Electronic Supplementary Information

A gaseous hydrogen chloride chemosensor based on a 2D covalent organic framework

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Section 1. Instruments and methods.

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

The ^{13}C CP/MAS NMR spectrum of the COF was recorded on an Agilent DD2 600 Solid NMR System with 4 mm zirconia rotors. The spinning rate is 8 kHz and the contact time is 3 ms.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was conducted on a Waters TGA Q500 instrument by heating the sample from room temperature to 1000 ℃ under nitrogen atmosphere with a heating rate of 10 ℃/min.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a FEI NOVA NANOSEM 450 scanning electron microscope. The sample was dispersed over the slice of silicon wafer adhered to flat copper platform sample holder and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in an nitrogen atmosphere, puttered for 30 s from a solid gold target at a current at 30 mA) before being submitted to SEM characterization.

Powder X-ray diffraction

Powder X-ray diffraction measurement was carried out with an PANalytical X'Pert Powder system using monochromated Cu/Kα(λ= 0.1542 nm). The sample was spread on the square recess of XRD sample holder as a thin layer.

Nitrogen adsorption-desorption isotherm measurement

The measurement was carried out using a Micromeritics ASAP 2020 system. Before

gas adsorption measurement, the as-synthesized COF was washed by anhydrous acetone using Soxhlet extractor. The sample was then dried under dynamic vacuum at 120 °C for 4 h. The resulting sample was activated by degassing at 200 ^{o}C for 4 h and used for gas adsorption measurement from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate its specific surface area. By using the non-local density functional theory model, the pore size distribution was derived from the sorption data.

Structural simulation and powder X-ray diffraction analysis

The Pawley refinement of the experimental PXRD was conducted by the Reflex module in the Materials Studio 7.0. Before the simulations, the structures were firstly optimized in Gaussian 09 package by semiempirical calculations at PM3 level. The simulations of the possible structures were carried out in Accelrys Materials Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. P1 space group was chosen for the primitive models in the initial simulations.

Section 2. Synthetic procedure

Synthesis of COF-ETBA-DAB

COF-ETBA-DAB was obtained with 4,4’,4’’,4’’’-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde (**ETBA**, 26.64 mg, 0.06 mmol, prepared according to the published procedure[1]) and p-phenylenediamine (**DAB**, 12.96 mg, 0.12 mmol,) as monomers in a mixture of mesitylene/1,4-dioxane(1:1, v/v, 2 mL), and acetic acid (aq. 6M, 0.2 mL) in a glass ampoule. After three freeze-pump-thaw cycles, the glass tube was sealed under vacuum. The mixture was then heated at 120 ℃ for 72 h to afford a yellow solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous acetone using Soxhlet extractor and then dried under dynamic vacuum at 120 ℃ for 4 h to afford a yellow powder (28 mg, 70.71%), which was insoluble in common organic solvents such as dichloromethane, ethanol, and N, N-dimethylformamide. Anal. Calcd. For chemical formula $C_{42}H_{28}N_4$: C, 85.69; H, 4.79; N, 9.52. Found: C, 81.03; H, 5.69; N, 8.31.

