BMIM][TFSI] at 100–170 ˚C.

Material	Temperature (ºC)	Proton conductivities (S cm^{-1})
[BMIM][TFSI]	100	0.008660258
	110	0.012381218
	120	0.016587874
	130	0.018909847
	140	0.021197668
	150	0.02281152
	160	0.024573043
	170	0.026576307

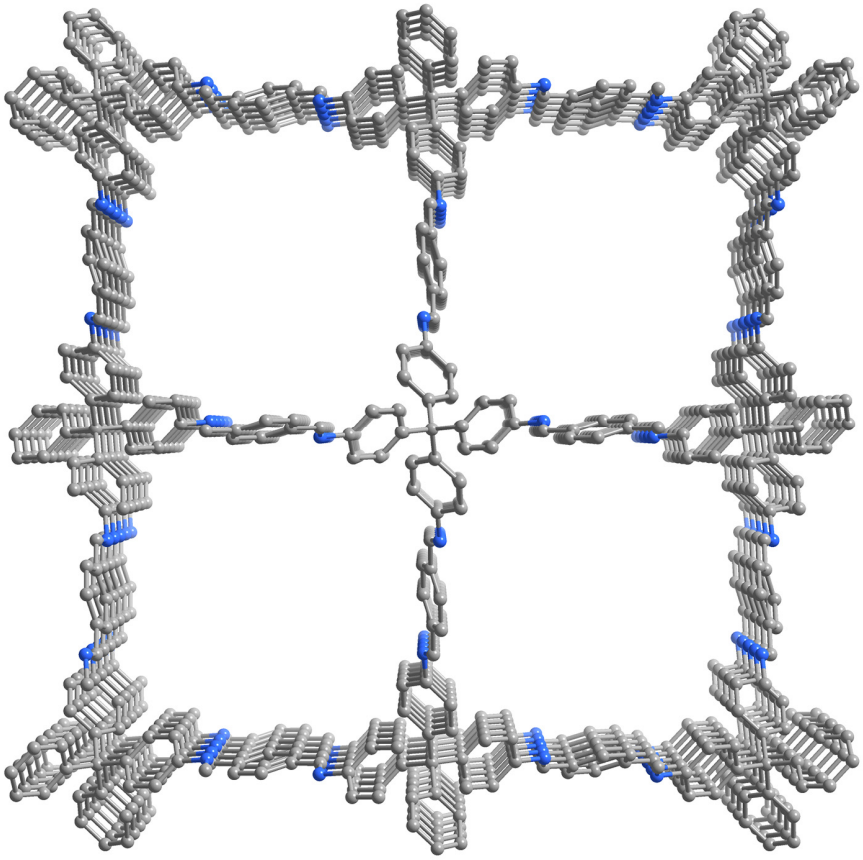
Supplementary Table 6. Comparison of proton conductivities of reported single-crystal proton-conducting materials under anhydrous conditions.

No.	Material	σ (S cm^{-1})	T (°C)	E_a (eV)	Ref.
1	$Li_3HMO_8W \cdot 18H_2O$	3.8×10^{-7}	20	0.62	(*1*)
2	C_{12}im-V_{10}	4.6×10^{-5}	100	Not provided	(*2*)
3	H_3PO_4@USTB-5o	6.3×10^{-2}	140	0.20	(*3*)
4	$[Eu_2(CO_3)(ox)_2(H_2O)_2]\cdot 4H_2O$	2.08×10^{-3}	150	0.28	(*4*)
5	$[Co_2Na(bptc)_2][EMIm]_3$	2.63×10^{-5}	25	0.49	(*5*)
6	$(Me_2NH_2)[Eu(L)]$	1.25×10^{-3}	150	0.21	(*6*)
7	$[Zn(H_2PO_4)_2(TzH)_2]_n$	1.1×10^{-4}	130	Not provided	(*7*)
8	$[Fe(ox)(H_2O)_2]$	1.5×10^{-3}	20	0.14	(*8*)
9	Im-Glu	2.40×10^{-6}	94	0.90	(*9*)
10	$Fe(H_2PO_4)_2F$	2.6×10^{-7}	25	0.43	(*10*)
11	$Ba(H_2PO_4)_2$	2×10^{-7}	160	0.80	(*11*)
	COF-300-123-triazole	**4.23×10^{-3}**	**170**	**0.153**	**This work**
	COF-300-124-triazole	**4.15×10^{-3}**	**170**	**0.187**	**This work**
	COF-300-pyrazole	**4.35×10^{-3}**	**170**	**0.155**	**This work**

COF-300: A pyramidal-shaped crystal of COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 22. Asymmetric unit in the single crystal structure of COF-300.

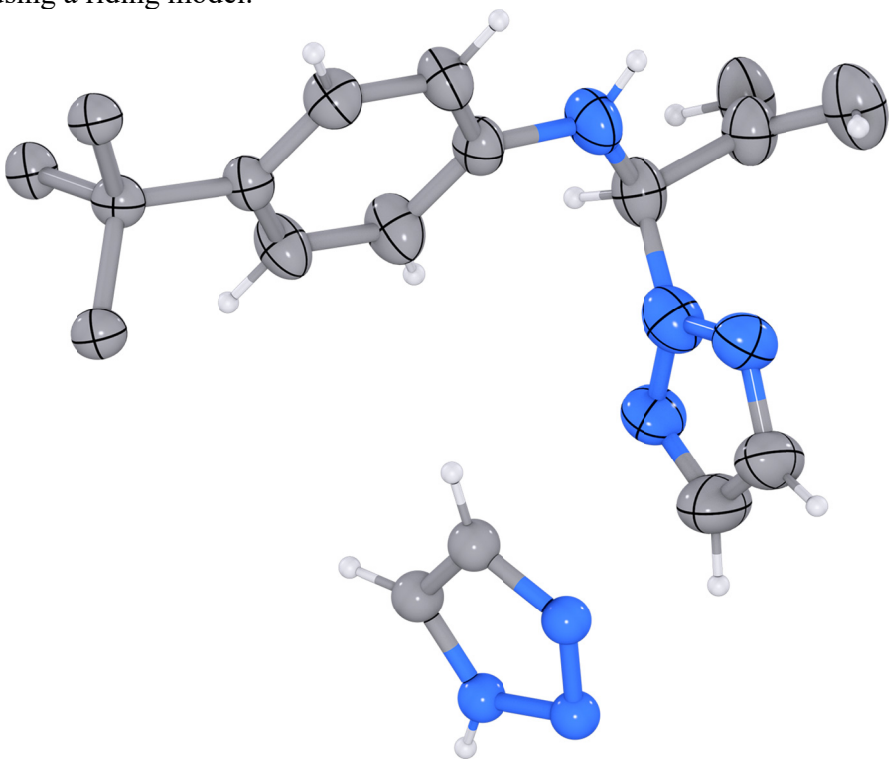


Supplementary Fig. 23. Single-crystal structure of COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

