

Electronic Supplementary Information

Trifluoromethyl-grafted ultra-stable fluorescent covalent organic framework for adsorption and detection of pesticides

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1. Characterization methods and instruments

Nitrogen adsorption isotherms of TPB-DMTP-COF, COF-Ph, and COF-(CF₃)₂ were measured with Micromeritics ASAP 2460 automated sorption analyzer, and all samples were degassed at 100 °C for 10 hours before the test. Powder X-ray diffraction analysis of TPB-DMTP-COF, COF-Ph, and COF-(CF₃)₂ were performed on Bruker AXS D8 Advance Labx diffractometer at 40 kV and 30 mA using Cu K α radiation over a 2 θ range of 4-40° at room temperature. Transmission electron microscopy analysis of COF-Ph, and COF-(CF₃)₂ were performed on a Tecnai G2 20 S-TWIN microscope. X-ray photoelectron spectroscopy analysis of COF-(CF₃)₂ was performed on Kratos AXIS SUPRA electron spectrometer. Fluorescence emission spectroscopy measurements of COF-(CF₃)₂ was recorded upon excitation at 440 nm by Hitachi F-7000 spectrometer.

2. Synthetic Procedures

Synthesis of TPB-DMTP-COF

An o-dichlorobenzene (o-DCB)/n-BuOH (0.5/0.5 ml) mixture of 1,3,5-tri-(4-aminophenyl)benzene (TAPB) (0.080 mmol, 28.1 mg) and DMTA (0.120 mmol, 23.3 mg) in the presence of an acetic-acid catalyst (6 M, 0.1 ml) in a Pyrex tube (10 ml) was degassed via three freeze–pump–thaw cycles. The tube was flame sealed and heated at 120 °C for three days. The precipitate was collected via centrifugation, washed six times with THF and then subjected to Soxhlet extraction with THF as the solvent for one day to remove the trapped guest molecules. The powder was collected and dried at 120 °C under vacuum overnight to produce TPB-DMTP-COF in an isolated yield of 81%.^{1,2}

Synthesis of COF-Ph in the Pyrex tube

COFs (4 mg), phenylacetylene (6 μL , 0.05 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (4 μL , 0.03 mmol), chloranil (8 mg, 0.03 mmol), and 2 mL of toluene were added to a Pyrex tube. The vial was sealed and heated under N_2 at 110 $^\circ\text{C}$. After 3 days, the mixture was cooled to room temperature and the precipitate was isolated via centrifugation. The reaction mixture was then washed with THF and quenched with saturated aqueous sodium bicarbonate (2 mL \times 3). Subsequently, the solids were washed with THF using a Soxhlet extractor for 12 h and dried under vacuum.^{2,3}

3. The relative calculation formula

The adsorption capacity of pesticide was calculated according to the following equation.

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where q_e (mg g^{-1}) is the sorption amount at equilibrium, C_0 (mg L^{-1}) and C_e (mg L^{-1}) represent the concentrations of pesticides at initial state and sorption equilibrium, respectively; V (L) and m (g) are the volume of solution and the weight of COFs, respectively.

The pseudo-second-order and pseudo-first-order models were analyzed by the following equations.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) represent the adsorbed pesticides amounts of COFs at the contact time t and sorption equilibrium, respectively. k_2 (g (mg min)^{-1}) and k_1 (min^{-1}) represent the corresponding rate constants.⁴

Table S1. Porosity data of COF-Ph prepared in the Pyrex tube from literature and this work.

Materials	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{Langmuir}}^{\text{b}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{c}}$ ($\text{m}^3 \text{g}^{-1}$)	$D_{\text{pore}}^{\text{d}}$ (nm)
COF-Ph (literature)	955 ^e	-	-	2.6 ^e
COF-Ph (this work)	1758	2217	0.6	2.8

^a Specific surface area calculated according to BET theory. ^b Specific surface area calculated by Langmuir theoretical model. ^c Total pore volume at $P/P_0=0.99$. ^d Data calculated with the NLDFT method. ^e data obtained from reference 2.

