Supporting Information

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

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Table of Contents

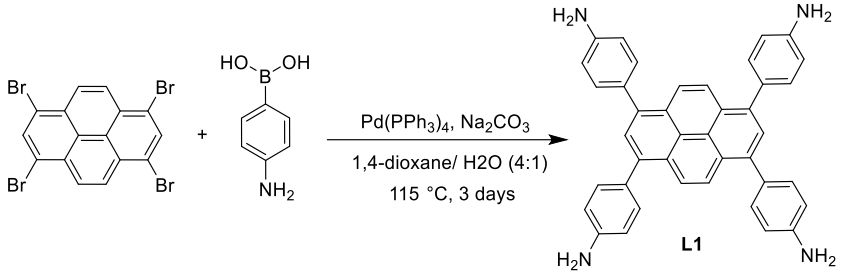
Section S1: Materials and General Methods

Chemicals. The chemicals utilized in this study include anhydrous tetrahydrofuran (THF), sodium carbonate (Na_2CO_3), 1,3,6,8-tetrabromopyrene ($C_{16}H_6Br_4$), 4-aminophenylboronic acid pinacol ester ($C_{12}H_{18}BNO_2$), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), 1,4-dioxane ($C_4H_8O_2$), methanol (CH_3OH), 1,1,2,2-tetra-*p*-tolylethene ($C_{30}H_{30}$), *N*-bromosuccinimide (NBS) ($C_4H_4BrNO_2$), benzoyl peroxide (BPO), and carbon tetrachloride (CCl_4), *o*-dichlorobenzene (*o*-DCB) ($C_6H_4Cl_2$), *n*-butanol ($C_4H_{10}O$), acetic acid (CH_3COOH), Mesitylene (C_9H_{12}), *p*-hydroxybenzaldehyde ($C_7H_6O_2$), potassium carbonate (K_2CO_3), acetonitrile (CH_3CN), hexachlorocyclotriphosphazene ($(NPCl_2)_3$), anhydrous magnesium sulfate ($MgSO_4$) and dichloromethane (CH_2Cl_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 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 gathered 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}H-NMR at 400 MHz and ^{13}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 (δ 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-Kα radiation at $\lambda = 1.542$ Å was utilized. Data collection spanned the 2θ range of 20–80° at a rate of 1 °C/min. These measurements were carried out under room temperature and atmospheric pressure conditions, as delineated in Sections S5, S6, and S7. 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 N_2 bath. Thermogravimetric analysis (TGA) involved heating a 0.2 g sample to 600 °C at a rate of 5 °C/min while continuously monitoring the weight relative to the temperature, following the procedures detailed in Section S6.

Section S2: Synthesis of raw materials

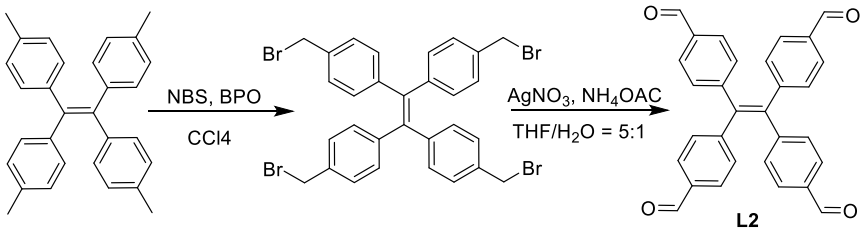
Synthesis of 1,3,6,8-tetra(aminophenyl)pyrene (L1)



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

The steps outlined in Scheme S1 will be 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_2CO_3 (10.9 g, 15.7 mmol, 5.5 eq.), and $Pd(PPh_3)_4$ (1.65 g, 1.45 mmol, 10 mol%) dissolved in 32 mL of 1,4-dioxane and 8 mL of H_2O. The mixture will be heated to reflux (115 °C) for a duration of 3 days. After cooling to room temperature, H_2O will be added. The resulting precipitate will be collected via filtration and washed with H_2O and MeOH. Recrystallization from 1,4-dioxane, followed by drying under high vacuum, will furnish the title compound, co-crystallized with approximately 1.5 dioxane molecules per formula unit, as a bright yellow powder; ^{1}H NMR (DMSO-d_6, 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); ^{13}C NMR (DMSO-d_6, 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)

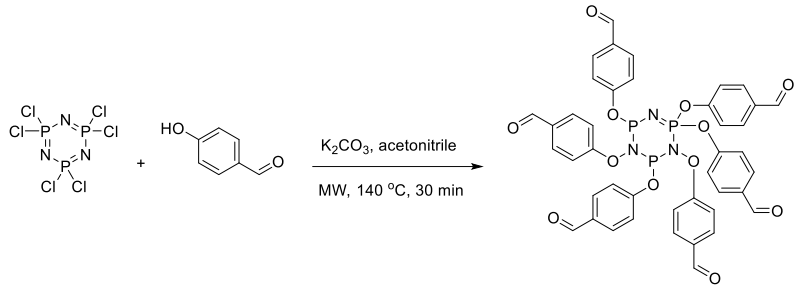


Scheme S2. Synthesis of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde

The procedure described in Scheme S2 begins 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_4 (30 mL) were

sequentially introduced. The resulting mixture underwent a reaction under an N_2 atmosphere at 80 °C for 2 hours. Following this, an additional portion 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 by 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_2O (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, brine, and dried with Na_2SO_4. A light yellow viscous liquid was obtained by rotary evaporation, and it was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5 : 1), resulting in a yellow-green product L4 (yield: 54%); ^{1}H NMR (DMSO-d_6, 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); ^{13}C NMR (DMSO-d_6, 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 starts by dissolving 14.92 g *p*-hydroxybenzaldehyde in 300 mL acetonitrile, 33.4 g potassium carbonate will be slowly added to the system, and stir in an ice bath for 30min. Then, 50 mL hexachlorocyclotriphosphazene (HCCP, 6.96 g) solution dissolve by acetonitrile will be slowly add, after 2 hours of ice bath, stirring reaction will conduct at room temperature for 2 days. The reaction ends with filtration, decompression distillation of the filtrate, and the obtained solid will be extracted with dichloromethane and wash with saturated salt water. The organic phase will be dried withanhydrous magnesium sulfate. The white solid will be obtained by decompression distillation, and the solid powder will be recrystallized in ethyl acetate. The powder will be dried at 50ºC under vacuum overnight to obtain compound **L3.**