Reference

1 H. Qu, Y. Wang, Z. Li, X. Wang, H. Fang, Z. Tian and X. Cao, *J. Am. Chem. Soc.*, 2017, **139**, 18142.

Section 3. Characterizations of the COF-ETBA-DAB

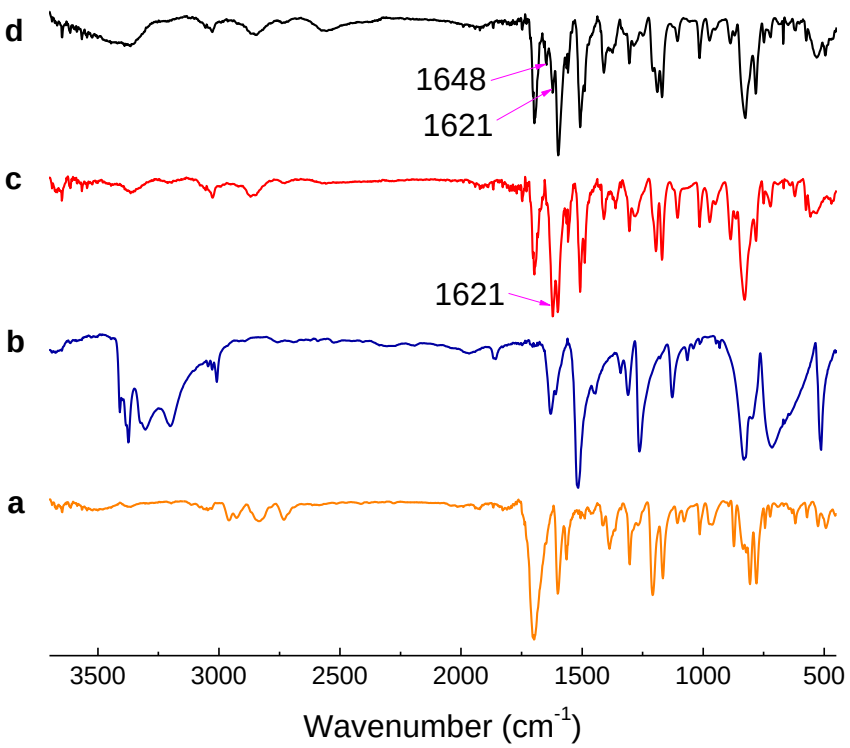


Figure S1. FT-IR spectra of (a) **ETBA**, (b) **DAB**, (c) **COF-ETBA-DAB**, and (d) **COF-ETBA-DAB -HCl**.

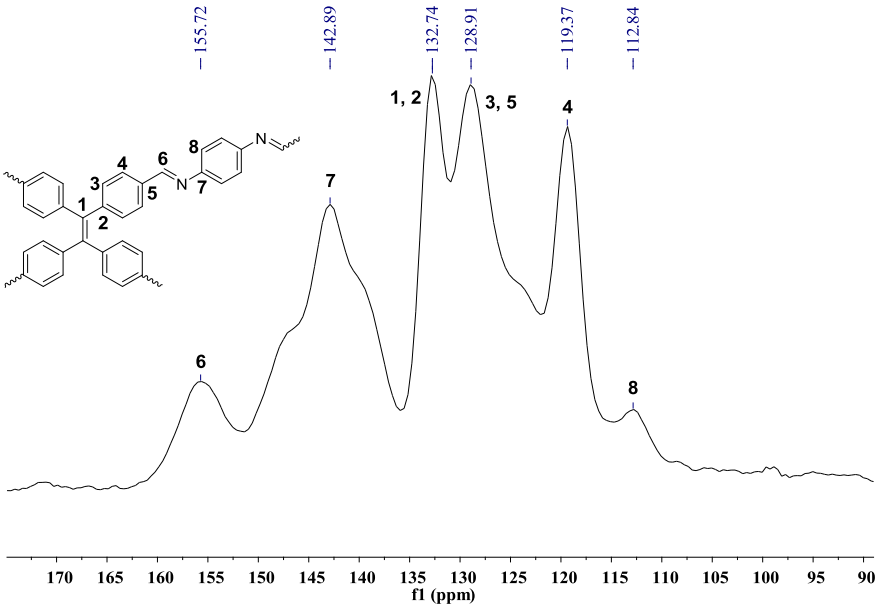


Figure S2. Solid-state ^{13}C CP/MAS NMR spectrum of **COF-ETBA-DAB**.

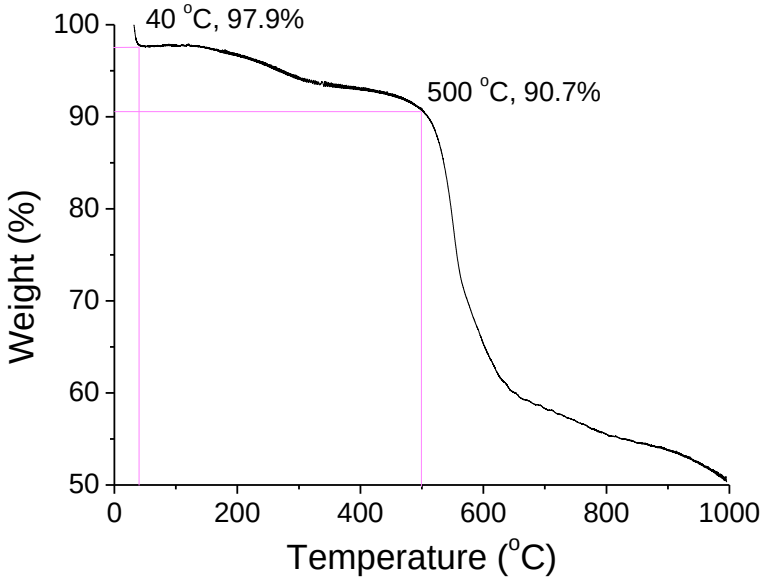


Figure S3. TGA profile of **COF-ETBA-DAB**. The decrease in weight before 40 °C might be attributed to the loss of small molecules encapsulated in the COF.

