Supporting information for

Removal of Pharmaceuticals and Personal Care Products (PPCPs) from Water and Wasteater Using Sulfonic Acid (-SO_3H) Functionalized Covalent Organic Frameworks

Jun Hao[a], Qianxin Zhang[a], Ping Chen[a,b], Xiaoshan Zheng[a], Yuliang Wu[a], Dan Ma[a], Dandan Wei[a], Haijin Liu[c], Guoguang Liu[a], Wenying Lv[a*]

[a]*School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou, 510006, China*

[b]*School of Environment, Tsinghua University, Beijing, 100084, China*

[c] *Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, School of Environment, Henan Normal University, Xinxiang 453007, China*

***Corresponding Author**:

Wenying Lv, E-mail: lvwy612@163.com , Telephone: +86-20-39322547, Fax: +86-13538982812.

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Text S1. Reagents

High purity reagents are purchased through commercial suppliers and are not further purified for use. The 1,4-dioxane, butanol, methanol, tetrahydrofuran 2,2-Azobisisobutyronitrile, 1,2-ethanedisulfonic acid and 1,3,5-tris (4-aminophenyl) benzene were purchased from Guangzhou Wei Gu Run Instrument Co., Ltd. The acetone and glacial acetic acid were obtained from Shanghai Panicle Test Company. The 2,5-divinylterephthalaldehyde (purity 98%) was procured from Shanghai Kai Yu Lin Pharmaceutical Technology Co., Ltd. The indomethacin, naproxen, ibuprofen, diclofenac, ciprofloxacin, enrofloxacin, ketoprofen, sulfamethoxazole, sulfisoxazole, sulfamethazine, bisphenol A, bisphenol B and bisphenol C were also purchased from Guangzhou Wei Gu Run Instrument Co., Ltd.

Text S2. Characterization methods

The Fourier transform infrared spectroscopy was determined by spectrometer of type Nicolet 6700 produced by Thermo-Filsher manufacturer in the United States, whose spectral resolution was better than 0.09 cm^{-1}. Hydrogen (^{1} H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectrum was recorded at 25 °C with 600 MHZ instruments, by Swiss Bruker factory production. Chloroform is used as tritium substitute solvent ($CDCl_3$: 7.26 ppm for ^{1}HNMR, 77.00 for ^{13}C NMR). The morphology and composition of the samples were observed using field emission transmission electron microscopy (TEM). The model is */Talos F200S, made in the Czech Republic. Scanning electron microscopy (SEM) images of TAB-DVA-COF and COF-SO_3H were taken on a */SU8220 SEM. The internal composition of the material is characterized by X-ray Diffractometer (XRD, */D8 ADVANCE, Germany). X-ray Photoelectron Spectroscopy (XPS) data were acquired through a model */Escalab 250Xi produced by a British manufacturer, Thermo Fisher. The concentration of Pharmaceuticals solutions was determined by high performance liquid chromatography (HPLC, Shimadzu, JAPAN). The specific surface area and pore distribution of adsorbents were analyzed by N_2 adsorption at 77 K with ASAP2020 (Micromeritics, USA). Thermal stability of materials is characterized by thermogravimetric analysis (TGA, */TG 209 F1, Germany). The isoelectric point (pHiep) of COF-SO_3H was measured by a Zeta potential instrument (Brookhaven, USA). Trace adsorbents were added to 100 mL eakers, then ultra-pure water was added and ultrasound was conducted for 20 minutes. Then pH was adjusted to 3, 4, 5, 6, 7, 8, 9 and 10 with 0.5 M HCl or 0.5 M NaOH, respectively.

Text S3. Material Synthesis

Synthesis of TAB-DVA-COF. 2,5-divinylterephthalaldehyde (22.3 mg, 0.12 mM) and 1,3,5-tris (4-aminophenyl) benzene (28.0 mg, 0.08 mM) were added to 4.5 mL 1,4-dioxane-butanol-methanol (v/v/v, 4:4:1) cosolvent system. Then, the mixture is ultrasonic for 30 min to make the resulting solution more uniform. After, 0.050 mL 12 M of acetic acid solution was added in drops and the mixture was left undisturbed at room temperature for 2 h. Subsequently, 0.45 mL 12 M acetic acid solution was added, and the mixture was reacted in the oven at 70 °C for 24 h. Finally, the product was removed and cooled to room temperature, washed several times with tetrahydrofuran and acetone, and dried in vacuum at room temperature for 12 h.

Synthesis of COF-SO_3H. TAB-DVA-COF (100 mg) and 2,2-Azobisisobutyronitrile (AIBN, 10 mg) was added in a 25 mL Schlenk tube. Then, 1,2-ethanedisulfonic acid (678.2, 600, 500, 300, 100, 25 mg) was dissolved in ethanol and then was added to the 25 mL Schlenk tube under nitrogen atmosphere. The mixture stirring 48 h under 80 °C, the target product is washed with acetone, and vacuum drying under 50 °C. Finally, we got six kinds of different COFs, the mass ratio of TAB-DVA-COF to 1,2-ethanedisulfonic acid is 1:6.8, 1:6, 1:5, 1:3, 1:1 and 4:1, separately.

Text S4. Sorption Experiments.

DCF solutions with different concentrations were obtained by diluting the prepared 1 g/L DCF mother liquor with ultra-pure water. The concentration of DCF was determined by high performance liquid chromatography (HPLC) and all experiments were performed at room temperature.

DCF sorption isotherms.

Adsorbent COF-SO_3H (8 mg) was added to the DCF solution of 50 mL with concentrations of 50, 70, 90, 110, 130 and 150 mg/L, respectively. The adsorbent was treated with ultrasound in 25 mL ultra-pure water for 5 min to make it completely dispersed in the solution. Then, the mixture is magnetically stirred for 60 min at 25 °C, 35 °C and 45 °C, respectively, which are assumed to be in equilibrium. Subsequently, 1 mL of the solution was filtered with 0.45 μm membrane, and the residual concentration of DCF was measured by HPLC. The amount of adsorbed DCF at equilibrium is calculated by the following formula:

$$Q_e = \frac{(C_i - C_e) * V}{m}$$

Where $V\ (mL)$ represents the volume of the treatment solution, $C_i\ (mg/L)$ is the initial concentration, $C_e\ (mg/L)$ is the equilibrium concentration, and $m\ (mg)$ is the mass of the adsorbent.

DCF sorption kinetics.

Adsorbent COF-SO_3H (10 mg), and DCF aqueous solution (50 mg/L, 50 mL) were added to a 100 mL beaker. Then the mixture was magnetically stirred for 90 min, during which sampling was conducted at appropriate time intervals. 1 mL of the mixture was taken at a time and filtered with a 0.45 μm membrane. The residual concentration of DCF was measured by HPLC. The removal rate of the DCF was calculated as follows:

$$Removal\,percentage(\%) = \frac{C0 - Ct}{C0} \times \%$$

Where C_o (mg/L) is the initial concentration, C_t (mg/L) is the concentration at time t (min).

Selective adsorption experiment.

