Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A π-electronic covalent organic framework catalyst: π-walls as catalytic beds for Diels-Alder reactions under ambient conditions

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Section A. Materials and Method

All the solvents were purchased from Kanto Chemicals. 9-Hydroxymethylanthracene, *N*-substituted maleimide derivatives, pyrene, tin, bromine, potassium carbonate, sodium borohydride, tetrakis(triphenylphosphine)-palladium(0), 2,6-diaminoanthraquinone, and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde were purchased from TCI. TFPPy and DAAn monomers were synthesized according to the previous literatures.[S1,S2]

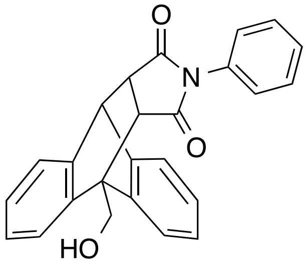
Py-An COF. A 10-mL pyrex tube was charged with TFPPy (15.0 mg, 0.024 mmol), DAAn (10 mg, 0.048 mmol), *o*-DCB/n-BuOH (0.5 mL, 1/1 by vol.) and 0.1 mL AcOH (6 M) and the mixture was sonicated for 2 minutes, degassed via three freeze–pump–thaw cycles, sealed under vacuum, and heated at 120 °C for 5 days. The reaction mixture was cooled to room temperature and the fluffy orange precipitate was collected by centrifugation. The solid was washed with DMF (2 mL × 3) and THF(2 mL × 5), and then dried under vacuum at 120 °C overnight. The yield is 88%. Elemental analysis Calc. for $(C_{72}H_{42}N_4)_n$: H, 4.40; C, 89.69; N, 5.82. Found for as-synthesized COF: H, 4.76; C, 81.63; N, 4.35. Found for the COF after 4th cycle use: H, 4.65; C, 83.14; N, 3.09.

Catalytic Diels-Alder Reactions. A mixture of 9-hydroxymethylanthracene (0.05 mmol), *N*-substituted maleimide derivative (0.05 mmol), Py-An COF (10 mol%), and ethanol (3 mL) in a tube was stirred at room temperature, 1 bar. After the reaction completed, the Py-An COF solid was removed using filtration, the reaction mixture was concentrated under vacuum and then subjected to ^1H NMR spectroscopy using $CDCl_3$ as solvent. The yield was calculated from the integrated proton ratio of the product and the unreacted 9-hydroxymethylanthracene.

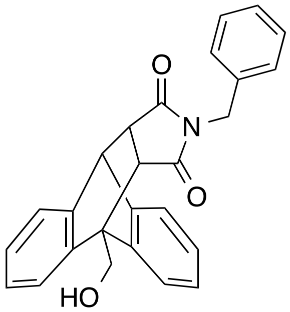
Cycle performance test. After the reaction completed, the COF sample was collected via centrifuge, washed with acetone (2 mL × 3), and dried under vacuum; the COF sample was then reused for the next-round reaction under ambient conditions.

Control experiments for the Diels-Alder reactions. A mixture of 9-hydroxymethylanthracene (0.05 mmol), *N*-substituted maleimide derivative (0.05 mmol), and ethanol (3 mL) in a tube was stirred at room temperature, 1 bar. After the reaction completed, the reaction mixture was concentrated under vacuum and then subjected to ^1H

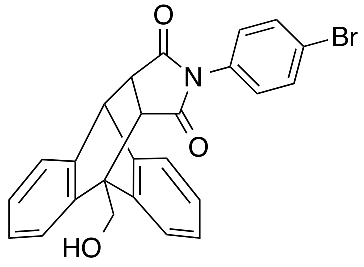
NMR spectroscopy using $CDCl_3$ as solvent. The yield was calculated from the integrated proton ratio of the product and the unreacted 9-hydroxymethylanthracene. The products were purified by preparative TLC using silica gel as stationary phase and hexane/CH_2Cl_2 mixture was used as eluent.



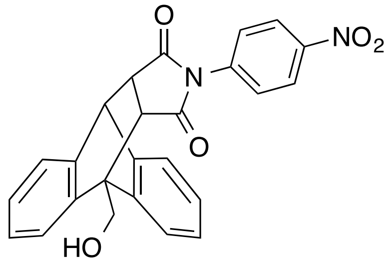
Isolated yield 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.64 (d, 1H), 7.43 (d, 1H), 7.37 (dd, 1H), 7.30-7.21(m, 9H), 6.50 (dd, 2H), 5.17 (dd, 1H), 5.00 (dd, 1H), 4.86 (d, 1H), 3.56 (d, 1H), 3.47 (dd, 1H), 2.78 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 176.51, 176.48, 142.30, 139.75, 139.37, 131.67, 129.56, 129.30, 127.54, 127.51, 127.20, 127.14, 126.84, 125.88, 124.62, 123.84, 122.84, 60.71, 50.23, 48.40, 46.71, 46.35. MALDI-TOF MS for $C_{25}H_{19}NO_3$ (Calc. 381.14), found m/z = 381.05 ($[M]^+$).



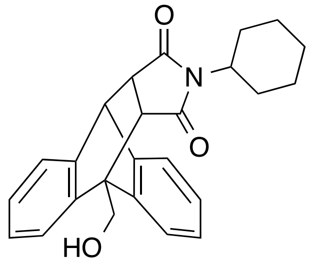
Isolated yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.55 (d, 1H), 7.36 (m, 1H), 7.24-7.13 (m, 7H), 7.09 (m, 2H), 6.61 (d, 2H), 5.11 (m, 1H), 4.95 (m, 1H), 4.74(d,1H), 4.31 (s, 2H), 3.37 (d, 1H), 3.33 (m, 1H), 2.69 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 177.16, 176.90, 142.70, 139.62, 139.30, 135.16, 128.87, 127.83, 127.74, 127.44, 127.06, 126.97, 125.62, 124.48, 123.54, 122.83, 61.01, 49.72, 48.29, 46.70, 45.86, 42.54. MALDI-TOF MS for $C_{26}H_{21}NO_3$ (Calc. 395.15), found m/z = 395.08 ($[M]^+$).



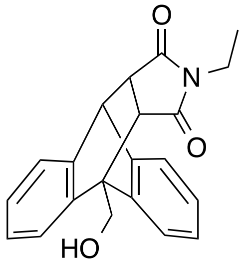
Isolated yield 80%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.65 (d, 1H), 7.43 (m, 3H), 7.35 (m, 1H), 7.28- 7.19 (m, 5H), 6.42 (d, 2H), 5.14 (q, 1H), 5.01 (q, 1H), 4.84 (d, 1H), 3.52 (d, 1H), 3.45 (m, 1H), 2.61 (br, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 175.82, 175.79, 141.82, 139.34, 139.04, 132.42, 130.29, 128.04, 127.21, 127.16, 126.92, 126.82, 125.51, 124.26, 123.64, 122.93, 122.40, 60.13, 49.91, 48.03, 46.15, 46.05. MALDI-TOF MS for $C_{25}H_{18}BrNO_3$ (Calc. 459.05), found m/z = 458.87 ([M]$^+$).



