Supporting Information

Pyrazine-cored covalent organic frameworks for efficient CO$_2$ adsorption and removal of organic dyes

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1 Synthesis of the linkers

1.1 Synthesis of 2,3,5,6-tetrakis (4-aminophenyl) pyrazine
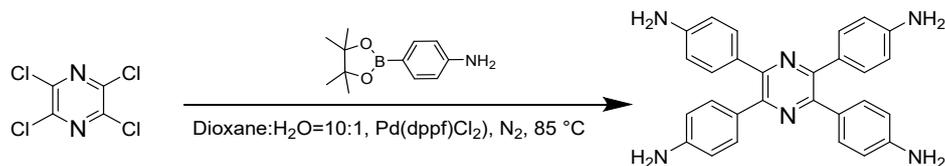
Scheme S1. Synthesis of 2,5-Dihydroxyterephthalaldehyde

To a 50 mL double-necked round bottom flask were added 0.22 g (1 mmol) tetrachloropyrazine, 1.05 g (4.8 mmol) 4-aminophenylborate, 0.55 g (4 mmol) potassium carbonate, 30 mL dioxane /water (V/V= 10:1) and 0.16 g (5% mmol) Pd(dppf)Cl$_2$ under N$_2$ atmosphere, then the mixed system was magnetically stirred in an oil bath at 85 °C for 24 h. When TLC monitoring showed that the reaction was completed, the reaction system was cooled to room temperature, filtered, and the filter residue was washed with dichloromethane three times. The combined organic phase was washed 3 times with water (100 mL x 3), dried over anhydrous sodium sulfate. The filtered solution was evaporated to remove the solvent in vacuo, and the residue was recrystallized from CH$_2$Cl$_2$/n-hexane to obtain the target compound (0.39 g, 87%).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 7.25 (d, J = 8.8 Hz, 8H, Ph-*H*), 6.49(d, J = 40.0 Hz, 8H, Ph-*H*), 5.30(s, 8H, -N*H$_2$*) (Fig. S18).

^{13}C NMR (100 MHz，DMSO-d$_6$): δ (ppm) 148.83, 145.17, 130.12, 126.29, 113.36, 66.38 (*C*-dioxane), 54.89 (C-dichloromethane)[1] (Fig. S19).

HRMS: caculated for C$_{28}$H$_{24}$N$_6$ [M+H]$^+$: 445.2135, found: 445.2130 (Fig. S20).

1.2 Synthesis of 2,3-dihydroxyterephthalaldehyde
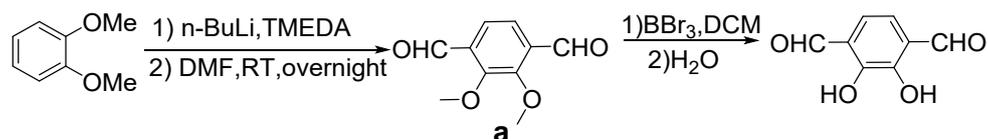
Scheme S2. Synthesis of 2,3-Dihydroxyterephthalaldehyde

6.9 g (50 mmol) phthalic ether, 37.73 mL (250 mmol) TMEDA and 150 mL dry ether were added to a 500 mL two-necked flask. Under the protection of nitrogen, 100 mL (250 mmol) n-hexane solution of n-butyllithium was slowly dropped into the reaction system at 0 °C. After the addition was completed, the system returned to room temperature and continued to stir for 24 h. 21.2 mL (275 mmol) anhydrous DMF was slowly dropped into the reaction system at 0 °C, then the mixture was stirred at room temperature overnight. The mixture was extracted 3 times with ether (100 mL × 3) after 100 mL of 1 mol L^{-1} HCl was added to the system to quench the reaction. The combined organic phase was dried with anhydrous sodium sulfate and filtered. The residue after removing the solvent was subjected to column chromatography (HE: EA = 10: 1) to obtain a dark yellow solid intermediate **a** (3.15 g) with a yield of 32.4%.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 10.44 (s, 2H, -C*H*O), 7.63 (s, 2H, Ph-*H*), 4.05 (s, 2H, -OC*H$_3$*).

