

## **Supporting Information**

# **Pyrene-Derived Covalent Organic Framework Films: Advancements in Acid Vapor Detection**

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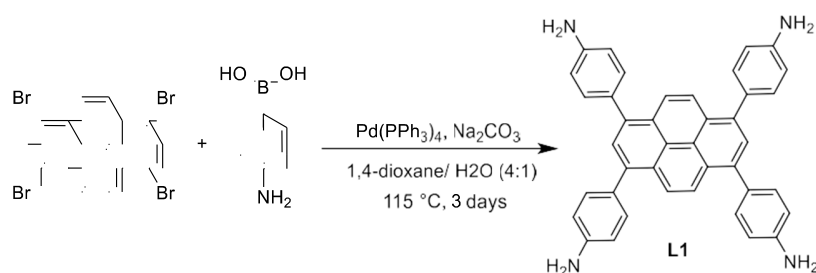
## Section S1: Materials and General Methods

**Chemicals.** The chemicals utilized in this study include anhydrous tetrahydrofuran (THF), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 1,3,6,8-tetrabromopyrene ( $\text{C}_{16}\text{H}_6\text{Br}_4$ ), 4-aminophenylboronic acid pinacol ester ( $\text{C}_{12}\text{H}_{18}\text{BNO}_2$ ), tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{PPh}_3)_4$ ), 1,4-dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ ), methanol ( $\text{CH}_3\text{OH}$ ), 1,1,2,2-tetra-*p*-tolylethene ( $\text{C}_{30}\text{H}_{30}$ ), *N*-bromosuccinimide (NBS) ( $\text{C}_4\text{H}_4\text{BrNO}_2$ ), benzoyl peroxide (BPO), carbon tetrachloride ( $\text{CCl}_4$ ), *o*-dichlorobenzene (*o*-DCB) ( $\text{C}_6\text{H}_4\text{Cl}_2$ ), *n*-butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), Mesitylene ( $\text{C}_9\text{H}_{12}$ ), *p*-hydroxybenzaldehyde ( $\text{C}_7\text{H}_6\text{O}_2$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ), hexachlorocyclotriphosphazene ( $(\text{NPCl}_2)_3$ ), anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). These chemicals were sourced from Sigma Aldrich (St. Louis, MO, USA) and were utilized as received without any additional purification. For sorption experiments, ultrahigh-purity grade  $\text{N}_2$  from Air Products (99.999% purity) was used.

**Analytical techniques.** Thin-layer chromatography utilized silica gel glass plates (Silica gel, 60 F254, Fluka, Merck, Darmstadt, Germany), while column chromatography employed Kieselgel S (silica gel S, 0.063–0.1 mm, Merck, Darmstadt, Germany) as specified in Section S2. Fourier-transform infrared (FTIR) spectra were recorded using KBr pellets on a Thermo Nicolet model 470 FT-IR spectrophotometer (Thermo Scientific, Waltham, MA, USA) following the procedures outlined in Sections S5 and S7. NMR spectra were recorded on an Agilent Technologies Varian-400 MHz spectrometer ( $^1\text{H}$ -NMR at 400 MHz and  $^{13}\text{C}$ -NMR at 100 MHz; Santa Clara, CA, USA), employing dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) as the solvent. Chemical shifts, reported in parts per million ( $\delta$  values, ppm), were referenced to tetramethylsilane (TMS) as the internal reference, as specified in Section S3. Absorption assessments were completed employing an Agilent 8453 spectrophotometer (Santa Clara, USA) fitted with 1.0 cm quartz cells (Varian, Austria) in accordance with the procedures outlined in Section S8. For Powder X-ray diffraction (PXRD) analysis, a Shimadzu-6100 PXRD diffractometer (Shimadzu-series, Kyoto, Japan) utilizing Cu-K $\alpha$  radiation at  $\lambda = 1.542 \text{ \AA}$  was utilized. Data collection spanned the  $2\theta$  range of  $3\text{--}40^\circ$  at a rate of  $1^\circ/\text{min}$ . These measurements were carried out under room temperature and atmospheric pressure conditions, as delineated in Sections S5, S6, and S7.  $\text{N}_2$  sorption measurements and pore size analyses were executed using PMI's BET Sorptometer (BET-201-AEL, PMI, USA). The assessments at 77 K were conducted employing a liquid  $\text{N}_2$  bath. Thermogravimetric analysis (TGA) involved heating a 0.2 g sample to  $600^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$  while continuously monitoring the weight relative to the temperature, following the procedures detailed in Section S6.

## Section S2: Synthesis of raw materials

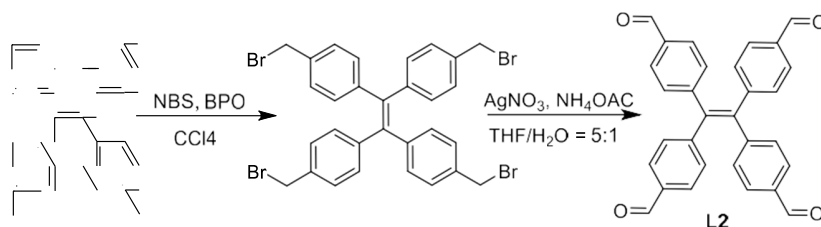
### Synthesis of 1,3,6,8-tetra(aminophenyl)pyrene (L1)



**Scheme S1.** Synthesis of 1,3,6,8-tetra(aminophenyl)pyrene

The steps outlined in Scheme S1 were carried out using a solution comprising 1,3,6,8-tetrabromopyrene (7.4 g, 14.3 mmol, 1.0 eq.), 4-aminophenylboronic acid pinacol ester (15 g, 68.5 mmol, 4.8 eq.), Na<sub>2</sub>CO<sub>3</sub> (10.9 g, 15.7 mmol, 5.5 eq.), and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.65 g, 1.45 mmol, 10 mol%) dissolved in 32 mL of 1,4-dioxane and 8 mL of H<sub>2</sub>O. The mixture was heated to reflux (115 °C) for a duration of 3 days. After cooling to room temperature, H<sub>2</sub>O was added. The resulting precipitate was collected via filtration and washed with H<sub>2</sub>O and MeOH. Recrystallization from 1,4-dioxane, followed by drying under high vacuum, was used to furnish the title compound, co-crystallized with approximately 1.5 dioxane molecules per formula unit, as a bright yellow powder; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 298 K, 400 MHz): 5.28 (s, 8 H), 6.73 (d, *J* = 8.5 Hz, 8 H), 7.30 (d, *J* = 8.4 Hz, 8 H), 7.79 (s, 2 H), 8.10 (s, 4 H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 298 K, 100 MHz): 114.3, 124.8, 126.5, 127.1, 127.9, 129.5, 131.5, 137.5, 148.6.