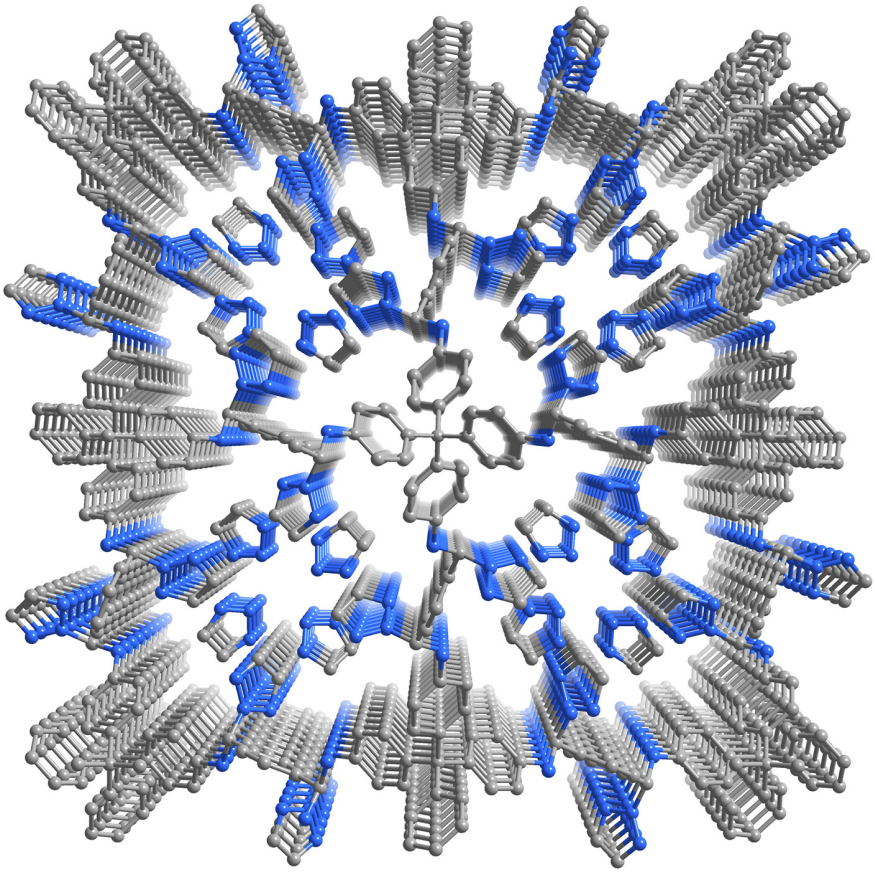
Supplementary Table 7. Crystallographic data and structural refinement parameters for COF-300.

Name	**COF-300**
Empirical formula	$C_{41}H_{28}N_4$
Formula weight	576.67
Temperature [K]	173.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	26.9202(13)
b [Å]	26.9202(13)
c [Å]	7.4244(5)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5380.4(6)
Z	4
ρ_{calc} [gcm^{-3}]	0.712
μ [mm^{-1}]	0.327
F(000)	1208.0
Crystal size [mm^3]	0.15 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.292 to 129.084
Index ranges	$-30 \le h \le 31$, $-24 \le k \le 31$, $-8 \le l \le 8$
Reflections collected	14925
Independent reflections	2196
	R_{int} = 0.0497, R_{sigma} = 0.0331
Data / Restraints / Parameters	2196/0/102
Goodness-of-fit on F^2	1.085
Final R indexes	R_1 = 0.0661
[$I \ge 2\sigma(I)$]	wR_2 = 0.2126
Final R indexes	R_1 = 0.0829
[all data]	wR_2 = 0.2272
Largest peak/hole [eÅ^{-3}]	0.18/-0.17
CCDC number	2375338

COF-300-1,2,3-triazole: A pyramidal -shaped crystal of COF-300-1,2,3-triazole was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 24. Asymmetric unit in the single-crystal structure of COF-300-1,2,3-triazole.

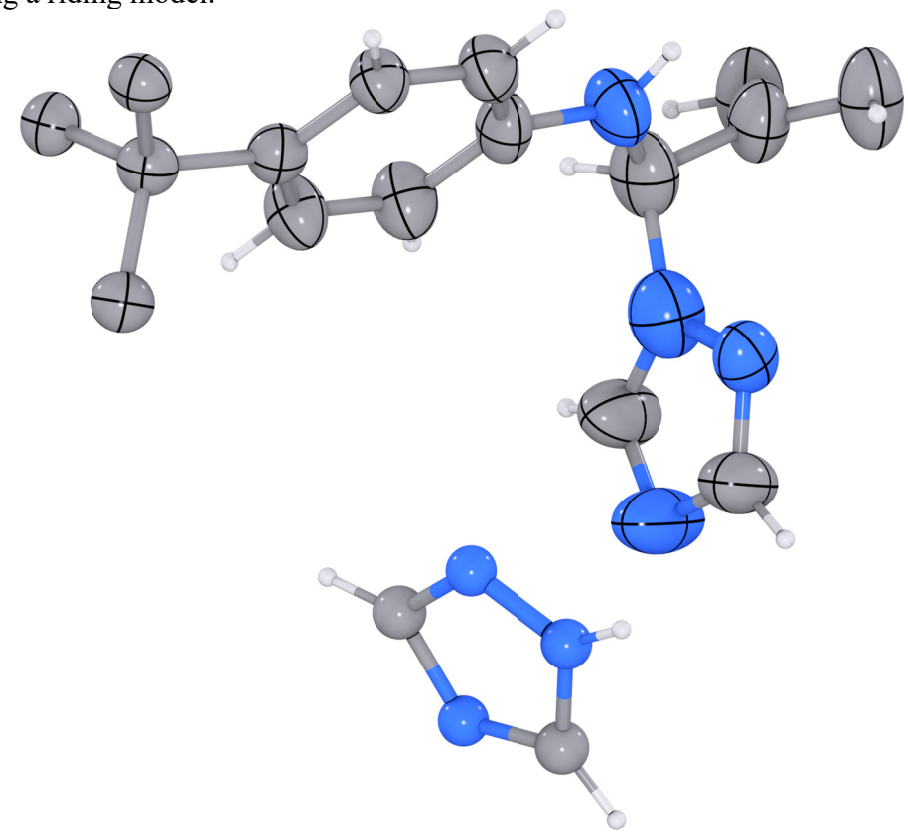


Supplementary Fig. 25. Single-crystal structure of COF-300-1,2,3-triazole viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