Section S3: Characterizations of raw materials

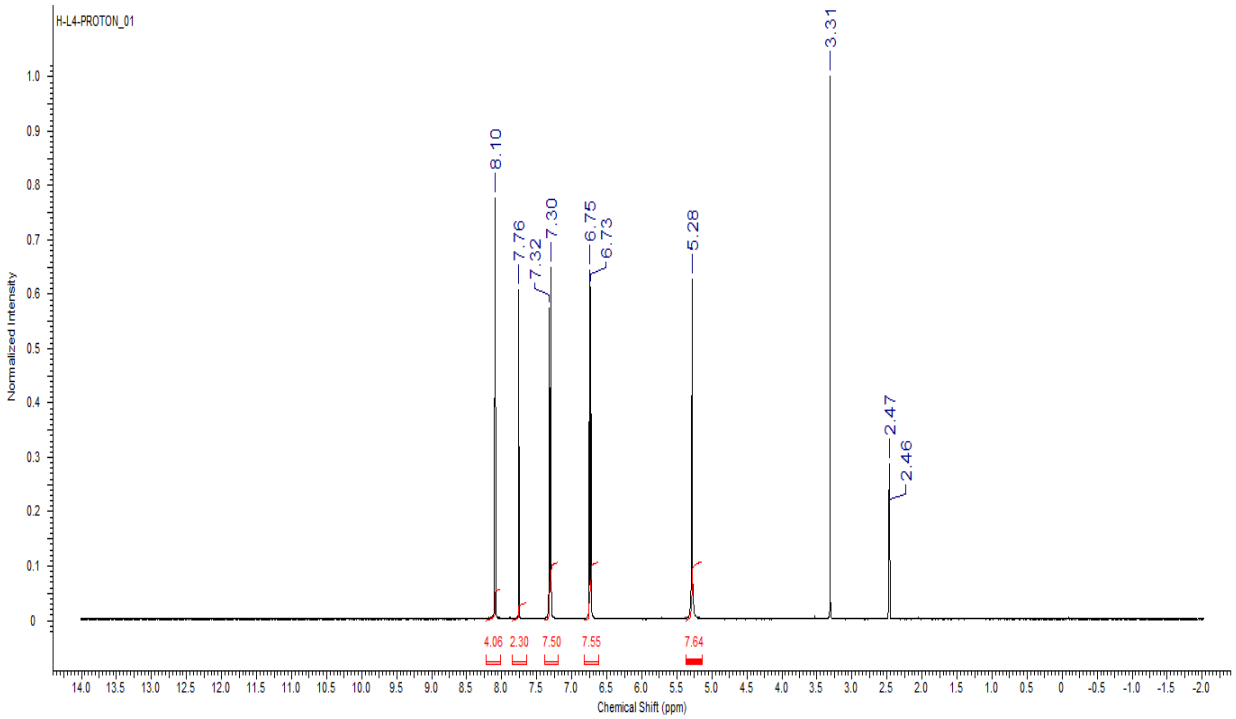


Fig S1. ^{1}H-NMR spectrum of L1

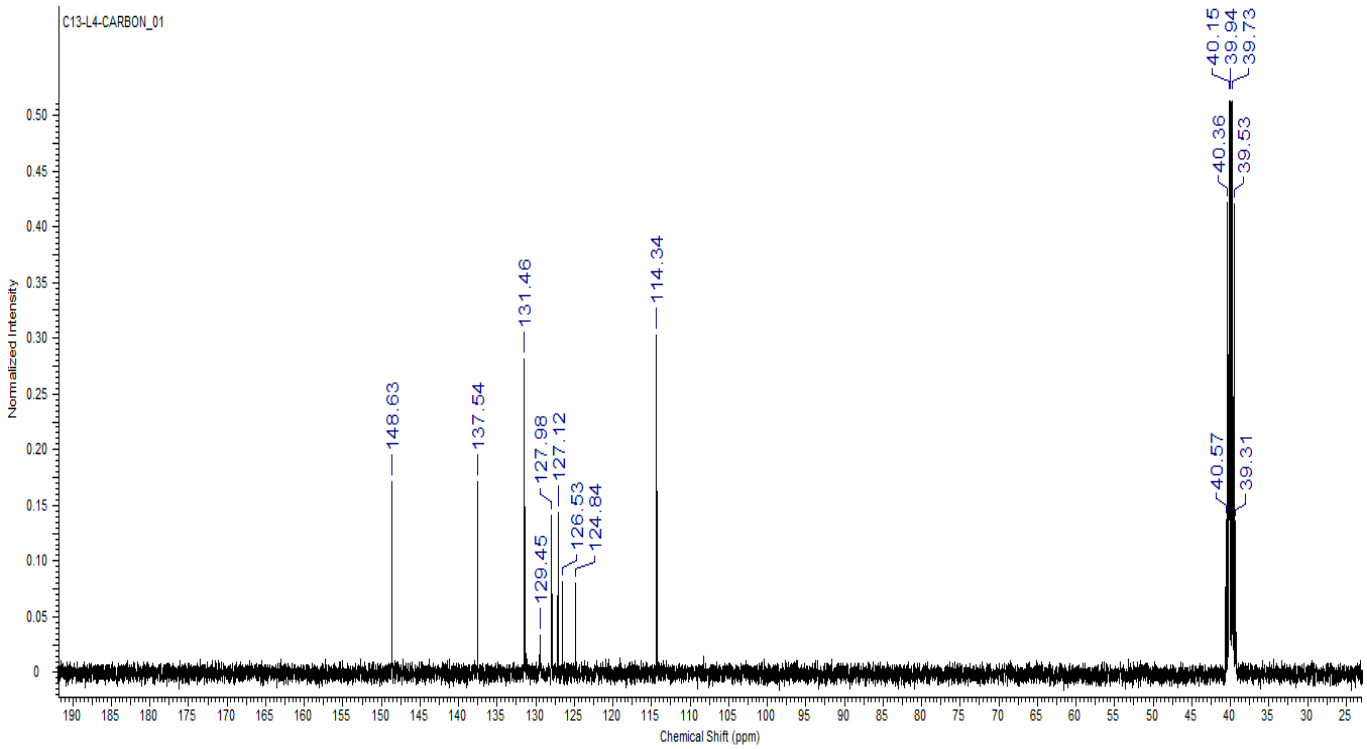


Fig S2. ^{13}C-NMR spectrum of L1

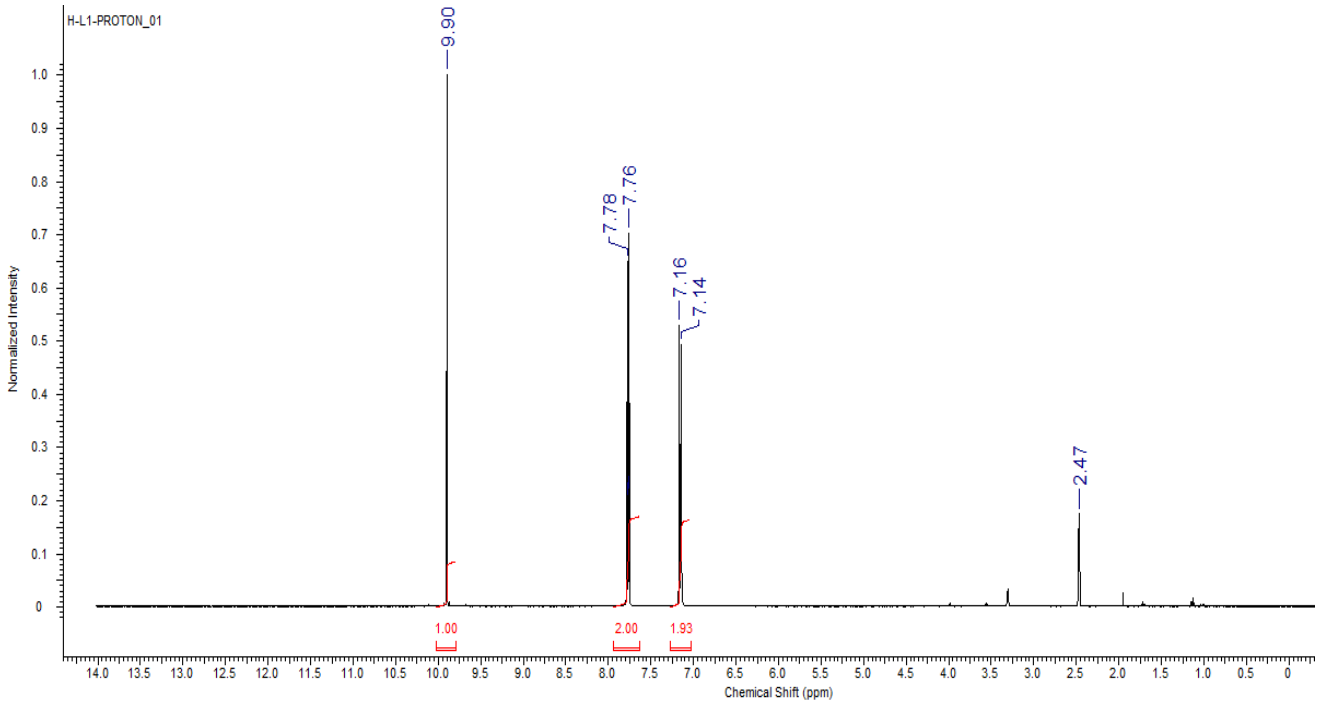


Fig S3. [1]H-NMR spectrum of L2

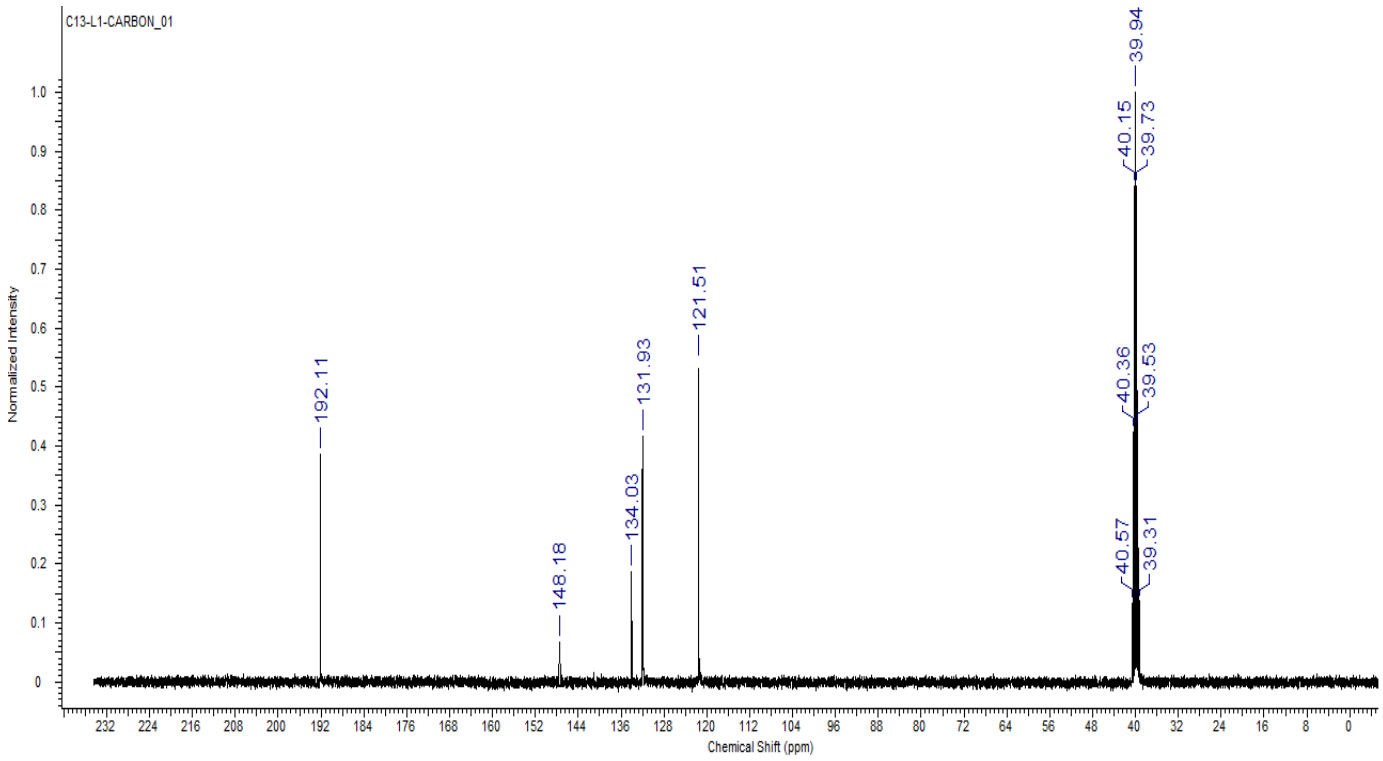


Fig S4. [13]C-NMR spectrum of L2

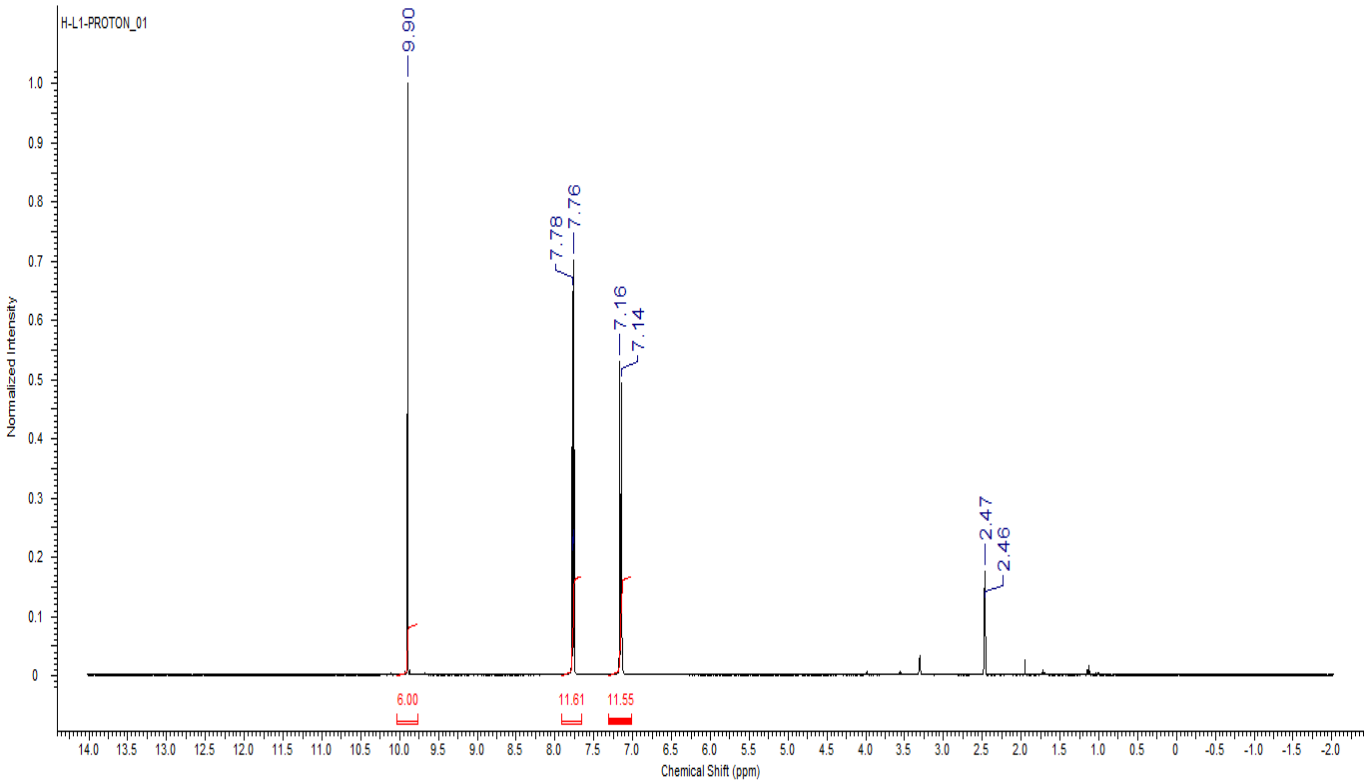


Fig S5. ^{1}H-NMR spectrum of L3

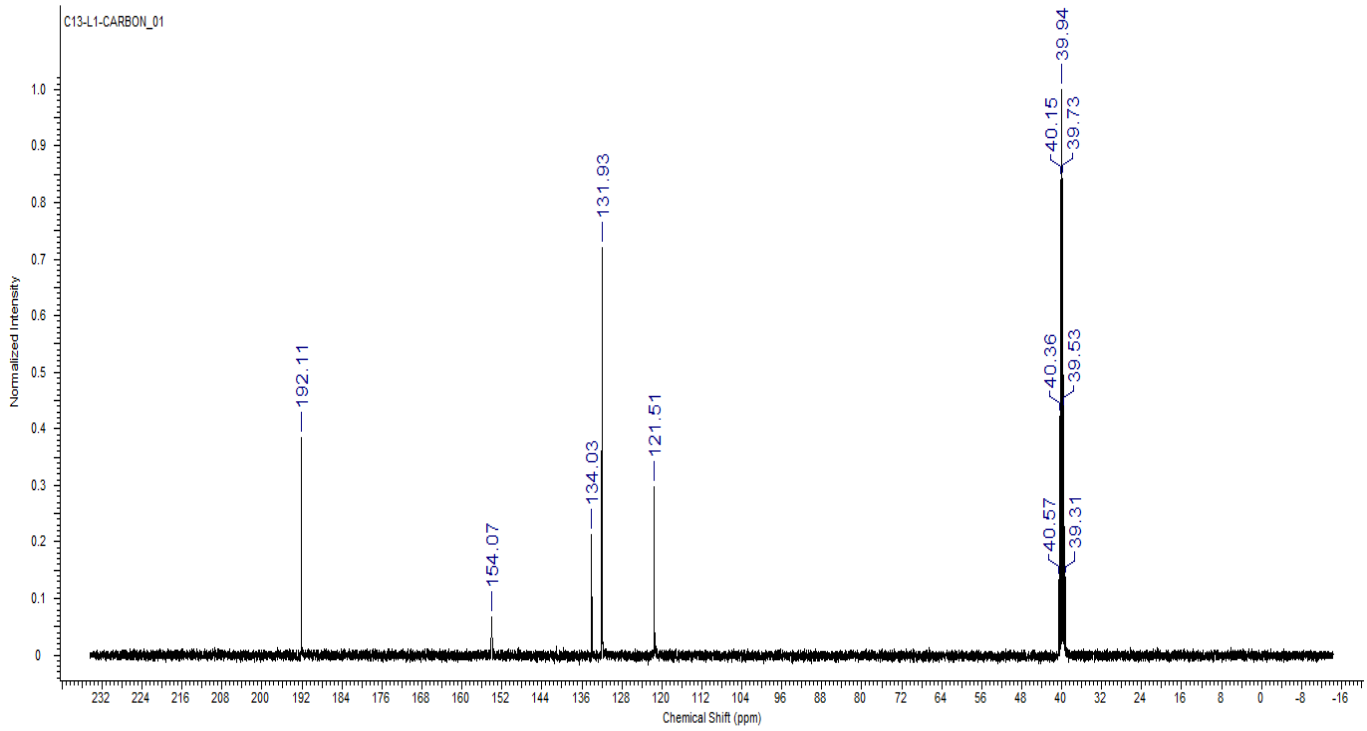


Fig S6. ^{13}C-NMR spectrum of L3

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