Isolated yield 47%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.16 (d, 2H), 7.68 (d, 1H), 7.43 (m, 1H), 7.26(m, 1H), 7.28- 7.20 (m, 5H), 6.81 (d, 2H), 5.17 (d, 1H), 5.03 (d, 1H), 4.86 (d, 1H), 3.58 (d, 1H), 3.50 (m, 1H), 2.56 (br, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 175.34, 175.23, 147.34, 141.59, 139.22, 138.95, 136.79, 127.33, 127.28, 127.17, 127.01, 126.91, 125.51, 124.42, 124.30, 123.71, 122.33, 59.98, 50.00, 48.09, 46.13, 46.09. MALDI-TOF MS for $C_{25}H_{18}N_2O_5$ (Calc. 426.12), found m/z = 426.05 ([M]$^+$).



Isolated yield 59%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.58 (d, 1H), 7.38 (d, 1H), 7.29 (d, 1H), 7.26 (d, 1H), 7.23 (dd, 1H), 7.17 (dd, 1H), 7.14 (m, 2H), 5.14 (dd, 1H), 4.97 (dd, 1H), 4.72 (d, 1H), 3.52 (m, 1H), 3.26 (d, 1H), 3.20 (dd, 1H), 2.77 (br, 1H), 1.68 (q, 2H), 1.64 (d, 2H), 1.58 (s, 1H), 1.07 (m, 3H), 0.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 177.69, 177.43, 142.61, 139.77, 139.42, 127.26, 127.05, 126.99, 125.77, 124.51, 123.62, 122.89, 60.97, 51.86, 49.95, 47.85, 46.26, 28.50, 28.45, 26.12, 25.36. MALDI-TOF MS for $C_{25}H_{25}NO_3$ (Calc. 387.18), found m/z = 387.03 ($[M]^+$).



Isolated yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.62 (d, 1H), 7.40 (d, 1H), 7.33-7.12 (m, 6H), 5.16 (d, 1H), 4.99 (d, 1H), 4.76 (d, 1H), 3.35 (m, 1H), 3.26 (m, 1H), 3.16 (q, 2H), 0.41 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 176.78, 176.61, 142.08, 142.01, 139.22, 138.87, 126.81, 126.77, 126.61, 126.53, 125.27, 124.01, 123.20, 122.40, 60.52, 49.37, 47.69, 46.14, 45.69, 33.16, 12.01. MALDI-TOF MS for $C_{21}H_{19}NO_3$ (Calc. 333.14), found m/z = 332.95 ($[M]^+$).

Fourier transform infrared (FT IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. Electronic absorption spectrum was recorded on a JASCO model V-670 spectrometer. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The sample was prepared by drop-casting a supersonicated THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. The sample was prepared by drop-casting a supersonicated THF suspension of the COFs onto a copper grid. X-ray diffraction (XRD) 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. Elemental analysis was performed on a Yanako CHN CORDER MT-6 elemental analyzer. TGA measurements were performed on a Mettler-Toledo model TGA/SDTA851^e under N_2, by heating to 1000 °C at a rate of 10 °C min^{-1}. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode.

Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Instrument Corporation model 3Flex surface characterization analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve.

The crystalline structure of COF 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.[S3] 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 p-stacking interactions. The lattice dimensions were optimized simultaneously with the geometry. Standard DFTB parameters for X–Y element pair (X, Y = C, O, H and N) interactions were employed from the mio-0-1 set.[S4]

9-Hydroxymethylanthracene adsorption experiment. An ethanol solution of 9-hydroxymethylanthracene (2 mL, 0.1 mM) in a capped cuvette (path length = 10 mm) was added with Py-An COF (10 mg). Time-dependent electronic absorption spectroscopy was used to monitor the spectral change of the solution (Figure S7).The concentration of 9-hydroxymethylanthracene in solution is defined by the equation, $c_{\mathrm{EtOH}} = c_0 I_t / I_0$, whereas c_0 is the initial concentration of 9-hydroxymethylanthracene in EtOH, I_t is the intensity of UV absorption spectra at 364nm at t hours after adding Py-An COF and I_0 is the initial intensity of UV absorption spectra at 364nm. By using the conditions of $c_0 = 0.1$ mM, $I_{4h} = 0.59$ and $I_0 = 0.70$, c_{EtOH} was evaluated to be 0.08 mM. On the other hand, the concentration of

9-hydroxymethylanthracene in the pores of COFs is defined by the equation, $c_{\mathrm{COF}} = c_0V_0(I_0\text{-}I_t)/(I_0V_gm_{\mathrm{COF}})$, whereas V_0 is the volume of EtOH, V_g is the pore volume of Py-An COF, m_{COF} is the mass of Py-An COF. By using the parameters of $V_0 = 2$ cm^3, $V_g = 0.7$ cm^{3}g^{-1}, $m_{\mathrm{COF}} = 10$ mg, the c_{COF} value was evaluated to be 4.5 mM, which resulted in a ratio of $c_{\mathrm{COF}}/c_{\mathrm{EtOH}}$ to be 56.

Section B. Supporting Tables

Table S1. Cycle performance of the Py-An COF at 25 °C, 1 bar

Cycle	Yield (%)	Reaction time (h)	XRD intensity of the COF at 3.14º (counts)	Recovery of COF (wt %)
0	> 99	6	20,838	97%
1	> 99	6	21,845	96%
2	> 99	6	20,401	98%
3	> 99	6	19,003	97%