### Synthesis of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde (L2)

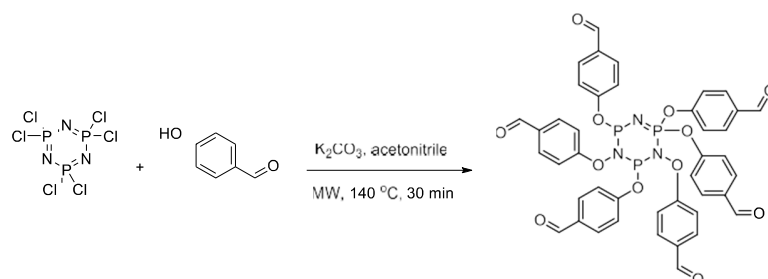


**Scheme S2.** Synthesis of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde

The procedure described in Scheme S2 began with the addition of 1,1,2,2-Tetra-*p*-tolylethene (770 mg, 2 mmol) into a 100 mL round-bottom flask. To this, NBS (1424 mg, 8 mmol), BPO (64 mg), and CCl<sub>4</sub> (30 mL) were

sequentially introduced. The resulting mixture underwent a reaction under an N<sub>2</sub> atmosphere at 80 °C for 2 hours. Following this, additional portions of NBS (1424 mg, 8 mmol) and BPO (64 mg) were added, prolonging the reaction at 80 °C for another 2 hours. After this 2-hour interval, NBS (1424 mg, 8 mmol) and BPO (64 mg) were added, and the mixture was allowed to stand for 24 hours. It was then rapidly filtered while the solution was still hot, and the solid was washed with ethyl acetate, while the filtrate was collected. The organic phase was obtained through the rotary evaporation of the yellow solid, and without further purification, the process was continued directly to the next step. In the subsequent step, the solid from the previous step (2.0 g), sodium acetate trihydrate (1500 mg, 18 mmol), silver nitrate (3400 mg, 20 mmol), THF (25 mL), and H<sub>2</sub>O (5 mL) were mixed and further refluxed at 75 °C for 24 hours. The solution was then cooled to room temperature and filtered. The filtrate was extracted with ethyl acetate, washed successively with water and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. A light yellow viscous liquid was obtained through rotary evaporation, and it was purified through column chromatography (silica gel, petroleum ether/ethyl acetate = 5 : 1), resulting in a yellow-green product L4 (yield: 54%); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 298 K, 400 MHz): 7.14 (d, *J* = 8.5 Hz, 8 H), 7.76 (d, *J* = 8.4 Hz, 8 H), 9.90 (s, 1 H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 298 K, 100 MHz): 121.5, 131.9, 134.0, 148.2, 192.11.

### Synthesis of hexa(4-formyl-phenoxy)cyclotriphosphazene (L3)



**Scheme S3.** Synthesis of hexa(4-formyl-phenoxy)cyclotriphosphazene

The reaction depicted in Scheme 3 started by dissolving 14.92 g *p*-hydroxybenzaldehyde in 300 mL acetonitrile. Then, 33.4 g potassium carbonate was slowly added to the system, and it was stirred in an ice bath for 30 min. Then, a 50 mL hexachlorocyclotriphosphazene (HCCP, 6.96 g) solution dissolved with acetonitrile was slowly added; after 2 hours of ice bath, a stirring reaction was conducted at room temperature for 2 days. The reaction ended with filtration and decompression distillation of the filtrate, and the obtained solid was extracted with dichloromethane and washed with saturated salt water. The organic phase was dried with anhydrous magnesium sulfate. The white solid was obtained through decompression distillation, and the solid powder was recrystallized in ethyl acetate. The powder was dried at 50 °C under vacuum overnight to obtain compound **L3**.

### Section S3: Characterizations of raw materials

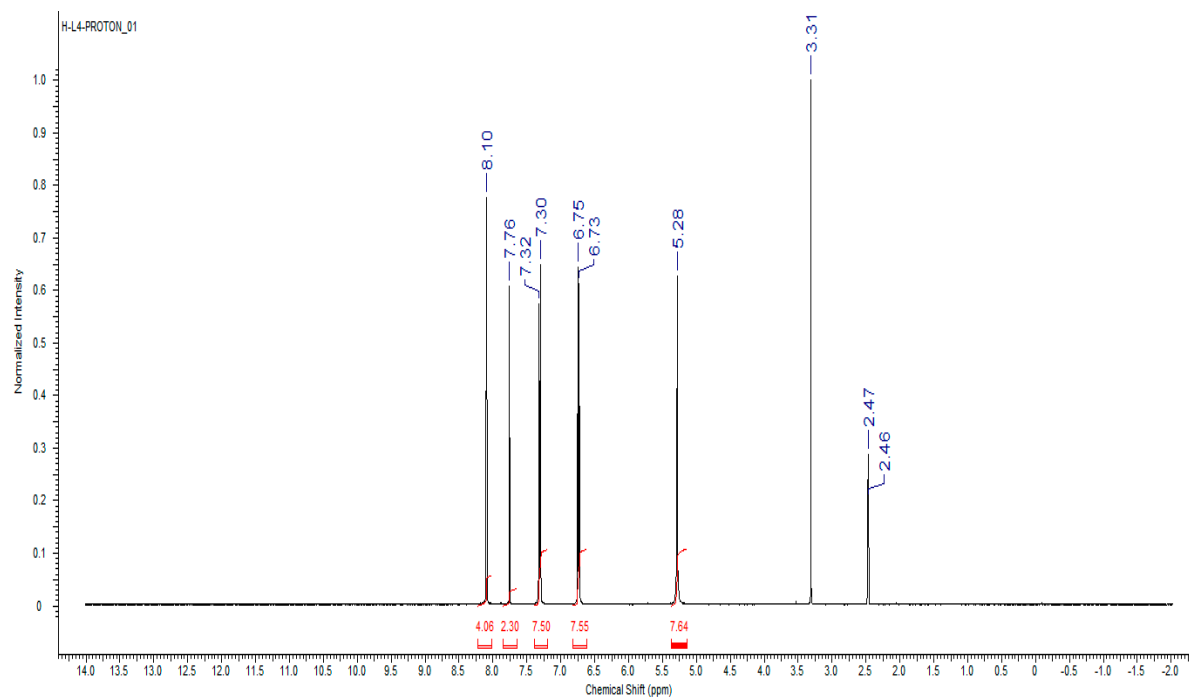


Figure S1. <sup>1</sup>H-NMR spectrum of L1.

