

Supplementary Information

2D covalent organic framework thin films via interfacial self-polycondensation of an A₂B₂ type monomer

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Section 1. General Information

Fourier transform infrared (FT-IR) spectra of COF films were recorded in transmission mode on a Bruker Alpha spectrometer using KBr pellets in the range 400-4000 cm^{-1} . As for recording the FT-IR spectra of the protonated Py-COF films, the as-synthesized Py-COF films were acidified by exposure to volatile acid vapor prior to each measurement.

Grazing-incidence X-ray diffraction (GI-XRD) and powder X-ray diffraction (PXRD) patterns of Py-COF films or powder were all recorded on Rigaku SmartLab 9KW X-ray diffractometer at 45 kV, 200 mA with 1D array detector using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in air. The GIXRD measurement were performed for Py-COF film with an incidence angle of 0.2° .

The two dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS) data were measured at beamline 1W1A, Beijing Synchrotron Radiation Facility (BSRF), using a Mar345 detector and a photon energy of 8 keV with an incident angle of 0.2° , where $q = 4\pi \sin\theta/\lambda$, θ is a half of the total scattering angle, and λ is the X-ray wavelength (0.15479 nm).

Transmission electron microscopies (TEM) of the film were performed on a FEI model Tecani 20 microscope and a JEOL model JEM-2100F.

Field emission scanning electron microscopies (FE-SEM) were performed on a Hitachi Limited Model S-4800 microscope. The COF films were fixed on the sample tray with conductive tap and then were sprayed gold before FE-SEM measurements.

Optical microscopy (OM) and polarizing optical microscopy (POM) of COF films were performed on a Nikon microscope (ECLIPSE LV100ND) with a microscope camera (Nikon DS-Ri2). The Py-COF films were placed on silicon wafers or SiO_2/Si substrates.

X-ray photoelectron spectroscopy (XPS) was measured by ThermoFisher ESCALAB 250XI system. The Py-COF films were transferred on silicon wafers ($5 \times 5 \times 3 \text{ mm}$) and measured.

Raman spectra were performed on DXR2xi and Renishaw Raman Imaging Microscope (laser wavelength, 532 nm).

UV-visible spectra were recorded on Perkin-Elmer Lambda 900. A tape was applied to fix the quartz slide and a background measurement was performed. The Py-COF film was then transferred on the same quartz and measured. Besides, the Py-COF films were placed inside a cuvette filled with the respective acid vapor. For the acid vapor sensing experiments, the acid was evaporated at room temperature inside a cuvette. The Py-COF films were handled and measured in air. Due to the concentration of gaseous acid is hard to precisely monitor, solution of acid in 1,4-dioxane was used for the sensitivity of sensing experiment. The films were washed thoroughly with 1,4-dioxane by immersion and dried before the experiments.

Atomic force microscopy (AFM) was performed on a Bruker MultiMode 8 instrument in tapping mode. The roughness was calculated by the software NanoScope Analysis 1.8.

Section 2. Materials and Methods

Materials

1,6-bis(4-formylphenyl)-3,8-bis(4-aminophenyl)pyrene (BFBAPy) was synthesized following the previously reported protocols.^{S1} All the commercially available reagents and solvents were purchased from Kermel and were used as received without any further purification. All the reactions were performed under ambient atmosphere using oven-dried glassware unless otherwise mentioned. Silicon wafers were purchased from Suzhou Crystal Silicon Electronic & Technology Co., Ltd.

Synthesis of Py-COF powder by the solvothermal method

Py-COF_{DCM} powder was synthesized following the previously reported protocols. BFBAPy (29.6 mg, 0.05 mmol) was added to a 10 mL Schlenk tube, dichloromethane (2.0 mL) was added. The mixture was sonicated for 2 min followed by addition of 6 M acetic acid (0.2 mL). The mixture was further sonicated for another 2 minutes and degassed by three freeze-pump-thaw cycles, purged with Ar and heated at 120 °C for 3 days. Upon cooling to r.t., the precipitate was collected by filtration and washed by dimethylacetamide (DMAc), methanol and tetrahydrofuran (THF), dried under vacuum to afford an orange-yellow powder.