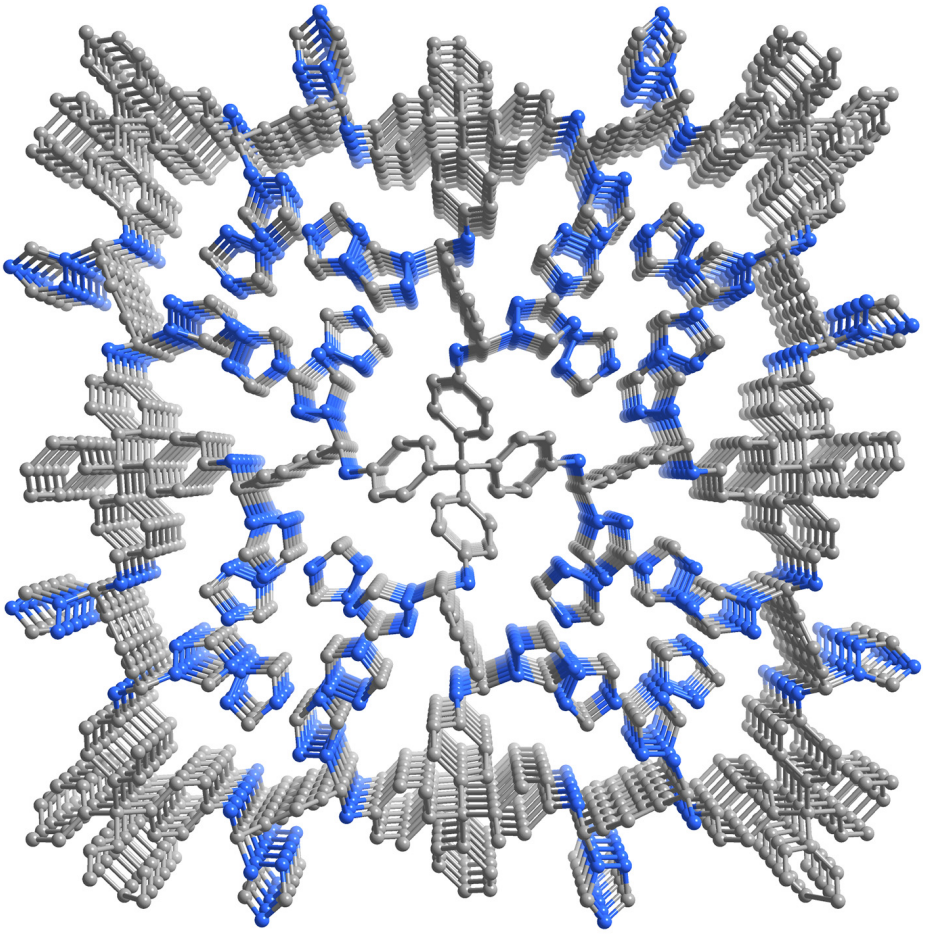
Supplementary Table 8. Crystallographic data and structural refinement parameters for COF-300-1,2,3-triazole.

Name	**COF-300-1,2,3-triazole**
Empirical formula	$C_{57}H_{52}N_{28}$
Formula weight	1129.26
Temperature [K]	293.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	26.0064(13)
b [Å]	26.0064(13)
c [Å]	7.7568(7)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5246.2(7)
Z	4
ρ_{calc} [gcm^{-3}]	1.430
μ [mm^{-1}]	0.763
F(000)	2360.0
Crystal size [mm^3]	0.2 × 0.15 × 0.13
Radiation	Cu $K\alpha$ (λ = 1.54178 Å)
2θ range [°]	6.798 to 128.11
Index ranges	$-25 \leq h \leq 23$, $-28 \leq k \leq 30$, $-8 \leq l \leq 9$
Reflections collected	13269
Independent reflections	2139
	R_{int} = 0.0539, R_{sigma} = 0.0358
Data / Restraints / Parameters	2139/97/185
Goodness-of-fit on F^2	1.102
Final R indexes	R_1 = 0.0855
[$I \geq 2\sigma(I)$]	wR_2 = 0.2411
Final R indexes	R_1 = 0.0993
[all data]	wR_2 = 0.2559
Largest peak/hole [eÅ^{-3}]	0.35/-0.38
CCDC number	2418811

COF-300-1,2,4-triazole: A pyramidal-shaped crystal of COF-300-1,2,4-triazole was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 26. Asymmetric unit in the single crystal structure of COF-300-1,2,4-triazole.

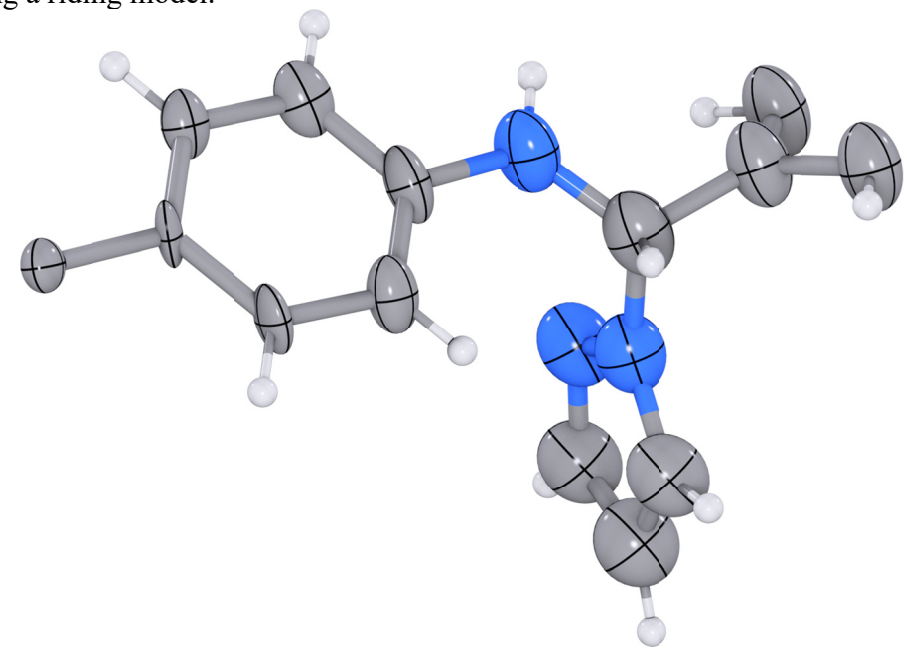


Supplementary Fig. 27. Single-crystal structure of COF-300-1,2,4-triazole viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

