

## Supporting Information

### **Post-synthetic Modification of Covalent Organic Framework via Thiol-Ene Reaction for Improving Fluorescence Detection and Removal of Cationic Crystal Violet Carcinogenic Dye**

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## Materials and Instruments.

Deionized water was used throughout the experiments. Selenium dioxide (99%), 1,3,5-triformylbenzene (98%), 2,5-Bis(allyloxy)terephthalohydrazide (98%), KCl (99%), MgCl<sub>2</sub> (99%), NaHCO<sub>3</sub> (99%), Na<sub>3</sub>PO<sub>4</sub> (99%), CH<sub>3</sub>COONa (99%), Cu(NO<sub>3</sub>)<sub>2</sub> (99%), Fe(NO<sub>3</sub>)<sub>2</sub> (99%), Fe(NO<sub>3</sub>)<sub>3</sub> (99%), Co(NO<sub>3</sub>)<sub>2</sub> (99%), Ni(NO<sub>3</sub>)<sub>2</sub> (99%) and Zn(NO<sub>3</sub>)<sub>2</sub> (99%) were purchased from Sigma-Aldrich. 2-mercaptoacetic acid (97%) and crystal violet were purchased from Aladdin Chemistry. 1,4-Dioxane was purchased from Greagent. The lake water used in the experiment was taken from the domestic wastewater of Tongji University.

Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA, and the scan range of 2 theta was 3 to 50°. Fourier transform infrared spectra (FT-IR) of the powder samples were obtained on a Nicolet IS10 infrared spectrum radiometer using ATR annex. Scanning electronic microscopy (SEM) images, energy-dispersive X-ray spectra (EDS) and mapping images were obtained using ZEISS GeminiSEM 300. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449C system analyzer under an N<sub>2</sub> atmosphere at a heating rate of 15 °C·min<sup>-1</sup> within the temperature ranging from 30 to 600 °C. Nitrogen adsorption/desorption isotherms were measured by a Tristar 2460 analyzer at the liquid nitrogen temperature. The samples were outgassed at 120 °C for 3 h before the measurements. The Brunauer Emmett Teller (BET) method was used to calculate the surface area from the adsorption data. The pore-size-distribution curves were obtained via the non-local density functional theory (NLDFT) method. X-ray photoelectron spectroscopy (XPS) was recorded by using Thermo Scientific K-Alpha photoelectron spectrometer. The fitting curve was carried out with the XPSPEAK41 program. UV-vis absorption spectra were recorded by a UV-1800 spectrometer. The fluorescence spectra were recorded on an Edinburgh FLS920 spectrophotometer with a xenon lamp (450 W) as an excitation source. Luminescence lifetime were measured at room temperature on an Edinburgh FLS920

phosphorimeter using a microsecond flashlamp (100 mW). The corresponding Commission International de l'Eclairage (CIE) color coordinates were calculated based on the international CIE standards.

### Luminescence lifetime analysis

0.75 mg of COF-A (COF-S-COOH) powder was added to gradient concentration of 1.5 mL DW and CV aqueous solutions ( $1 \times 10^{-4}$ ). The curve was fitted with two-phase exponential decay function with time constant parameters (Equation (1)) and the average lifetime was calculated by Equation (2).

$$I(t) = I_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

$$\tau_{ave} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \quad (2)$$

### Adsorption isotherm

The Langmuir isotherm is based on the assumption that the adsorbent can only be adsorbed in a single layer on the adsorbent. The linear fitting of the Langmuir isotherm model is represented as following:

$$Q_e = Q_m C_e K_L / (1 + C_e K_L) \quad (3)$$

Where  $C_e$  ( $\text{mg} \cdot \text{L}^{-1}$ ) and  $Q_e$  ( $\text{mg} \cdot \text{g}^{-1}$ ) are the concentration of CV and the amount of CV adsorbed by adsorbent at equilibrium time respectively,  $Q_m$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the largest and the single layer saturated amount of CV adsorbed by adsorbent.  $K_L$  ( $\text{L} \cdot \text{mg}^{-1}$ ) is Langmuir equilibrium constant related to the properties and temperature of adsorbents.

The Freundlich model is an empirical equation based on multilayer adsorption on a heterogeneous surface. The linear fitting of the Freundlich isotherm model is expressed by equation.

$$Q_e = K_F C_e^{1/n} \quad (4)$$

Both  $K_F$  and  $n$  are adsorption equilibrium constant related to system and temperature.

## Adsorption kinetics

Pseudo-first-order kinetic model and pseudo-second-order kinetic model were described as the following function:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (5)$$

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (6)$$

Where  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is equilibrium concentration of CV,  $Q_t$  and  $Q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) are the amount of CV adsorbed by adsorbent at  $t$  time and after reaching equilibrium respectively,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{mg}\cdot\text{g}^{-1}$ ) are the rate constants of the pseudo first and second order kinetics models, respectively.

## 2. Experimental Section

### 2.1. Luminescent sensing experiments

Detection in deionized water. The prepared COF-A and COF-S-COOH were ground to be homogeneous powder. 0.75 mg of COF (COF-S-COOH) powder was added to gradient concentration of 1.5 mL CV aqueous solutions ( $1 \times 10^{-4} \sim 1 \times 10^{-7}$  M) and the fluorescence test was performed immediately after sonication for 1 min.

Detection in actual samples (river water). The river water sample was obtained from Sanhaowu of Tongji University. Then deionized water in the above detection was replaced with treated river water for subsequent configuration of gradient concentration solution ( $1 \times 10^{-4} \sim 1 \times 10^{-7}$  M).

Selective test of CV. Several common anionic and cationic ions in river water ( $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{COO}^-$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ) and CV were prepared to aqueous solutions ( $2 \times 10^{-4}$  M). Then 0.75 mL of above solutions were mixed with 0.75 mL of COF-A (COF-S-COOH) aqueous solutions (1 mg/mL) respectively for selective test.

Anti-interference test of CV. 0.75 mL of above solutions of the chemicals in river water including a

blank were mixed with 0.75 mL of CV ( $10^{-4}$  M). 0.75 mg of COF (COF-S-COOH) was added to each solution for following test after being sonicated for 1 min.

Response time experiments. Fluorescence kinetic test is performed on the configured COF-A and COF-S-COOH suspensions. After the curve stabilized, the substrate solution was quickly added with a dropper. The test was stopped when the intensity decreased to a stable value, and the time of change between the two equilibria was the response time.

### *2.2. Adsorption experiments*

As a whole, 5 mg of well ground COF (COF-S-COOH) powder was dispersed in 10 mL of treated CV solution which was packed in a flask. In order to investigate the effect of pH on adsorption, ten CV solutions in the conical flask were modulated with HCl and NaOH for pH 3 ~ 11 respectively. For absorption isotherm data, eight CV solutions were configured with different initial concentrations from 2 to 100 mg/L (2, 5, 10, 20, 40, 50, 70 and 100 mg/L). In order to explore the adsorption kinetics, 5 mg COF-A (COF-S-COOH) was added in eleven CV solutions with initial concentration of  $10^{-4}$  M separately and shaken for different time from 10 s to 2 h (10 s, 0.5 min, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, 60 min, 90 min and 120 min). In addition to the above, all the mixtures were shaken for 2 h and filtered through a 0.22  $\mu$ m needle filter, and 3 mL of the filtrate was taken for UV-absorption spectroscopy quantification.

### *2.3. Cycle experiments*

After fluorescence sensing as well as adsorption experiments, the solid filtrate was filtered out and washed with an acidic ethanol solution (pH = 2) ( $5 \times 10$  mL), and then centrifuged to obtain a yellow solid, dried at 80°C for 5h

Figures and tables.

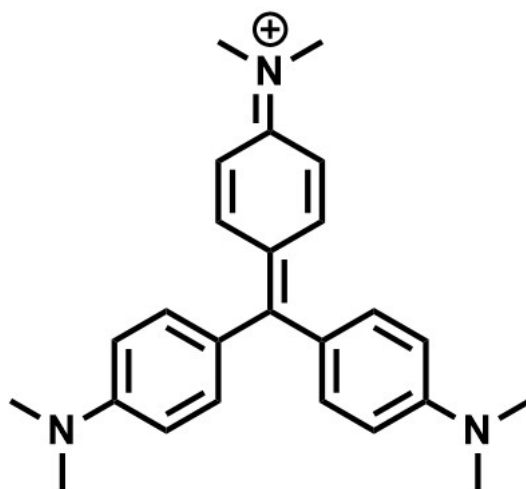


Fig. S1 Molecular formula of crystal violet (CV).