Fabrication Procedure of Py-COF films at liquid/liquid interface in simplex solvents^{S2}

The thin films were synthesized in 25 mL glass beakers. First, 1,6-bis(4-formylphenyl)-3,8-bis(4-aminophenyl)pyrene (BFBAPy, 14.8 mg, 0.025 mmol) was dissolved in 50 mL dichloromethane. Then the liquid transferred to a filter to remove any residual particulate. The solution of BFBAPy in 10 mL dichloromethane was poured into the beaker, followed by overlaying 6 mL water. Finally, 3 mL dilute acetic acid (6 M) was added slowly on top of water layer. The beaker was sealed by plastic wrap and kept undisturbed at room temperature for 4 days. The as-synthesized Py-COF films were transferred onto different substrates by immersing into the reaction solution and passing through the CH₂Cl₂/aqueous interface horizontally and slowly. Then, the aqueous solution was removed before the substrate was taken out of the CH₂Cl₂

solution.^{S3}The films was washed thoroughly with DCM by immersion and dried for further characterization. The same procedure was used to fabricating films in dichloroethane.

Fabrication Procedure of Py-COF thin films at liquid/liquid interface in mixed solvent

The thin films were synthesized in 25 mL glass beakers. First, BFBAPy (7.1 mg, 0.012 mmol) was added in 50 mL mesitylene and benzyl alcohol mixed solvent. The liquid was filtered using a syringe filter to remove undissolved reactants after sonication. 9 mL water containing 3 mL dilute acetic acid (6 M) was poured into the beaker. Finally, 10 mL mixed solution of BFBAPy was added slowly on top of water layer. The beaker was sealed by plastic wrap and kept undisturbed at room temperature for 4 days. The as-synthesized Py-COF thin films were transferred onto different substrates of interest for characterization.

Fabrication Procedure of 2D Py-COF films at air/liquid interface

Glass sample vials (60 mm × 30 mm) were used as the containers to grow the 2D Py-COF. The vials were cleaned twice by ethanol. 25 mL of water containing acetic acid was added into the vials as a liquid substrate for film growth. 100 μ L of BFBAPy solution (0.10 mM in mixed solvent) was slowly dropped on the surface and then undisturbed for 24 h. After the solvent evaporated completely, 2D polymer films of BFBAPy floating on the surface of water were obtained. SiO₂/Si wafers were used as the substrates. The films were transferred to the SiO₂/Si substrates by dipping the substrate up-side-down and fishing the films out.^{S4}

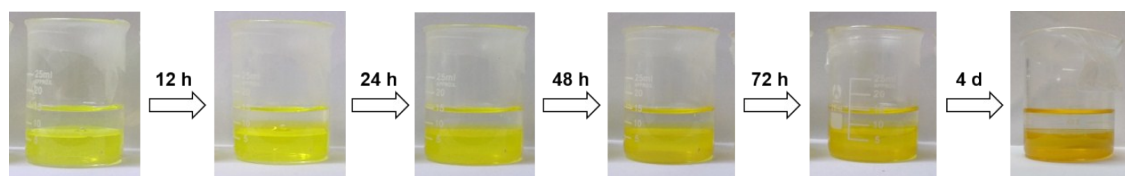


Figure S1 The digital images of the interfacial crystallization process for Py-COF film at water/dichloromethane interface.

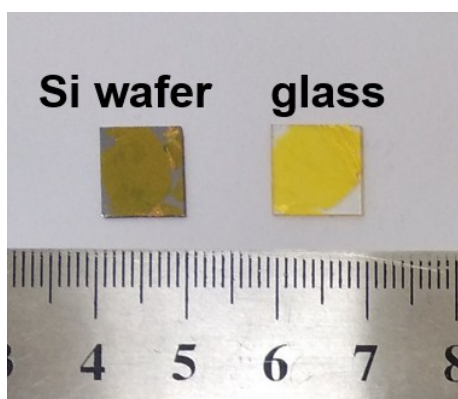


Figure S2 Photograph of Py-COF-DCM thin films transferred on various substrates.