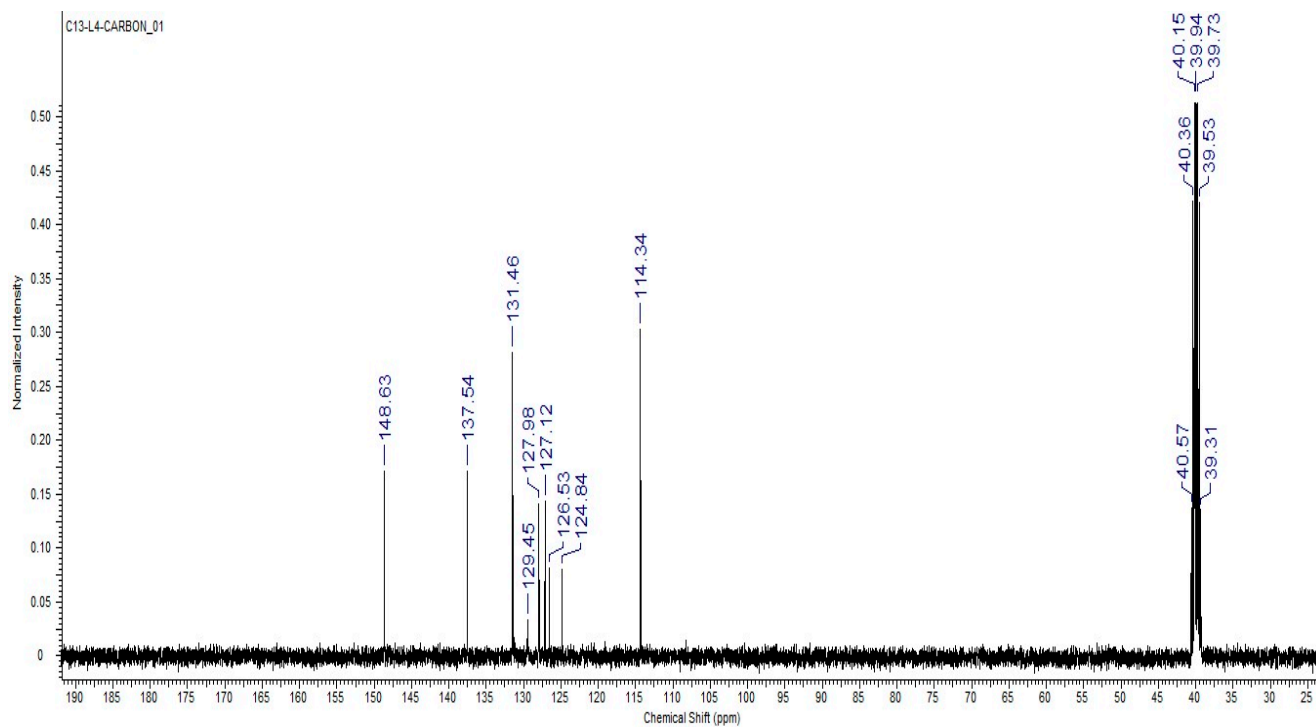
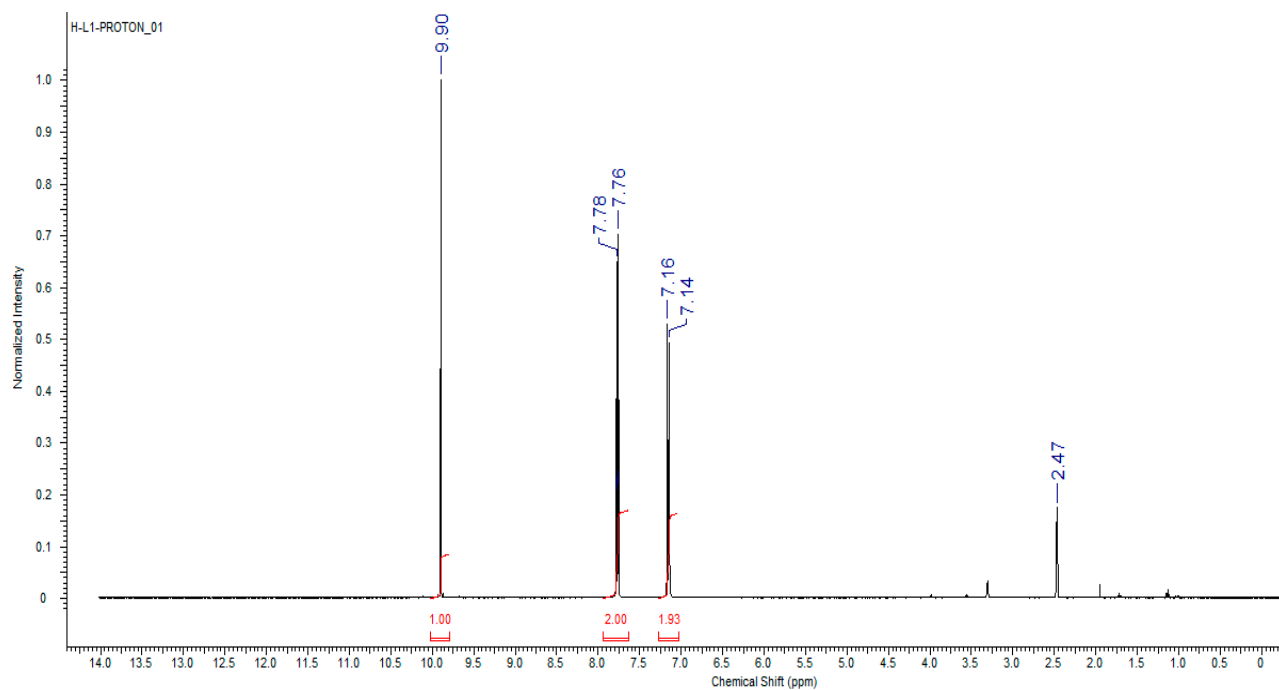
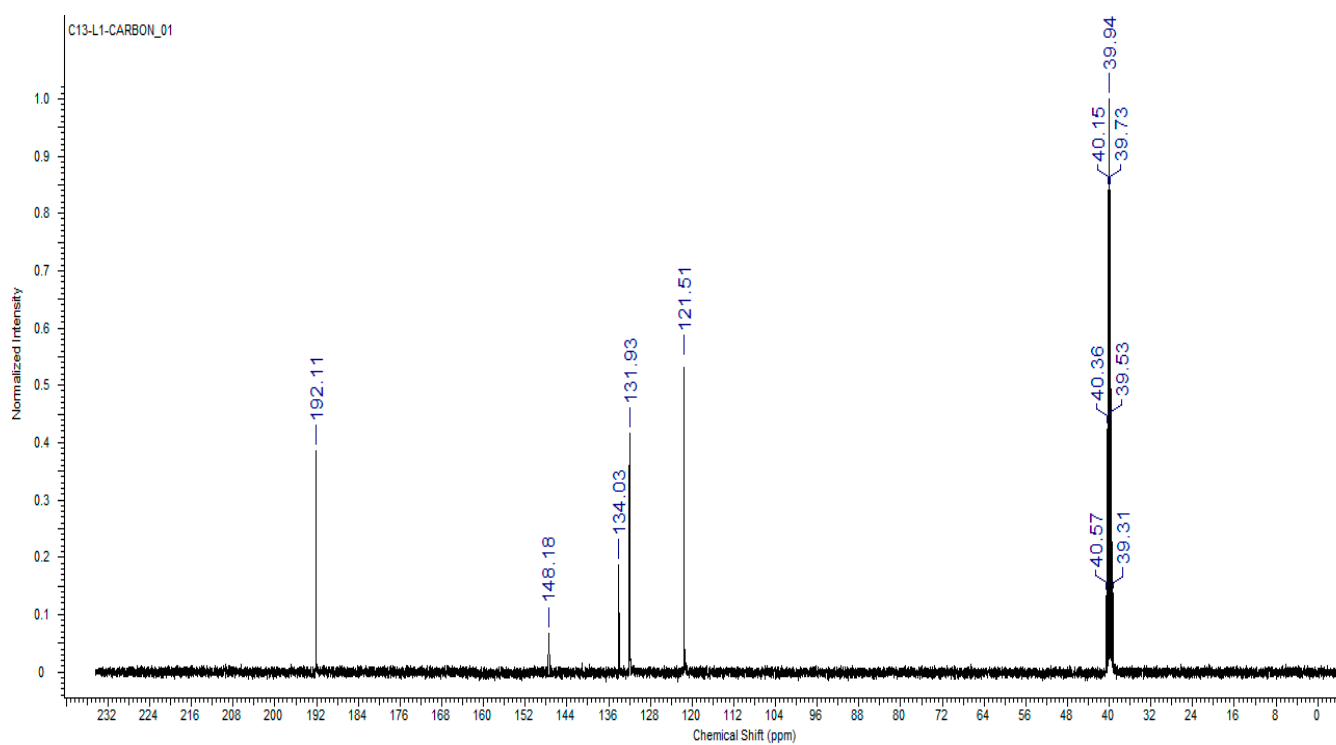