Adsorbent COF-SO_3H (5 mg), BPA, BPB, BPC, NPX, SIZ, SMZ, ENX, SMT, DCF, IDM, IBU, KP and CIP (60 mL, 10 mg/L) were added to 100 mL beaker respectively. Subsequently, the mixture was magnetically stirred for 30 min. Then samples were taken at a fixed time, 1 mL of which were filtered with 0.45 μm membrane. Finally, after adsorption, the residual concentrations of these pollutants were measured by high performance liquid chromatography (HPLC). Each experiment was repeated three times, the final mean value was taken, and the standard deviation was calculated.

Adsorption and desorption experiments.

Adsorption. The adsorbent was dissolved into 10 mL ultra-pure water, the suspension was ultrasonic for 1 min, and then magnetic stirring for 1 h. Subsequently, take 1mL of the mixture with a 1 mL syringe and filter it with a 0.45 um filter membrane to concentrate the adsorbent on the filter membrane. Then take 1 mL of 10 mg/L DCF solution to pass through the adsorbent at a rate of 1 seconds per drop, collect the filtrate and measure the residual concentration of DCF.

Desorption. The adsorbent loaded with DCF is washed with ultrapure water and methanol. The methanol solution was collected to measure the concentration of DCF.

Effect of pH on adsorption.

In order to inquiry the influence of pH for adsorption experiments, adjust the pH from 6-10 of DCF solutions (40 mL, 20 mg/L) with either 0.5 M HCL and 0.5 M NaOH, adsorbent (5 mg) was added to the solutions.

Adsorbent recycling.

The reusability of sorbent (COF-SO_3H) was estimated after the adsorption of DCF. The COFs (67 mg) loaded in DCF (20 mg/L, 50 mL) was separated by filter and then eluted with ultra-pure water for two times, after that, add 50 mL methanol to the residual solids and magnetic stirrer 2 h. Finally, adsorbent by sucking filtration was collected and vacuum drying 2 h at 45 °C for the next round of adsorption.

The application of COFs in real water or wastewater treatment

In order to study the ability of adsorbent to degrade PPCPs in actual water bodies, tap water, sea water, pearl river water and secondary effluent (Guangzhou, China) were taken, and the suspended matters were removed by filtration with a 0.22 μm membrane. The wastewater was used as the solution for the preparation of DCF-containing solution; the adsorption experiments were conducted with 0.25 g/L COF-SO_3H in 10 mg/L DCF solution at 27 °C for 2 h.

Text S5. Adsorption analysis of diclofenac by adsorbent

Diclofenac concentrations were measured by HPLC with photodiode array (PDA) detection (Shimadzu UV model with SPD-M20A). Analytes were separated on a BEH-C18 column (250×2.1 mm, 1.7 μm). Isocratic elution was carried out at a flow rate of 1 mL min^{-1} with 80% (v/v) HPLC-grade methanol and 20% (v/v) Milli-Q water containing 0.2% formic acid, and the column temperature is 35 °C. A 20-μL aliquot was injected for analysis, and the PDA detector was set to 276 nm. Analytical parameters for HPLC analysis of the other pharmaceuticals are shown in Table S2 of the Supporting Information (SI).

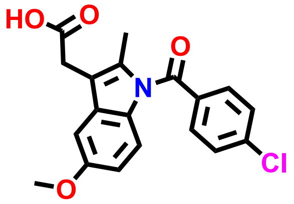
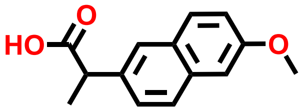
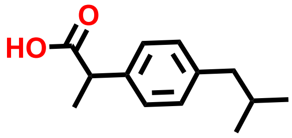
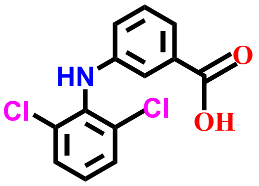
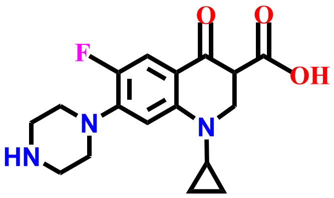
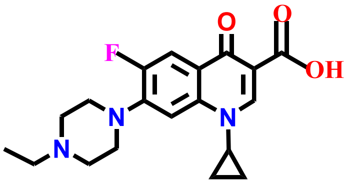
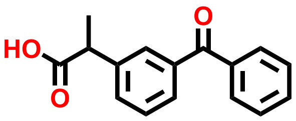
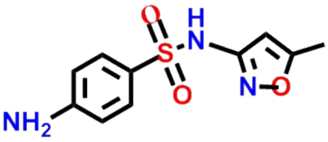
Table S1. DCF sorption performance of various sorbent materials

Adsorbents	**SA_{BET} (m^2/g)**	**Q_{max} (mg/g)**	**References**
UiO-66	1082	189	[1]
18%SO3-UiO-66	910	263	[2]
Commercial AC	1016	83	[3]
OAC (2.0)	704	487	[2]
Polyaniline	-	43.146	[4]
ZHB-30	-	67.4	[5]
GO	-	500	[6]
r GO	98 cm^2/g	59.67	[7]
Grape bagasse	2	77	[8]
AC from agricultural by-product	793	56	[9]
Mercapto-functionalized hexagonal mesoporous silicate	912	80	[10]
CTAB-ZIF-67	871	54.31	[1]
Zeolite modified with Cetylpyridiumchloride	68.6	160	[11]
TAB-DVA-COF	457	90.7	This work
COF-SO_3H	15	**770**	This work

Table S2. HPLC-UV parameters for drugs analysis

Pharmaceuticals	Mobile phase composition		Detection wavelength (nm)
	Methanol	H_2O (0.2% formic acid)	
Indomethacin	75%	25%	270
Naproxen	70%	30%	262
Ibuprofen	75%	25%	220
Diclofenac	80%	20%	276
Ciprofloxacin	35%	65%	278
Enrofloxacin	23%	77%	278
Ketoprofen	70%	30%	254
Sulfamethoxazole sulfisoxazole	40%	60%	275
Sulfamethazine	30%	70%	262
Bisphenol A	60%	40%	230
Bisphenol B	Acetonitrile 50%	H_2O (0.2% Acetic acid) 50%	223
Bisphenol C	Acetonitrile 50%	H_2O (0.2% Acetic acid) 50%	225

Table S3. Structures and physicochemical properties of pharmaceuticals.

Sequence Number	Pharmaceuticals	Structure	Molar Weight [g/mol]
P1	Indomethacin		357.79
P2	Naproxen		230.26
P3	Ibuprofen		206.28
P4	Diclofenac		296.15
P5	Ciprofloxacin		331
P6	Enrofloxacin		359.4
P7	Ketoprofen		254.28
P8	Sulfamethoxazole		253.28

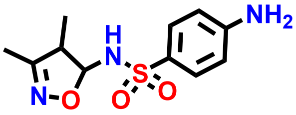
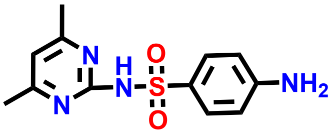
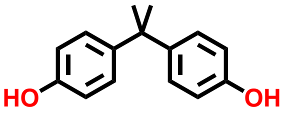
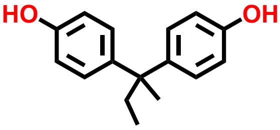
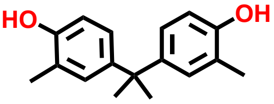
P9	Sulfafurazole		267.30
P10	Sulfamethazine		278.33
P11	Bisphenol A		228.29
P12	Bisphenol B		242.31
P13	Bisphenol C		256.34

Table S4. Pseudo-first order, Pseudo-second order, Intra-particle diffusion and Liquid film diffusion kinetic model parameters with respect to adsorption of DCF.