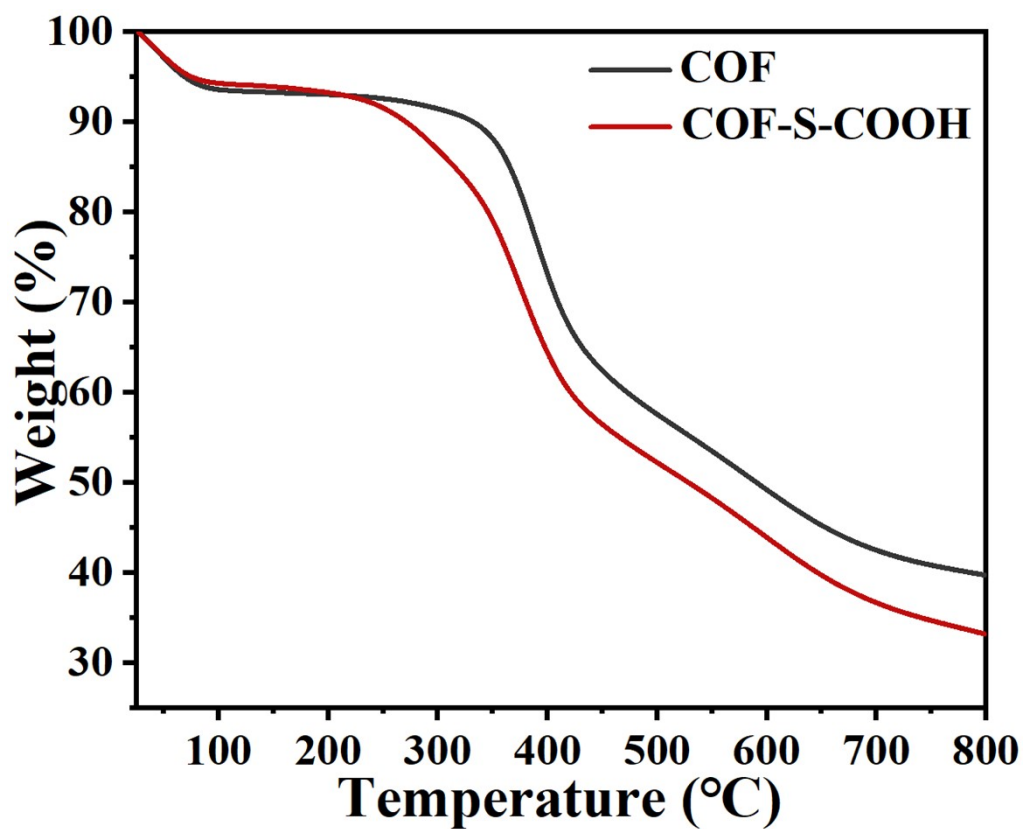


Fig. S2 TGA curves of COF-A and COF-S-COOH.

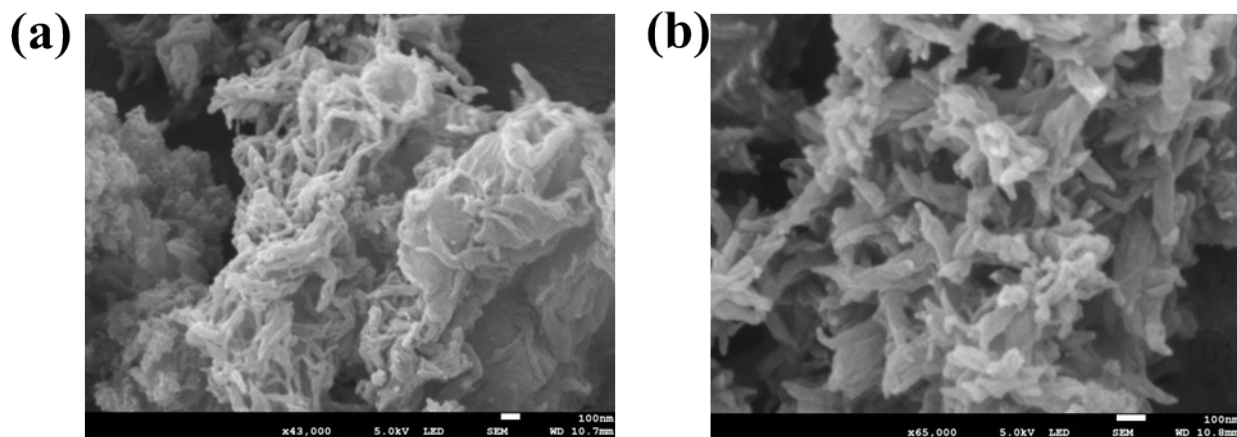


Fig. S3 SEM images of (a) COF-A and (b) COF-S-COOH.