Section C. Supporting Figures

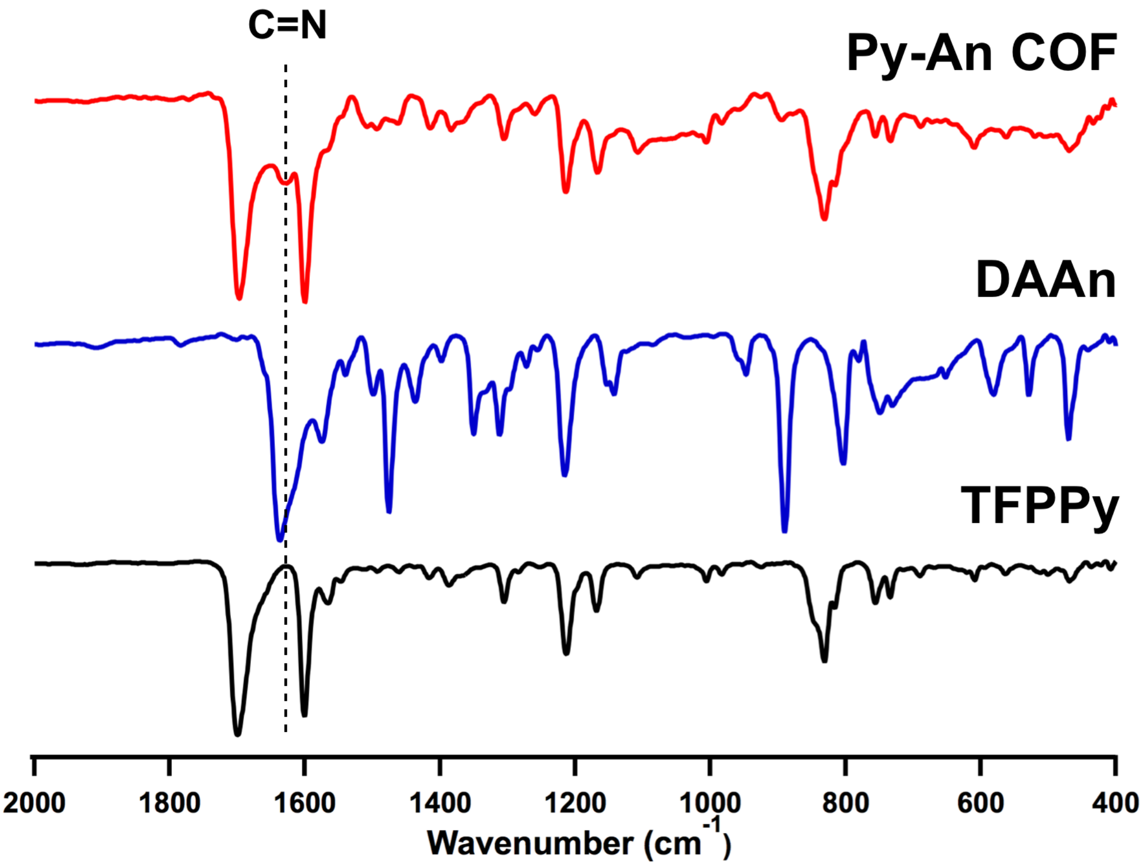


Figure S1. FT IR spectra of TFPPy (black), DAAn (blue), and Py-An COF (red).

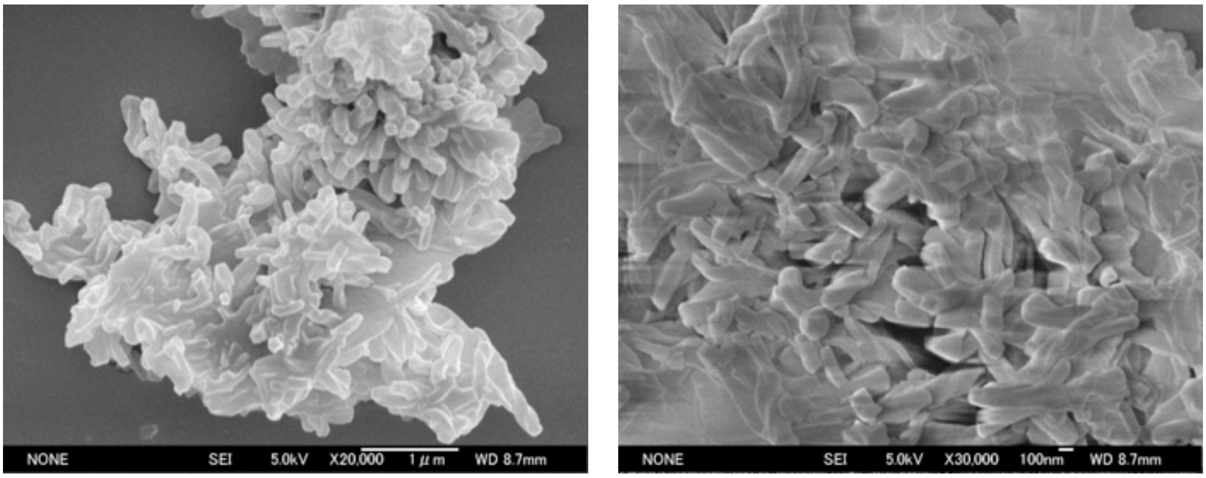


Figure S2. FE SEM images of the Py-An COF.

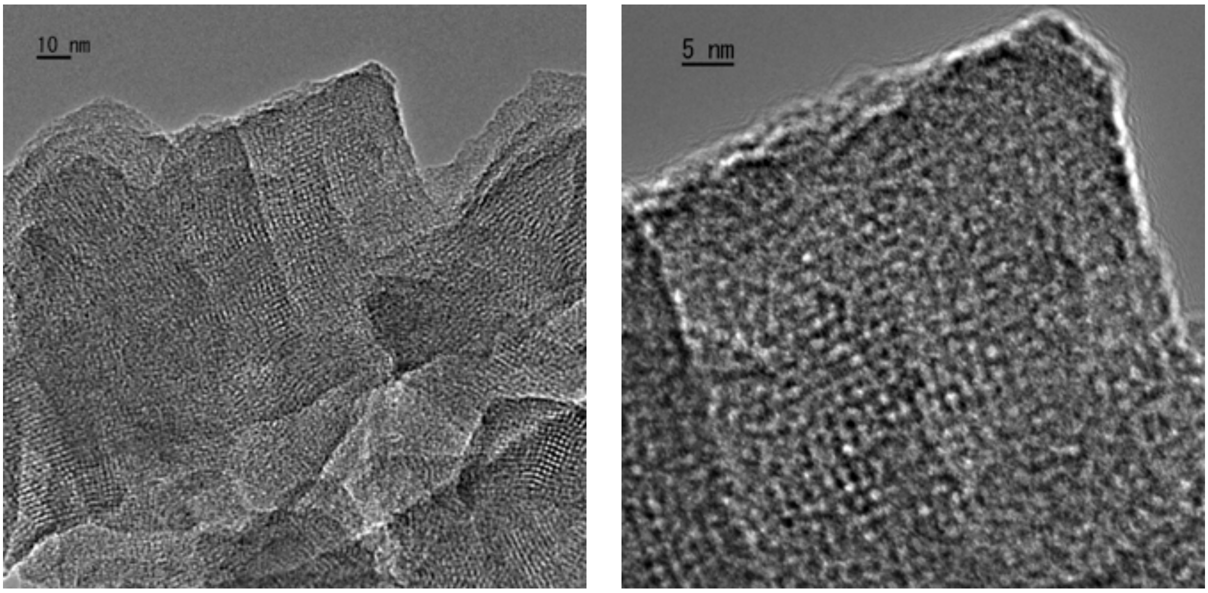


Figure S3. HR TEM images of the Py-An COF.

