

Electronic Supplementary Information (ESI)

A covalent organic framework bearing thioether pendant arms for selective detection and recovery of Au from ultra-low concentration aqueous solution

Zhiming Zhou,^{ab} Wanfu Zhong,^{ab} Kaixun Cui,^{ab} Zanyong Zhuang,^{ab} Lingyun Li,^{ab} Liuyi Li,^{*ab} Jinhong Bi^b and Yan Yu^{*ab}

^a College of Materials Science and Engineering, Fuzhou University, Minhou, Fujian 350108, China.

^b Key Laboratory of Eco-materials Advanced Technology, Fuzhou University, Fuzhou, Fujian 350108, China.

E-mail address: lyli@fzu.edu.cn; yuyan@fzu.edu.cn

Section 1. Materials and Methods

All starting materials and solvents, unless otherwise specified, were purchased in high purity from commercial sources and used without further purification. 1,3,5-triformylbenzene (TFB) was synthesized according to the reported procedure.¹

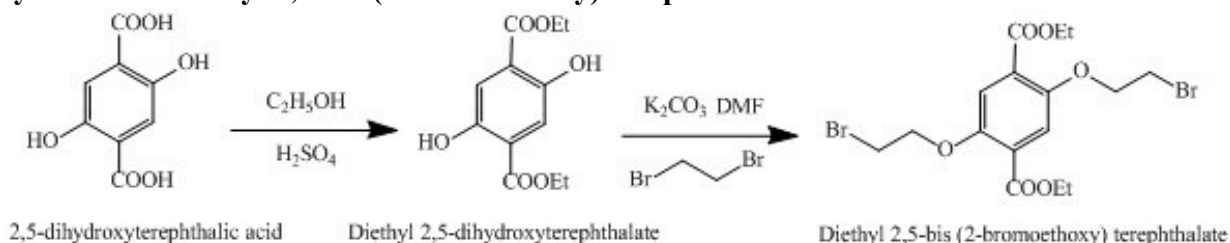
Powder X-ray diffraction (PXRD) data were recorded on a DY5261/Xpert3 diffractometer (Scan step size: 0.013°, Time per step: 18.87 s). FT-IR spectra were recorded with a Nicolet 5700 instrument and was used to study the changes of the characteristic functional groups to determine if the condensation reaction occurred. Elemental analysis was carried out on a Vario EL Cube elemental analyzer. The morphology of the TTB-COF was examined by scanning electron microscopy (SEM, Philips XL30) and transmission electron microscopy (TEM, FEI Tecnai G2 F30) operated at an accelerating voltage of 200 kV. Liquid ¹H and ¹³C NMR spectra were collected on a Bruker Avance III 500 MHz NMR in CDCl₃ at 25 °C. The solid-state ¹³C NMR experiments were performed on a Bruker Avance III 500 NMR spectrometer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 system. The samples were outgassed at 120 °C for 12 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore size distribution was calculated by using the nonlocal density functional theory (NLDFT)

method. The thermal properties of TTB-COF material were evaluated using a DIL402C thermogravimetric analysis (TGA) instrument over the temperature range of 25 to 800 °C under Argon atmosphere with a heating rate of 10 °C/min. The species of the elements in the samples before and after the adsorption of metal ions and Changes in valence were investigated by X-ray photoelectron spectrometry (XPS, ESCALAB 250). UV-Vis spectra were recorded using a Agilent Cary 5000 spectrometer. Fluorescence spectra were recorded at room temperature using a FM-4 spectrophotometer, and the slit width for both excitation and emission was 3 nm.

Theoretical Calculations: The density functional theory (DFT) method at the hybrid Becke three-parameter Lee-YangParr (B3LYP)² functional level was used to optimize the geometrical structures firstly. During the optimization processes, the convergent values of maximum force, root-mean-square (RMS) force, maximum displacement, and RMS displacement were set by default. Then, the natural bond orbital (NBO) analysis³ was implemented. In these calculations, the all-electron basis set of 6311G**⁴ was used. All calculations were implemented in Gaussian 09 program.⁵ Visualization of the optimized geometrical structures, frontier molecular orbitals, and electrostatic potential (ESP) mapped onto electron density surfaces were performed by GaussView.

Section 2. Synthetic Procedures

Synthesis of Diethyl 2,5-bis (2-bromoethoxy) terephthalate.

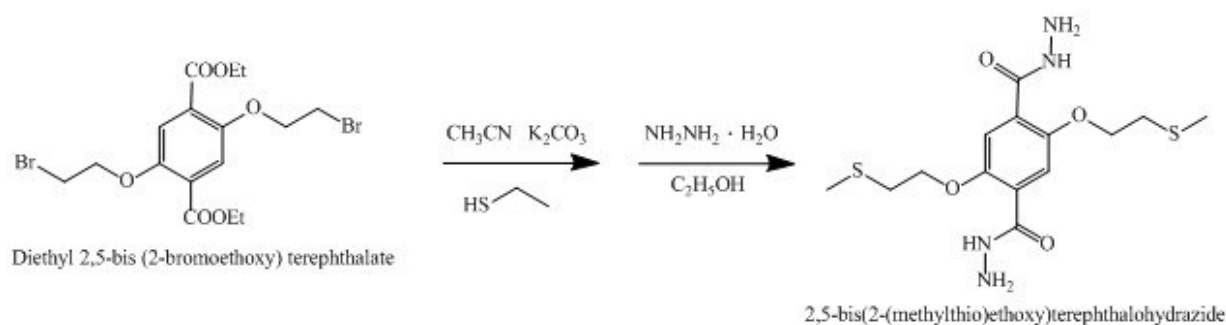


Scheme S1. Synthesis of diethyl 2,5-bis (2-bromoethoxy) terephthalate.

A mixture of 2,5-dihydroxyterephthalic acid (3.0 g, 15.1 mmol), concentrated sulfuric acid (5 mL, 93.88 mmol) in ethanol (100 mL) were heated to 80 °C for 15 h. After cooling to room temperature, the mixture was filtered and washed with water to give diethyl 2,5-dihydroxyterephthalate as a yellow-green crystal.

A mixture of diethyl 2,5-dihydroxyterephthalate (1 g) potassium carbonate (5.44 g), 1,2-dibromoethane (14.78 g) in N,N-dimethylamide (10 mL) was stirred at room temperature for 16 h. After filtration, the filtrate was diluted with dichloromethane, and then washed 5 times with saturated saline, dried over anhydrous sodium sulfate. After evaporation, the solid was purified by column chromatography on silica gel to give 2,5-bis(2-bromoethoxy) terephthalate as a white solid.

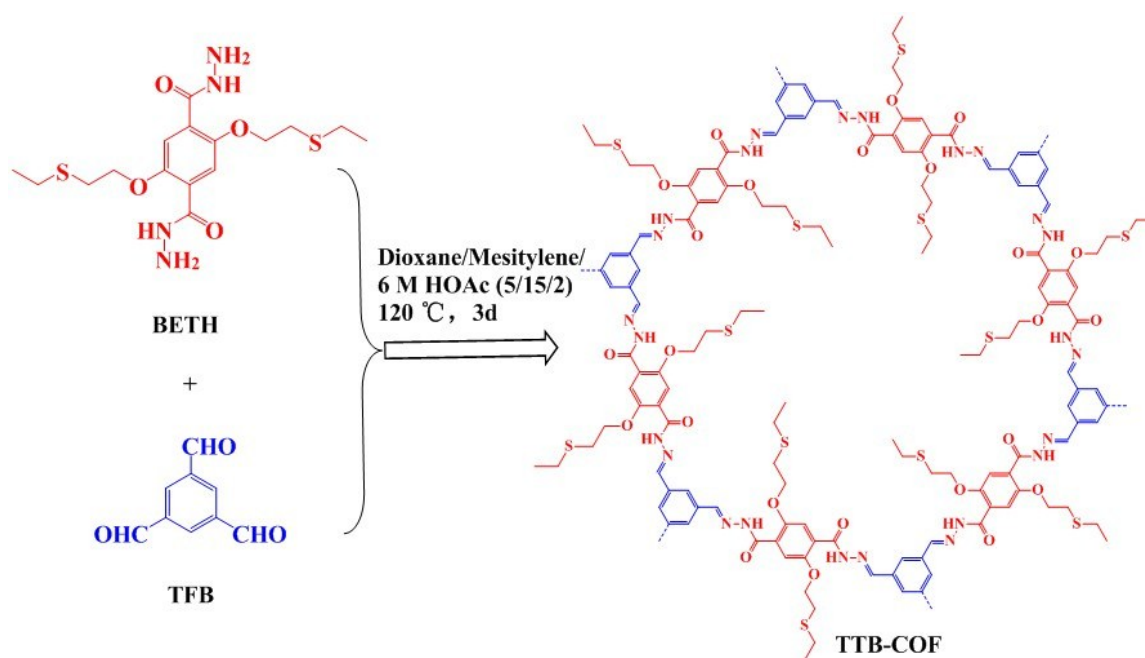
Synthesis of 2,5-bis(2-(ethylthio)ethoxy)terephthalohydrazide (BETH).



