[*Supporting Information*]

Synthesis of pyridine-based covalent organic framework as efficient adsorbent for rhodamine B removal

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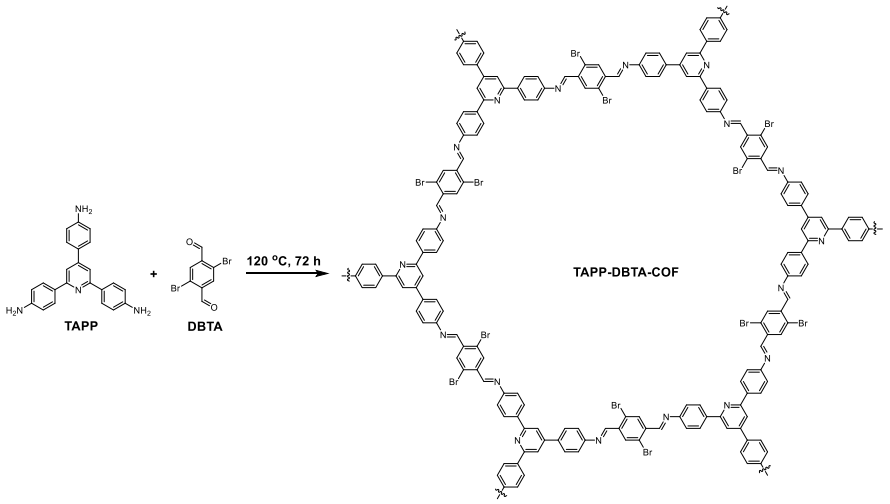
Section I. Materials and Instrumentation

All chemicals and solvents were commercially sourced and used without further purification. Deionized water was used throughout all experiments. 2,4,6-tris(4-aminophenyl)pyridine (TAPP) and 2,5-dibromobenzene-1,4-dicarbaldehyde (DBTA) were synthesized according to reported literature method.[1,2]

Fourier transform Infrared (FT-IR) spectra were recorded on a Shimadzu 8400S instrument. Solid-state NMR measurements were carried out on a Bruker WB Avance III 400 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on an Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) and operated at 40 kV and 40 mA. Scanning Electron Micrograph (SEM) images were obtained with a Zeiss Gemini 300 microscope operated at an accelerating voltage of 3.0 kV. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. The thermogravimetric analysis (TGA) were measured with a TGA5500 instrument over the temperature range of 30 to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 system. The surface area was calculated from the adsorption data using Brunauer-Emmett-Teller (BET) method. UV-vis spectra were recorded on an Agilent Cary 60 Spectrophotometer. X-ray photoelectron spectroscopy (XPS) data were recorded with an ESCALAB 250Xi spectrometer (ThermoFisher Scientific).

Section II. Synthetic procedures and characterizations of TAPP-DBTA-COF and TAPP-DBTA-COP.

Synthesis of TAPP-DBTA-COF.



2,4,6-tris(4-aminophenyl)pyridine (188 mg, 0.5 mmol), 2,5-dibromobenzene-1,4-dicarbaldehyde (233 mg, 0.8 mmol) and 6 mL *o*-dichlorobenzene/mesitylene (4 mL/2 mL) were charged into a 20 mL vial. The resulting mixture was sonicated for 5 min and then 0.8 mL of 6 M acetic acid was added. The vial was sealed and heated at 120 ℃ for 72 h. The precipitate was collected by filtration and washed with dichloromethane, acetone, methanol respectively. Further purification was conducted *via* Soxhlet extraction with THF for 12 h. After being dried at 80℃ for 10 h, the final **TAPP-DBTA-COF** was obtained as a yellow powder in 85% yield. **Elemental Analysis**: calcd. for $C_{70}H_{40}N_8Br_6$: C, 57.10; H, 2.74; N, 7.61. Found: C, 56.04; H, 2.64; N, 7.89.

Synthesis of TAPP-DBTA-COP.

2,4,6-tris(4-aminophenyl)pyridine (106 mg, 0.30 mmol), 2,5-dibromobenzene-1,4-dicarbaldehyde (131 mg, 0.45 mmol) and 8 mL DMSO were charged into a 50 mL vial. The resulting mixture was heated at 80 ℃ for 24 h. After that, the precipitate was collected by filtration and washed with dichloromethane, acetone, methanol respectively. Further purification was conducted *via* Soxhlet extraction with THF for 12 h. After being dried at 80℃ for 10 h, the final **TAPP-DBTA-COP** was obtained as

a pale brown powder in 83% yield. **Elemental Analysis**: calcd. for $C_{70}H_{40}N_8Br_6$: C, 57.10; H, 2.74; N, 7.61. Found: C, 55.72; H, 2.82; N, 7.92.

*The deviations in elemental analysis of **TAPP-DBTA-COF** and **TAPP-DBTA-COP** may be caused by trace amounts solvent trapped in porous network.*