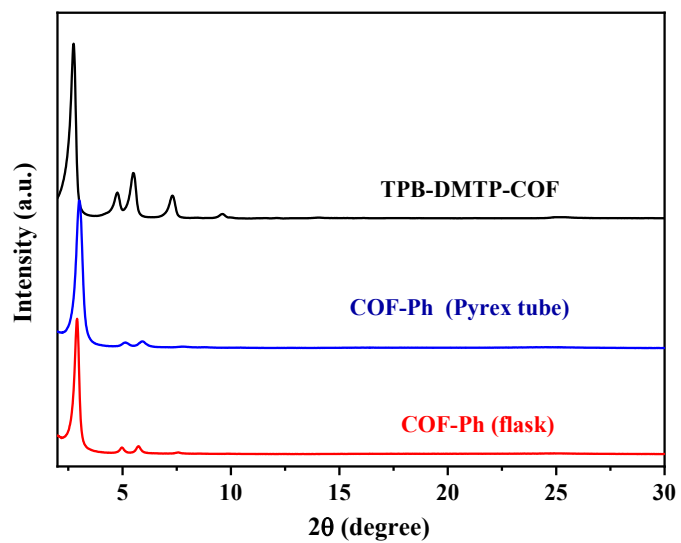


Figure S1. Powder X-ray diffraction (PXRD) pattern of original TPB-DMTP-COF and COF-Ph prepared in the flask and Pyrex tube.