Scheme S2. Scheme of synthesis of 2,5-bis(2-(ethylthio)ethoxy)terephthalohydrazide (BETH).

To a solution of diethyl 2,5-bis(2-bromoethoxy) terephthalate (1.0 g, 2.1 mmol) and excess potassium carbonate (0.89 g, 6.3 mmol) in CH₃CN (10 mL) was added ethylthiol (6.9 mmol, 0.50 mL). The mixture was stirred and heated at 80 °C for 48 h. After the reaction was completed, the mixture was cooled in an ice-water bath, then filtered. The mixture was rotary evaporated, and then the crude product was purified by flash chromatography (ethyl acetate) to gain a pale yellow oil. To a solution of the yellow oil in absolute ethanol (10 mL) was added hydrazine hydrate (42 mmol, 2.0 mL). The mixture was stirred and heated at 80 °C for 12 h. After cooling to room temperature, the precipitate was separated by filtration, washed with water and dried to give 2,5-bis(2-(ethylthio)ethoxy)terephthalohydrazide as a white solid (0.71 g, 82% yield). ¹H NMR (400MHz, DMSO-d₆): 1.21 (t, J = 7.3 Hz, 6H), 2.96 (t, J = 6.3 Hz, 4H), 3.34 (s, 4H), 4.23 (t, J = 6.3 Hz, 4H), 4.60 (4H, NHNH₂), 7.47 (2H, s, H-Ar), 9.36 (2H, CONHNH₂). ¹³C NMR (100MHz, DMSO-d₆): δ=15.31, 25.53, 30.09, 69.76, 115.59, 125.40, 150.03, 163.89.

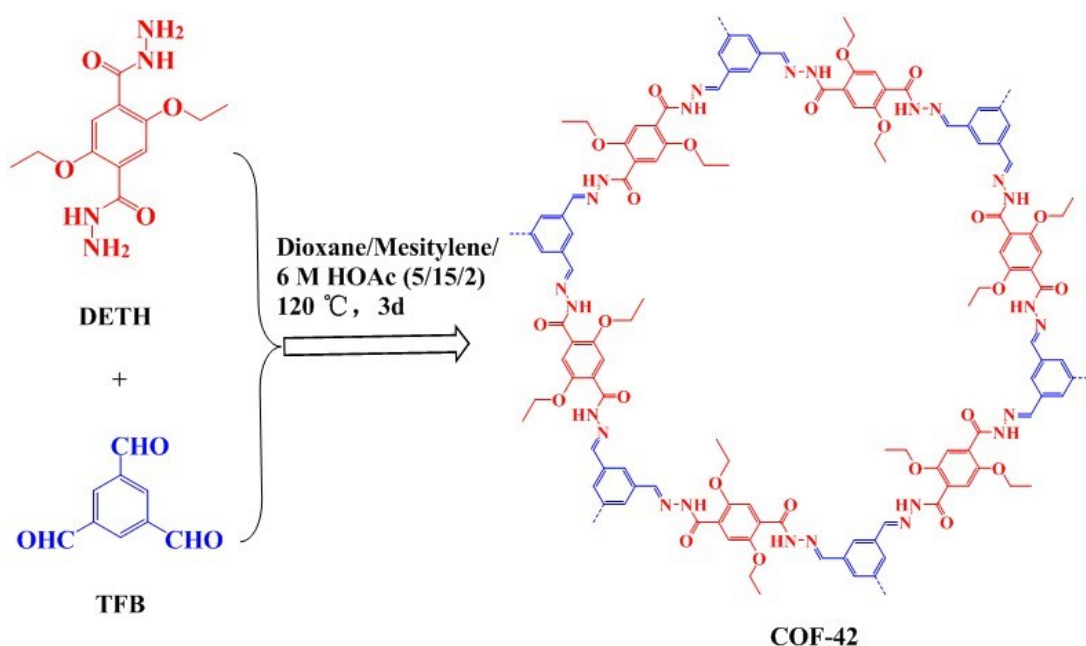
Synthesis of TTB-COF.



Scheme S3. Scheme of synthesis of TTB-COF.

An 1,4-dioxane/mesitylene/6.0 M aqueous acetic acid (v:v:v=5/15/2 by vol: 1.2 mL) mixture of 2,5-bis(2-(ethylthio)ethoxy)terephthalohydrazide BETH (30 mg, 0.075 mmol) and 1,3,5-triformylbenzene TFB (8 mg, 0.050 mmol) in a Pyrex tube was degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days, yielding a yellow solid. The precipitate was collected by filtration, washed three times with anhydrous THF and three times with acetone. The yellow powder was dried at 80 °C under vacuum overnight to yield the TTB-COF (31 mg, 80% yield). TTB-COF could also be successfully synthesized with high crystallinity under other different conditions, such as in ethanol (EtOH/mesitylene/6.0 M HOAc) and in N,N-dimethylformamide (DMF/mesitylene/6.0 M HOAc) (see Figure S4). Anal. Cald for $(C_{11}H_{13}N_2O_2S)_n$: C 55.68; H 5.52; N 11.81, S 13.51. Found: C 55.59; H 5.68; N 10.42, S 9.32. IR (powder, cm^{-1}) : 3448, 3277, 2967, 2924, 1671, 1618, 1535, 1490, 1459, 1413, 1383,1215, 1076, 1007, 772, 578.

Synthesis of COF-42. COF-42 was synthesized according to the reported procedure.⁶



Scheme S4. Scheme of synthesis of COF-42.

Stability test of TTB-COF. A 10 mg sample of COFs was immersed in 5 mL of ethanol, acetone, tetrahydrofuran (THF), methanol (MeOH), N,N-dimethylformamide (DMF), and H₂O, at 25 °C for 48 hours. Then, the samples were rinsed with acetone, dried under vacuum at 80 °C for 24 h, and characterized by PXRD.

Detection of fluorescence selective quenching. Stock solution of TTB-COF (0.05 mg/mL) was prepared by dispersion of TTB-COF in acetonitrile. For the sensing (sensitivity and selectivity) tests, 3 mL of TTB-COF stock solution (0.05 mg/mL) was placed in a 4 mL quartz cuvette. The

fluorescence spectra were recorded immediately after an appropriate aliquot of the solution of metal ions (Au^{3+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Co^{2+} , and Ni^{2+}) was added. The shape of the emission spectra was not changed upon the addition of the stock solutions of metal ions. All the measurements, unless otherwise noted, were excited at $\lambda_{\text{ex}} = 394$ nm and the corresponding emission wavelength was tested from $\lambda_{\text{em}} = 420$ to 720 nm.

Metal ions sorption experiments. Unless otherwise specified, aqueous solutions of metal ions with different concentrations are obtained by diluting the starting metal solution with the suitable amount of distilled water. The concentration of metal ions in the aqueous metal ions solution was tested by Atomic Absorption Spectrometry (AAS) for all Adsorption experiments. All adsorption experiments were carried out under ambient conditions.

Au(III) sorption isotherms. TTb-COF (10.0 mg) was added to each glass beaker (100 mL) containing the stock solution (50 mL) of Au(III) at different concentrations. The mixture was stirred for 12 h at room temperature with a magnetic stirrer, at which time it was assumed that adsorption equilibrium had been reached and then filtered through filter paper. The filtrate was collected and analyzed by AAS to determine the remaining Au content.

Au(III) sorption kinetics. TTb-COF (10.0 mg) was added to a glass beaker (100 mL) containing 10 ppm Au(III) aqueous solution (50 mL). The mixture was stirred at room temperature for 90 minutes. At given time intervals, an aliquot (3 mL) was taken from the mixture. Aliquots were centrifuged through a centrifuge and the supernatant was taken. The resulting solution was analyzed for Au(III) concentration by AAS.

The equilibrium capacity (Q_e , mg g^{-1}) and the capture efficiency (R_e , %) of all adsorbents were calculated according to eqn (1) and (2), respectively:

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$R_e = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

where C_o and C_e are the initial and the equilibrium concentration (mg L^{-1}) of Au(III), respectively, V is the volume of solution (mL), and m is the weight of the adsorbent (mg).

Selective au(iii) adsorption tests. TTb-COF (10.0 mg) was added to each glass beaker (100 mL) containing a 50-mL aqueous solution of Au^{3+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Co^{2+} , and Ni^{2+} with each concentration at 10 ppm. The mixture is stirred at room temperature for 90 minutes. At given

time intervals, an aliquot (3 mL) was taken from the mixture. Aliquots were centrifuged through a centrifuge and the supernatant was taken. The resulting solution was analyzed for metal ions concentration by Atomic Absorption Spectrometry (AAS).

Recycling experiment. TTB-COF (100.0 mg) was added to each glass beaker (100 mL) containing Au^{3+} solution (50 mL) at 100 ppm. The mixture was stirred at room temperature for 6 h, filtered through filter paper and washed with water (30 mL). The recycled Au/TTB-COF was stirred in 50 mL aqueous Na_2S solution (1.0 M) for 6 h, filtered and washed with water (30 mL), the TTB-COF was regenerated and used for the next cycle until 4 cycles.