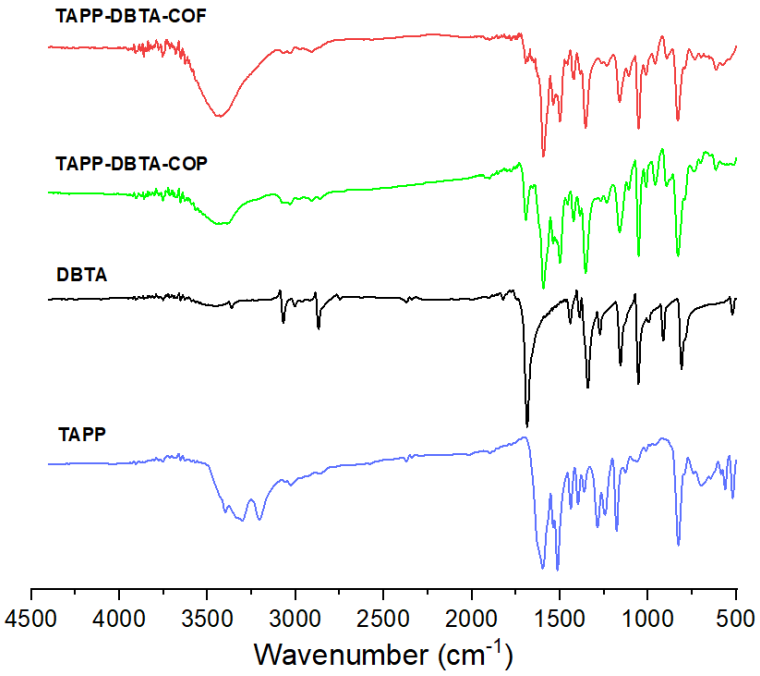


Fig. S1. FT-IR spectra of TAPP-DBTA-COF, TAPP-DBTA-COP and monomers.

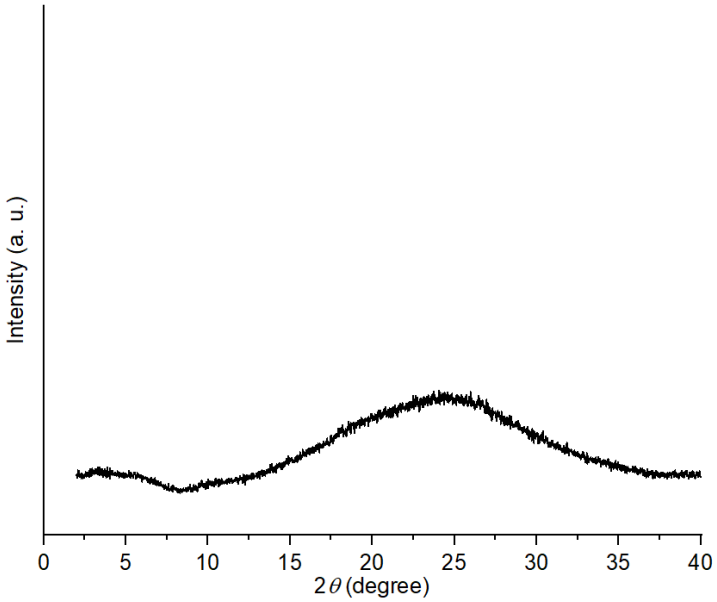


Fig. S2. PXRD patterns of TAPP-DBTA-COP.

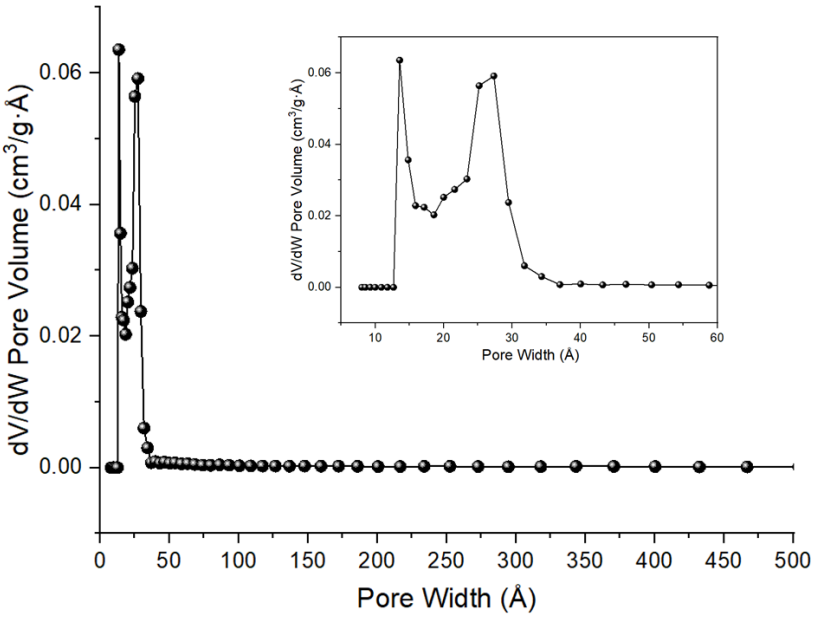


Fig. S3. Pore diameter of TAPP-DBTA-COF calculated from desorption isotherm with DFT method.

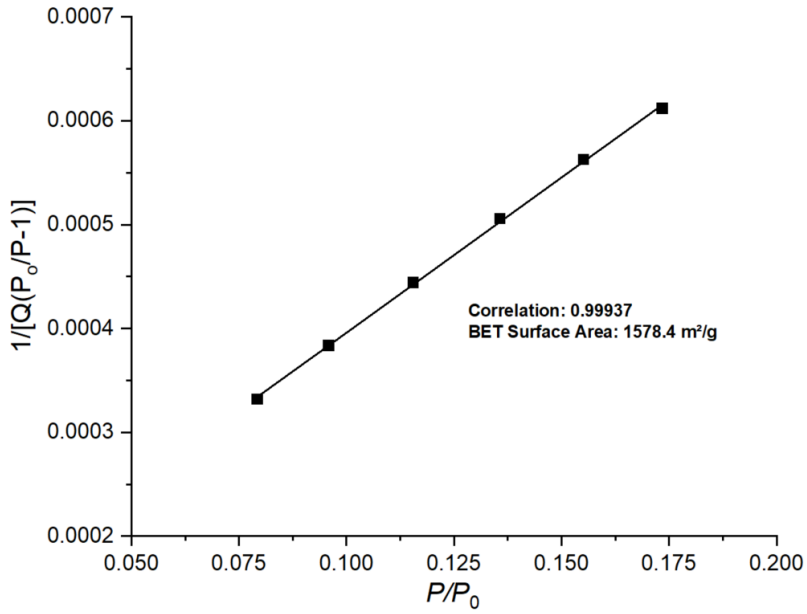


Fig. S4. BET surface area plot of TAPP-DBTA-COF.