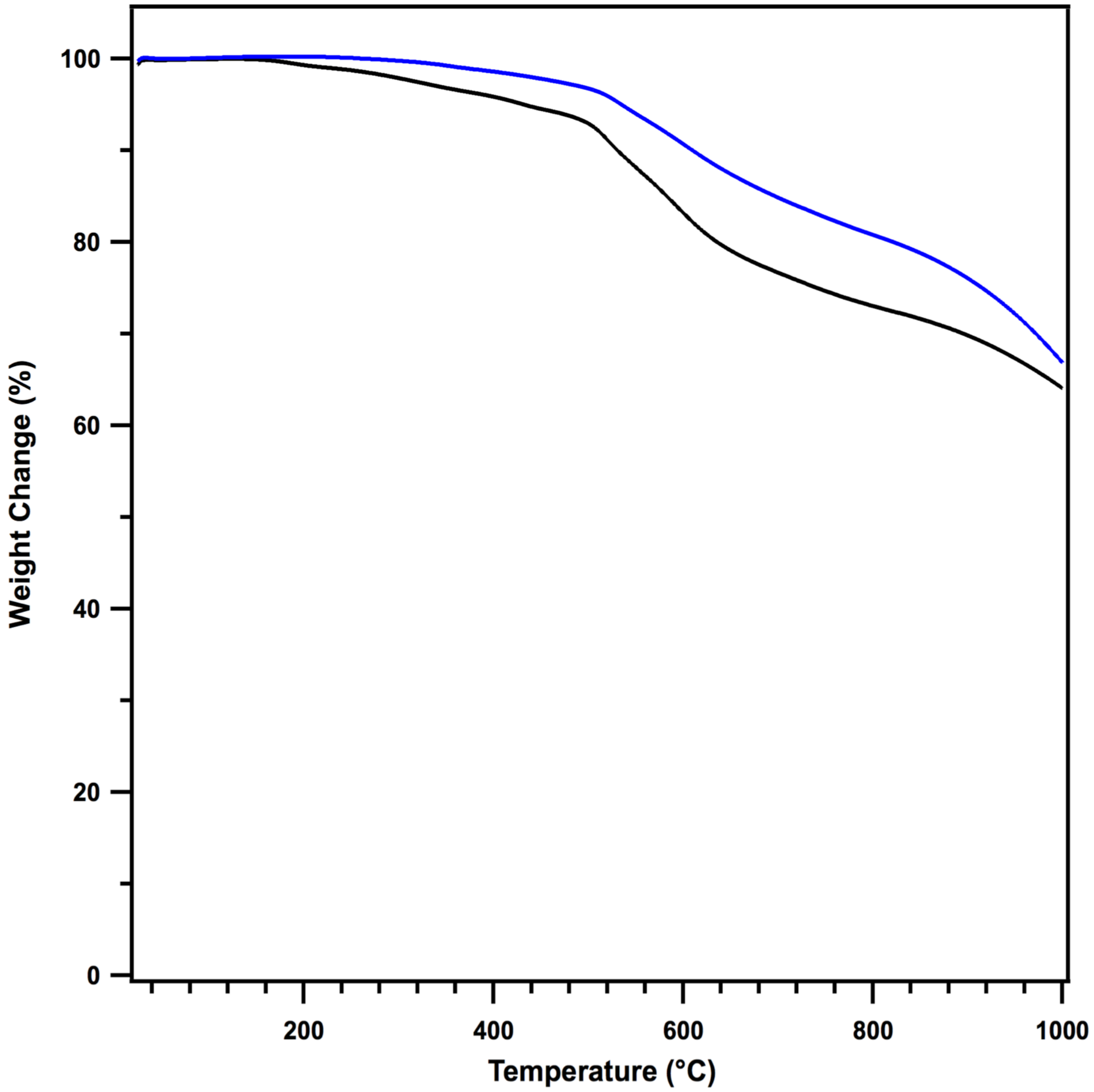


Figure S4. TGA curves of the Py-An COF samples (black: as synthesized, blue: after 4th cycle use as catalyst).

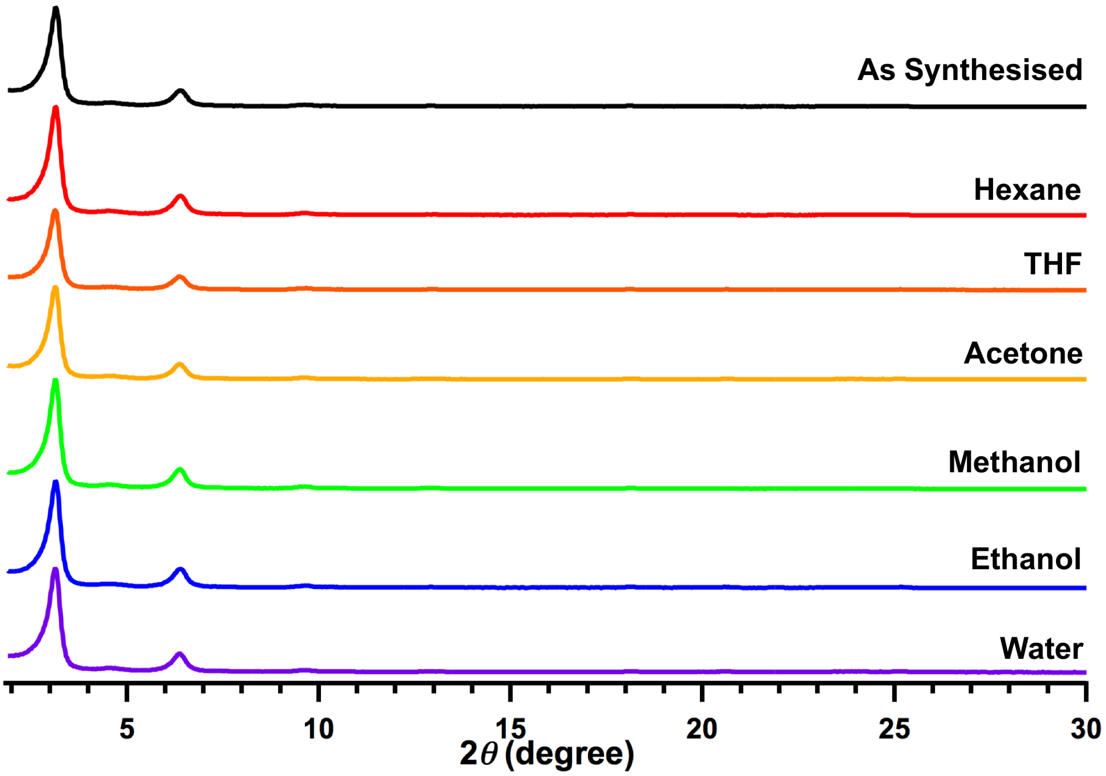


Figure S5. XRD patterns of the Py-An COF upon 1-day treatment in different solvents.

