Electronic Supplementary Information

Rapid synthesis of aminal-linked covalent organic frameworks for CO_2/CH_4 separation

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1. Screening conditions and characterization for COF-TA-PA

Table S1. Synthesis of COF-TA-PA obtained under different solvents.

Entry	Solvent (1 mL)	Temperature	Time
1	Mesitylene (Mes)	120 °C	72 h
2	Toluene (Tol)		
3	Dioxane (Dio)		
4	*o*-dichlorobenzene (*o*-DCB)		
5	Mes/Dio = 1/1		
6	Dimethylacetamide (DMAc)/Mes = 1/1		
7	DMAc/Tol = 1/1		
8	Mes/*n*-Butanol (*n*-BuOH) = 1/1		

Table S2. Synthesis of COF-TA-PA obtained under different temperatures.

Entry	Temperature	Solvent (1 mL)	Time
1	120 ºC		
2	100 ºC	*o*-DCB	72 h
3	80 ºC		

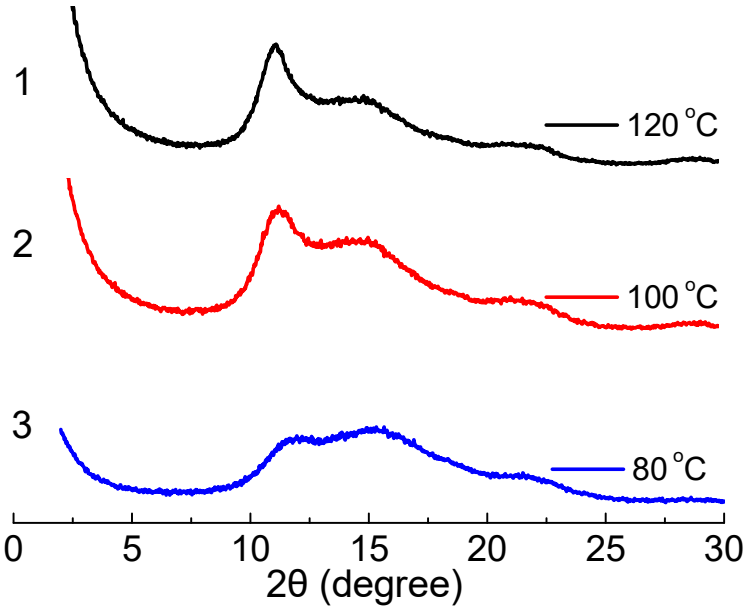

Fig. S1. PXRD patterns of COF-TA-PA prepared under different temperatures.

Table S3. Synthesis of COF-TA-PA obtained under different monomer concentrations.

Entry	Weight (TA, mg)	Weight (PA, mg)	Temperature	Solvent (1 mL)
1	13.4	17.2	120 °C	*o*-DCB
2	26.8	34.4		
3	40.2	51.6		
4	67	86		

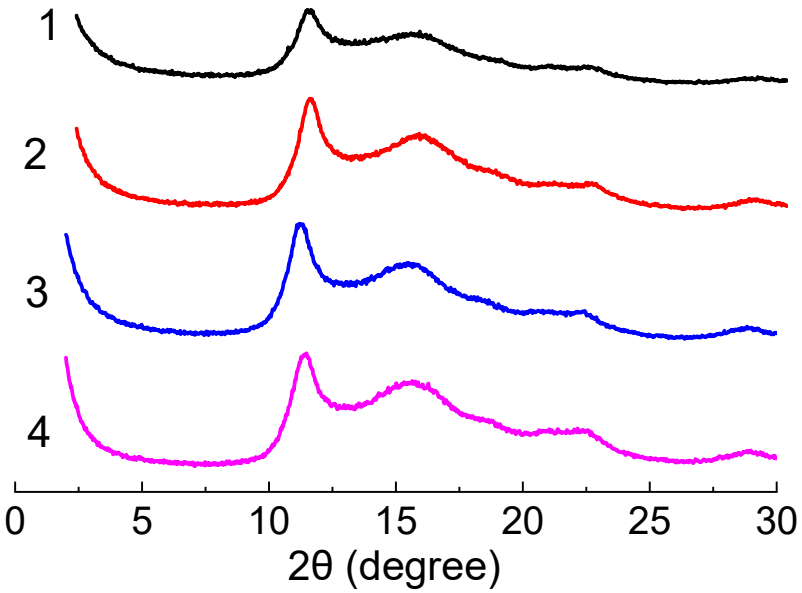

Fig. S2. PXRD patterns of **COF-TA-PA** obtained by using different monomer concentrations.

Table S4. Synthesis of COF-TA-PA under different equivalents of PA.

Entry	Weight (TA, mg)	Weight (PA, mg)	Temperature	Solvent (1 mL)
1	26.8	34.4	120 °C	*o*-DCB
2	26.8	68.8		
3	26.8	103.2		
4	26.8	137.6		

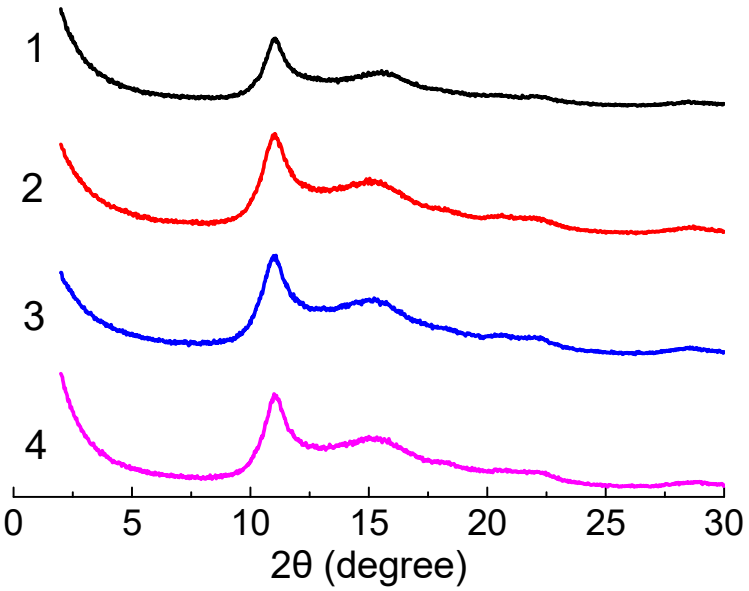

Fig. S3. PXRD patterns of **COF-TA-PA** obtained by using different equivalents of PA.

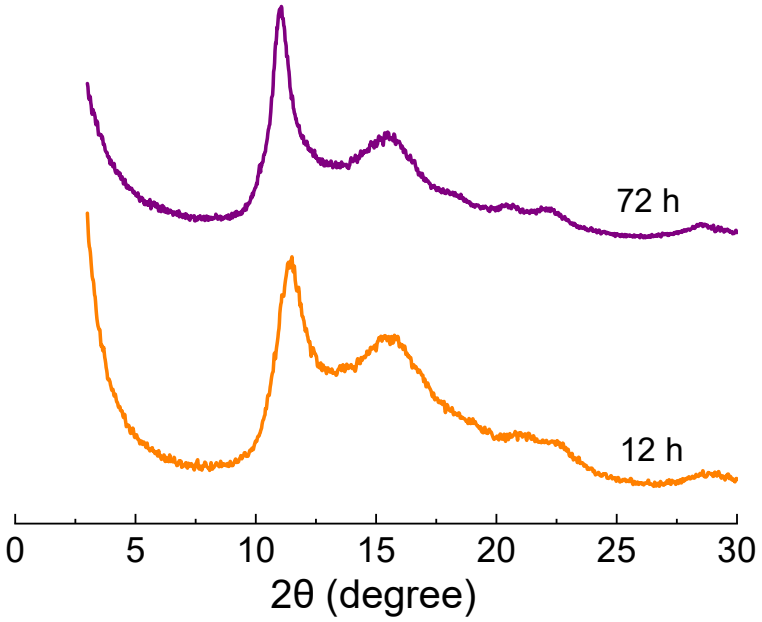

Fig. S4. PXRD patterns of **COF-TA-PA** after 12 and 72 hours.