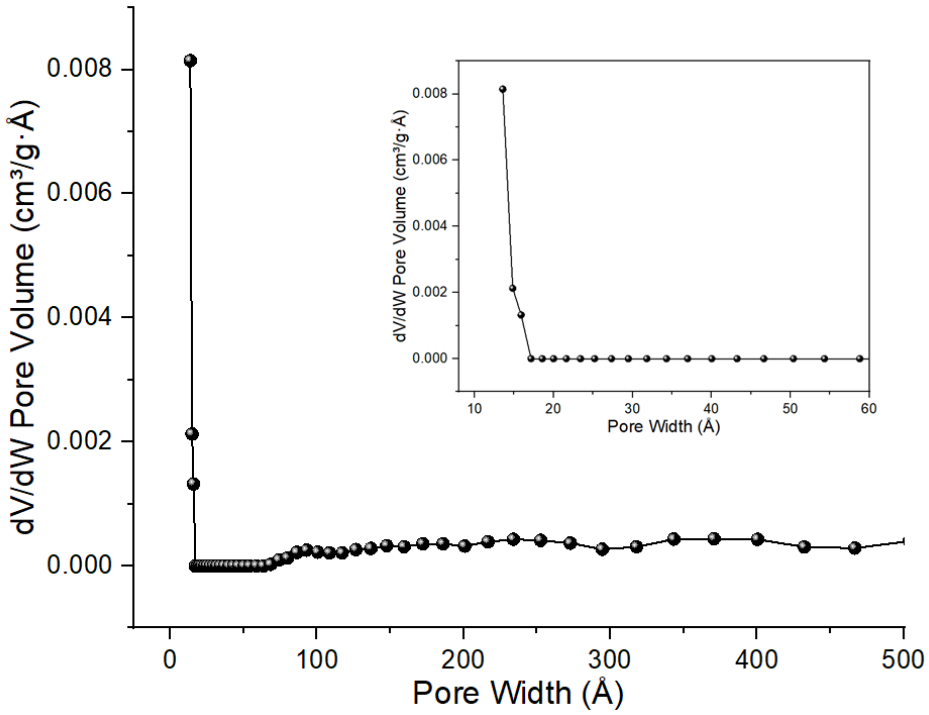


Fig. S5. Pore diameter of TAPP-DBTA-COP calculated from desorption isotherm with DFT method.

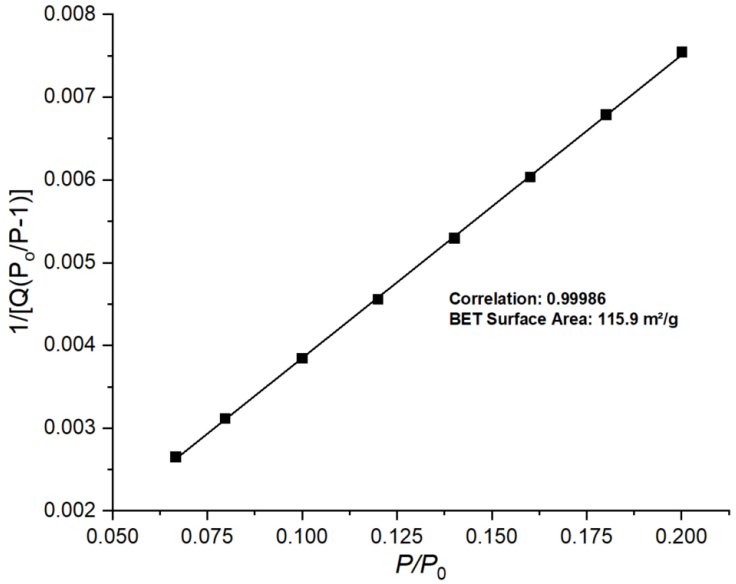


Fig. S6. BET surface area plot of TAPP-DBTA-COP.

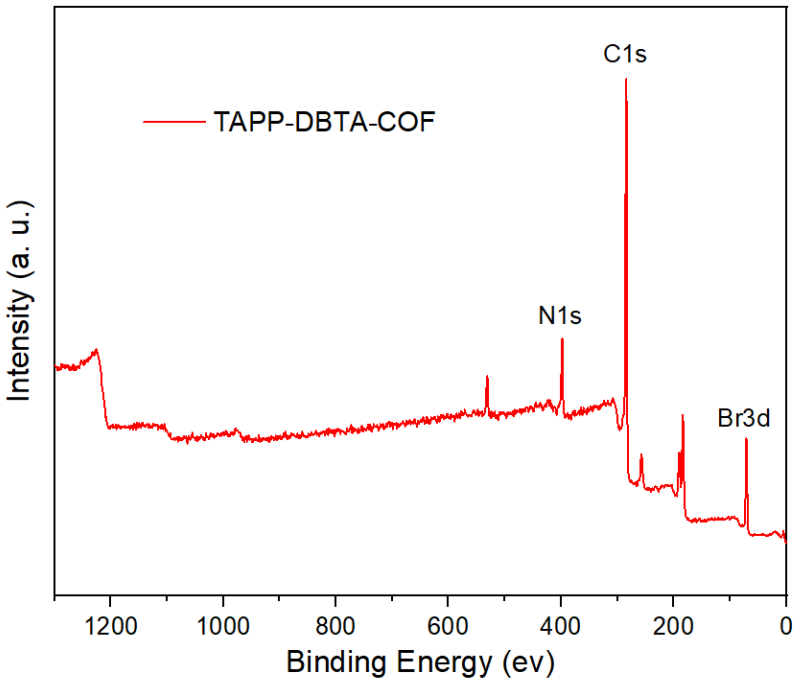


Fig. S7. XPS survey spectra of TAPP-DBTA-COF.