2.91 g (15 mmol) intermediate **a** was dissolved in 140 mL anhydrous dichloromethane, and the temperature of the system was reduced to 0 °C. Under the protection of nitrogen, 45 mL of 1 mol L^{-1} dichloromethane solution of boron tribromide was slowly dropped into the system. The reaction system was stirred at 0 °C for 0.5 hours and at room temperature for 3.5 hours. When the end of the reaction was verified by TLC, 140 mL ice water was added to the reaction solution to destroy the excess BBr$_3$. The mixture was extracted twice with dichloromethane (100 mL × 2), and the combined organic phases were dried with anhydrous sodium sulfate, then filtered. The solvent of the filtrate was removed in vacuo, and the residue was recrystallized from CH$_2$Cl$_2$/n-hexane to obtain the target compound (2.3 g, 92%).

^{1}H NMR (400 MHz，CDCl$_3$): δ (ppm) 10.90 (s, 2H, -O*H*), 10.02 (s, 2H, -C*H*O), 7.27 (s, 2H, Ph-*H*).

^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 196.45, 150.81, 123.17, 122.32.

1.3 Synthesis of 2,5-Dihydroxyterephthalaldehyde
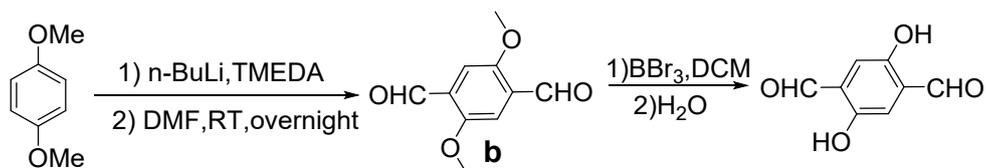
Scheme S3. Synthesis of 2,5-Dihydroxyterephthalaldehyde

6.9 g (50 mmol) terephthalic ether, 150 mL anhydrous ether, and 37.73 mL (250 mmol) TMEDA were added to a 500-mL double-necked flask in sequence. The temperature of the reaction system was lowered to 0 °C, and 100 mL (250 mmol) n-butyllithium in n-hexane was slowly added to the system under nitrogen atmosphere. After the addition was completed, the reaction solution was stirred and refluxed for 24 hours. To this mixture was added dropwise 21.2 mL (275 mmol) anhydrous DMF at 0°C over a period of 30 mins, and the system was warmed to room temperature and stirred overnight. 100 mL of 1 mol L^{-1} HCl was added to the system to adjust the pH to near neutral, and the precipitation was filtered, washed with ethyl acetate, dried in vacuum. At last, 4.14 g of white solid **b** was obtained with a yield of 42.6%.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 10.49 (s, 2H, -CHO), 7.44 (s, 2H, Ph-H), 3.94 (s, 2H, -OCH_3).

4.53 g (23.3 mmol) intermediate **b** and 200 mL dry dichloromethane were added to a 500 mL two-neck flask, then 70 mL (1 M) dichloromethane solution of boron tribromide was added dropwise to the reaction system under the protection of nitrogen at 0°C. The reaction system was stirred at 0 °C for 0.5 hours and at room temperature for 3.5 hours when the addition was complete. When the end of the reaction was verified by TLC, the reaction system was poured into 200 mL ice water to destroy the excess BBr$_3$, then the precipitate was filtered and dried under vacuum at 40°C. At last, the target product was obtained as a dark yellow solid (3.4 g) with a yield of 88%.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.30 (s, 4H, -CHO, -OH), 7.22 (s, 2H, Ph-H).

^{13}C NMR (100 MHz，DMSO-d$_6$): δ (ppm) 190.63, 153.27, 128.11, 115.50.

2 FT-IR spectra
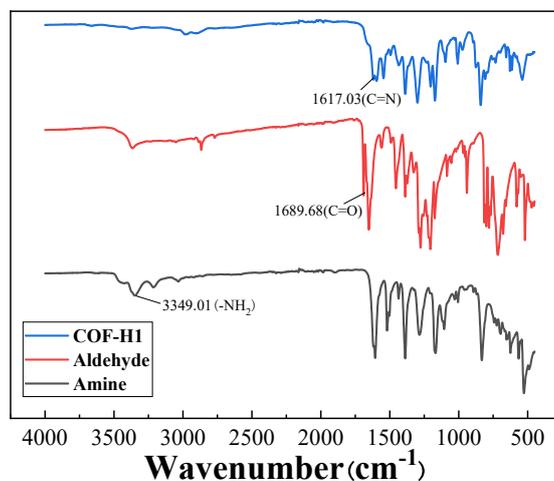
Fig. S1 FT-IR spectra of 2,3,5,6-tetrakis(4-aminophenyl)pyrazine, 2,3-dihydroxyterephthalaldehyde, and COF-H1.