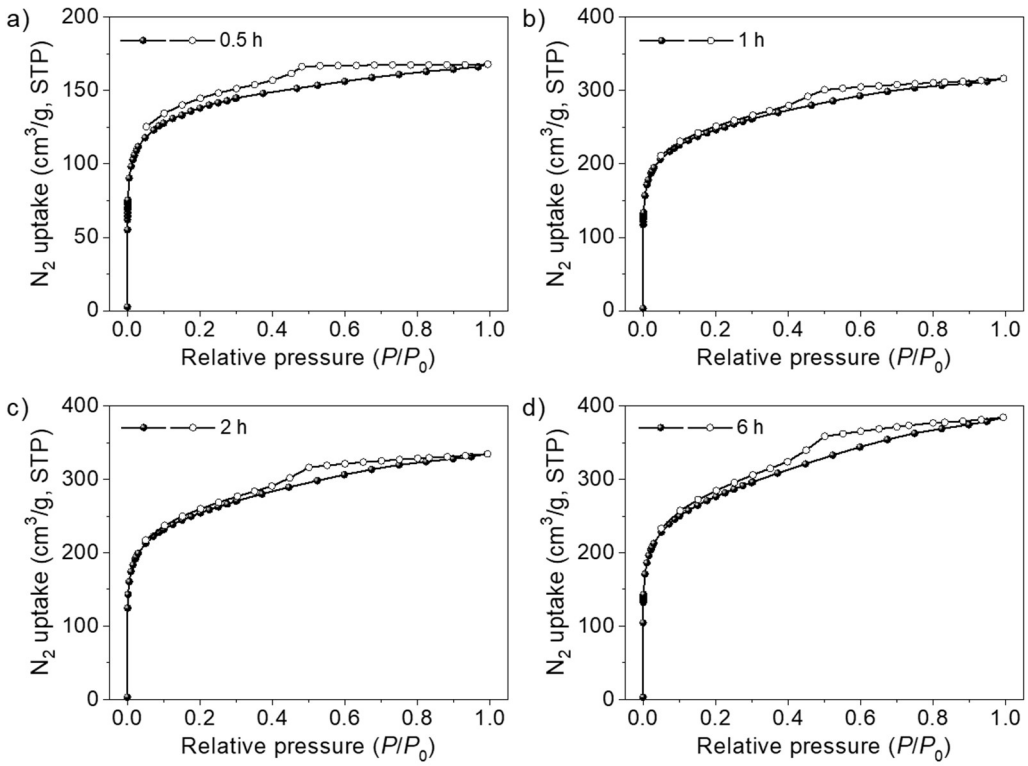

Fig. S5. N_2 adsorption-desorption isotherms (77 K) of **COF-TA-PA** at different time intervals.

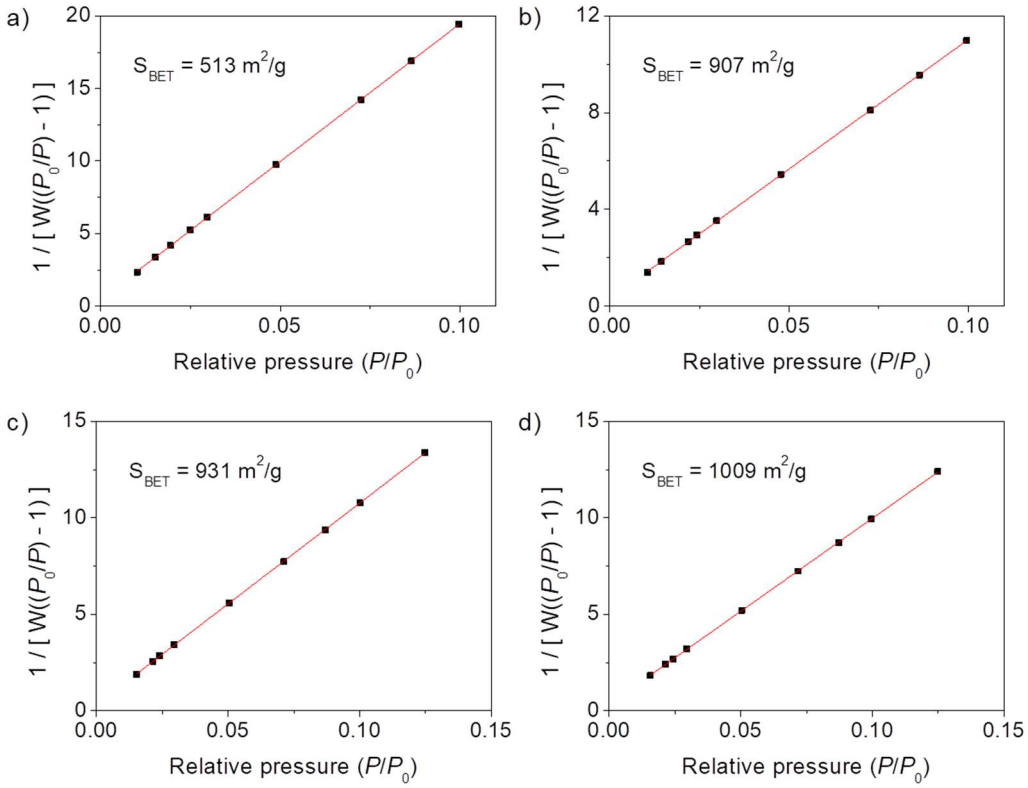

Fig. S6. BET surface area plots of **COF-TA-PA** at (a) 0.5 h, (b) 1 h, (c) 2 h, and (d) 6 h.

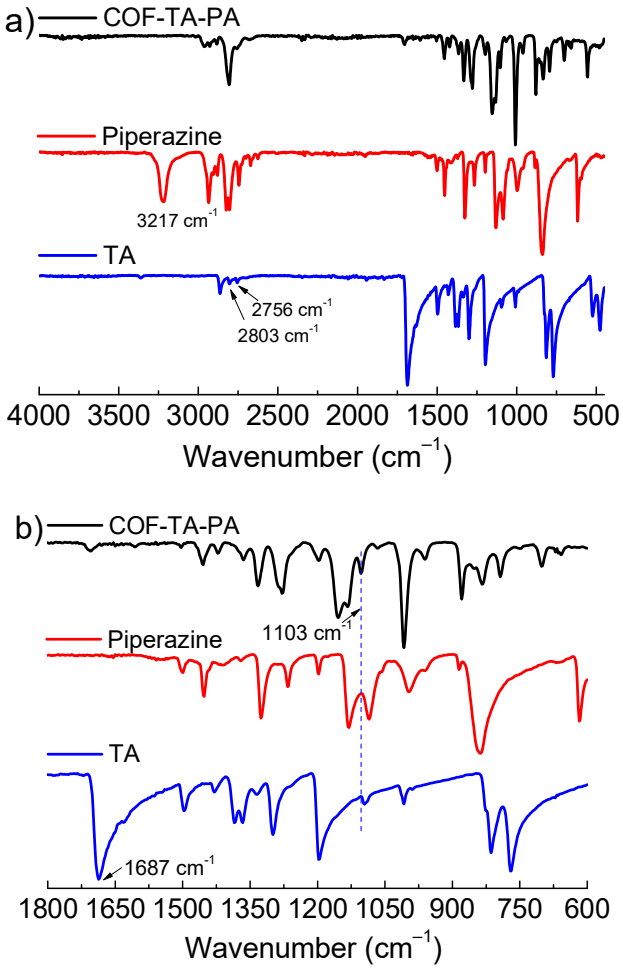

Fig. S7. FT-IR spectra of **COF-TA-PA** (black), piperazine (red), and terephthalaldehyde (TA, blue) at the wavenumber of (a) 4000–450 cm^{-1} and (b) 1800–600 cm^{-1}.

Table S5. Paek assignment and notes for COF-TA-PA.

Paek (cm^{-1})	**Assignment and notes for COF-BDA-PA**
3016	aromatic C–H stretch
2962 and 2929	aliphatic C–H stretch
2806 and 2756	C–H stretch from residual H–C=O in COF terminal group
1704	residual C=O stretch from COF terminal group
1504	phenyl ring C=C vibrational mode (ν_a)
1456	phenyl ring C=C vibrational mode (ν_b)
1332	phenyl ring C–C vibrational mode
1154	C–Ph stretching
1103	**C(H)–N stretching**
961	aromatic ring stretching
879	aromatic C-H out of plane wagging

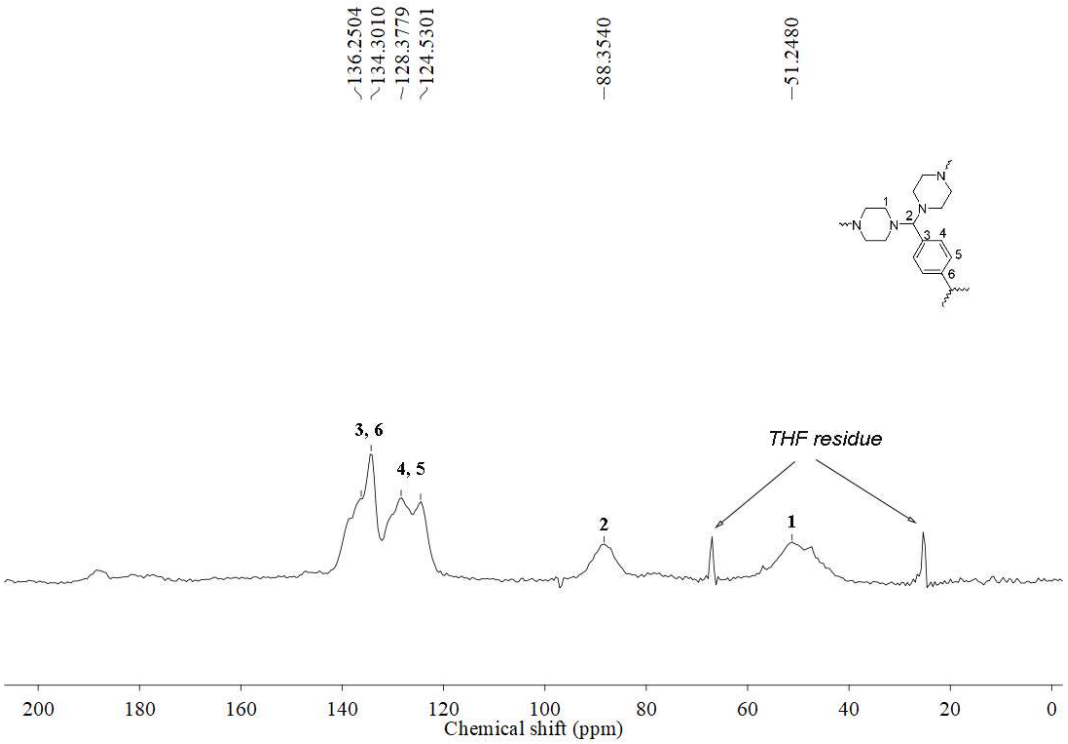

Fig. S8. Solid-state ^{13}C CP/MAS NMR spectrum of **COF-TA-PA**.