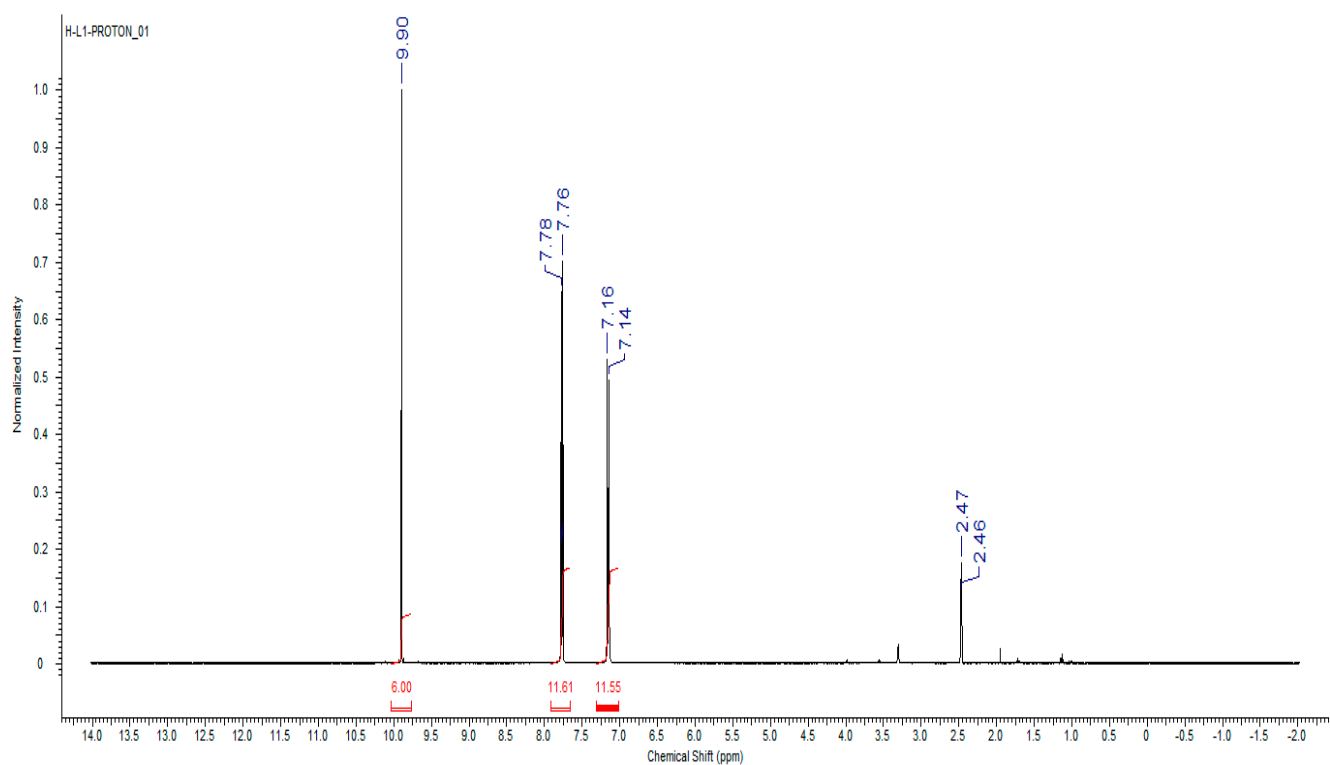
Figure S2. <sup>13</sup>C-NMR spectrum of L1.



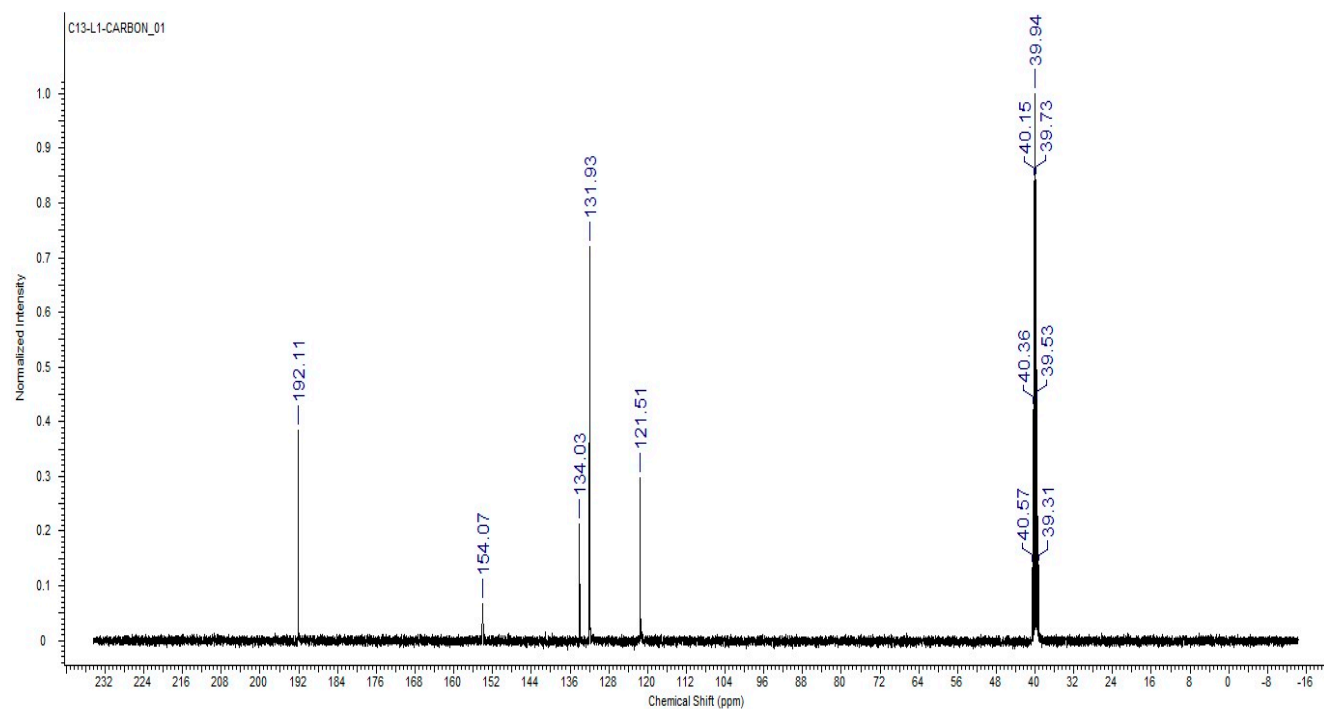
**Figure S3.** <sup>1</sup>H-NMR spectrum of L2.



**Figure S4.** <sup>13</sup>C-NMR spectrum of L2.



**Figure S5.** <sup>1</sup>H-NMR spectrum of L3.



**Figure S6.** <sup>13</sup>C-NMR spectrum of L3.



## Section S4: Fabrication Methods for Covalent Organic Framework Powders and Films

**PT-COF.** The COF was synthesized by weighing 4,4',4''-(pyrene-1,3,6,8-tetrayl)tetraaniline **L1** (0.03 mmol, 0.022 g) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (0.04 mmol, 0.013 g) into a centrifuge tube. Then, a mixture of *o*-DCB (0.2 mL) and *n*-BuOH (0.8 mL) was added to the tube. The mixture was sonicated for 20 minutes to ensure a homogenous dispersion. Afterward, 0.1 mL of aqueous acetic acid (9.0 mol/L) was added. Next, the tube was degassed through three freeze–pump–thaw cycles in 77 K liquid nitrogen. Subsequently, the mixture was transferred to an autoclave and heated at 120 °C for 5 days. Following this process, a pale brown powder was isolated through centrifugation and washed with acetone (3 × 5.0 mL) to obtain the final product.

**PE-COF.** 4,4',4''-(pyrene-1,3,6,8-tetrayl)tetraaniline **L1**, a yellow solid, was obtained using 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde **L2** (ETBA, 26.64 mg, 0.06 mmol), and hydrazine (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) inside a glass ampoule. The glass tube was sealed under vacuum after three freeze–pump–thaw cycles. The mixture was then heated at 120 °C for 72 hours, resulting in the formation of the yellow solid at the bottom of the tube. After cooling to room temperature, the solvent was decanted, and the solid was washed with anhydrous acetone using a Soxhlet extractor and subsequently dried under dynamic vacuum at 120 °C for 4 hours, resulting in a yellow powder.