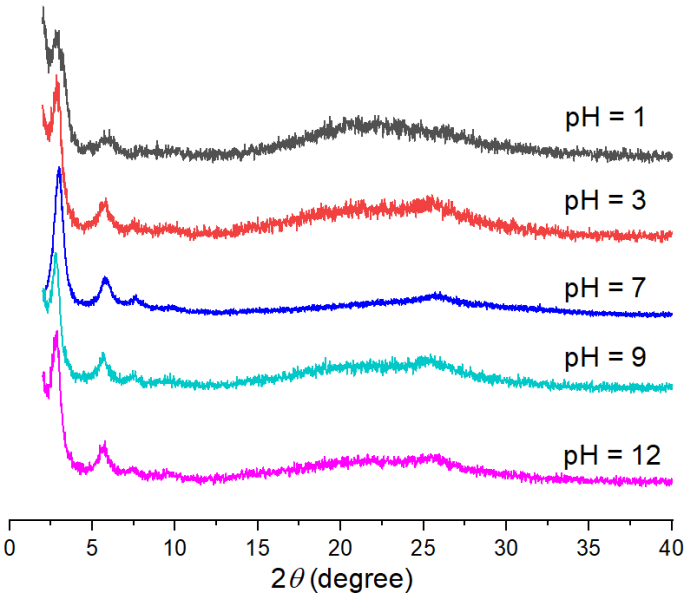


Fig. S8. PXRD patterns of TAPP-DBTA-COF before and after treatment with different aqueous solutions (pH = 1, 3, 7, 9, 12).

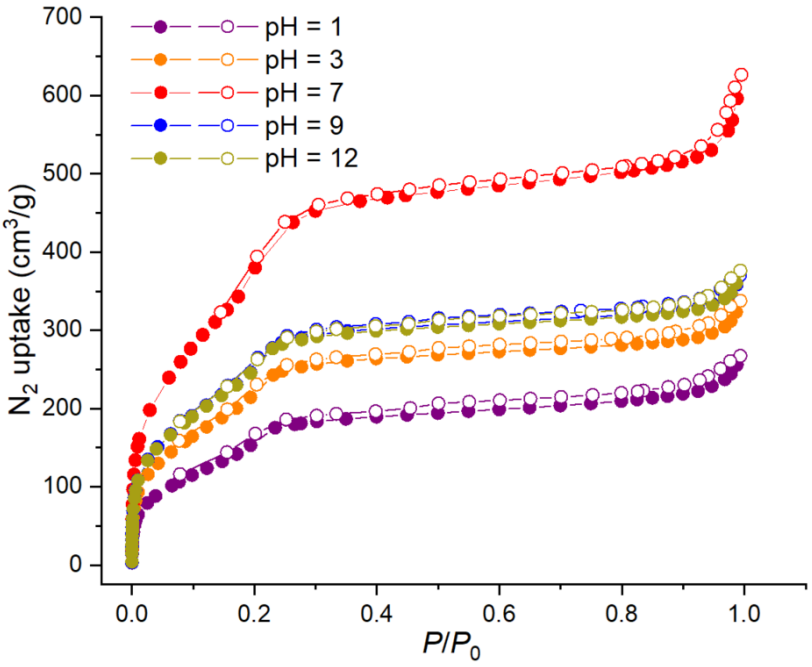


Fig. S9. Nitrogen sorption isotherm curves of TAPP-DBTA-COF before and after treatment with different aqueous solutions (pH = 1, 3, 7, 9, 12). The BET surface areas were 664.7, 933.5, 1578.4, 1036.3 and 1053.0 m^2 g^{-1}, respectively.

Table S1. Fractional atomic coordinates for the unit cell of TAPP-DBTA-COF.

Space group: *P*2/m *a* = 38.7109 Å, *b* = 3.5765 Å, *c* = 35.7454 Å, $\alpha = \gamma = 90°$, $\beta = 117.4762°$							
Atom	X (Å)	Y (Å)	Z (Å)	Atom	X (Å)	Y (Å)	Z (Å)
C1	-0.1587	0	1.20326	H32	-0.04349	0	1.12984
N2	-0.14142	0	1.17768	H33	-0.08246	0	1.16675
C3	-0.1331	0	1.25019	C34	-0.03372	0	1.05747
C4	-0.09225	0	1.26603	H35	-0.01447	0	1.091
C5	-0.06732	0	1.30946	C36	-0.01634	0	1.02821
C6	-0.08217	0	1.3384	C37	0.02443	0	1.04369
C7	-0.12283	0	1.32319	C38	0.0404	0	1.01571
C8	-0.14795	0	1.27972	Br39	0.05998	0	1.10271
H9	-0.0794	0	1.24474	H40	0.07185	0	1.02869
H10	-0.03604	0	1.32097	C41	-0.22255	0	1.14008
N11	-0.05479	0	1.38258	C42	-0.19967	0	1.18448
H12	-0.13567	0	1.34435	C43	-0.26692	0	1.11951
H13	-0.17876	0	1.27022	C44	-0.28735	0	1.14387
C14	-0.0626	0	1.41435	C45	-0.3281	0	1.12478
H15	-0.09232	0	1.40943	C46	-0.35017	0	1.08105
C16	-0.03069	0	1.45821	C47	-0.33077	0	1.05616
C17	-0.03884	0	1.49283	C48	-0.29	0	1.07499
C18	-0.00844	0	0.534	H49	-0.27295	0	1.1778
Br19	-0.09086	0	1.48608	H50	-0.34291	0	1.14416
H20	-0.01575	0	0.55987	N51	-0.39193	0	1.06375
C21	-0.16133	0	1.13487	H52	-0.34659	0	1.02214
C22	-0.20231	0	1.11565	H53	-0.27767	0	1.05347
C23	-0.13847	0	1.11039	C54	-0.41753	0	1.02406
C24	-0.15616	0	1.06579	H55	-0.40858	0	0.99954
C25	-0.1334	0	1.04462	C56	-0.45974	0	1.0116
C26	-0.09277	0	1.06686	C57	-0.48769	0	0.9687
C27	-0.07478	0	1.11122	C58	0.47261	0	0.95744
C28	-0.09737	0	1.13256	Br59	-0.47363	0	0.92389
H29	-0.18733	0	1.04649	H60	0.45191	0	0.92417
H30	-0.14737	0	1.01044	H61	0.21325	0	0.79548
N31	-0.0714	0	1.04288	H62	0.21793	0	0.91793