Section 3. FT-IR and Raman Spectra Analysis of BFBAPy and Py-COF Film

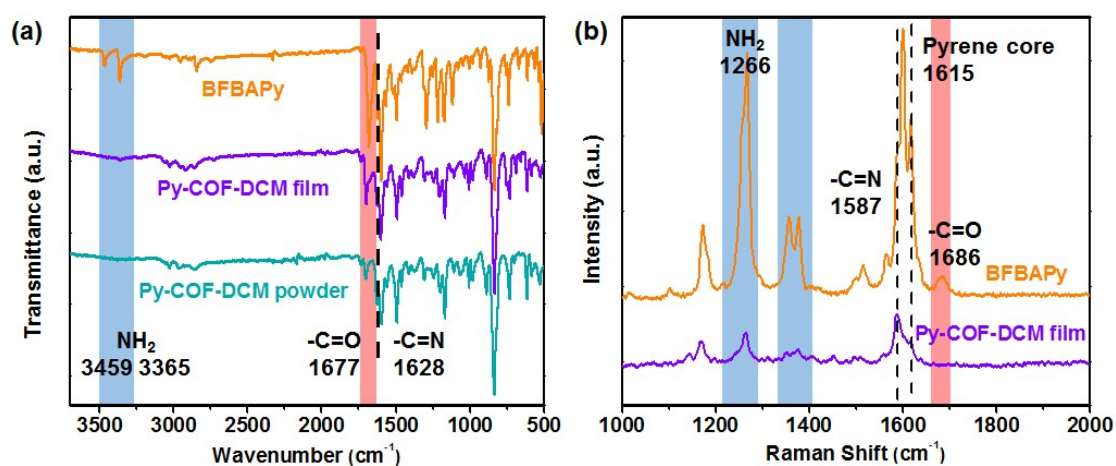


Figure S3 (a) FT-IR and (b) Raman spectra of Py-COF thin film (ca. 150 nm thickness).

Section 4. UV-vis and XPS Spectra Analysis of BFBAPy and Py-COF Film

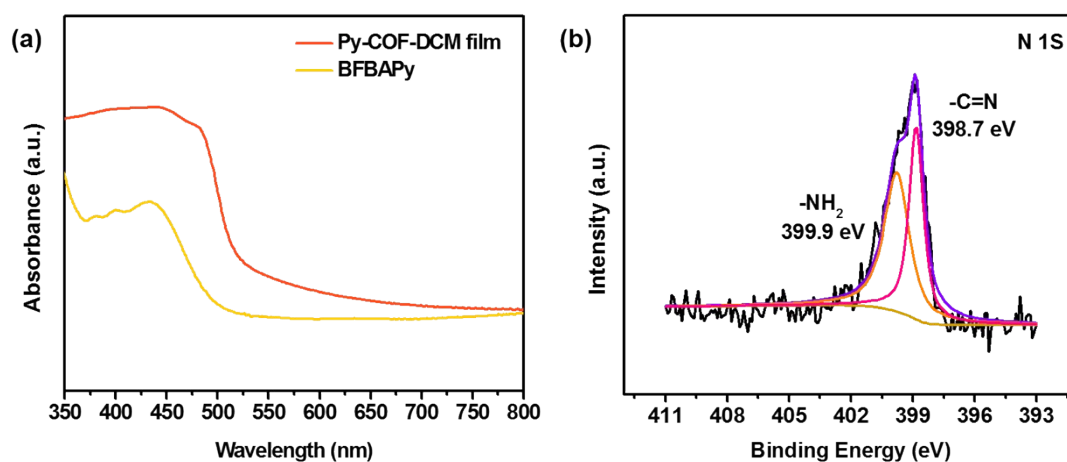


Figure S4 (a) UV-vis and (b) XPS spectra of Py-COF thin film (ca. 150 nm thickness).

Section 5. Optical Microscopy, SEM and TEM images of Py-COF film

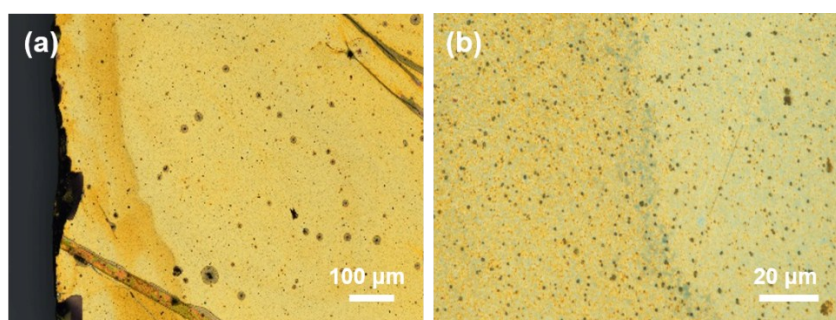


Figure S5 Optical microscopy of Py-COF film on a silicon wafer.