**PP-COF.** 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline **L1** (86 mg, 0.1 mmol) and hexa(4-formylphenoxy)cyclotriphosphazene **L3** (33 mg, 0.3 mmol) were placed in a 15 mL pressure vessel, respectively; then, 1,2-dichlorobenzene/*n*-butanol (9:1 v/v, 1.5 mL) was added, and the two mixtures were sonicated for 5 min to enable a homogeneous dispersion. Afterwards, the L1 dispersion was added to the L4 or L5 dispersion, and the resultant suspension was briefly shaken (about 10 s). Subsequently, acetic acid (6 M, 0.3 mL) was slowly added and protected with nitrogen; the vessel was then sealed and left undisturbed for 7 days at 120 °C. The solid was collected through filtration and washed with DMF, acetone, and THF separately. The powder was dried at 50 °C under vacuum overnight to obtain a yellowish crystalline solid.

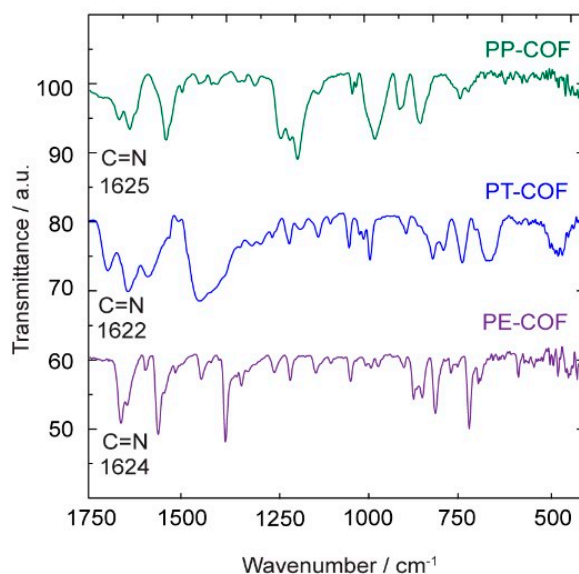
**PT-COF film.** A PT-COF film was created through a process involving the loading of 1,3,6,8-tetra(aminophenyl)pyrene **L1** (10 mg, 18.6 μmol, 1.0 eq.) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde **L4** (5.2 mg, 14.3 μmol, 0.7 eq.) into an autoclave, along with *o*-DCB (0.2 mL) and *n*-BuOH (0.8 mL). Following this, a fused silica substrate was inserted, and 0.1 mL of aqueous acetic acid (9.0 mol/L) was added. The sealed autoclave was heated at 120 °C for 5 days. After cooling to room temperature, the resulting COF film was rinsed with dry MeCN and dried using compressed air.

**PE-COF film.** A PE-COF film was created using a process that involved loading 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline **L1** (7.0 mg, 10  $\mu\text{mol}$ , 1.0 eq.) and 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde **L2** (4.0 mg, 10  $\mu\text{mol}$ , 1.0 eq.) into an autoclave with mesitylene/1,4-dioxane (1:1, v/v, 2 mL). The procedure included inserting a fused silica substrate followed by adding 6 M acetic acid (200  $\mu\text{L}$ ). The autoclave was then sealed and subjected to heating at 120  $^{\circ}\text{C}$  for 3 days. Post cooling to room temperature, the resulting COF film underwent a rinse with dry MeCN and was dried using compressed air.

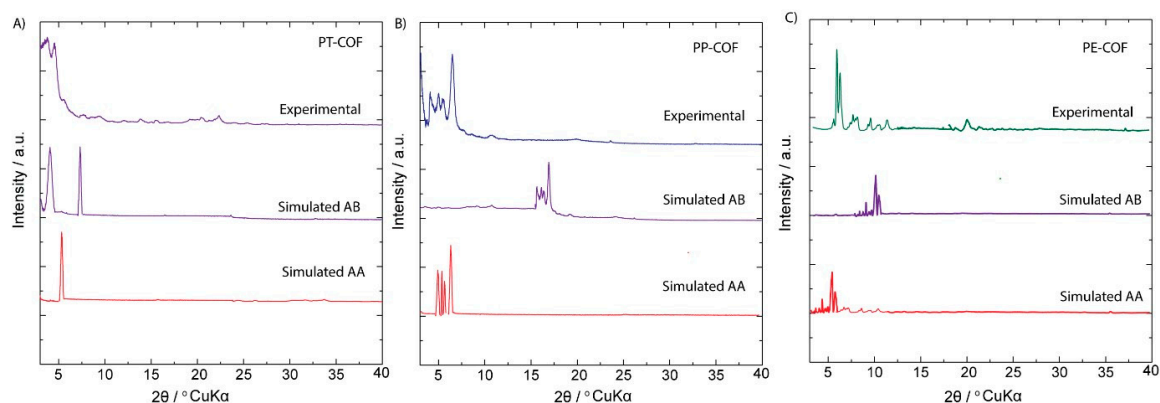
**PP-COF film.** A PP-COF film was produced by loading 1,3,6,8-tetra(aminophenyl)pyrene **L1** (30 mg, 55.8  $\mu\text{mol}$ , 3.0 eq.) and hexa(4-formyl-phenoxy)cyclotriphosphazene **L3** (19.6 mg, 18.6  $\mu\text{mol}$ , 1.0 eq.) into an autoclave along with 1,2-dichlorobenzene/n-butanol (9:1 v/v, 1.5 mL). Subsequently, a fused silica substrate was introduced, followed by the addition of 6 M of acetic acid (200  $\mu\text{L}$ ). The autoclave was sealed and heated at 120  $^{\circ}\text{C}$  for 7 days. Post cooling to room temperature, the resulting COF film underwent rinsing with dry MeCN and drying using compressed air.

## Section S5: Characterization of COFs

### Fourier-Transform Infrared (FT-IR) analysis



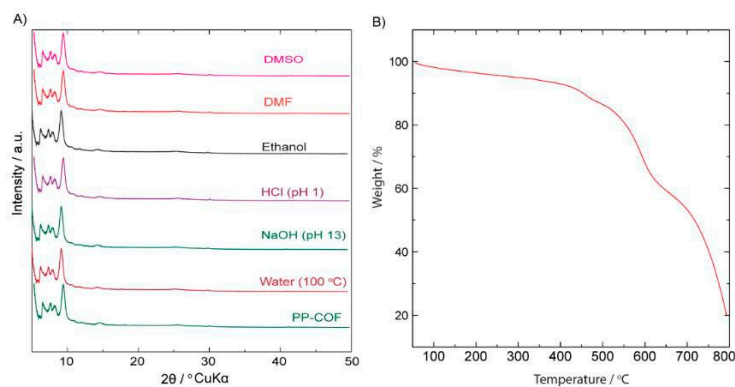
**Figure S7.** FTIR spectra of PT-COF (blue), PP-COF (green), and PE-COF (purple), respectively.



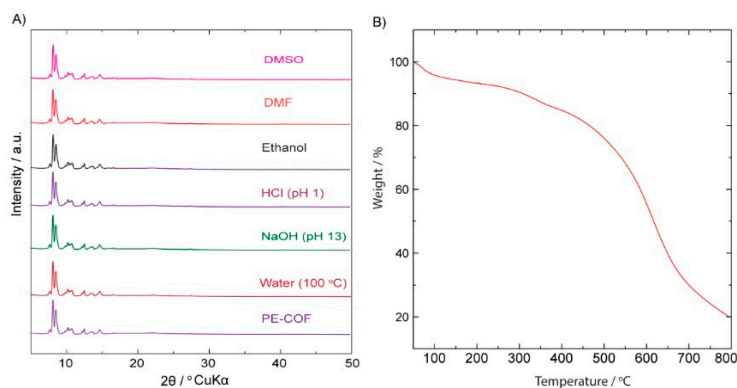
**Figure S8.** Comparison of PXRD patterns of A) PT-COF, B) PP-COF, and C) PE-COF.

