Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A backbone design principle for covalent organic frameworks: the impact of weakly interacting units on CO_2 adsorption

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Section A. Methods

Fourier transforms Infrared (FT IR) spectra were recorded on a JASCO model FT IR-6100 infrared spectrometer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. TGA measurements were performed on a Mettler-Toledo model TGA/SDTA851e under N_2, by heating to 800 °C at a rate of 10 °C min^{-1}. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve.

The isosteric heat of adsorption, Q_{st}, defined as $Q_{st} = RT^2 (\frac{\partial lnp}{\partial T})_q$, was determined using the pure component isotherm fits using the Clausius-Clapeyron equation. R is the gas constant, 8.314 J mol^{-1} K^{-1}.

The crystalline structures were determined using the density-functional tight-binding (DFTB+) method including Lennard-Jones (LJ) dispersion. The calculations were carried out with the DFTB+ program package version 1.2. [S1] DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism. Lennard-Jones type dispersion was employed in all calculations to describe van der Waals (vdW) and π-stacking interactions. The lattice dimensions were optimized simultaneously with the geometry. Standard DFTB parameters for X–Y element pair (X, Y = C, S, H and N) interactions were employed from the mio-0-1 set. [S2]

Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from XRD pattern, implemented in MS modeling version 4.4 (Accelrys Inc.).[S3] Initially, unit cell dimensions for hexagonal lattices were taken from the DFTB calculation and the space group for hexagonal crystal system were selected as *P*3, respectively. We performed Pawley refinement for hexagonal lattice to optimize the lattice parameters iteratively until the R_{WP} value converges. The pseudo–Voigt profile function was used for whole profile fitting and Berrar–Baldinozzi function was used for asymmetry correction during the refinement processes. The final *R*wp and *R*p values were R_{WP} = 9.56% and R_P = 6.56% for TFPB-TAPB-COF, R_{WP} = 21.7% and R_P = 15.08% for TFPA-TAPB-COF, R_{WP} = 15.60%; R_P = 12.77% for BTMA-TAPA-COF and R_{WP} = 9.90%; R_P = 7.65% for TFPA-TAPA-COF, respectively. The high *R*wp and *R*p values of TFPA-TAPB-COF are associated with the unclear shoulder peak at around 6°.

Section B. Materials and synthetic procedures

Mesitylene, 1,4-dioxane and tetrahydrofuran (THF) were purchased from Wako chemicals. Tris(4-aminophenyl)amine(TAPA), 1,3,5-tris(4-aminophenyl)benzene (TAPB), tris(4-formylphenyl)amine(TFPA) and acetic acid were purchased from TCI. 1,3,5-Tris (4-formylphenyl)benzene (TFPB) was synthesized according to a reported method.[S4] tris(bromoduryl)borane was synthesized according to a reported method.[S5]

Synthesis of 4,4',4''-boranetriyltris(2,3,5,6-tetramethylbenzaldehyde) (BTMA). To an anhydrous THF solution (40 mL) of tris(bromoduryl)borane (1 g, 1.6 mmol) was added dropwise with a pentane solution of t-BuLi (1.5 M, 5 mL, 7.5mmol) at –78 ^{o}C. The mixture was stirred for 2 h and anhydrous DMF (5 mL) was added at –78 ^{o}C. The mixture was warmed up to room temperature over 1 h and stirred overnight. The mixture was charged with concentrated HCl and stirred for 1 h. After addition of water (100 mL), the mixture was extracted with CH_2Cl_2 (100 mL x 3). The extract was combined and washed with brine and water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of CH_2Cl_2 and hexane (1:1 to 3:1) as eluent to obtain the product 4,4',4''-boranetriyltris(2,3,5,6-tetramethylbenzaldehyde) as a white soild (220 mg, 27% yield). ^{1}HNMR ($CDCl_3$): 10.64 (s, 3H), 2.28 (s, 18H) and 1.97 (s, 18H).

TFPB-TAPB-COF. A mesitylene/1,4-dioxane (0.9 mL/0.1 mL) mixture of TFPB (0.048 mmol, 18.9 mg) and TAPB (0.048 mmol, 17 mg) in the presence of acetic acid (6 M, 0.1mL) in a Pyrex tube (10mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame sand heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding TFPB-TAPB-COF in 87% isolated yield.

TFPA-TAPB-COF. A mesitylene/1,4-dioxane (0.5 mL/0.5 mL) mixture of TFPA (0.048 mmol, 15.94 mg) and TAPB (0.048 mmol, 17 mg) in the presence of acetic acid (6 M, 0.1 mL) in a

Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding TFPA-TAPB-COF in 84% isolated yield.

BTMA-TAPA-COF. An *o*-DCB/n-BuOH (0.5 mL/0.5 mL) mixture of TAPA (17.8 mg, 0.0617 mmol) and BTMA (30.37 mg, 0.0617 mmol) in the presence of acetic acid (6 M, 0.1 mL) in a Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding BTMA-TAPA-COF in 78% isolated yield.

TFPA-TAPA-COF. A mesitylene/1,4-dioxane (0.5 mL/0.5 mL) mixture of TAPA (0.049 mmol, 14.1 mg) and TFPA (0.048 mmol, 15.94 mg) in the presence of acetic acid (6 M, 0.1 mL) in a Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding TFPA-TAPA-COF in 85% isolated yield.