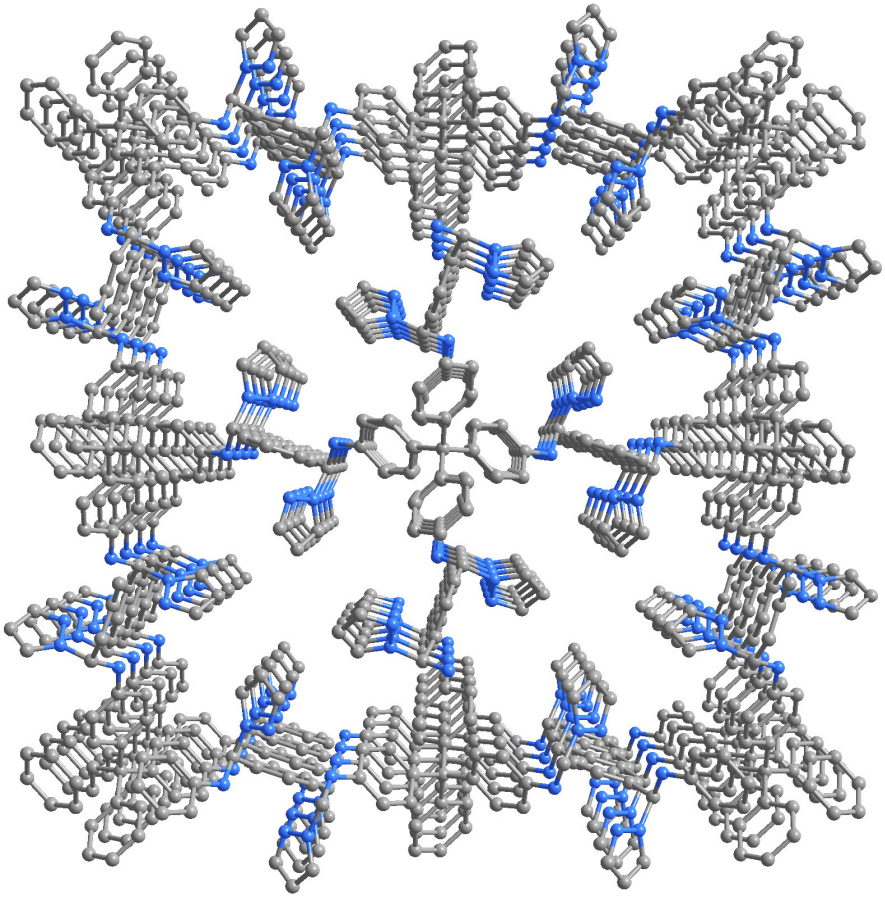
Supplementary Table 9. Crystallographic data and structural refinement parameters for COF-300-1,2,4-triazole.

Name	**COF-300-1,2,4-triazole**
Empirical formula	$C_{57}H_{52}N_{28}$
Formula weight	1129.26
Temperature [K]	173.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	25.844(9)
b [Å]	25.844(9)
c [Å]	7.879(6)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5263(6)
Z	4
ρ_{calc} [gcm^{-3}]	1.425
μ [mm^{-1}]	0.760
F(000)	2360.0
Crystal size [mm^3]	0.2 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.68 to 99.44
Index ranges	$-25 \leq h \leq 24$, $-25 \leq k \leq 20$, $-7 \leq l \leq 7$
Reflections collected	7182
Independent reflections	1330
	R_{int} = 0.0728, R_{sigma} = 0.0509
Data / Restraints / Parameters	1330/108/193
Goodness-of-fit on F^2	1.063
Final R indexes	R_1 = 0.1121
[$I \geq 2\sigma(I)$]	wR_2 = 0.3108
Final R indexes	R_1 = 0.1299
[all data]	wR_2 = 0.3318
Largest peak/hole [eÅ^{-3}]	0.36/-0.36
CCDC number	2468192

COF-300-pyrazole: A pyramidal-shaped crystal of COF-300-pyrazole was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 28. Asymmetric unit in the single crystal structure of COF-300-pyrazole.

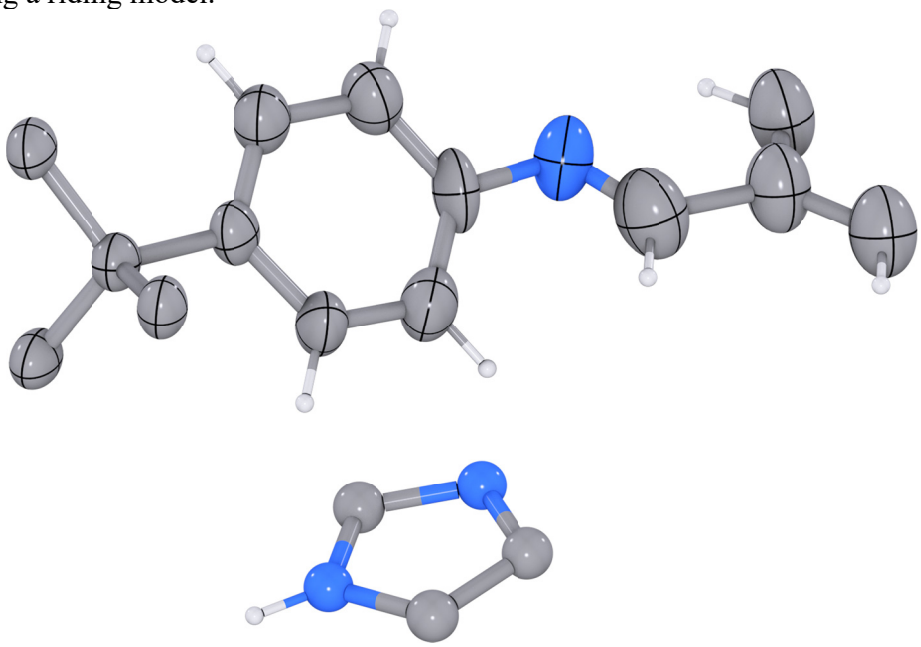


Supplementary Fig. 29. Single-crystal structure of COF-300-pyrazole viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

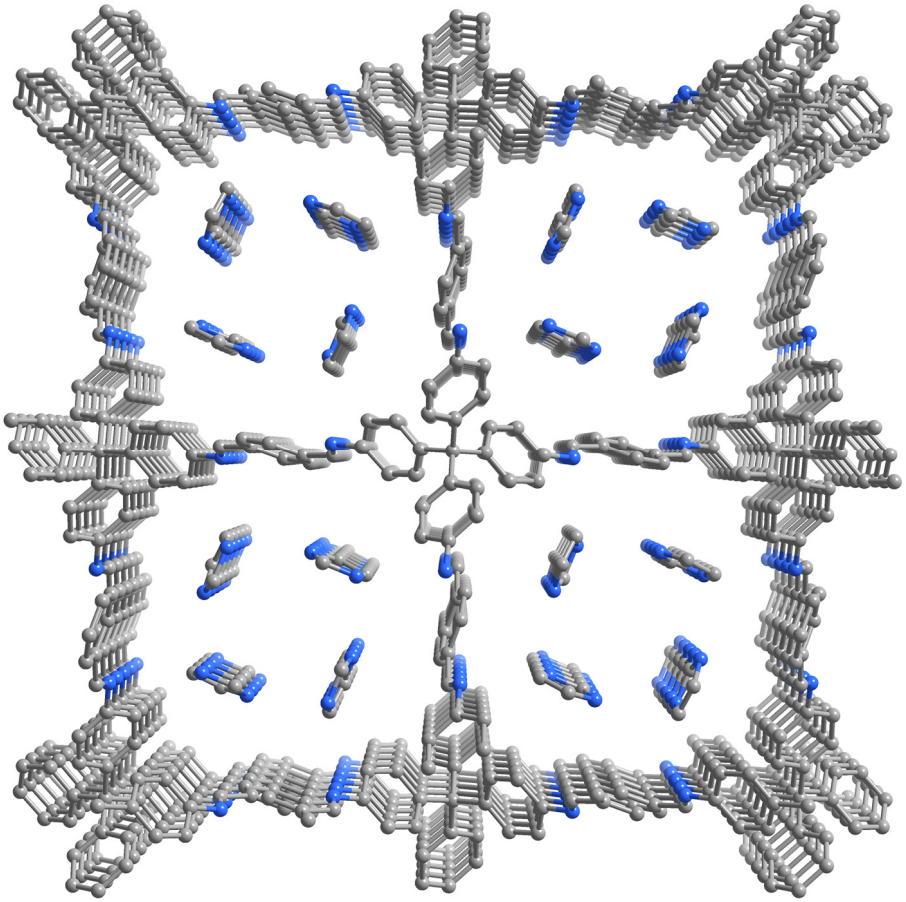
Supplementary Table 10. Crystallographic data and structural refinement parameters for COF-300-pyrazole.