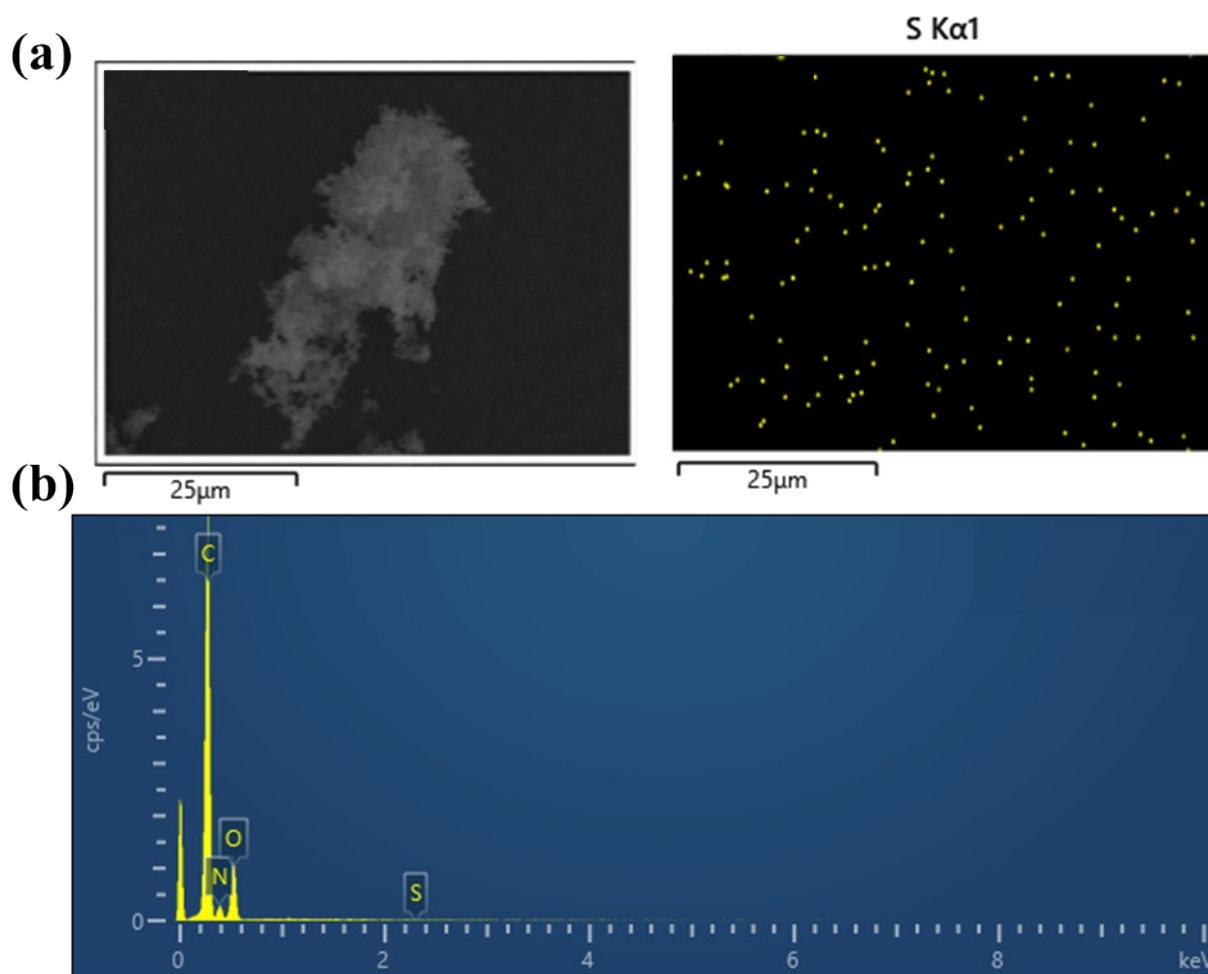
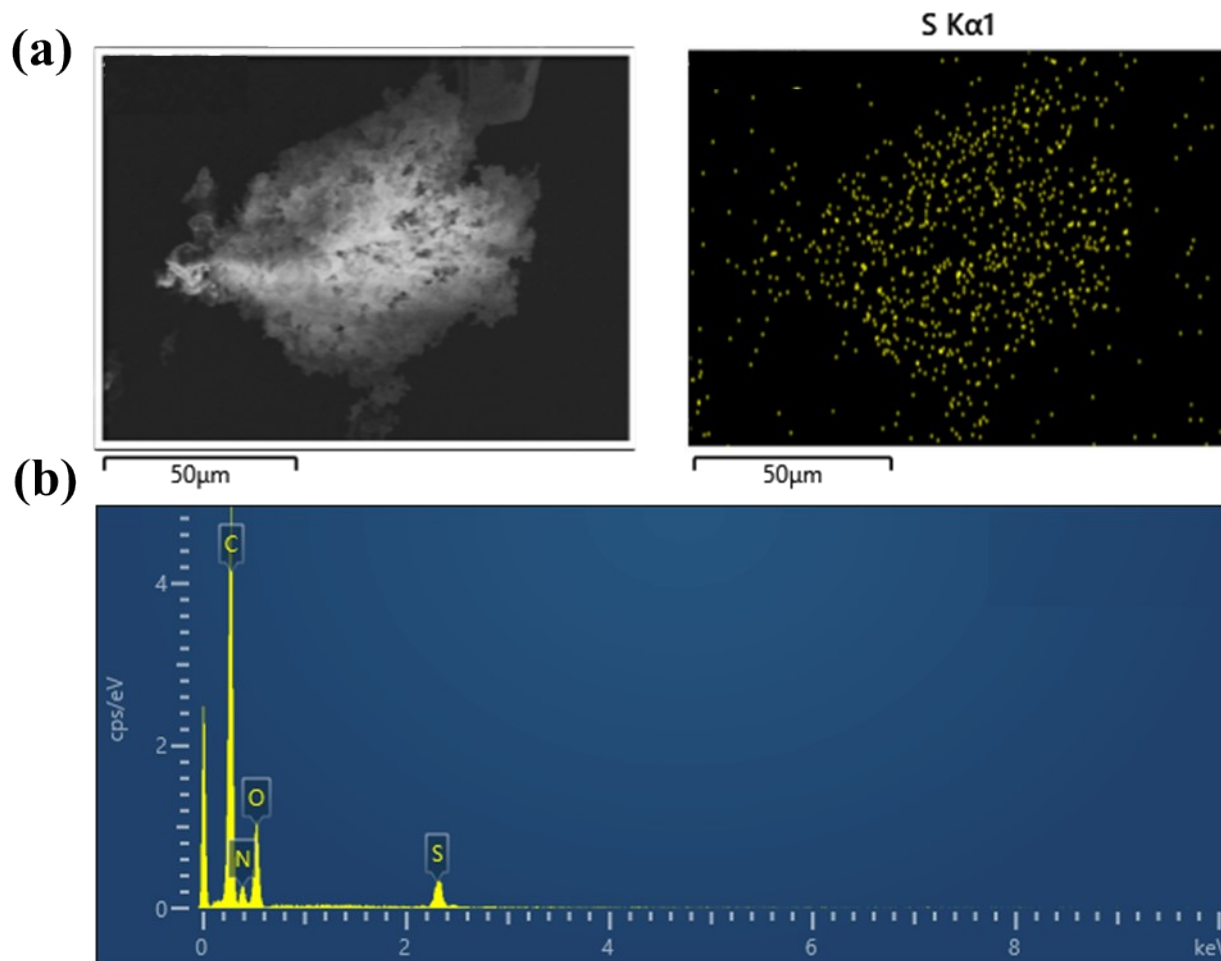
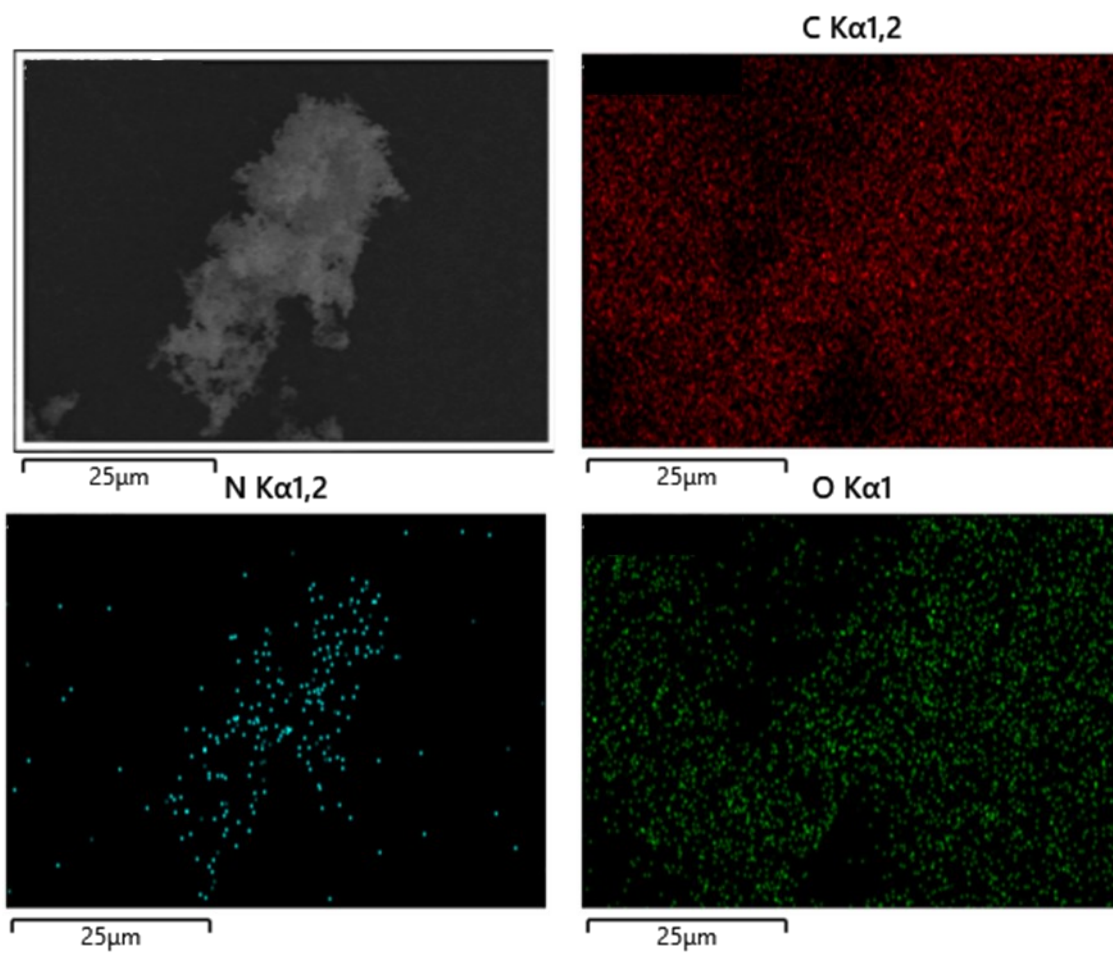


Fig. S4 (a) EDX mapping image of S element in COF-A. (b) The element content of S (0%) element in EDX energy spectrum of COF-A.



**Fig. S5** (a) EDX mapping image of S element in COF-S-COOH. (b) The element content of S (5.14%) element in EDX energy spectrum of COF-S-COOH.