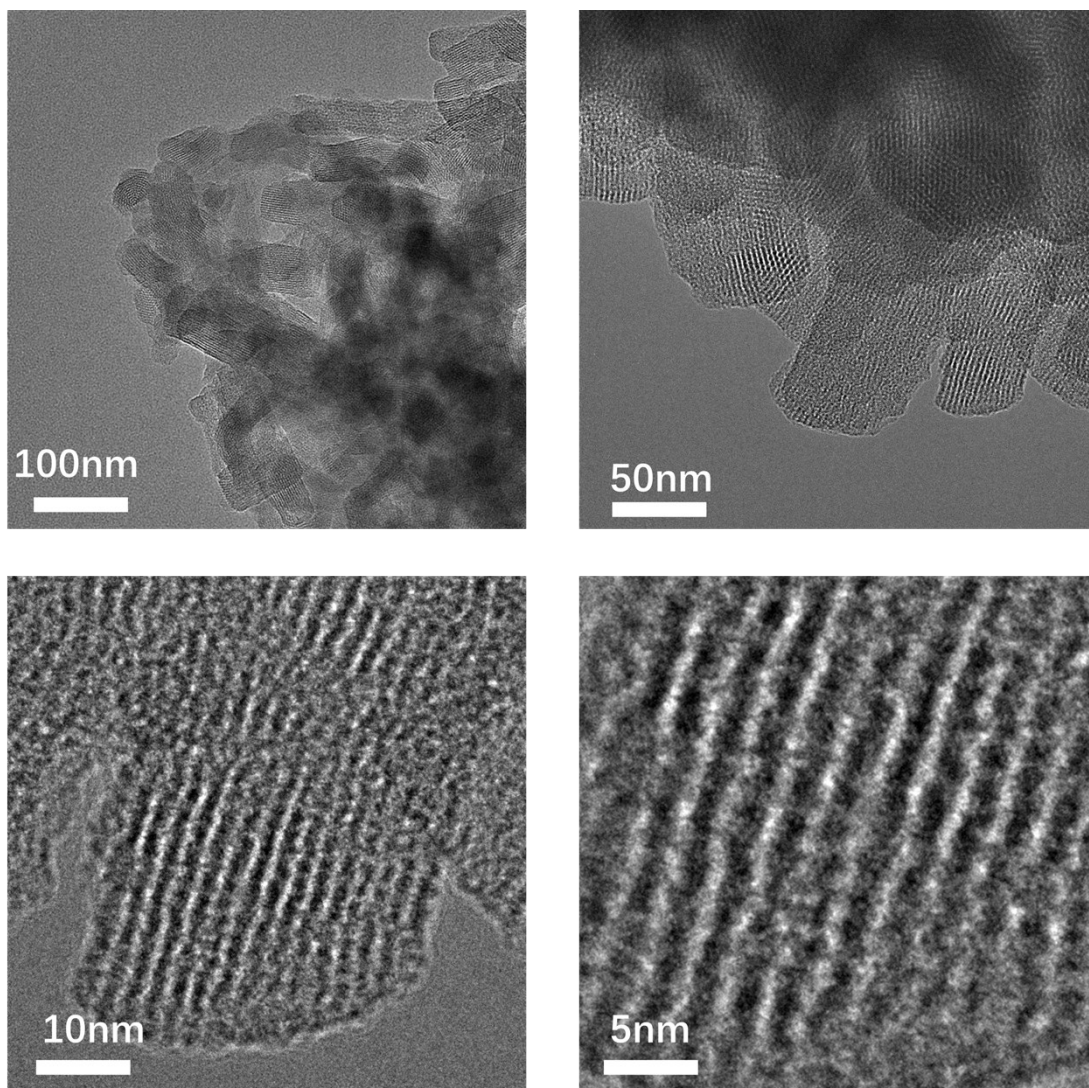


Figure S2. TEM images of the COF-(CF₃)₂.

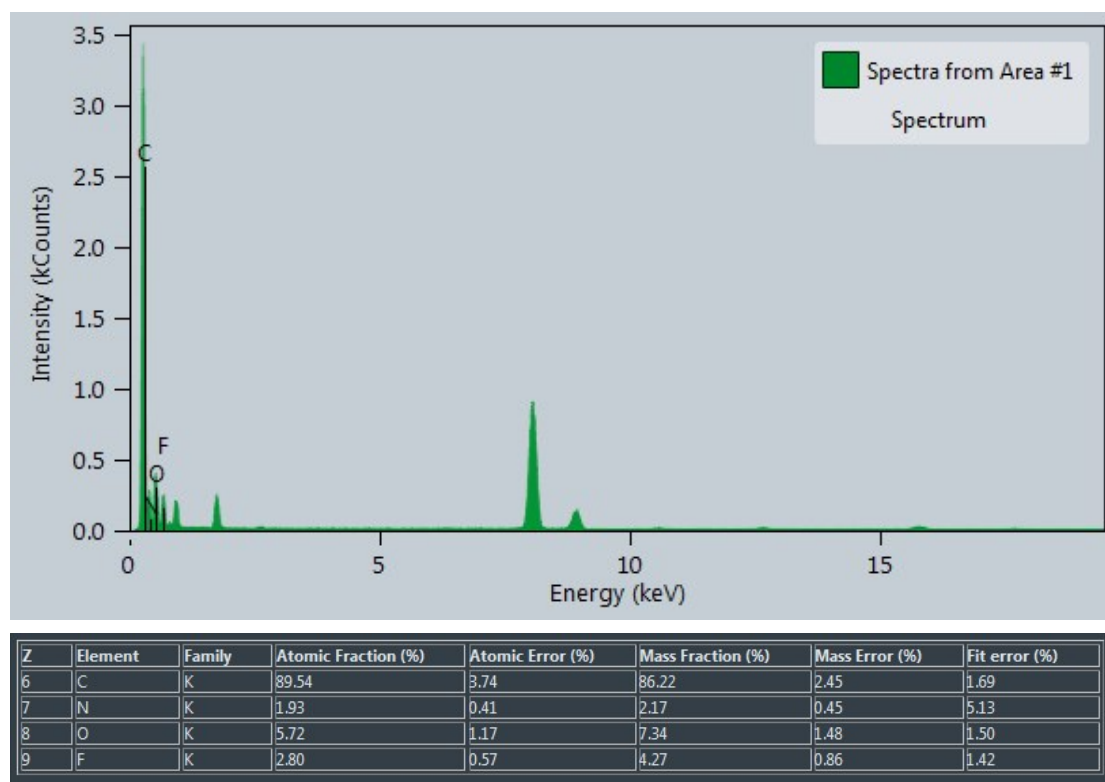


Figure S3. EDS spectra of COF-(CF₃)₂.