Section C. Elemental analysis

Table S1. Elemental analysis results of TFPB-TAPB-COF, TFPA-TAPB-COF, BTMA-TAPA-COF and TFPA-TAPA-COF

COFs		C%	H%	N%
TFPB-TAPB-COF	Calcd.	88.44	5.35	6.07
	Found	86.16	5.22	5.39
TFPA-TAPB-COF	Calcd.	85.71	5.39	7.61
	Found	83.69	4.85	8.41
BTMA-TAPA-COF	Calcd.	83.84	6.99	7.67
	Found	81.57	5.68	7.34
TFPA-TAPA-COF	Calcd.	82.25	5.44	12.28
	Found	79.22	3.89	11.44

Section D. NMR spectra

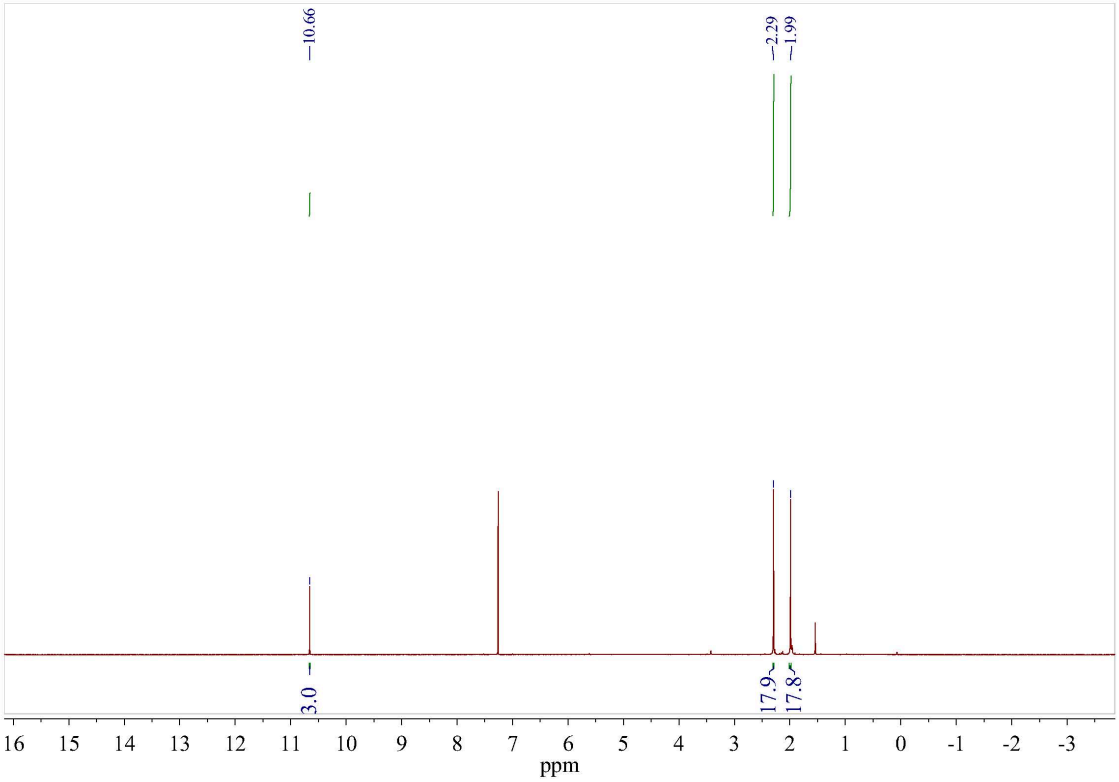

Figure S1. ^{1}HNMR of 4,4',4"-boranetriyltris(2,3,5,6-tetramethylbenzaldehyde, BTMA) ($CDCl_3$)

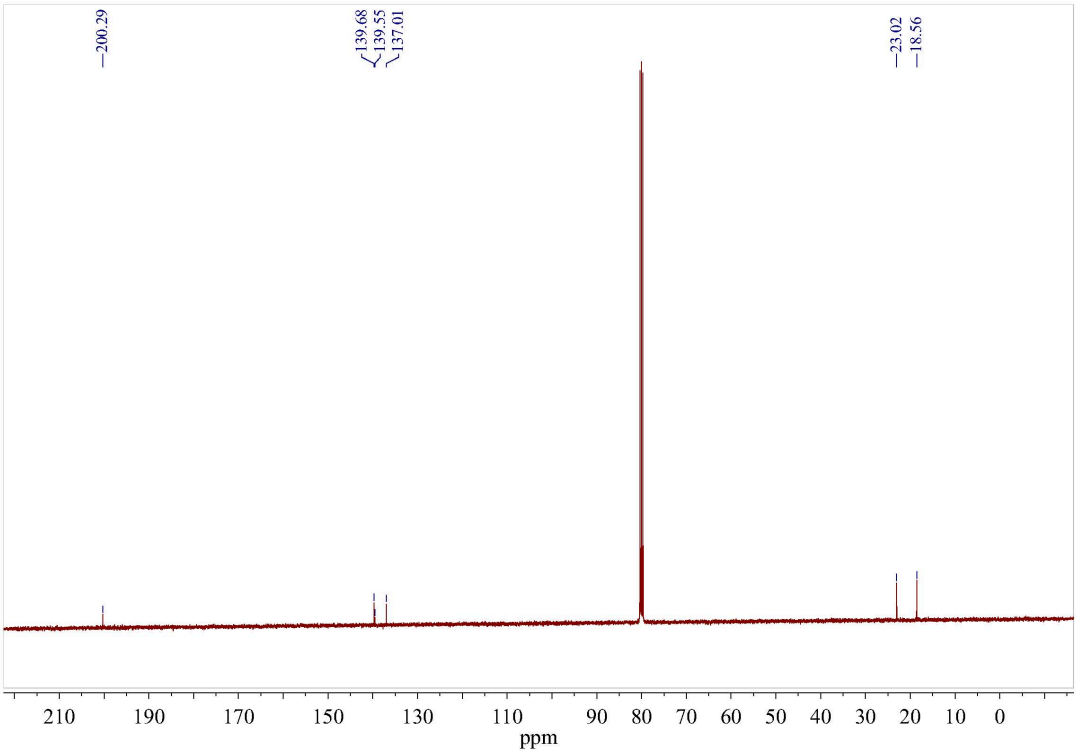

Figure S2. ^{13}C NMR of 4,4',4"-boranetriyltris(2,3,5,6-tetramethylbenzaldehyde, BTMA) ($CDCl_3$)