## Section S6: COF stability

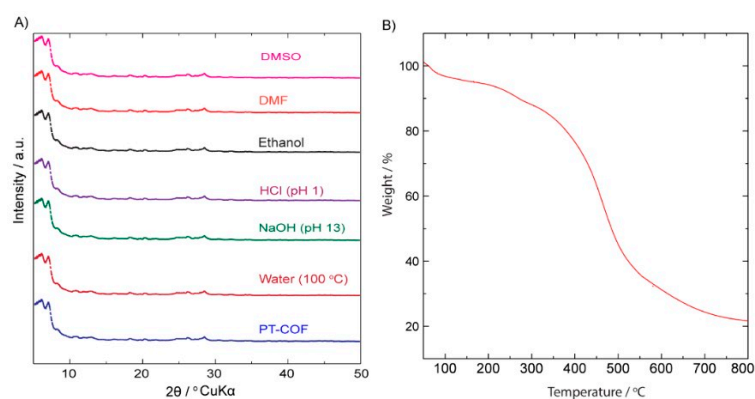
**Stability Test.** A total of 10 mg of each COF was immersed in 10 ml of the following solvents: boiling water (100 °C), strong acid (HCl, pH 1), strong base (NaOH, pH 13), ethanol, DMF, and DMSO. The mixtures were then gently shaken and allowed to stand for 24 h. The sample was then centrifuged and dried for subsequent PXRD characterization.