**Fig. S6.** EDX mapping images of C, N, O element in COF-A.

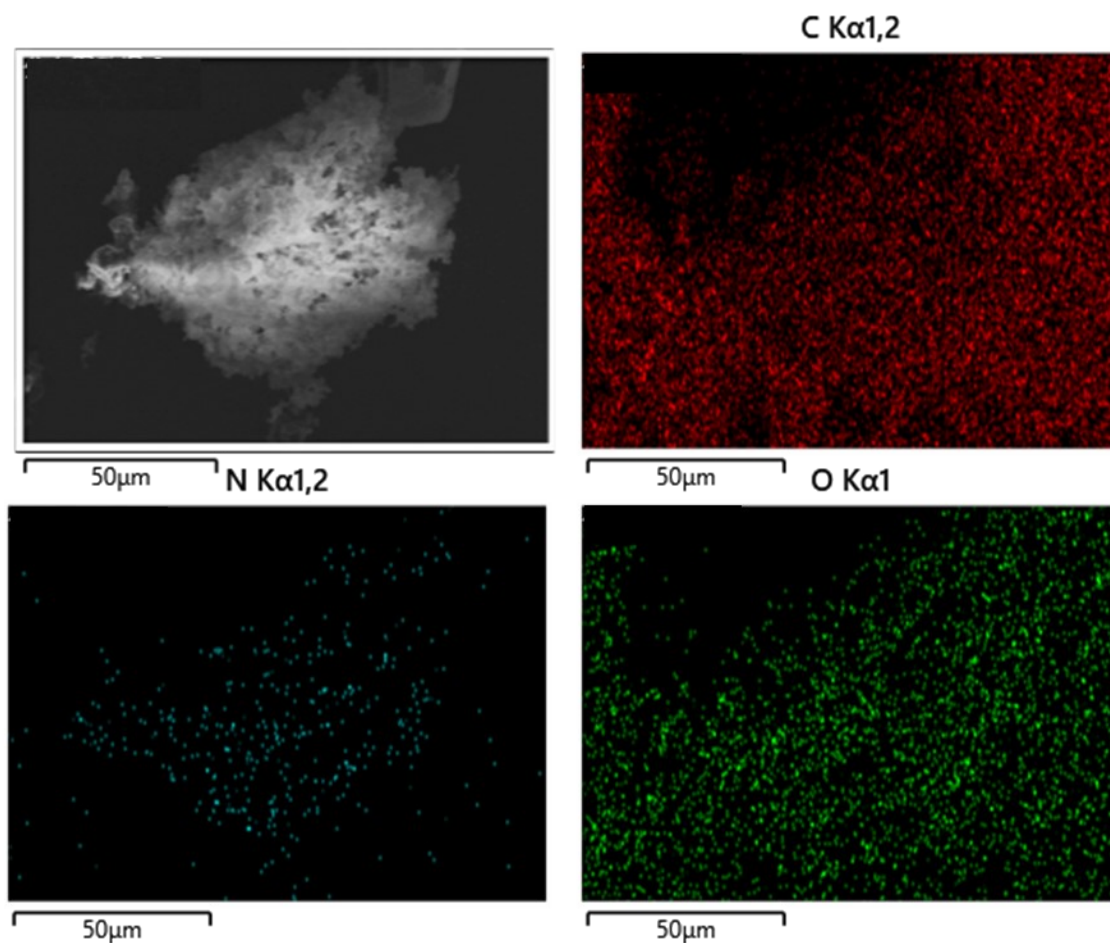


Fig. S7 EDX mapping images of C, N, O element in COF-S-COOH.