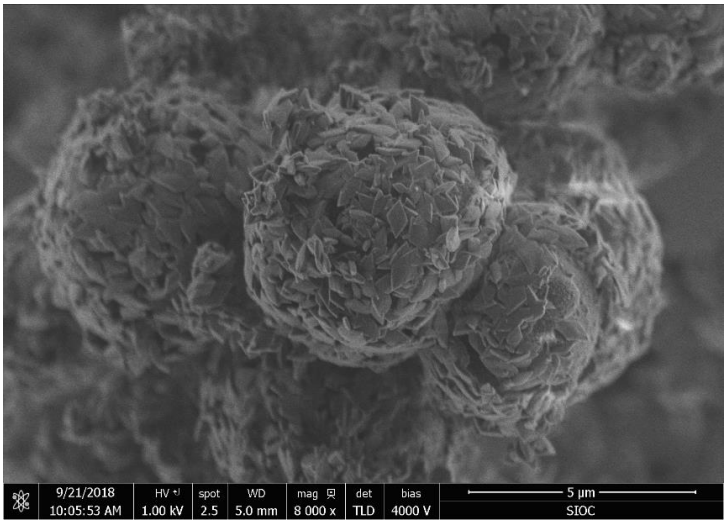
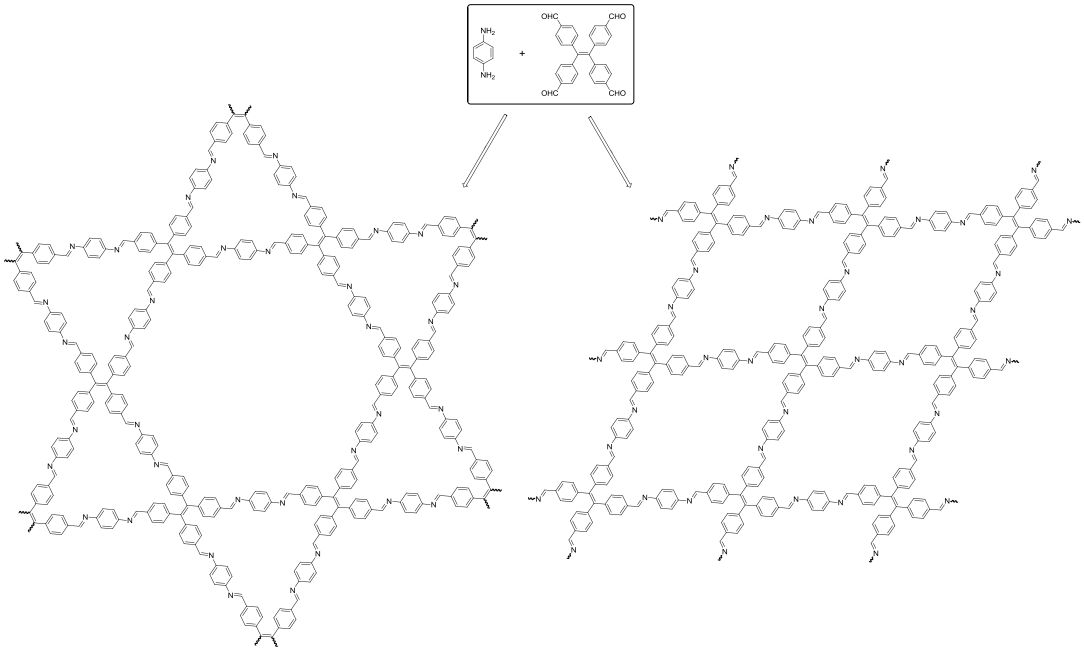


Figure S4. SEM image of **COF-ETBA-DAB**.



Scheme S1. The two possible framework structures which theoretically can be assembled from **ETBA** and **DAB**.

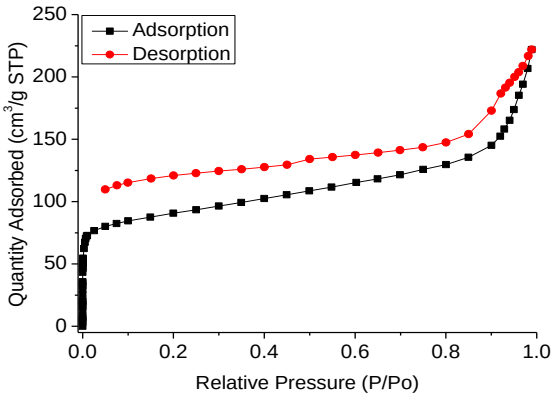


Figure S5. N_2 adsorption–desorption isotherm (77 K) of **COF-ETBA-DAB**.