Kinetic Model	Parameters	DCF
Pseudo-first order	$Q_{e, exp}$	399.3
	$Q_{e, cal}$	263.57
	K_1	0.2156
	R^2	0.9124
Pseudo-second order	$Q_{e, exp}$	399.3
	$Q_{e, cal}$	434.78
	K_2	$1.13*10^{-3}$
	R^2	0.9979
Intra-particle diffusion	K_i	70.203
	C	83.758
	R^2	0.8318
Liquid film diffusion	K_{fd}	0.2562
	R^2	0.9654

Table S5: Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm parameters with respect to adsorption of DCF.

Isotherm Model	Parameters	25 °C	35 °C	45 °C
Langmuir	$Q_{e, exp}$	770	736.7	701.5
	Q_{max}	775.2	740.7	740.7
	K_L	4.62	4.48	0.42
	R^2	0.9996	0.9996	0.9836
Freundlich	n	9.42	10.22	4.89
	K_F	570.24	550.62	346.20
	R^2	0.8944	0.9152	0.4547
Temkin	B	63.82	57.25	104.88
	a_T	9276.01	$1.82*10^4$	24.24
	b_T	38.82	43.28	23.62
	R^2	0.9404	0.9479	0.5573
Dubinin-Redushkevich	Q_m	743.30	715.52	679.49
	β	$4.81*10^{-9}$	$2.15*10^{-8}$	$5.28*10^{-7}$
	R^2	0.8971	0.9014	0.2677

Table S6: Thermodynamic values of $\Delta G°, \Delta H°\ and\ \Delta S°$ at three temperature of 298, 308, and 318 K with respect to adsorption of DCF.

Adsorbent	Pollutants	T, K	Kc	$\Delta G°$, KJmol^{-1}	$\Delta H°$, KJmol^{-1}	$\Delta S°$, Jmol^{-1} K^{-1}
COF-SO_3H	DCF	298	28.73	-8324.6	-1.18*10^4	-12.13
		308	22.93	-8015		
		318	18.58	-7720		

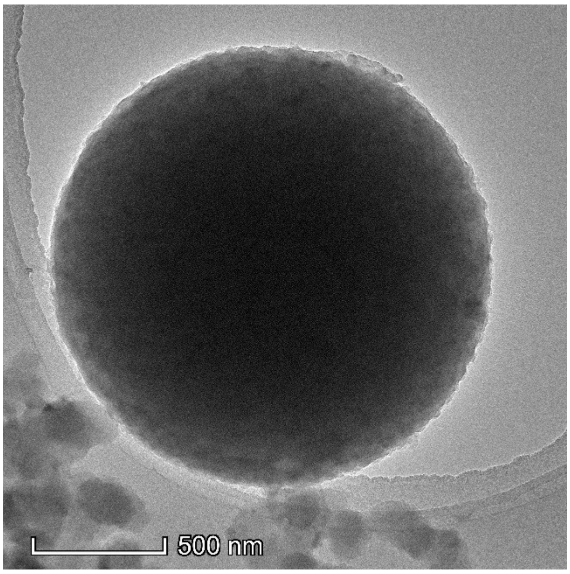
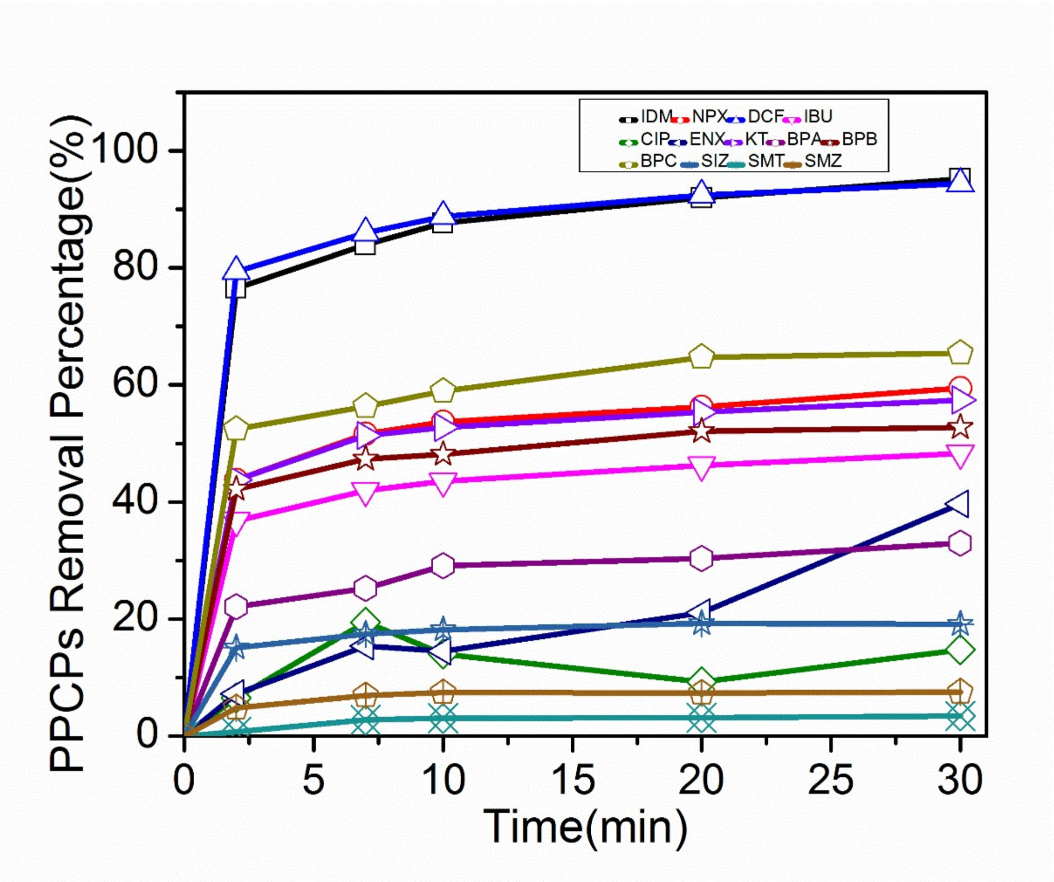
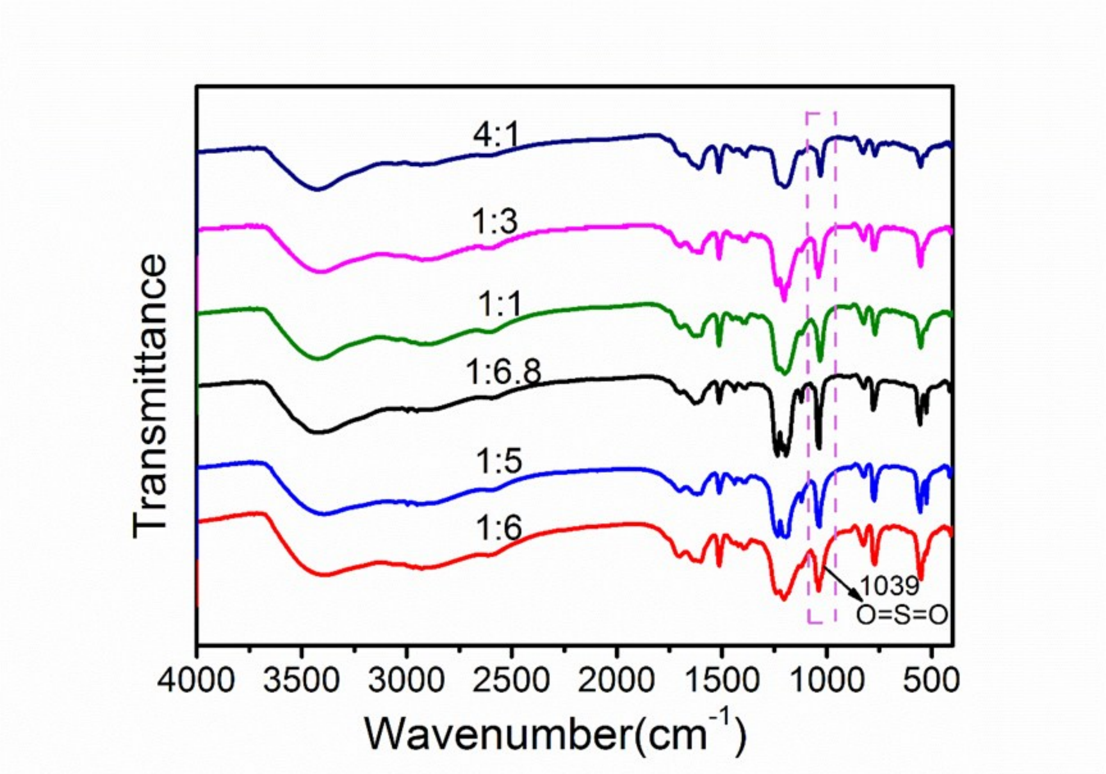