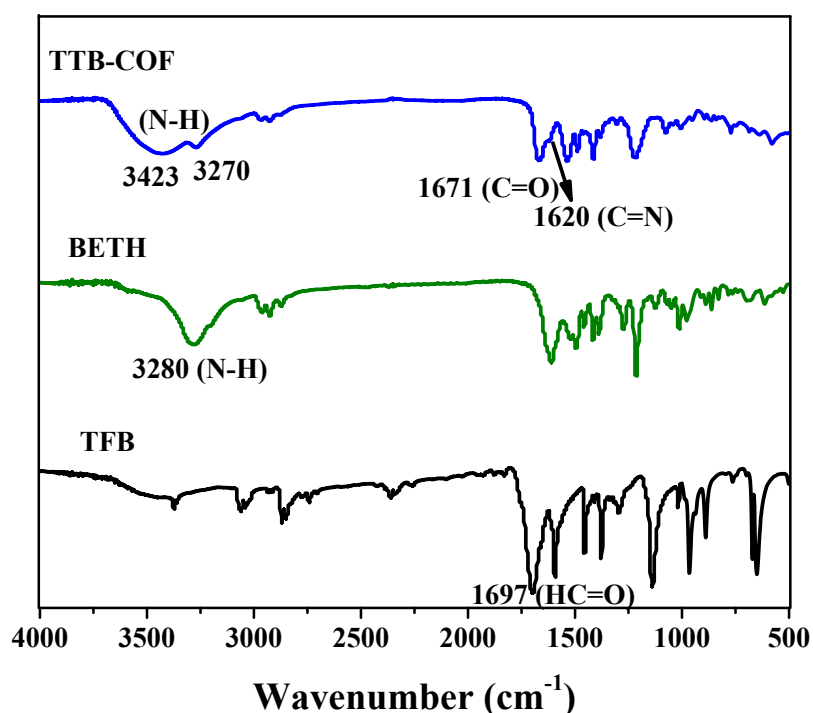


Figure S1. FT-IR spectra for TTB-COF (blue), BETH (green), and TFB (black).

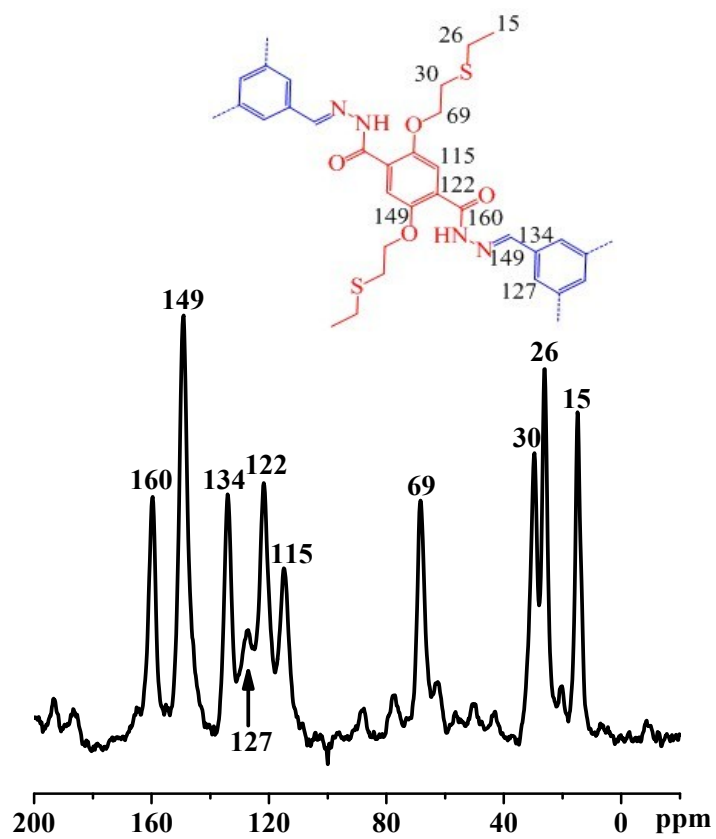


Figure S2. Solid state ¹³C NMR spectrum of TTB-COF.

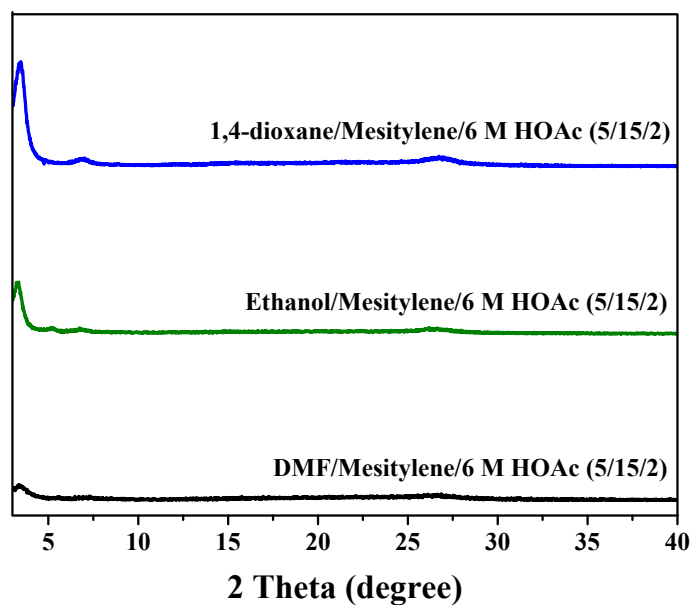


Figure S3. XRD patterns of TTB-COF synthesized under different solvent conditions.

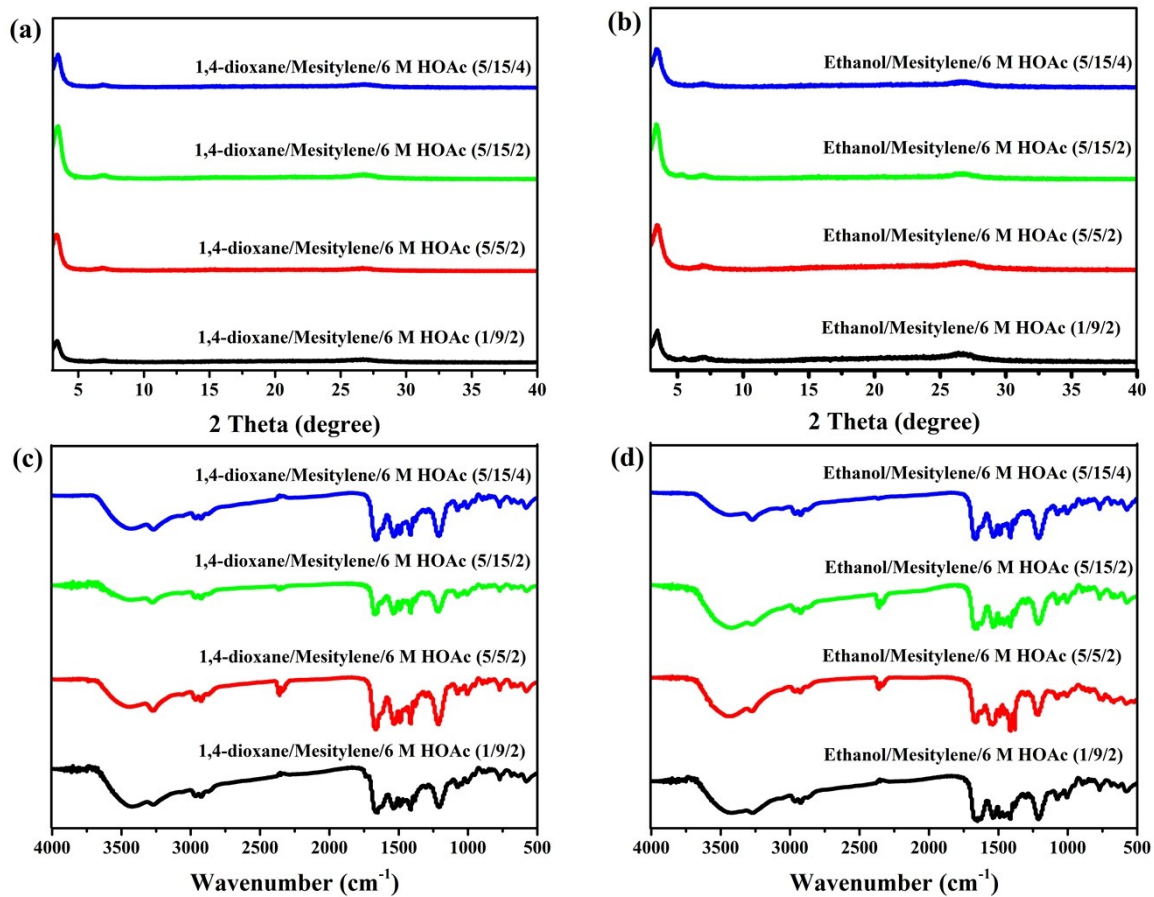


Figure S4. (a, b) XRD patterns of TTB-COF synthesized under different solvent conditions. (c, d) FT-IR spectra for TTB-COF synthesized under different solvent conditions.