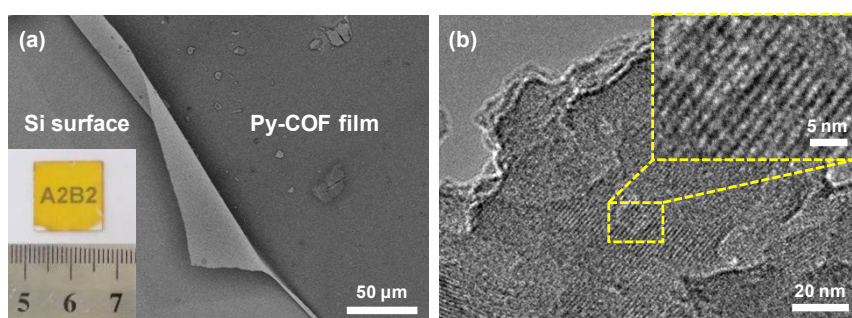


Figure S6 (a) SEM image of Py-COF film transferred on Si wafer. (Inset: photography of Py-COF film on a glass substrate) and (b) TEM image of Py-COF film.

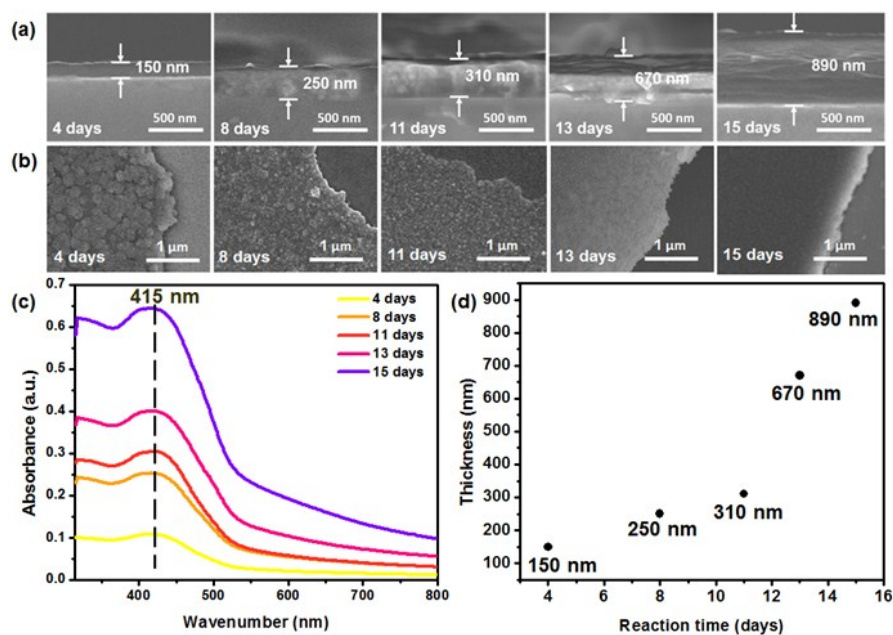


Figure S7 (a) Cross-section and (b) Top-view SEM images of Py-COF films with different thickness, (c) UV-vis spectra and (d) The thickness of Py-COF films growth over different reaction time.

Section 6. XRD, Raman, FT-IR, UV-vis Spectra Analysis of BFBAPy and Py-COF Films Prepared in Different Solvents

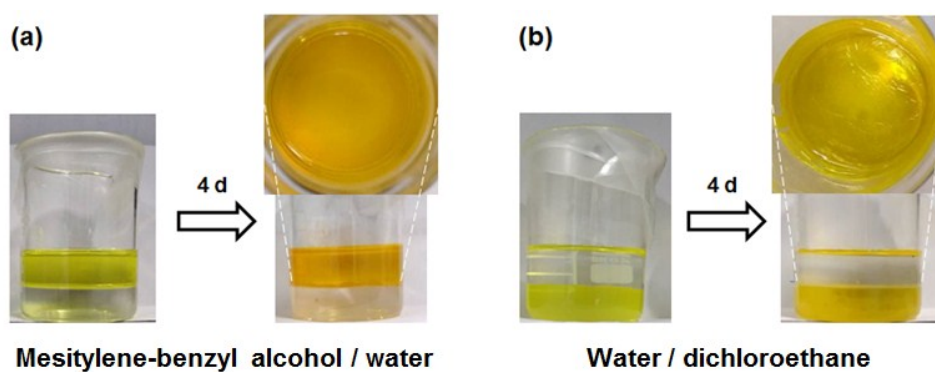


Figure S8 The digital images of the interfacial synthesis for Py-COF films prepared in different solvents.