Section E. IR spectroscopy

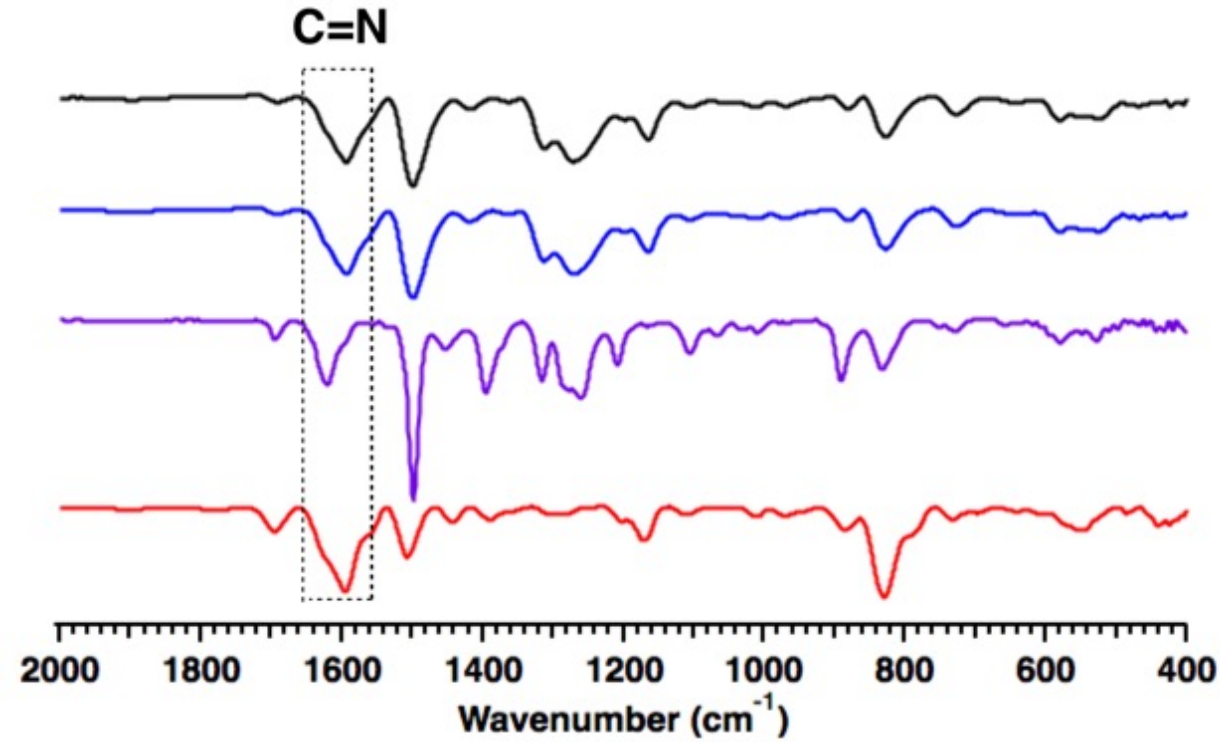

Figure S3. FT-IR spectra of TFPB-TAPB-COF (black), TFPA-TAPB-COF (blue), BTMA-TAPA-COF (purple) and TFPA-TAPA-COF (red).

Section F. Thermal gravimetric analysis

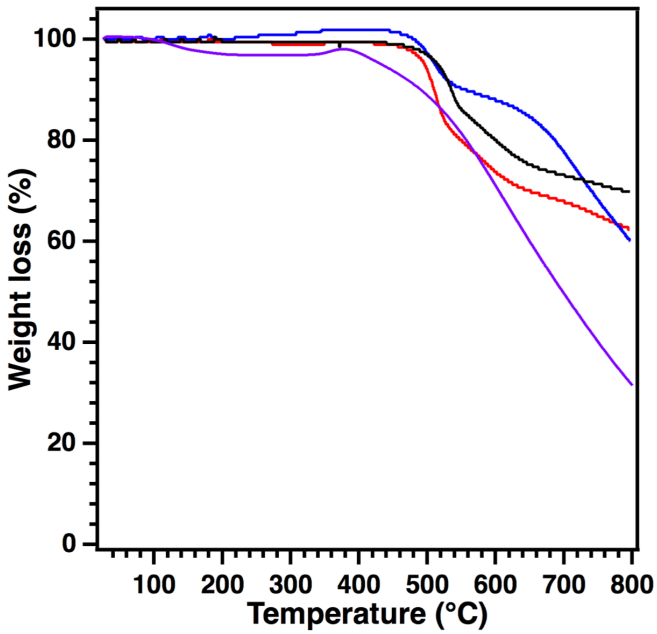

Figure S4. TGA curve of TFPB-TAPB-COF (black curves), TFPA-TAPB-COF (blue curves), BTMA-TAPA-COF (purple curves) and TFPA-TAPA-COF (red curves).