Section III. Organic dyes adsorption experiments

Sorption kinetics study

Typically, TAPP-DBTA-COF or TAPP-DBTA-COP (3 mg) was dispersed in 5 mL Rh B aqueous solution (200 ppm) and stirred under room temperature. After stirring for a desired time, the sorbent was filtered with a syringe filter (PTFE, 0.45 μm), and the solution was detected by UV-vis spectrophotometer. The adsorption percentage was obtained by comparing the maximum absorbance (λ = 554 nm) with the original Rh B aqueous solution.

$$Q_t = \left(\frac{C_0 - C_t}{m}\right) \times V$$

where Q_t is the adsorption capacity at contact time t, C_0 is the initial concentration of Rh B solution, C_t is the concentration of Rh B at time t, m is the mass of TAPP-DBTA-COF or TAPP-DBTA-COP, and the V is the volume of Rh B aqueous solution.

Two kinetic models, including pseudo-first order model and pseudo-second order model were used to fit the sorption kinetics data. These two models can be expressed in the following equations:

Pseudo-first order equation:

$$Q_t = Q_e - Q_e e^{-k_1 t}$$

Pseudo-second order equation:

$$Q_t = \frac{K_2 Q_e^2 t}{1 + k_2 Q_e t}$$

where k_1 and k_2 (g mg^{-1} min^{-1}) are the rate constants of pseudo-first order and pseudo-second order, respectively.

Sorption isotherm study

The sorption isotherm experiments of TAPP-DBTA-COF and TAPP-DBTA-COP were conducted by varying the initial concentrations of Rh B (400-2200 ppm for TAPP-DBTA-COF, or 40-120 ppm for TAPP-DBTA-COP). Typically, adsorbent (5 mg) was

dispersed in 6 mL Rh B aqueous solution. The solution was stirred for 2.5 h under room temperature, and then the solution was filtered with a syringe filter (PTFE, 0.45 μm). After being diluted with deionized water, the solution was measured with UV-vis spectrophotometer. The equilibrium adsorption capacity (Q_e) was calculated by using the following equation.

$$Q_e = \left(\frac{C_0 - C_e}{m}\right) \times V$$

where the C_e is the equilibrium concentration of Rh B solution.

The adsorption isotherm curves of Rh B were fitted by LangmuirEXT1, Langmuir, and Freundlich models respectively.

LangmuirEXT1 equation:

$$Q_e = \frac{Q_m K_s C_e^{\gamma}}{1 + K_s C_e^{\gamma}}$$

Langmuir equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

Freundlich equation:

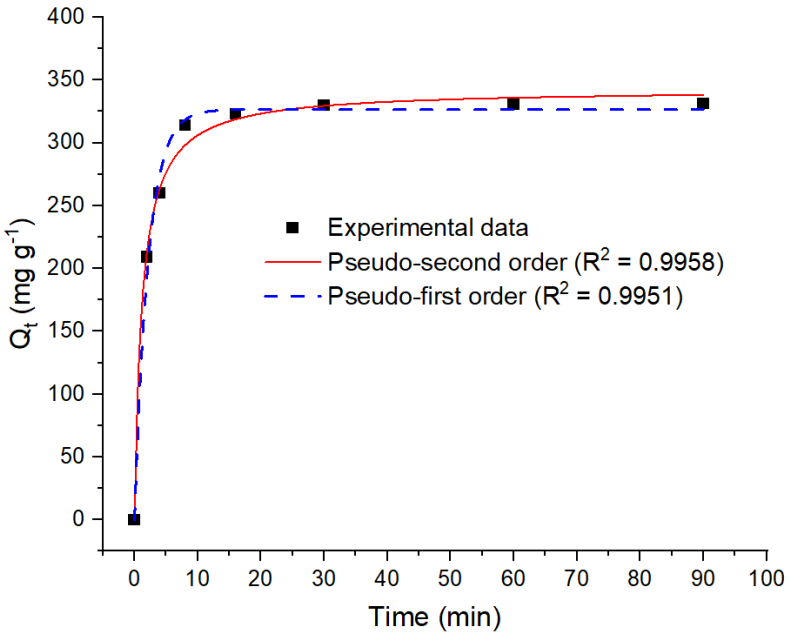
$$Q_e = K_F C_e^{1/n}$$

where Q_m is the maximum adsorption capacity, K_S and γ are the constants of LangmuirEXT1 model, K_L is the constant of Langmuir model, K_F and n are constants of Freundlich model.