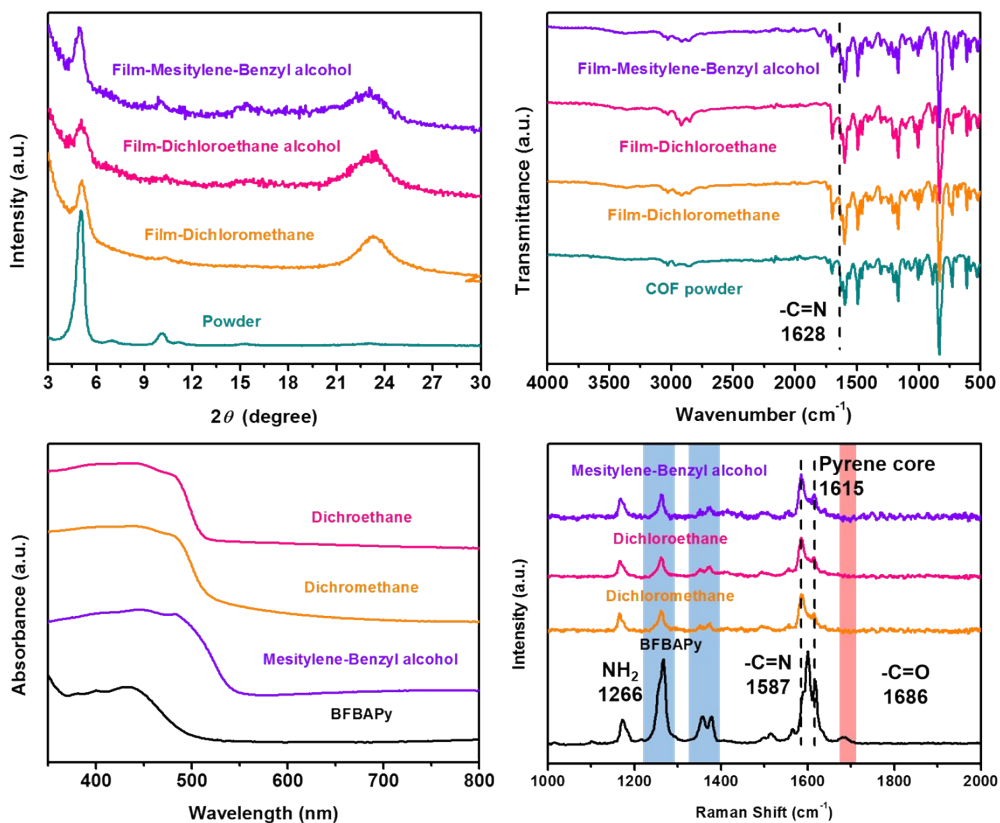


Figure S9 (a) XRD patterns, (b) FT-IR, (c) UV-vis and (d) Raman spectra of Py-COF films prepared in different solvents.

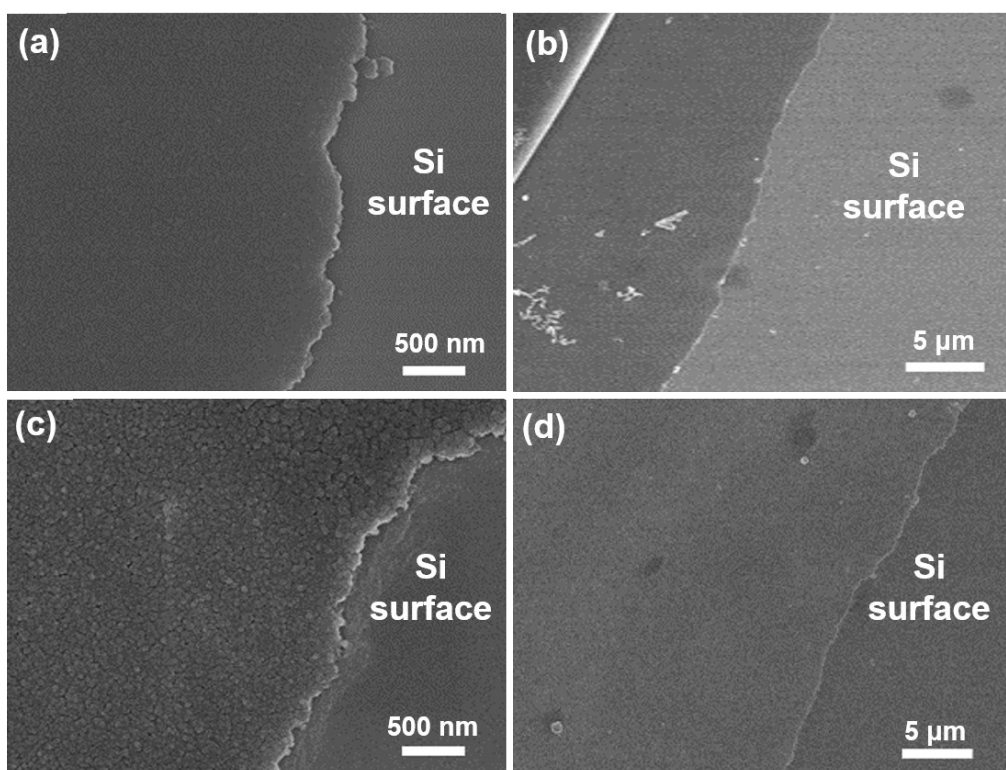


Figure S10 SEM images of Py-COF films prepared at (a), (b) mesitylene-benzyl alcohol mixed solvent/water and (c), (d) dichloroethane/water interfaces.