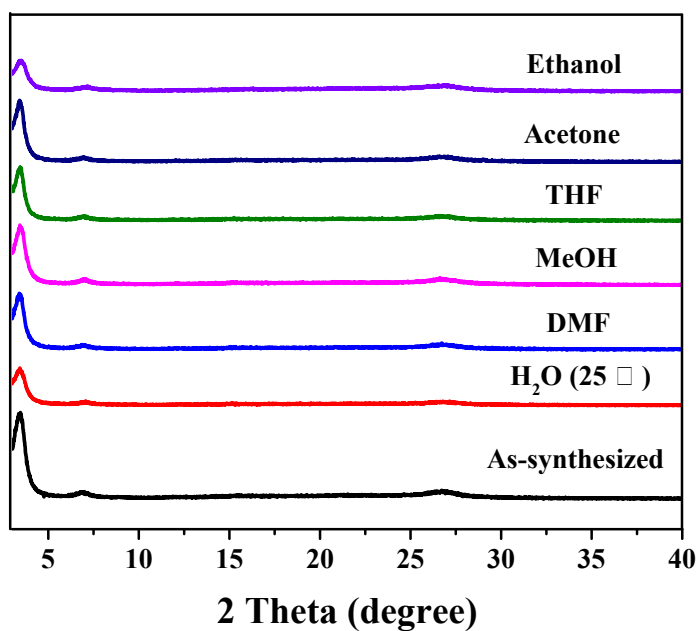


Figure S5. XRD patterns of TTB-COF before and after treatment for 48 h in various solvents.

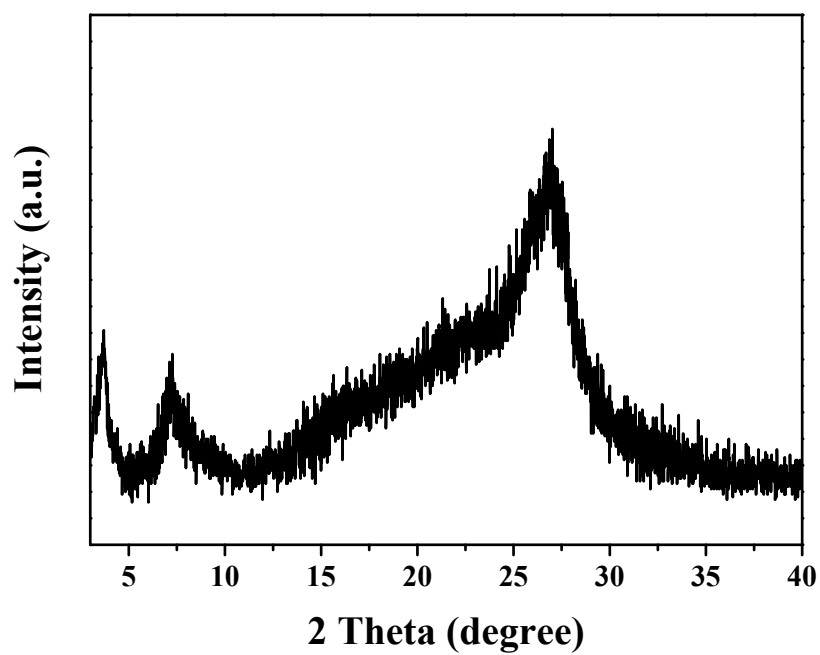


Figure S6. XRD pattern of TTB-COF after heating at 100°C in 1M HCl for 24 h.

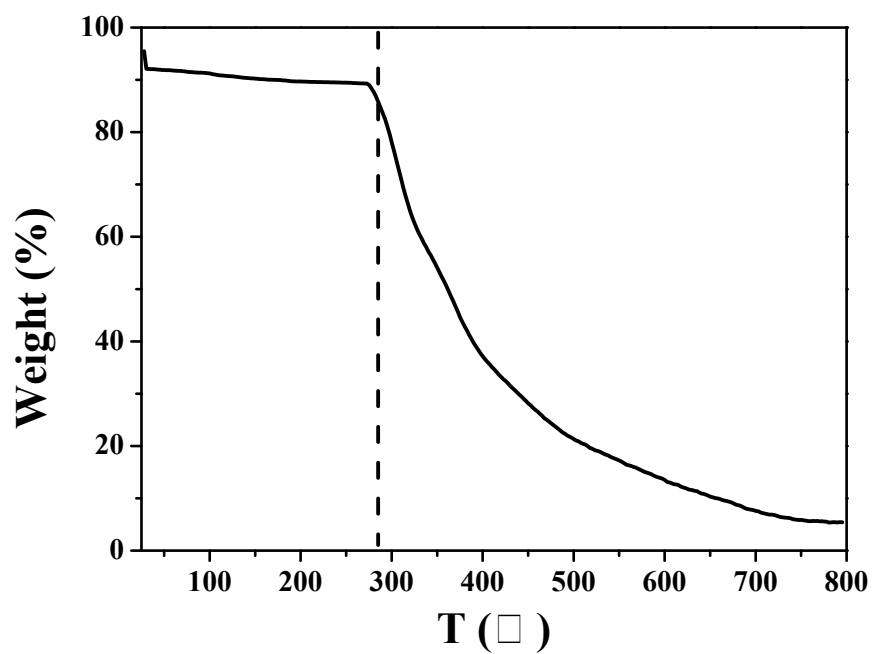


Figure S7. TGA data for TTB-COF.

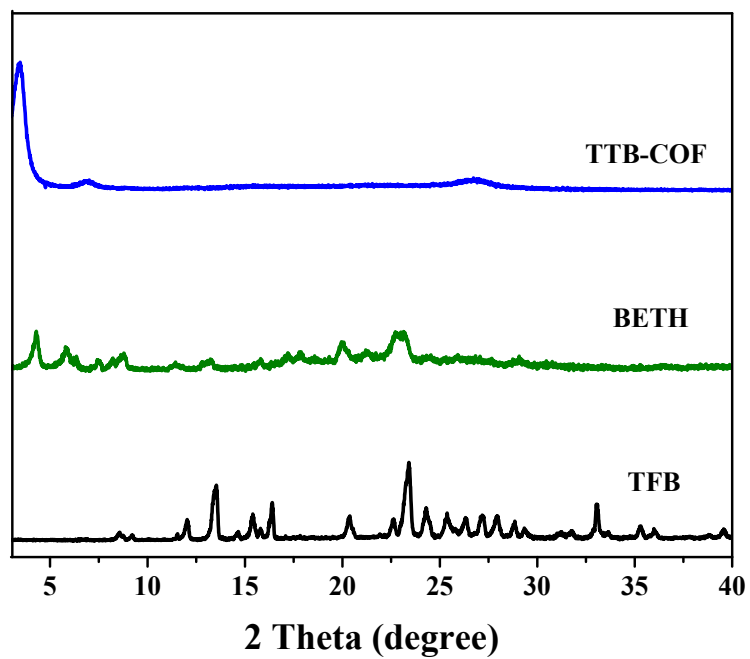


Figure S8. PXRD patterns of TTB-COF, BETH and TFB.

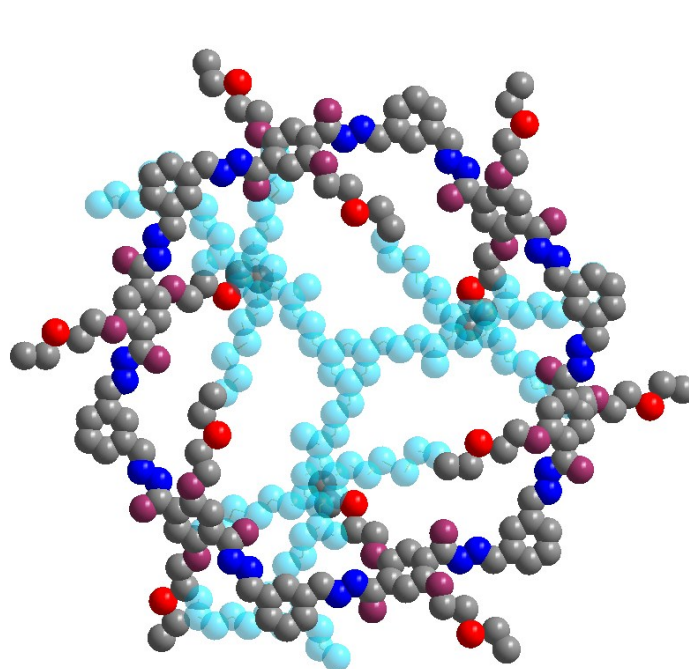


Figure S9. Top view of the staggered stacking mode of TTB-COF (red, S; blue, N; gray, C; purple, O).