PT-COF. The COF will be synthesized by weighing 4,4',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) will be added to the tube. The mixture will be sonicated for 20 minutes to ensure a homogenous dispersion. Afterward, 0.1 mL of aqueous acetic acid (9.0 mol/L) will be added. Next, the tube will be degassed through three freeze-pump-thaw cycles under 77 K liquid nitrogen. Subsequently, the mixture will be transferred to an autoclave and heated at 120℃ for 5 days. Following this process, a pale brown powder will be isolated by centrifugation and washed with acetone (3 × 5.0 mL) to obtain the final product.

PE-COF. 4,4',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-formyl-phenoxy)cyclotriphosphazene **L3** (33 mg, 0.3 mmol) will be placed in 15 mL pressure vessel respectively, then 1,2-dichlorobenzene/n-butanol (9:1 v/v, 1.5 mL) will be added and the two mixtures will be sonicated for 5 min to afford homogeneous dispersion. Afterwards, the L1 dispersion will be added to the L4 or L5 dispersion and the resultant suspension will be briefly shaken (about 10 s). Subsequently, acetic acid (6 M, 0.3 mL) will be slowly added and protect by nitrogen, the vessel will be then sealed and left undisturbed for 7 days at 120°C. The solid will be collected by filtration and wash with DMF, acetone, and THF separately. The powder will be dried at 50ºC under vacuum overnight to afford 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 µmol, 1.0 eq.) and 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzaldehyde **L2** (4.0 mg, 10 µmol, 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 µL). The autoclave was then sealed and subjected to heating at 120 °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 µmol, 3.0 eq.) and hexa(4-formyl-phenoxy)cyclotriphosphazene **L3** (19.6 mg, 18.6 µmol, 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 acetic acid (200 µL). The autoclave was sealed and heated at 120 °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