Section 7. Raman Spectra and AFM Image of Py-COF Thin Film Obtained at The Air/Water Interface

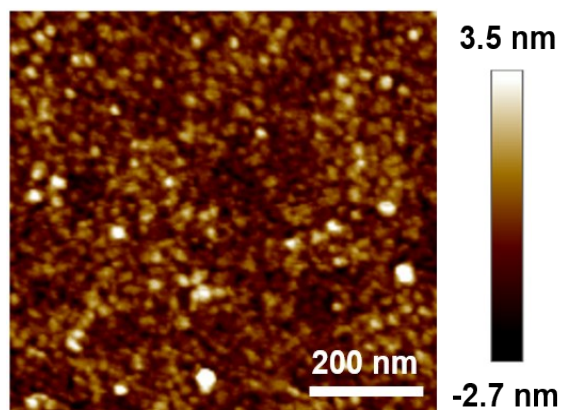


Figure S11 AFM image of Py-COF thin film grown at the air/water interface.

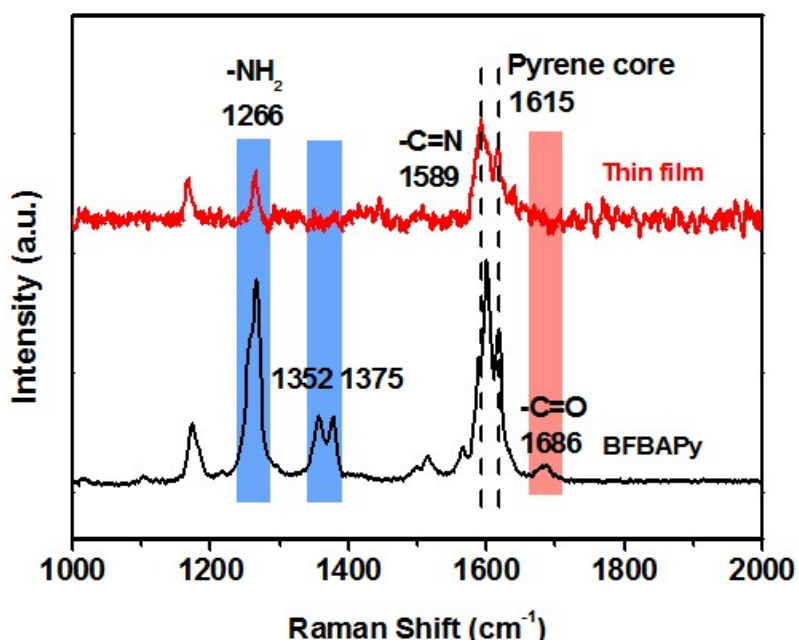


Figure S12 Raman spectra of Py-COF thin film grown at the air/water interface.

Section 8. Py-COF Thin Films Obtained from Liquid/Liquid Interface for Protonation-Acid Sensing^{S5}

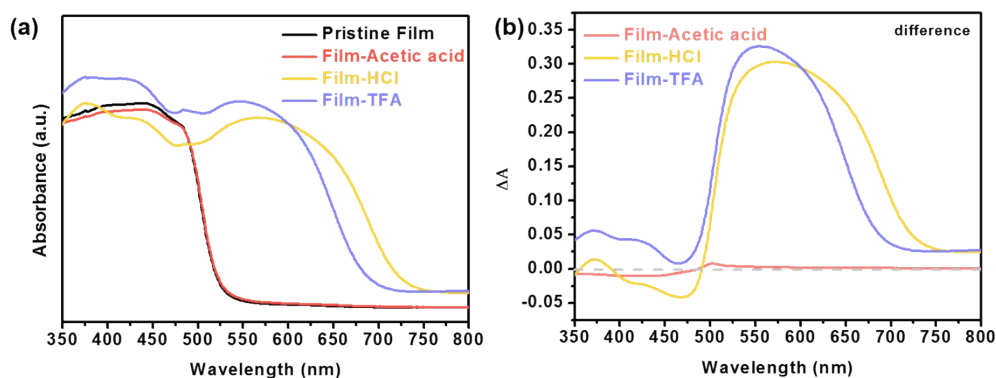


Figure S13 (a) UV-vis spectra of the Py-COF films exposed by various acid vapors and (b) the corresponding absorption difference between the protonated and the non-protonated states.