### Solid-State $^{13}\text{C}$ CP-MAS of COF-A

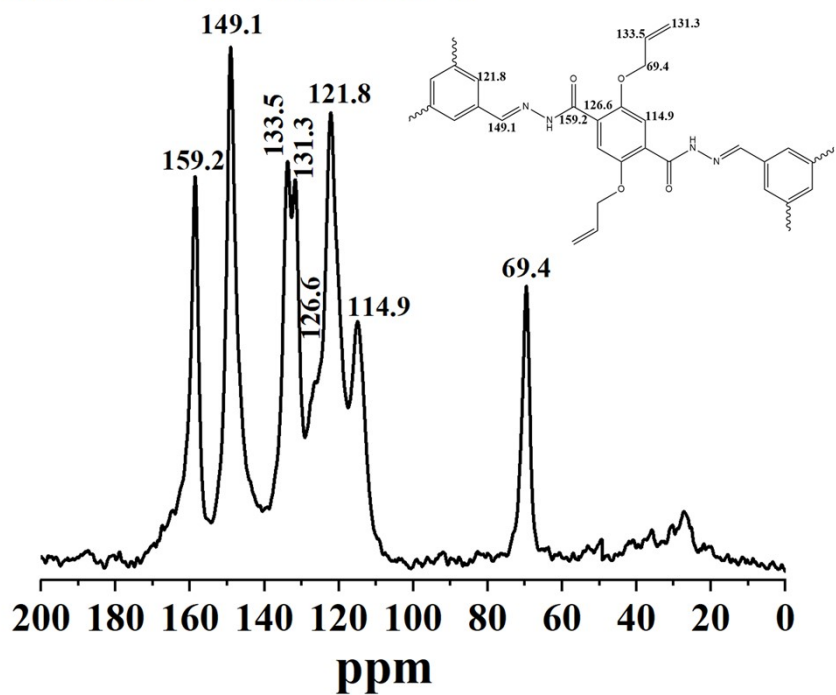


Fig. S8 Solid-State  $^{13}\text{C}$  CP-MAS of COF-A

### Solid-State $^{13}\text{C}$ CP-MAS of COF-S-COOH

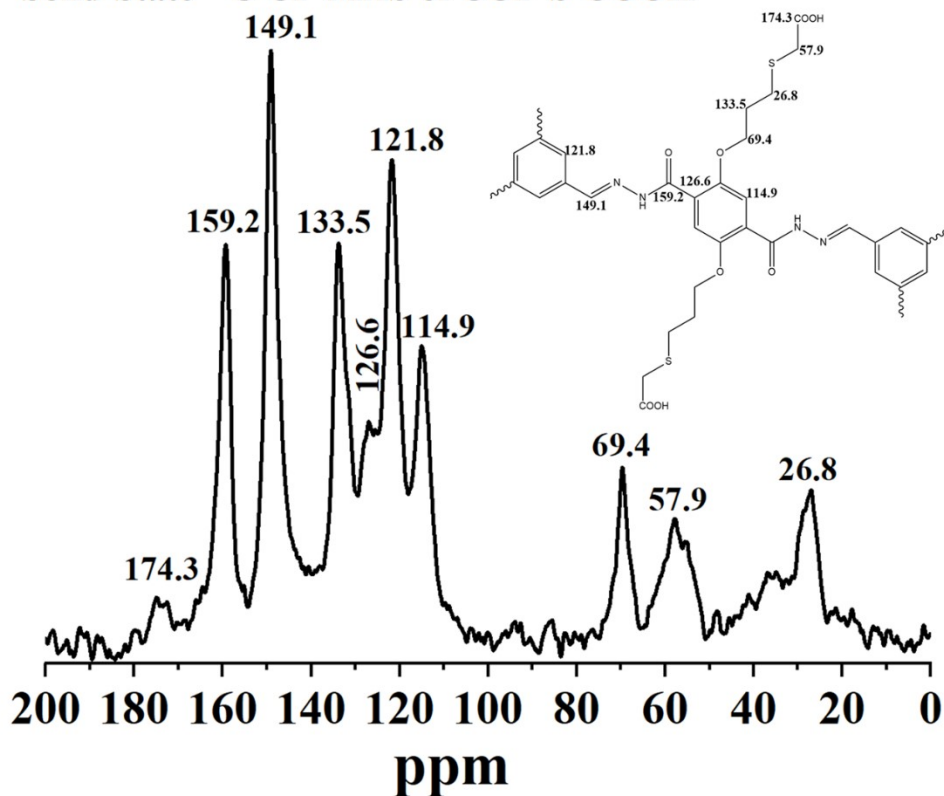


Fig. S9 Solid-State  $^{13}\text{C}$  CP-MAS of COF-S-COOH

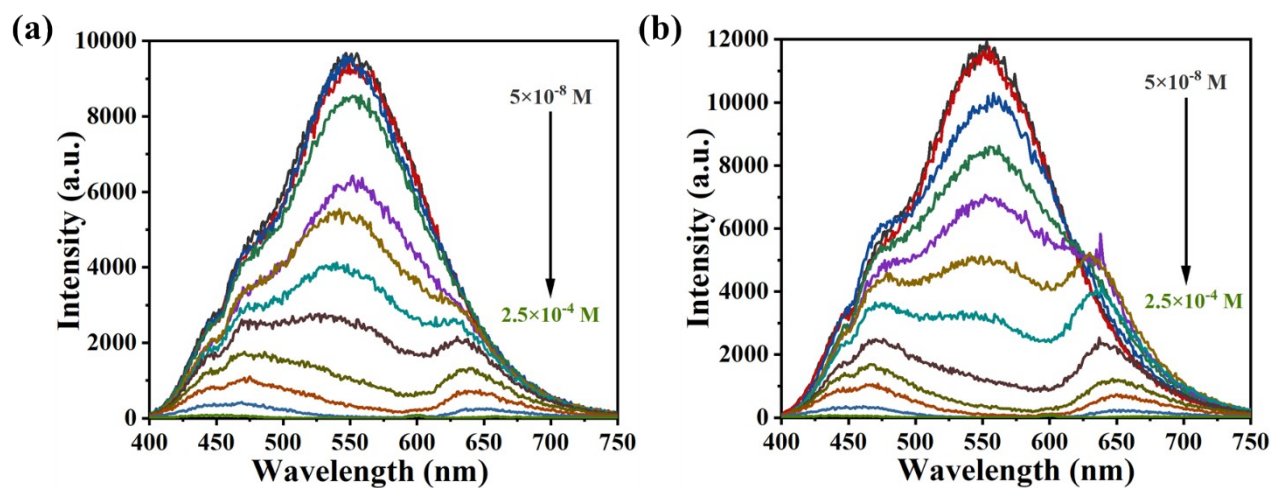
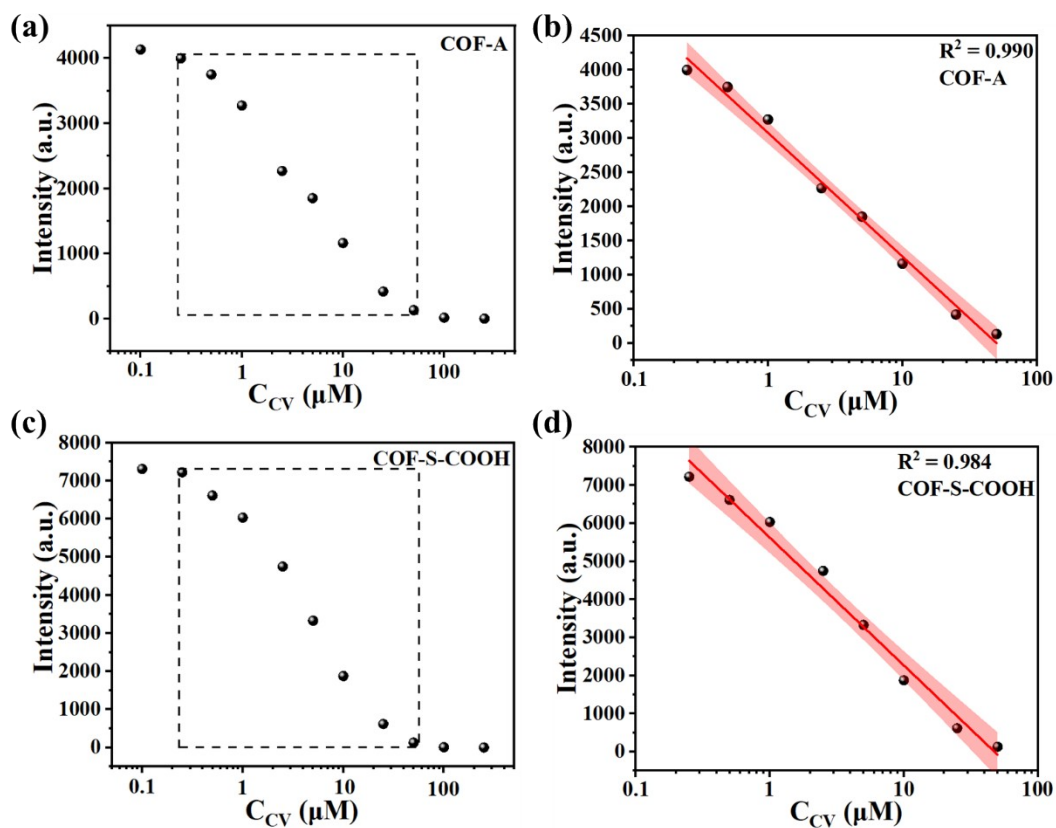
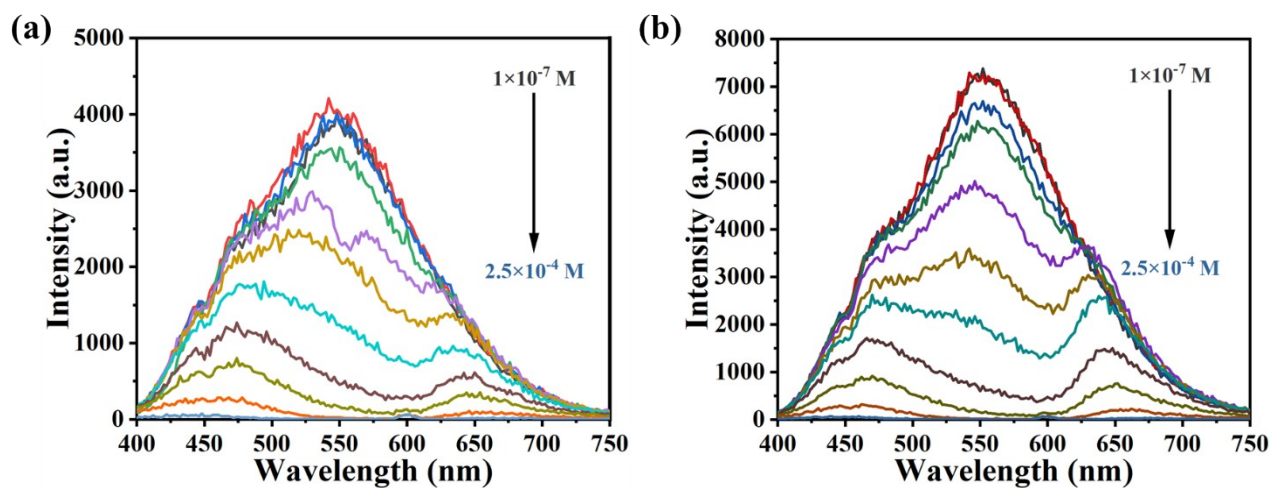


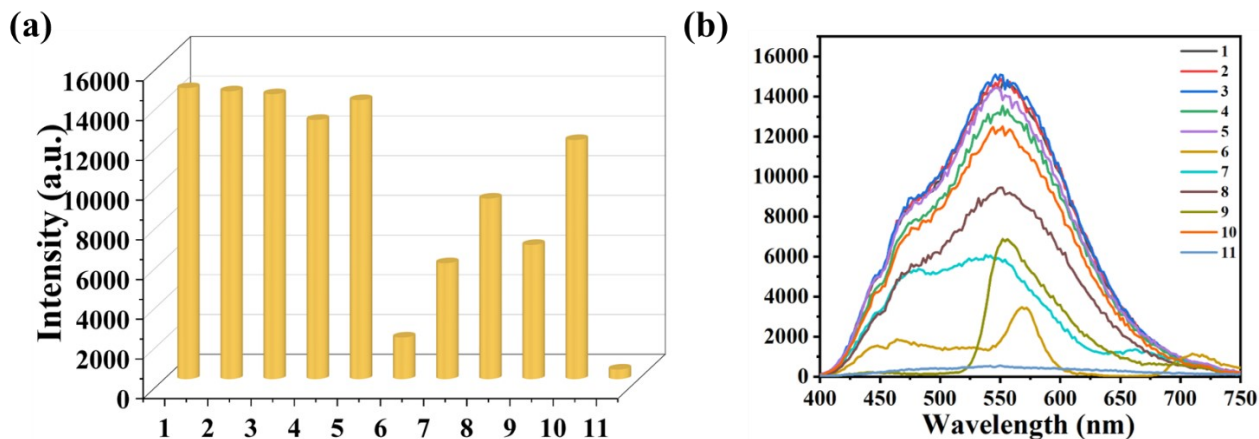
Fig. S10 Fluorescence spectra at different CV concentrations from  $5 \times 10^{-8}$  to  $2.5 \times 10^{-4}$  M of (a) COF-A and (b) COF-S-COOH in DW.



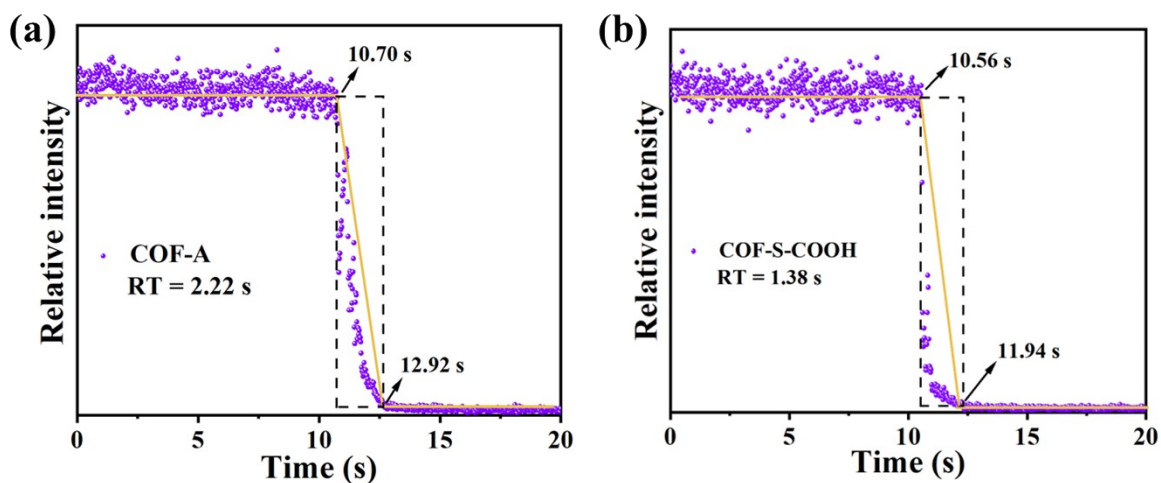
**Fig. S11** Dependences of the emission intensity of (a) COF-A and (d) COF-S-COOH at 556 nm on  $C_{CV}$  and labelling of linear range. Corresponding calibration curve of Intensity of (b) COF-A and (e) COF-S-COOH toward  $C_{CV}$  in real sample (lake water).