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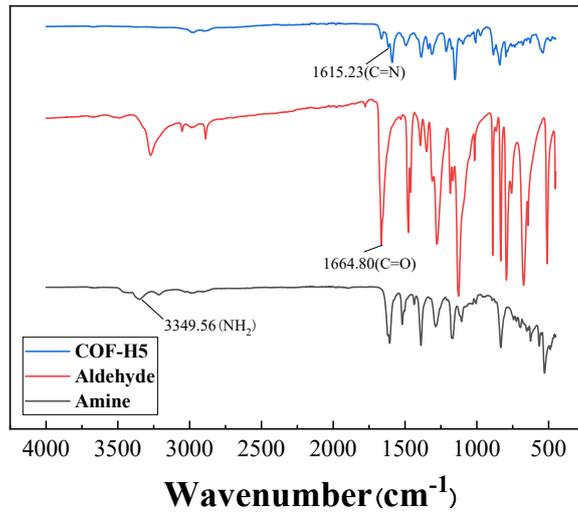
Fig. S2 FT-IR spectra of 2,3,5,6-tetrakis(4-aminophenyl)pyrazine, 2,5-dihydroxyterephthalaldehyde, and COF-H2.

3 SEM images
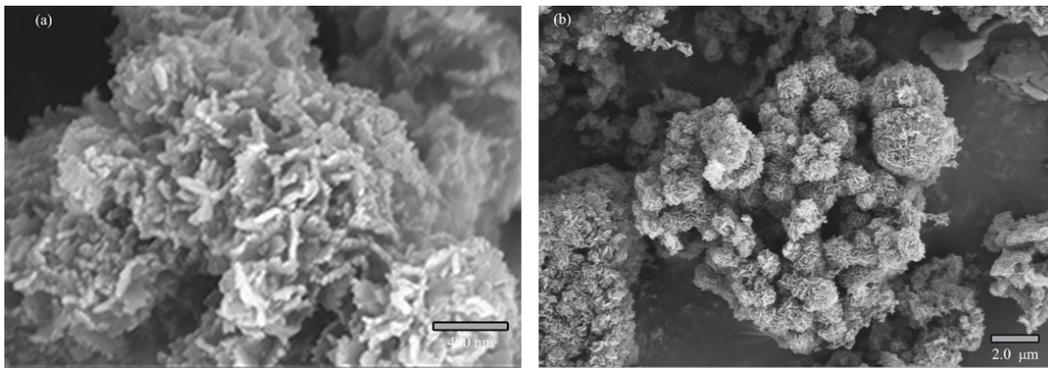
Fig. S3. SEM images of the prepared COF-H1.
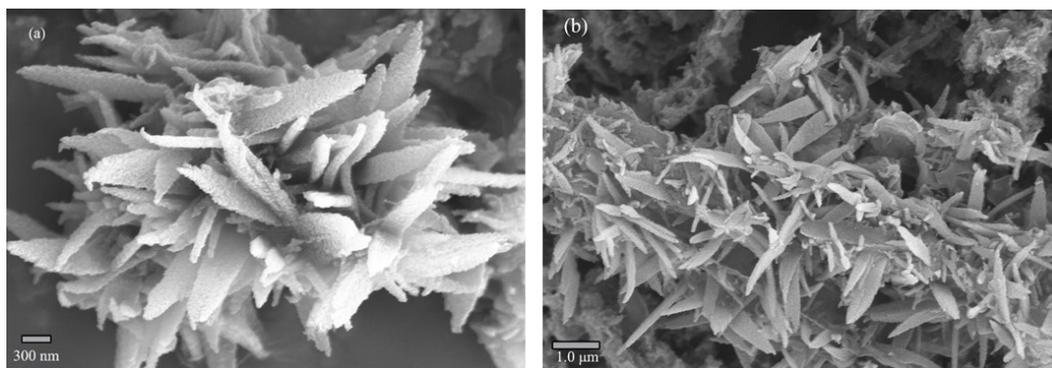
Fig. S4 SEM images of the prepared COF-H2.