The influence of pH value of the solution was studied by dispersing TAPP-DBTA-COF (5 mg) in 6 mL Rh B aqueous solution (1400 ppm) with different pH values (pH = 1, 3, 7, 9, 12). The pH values of the solution were adjusted *via* adding 0.1 M HCl or 0.1 M NaOH. After stirring for 2 hours, the sorbent was filtered with a syringe filter (PTFE, 0.45 μm), and the solutions were detected by UV-vis spectrophotometer, the adsorption percentage was determined based on the intensity reduction of the

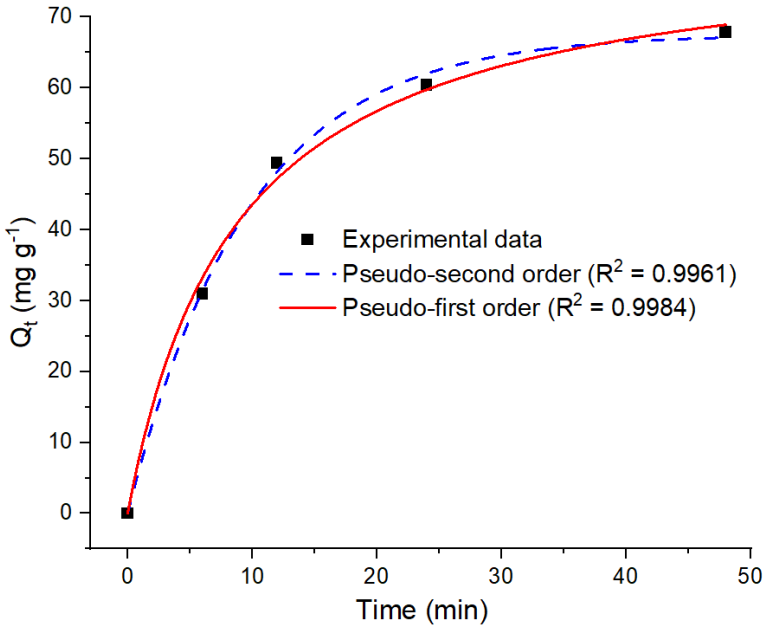
characteristic peak of Rh B.

The recyclability of TAPP-DBTA-COF was studied in an amplified experiment. 28 mg of TAPP-DBTA-COF was dispersed in 40 mL Rh B aqueous solution (1400 ppm), and stirred for adsorption. The adsorbed Rh B can be desorbed *via* directly eluting with ethanol until the eluent was changed to colorless. The ethanol solution was collected and detected by UV-vis spectrophotometer to determine desorption efficiency. After thoroughly washing with ethanol, the regenerated adsorbent TAPP-DBTA-COF-Regenerated was obtained and dried at 80 ℃. The next adsorption cycle was performed under the same conditions.



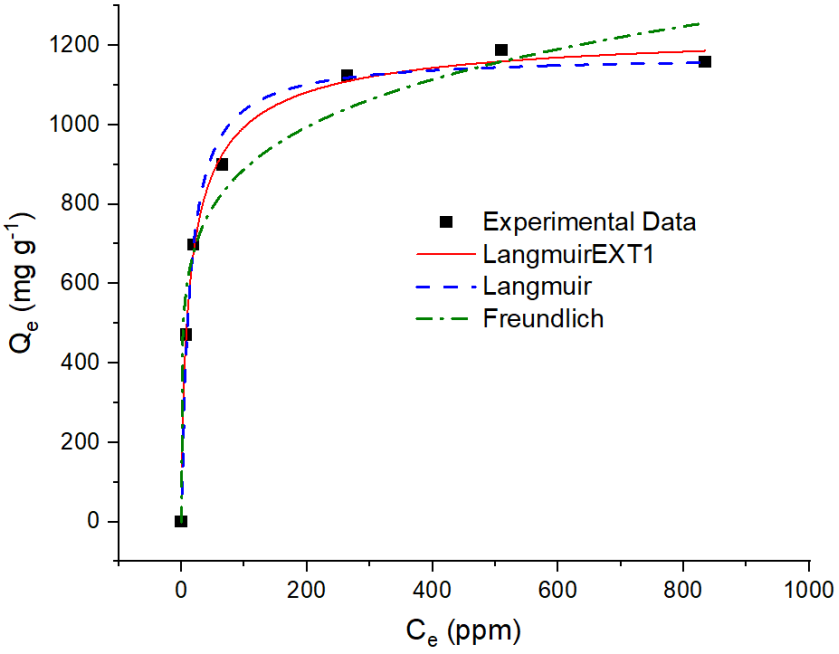
Fitting model	**Parameter**	**correlation coefficient**
Pseudo-first order	**Q_e = 326.6 mg g^{-1}** **k_1 = 0.460 min^{-1}**	**R^2 = 0.9951**
Pseudo-second order	**Q_e = 342.7 mg g^{-1}** **k_2 = 0.00244 g mg^{-1} min^{-1}**	**R^2 = 0.9958**

Fig. S10. The kinetics for adsorption of Rh B by **TAPP-DBTA-COF** fitted by pseudo-first and pseudo-second order models respectively.