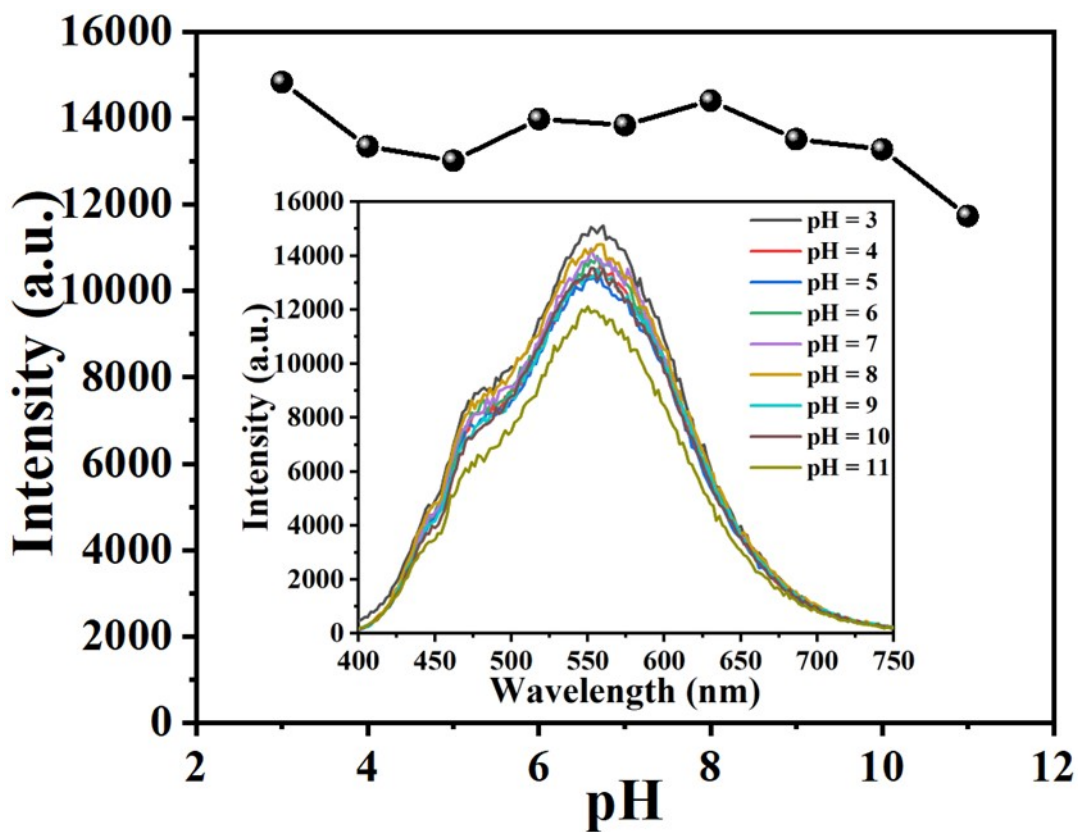
**Fig. S12** Fluorescence spectra at different CV concentrations from  $1 \times 10^{-7}$  to  $2.5 \times 10^{-4}$  M of (a) COF-A and (b) COF-S-COOH in lake water.



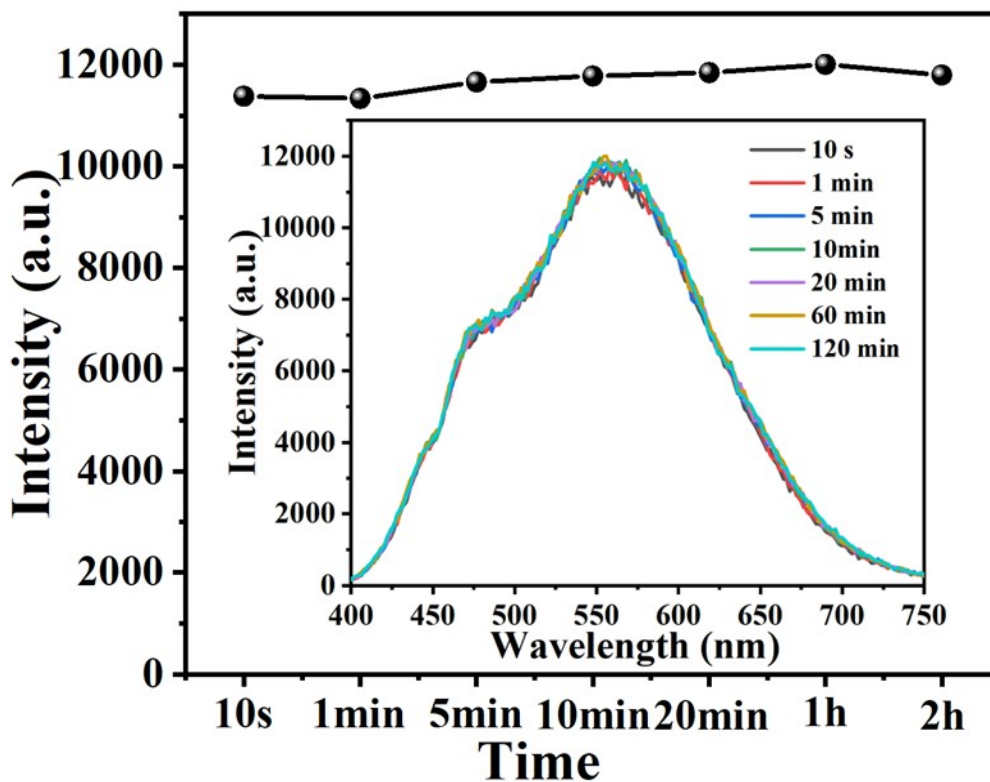
**Fig. S13** Selectivity of COF-S-COOH for some co-existing dyes or organic molecules. (1 blank; 2 aminobenzene; 3 nitrobenzene; 4 mesotrione; 5 ciprofloxacin; 6 methyl blue; 7 malachite green; 8 tetracycline; 9 rhodamine B; 10 diclofenac sodium; 11 CV)



**Fig. S14** Response times to CV of (a) COF-A and (b) COF-S-COOH.



**Fig. S15** Fluorescence intensity of COF-S-COOH at 556 nm in aqueous solutions of different pH values and their fluorescence spectra.



**Fig. S16** Emission spectra at 556 nm of COF-S-COOH over time (10 s ~ 2 h).

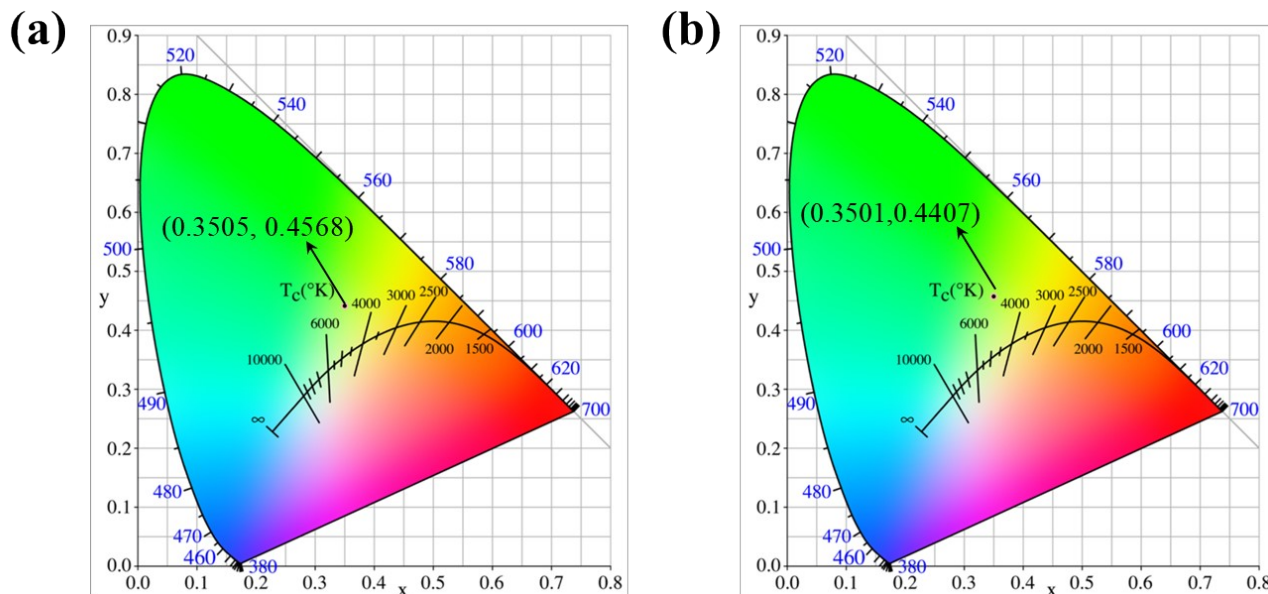


Fig. S17 CIE chromaticity coordinate and fluorescence photographs of (a) COF-A and (b) COF-S-COOH.