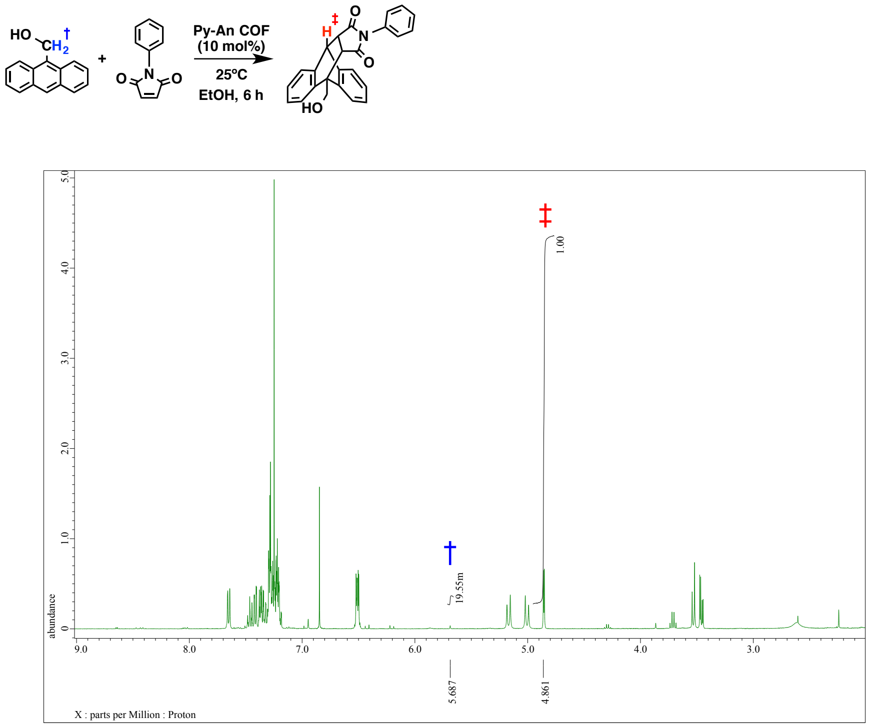


Figure S6A. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-phenylmaleimide catalysed by the Py-An COF.

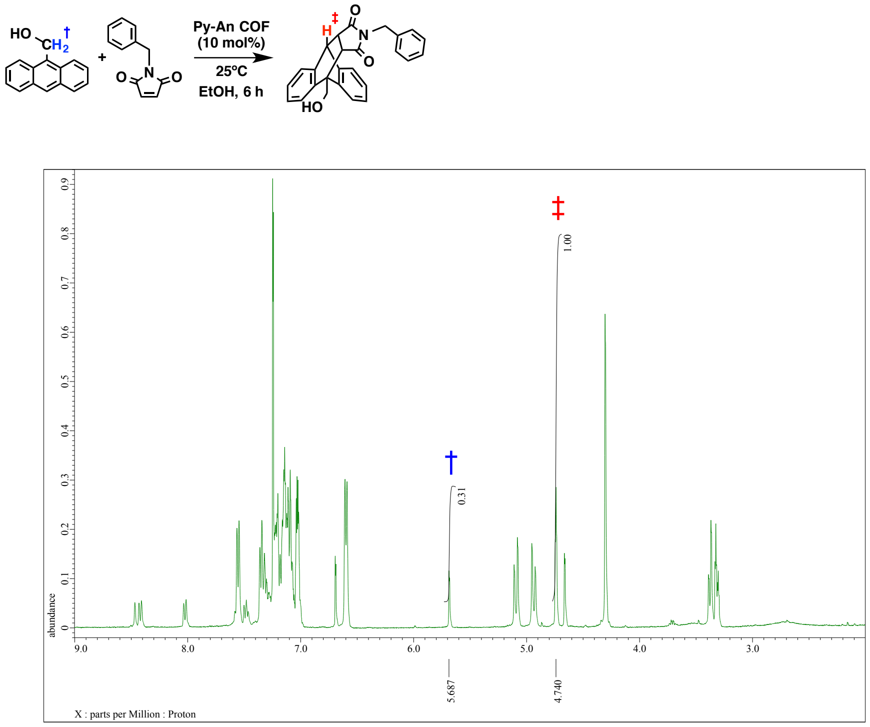


Figure S6B. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-benzylmaleimide catalysed by the Py-An COF.

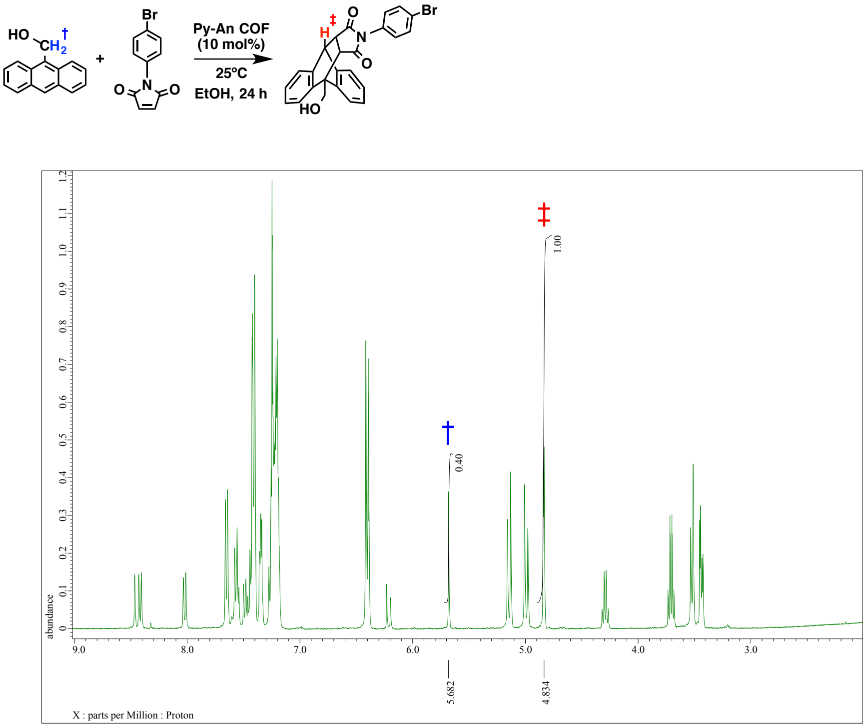


Figure S6C. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-(p-boromo)phenylmaleimide catalysed by the Py-An COF.