Section G. PXRD patterns

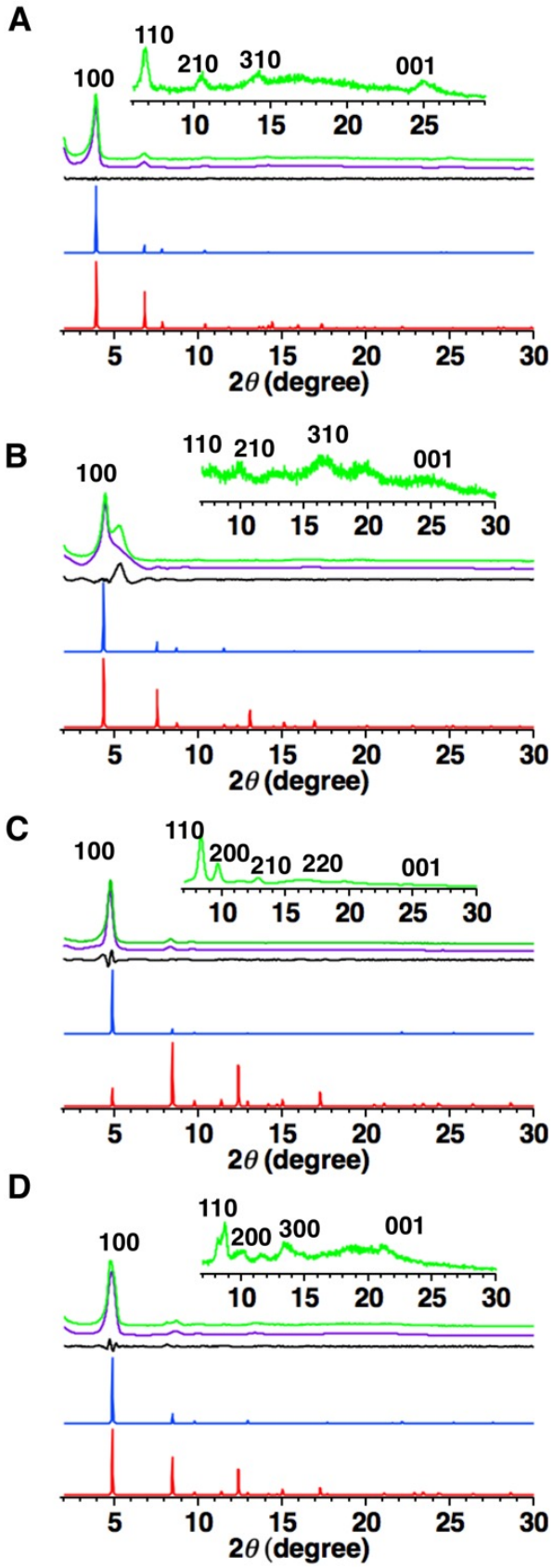

Figure S5. PXRD assignments of (A) TFPB-TAPB-COF, (B) TFPA-TAPB-COF, (C) BTMA-TAPA-COF and (D) TFPA-TAPA-COF. The originality of the shoulder peak around 6° in (B) is unclear.

Section H. Nitrogen adsorption isotherm

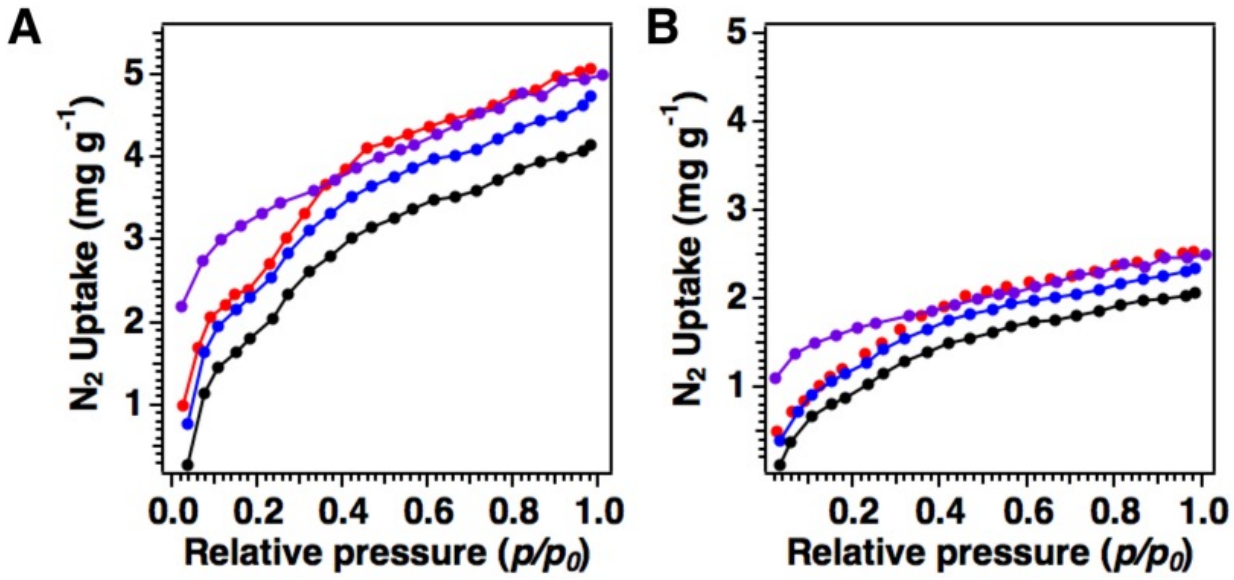

Figure S6. Nitrogen adsorption isotherm curves of TFPB-TAPB-COF (black curve), TFPA-TAPB-COF (blue curve), BTMA-TAPA-COF (purple curve) and TFPA-TAPA-COF (red curve) at (A) 273 K and (B) 298 K.

Section I. Cycling performance of CO_2 capture capacity

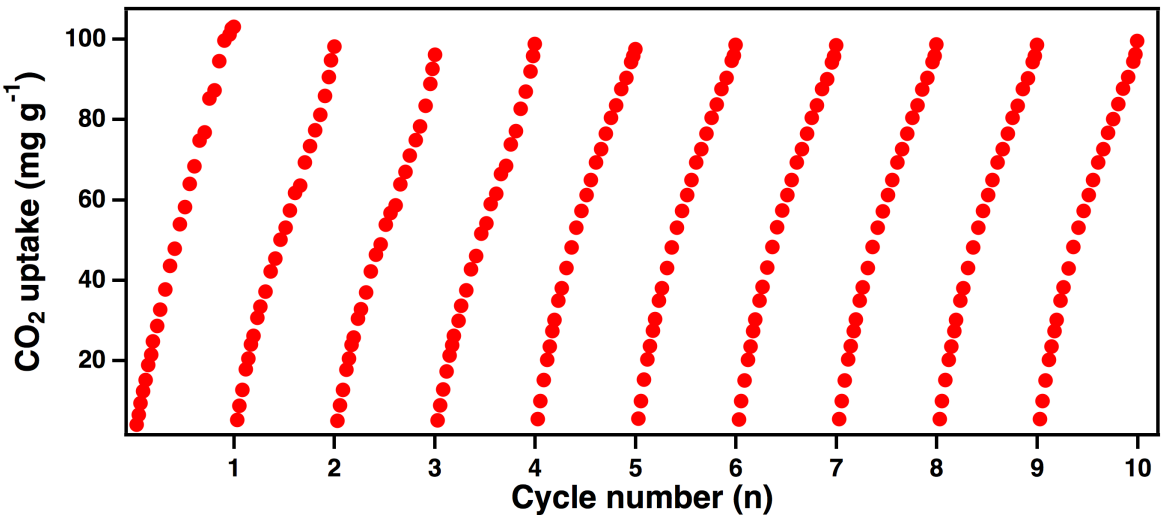

Figure S7. CO_2 uptake cycling performance of TFPA-TAPA-COF at 273 K.