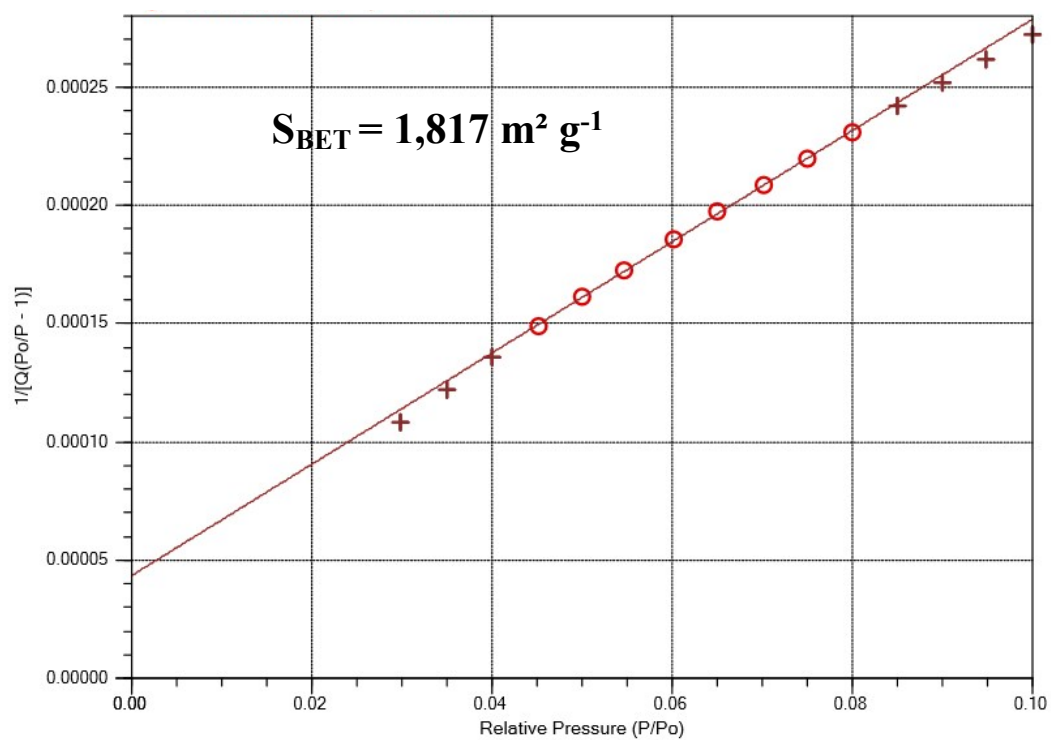


Figure S4. BET plot for COF-Ph.