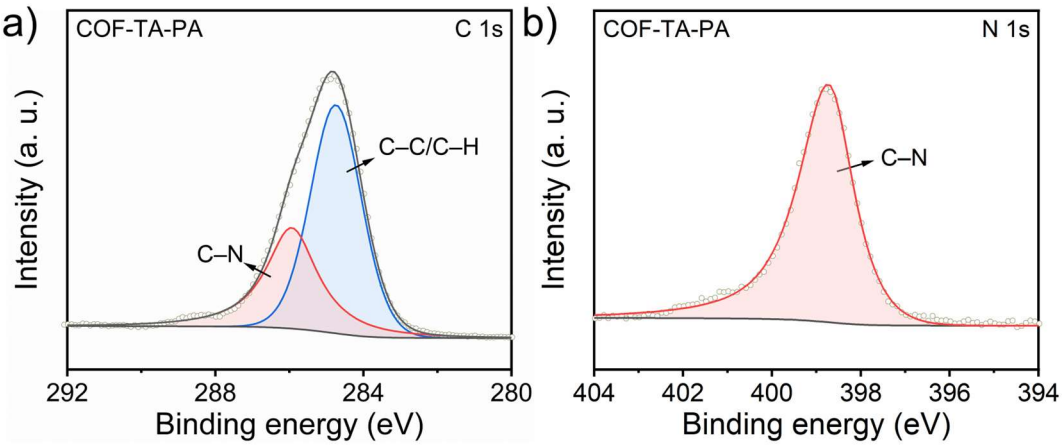

Fig. S9. (a) C 1s and (b) N 1s XPS spectra of **COF-TA-PA**.

2. Screening conditions and characterization for COF-BDA-PA

Table S6. Synthesis of **COF-BDA-PA** obtained under different solvents.

Entry	Solvent (1 mL)	Temperature	Time
1	*o*-DCB		
2	Tol		
3	Mes/Dio = 1/1	120 °C	72 h
4	DMAc/Mes = 1/1		
5	DMAc/Tol= 1/1		

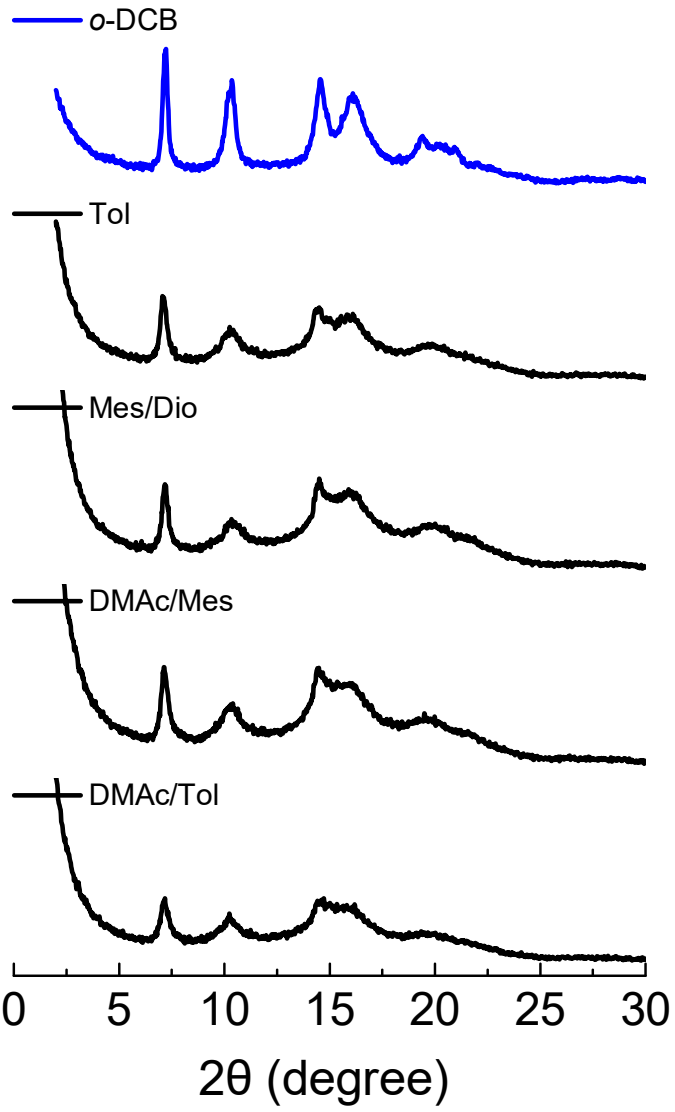

Fig. S10. PXRD patterns of **COF-BDA-PA** obtained under different solvents.

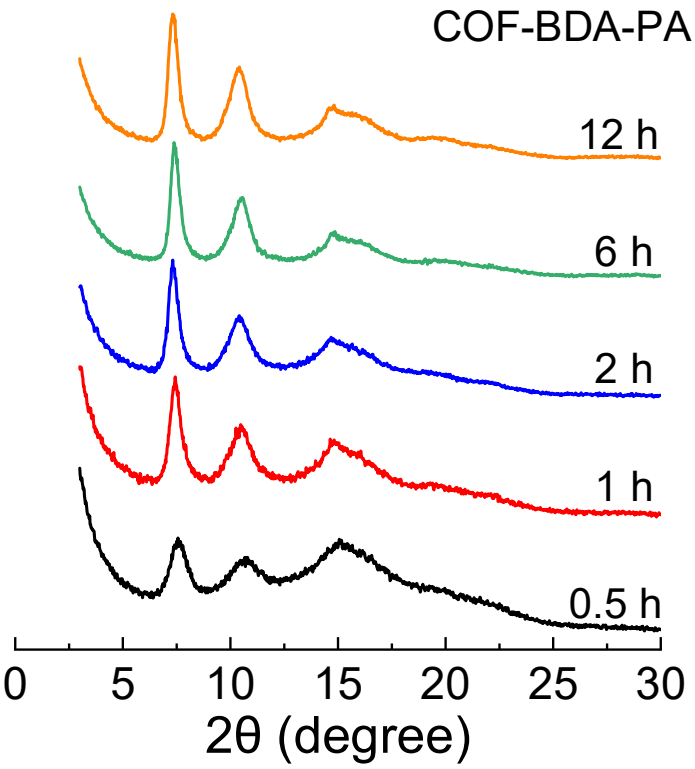

Fig. S11. PXRD patterns of **COF-BDA-PA** obtained by using different reaction times.

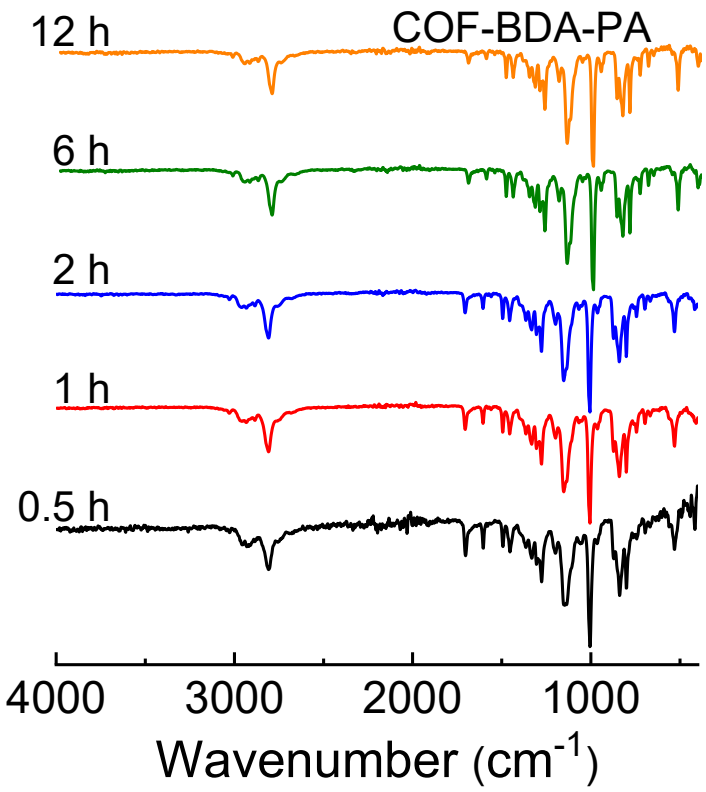

Fig. S12. FT-IR spectra of **COF-BDA-PA** obtained by using different reaction times.