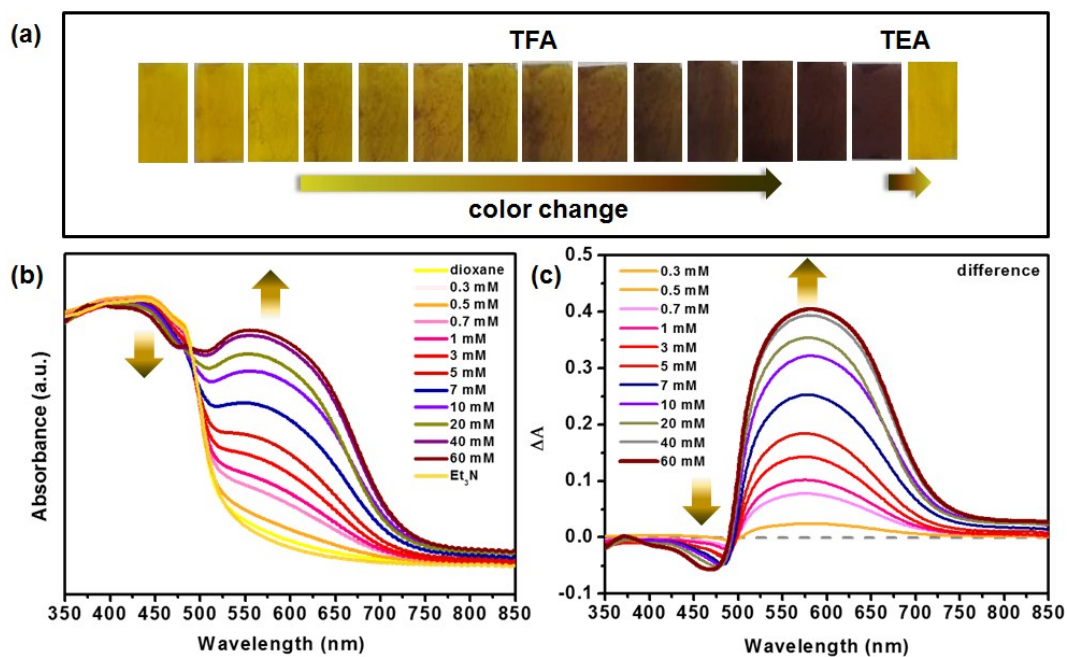


Figure S14 (a) Digital images of pristine, protonated and deprotonated Py-COF films, (b) UV-vis spectra of the Py-COF films in a series of trifluoroacetic acid solutions and (c) the corresponding absorption difference between the protonated and the non-protonated states.