Section J. Atomistic coordinates

Table S2. Atomistic coordinates for the AA-stacking mode of TFPB-TAPB-COF optimized by using DFTB+ method. Space group: *P*3*;a* = 26.0324 Å, *b* = 26.0324 Å, and *c* = 3.6329 Å.

Atom	*x/a*	*y/b*	*z/c*
C	2.26456	2.82035	0.34858
C	2.29494	2.78951	0.33548
C	2.26886	2.73077	0.46047
C	2.21047	2.70421	0.59277
C	2.1795	2.73449	0.60274
C	2.20648	2.79378	0.48562
C	2.30197	2.69774	0.45481
C	2.27181	2.63577	0.45448
N	2.64962	2.82033	0.48383
C	3.09128	3.226	0.50235
C	3.05551	3.16506	0.49663
C	3.07555	3.12784	0.63497
C	3.13327	3.15455	0.77787
C	3.1692	3.21552	0.78291
C	3.14892	3.25249	0.64562
C	3.03669	3.06206	0.63223
C	2.97498	3.03618	0.63205
C	3.13016	2.813	0.65488
H	2.28576	2.86612	0.24944
H	2.33962	2.81162	0.21776
H	2.18848	2.65877	0.69867
H	2.13401	2.7114	0.70749
H	2.22332	2.61138	0.45511
H	3.07485	3.25417	0.39098
H	3.01136	3.14621	0.37365
H	3.15039	3.12749	0.89736
H	3.21387	3.23499	0.89987
H	2.95527	3.0647	0.63236
H	3.10563	2.77081	0.81586

Table S3. Atomistic coordinates for the refined unit cell parameters for TFPB-TAPB-COF via Pawley refinement. Space group: *P*3*; a* = 26.0077 Å, *b* = 26.0077 Å, and *c* = 3.6347 Å.

Atom	***x/a***	***y/b***	***z/c***
C	2.26456	2.82035	0.34858
C	2.29494	2.78951	0.33548
C	2.26886	2.73077	0.46047
C	2.21047	2.70421	0.59277
C	2.1795	2.73449	0.60274
C	2.20648	2.79378	0.48562
C	2.30197	2.69774	0.45481
C	2.27181	2.63577	0.45448
N	2.64962	2.82033	0.48383
C	3.09128	3.226	0.50235
C	3.05551	3.16506	0.49663
C	3.07555	3.12784	0.63497
C	3.13327	3.15455	0.77787
C	3.1692	3.21552	0.78291
C	3.14892	3.25249	0.64562
C	3.03669	3.06206	0.63223
C	2.97498	3.03618	0.63205
C	3.13016	2.813	0.65488
H	2.28576	2.86612	0.24944
H	2.33962	2.81162	0.21776
H	2.18848	2.65877	0.69867
H	2.13401	2.7114	0.70749
H	2.22332	2.61138	0.45511
H	3.07485	3.25417	0.39098
H	3.01136	3.14621	0.37365
H	3.15039	3.12749	0.89736
H	3.21387	3.23499	0.89987
H	2.95527	3.0647	0.63236
H	3.10563	2.77081	0.81586

Table S4. Atomistic coordinates for the AB-stacking mode of TFPB-TAPB-COF optimized by using DFTB+ method. Space group: *P*3*; a* = 25.9516 Å, *b* = 25.9516 Å, and *c* = 6.3891 Å.

Atom	***x/a***	***y/b***	***z/c***
C	0.25086	0.80492	0.00839
C	0.27908	0.77163	0.00833
C	0.27543	0.73747	0.18289
C	0.24367	0.73792	0.35881
C	0.21532	0.77111	0.36023
C	0.21777	0.80408	0.18286
C	0.30549	0.70086	0.18225
C	0.27147	0.6389	0.18223
N	0.64887	0.80895	0.17686
C	0.0863	0.22537	0.16224
C	0.05162	0.16411	0.16178
C	0.07225	0.12843	0.25135
C	0.12902	0.15674	0.34209
C	0.16374	0.21802	0.34322
C	0.14304	0.25346	0.25309
C	0.03504	0.06232	0.25004
C	0.97303	0.03465	0.24989
C	0.13826	0.81976	0.25354
H	0.25316	0.83096	-0.12953
H	0.30417	0.77185	-0.1297
H	0.24155	0.71221	0.49766
H	0.19195	0.77205	0.50154
H	0.22287	0.61707	0.18243
H	0.06953	0.2524	0.09028
H	0.00778	0.14384	0.08798
H	0.14673	0.13069	0.41458
H	0.2078	0.23882	0.41636
H	0.9518	0.06194	0.24985
H	0.11133	0.77373	0.31929
C	0.93793	0.15908	0.66745

C	0.96657	0.12625	0.66449
C	0.94017	0.06903	0.75186
C	0.88361	0.04607	0.84178
C	0.85504	0.07894	0.84912
C	0.88234	0.13641	0.76421
C	0.97097	0.03348	0.74929
C	0.93828	0.97133	0.74917
N	0.3168	0.14609	0.75869
C	0.75994	0.55639	0.74102
C	0.72885	0.49483	0.73766
C	0.73092	0.4624	0.90908
C	0.76429	0.49299	1.08485
C	0.79454	0.55457	1.08966
C	0.79318	0.58727	0.91736
C	0.69763	0.39553	0.90578
C	0.63554	0.36419	0.90569
C	0.82625	0.17355	0.9229
H	0.95941	0.2036	0.59851
H	0.01023	0.14565	0.58963
H	0.861	1.00142	0.90945
H	0.81066	0.05918	0.91886
H	0.88967	0.9487	0.74906
H	0.75843	0.5814	0.6054
H	0.70291	0.47139	0.59899
H	0.76606	0.46818	1.22054
H	0.82004	0.57779	1.22953
H	0.61109	0.38843	0.90638
H	0.82575	0.15175	1.07491