Name	**COF-300-pyrazole**
Empirical formula	$C_{65}H_{60}N_{20}$
Formula weight	1121.33
Temperature [K]	293.02
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	25.946(3)
b [Å]	25.946(3)
c [Å]	7.6916(14)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5178.1(14)
Z	4
ρ_{calc} [gcm^{-3}]	1.438
μ [mm^{-1}]	0.722
F(000)	2360.0
Crystal size [mm^3]	0.2 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.642 to 86.872
Index ranges	$-23 \le h \le 19$, $-22 \le k \le 9$, $-6 \le l \le 6$
Reflections collected	4044
Independent reflections	939
	R_{int} = 0.0764, R_{sigma} = 0.0737
Data / Restraints / Parameters	939/399/127
Goodness-of-fit on F^2	1.039
Final R indexes	R_1 = 0.2502
[$I \ge 2\sigma(I)$]	wR_2 = 0.5631
Final R indexes	R_1 = 0.28830
[all data]	wR_2 = 0.6022
Largest peak/hole [eÅ^{-3}]	0.90/-0.80
CCDC number	2468193

imidazole@COF-300: A pyramidal-shaped crystal of imidazole@COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 38. Asymmetric unit in the single crystal structure of imidazole@COF-300.

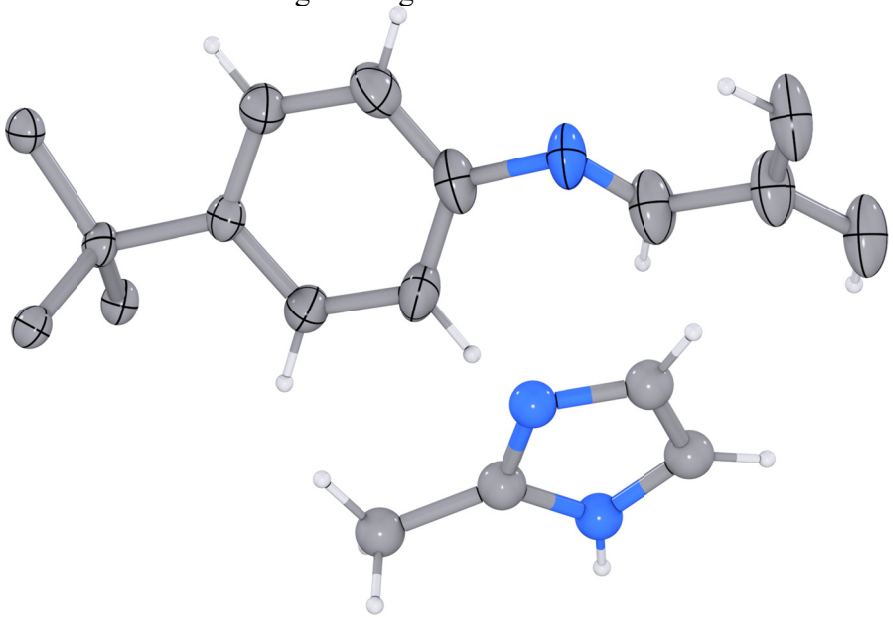


Supplementary Fig. 39. Single-crystal structure of imidazole@COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

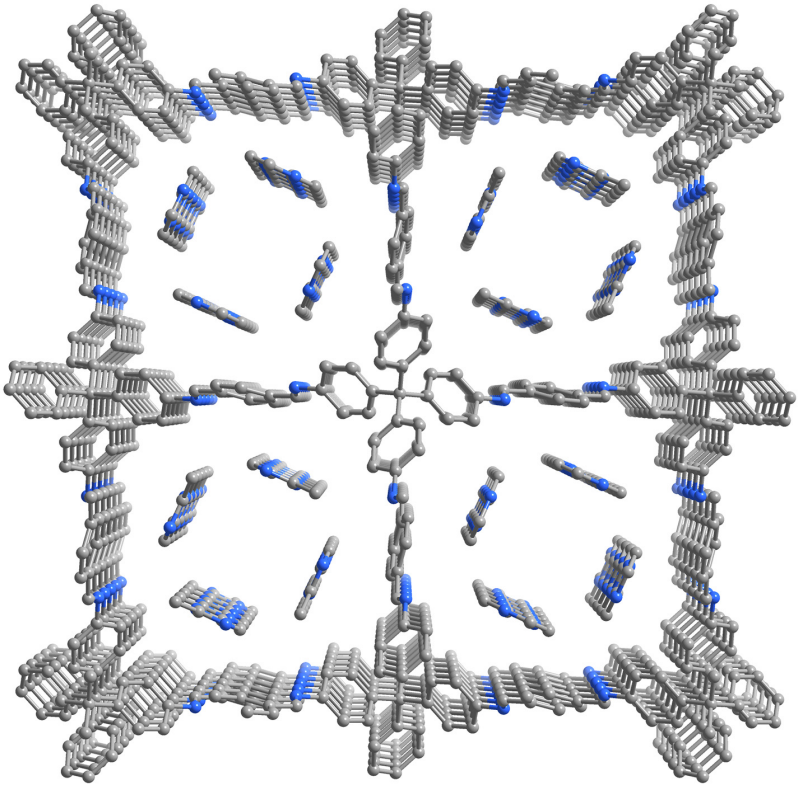
Supplementary Table 15. Crystallographic data and structural refinement parameters for imidazole@COF-300.

Name	**imidazole@COF-300**
Empirical formula	$C_{44}H_{29}N_6$
Formula weight	641.73
Temperature [K]	173.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	26.166(4)
b [Å]	26.166(4)
c [Å]	7.6048(19)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5206.6(19)
Z	4
ρ_{calc} [gcm^{-3}]	0.819
μ [mm^{-1}]	0.385
F(000)	1340.0
Crystal size [mm^3]	0.2 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.56 to 96.458
Index ranges	$-25 \le h \le 24$, $-25 \le k \le 25$, $-6 \le l \le 7$
Reflections collected	10417
Independent reflections	1224
	R_{int} = 0.0648, R_{sigma} = 0.0352
Data / Restraints / Parameters	1224/119/140
Goodness-of-fit on F^2	0.998
Final R indexes	R_1 = 0.1653
[$I \ge 2\sigma(I)$]	wR_2 = 0.3934
Final R indexes	R_1 = 0.1854
[all data]	wR_2 = 0.4124
Largest peak/hole [eÅ^{-3}]	0.38/-0.28
CCDC number	2468194

2-methylimidazole@COF-300: A pyramidal-shaped crystal of 2-methylimidazole@COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 32. Asymmetric unit in the single crystal structure of 2-methylimidazole@COF-300.