**Figure S9.** A) PXRD patterns of PP-COF after treatment in different organic solvents for 24; B) TGA of PP-COF.

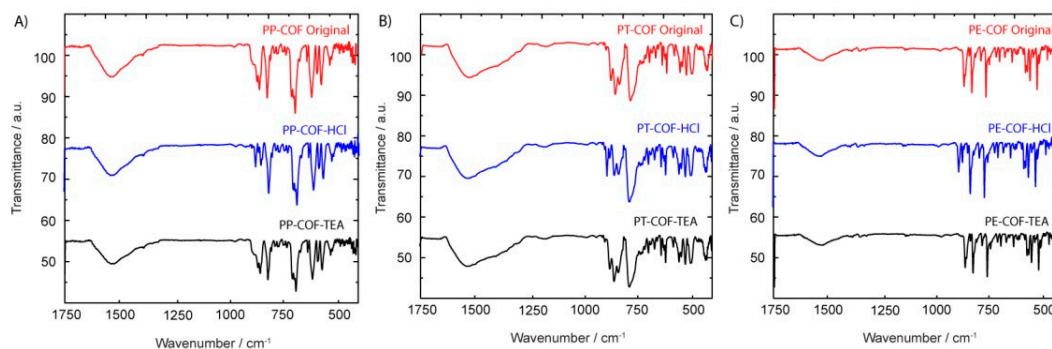


**Figure S10.** A) PXRD patterns of PE-COF after treatment in different organic solvents for 24; B) TGA of PE-COF.

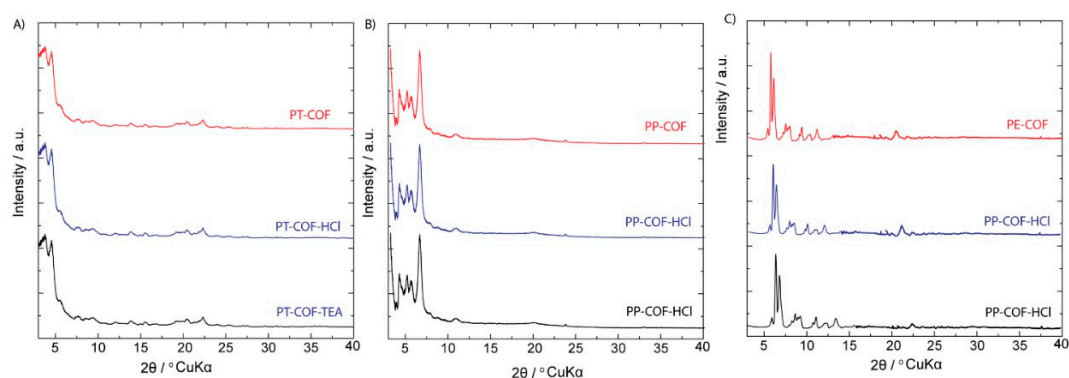


**Figure S11.** A) PXRD patterns of PT-COF after treatment in different organic solvents for 24; B) TGA of PT-COF.

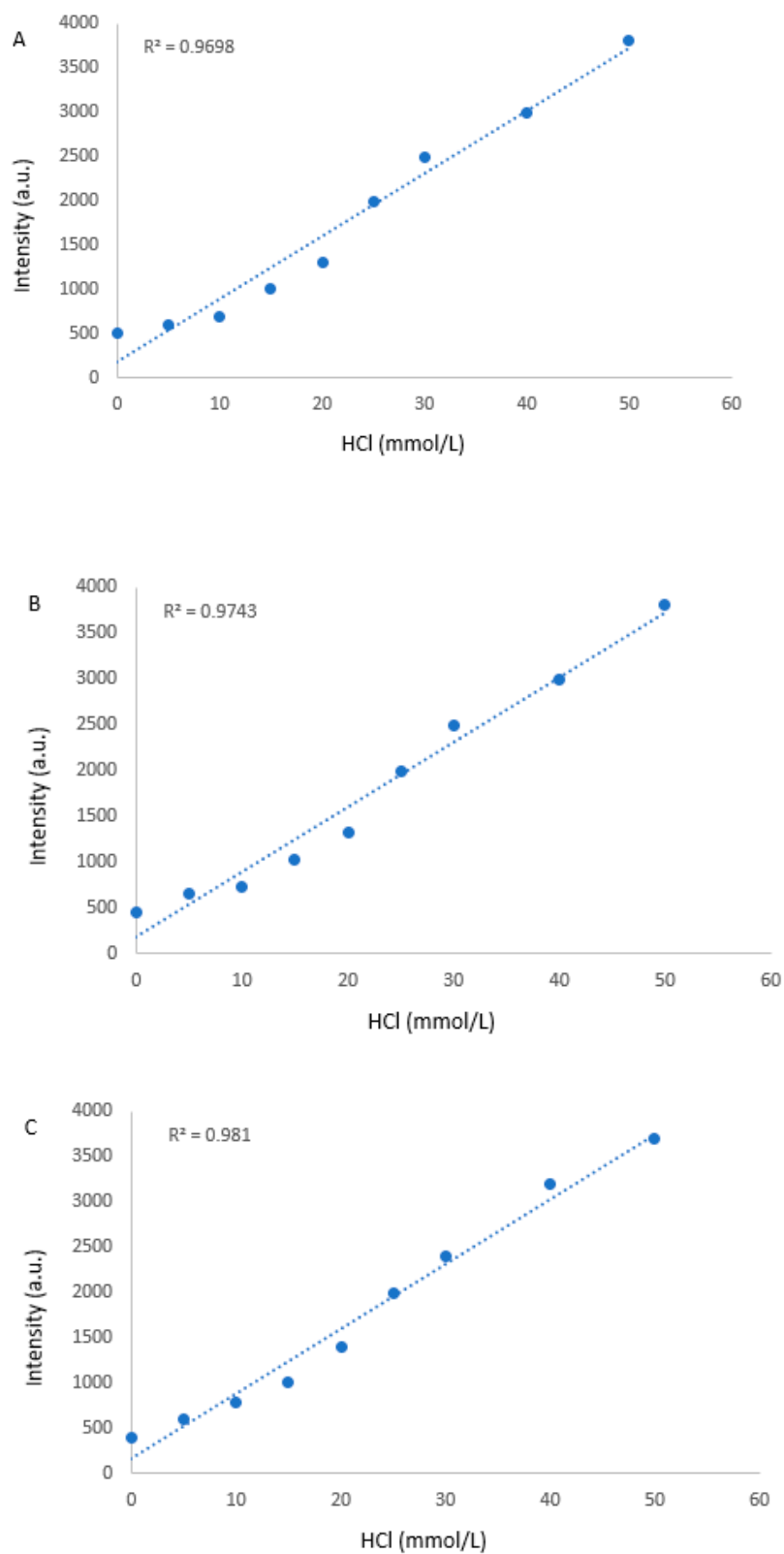
## Section S7: Recovery and reusability



**Figure S12.** FT-IR spectra of the A) PP-COF, B) PT-COF, and C) PE-COF powders before and after exposure to HCl gas, and recovery with TEA gas.

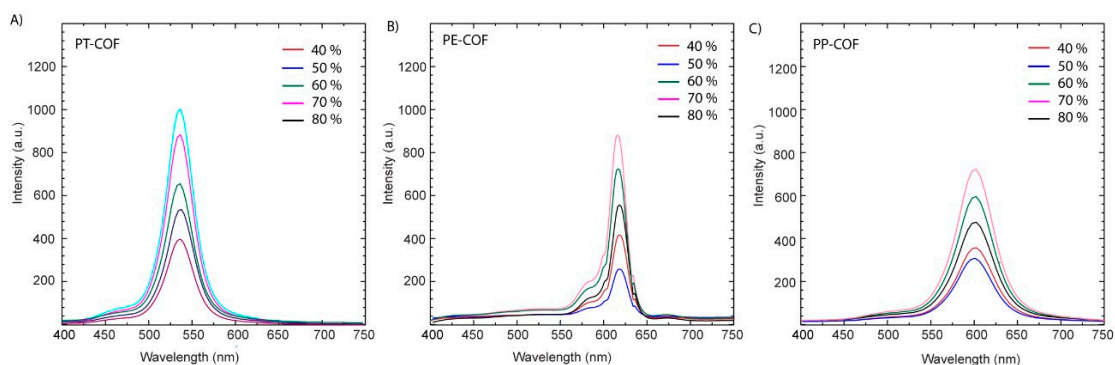


**Figure S13.** Powder XRD patterns of the A) PT-COF, B) PP-COF, and C) PE-COF powders before and after exposure to HCl gas, and recovery with TEA gas.



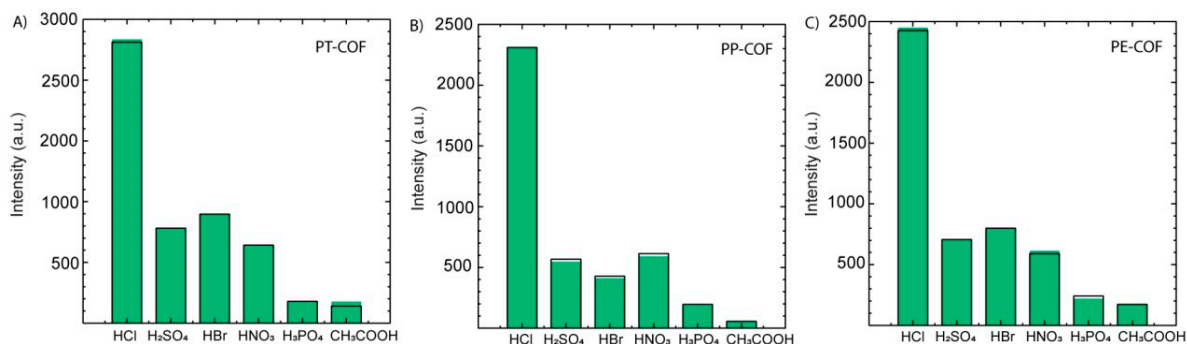
**Figure S14.** Calibration curves of the fluorescence intensities of the A) PT-COF, B) PP-COF, and C) PE-COF plotted with respect to the HCl concentration.

## Section S8: Humidity test



**Figure S15.** Detection of HCl gas under different humidity environments (40%, 50%, 60%, 70%, and 80%) with A) PT-COF, B) PE-COF, and C) PP-COF films.

## Section S9: Comparison with Other Acids



**Figure S16.** Illustrates the fluorescence emission peaks at 540, 625, and 611 nm for (A) PT-COF, (B) PP-COF, and (C) PE-COF when dispersed in 1,4-dioxane (concentration: 1 mg mL<sup>-1</sup>; excitation wavelength: 366 nm) following the introduction of an acid concentration of 20 mmol L<sup>-1</sup>.

## Section S10: Unit cell parameters

**Table S1. Fractional atomic coordinates in the refined unit cell of PT-COF.**

Space group P3 and unit cell dimensions  $a = b = 19.46 \text{ \AA}$ ,  $c = 3.64 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$

Atom	x	y	z
C1	-0.37444	-0.63645	0.55262
C2	-0.23123	-0.56122	0.69341
C3	-0.16293	-0.52157	0.69101
C4	-0.12379	-0.54581	0.55312
C5	-0.15349	-0.60986	0.41425
C6	-0.22183	-0.64899	0.41171
C7	-0.49657	-0.54881	0.55602
C8	-0.47420	-0.48786	0.46745
N9	-0.51422	-0.45782	0.46298
C10	-0.58264	-0.49485	0.50874
C11	-0.62035	-0.46408	0.50266
C12	-0.59028	-0.39597	0.45230
C13	-0.52199	-0.35916	0.40641
C14	-0.48428	-0.38996	0.41064
C15	-0.62997	-0.36343	0.44952
C16	-0.69661	-0.39978	0.44962
H17	-0.26303	-0.54158	0.81081
H18	-0.13906	-0.46927	0.80193
H19	-0.12183	-0.63013	0.30299
H20	-0.24594	-0.70085	0.29414
H21	-0.55031	-0.58054	0.63806
H22	-0.60746	-0.55023	0.55099
H23	-0.67590	-0.49437	0.53877
H24	-0.49712	-0.30374	0.36542
H25	-0.42881	-0.35964	0.37122
C26	-0.33333	-0.66667	0.55264
H27	-0.54914	-0.58065	0.64244
H28	-0.47363	-0.48870	0.46575
H29	-0.60598	-0.55036	0.56298
H30	-0.47363	-0.48870	0.46575
H31	-0.72266	-0.45707	0.44884
C32	-0.57761	-0.54316	0.45005
C33	-0.41552	-0.53421	0.41296

**Table S2 Fractional atomic coordinates in the refined unit cell of PP-COF.**Space group P1 and unit cell dimensions  $a = b = 30.17 \text{ \AA}$ ,  $c = 3.43 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ 