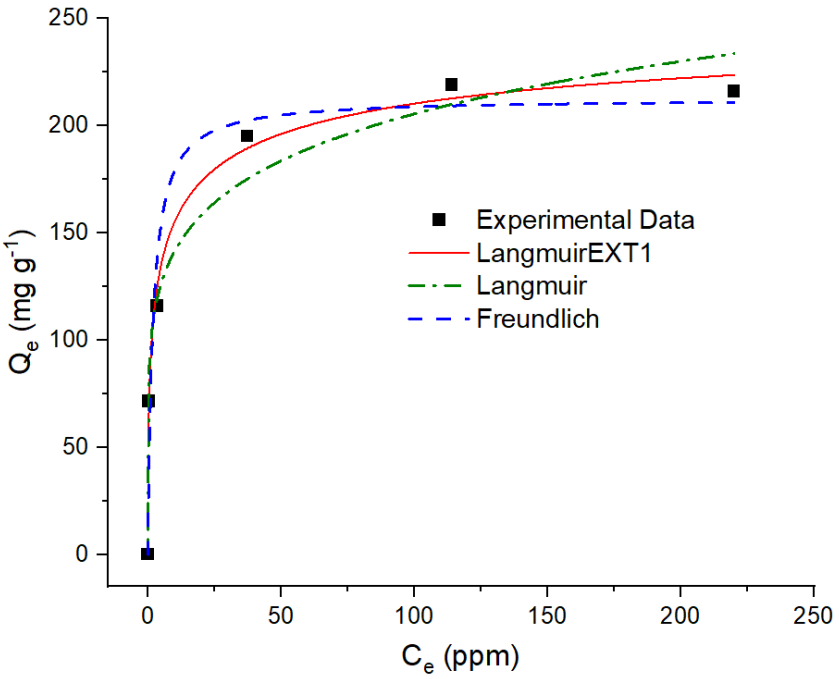
Fitting model	Parameter	correlation coefficient
Pseudo-first order	**Q_e = 67.5 mg g^{-1}** **k_1 = 0.104 min^{-1}**	**R^2 = 0.9984**
Pseudo-second order	**Q_e = 81.4 mg g^{-1}** **k_2 = 0.00141 g mg^{-1} min^{-1}**	**R^2 = 0.9961**

Fig. S11. The kinetics for adsorption of Rh B by **TAPP-DBTA-COP** fitted by pseudo-first and pseudo-second order models respectively.



Fitting model	Parameter	correlation coefficient
LangmuirEXT1	**Q_m = 1254.1 mg g^{-1} K_s = 0.14 γ = 0.72**	**R^2 = 0.9924**
Langmuir	**Q_m = 1174.6 mg g^{-1} K_L = 0.08**	**R^2 = 0.9919**
Freundlich	**K_F = 418.6 n = 6.12**	**R^2 = 0.9689**

Fig. S12. The adsorption isotherm of Rh B by **TAPP-DBTA-COF** fitted with three different models. As listed above, LangmuirEXT1 model displayed a better correlation coefficient than other two models, suggesting LangmuirEXT1 model can well describe the adsorption process.



Fitting model	Parameter	correlation coefficient
LangmuirEXT1	**Q_m = 263.7 mg g^{-1} K_s = 0.52 γ = 0.44**	**R^2 = 0.9871**
Langmuir	**Q_m = 212.7 mg g^{-1} K_L = 0.53**	**R^2 = 0.9514**
Freundlich	**K_F = 97.22 n = 6.15**	**R^2 = 0.9765**

Fig. S13. The adsorption isotherm of Rh B by **TAPP-DBTA-COP** fitted with three different models. As listed above, LangmuirEXT1 model displayed a better correlation coefficient than other two models, suggesting LangmuirEXT1 model can well describe the adsorption process.

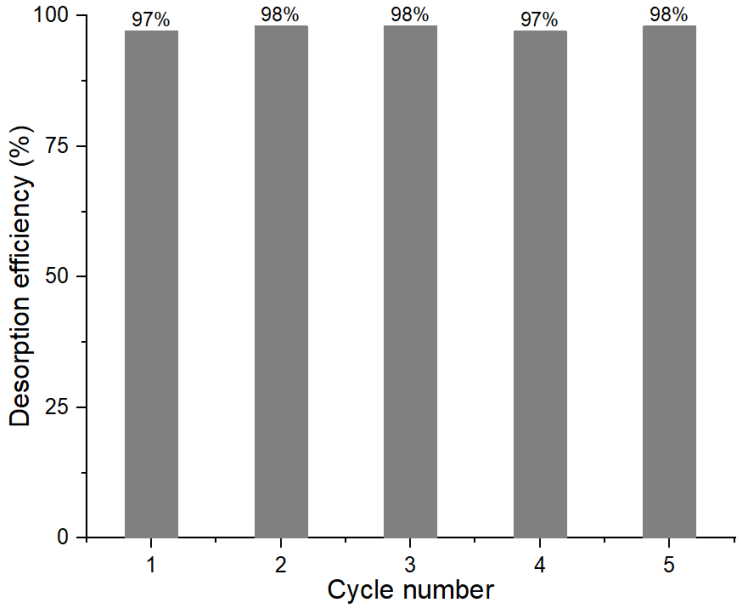


Fig. S14. Desorption efficiency of Rh B on TAPP-DBTA-COF with ethanol after each cycle.