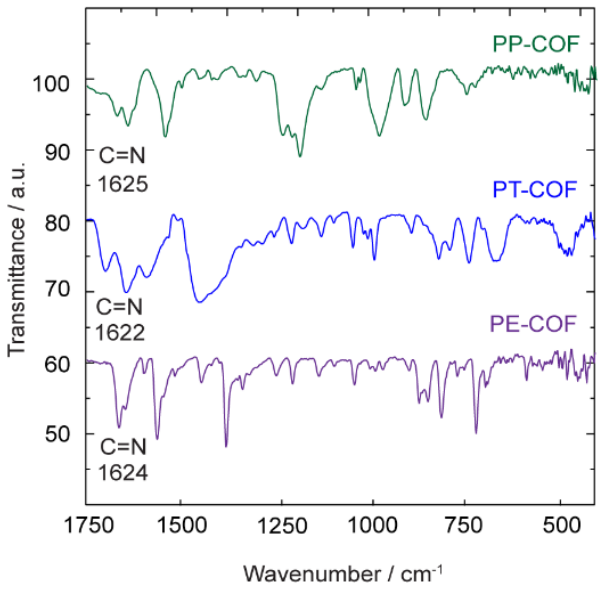


Fig S7. FTIR spectra of PT-COF (blue), PP-COF (green) and PE-COF (purple), respectively.

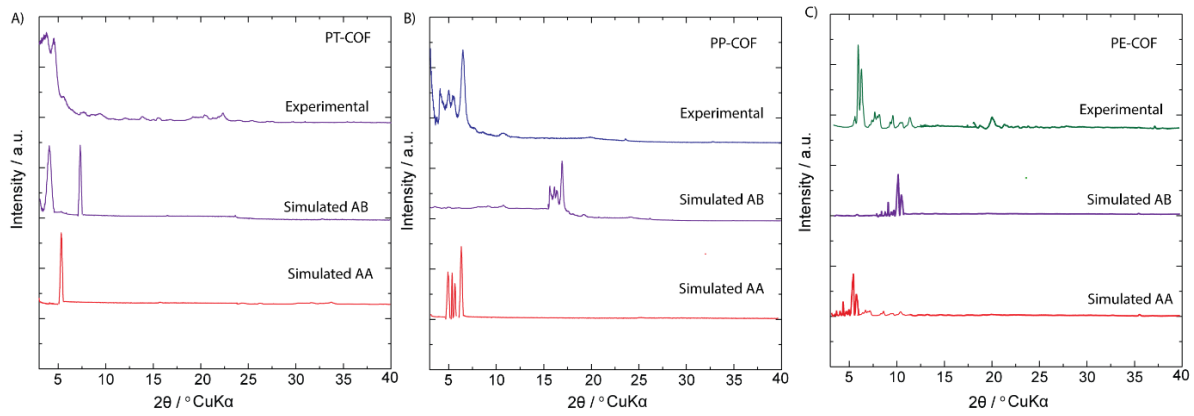


Fig S8. Comparison of PXRD patterns of A) PT-COF, B) PP-COF and C) PE-COF.

Section S6: COF stability

Stability Test. 10 mg of each COF was immersed at 10 ml of the following solvent: boiling water (100 °C), strong acid (HCl, pH 1) and 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.

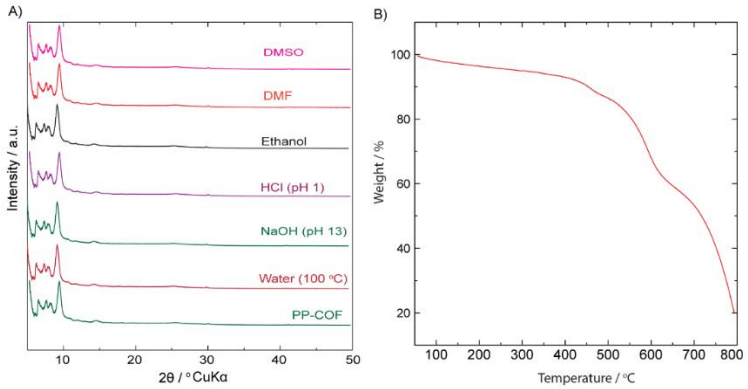


Fig S9. A) PXRD patterns of PP-COF after the treatment in different organic solvents for 24; B) TGA of PP-COF

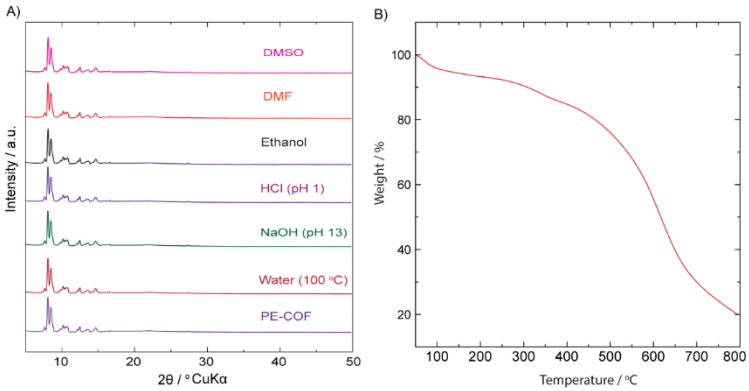


Fig S10. A) PXRD patterns of PE-COF after the treatment in different organic solvents for 24; B) TGA of PE-COF.