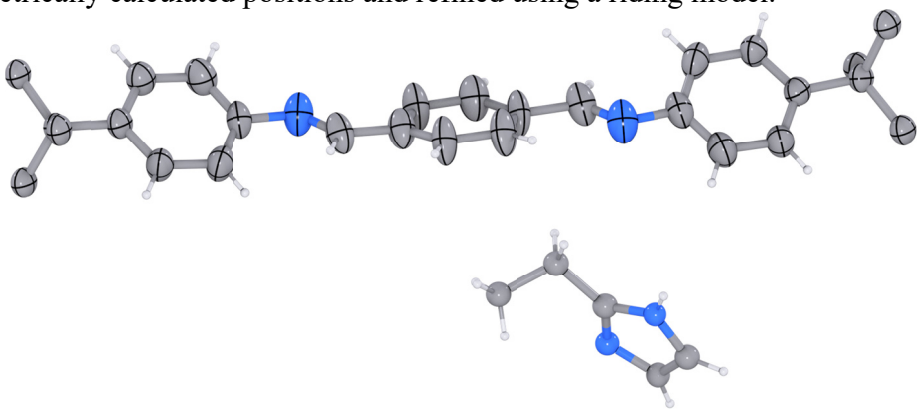


Supplementary Fig. 33. Single-crystal structure of 2-methylimidazole@COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

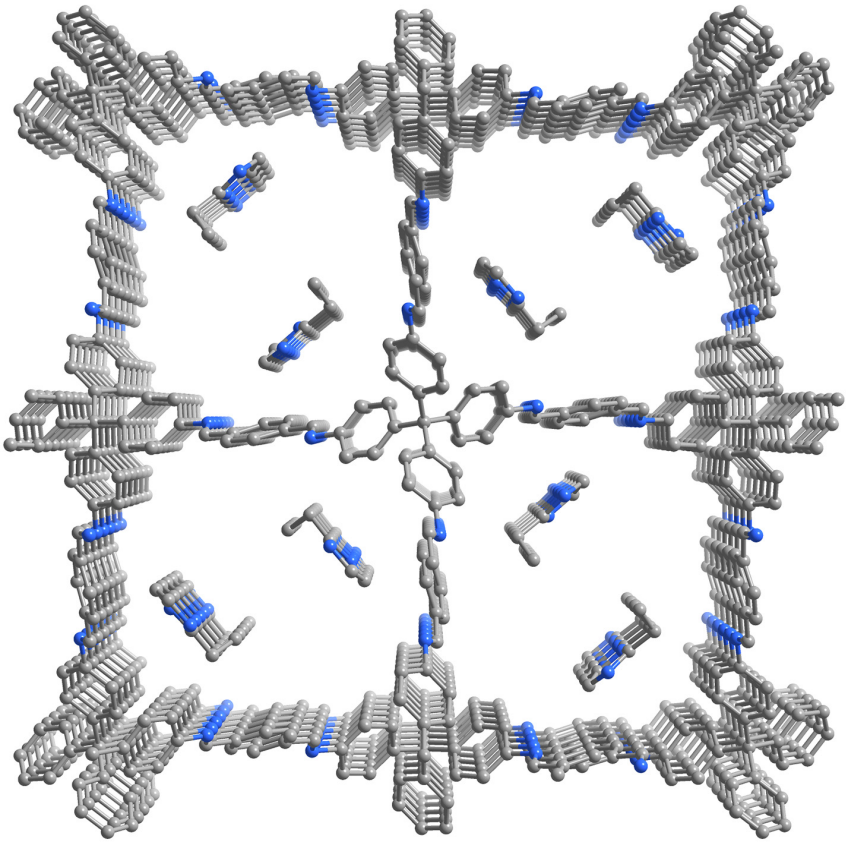
Supplementary Table 12. Crystallographic data and structural refinement parameters for 2-methylimidazole@COF-300.

Name	**2-methylimidazole@COF-300**
Empirical formula	$C_{45}H_{34}N_6$
Formula weight	658.78
Temperature [K]	293.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	27.2075(11)
b [Å]	27.2075(11)
c [Å]	7.3528(5)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5442.9 (6)
Z	4
ρ_{calc} [gcm^{-3}]	0.804
μ [mm^{-1}]	0.375
F(000)	1384.0
Crystal size [mm^3]	0.15 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range [°]	12.47 to 127.656
Index ranges	$-22 \le h \le 31$, $-26 \le k \le 31$, $-7 \le l \le 7$
Reflections collected	13809
Independent reflections	2110
	R_{int} = 0.0571, R_{sigma} = 0.0389
Data / Restraints / Parameters	2110/82/148
Goodness-of-fit on F^2	1.013
Final R indexes	R_1 = 0.1518
[$I \ge 2\sigma(I)$]	wR_2 = 0.3825
Final R indexes	R_1 = 0.1826
[all data]	wR_2 = 0.4121
Largest peak/hole [eÅ^{-3}]	0.51/-0.30
CCDC number	2498195

2-ethylimidazole@COF-300: A pyramidal-shaped crystal of 2-ethylimidazole@COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer with a resolution of 0.86 Å. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 30. Asymmetric unit in the single crystal structure of 2-ethylimidazole@COF-300.

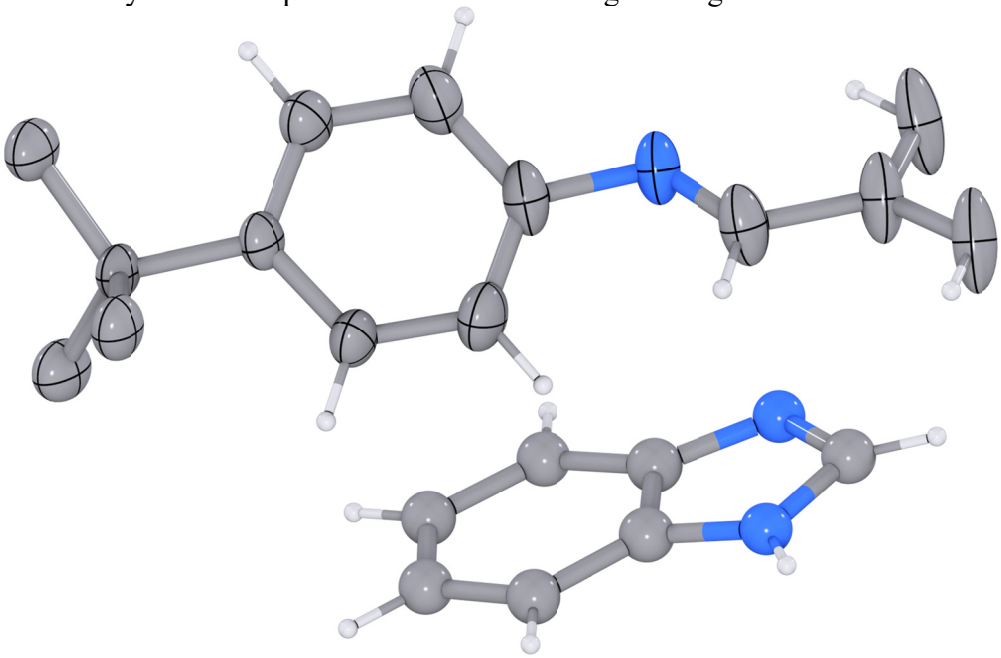


Supplementary Fig. 31. Single-crystal structure of 2-ethylimidazole@COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