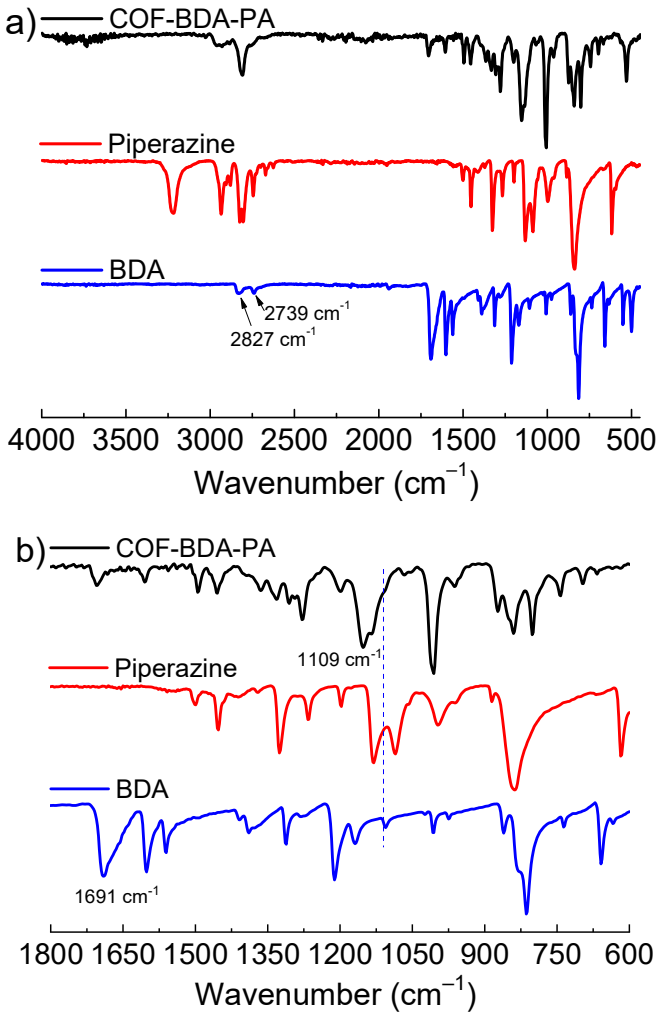

Fig. S13. FT-IR spectra of **COF-BDA-PA** (black), piperazine (red), and 4,4'-Biphenyldicarboxaldehyde (BDA, blue) at the wavenumber of (a) 4000–450 cm^{-1} and (b) 1800–600 cm^{-1}.

Table S7. Paek assignment and notes for COF-BDA-PA.

Paek (cm^{-1})	**Assignment and notes for COF-BDA-PA**
3027	aromatic C–H stretch
2960 and 2931	aliphatic C–H stretch
2810 and 2753	C–H stretch from residual H–C=O in COF terminal group
1704	residual C=O stretch from COF terminal group
1495	phenyl ring C=C vibrational mode (ν_a)
1455	phenyl ring C=C vibrational mode (ν_b)
1305	phenyl ring C–C vibrational mode
1153	C–Ph stretching
1109	**C(H)–N stretching**
962	aromatic ring stretching
873	aromatic C-H out of plane wagging

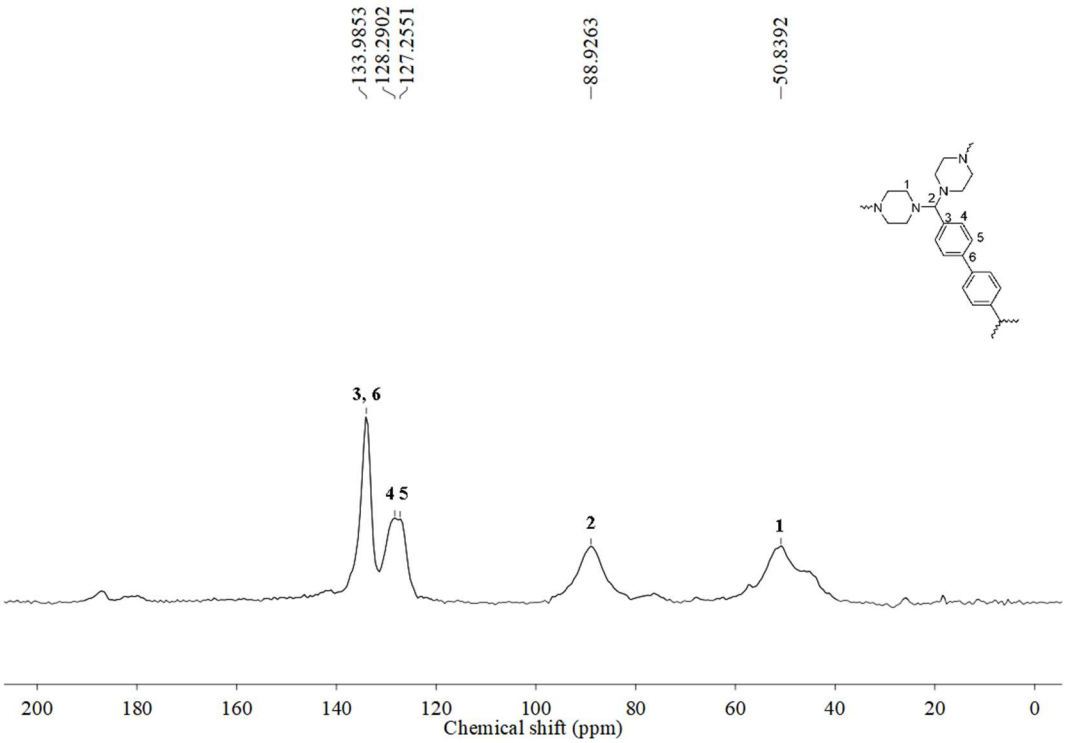

Fig. S14. Solid-state ^{13}C CP/MAS NMR spectrum of **COF-BDA-PA**.

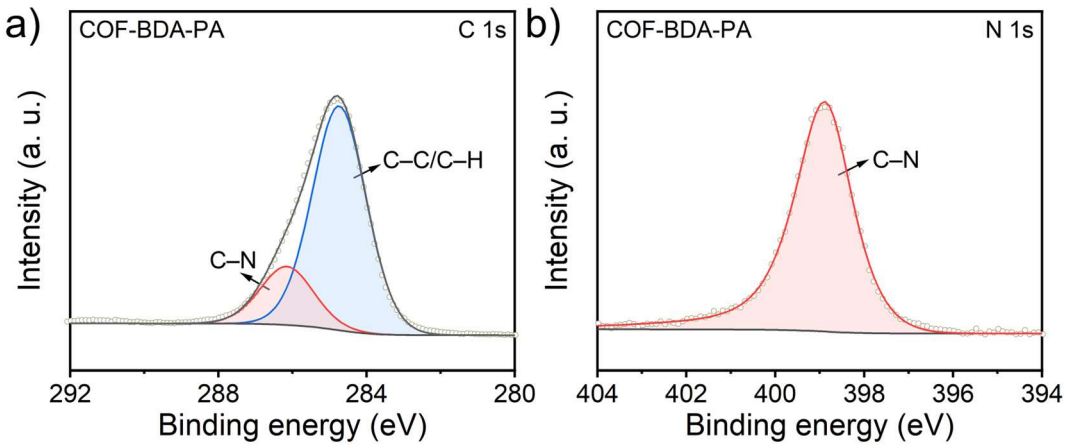

Fig. S15. (a) C 1s and (b) N 1s XPS spectra of **COF-BDA-PA**.