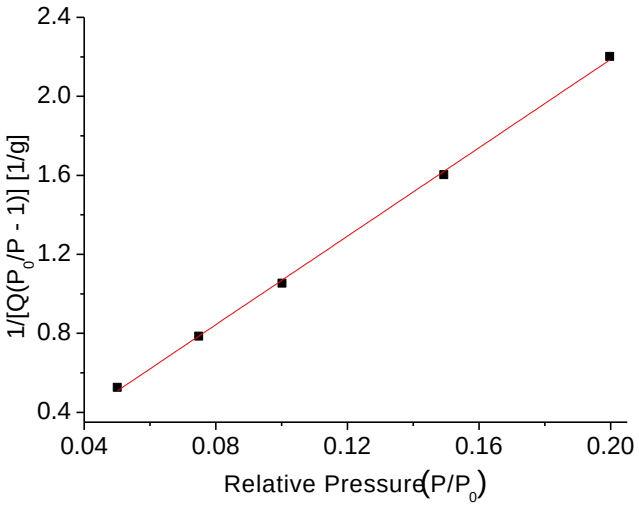


Figure S6. BET surface area plot for **COF-ETBA-DAB**.

Table S1. Fractional atomic coordinates for the unit cell of **COF-ETBA-DAB** with AA stacking.

P1							
a = b = 19.50 Å, and c = 4.60 Å, and α = β = 90° and γ = 113°							
H1	0.429759	1.583347	1.28226	C10	0.538537	1.699632	0.630735
H2	0.551224	1.586118	1.172744	C11	0.467367	1.695551	0.686481
H3	0.568282	1.733006	0.443443	C12	0.410139	1.801066	0.980539
H4	0.443508	1.724452	0.537107	C13	0.409882	1.870339	1.040371
H5	0.4592	1.802552	0.862038	C14	0.35151	1.879533	1.190824
H6	0.457135	1.919058	0.960161	C15	0.294527	1.814053	1.291593
H7	0.248078	1.817155	1.418686	C16	0.295031	1.744315	1.234378
H8	0.24908	1.695856	1.321258	C17	0.192948	1.645855	0.839902
H9	0.237621	1.695932	0.756712	C18	0.121053	1.642841	0.814766
H10	0.113174	1.690572	0.715749	C19	0.059531	1.580994	0.913077
H11	0.029193	1.471181	1.104619	C20	0.074796	1.521931	1.029364
H12	0.15007	1.474433	1.143618	C21	0.146483	1.524898	1.055207
H13	0.233178	1.476955	1.399725	C22	0.264114	1.464867	1.220534

H14	0.241111	1.356744	1.394011	C23	0.270006	1.396324	1.221045
H15	0.384212	1.422211	0.636285	C24	0.313042	1.377813	1.013521
H16	0.368028	1.538639	0.620753	C25	0.349123	1.432452	0.804102
H17	0.673742	1.701569	0.541677	C26	0.340301	1.49952	0.794575
H18	0.35736	1.300501	0.830374	C27	0.646346	1.666997	0.73012
H19	0.728288	1.546823	1.193295	C28	0.749548	1.63284	0.866072
H20	0.851147	1.543437	1.17107	C29	0.322306	1.307426	1.006082
H21	0.915728	1.716176	0.513136	C30	0.293241	1.185546	1.220361
H22	0.792518	1.719828	0.53697	C31	0.769041	1.584171	1.040293
H23	0.205527	1.144995	1.544304	C32	0.83911	1.582137	1.025952
H24	0.209272	1.021637	1.58912	C33	0.89378	1.628818	0.835417
H25	0.384855	1.082596	0.943564	C34	0.874571	1.678221	0.663552
H26	0.382143	1.204308	0.903465	C35	0.804312	1.68013	0.677355
H27	0.941044	1.520136	0.980974	C36	0.245644	1.131738	1.411195
H28	0.410545	0.999069	1.167319	C37	0.247772	1.061679	1.436852
C1	0.351331	1.657885	0.996631	C38	0.298019	1.041371	1.274357
C2	0.288652	1.591984	0.996381	C39	0.345337	1.095211	1.082254
C3	0.350992	1.73506	1.064581	C40	0.343285	1.165126	1.056861
C4	0.427216	1.656921	0.929427	C41	0.982595	1.573237	0.902018
C5	0.297185	1.517576	1.00128	C42	0.356886	0.955341	1.229036
C6	0.208686	1.588336	0.971655	N1	0.677593	1.632669	0.890409
C7	0.459196	1.616819	1.096649	N2	0.289526	1.256257	1.198018
C8	0.529171	1.61842	1.032374	N3	0.965641	1.628133	0.817431
C9	0.571859	1.661264	0.801191	N4	0.299389	0.96965	1.300744