Atom	x	y	z
N1	2.4488	0.31995	0.21385
P2	2.43019	0.26045	-0.00306
N3	2.48559	0.28318	-0.25326
P4	2.55073	0.32256	-0.08084
N5	2.53943	0.37798	-0.18218
P6	2.48722	0.39207	0.01288
O7	2.51546	0.44186	0.26372
O8	2.43475	0.38158	-0.24356
O9	2.56253	0.28054	-0.40481
O10	2.61332	0.37104	-0.29282
O11	2.36674	0.23101	-0.22037
O12	2.43099	0.20506	0.22053
C13	2.42943	0.43126	-0.23263
C14	2.57537	0.48173	0.21754
C15	2.66729	0.38195	-0.17493
C16	2.5622	0.2382	-0.35439
C17	2.32176	0.24739	-0.09321
C18	2.38227	0.1486	0.21231
C19	2.47849	0.48669	-0.26024
C20	2.47258	0.53579	-0.26954
C21	2.41734	0.5303	-0.25194
C22	2.36786	0.46499	-0.2266
C23	2.38395	0.42547	-0.22093
C24	2.61875	0.46735	0.27481
C25	2.67767	0.50945	0.24064
C26	2.6932	0.5661	0.15032
C27	2.64992	0.58042	0.09912
C28	2.59142	0.53866	0.13581
C29	2.67177	0.34397	0.03082
C30	2.72612	0.35239	0.11597
C31	2.77715	0.39912	0.11967
C32	2.77741	0.44928	0.0281
C33	2.72425	0.45951	-0.04984
C34	2.67388	0.41247	-0.04725
C35	2.72708	0.24983	0.10244
C36	2.77691	0.20017	0.09309
C37	2.77802	0.15055	-0.01482
C38	2.72736	0.14068	-0.11384
C39	2.67686	0.18989	-0.11715
C40	2.62373	0.23919	-0.00531
C41	2.57395	0.28812	0.00748
C42	2.50788	0.29989	-0.09591
C43	2.56731	0.42345	-0.41296



C44	2.61744	0.44877	-0.43568
C45	2.65165	0.39448	-0.46142
C46	2.60166	0.36942	-0.43962
C47	2.63172	0.2726	-0.53065
C48	2.68046	0.24422	-0.54532
C49	2.72723	0.24811	-0.46647
C50	2.67889	0.27653	-0.45052
N51	2.45012	0.63842	-0.34144
N52	2.7981	0.60688	0.18687
C53	2.46014	0.6868	-0.33276
C54	2.85656	0.65421	0.14369
C55	2.50884	0.735	-0.46027
C56	2.51525	0.79023	-0.4352
C57	2.47349	0.7985	-0.28425
C58	2.42433	0.75	-0.16123
C59	2.41769	0.69456	-0.18488
C60	2.90409	0.65336	0.28011
C61	2.96038	0.70167	0.25274
C62	2.9702	0.75083	0.15159
C63	2.92714	0.7621	0.09992
C64	2.87083	0.71421	0.12984
C65	2.95025	0.60556	0.03121
C66	3.00693	0.61388	0.1121
C67	3.0576	0.66036	0.11478
C68	3.05747	0.70989	0.02423
C69	3.00652	0.71872	-0.07069
C70	2.95134	0.6721	-0.06748
C71	3.00748	0.55631	0.09553
C72	3.05684	0.50672	0.0839
C73	3.05631	0.45716	-0.02779
C74	3.00709	0.4074	-0.10957
C75	2.95054	0.45718	-0.12085
C76	2.8999	0.50689	-0.00934
C77	2.84948	0.55647	0.0059
C78	2.78366	0.54503	-0.09659
C79	2.84378	0.66091	-0.41386
C80	2.89414	0.68634	-0.43654
C81	2.92829	0.63205	-0.46228
C82	2.87828	0.607	-0.44048
C83	2.90833	0.51018	-0.53151
C84	2.95705	0.4818	-0.54618
C85	3.00382	0.48569	-0.46733
C86	2.95548	0.51411	-0.45138
N87	2.72731	0.87593	-0.3423
P88	3.07499	0.84438	0.18598
N89	2.73719	0.92436	-0.33308
P90	3.13362	0.89177	0.14346

N91	2.78594	0.97256	-0.45984
P92	3.14134	0.92855	0.01351
O93	2.79235	1.02779	-0.43476
O94	2.75059	1.03606	-0.28381
O95	2.70143	0.98755	-0.16079
O96	2.69479	0.93212	-0.18444
O97	3.18118	0.89091	0.28056
O98	3.23747	0.93923	0.25319
O99	3.24729	0.98838	0.15204
O100	3.20423	0.99966	0.10037
O101	3.14792	0.95176	0.13029
O102	3.22734	0.84312	0.03166
O103	3.28402	0.85143	0.11255
O104	3.33469	0.89792	0.11523
O105	3.33456	0.94744	0.02468
O106	3.28361	0.95628	-0.07024
O107	3.22843	0.90965	-0.06703
O108	3.28457	0.79387	0.09608
O109	3.33393	0.74428	0.08445
O110	3.3334	0.69472	-0.02724
O111	3.28418	0.64495	-0.10902
O112	3.22763	0.69474	-0.1203
O113	3.17699	0.74445	-0.00879
O114	3.12657	0.79403	0.00645
O115	3.06075	0.78259	-0.09604
O116	3.12087	0.89846	-0.41331
O117	3.17123	0.92389	-0.43599
O118	3.20538	0.8696	-0.46173
O119	3.15537	0.84455	-0.43993
O120	3.18542	0.74773	-0.53096
O121	3.23414	0.71935	-0.54563
O122	3.28091	0.72324	-0.46678
O123	3.23257	0.75166	-0.45083
C124	3.0047	1.11313	-0.34125
C125	3.35238	1.08159	0.18603
C126	3.01458	1.1615	-0.33257
C127	3.411	1.12891	0.14368
C128	3.06322	1.2077	-0.45966
C129	3.06963	1.26293	-0.43459

**Table S3 Fractional atomic coordinates in the refined unit cell of PE-COF.**

Space group P4 and unit cell dimensions  $a = 21.23 \text{ \AA}$ ,  $b = 21.20 \text{ \AA}$ ,  $c = 4.37 \text{ \AA}$ , with  $\alpha = \beta = \gamma = 90^\circ$

Atom	x	y	z
N1	-0.35894	-0.38042	2.63619
C2	-0.43782	-0.47476	3.06097

C3	-0.46893	-0.47466	3.27774
C4	-0.48486	-0.45007	3.39447
C5	-0.41846	-0.4495	2.95891
C6	-0.42769	-0.42683	2.79566
C7	-0.40889	-0.40371	2.6943
C8	-0.37979	-0.40315	2.74415
C9	-0.37019	-0.42597	2.89833
C10	-0.38928	-0.44884	3.00653
C11	-0.36413	-0.35701	2.50468
C12	-0.34018	-0.33561	2.4048
C13	-0.31074	-0.34046	2.42846
C14	-0.34692	-0.3099	2.28398
C15	-0.71257	-0.31863	4.67476
C16	-0.70482	-0.29312	4.7887
C17	-0.67514	-0.28903	4.80993
C18	-0.75636	-0.7236	5.14351
C19	-0.77871	-0.74432	5.25482
C20	-0.72787	-0.72913	4.8925
C22	-0.81517	-0.71286	5.65747
H23	-0.47433	-0.43019	3.32791
H24	-0.44935	-0.42706	2.74285
H25	-0.41704	-0.38696	2.56782
H26	-0.34791	-0.42571	2.93926
H27	-0.38144	-0.46592	3.13273
H28	-0.38603	-0.3525	2.4681
H29	-0.30496	-0.35999	2.52379
H30	-0.36949	-0.30592	2.26152
H31	-0.73525	-0.32234	4.65483
H32	-0.66919	-0.26943	4.90345
H33	-0.7606	-0.70314	5.25402
H34	-0.81646	-0.69842	5.44359
H35	-0.79873	-0.7052	5.79208
H36	-0.8381	-0.7136	5.86022
C37	-0.57661	-0.5	4.05005
C38	-0.51552	-0.5	3.61296