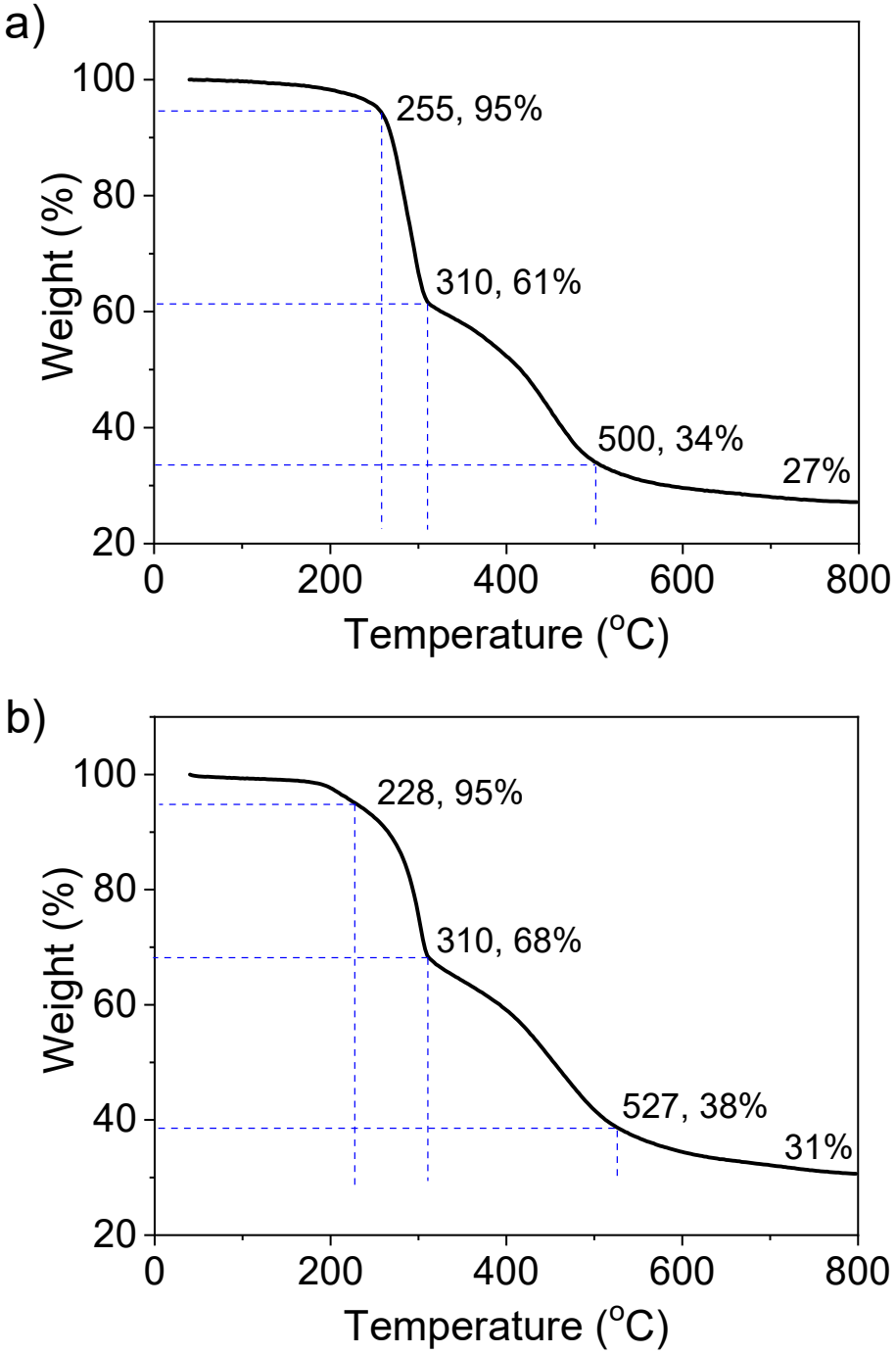

Fig. S16. TGA profiles of (a) **COF-TA-PA** and (b) **COF-BDA-PA**.

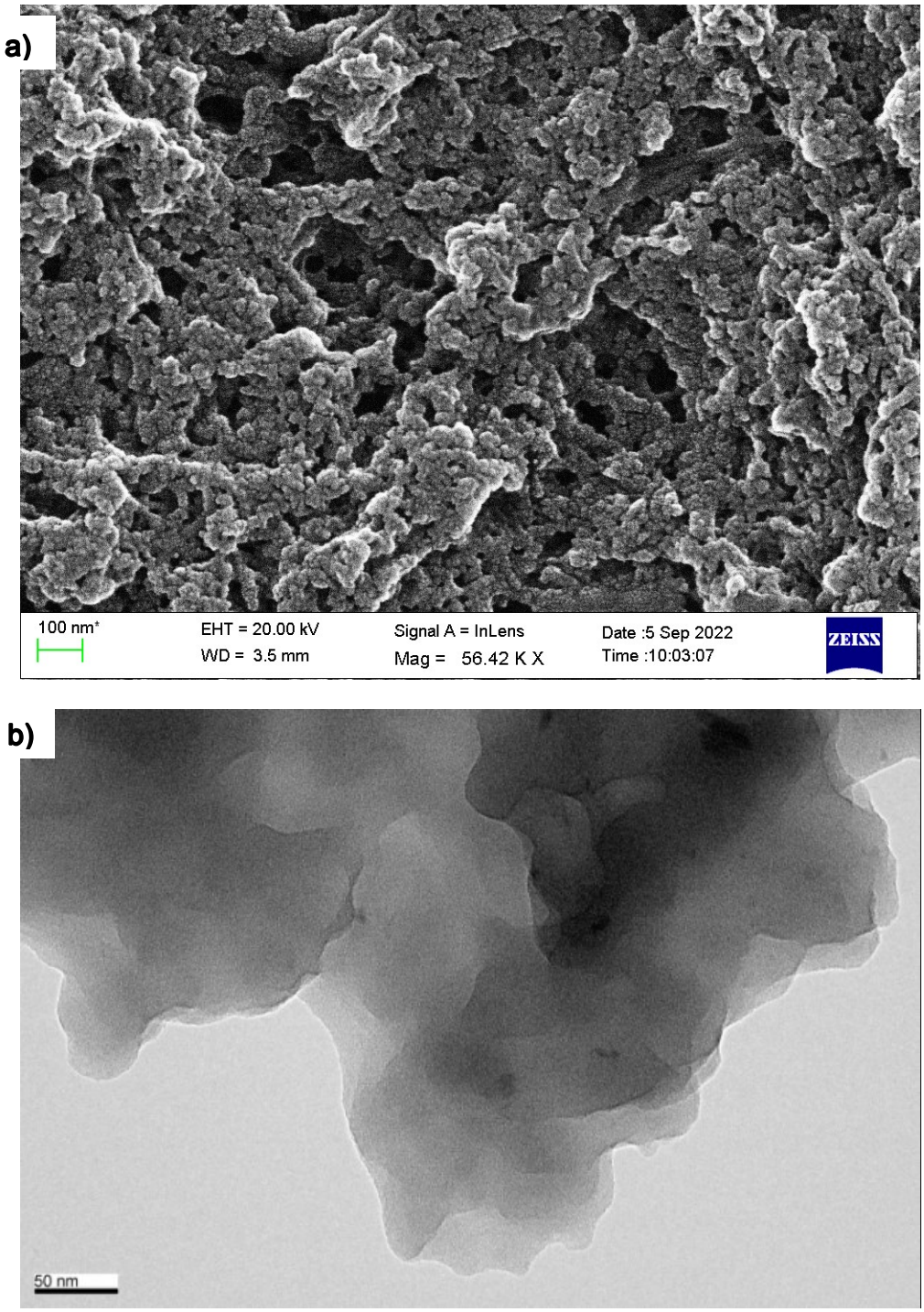

Fig. S17. (a) Field-emission SEM and (b) TEM images of **COF-TA-PA**.

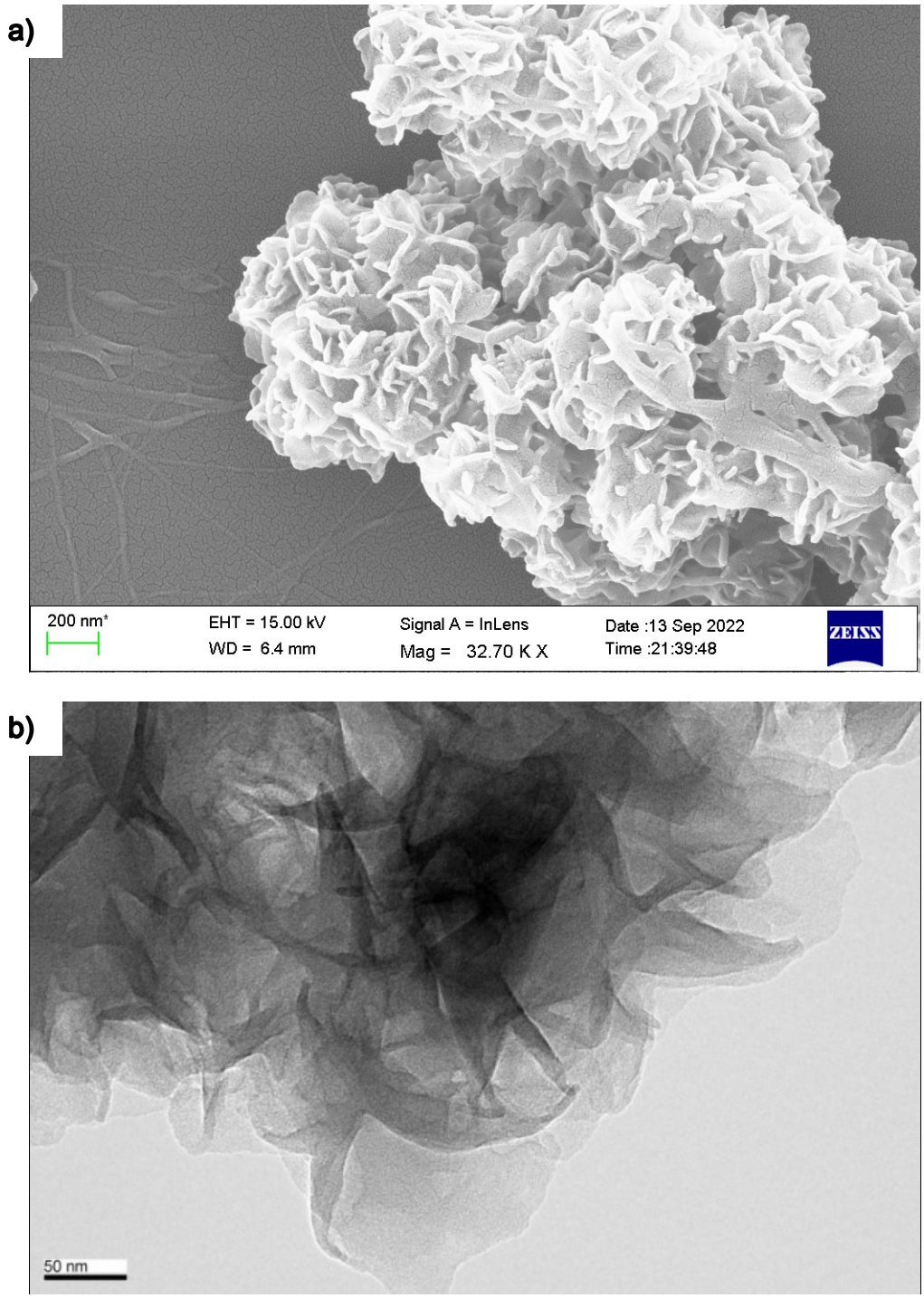

Fig. S18. (a) Field-emission SEM and (b) TEM images of **COF-BDA-PA**.