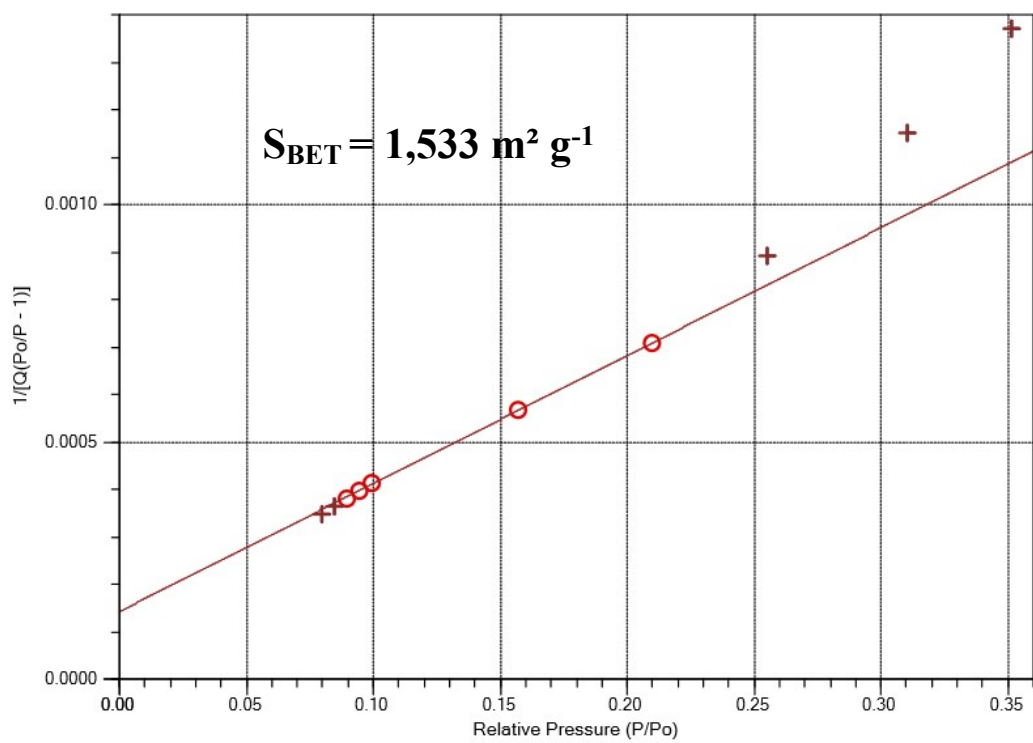


Figure S5. BET plot for COF-(CF₃)

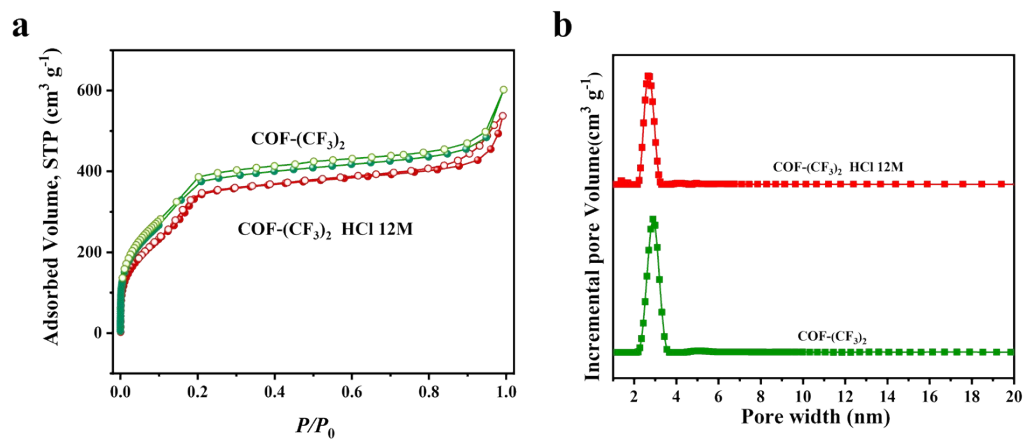


Figure S6. Nitrogen adsorption and desorption isotherms of COF-(CF₃)₂ treated in HCl (12 M).