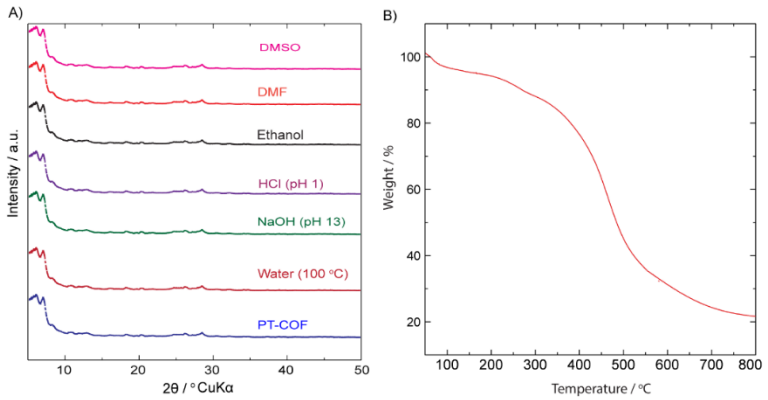


Fig S11. A) PXRD patterns of PT-COF after the treatment in different organic solvents for 24; B) TGA of PT-COF.

Section S7: Recovery and reusability

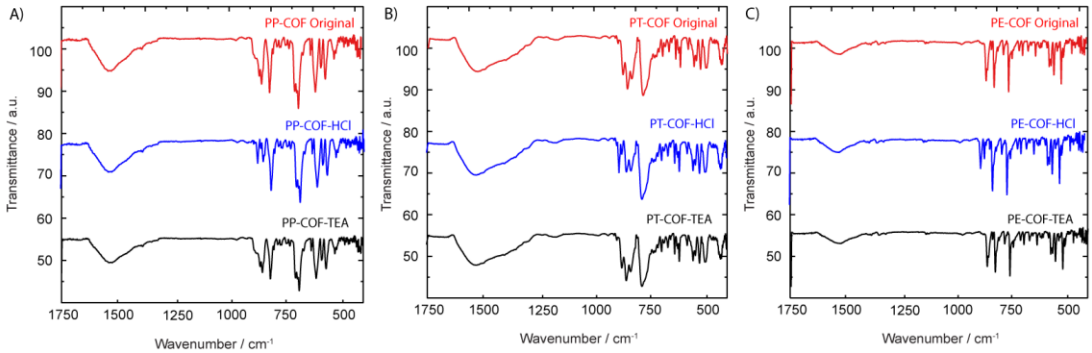


Fig S12. FT-IR spectra of the A) PP-COF, B) PT-COF and C) PE-COF powders before and after exposed to HCl gas, and recovery by TEA gas.

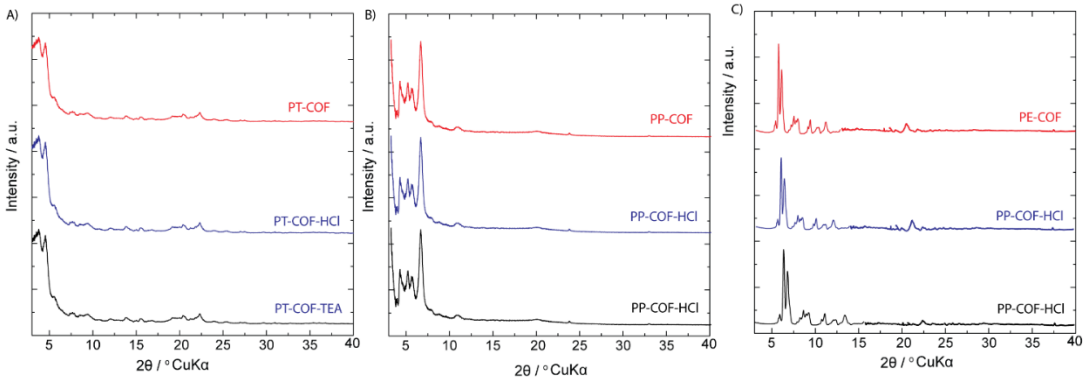


Fig S13. Powder XRD patterns of the A) PT-COF, B) PP-COF and C) PE-COF powders before and after exposed to HCl gas, and recovery by TEA gas.