3. Characterization of gram-scale aminal-linked COFs

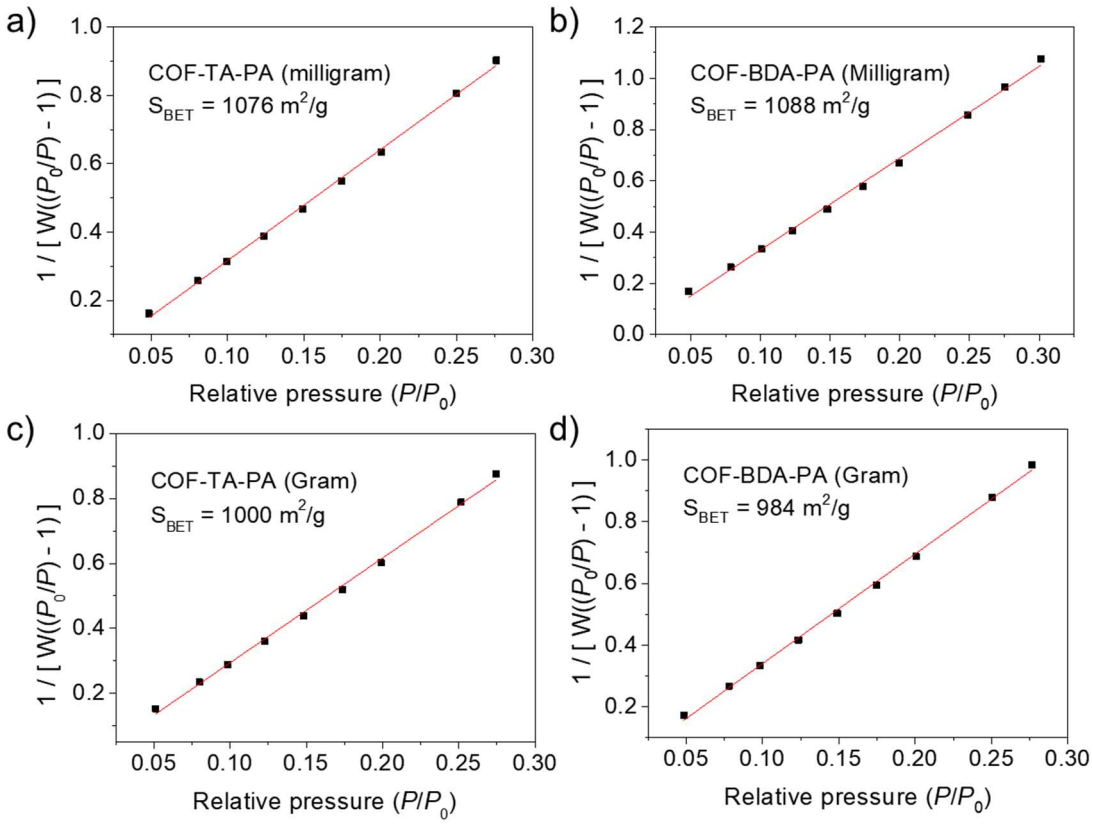

Fig. S19. BET surface area plots of (a, b) milligram-scale and (c, d) gram-scale synthesis of COF-TA-PA and COF-BDA-PA calculated from N_2 adsorption isotherms.

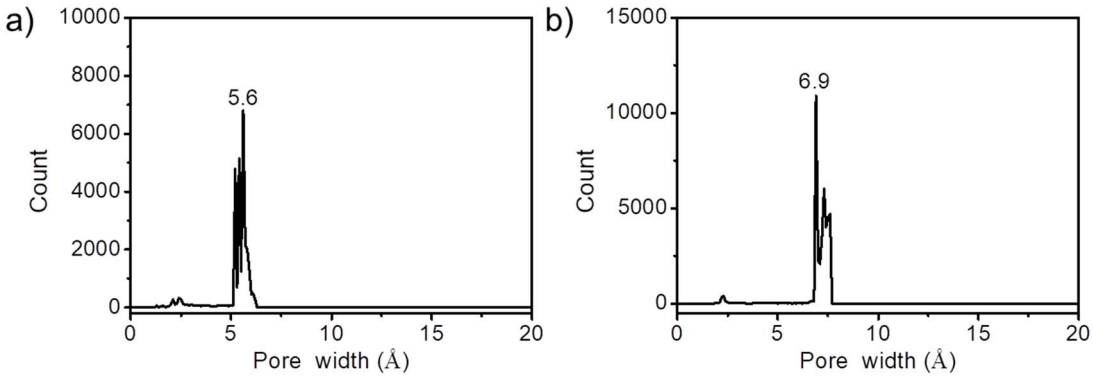

Fig. S20. Illustration of the theoretical pore sizes for (a) **COF-TA-PA** and (b) **COF-BDA-PA** with eclipsed AA stacking based on Zeo^{++} calculations.

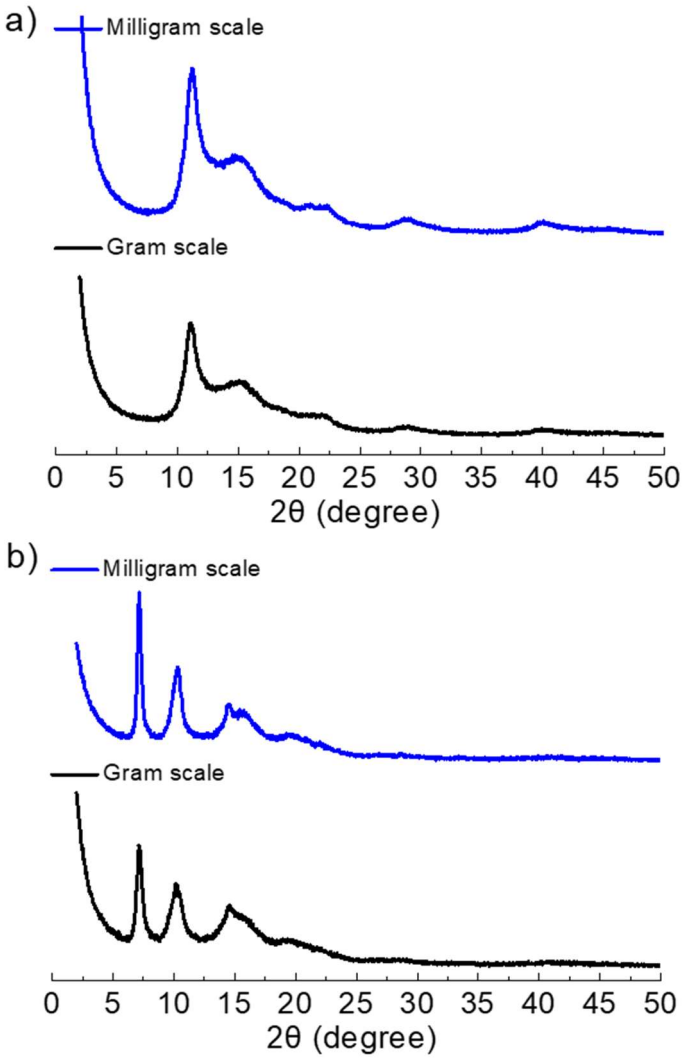

Fig. S21. PXRD patterns of (a) **COF-TA-PA** and (b) **COF-BDA-PA** on a milligram scale (blue) and gram scale (black) synthesis.

4. CO_2 and CH_4 adsorption isotherm

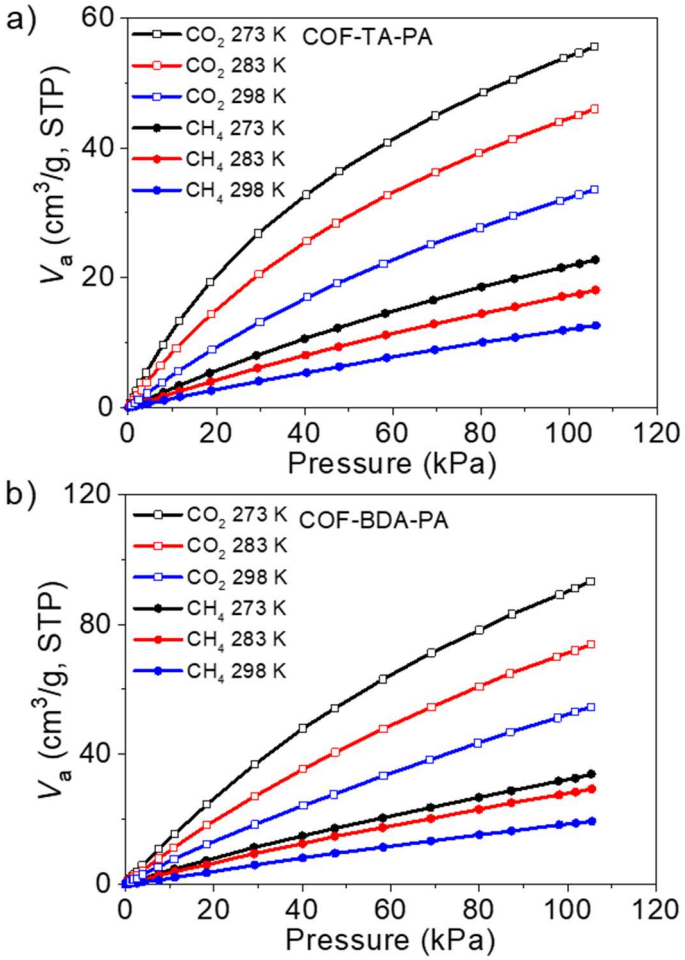

Fig. S22. CO_2 and CH_4 sorption isotherm curves of (a) **COF-TA-PA** and (b) **COF-BDA-PA** at 273, 283, and 298 K, respectively.