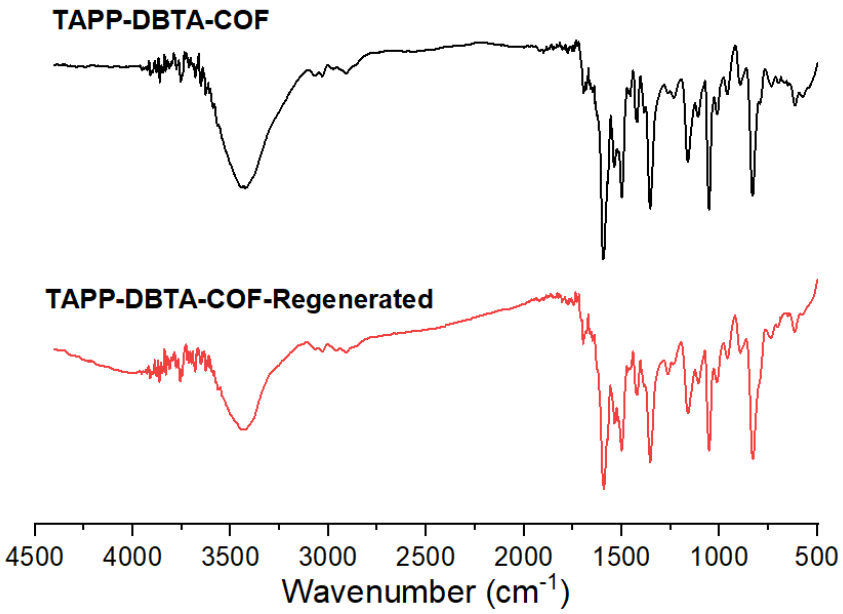


Fig. S15. FT-IR spectra of TAPP-DBTA-COF and TAPP-DBTA-COF-Regenerated.

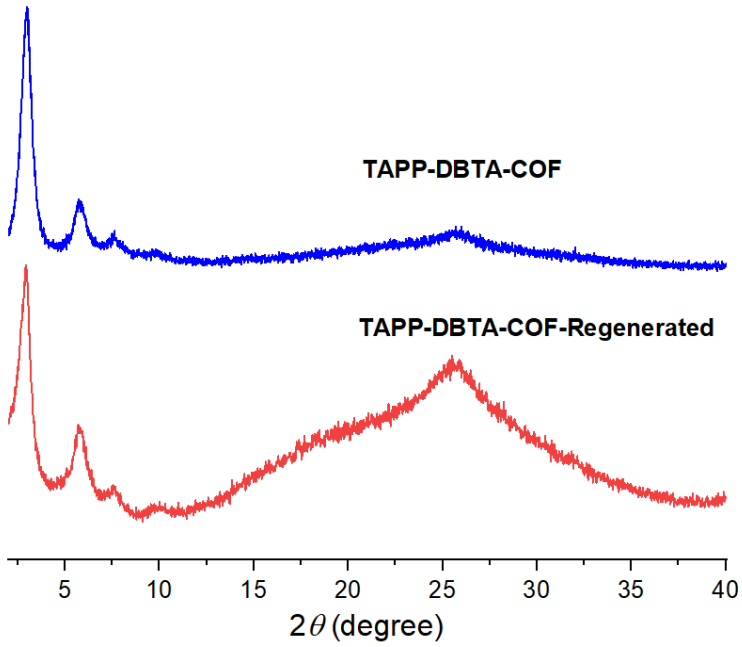


Fig. S16. PXRD patterns of TAPP-DBTA-COF and TAPP-DBTA-COF-Regenerated.

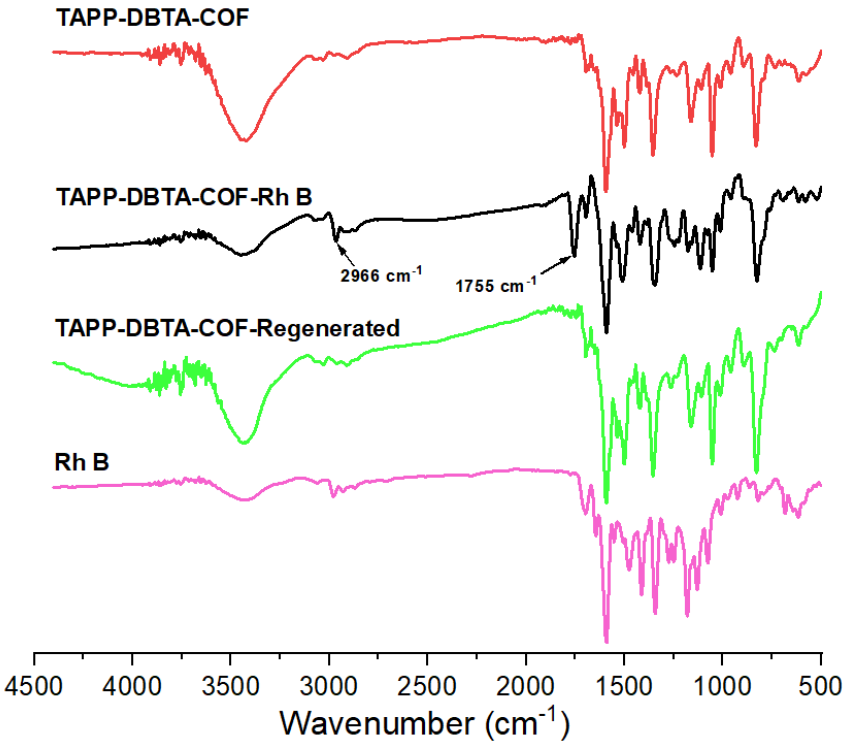


Fig. S17. FT-IR spectra of TAPP-DBTA-COF, TAPP-DBTA-COF-Rh B, TAPP-DBTA-COF-Regenerated and Rh B.

Section IV. References

(1) Shen, D.; Liu, J.; Yang, H.; Yang, S. Highly Thermally Resistant and Flexible Polyimide Aerogels Containing Rigid-rod Biphenyl, Benzimidazole, and Triphenylpyridine Moieties: Synthesis and Characterization. *Chem. Lett.* **2013**, *42*, 1545-1547.

(2) Deng, Y.; Zhang, Z.; Du, P. Y.; Ning, X. M.; Wang, Y.; Zhang, D. X.; Liu, J.; Zhang, S. T.; Lu, X. Q. Embedding Ultrasmall Au Clusters into the Pores of a Covalent Organic Framework for Enhanced Photostability and Photocatalytic Performance. *Angew. Chem., Int. Ed.* **2020**, *59*, 6082-6089.