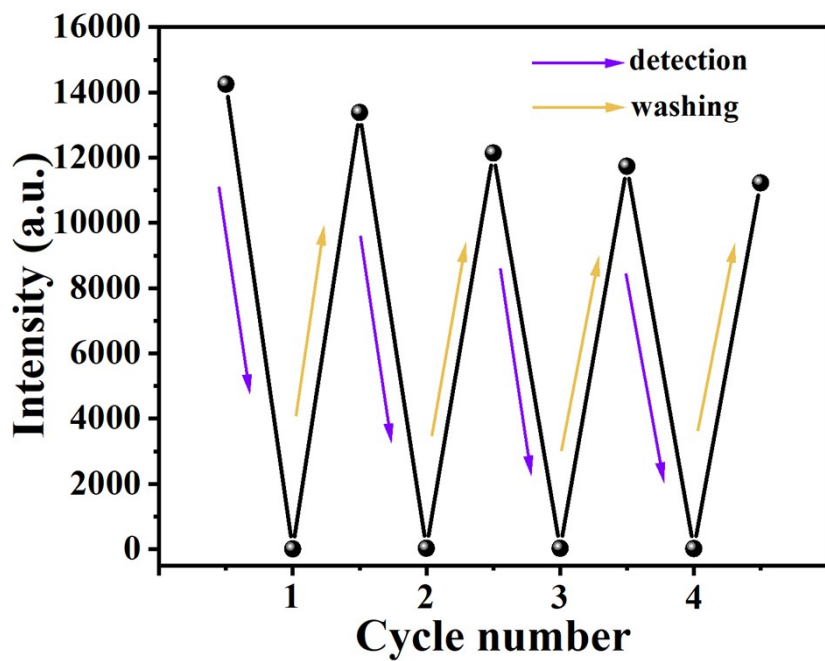


Fig. S18 Cyclicity of fluorescence detection of COF-S-COOH.

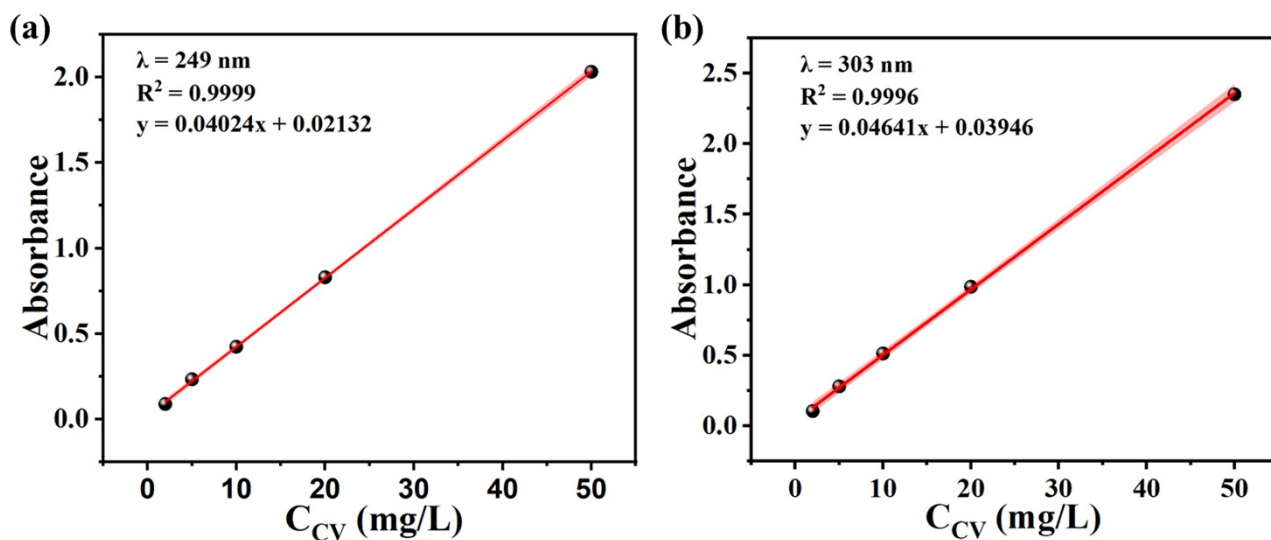


Fig. S19 Standard concentration curves for quantification in adsorption experiments of CV at (a) 249 nm and (b) 303 nm.

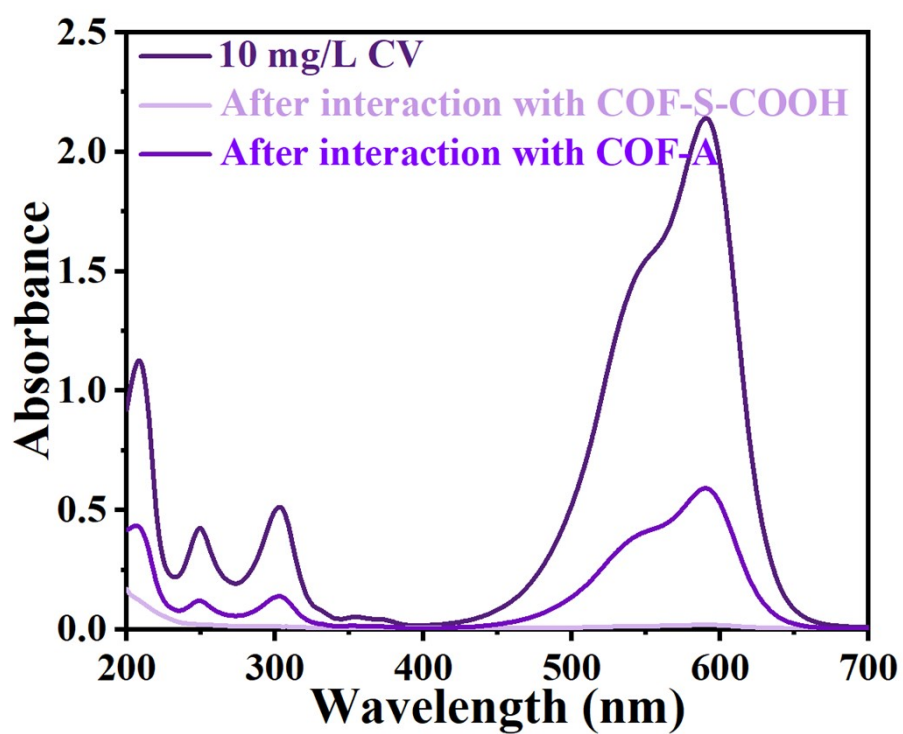
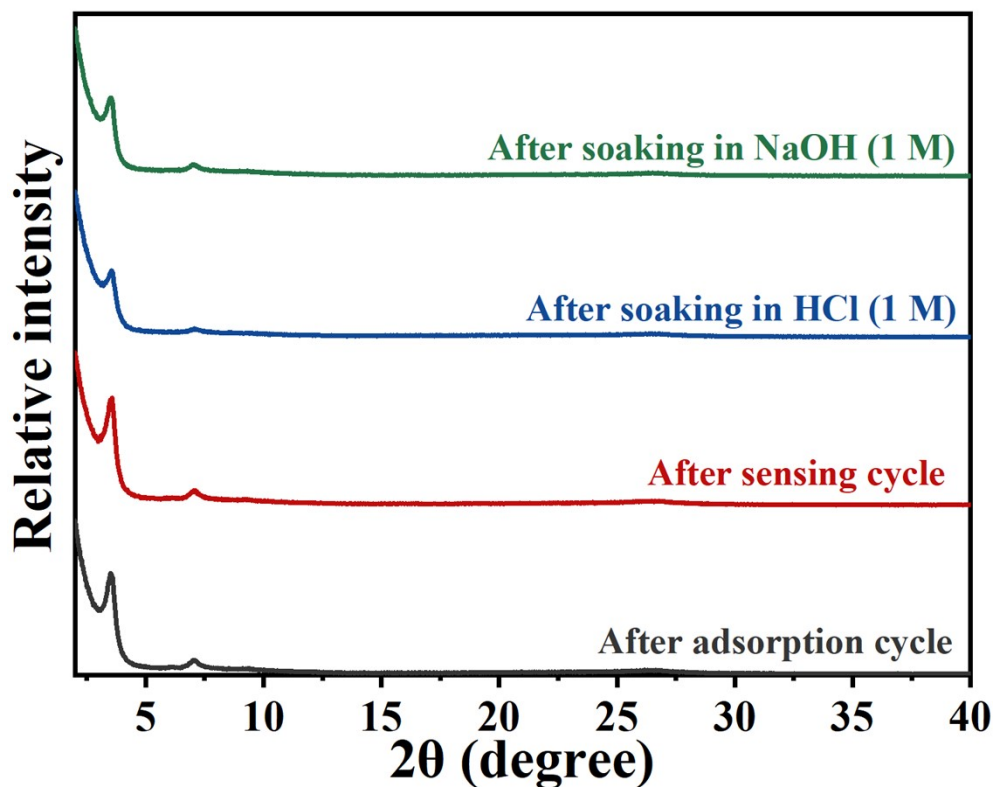
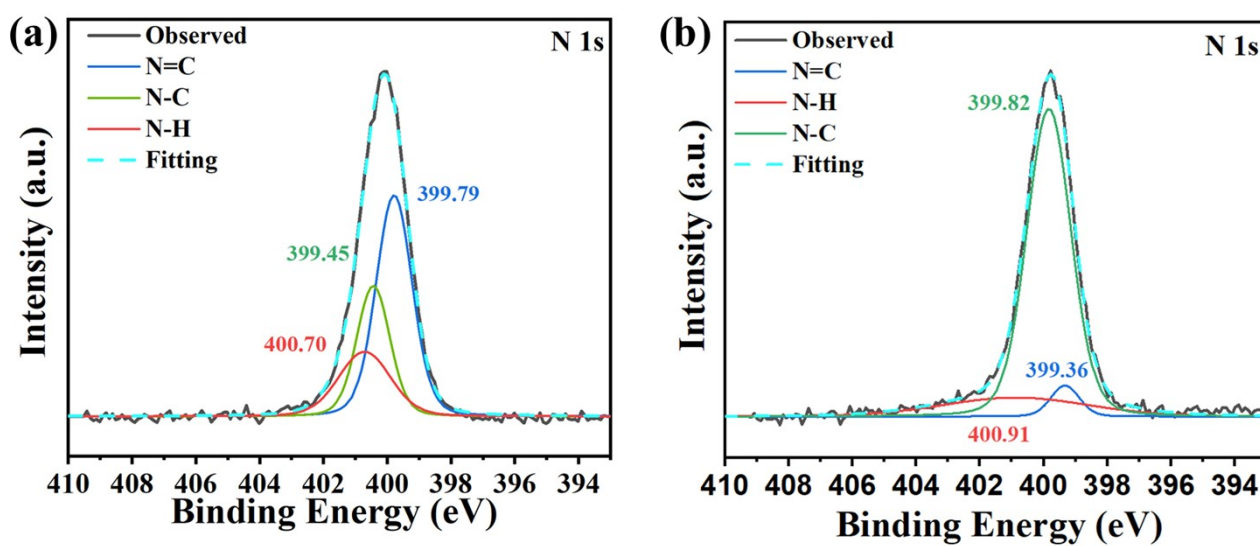