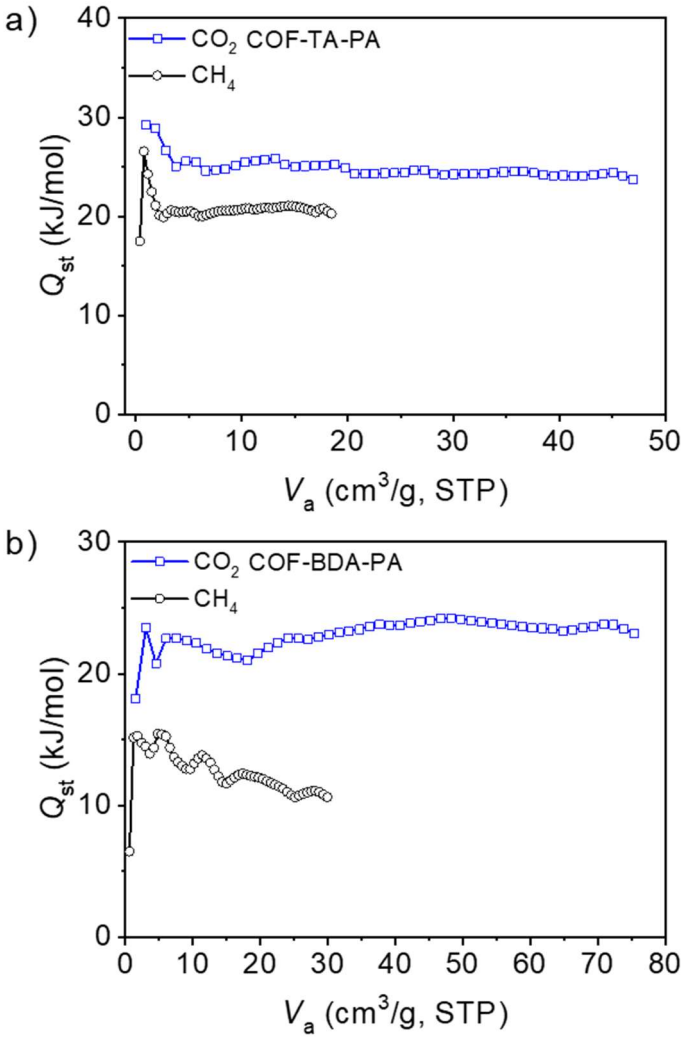

Fig. S23. The adsorption enthalpy (Q_{st}) for CO_2 for (a) **COF-TA-PA**, and (b) **COF-BDA-PA** calculated at low coverage by the Clausius–Clapeyron equation.

Table S8. Fitting parameters of the dual-site Langmuir and single site Langmuir-Freundlich model.

	Parameters	q_1	b_1	n_1	q_2	b_2	n_2	R^2
COF-TA-PA	**CO_2 (273 K)**	4.34109	0.00395	--	1.57687	0.03015	--	1
	CH_4 (273 K)	1.6728	0.00411	--	1.6728	0.00411	--	0.99998
	CO_2 (298 K)	4.05398	0.00608	0.97898	--	--	--	0.99997
	CH_4 (298K)	2.61698	0.00223	1.03198	--	--	--	0.99997
COF-BDA-PA	**CO_2 (273 K)**	10.24658	0.00676	0.99071	--	--	--	0.99998
	CH_4 (273 K)	12.58062	0.00181	0.92652	--	--	--	0.99993
	CO_2 (298 K)	19.68224	0.00192	0.92291	--	--	--	0.99997
	CH_4 (298K)	3.1178	0.00201	1.12576	--	--	--	0.99984

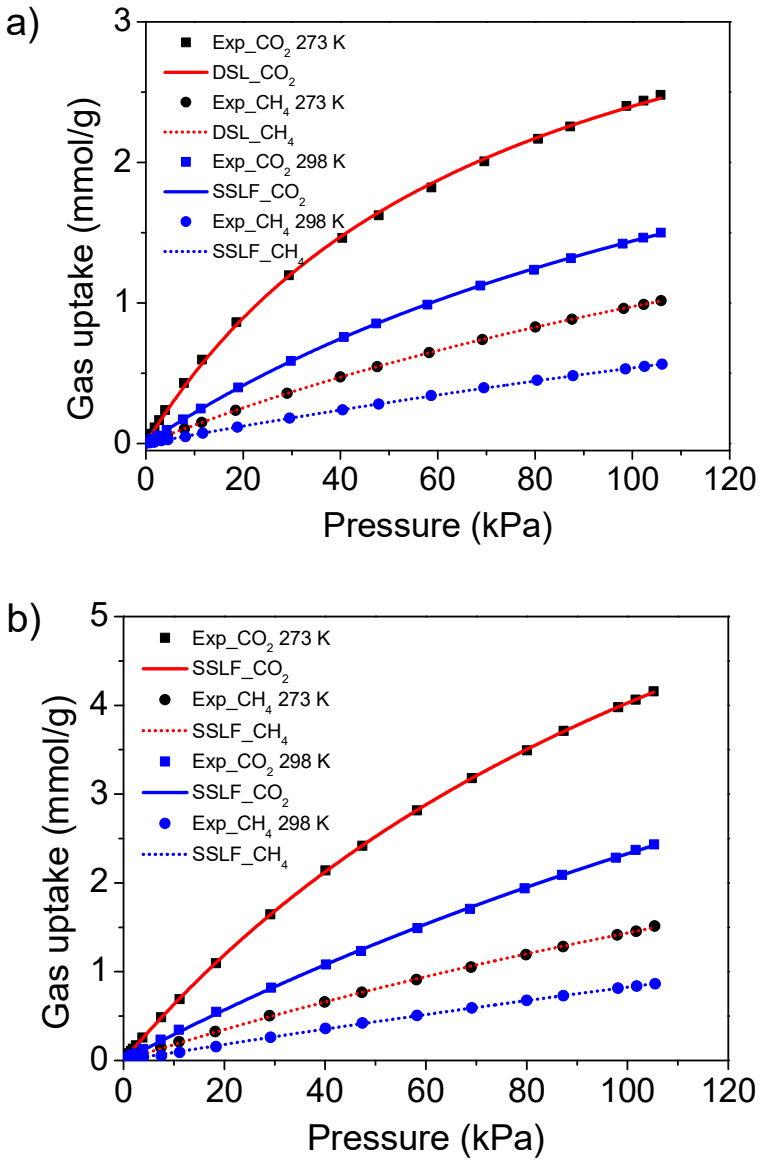

Fig. S24. Experimental and fitted isotherms of CO_2 and CH_4 for (a) **COF-TA-PA** and (b) **COF-BDA-PA** measured at 273 (red) and 298 K (blue).

5. Fractional atomic coordinates

Table S9. The space groups and cell parameters of the possible structures for **COF-TA-PA**

Structure	Space Group	Cell Parameters
AA	P1	a = 17.41 Å, b = 16.23 Å, c = 5.86 Å, $\alpha = \beta$ = 90° and γ = 120°
AB	P1	a = 17.41 Å, b = 16.23 Å, c = 14.00 Å, $\alpha = \beta$ = 90° and γ = 120°

Table S10. The space groups and cell parameters of the possible structures for **COF-BDA-PA**

Structure	Space Group	Cell Parameters
AA	P1	a = 9.79 Å, b = 13.96 Å, c = 6.45 Å, $\alpha = \beta$ = 90° and γ = 114.6°
AB	P1	a = 9.79 Å, b = 13.96 Å, c = 13.79 Å, $\alpha = \beta$ = 90° and γ = 114.6°

Table S11. Fractional atomic coordinates for the unit cell of **COF-TA-PA** with AA stacking.

P1 (C1-1)

a = 17.41 Å, b = 16.23 Å, c = 5.86 Å, $\alpha = \beta = 90°$ and $\gamma = 120°$; R_p = 2.13 %, R_{wp} = 2.70 %.