Table S5. Atomistic coordinates for the AA-stacking mode of TFPA-TAPB-COF optimized by using DFTB+ method. Space group: *P*3*; a* = 23.4586 Å, *b* = 23.4586 Å, and *c* = 3.8991 Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.13052	-0.17467	0.30775
C	-0.09667	-0.10678	0.29438
C	-0.03459	-0.07013	0.44937
C	-0.00766	-0.10487	0.61074
C	-0.04109	-0.1728	0.62013
C	-0.10396	-0.20927	0.47314
N	-0.13546	0.14292	0.46933
C	0.4164	0.18581	0.47434
C	0.48406	0.21405	0.46698
C	0.52486	0.27475	0.62632
C	0.49507	0.30611	0.79253
C	0.42736	0.27787	0.80043
C	0.38671	0.21718	0.64162
C	0.59786	0.30492	0.62192
C	0.62673	0.26531	0.62164
C	-0.12771	-0.31495	0.65322
H	-0.17873	-0.20216	0.18476
H	-0.11887	-0.08211	0.15764
H	0.04026	-0.07848	0.73652
H	-0.01765	-0.19706	0.74994
H	0.38538	0.13867	0.34601
H	0.50552	0.18889	0.32669
H	0.52507	-0.6473	0.92758
H	0.40542	0.30309	0.93632
H	0.59526	0.21173	0.62215
H	-0.08388	-0.29507	0.82666
N	0	0	0.44289

Table S6. Atomistic coordinates for the refined unit cell parameters for TFPA-TAPB-COF via Pawley refinement. Space group: *P*3*; a* = 23.4694 Å, *b* = 23.4694 Å, and *c* = 3.8935 Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.13052	-0.17467	0.30775
C	-0.09667	-0.10678	0.29438
C	-0.03459	-0.07013	0.44937
C	-0.00766	-0.10487	0.61074
C	-0.04109	-0.1728	0.62013
C	-0.10396	-0.20927	0.47314
N	-0.13546	0.14292	0.46933
C	0.4164	0.18581	0.47434
C	0.48406	0.21405	0.46698
C	0.52486	0.27475	0.62632
C	0.49507	0.30611	0.79253
C	0.42736	0.27787	0.80043
C	0.38671	0.21718	0.64162
C	0.59786	0.30492	0.62192
C	0.62673	0.26531	0.62164
C	-0.12771	-0.31495	0.65322
H	-0.17873	-0.20216	0.18476
H	-0.11887	-0.08211	0.15764
H	0.04026	-0.07848	0.73652
H	-0.01765	-0.19706	0.74994
H	0.38538	0.13867	0.34601
H	0.50552	0.18889	0.32669
H	0.52507	-0.6473	0.92758
H	0.40542	0.30309	0.93632
H	0.59526	0.21173	0.62215
H	-0.08388	-0.29507	0.82666
N	0	0	0.44289

Table S7. Atomistic coordinates for the AB-stacking mode of TFPA-TAPB-COF optimized by using DFTB+ method. Space group: *P3; a* = 23.394 Å, *b* = 23.394 Å, and *c* = 7.179 Å.

Atom	***x/a***	***y/b***	***z/c***
C	0.54067	0.16046	0.10875
C	0.57483	0.22862	0.10776
C	0.63133	0.26324	0.21893
C	0.65238	0.22814	0.33119
C	0.61823	0.15995	0.33095
C	0.56218	0.12498	0.21769
N	0.53272	0.47695	0.21129
C	0.08174	0.52269	0.17064
C	0.14933	0.54936	0.16493
C	0.19162	0.61112	0.24511
C	0.16355	0.64519	0.33034
C	0.09587	0.61869	0.33495
C	0.05374	0.55684	0.25582
C	0.26462	0.63977	0.2398
C	0.29197	0.59866	0.23897
C	0.54629	0.0181	0.2615
H	0.497	0.13347	0.02078
H	0.55793	0.25551	0.02015
H	0.69561	0.25483	0.42099
H	0.63477	0.13398	0.42365
H	0.04941	0.4745	0.10711
H	0.16944	0.52185	0.09382
H	0.19482	0.6929	0.39734
H	0.07528	0.64622	0.40361
H	0.25943	0.5451	0.23901
H	0.59838	0.03717	0.3088
C	0.19913	0.49214	0.66251
C	0.23412	0.56022	0.65325
C	0.29725	0.59637	0.73307
C	0.32389	0.561	0.81895

C	0.28878	0.49293	0.83004
C	0.22506	0.45725	0.75464
N	0.201	0.81323	0.75503
C	0.75193	0.85768	0.74858
C	0.82009	0.8887	0.74823
C	0.85707	0.93482	0.88613
C	0.82385	0.94868	1.02511
C	0.75558	0.91679	1.02731
C	0.71843	0.87095	0.88869
C	0.93098	0.96856	0.88545
C	0.96263	0.93136	0.88543
C	0.19147	0.35402	0.89129
H	0.15003	0.46517	0.59978
H	0.21185	0.58528	0.58076
H	0.37299	0.58701	0.88114
H	0.31211	0.46776	0.89695
H	0.72353	0.82204	0.63924
H	0.84526	0.87754	0.63765
H	0.85185	0.98425	1.13494
H	0.73051	0.92783	1.13864
H	0.93325	0.87739	0.88555
H	0.22375	0.37739	1.01594
N	0.66667	0.33333	0.2194
N	0.33333	0.66667	0.72637