Figure S1. The TEM of COF-SO3H (for mapping).



FigureS2.Time-dependent removal efficiency of various PPCPs in the presence of COF-SO$_3$H. adsorbent (5 mg), PPCPs concentration (10 mg/L), volume of the solution (60 mL).



FigureS3. FT-IR spectrum of different COF-SO_3H.

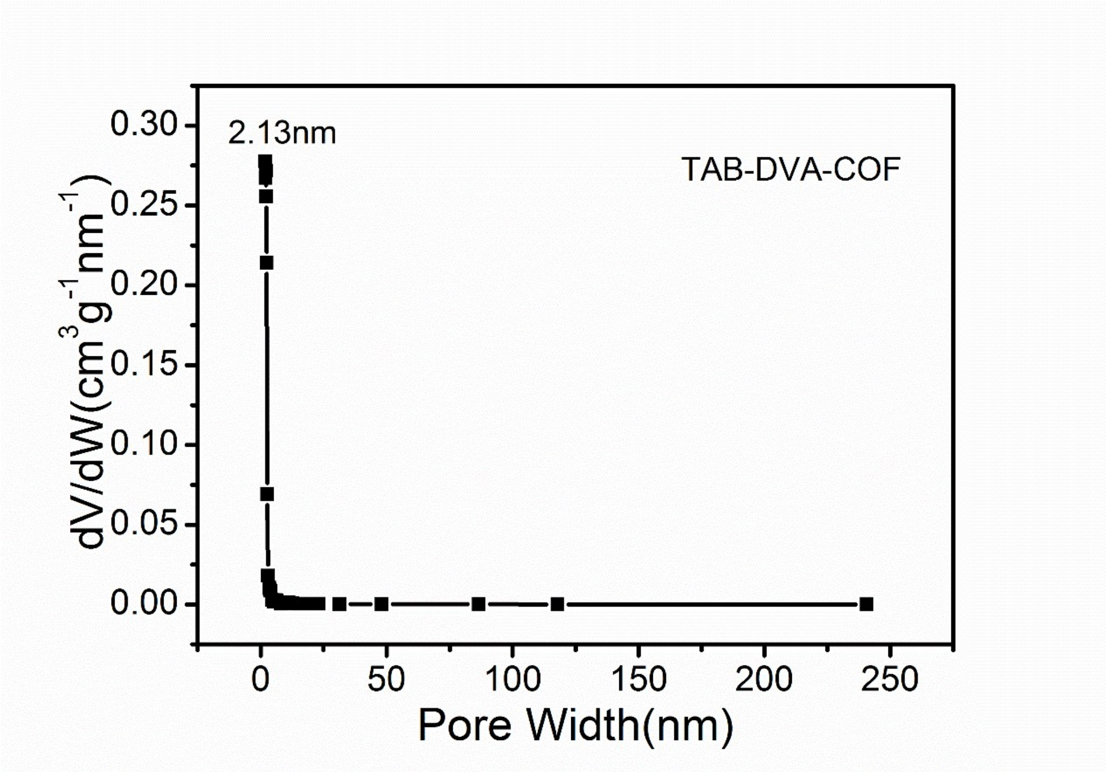


Figure S4. Pore size distribution of TAB-DVA-COF calculation based upon NLDFT.

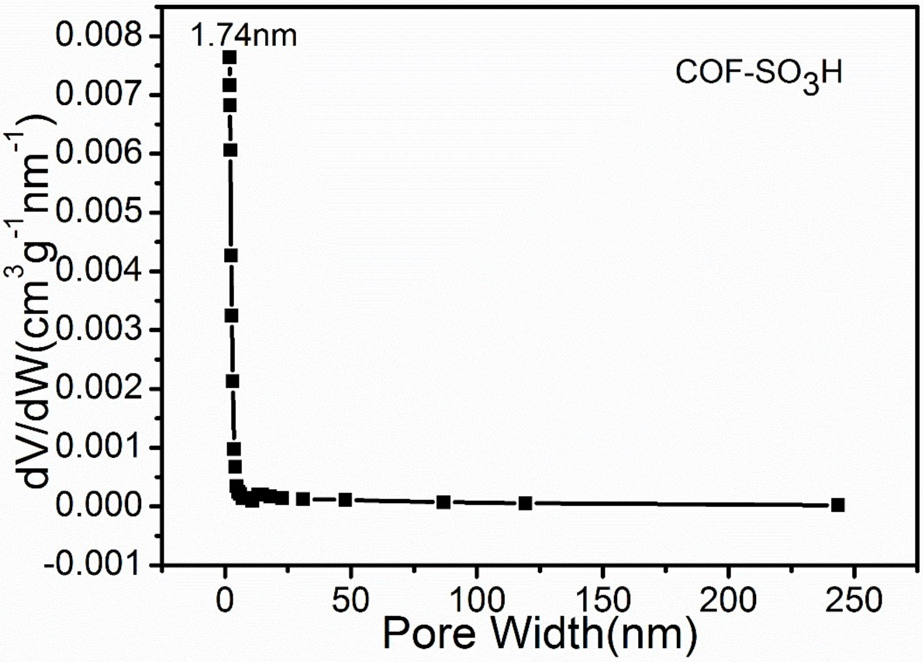


Figure S5. Pore size distribution of COF-SO_3H calculation based upon NLDFT.