Element	Atom number	x	y	z	Element	Atom number	x	y	z
H	1	1.73077	-0.03399	-0.36366	H	64	1.34393	-0.18061	0.35209
H	2	1.63521	-0.14702	-0.32488	H	65	1.21274	-0.32566	0.25763
H	3	1.59232	-0.02848	-0.28034	H	66	1.4915	-0.06757	0.28824
H	4	1.68226	0.04114	-0.09875	C	1	1.68278	-0.08164	-0.238
H	5	1.54869	-0.22119	0.07572	C	2	1.63321	-0.03197	-0.14326
H	6	1.56259	-0.16828	0.34752	C	3	1.58796	-0.1556	0.17298
H	7	1.68786	-0.19323	0.24602	C	4	1.68584	-0.13218	0.17491
H	8	1.72403	-0.07142	0.28636	C	5	1.81565	-0.09923	-0.10471
H	9	1.82637	-0.09013	-0.2896	C	6	1.81416	-0.19011	-0.04534
H	10	1.96195	0.12703	0.32657	C	7	1.96836	0.15302	0.15107
H	11	1.96257	0.21683	0.15778	C	8	1.89039	0.07699	0.00677
H	12	1.89383	0.10397	-0.16636	C	9	1.98123	0.00541	-0.09295
H	13	1.82887	0.06553	0.08407	C	10	2.05947	0.08306	0.04538
H	14	1.98811	0.02846	-0.27131	C	11	1.84157	-0.20386	0.17208
H	15	1.98695	-0.05868	-0.0885	C	12	1.84428	-0.2871	0.22327
H	16	2.11983	0.09349	-0.03796	C	13	1.81911	-0.36003	0.05888
H	17	2.05836	0.05729	0.21879	C	14	1.79081	-0.34675	-0.15774
H	18	1.86066	-0.15222	0.29431	C	15	1.78737	-0.26387	-0.20811
H	19	1.86556	-0.29382	0.3812	C	16	1.82218	-0.44923	0.11205
H	20	1.77213	-0.39833	-0.28005	C	17	1.64188	-0.69007	-0.15317
H	21	1.7654	-0.25742	-0.36535	C	18	1.72884	-0.62447	-0.02486
H	22	1.82507	-0.45424	0.29828	C	19	1.65498	-0.54812	0.17118
H	23	1.63969	-0.75741	-0.18762	C	20	1.56814	-0.61341	0.04017
H	24	1.64281	-0.65761	-0.31766	C	21	1.47703	-0.78591	-0.10841
H	25	1.78367	-0.61266	-0.13663	C	22	1.39389	-0.7861	-0.03862
H	26	1.73089	-0.66119	0.12947	C	23	1.55481	-0.95061	0.12239
H	27	1.6564	-0.4812	0.20636	C	24	1.50249	-0.8981	0.16629
H	28	1.65392	-0.58073	0.33545	C	25	1.44475	-0.95244	-0.23875
H	29	1.56542	-0.57776	-0.11576	C	26	1.42535	-1.05039	-0.14559
H	30	1.51315	-0.62423	0.14995	C	27	1.34811	-0.76006	-0.19634
H	31	1.48146	-0.77801	-0.29467	C	28	1.26874	-0.76259	-0.13654
H	32	1.5806	-0.95983	0.28475	C	29	1.23299	-0.78895	0.08555
H	33	1.61201	-0.90556	0.01537	C	30	1.27977	-0.81293	0.24501
H	34	1.54431	-0.83248	0.26042	C	31	1.35905	-0.81072	0.1848
H	35	1.44539	-0.94326	0.27347	C	32	1.14637	-0.79517	0.14976

H	36	1.5004	-0.92665	-0.35759	C	33	1.15845	-0.59427	-0.23092
H	37	1.3866	-0.9611	-0.33121	C	34	1.10758	-0.69384	-0.11935
H	38	1.41389	-1.0974	-0.29073	C	35	1.22382	-0.61369	0.19079
H	39	1.36457	-1.08053	-0.04381	C	36	1.20946	-0.52699	0.17037
H	40	1.37264	-0.73855	-0.35722	C	37	1.17126	-0.43225	-0.13035
H	41	1.23709	-0.74502	-0.25692	C	38	1.25455	-0.3417	-0.07126
H	42	1.25541	-0.8338	0.40626	C	39	0.94485	-0.50557	0.15362
H	43	1.39116	-0.82768	0.30532	C	40	1.00997	-0.52433	0.01397
H	44	1.13949	-0.80347	0.33553	C	41	1.06596	-0.36864	-0.17191
H	45	1.11822	-0.59273	-0.37197	C	42	0.99361	-0.35595	-0.04948
H	46	1.22128	-0.58299	-0.29916	C	43	1.32683	-0.29929	-0.22504
H	47	1.10063	-0.74694	-0.24495	C	44	1.40442	-0.21374	-0.16933
H	48	1.04095	-0.70733	-0.08159	C	45	1.41284	-0.168	0.04246
H	49	1.28354	-0.59731	0.094	C	46	1.34085	-0.21126	0.19719
H	50	1.23619	-0.62317	0.36855	C	47	1.26337	-0.29646	0.14145
H	51	1.27211	-0.46328	0.21263	C	48	1.49448	-0.07556	0.1034
H	52	1.16043	-0.53385	0.29557	N	1	1.72657	-0.10873	-0.05748
H	53	1.16571	-0.4338	-0.31684	N	2	1.89373	-0.01343	0.00223
H	54	0.97819	-0.46651	0.30896	N	3	2.05551	0.17352	0.05024
H	55	0.89024	-0.5739	0.20866	N	4	1.73429	-0.53218	0.03472
H	56	0.97811	-0.56307	-0.14273	N	5	1.56303	-0.70608	-0.01531
H	57	1.02646	-0.56925	0.11702	N	6	1.46869	-0.8807	-0.05313
H	58	1.04127	-0.39934	-0.34079	N	7	1.49978	-1.04308	-0.00115
H	59	1.12399	-0.29802	-0.19669	N	8	1.14674	-0.70337	0.10064
H	60	0.97506	-0.31661	-0.16708	N	9	1.17847	-0.51764	-0.06148
H	61	1.0222	-0.31209	0.1031	N	10	1.09054	-0.43119	-0.03902
H	62	1.32336	-0.33069	-0.3791	N	11	0.91394	-0.44981	0.01381
H	63	1.45509	-0.18476	-0.28486	N	12	1.57962	-0.07663	0.0673

Table S12. Fractional atomic coordinates for the unit cell of **COF-BDA-PA** with AA stacking.

P1 (C1-1)

a =9.79 Å, b = 13.96 Å, c = 6.45 Å, $\alpha = \beta = 90°$ and $\gamma = 114.6°$; R_p = 3.73 %, R_{wp} = 4.75 %.

Element	Atom number	x	y	z	Element	Atom number	x	y	z
H	1	1.08604	0.75821	0.7899	C	1	-1.87297	-3.21157	-0.07385
H	2	1.09011	0.65876	0.94929	C	2	-1.93483	-3.16959	0.11
H	3	1.10746	0.7642	1.26417	C	3	-1.71293	-3.00127	0.09582
H	4	0.94862	0.74597	1.1184	C	4	-1.65069	-3.04176	-0.09001
H	5	1.33714	0.93702	1.24818	C	5	-1.61867	-3.20331	0.04952
H	6	1.33667	1.0402	1.09688	C	6	-1.66276	-3.31981	0.02769
H	7	1.47755	0.95437	0.91913	C	7	-1.19713	-3.06619	0.18399
H	8	1.31931	0.93707	0.77364	C	8	-1.3563	-3.15562	0.19623
H	9	1.87714	0.87852	1.31576	C	9	-1.38552	-3.14311	-0.18288
H	10	1.80009	0.96423	1.21798	C	10	-1.22333	-3.05566	-0.19595
H	11	1.60222	0.80382	1.3559	C	11	-1.71165	-3.37328	-0.16288
H	12	1.65724	0.72433	1.19166	C	12	-1.75921	-3.48314	-0.17707
H	13	1.55235	0.82665	0.70528	C	13	-1.7536	-3.54412	-0.00372
H	14	1.62246	0.73612	0.79525	C	14	-1.69665	-3.48865	0.18387
H	15	1.77946	0.97747	0.82009	C	15	-1.65577	-3.37985	0.20061
H	16	1.82992	0.89353	0.66306	C	16	-1.80373	-3.65554	-0.01544
H	17	1.29045	0.62358	0.71609	C	17	-1.79294	-3.70701	-0.20055
H	18	1.20584	0.4376	0.69193	C	18	-1.84642	-3.81743	-0.21175
H	19	1.32226	0.42891	1.32089	C	19	-1.90911	-3.88158	-0.03617
H	20	1.38632	0.61133	1.3495	C	20	-1.91425	-3.83043	0.15068
H	21	1.26127	0.29121	0.67795	C	21	-1.86738	-3.72078	0.15923
H	22	1.16819	0.10501	0.65887	C	22	-1.96334	-3.99944	-0.04595
H	23	1.05386	0.08279	1.29201	N	1	-1.8816	-3.05203	0.10409
H	24	1.12453	0.26623	1.30507	N	2	-1.70436	-3.15956	-0.08875
H	25	1.06763	-0.06407	0.80775	N	3	-1.45116	-3.14263	0.02642
H	26	0.35682	0.76599	1.21612	N	4	-1.12973	-3.06762	-0.02322