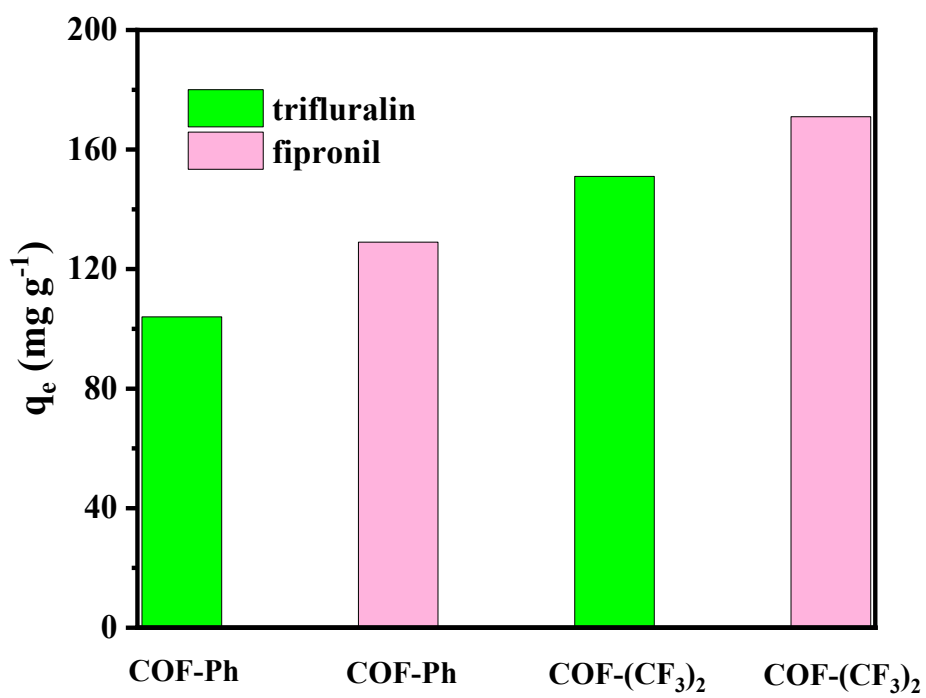


Figure S7. Maximum adsorption capacity of COF-Ph and COF-(CF₃)₂ for trifluralin and fipronil.

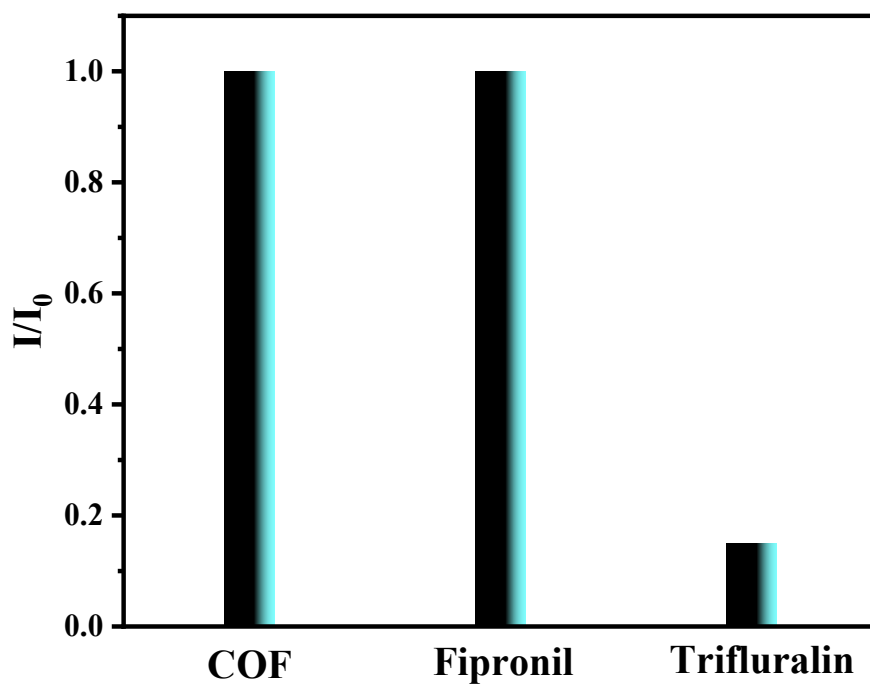


Figure S8. Fluorescence change of COF-(CF₃)₂ when different pollutants are added.

References

1. H. Xu, J. Gao and D. Jiang, *Nat. Chem.*, 2015, **7**, 905-912.
2. X. Li, C. Zhang, S. Cai, X. Lei, V. Altoe, F. Hong, J. J. Urban, J. Ciston, E. M. Chan and Y. Liu, *Nat. Commun.*, 2018, **9**, 2998.
3. X.-T. Li, J. Zou, T.-H. Wang, H.-C. Ma, G.-J. Chen and Y.-B. Dong, *J. Am. Chem. Soc.*, 2020, **142**, 6521-6526.
4. S. Shi, Y. Qian, P. Mei, Y. Yuan, N. Jia, M. Dong, J. Fan, Z. Guo and N. Wang, *Nano. Energy*, 2020, **71**, 104629.