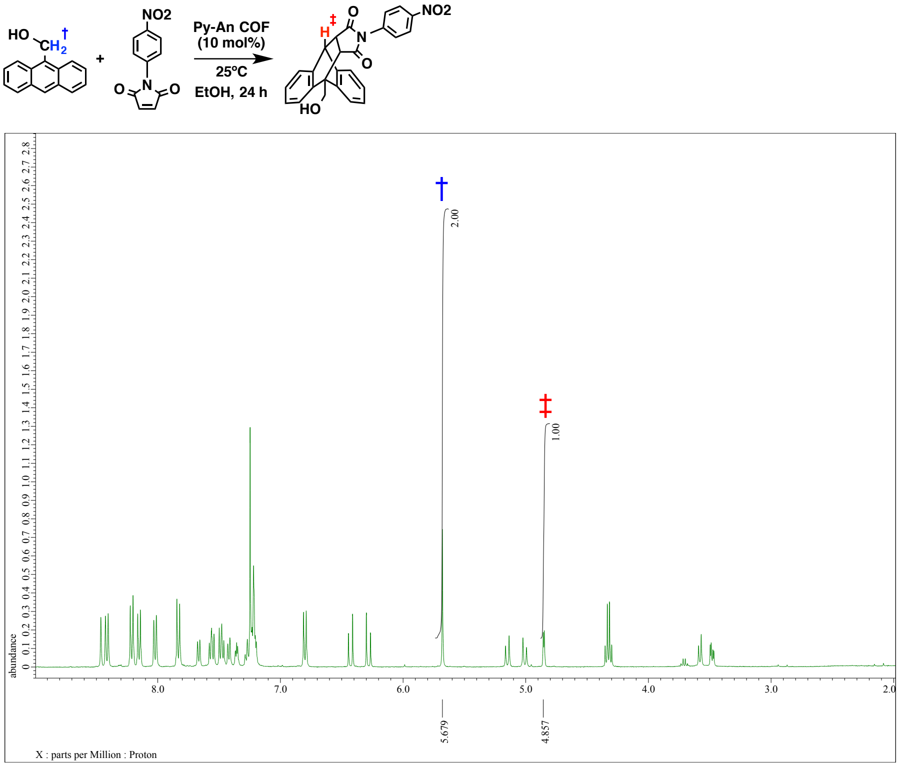


Figure S6D. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-(p-nitro)phenylmaleimid catalysed by the Py-An COF.

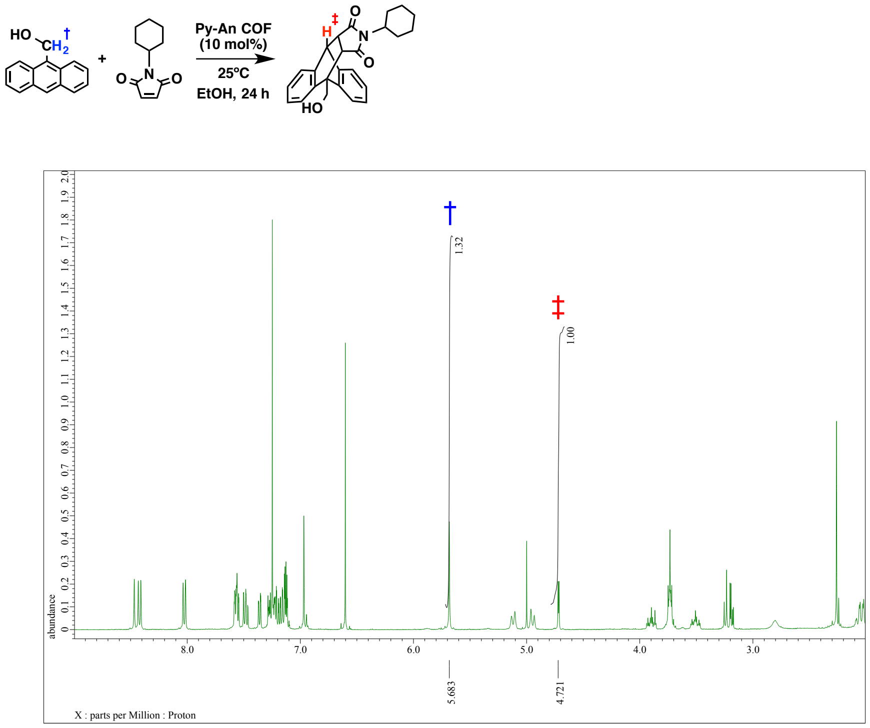


Figure S6E. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-cyclohexylmaleimide catalysed by the Py-An COF.

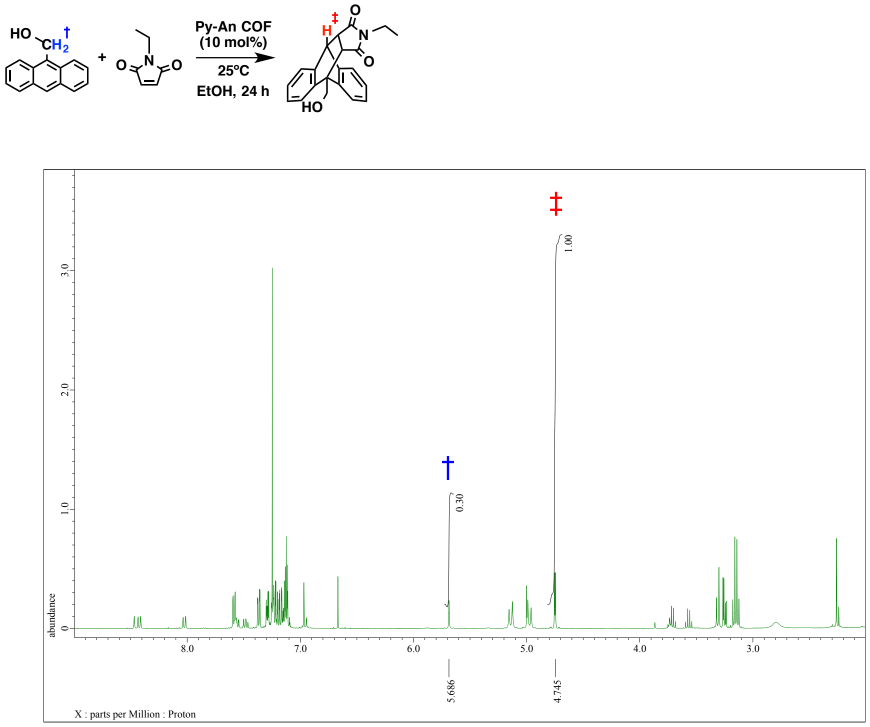


Figure S6F. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-ethylmaleimide catalysed by the Py-An COF.