Table S8. Atomistic coordinates for the AA-stacking mode of TFPA-TAPA-COF optimized by using DFTB+ method. Space group: *P*3*; a* = 20.8677 Å, *b* = 20.8677 Å, and *c* = 4.1175 Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.04977	1.14634	0.29258
C	-0.01204	1.10778	0.27472
C	-0.03955	1.0392	0.43122
C	-0.10701	1.01025	0.59848
C	-0.14504	1.04857	0.61396
C	-0.11634	1.11823	0.46594
N	0.31234	1.1499	0.46794
C	-0.26369	0.53303	0.49259
C	-0.30847	0.45708	0.48958
C	-0.28721	0.41168	0.65389
C	-0.21956	0.44534	0.82123
C	-0.17534	0.52143	0.82573
C	-0.19628	0.56684	0.66105
C	-0.20338	1.14907	0.66684
H	-0.02763	1.19966	0.16914
H	0.03936	1.1312	0.13557
H	-0.1301	0.95696	0.72237
H	-0.19731	1.02359	0.74764
H	-0.2807	0.56749	0.35972
H	0.63949	0.43264	0.35498
H	-0.20155	0.41176	0.95348
H	-0.12341	0.54625	0.96267
H	-0.2262	1.10306	0.84866
N	0	1	0.42
N	-0.33333	0.33333	0.65134

Table S9. Atomistic coordinates for the refined unit cell parameters for TFPA-TAPA-COF via Pawley refinement. Space group: *P*3*; a* = 20.0691 Å, *b* = 20.0691 Å, and *c* = 4.1936Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.04977	1.14634	0.29258
C	-0.01204	1.10778	0.27472
C	-0.03955	1.0392	0.43122
C	-0.10701	1.01025	0.59848
C	-0.14504	1.04857	0.61396
C	-0.11634	1.11823	0.46594
N	0.31234	1.1499	0.46794
C	-0.26369	0.53303	0.49259
C	-0.30847	0.45708	0.48958
C	-0.28721	0.41168	0.65389
C	-0.21956	0.44534	0.82123
C	-0.17534	0.52143	0.82573
C	-0.19628	0.56684	0.66105
C	-0.20338	1.14907	0.66684
H	-0.02763	1.19966	0.16914
H	0.03936	1.1312	0.13557
H	-0.1301	0.95696	0.72237
H	-0.19731	1.02359	0.74764
H	-0.2807	0.56749	0.35972
H	0.63949	0.43264	0.35498
H	-0.20155	0.41176	0.95348
H	-0.12341	0.54625	0.96267
H	-0.2262	1.10306	0.84866
N	0	1	0.42
N	-0.33333	0.33333	0.65134

Table S10. Atomistic coordinates for the AB-stacking mode of TFPA-TAPA-COF optimized by using DFTB+ method. Space group: *P3; a* = 20.8778 Å, *b* = 20.8778 Å, and *c* = 7.7734 Å.

Atom	***x/a***	***y/b***	***z/c***
C	0.28632	0.81315	0.10156
C	0.32206	0.7726	0.09417
C	0.29656	0.70843	0.19413
C	0.23491	0.68617	0.30129
C	0.19915	0.72675	0.30769
C	0.22382	0.79054	0.20617
N	0.64421	0.80766	0.20705
C	0.06927	0.19989	0.18339
C	0.02397	0.12403	0.18154
C	0.04628	0.07815	0.26255
C	0.11559	0.11113	0.34381
C	0.16134	0.18693	0.34145
C	0.13909	0.23286	0.2619
C	0.12508	0.81191	0.25967
H	0.30591	0.86286	0.02263
H	0.37028	0.79061	0.01074
H	0.2155	0.637	0.38213
H	0.15255	0.70907	0.39616
H	0.05116	0.23479	0.11929
H	0.97101	0.10026	0.11429
H	0.13403	0.07729	0.41101
H	0.21508	0.21103	0.40599
H	0.08778	0.75361	0.30352
C	0.95794	0.15206	0.69045
C	0.99387	0.11167	0.68189
C	0.96317	0.04183	0.76054
C	0.89466	0.01377	0.84379
C	0.85829	0.05372	0.85013
C	0.88999	0.12442	0.77603
N	0.31218	0.14336	0.7733

C	0.73367	0.53147	0.77199
C	0.69095	0.45529	0.76737
C	0.71057	0.41179	0.86761
C	0.77374	0.44636	0.97216
C	0.81563	0.52265	0.97701
C	0.79664	0.56661	0.87705
C	0.80562	0.15813	0.88361
H	0.98285	0.20646	0.6293
H	0.04611	0.13469	0.61173
H	0.86913	0.95971	0.90629
H	0.8045	0.0287	0.91425
H	0.71842	0.56511	0.6927
H	0.64198	0.42889	0.68484
H	0.78949	0.41318	1.05151
H	0.86439	0.54889	1.0605
H	0.78637	0.11535	0.98778
N	0.33333	0.66667	0.18782
N	0	0	0.26174
N	0	0	0.75461
N	0.66667	0.33333	0.86317

Table S11. Atomistic coordinates for the AA-stacking mode of BTMA-TAPA-COF optimized by using DFTB+ method. Space group: *P*3*;a* = 20.7444 Å, *b* = 20.7444 Å, and *c* = 4.1175 Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.04977	1.14634	0.29258
C	-0.01204	1.10778	0.27472
C	-0.03955	1.0392	0.43122
C	-0.10701	1.01025	0.59848
C	-0.14504	1.04857	0.61396
C	-0.11634	1.11823	0.46594
N	0.31234	1.1499	0.46794
C	-0.26369	0.53303	0.49259
C	-0.30847	0.45708	0.48958
C	-0.28721	0.41168	0.65389
C	-0.21956	0.44534	0.82123
C	-0.17534	0.52143	0.82573
C	-0.19628	0.56684	0.66105
C	-0.20338	1.14907	0.66684
H	-0.02692	1.20204	0.16513
H	-0.13127	0.95424	0.7244
H	-0.20019	1.02369	0.74767
H	-0.22402	1.10087	0.84458
C	0.45874	0.36486	0.85463
H	0.41573	0.35006	1.05431
H	0.43522	0.37078	0.61385
H	0.51058	0.41936	0.91712
C	0.58699	0.41828	0.88764
H	0.60984	0.45057	0.65224
H	0.63341	0.43756	1.07403
H	0.54165	0.42828	0.98581
C	0.40712	0.12309	0.41526
H	0.42505	0.08341	0.51369
H	0.39929	0.11586	0.14105
H	0.35272	0.11064	0.53379