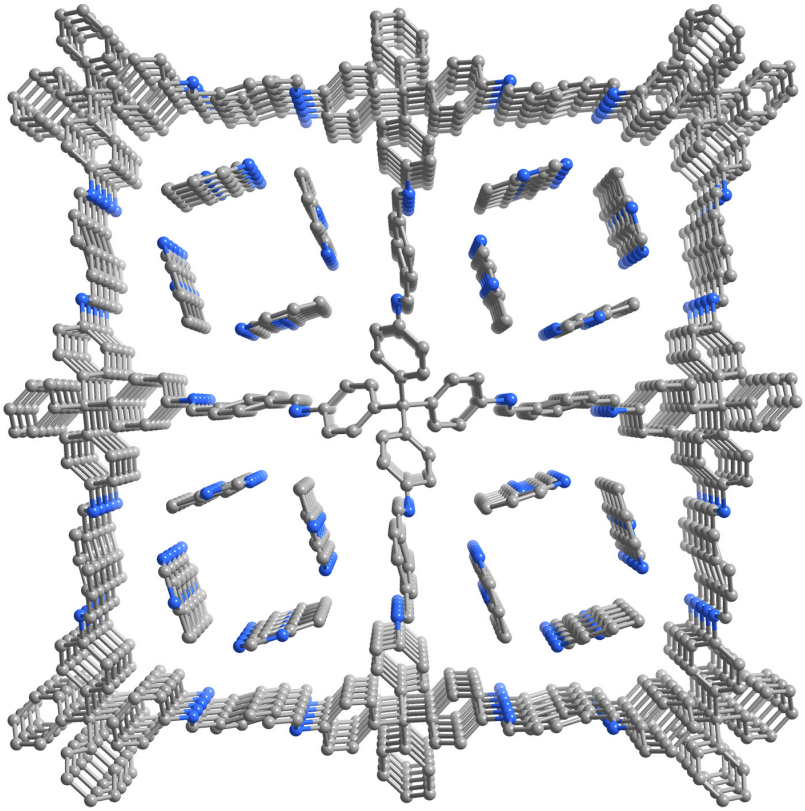
Supplementary Table 11. Crystallographic data and structural refinement parameters for 2-ethylimidazole@COF-300.

Name	**2-ethylimidazole@COF-300**
Empirical formula	$C_{51}H_{42}N_8$
Formula weight	766.92
Temperature [K]	293.00
Crystal system	tetragonal
Space group (number)	$I\bar{4}$
a [Å]	26.5843(17)
b [Å]	26.5843(17)
c [Å]	7.4767(8)
α [°]	90
β [°]	90
γ [°]	90
*V*olume [Å^3]	5284.0(9)
Z	4
ρ_{calc} [gcm^{-3}]	0.964
μ [mm^{-1}]	0.454
F(000)	1616.0
Crystal size [mm^3]	0.2 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.41 to 128.116
Index ranges	$-23 \le h \le 30$, $-26 \le k \le 22$, $-7 \le l \le 8$
Reflections collected	12929
Independent reflections	4240
	R_{int} = 0.0705, R_{sigma} = 0.0805
Data / Restraints / Parameters	4240/191/259
Goodness-of-fit on F^2	1.205
Final *R* indexes	R_1 = 0.1229
[$I \ge 2\sigma(I)$]	wR_2 = 0.3108
Final *R* indexes	R_1 = 0.1694
[all data]	wR_2 = 0.3477
Largest peak/hole [eÅ^{-3}]	0.42/-0.31
Flack parameter	2(3)
CCDC number	2468196

benzimidazole@COF-300: A pyramidal-shaped crystal of benzimidazole@COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer with a resolution of 0.98 Å. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 34. Asymmetric unit in the single crystal structure of benzimidazole@COF-300.

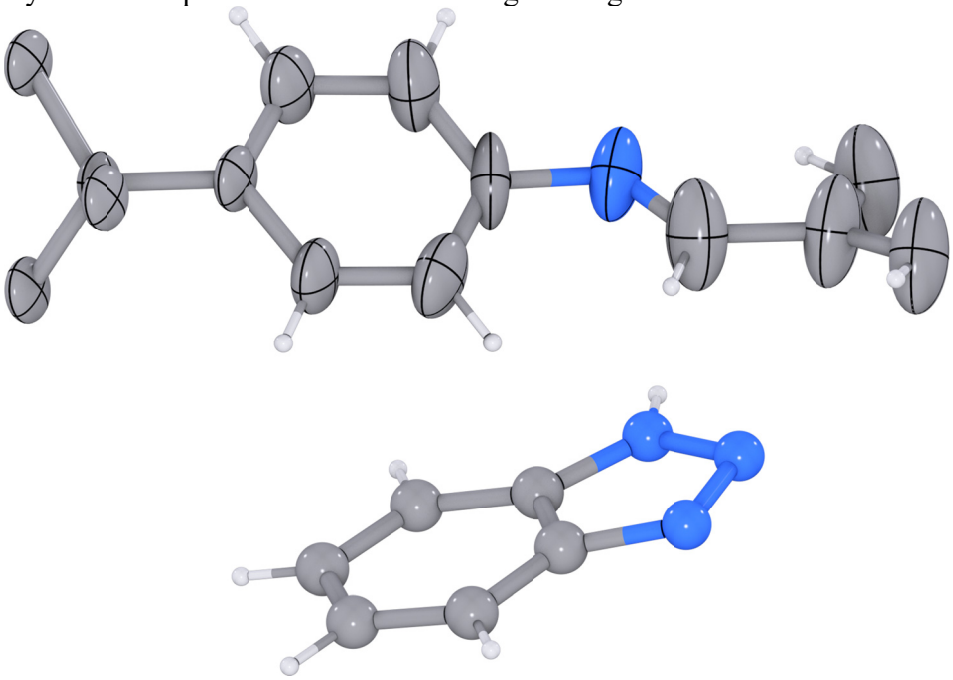


Supplementary Fig. 35. Single-crystal structure of benzimidazole@COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