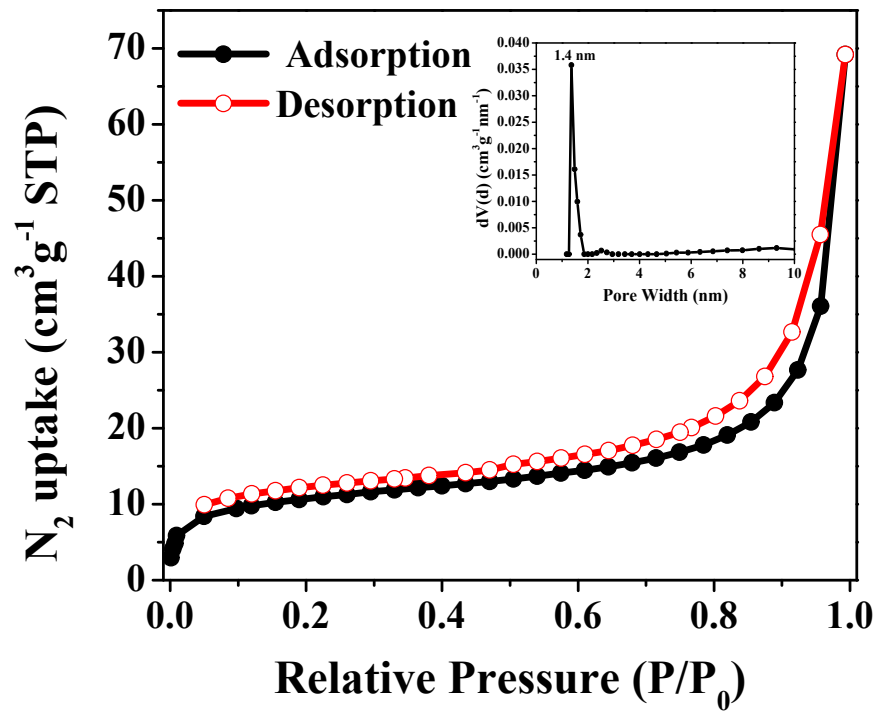


Figure S10. N_2 sorption isotherms of TTB-COF at 77 K. Inset: pore size distribution of TTB-COF

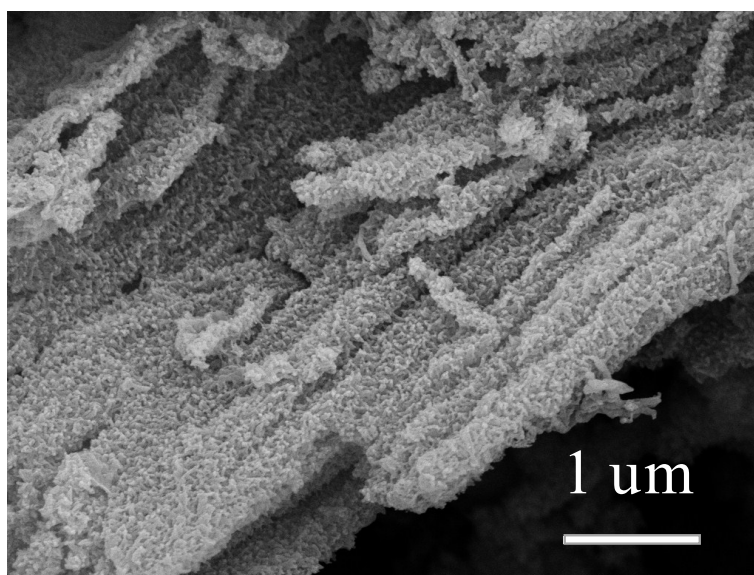


Figure S11. SEM image of TTB-COF.

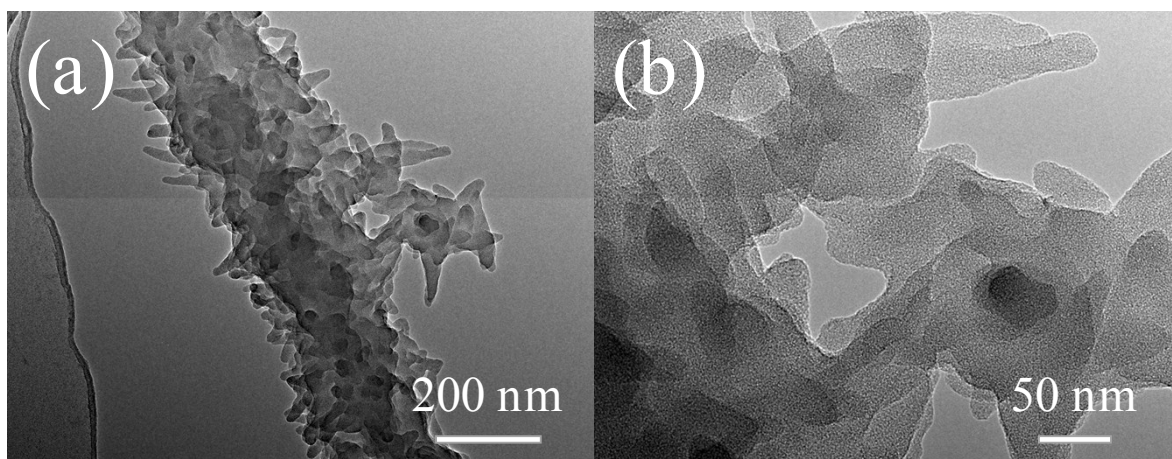


Figure S12. TEM images of TTB-COF.

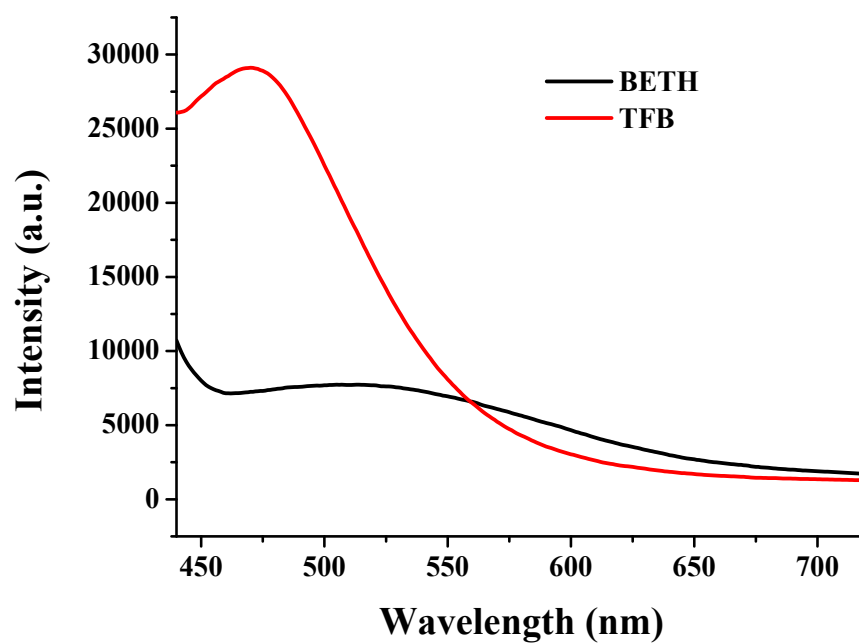


Figure S13. Fluorescence spectra of BETH (black), TFB (red) in the solid state ($\lambda_{\text{ex}} = 394$ nm).

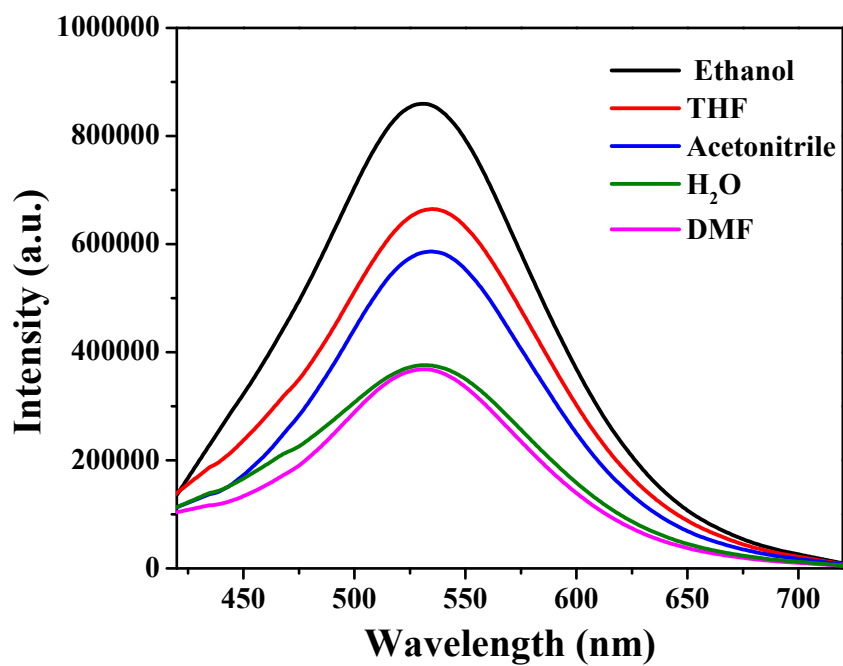


Figure S14. Fluorescence spectra of TTB-COF dispersed in various solvents ($\lambda_{\text{ex}} = 394$ nm).