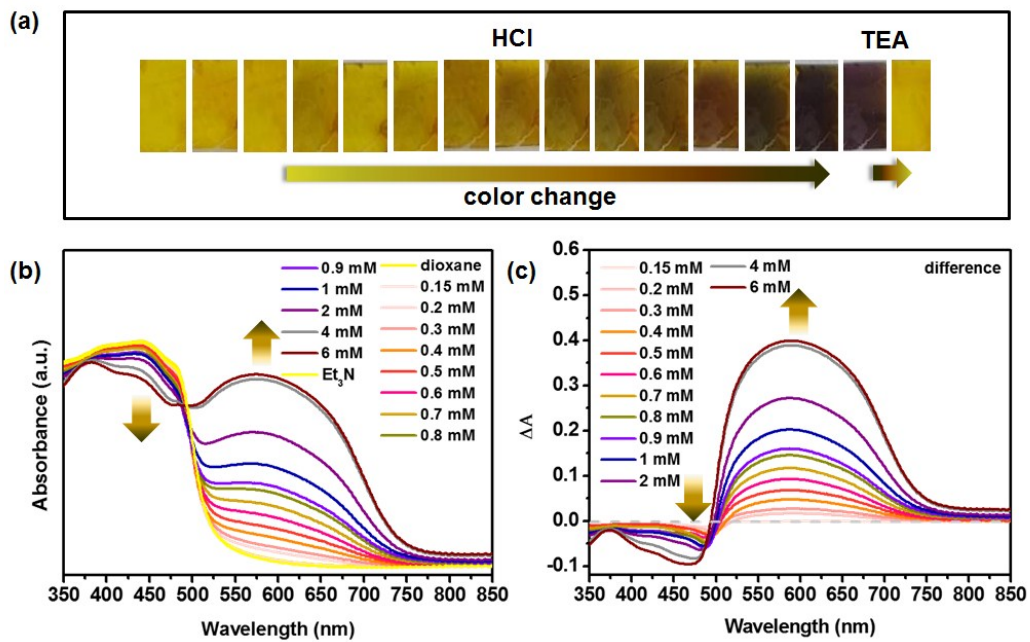


Figure S15 (a) Digital images of pristine, protonated and deprotonated Py-COF films, (b) UV-vis spectra of the Py-COF films in a series of hydrochloric acid solutions and (c) the corresponding absorption difference between the protonated and the non-protonated states.

Section 9. Stability and Recyclable of Py-COF Films for Sensing

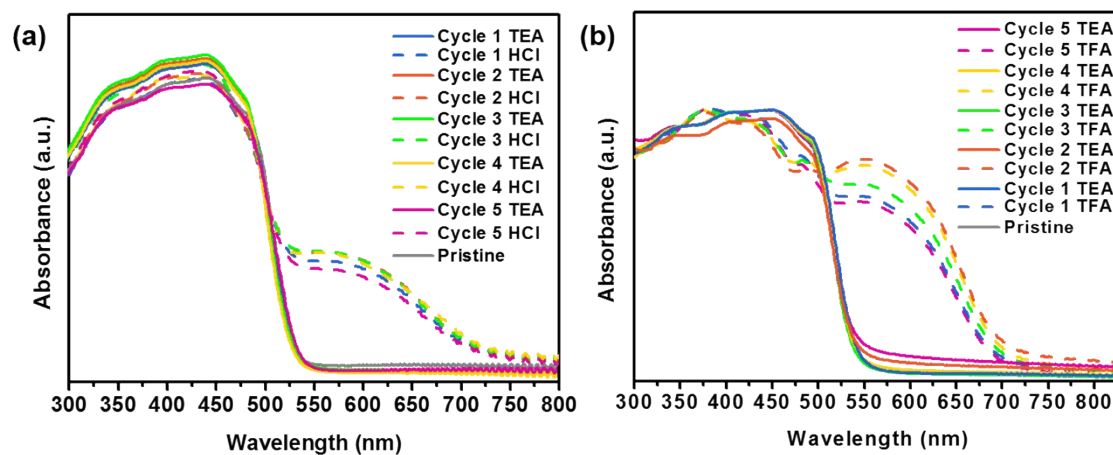


Figure S16 UV-vis spectra of protonated Py-COF thin films by different acid vapours.

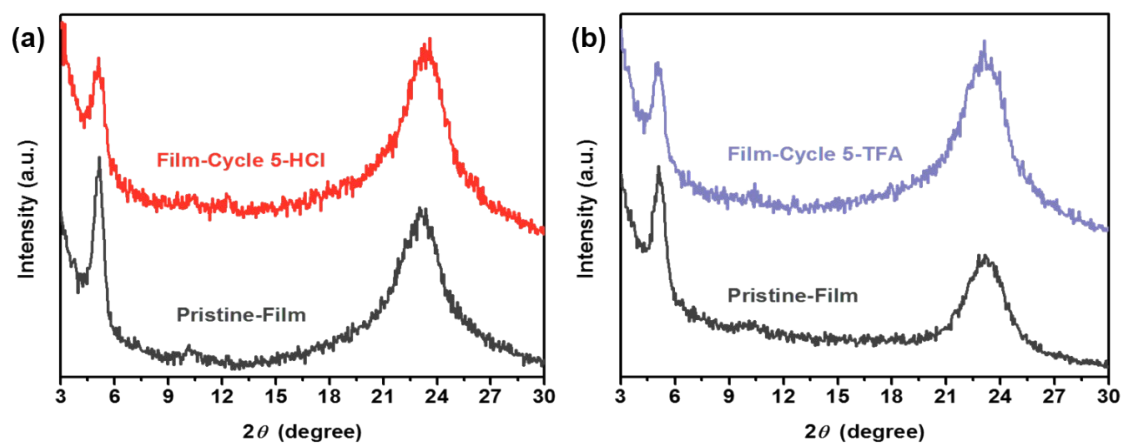


Figure S17 XRD patterns of (a) pristine and (b) treated Py-COF films by HCl, TFA vapour and restored by TEA solution after 5 cycles.

Section 10. Supporting References

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