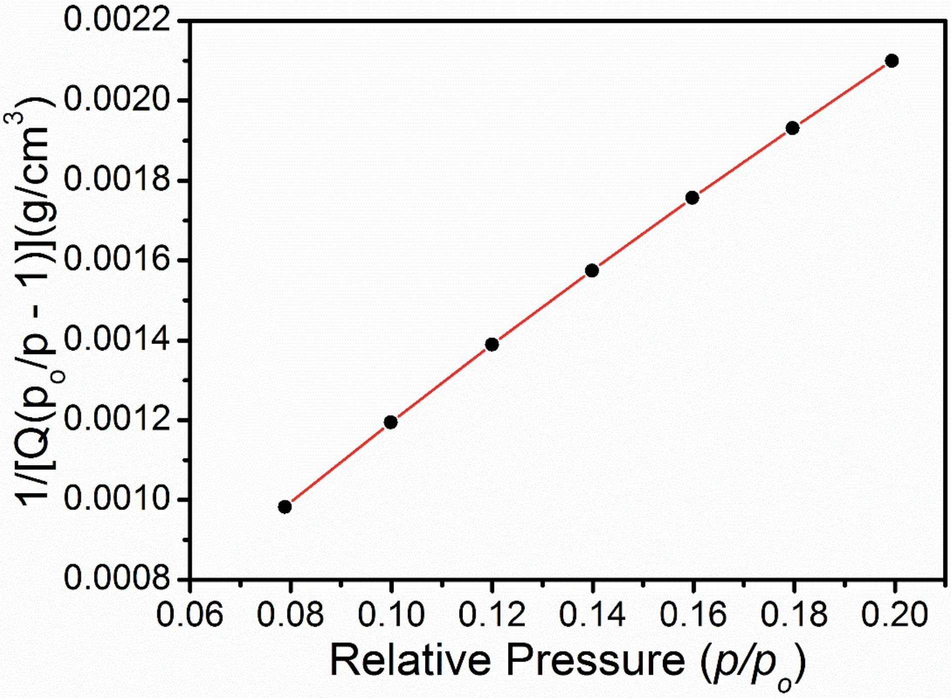


Figure S6. BET plot for TAB-DVA-COF.

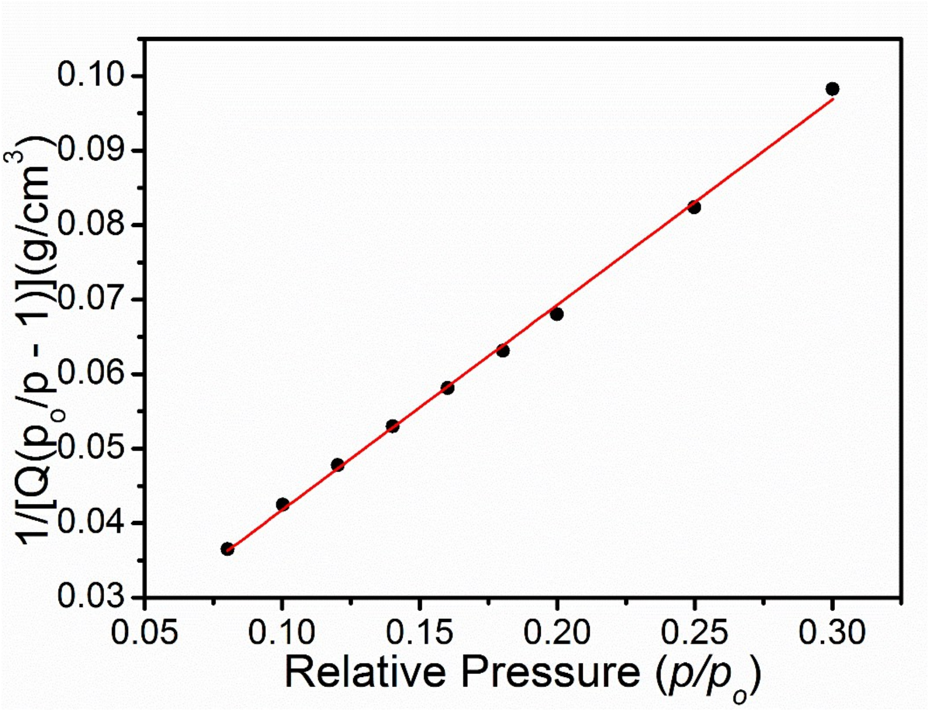


Figure S7. BET plot for COF-SO_3H.

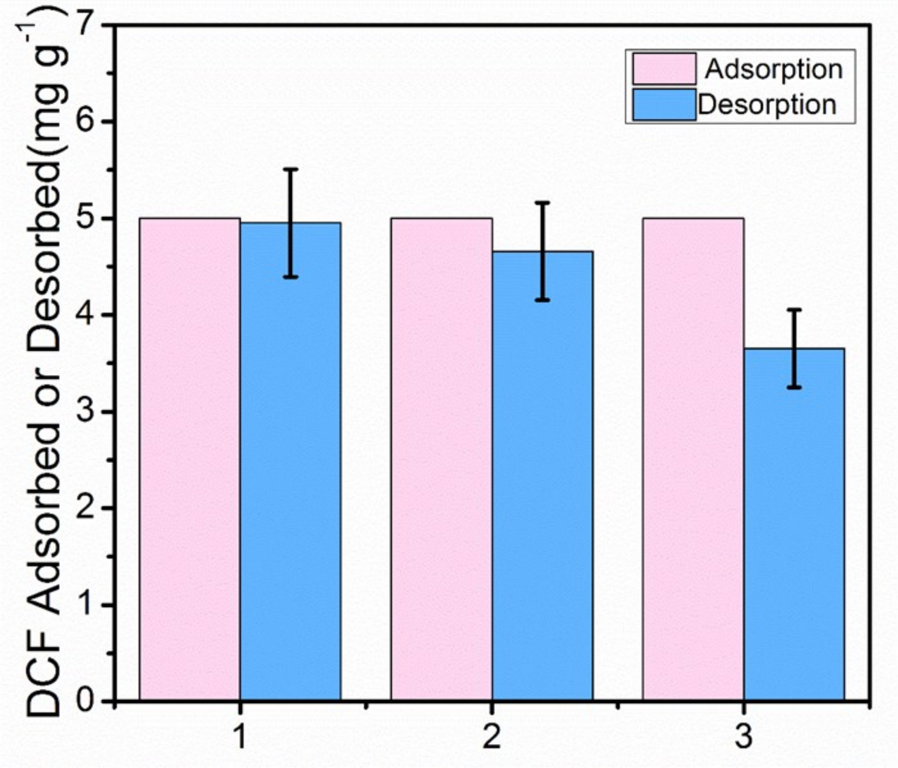


Figure S8. Adsorption and desorption experiment of DCF. Adsorption: Adsorbent (2 g/L), DCF concentration is 10 mg/L. Desorption: The COF-SO_3H was washed with CH_3OH. Error bars: standard deviation of 3 experiment