C	0.53494	0.18172	0.76823
H	0.56011	0.14655	0.69146
H	0.47383	0.14416	0.82695
H	0.56498	0.21541	0.99255
H	0.0419	1.13159	0.13207
N	0	1	0.42
B	-0.33333	0.33333	0.65134

Table S12. Atomistic coordinates for the refined unit cell parameters for BTMA-TAPA-COF via Pawley refinement. Space group: *P*3*; a* = 20.7444 Å, *b* = 20.7444 Å, and *c* = 4.1175 Å.

Atom	***x/a***	***y/b***	***z/c***
C	-0.04977	1.14634	0.29258
C	-0.01204	1.10778	0.27472
C	-0.03955	1.0392	0.43122
C	-0.10701	1.01025	0.59848
C	-0.14504	1.04857	0.61396
C	-0.11634	1.11823	0.46594
N	0.31234	1.1499	0.46794
C	-0.26369	0.53303	0.49259
C	-0.30847	0.45708	0.48958
C	-0.28721	0.41168	0.65389
C	-0.21956	0.44534	0.82123
C	-0.17534	0.52143	0.82573
C	-0.19628	0.56684	0.66105
C	-0.20338	1.14907	0.66684
H	-0.02692	1.20204	0.16513
H	-0.13127	0.95424	0.7244
H	-0.20019	1.02369	0.74767
H	-0.22402	1.10087	0.84458
C	0.45874	0.36486	0.85463
H	0.41573	0.35006	1.05431
H	0.43522	0.37078	0.61385
H	0.51058	0.41936	0.91712
C	0.58699	0.41828	0.88764
H	0.60984	0.45057	0.65224
H	0.63341	0.43756	1.07403
H	0.54165	0.42828	0.98581
C	0.40712	0.12309	0.41526
H	0.42505	0.08341	0.51369
H	0.39929	0.11586	0.14105
H	0.35272	0.11064	0.53379

C	0.53494	0.18172	0.76823
H	0.56011	0.14655	0.69146
H	0.47383	0.14416	0.82695
H	0.56498	0.21541	0.99255
H	0.0419	1.13159	0.13207
N	0	1	0.42
B	-0.33333	0.33333	0.65134

Table S13. Atomistic coordinates for the AB-stacking mode of BTMA-TAPA-COF optimized by using DFTB+ method. Space group: *P3; a* = 20.878 Å, *b* = 20.8778 Å, and *c* = 7.7734 Å.

Atom	***x/a***	***y/b***	***z/c***
C	0.28632	0.81315	0.10156
C	0.32206	0.7726	0.09417
C	0.29656	0.70843	0.19413
C	0.23491	0.68617	0.30129
C	0.19915	0.72675	0.30769
C	0.22382	0.79054	0.20617
C	0.64421	0.80766	0.20705
C	0.06927	0.19989	0.18339
C	0.02397	0.12403	0.18154
C	0.04628	0.07815	0.26255
C	0.11559	0.11113	0.34381
C	0.16134	0.18693	0.34145
C	0.13909	0.23286	0.2619
N	0.12508	0.81191	0.25967
C	0.30591	0.86286	0.02263
C	0.37028	0.79061	0.01074
C	0.2155	0.637	0.38213
C	0.15255	0.70907	0.39616
H	0.05012	0.23677	0.12047
H	0.96805	0.09818	0.11402
H	0.13454	0.07526	0.41256
H	0.21814	0.21301	0.40482
C	0.95794	0.15206	0.69045
C	0.99387	0.11167	0.68189
C	0.96317	0.04183	0.76054
C	0.89466	0.01377	0.84379
C	0.85829	0.05372	0.85013
C	0.88999	0.12442	0.77603
N	0.31218	0.14336	0.7733
C	0.73367	0.53147	0.77199

C	0.69095	0.45529	0.76737
C	0.71057	0.41179	0.86761
C	0.77374	0.44636	0.97216
C	0.81563	0.52265	0.97701
C	0.79664	0.56661	0.87705
C	0.80562	0.15813	0.88361
H	0.98347	0.20887	0.62733
H	0.04878	0.13495	0.61069
H	0.86807	0.95706	0.90773
H	0.8021	0.02933	0.91589
C	0.71842	0.56511	0.6927
C	0.64198	0.42889	0.68484
C	0.78949	0.41318	1.05151
C	0.86439	0.54889	1.0605
H	0.78833	0.11344	0.98617
H	0.67018	0.77392	0.16111
H	0.28056	0.84669	-0.11132
H	0.36875	0.89218	0.01221
H	0.28883	0.90152	0.08474
H	0.35652	0.80155	-0.12414
H	0.38588	0.74555	0.00492
H	0.41869	0.84351	0.06451
H	0.26461	0.63089	0.42305
H	0.17469	0.58598	0.3064
H	0.18697	0.64289	0.50117
H	0.13545	0.65158	0.44762
H	0.104	0.70747	0.32516
H	0.16964	0.74973	0.50791
H	0.6557	0.53931	0.69201
H	0.73891	0.56763	0.55557
H	0.74477	0.62343	0.74794
H	0.6216	0.36714	0.67551
H	0.65676	0.45453	0.55097

H	0.59655	0.43749	0.74205
H	0.82186	0.39363	0.97008
H	0.7376	0.36318	1.10412
H	0.82542	0.44814	1.16304
H	0.91342	0.59309	0.98494
H	0.87791	0.50538	1.10838
H	0.85259	0.57551	1.17507
B	0.33333	0.66667	0.18782
N	0	0	0.26174
N	0	0	0.75461
B	0.66667	0.33333	0.86317

Section K. Supporting references

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