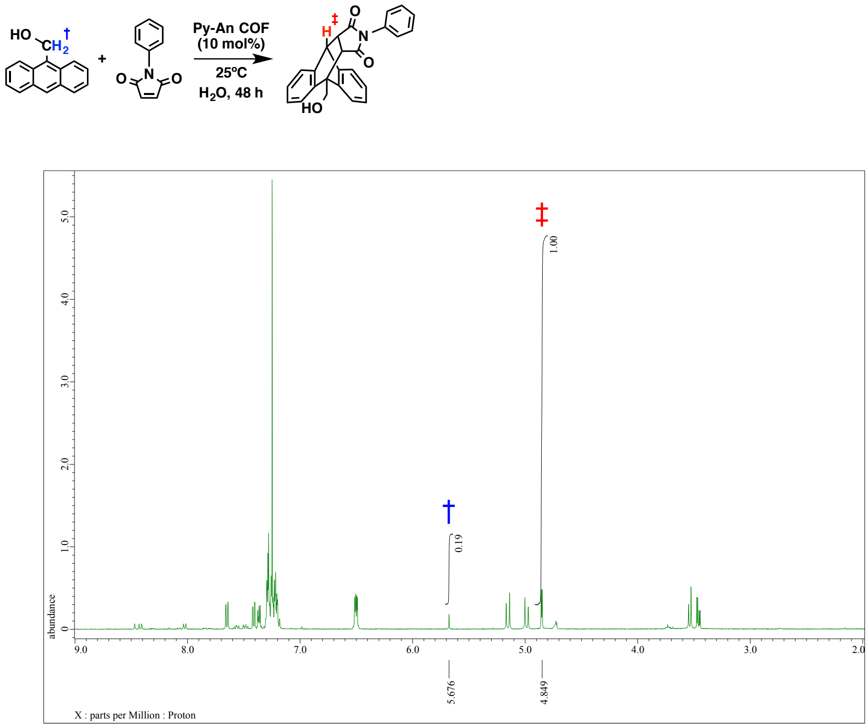


Figure S6G. The ^{1}H NMR spectrum of the reaction of 9-hydroxymethylanthrancene and *N*-phenylmaleimide catalysed by the Py-An COF.

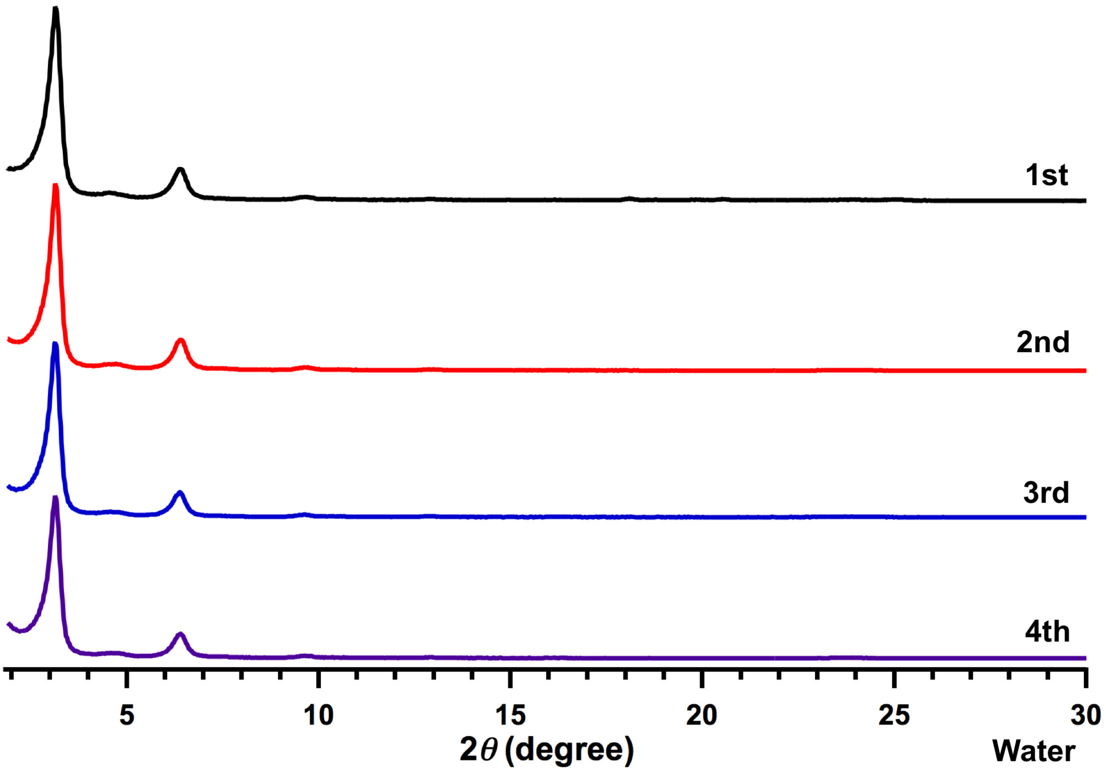


Figure S7. XRD patterns of the Py-An COF upon cycle use.

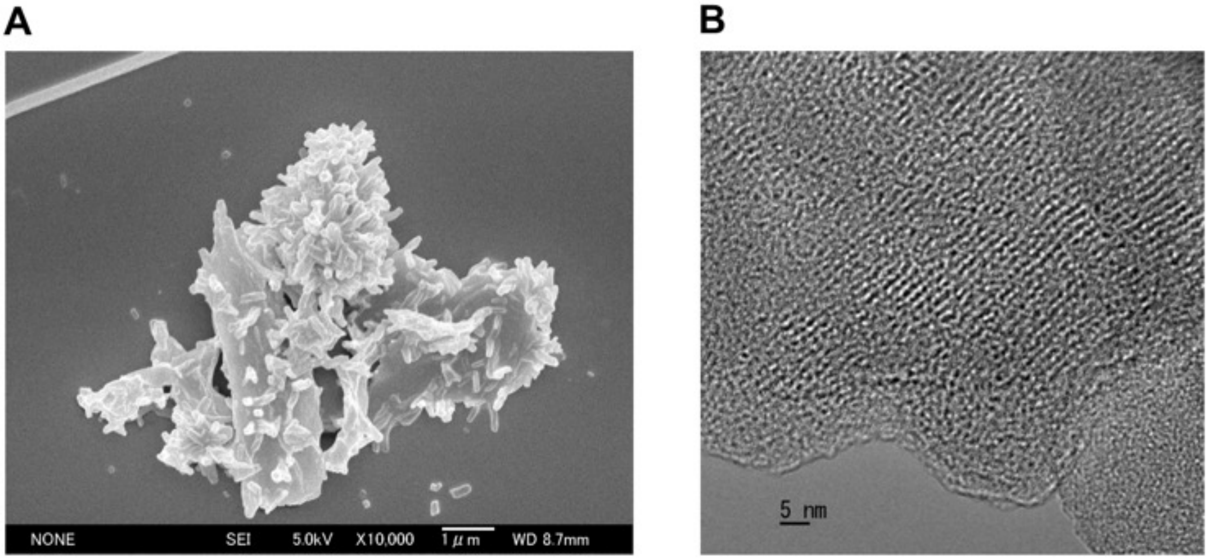


Figure S8. A) FE-SEM and B) HR TEM images of the Py-An COF upon catalytic use.