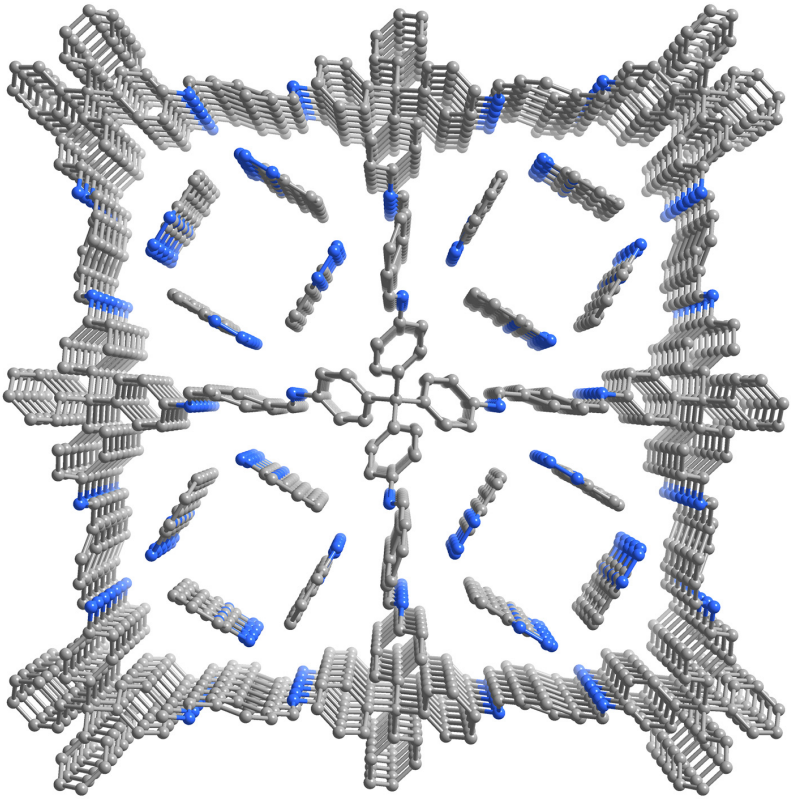
Supplementary Table 13. Crystallographic data and structural refinement parameters for benzimidazole@COF-300.

Name	**benzimidazole@COF-300**
Empirical formula	$C_{69}H_{52}N_{12}$
Formula weight	1049.22
Temperature [K]	173.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	27.031(5)
b [Å]	27.031(5)
c [Å]	7.394(2)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5402(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.290
μ [mm^{-1}]	0.616
F(000)	2200.0
Crystal size [mm^3]	0.15 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range [°]	9.254 to 104.424
Index ranges	$-23 \leq h \leq 26$, $-27 \leq k \leq 27$, $-7 \leq l \leq 7$
Reflections collected	10614
Independent reflections	1501
	R_{int} = 0.0572, R_{sigma} = 0.0337
Data / Restraints / Parameters	1501/261/175
Goodness-of-fit on F^2	1.071
Final R indexes	R_1 = 0.1172
[$I \geq 2\sigma(I)$]	wR_2 = 0.3386
Final R indexes	R_1 = 0.1295
[all data]	wR_2 = 0.3523
Largest peak/hole [eÅ^{-3}]	0.24/-0.20
CCDC number	2468197

benzotriazole@COF-300: A pyramidal-shaped crystal of benzotriazole@COF-300 was coated with silicone oil and mounted on a 0.050 mm diameter loop. The crystal data was measured on the single-crystal X-ray diffractometer with a resolution of 1.04 Å. All the non-hydrogen atoms of the framework were refined anisotropically. Hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.



Supplementary Fig. 36. Asymmetric unit in the single crystal structure of benzotriazole@COF-300.



Supplementary Fig. 37. Single-crystal structure of benzotriazole@COF-300 viewed along c-axis. C atoms, gray; N atoms, blue. H atoms were omitted for clarity.

Supplementary Table 14. Crystallographic data and structural refinement parameters for benzotriazole@COF-300.

Name	**benzotriazole@COF-300**
Empirical formula	$C_{65}H_{48}N_{16}$
Formula weight	1053.19
Temperature [K]	173.00
Crystal system	tetragonal
Space group (number)	$I4_1/a$
a [Å]	26.659(2)
b [Å]	26.659(2)
c [Å]	7.4645(8)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5304.9(10)
Z	4
ρ_{calc} [gcm^{-3}]	1.319
μ [mm^{-1}]	0.652
F(000)	2200.0
Crystal size [mm^3]	0.15 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range [°]	12.314 to 95.58
Index ranges	$-20 \leq h \leq 25$, $-19 \leq k \leq 25$, $-7 \leq l \leq 6$
Reflections collected	7601
Independent reflections	1220
	R_{int} = 0.0784, R_{sigma} = 0.0512
Data / Restraints / Parameters	1220/99/176
Goodness-of-fit on F^2	1.069
Final R indexes	R_1 = 0.1510
[$I \geq 2\sigma(I)$]	wR_2 = 0.3837
Final R indexes	R_1 = 0.1765
[all data]	wR_2 = 0.4085
Largest peak/hole [eÅ^{-3}]	0.26/-0.25
CCDC number	2468198

References

1. Dolbecq A, *et al.* Synthesis, X-ray and Neutron Diffraction Characterization, and Ionic Conduction Properties of a New Oxothiomolybdate $Li_3[Mo_8S_8O_8(OH)_8\{HWO_5(H_2O)\}]\cdot 18\ H_2O$. *Chemistry-A European Journal* **8**, 349–356 (2002).
2. Misawa T, *et al.* Conductive hybrid crystal composed of polyoxovanadate and deprotonatable ionic-liquid surfactant. *Inorganic Chemistry Communications* **96**, 24–29 (2018).
3. Yu B, *et al.* Linkage conversions in single-crystalline covalent organic frameworks. *Nature Chemistry* **16**, 114–121 (2023).
4. Tang Q, *et al.* High Proton Conduction at above 100 °C Mediated by Hydrogen Bonding in a Lanthanide Metal–Organic Framework. *Journal of the American Chemical Society* **136**, 12444–12449 (2014).
5. Chen W-X, *et al.* Temperature-dependent conductivity of Emim+ (Emim+ = 1-ethyl-3-methyl imidazolium) confined in channels of a metal–organic framework. *Chemical Communications* **47**, 11933–11935 (2011).
6. Wei Y-S, *et al.* Unique Proton Dynamics in an Efficient MOF-Based Proton Conductor. *Journal of the American Chemical Society* **139**, 3505–3512 (2017).
7. Umeyama D, Horike S, Inukai M, Itakura T, Kitagawa S. Inherent Proton Conduction in a 2D Coordination Framework. *Journal of the American Chemical Society* **134**, 12780–12785 (2012).
8. Tominaka S, Cheetham AK. Intrinsic and extrinsic proton conductivity in metal-organic frameworks. *RSC Adv.* **4**, 54382–54387 (2014).
9. Sunairi Y, Ueda A, Yoshida J, Suzuki K, Mori H. Anisotropic Proton Conductivity Arising from Hydrogen-Bond Patterns in Anhydrous Organic Single Crystals, Imidazolium Carboxylates. *The Journal of Physical Chemistry C* **122**, 11623–11632 (2018).
10. Ma Z, *et al.* Synthesis, crystal structure and possible proton conduction of Fe(H2PO4)2F. *Solid State Ionics* **338**, 134–137 (2019).
11. Bagryantseva IN, Ponomareva VG. Ponomareva, Proton Conductivity and Thermal Properties of Ba(H2PO4)2. *Inorganic Materials* **54**, 366–373 (2018).