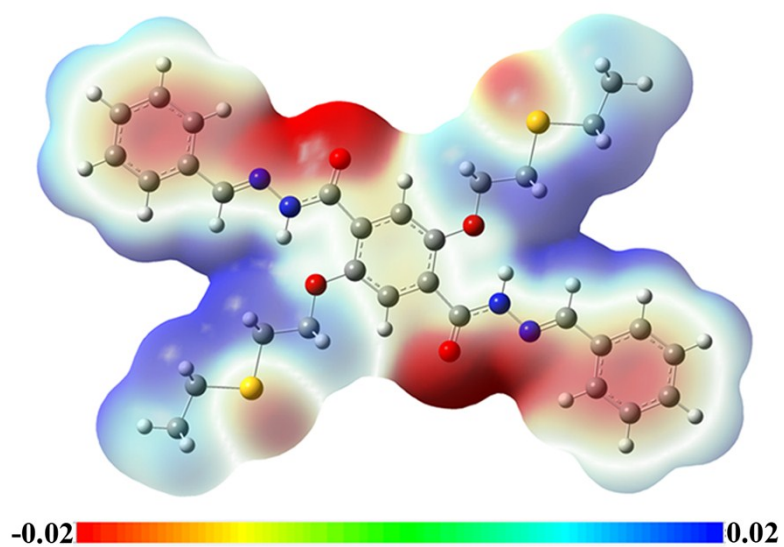


Figure S15. Electrostatic potential map of the optimized structure of building block.

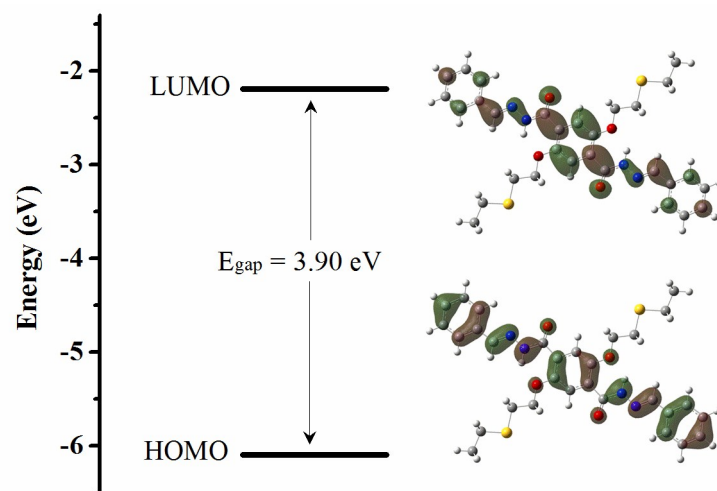


Figure S16. HOMO-LUMO energy separation of the optimized structure of building block.

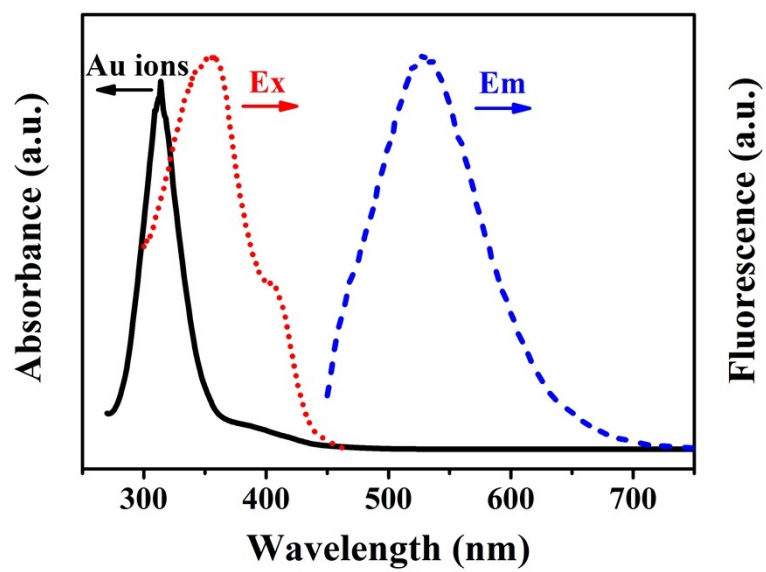


Figure S17. UV-vis spectrum of Au ions, fluorescence excitation and emission spectra of TTB-COF in CH_3CN .

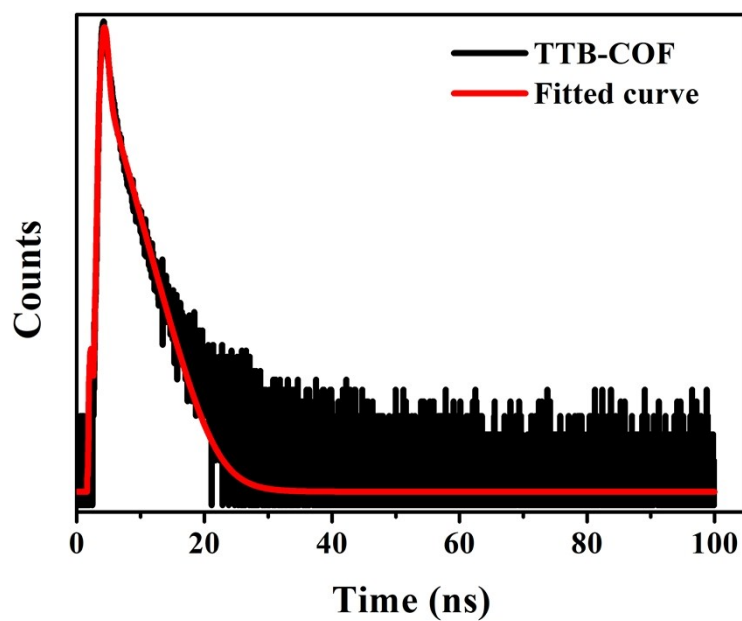


Figure S18. Time-resolved decays of TTB-COF in CH₃CN.

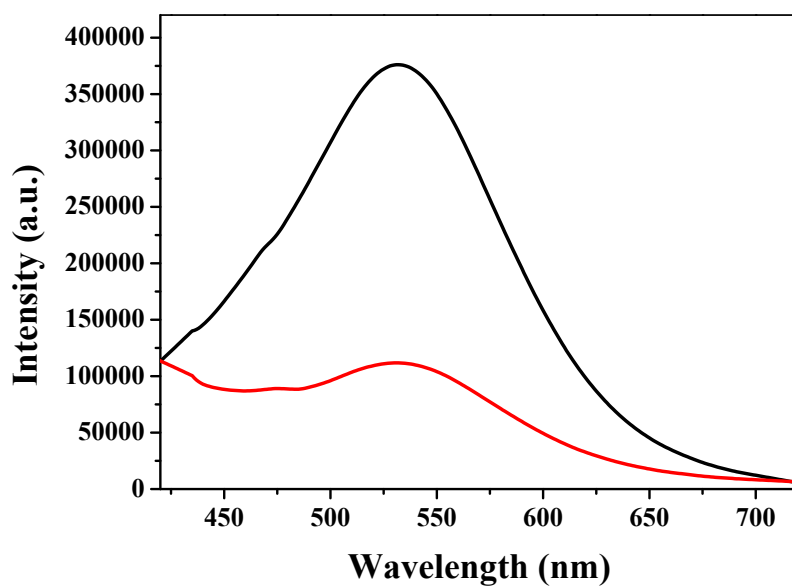


Figure S19. Fluorescence spectra of TTB-COF (black) dispersed in H₂O and after (red) the addition of Au³⁺ (10.0 μM, $\lambda_{\text{ex}} = 394$ nm).

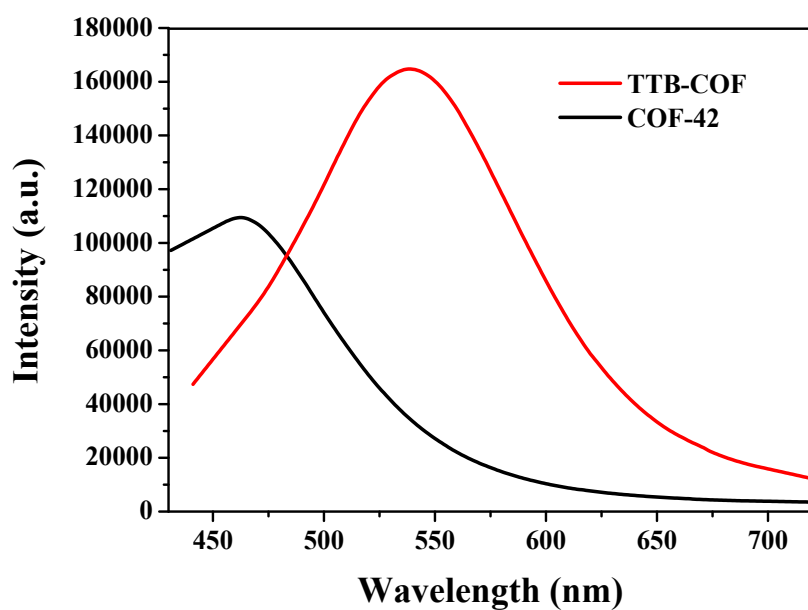


Figure S20. Fluorescence spectra of TTB-COF (red) and COF-42 (Black) in the solid state.