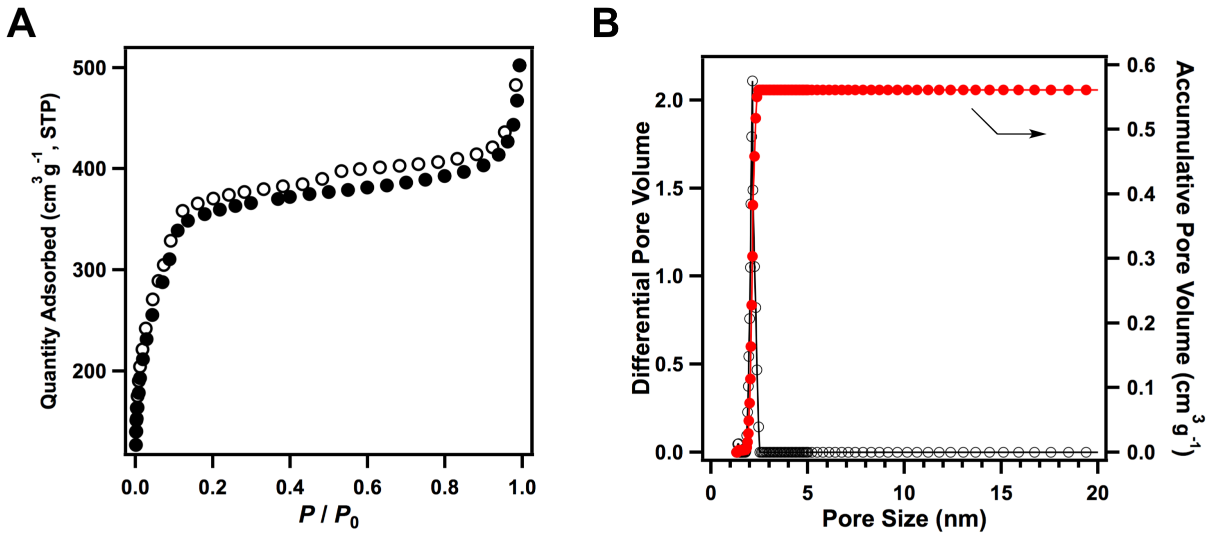


Figure S9. Porosity of the Py-An COF after 4th cycle use. A) Nitrogen sorption isotherm curves measured at 77 K (red circle: desorption, blue circle: adsorption). (B) Pores size (red circle) and pore size distribution (blue circle) profiles.

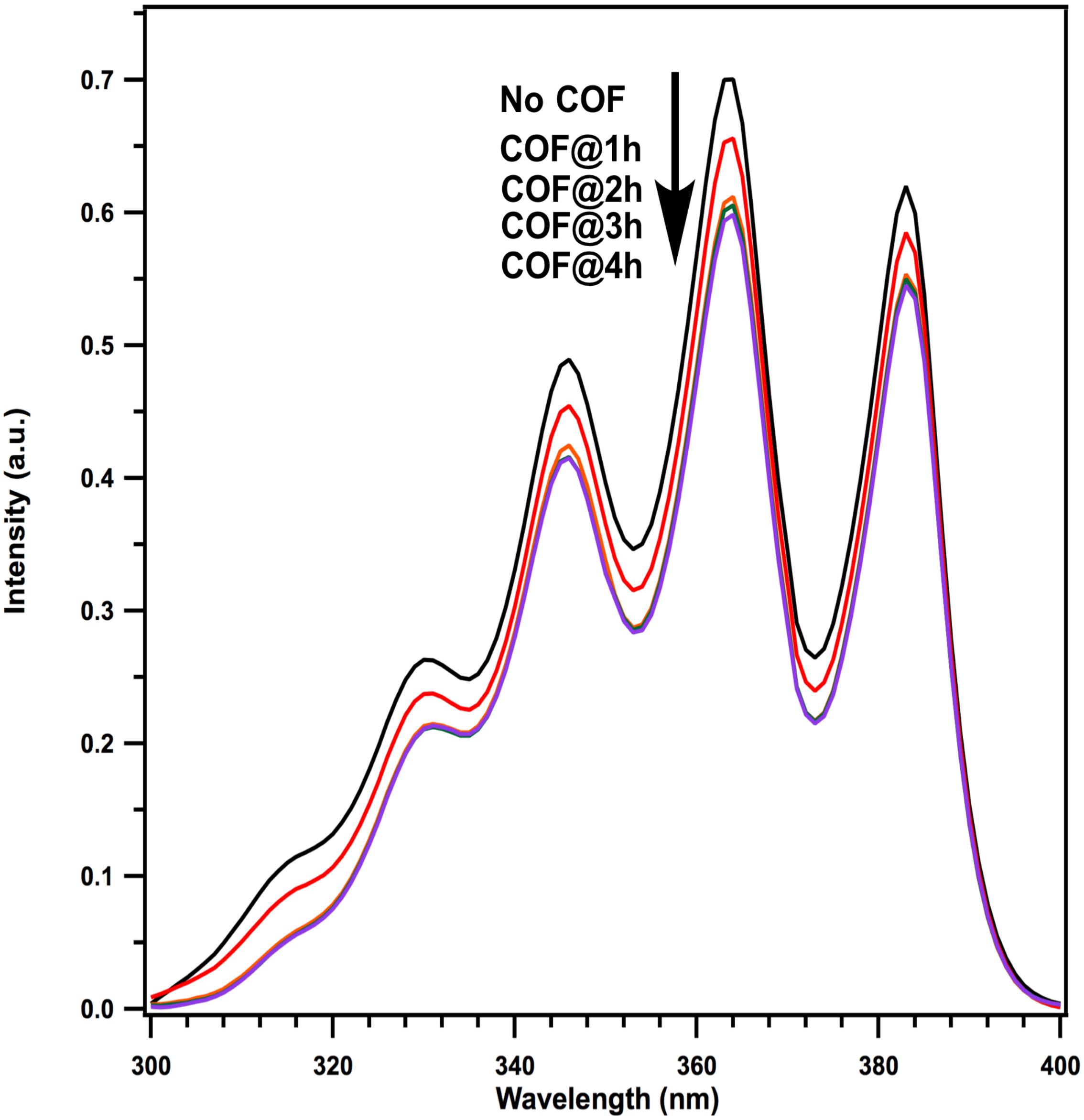


Figure S10. Time-dependent electronic absorption spectral change of ethanol solution of 9-hydroxymethylanthracene (0.1 mM) upon addition of the Py-An COF (10 mg).

Section D. Supporting References

S1. M. G. Rabbani, A. K. Sekizkardes, Z. Kahveci, T. E. Reich, R. Ding and H. M. El-Kaderi, *Chem. Eur. J.* 2013, **19**, 3324.

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S4. B. Lukose, A. Kuc and T. Heine, T. *J. Mol. Model.* 2013, **19**, 2143.