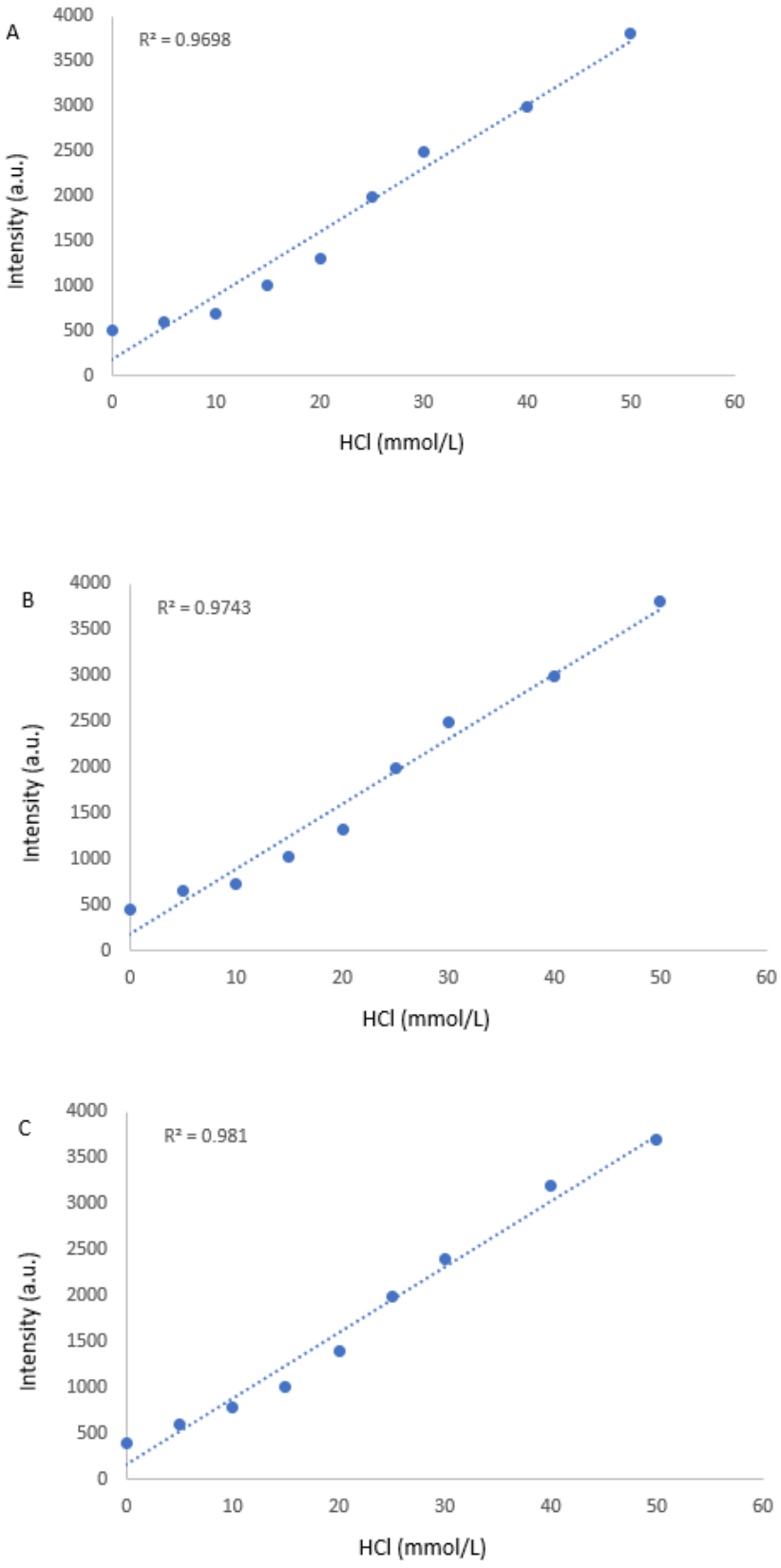


Fig S14. Calibration curves of the fluorescence intensities of the A) PT-COF, B) PP-COF and C) PE-COF plotted with respect to the HCl concentration.

Section S8: Humidity test

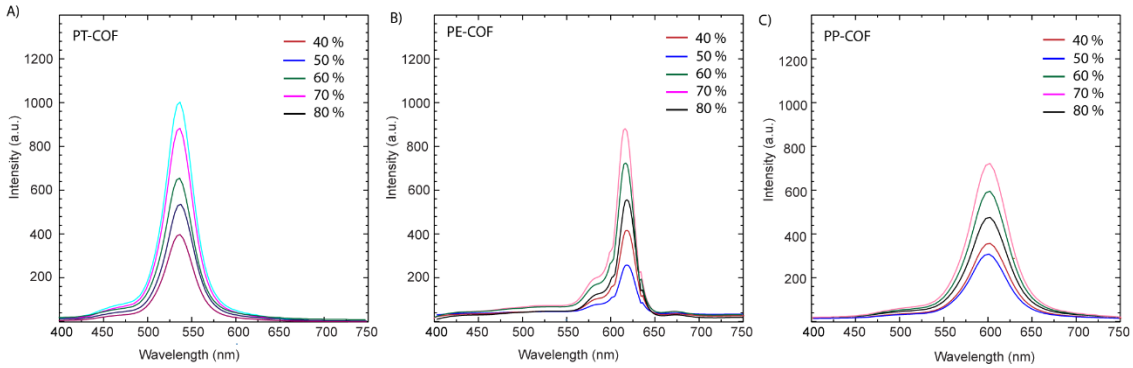


Fig S15. Detection of HCl gas under different humidity environments (40%, 50%, 60%, 70% and 80%) by A) PT-COF, B) PE-COF and C) PP-COF films

Section S9: Comparison with Other Acids

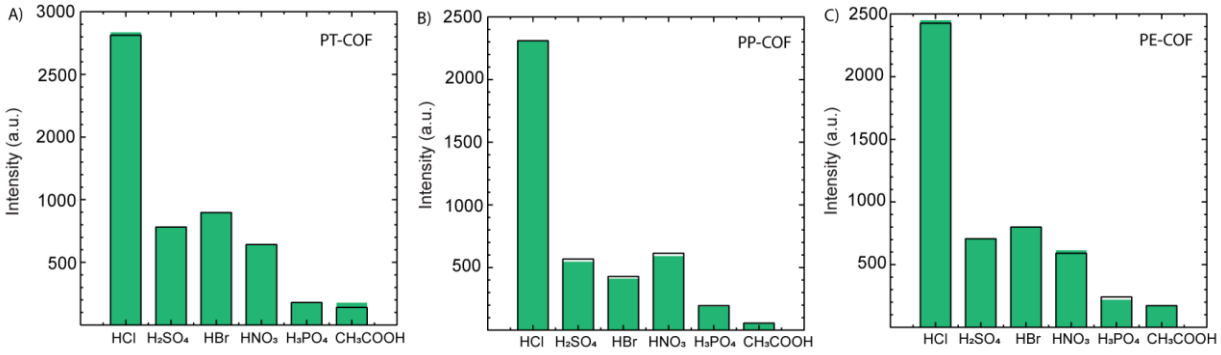


Fig S16. Illustrates the fluorescence emission peaks at 540, 625 and 611 nm for (A) PT-COF, (B) PP-COF, and (C) PE-COF when dispersed in 1,4-dioxane (concentration: 1 mg mL^{-1}; excitation wavelength: 366 nm) following the introduction of an acid concentration of 20 mmol L^{-1}.