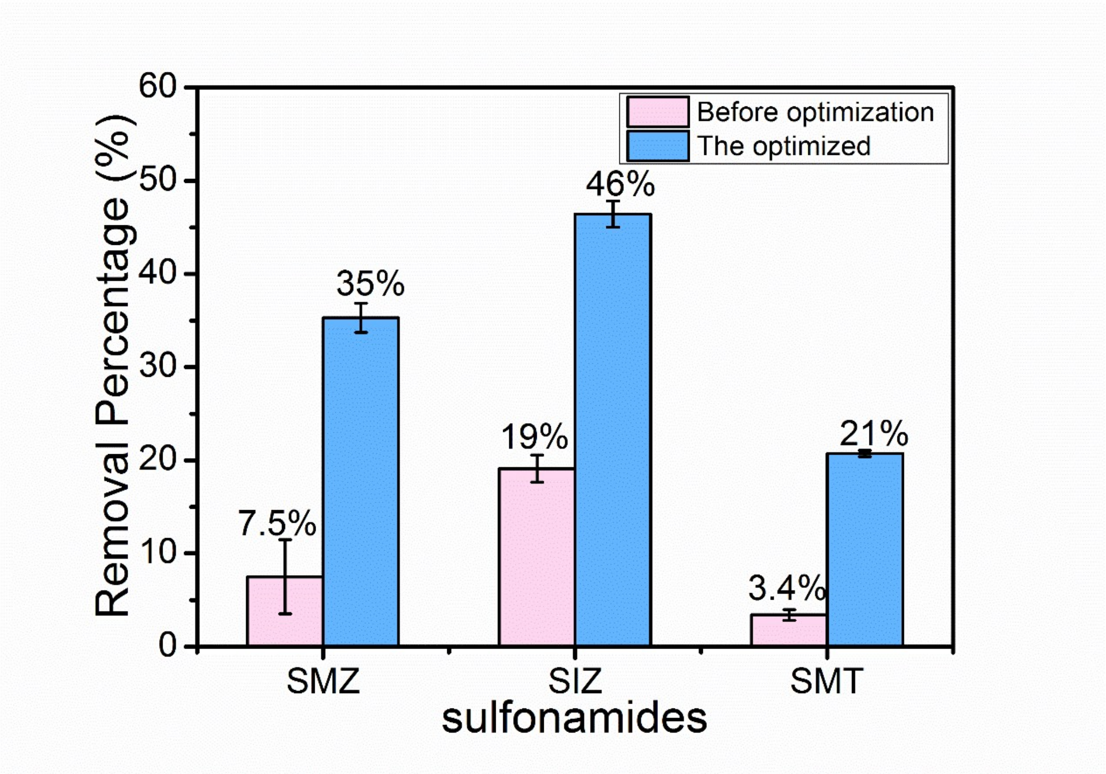


Figure S9. Adsorption of sulfonamides by optimized conditions: COF-SO_3H concentration (0.25 g/L), pollutant concentration (10 mg/L), pH=6.5, reaction time (7 h).

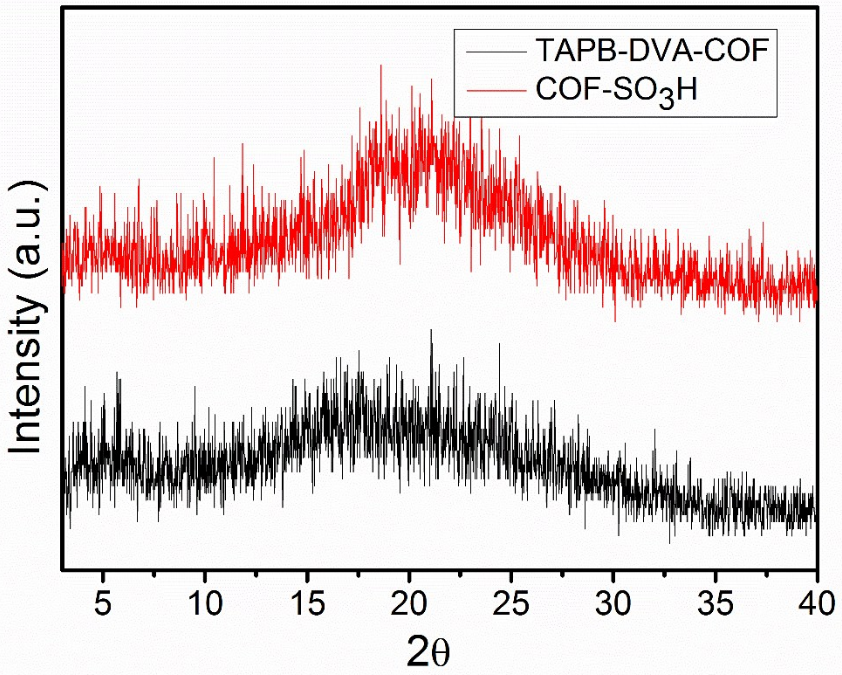


Figure S10. XRD profiles of TAPB-DVA-COF and COF-SO$_3$H.

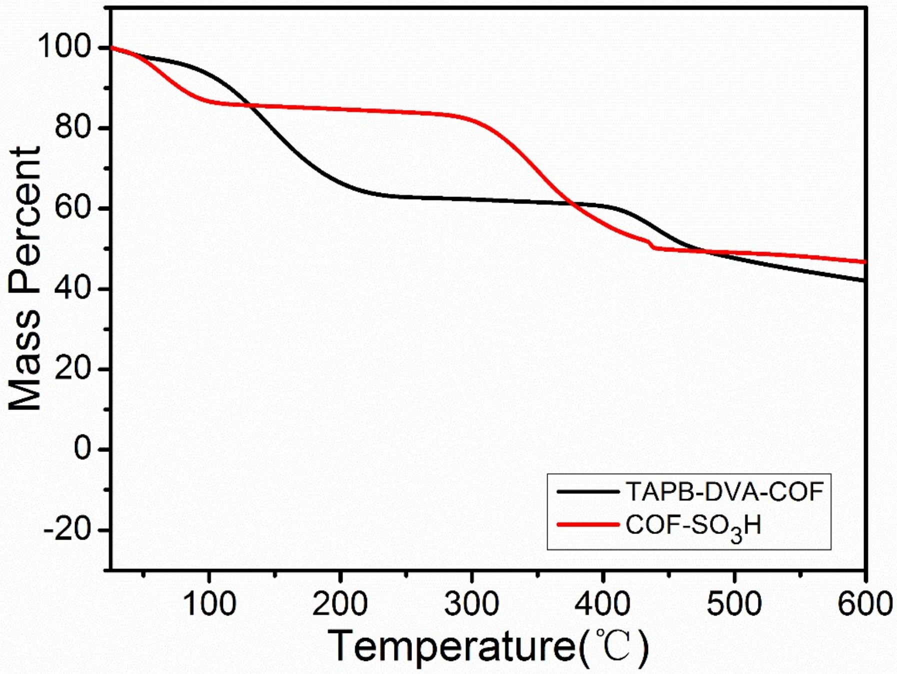


Figure S11. The TGA analysis of TAPB-DVA-COF and COF-SO$_3$H.