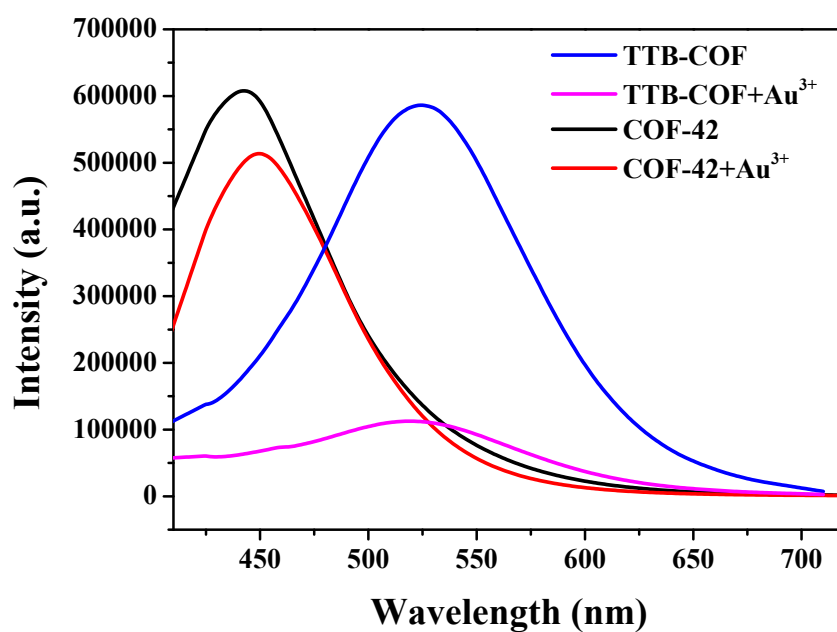


Figure S21. Fluorescence spectra of TTB-COF (blue), COF-42 (black) dispersed in acetonitrile and TTB-COF (pink), COF-42 (red) after the addition of Au^{3+} (50.0 μM , $\lambda_{\text{ex}} = 394 \text{ nm}$).

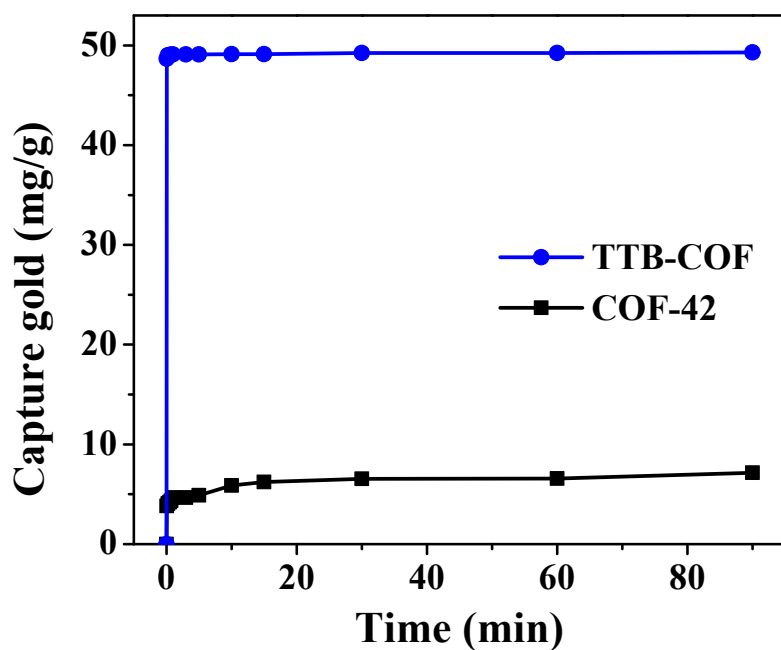


Figure S22. TTB-COF and COF-42 pairs of gold ions in aqueous solution adsorption curve and the contact time.

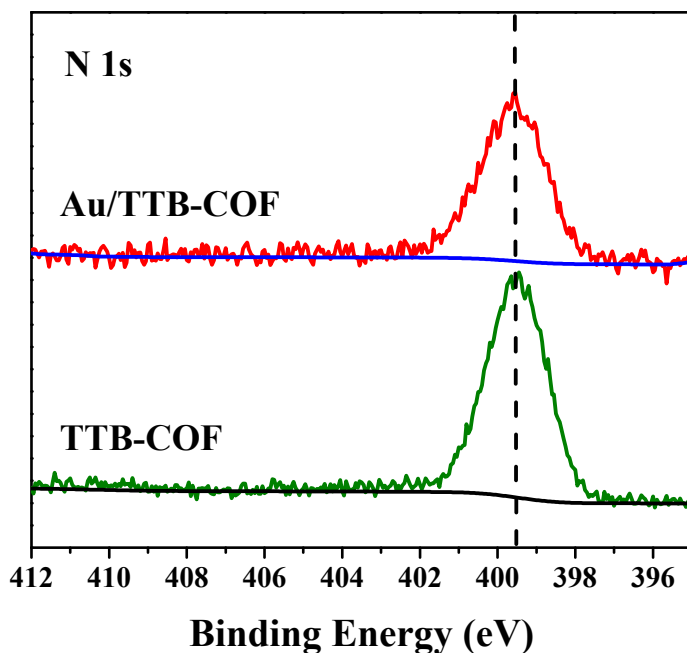


Figure S23. N 1s XPS spectra of TTB-COF and Au/TTB-COF.

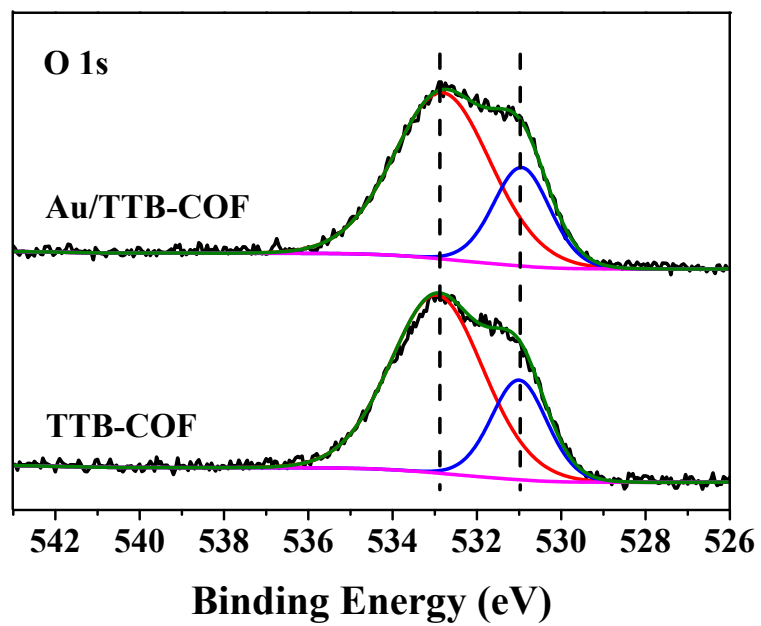


Figure S24. O 1s XPS spectra of TTB-COF and Au/TTB-COF.

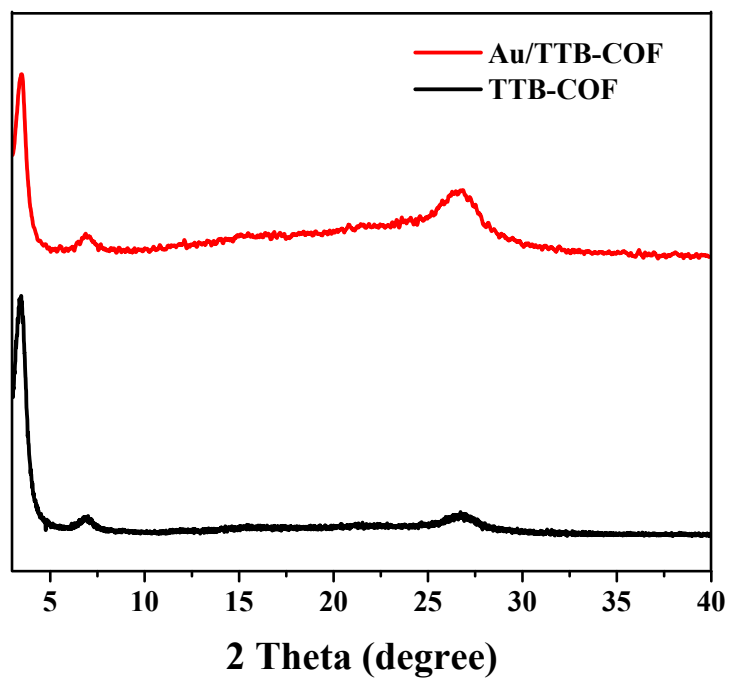


Figure S25. XRD patterns of TTB-COF (black), Au/TTB-COF (red).