Fig. S20 UV absorption spectrum of 10 mg/L CV after adsorption by COF-A and COF-S-COOH





**Fig. S21** PXRD of COF-S-COOH after being soaked in 1 M NaOH and 1 M HCl for 2 h and after sensing and adsorption cycles.



**Fig. S22** N1s spectra of COF-S-COOH before (a) and after (b) adsorption of CV.

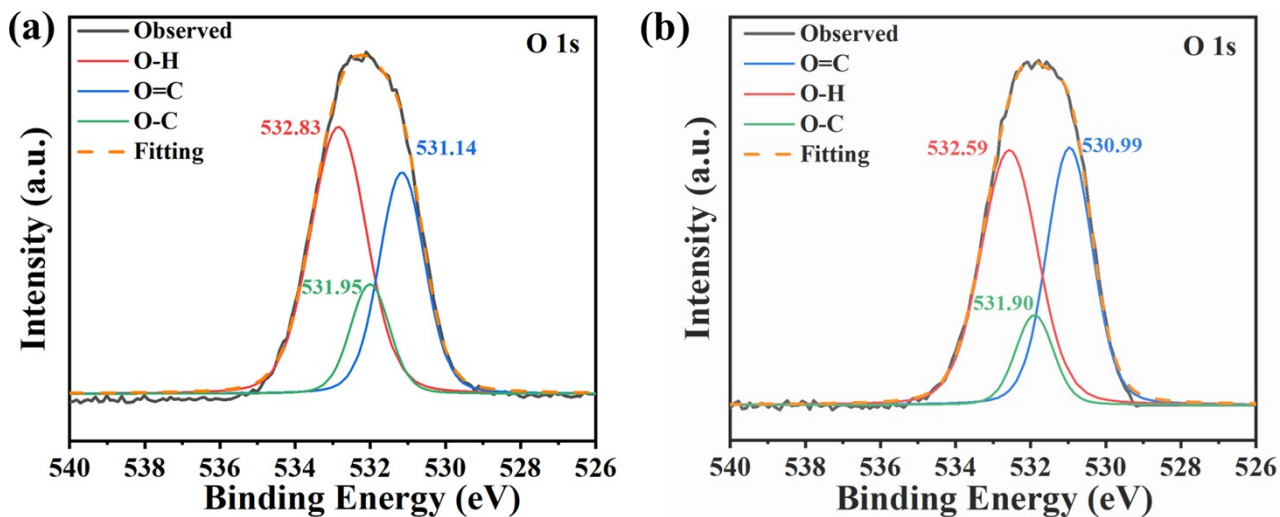


Fig. S23 O1s spectra of COF-S-COOH before (a) and after (b) adsorption of CV.

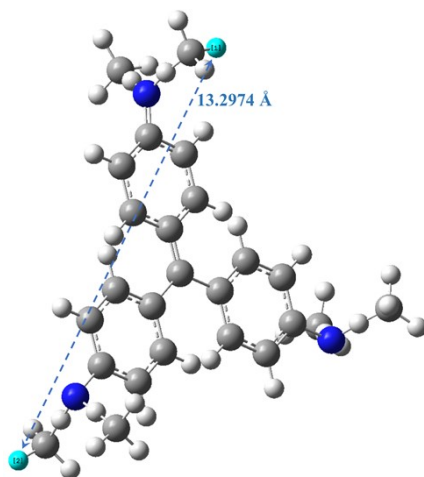


Fig. S24 Ball-and-stick modelling and molecular size of CV molecules

Table S1. EDX analysis of COF-S-COOH

Element	Signal Type	Wt%	Wt% Sigma
C	EDS	61.49	1.42
N	EDS	13.58	1.62
O	EDS	19.74	0.90
S	EDS	5.19	0.35
Total amount		100.00	

Table S2. EDX analysis of COF-A.

Element	Signal Type	Wt%	Wt% Sigma
C	EDS	66.45	0.98
N	EDS	13.32	1.10

O	EDS	20.23	0.59
S	EDS	0.00	0.07
Total amount		100.00	

**Table S3** Comparison of other methods for sensing CV.

	Method	DL	Ref
MG	Fluorescence (Eu-TDA MOF)	0.0221 $\mu\text{M}$	[S7]
CV	Fluorescence (COF-TPDD)	0.007 $\mu\text{g}\cdot\text{mL}^{-1}$	[S3]
CV	SCP-nanoESI-MS	0.077 $\text{ng mL}^{-1}$	[S8]
CV	Fluorescence (Se,N-codoped carbon dots)	0.02 $\mu\text{M}$	[S9]
CV	SERS (MIL-101(Cr)/silver nanocomposites)	$9.2\times 10^{-12}\text{ M}$	[S10]
CV	SERS (Au@PB NPs)	0.2 nM	[S11]

**Table S4** Comparison of other for adsorption of CV.

Materials	Adsorption Capacity	Ref
CPCM@MXene/CV	2750 mg/g	[S1]
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> magnetic nanoparticles	16.37mg/g	[S2]
COF-TPDD-COOH	88.02 mg/g	[S3]
carboxylated activated carbon	255.8 mg/g	[S4]
TpStb-SO <sub>3</sub> Na	1831 mg/g	[S5]
ZIF-201	10.83 mg/g	[S6]

## Reference

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