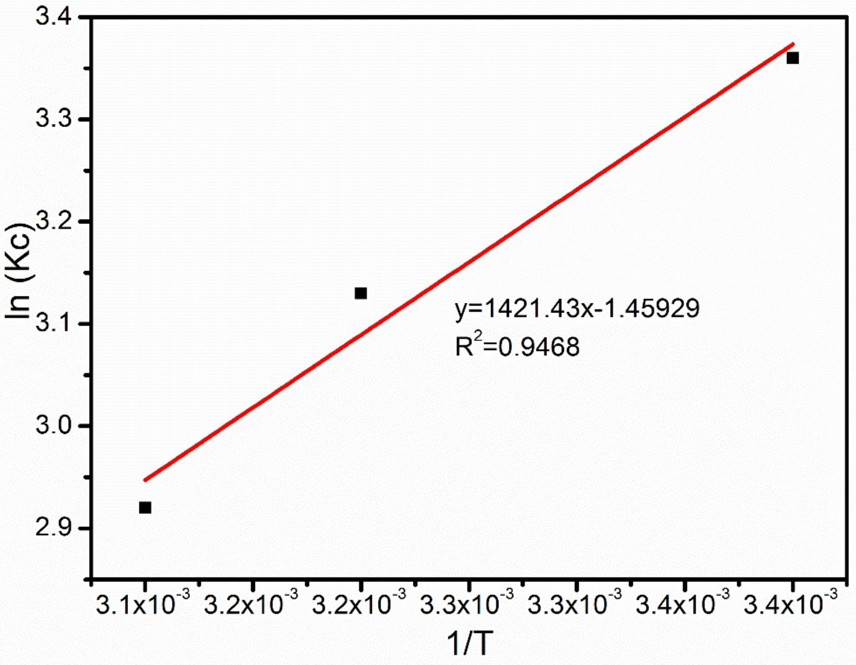


Figure S12. Van’t Hoff plots to obtain the ΔHº and ΔSº values of the DCF.

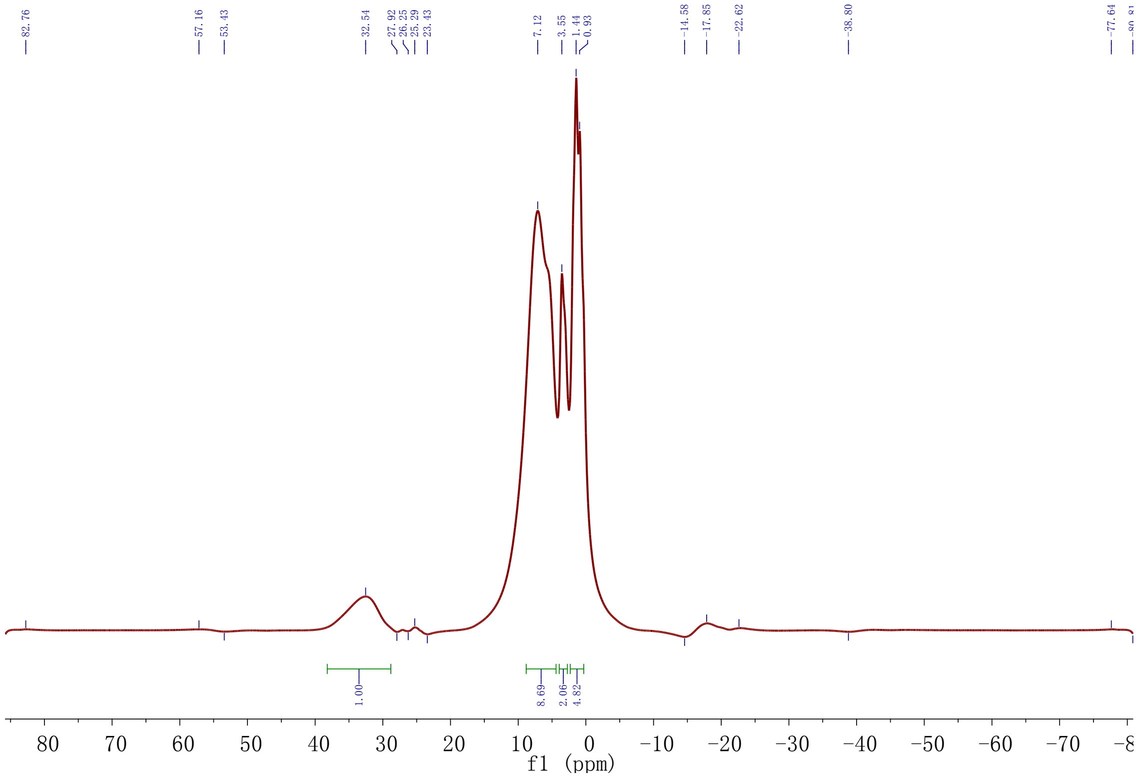


Figure S13. ^{1}H NMR Spectra of COF-SO$_3$H.