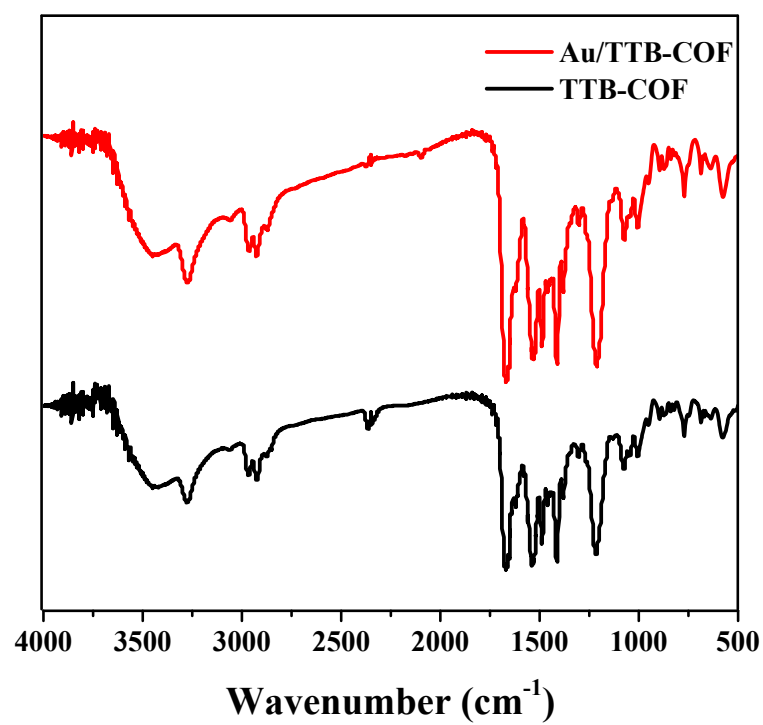


Figure S26. FT-IR spectra for TTB-COF (black) and Au/TTB-COF (red).

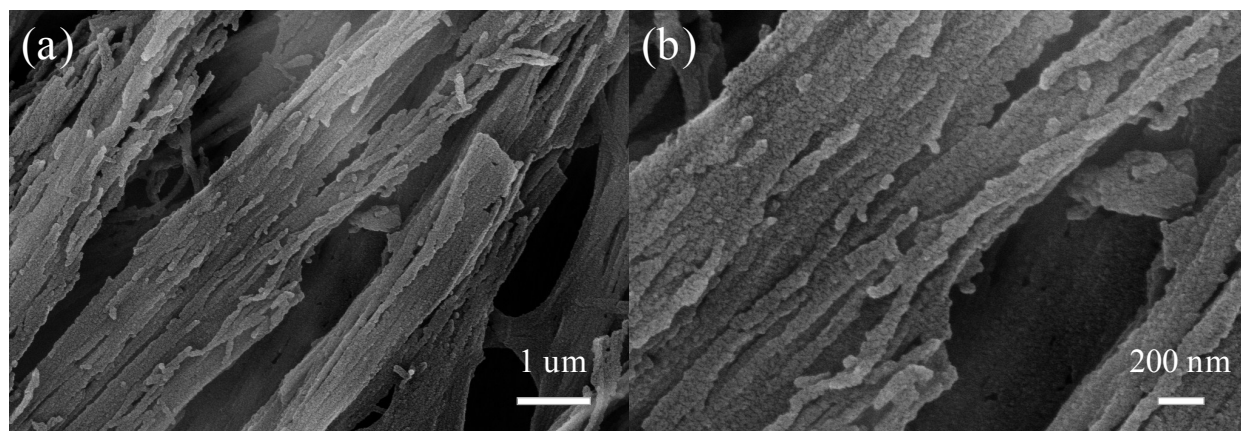


Figure S27. SEM images of Au/TTB-COF.

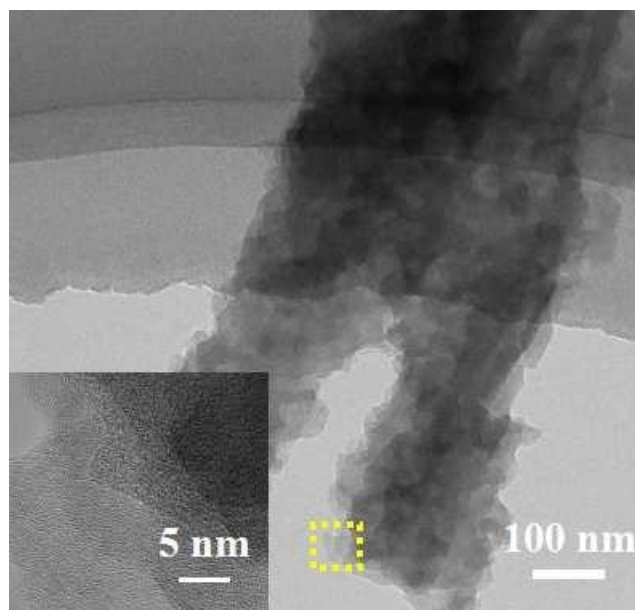


Figure S28. TEM images of Au/TTB-COF.

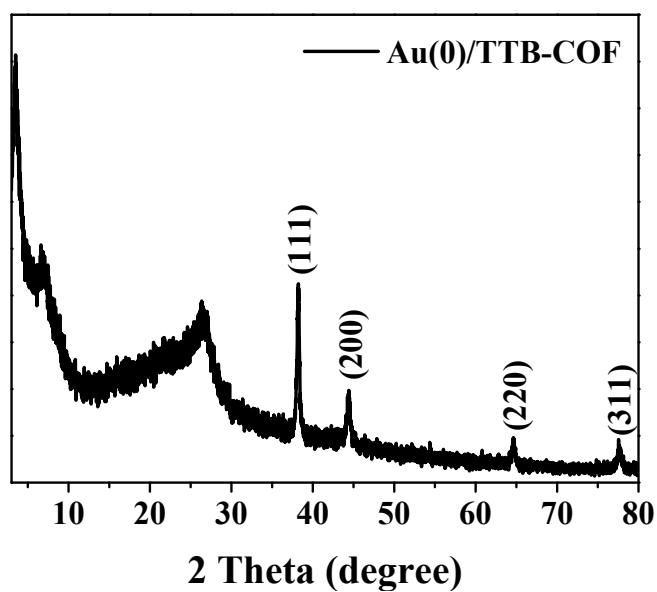


Figure S29. XRD pattern of Au(0)/TTB-COF recycled after the fourth treatment with aqueous Na_2S solution.

Table S1 Maximal sorption capacities of different sorption materials

Entry	adsorbents	Au uptake (mg g^{-1})	Initial concentration of Au in solvent	Au sensing	Ref.
1	TTB-COF	560	400 ppm in water	√	this work
	Methionine-Decorated Metal-Organic Framework	598	20 mmol L^{-1} in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1:1) solution	X	[7]
2	PEC	965	1.5 mmol L^{-1} in water	X	[8]

3	PEPEI	689	4 mmol L ⁻¹ in water	X	[8]
5	Carbon nitride	22.3	0.4 mmol L ⁻¹ in water,	X	[9]
6	E. coli surface-displayed GolB protein	0.91	0.05 mmol L ⁻¹ in water	√	[10]
7	N12 powder	66	200 ppm in 5% hydrochloric acid	X	[11]
8	D301-g-THIOPGMA	300.4	15 mg L ⁻¹ in water	X	[12]
9	Lysine modified crosslinked chitosan resin	70.34	130 mg L ⁻¹ in water	X	[13]
10	UiO-66-TU	326	700 mg L ⁻¹ in water	X	[14]
11	NH ₂ -MCM-41b	226	3 mM in water	X	[15]

REFERENCES

- [1] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, *J. Am. Chem. Soc.* **2011**, 133, 19816-19822.
- [2] (a) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785-789; (b) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- [3] (a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, 78, 4066; (b) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, 83, 735; (c) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, 88, 899.
- [4] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, 77, 3654.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al Gaussian 09, revision D.01.Gaussian, Inc., Wallingford CT, **2013**.
- [6] F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, 133, 11478-11481.
- [7] M. Mon, J. Ferrando-Soria, T. Grancha, F. R. Fortea-Pérez, J. Gascon, A. Leyva-Pérez, D. Armentano, E. Pardo, *J. Am. Chem. Soc.*, **2016**, 138, 7864-7867.
- [8] S. Bratskaya, Y. Privar, A. Ustinov, Y. Azarova and A. Pestov, *Ind. Eng. Chem. Res.*, **2016**, 55, 10377-10385.
- [9] Y. Guo, L. Zhang, K. Zhou, Y. Shen, Q. Zhang, C. Gu, *J. Mater. Chem. A*, **2014**, 2, 19594-19597.
- [10] W. Wei, T. Zhu, Y. Wang, H. Yang, Z. Hao, P. R. Chen, J. Zhao, *Chem. Sci.*, **2012**, 3, 1780-1784.
- [11] E. Lahtinen, L. Kivijärvi, R. Tatikonda, A. Väisänen, K. Rissanen, M. Haukka, *ACS Omega*, **2017**, 2, 7299-7304.
- [12] F. An, M. Li, X. Guo, H. Wang, R. Wu, T. Hu, J. Gao, W. Jiao, *Journal of Environmental Chemical Engineering*, 2017, 5, 10-15.

- [13] K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, K. Ueda, *J. Hazard. Mater.* , **2007**, *146*, 39-50.
- [14] C. Wu, X. Zhu, Z. Wang, J. Yang, Y. Li and J. Gu, *Ind. Eng. Chem. Res.*, **2017**, *56*, 13975-13982.
- [15] Lam, K. F.; Fong, C. M.; Yeung, K. L.; McKay, G., *Chem. Eng. J.* **2008**, *145*, 185-195.