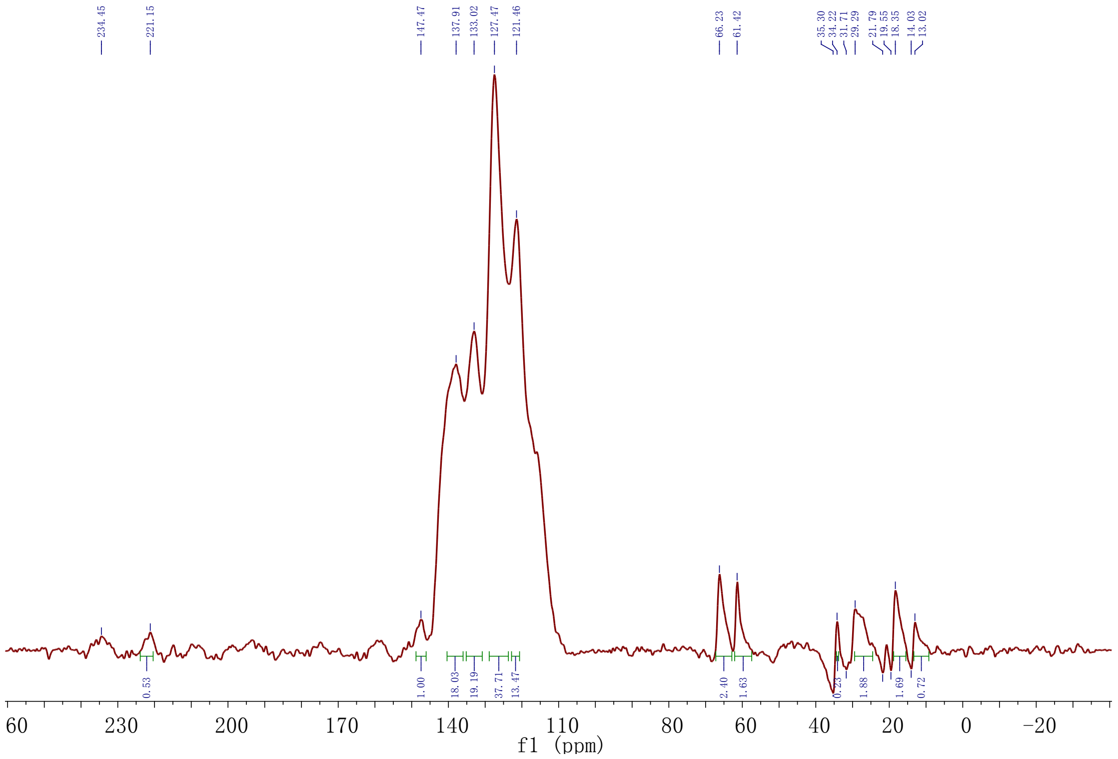


Figure S14. ^{13}C NMR Spectra of TAB-DVA-COF.

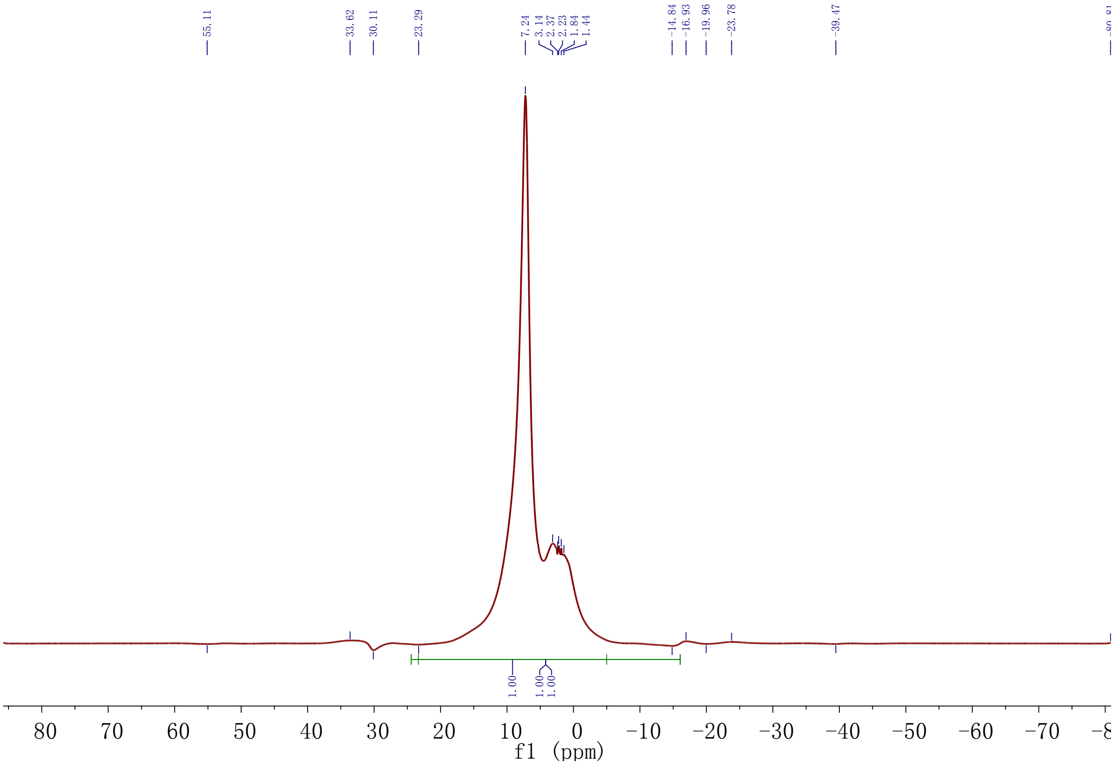


Figure S15. ^{1} H NMR Spectra of TAB-DVA-COF.

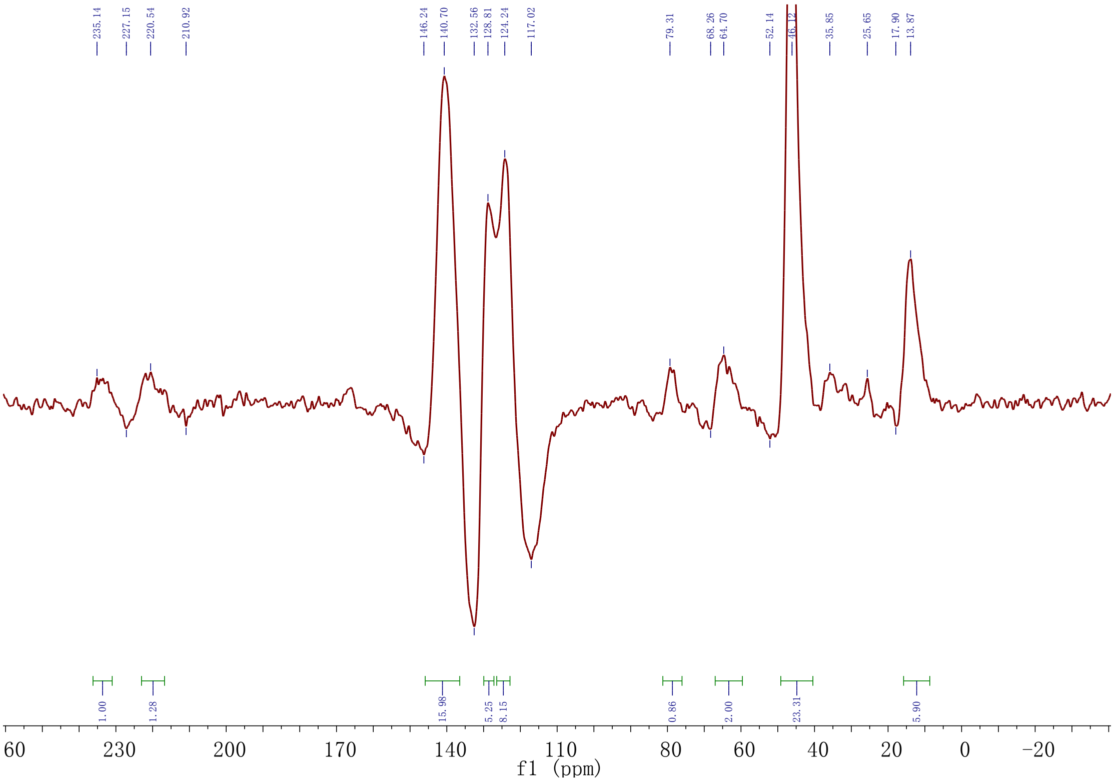


Figure S16. ^{13} C NMR Spectra of COF-SO_3H.

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