4 TGA curves
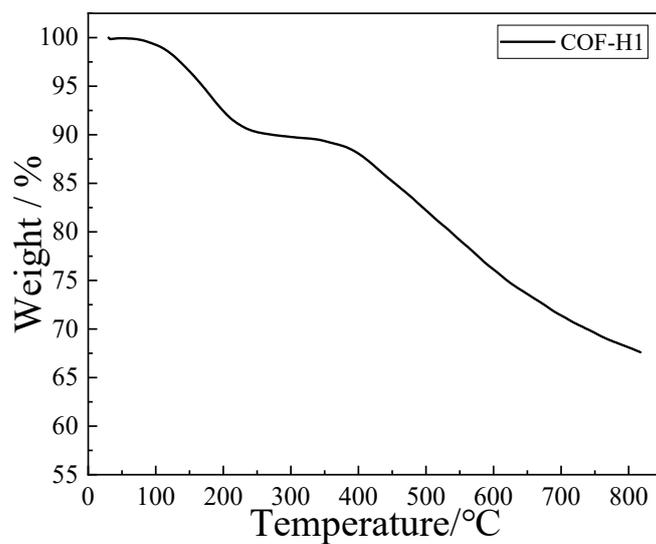
Fig. S5 TGA curve of COF-H1.
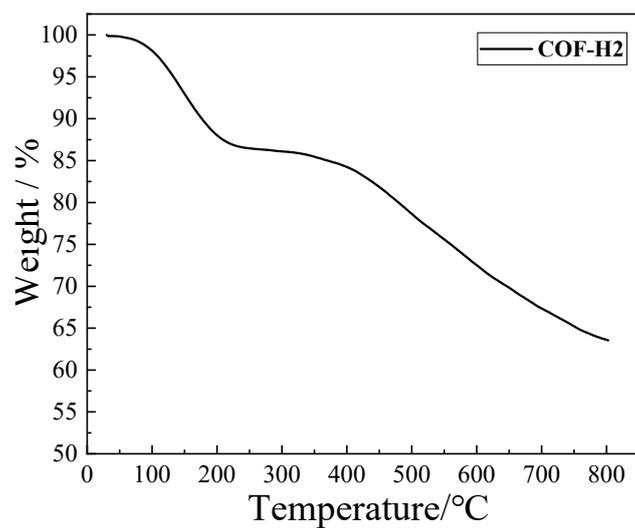
Fig. S6 TGA curve of COF-H2.

5 PXRD patterns of COF-H1 and COF2 soaked in different solvents
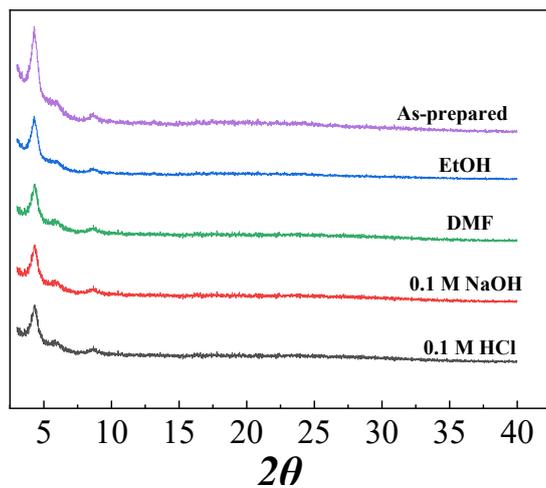
Fig. S7 PXRD patterns of COF-H1 soaked in different solvents for 24 h at room temperature.
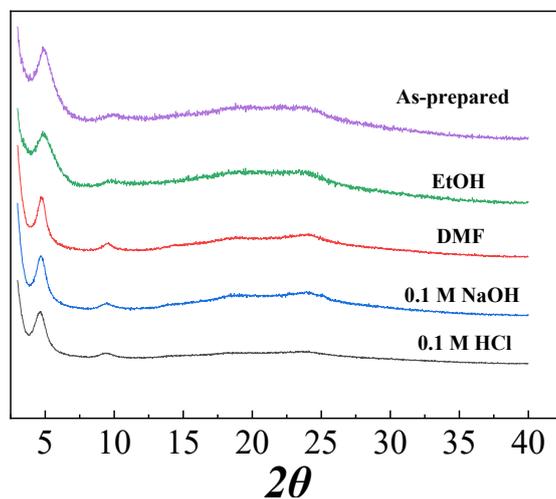
Fig. S8 PXRD patterns of COF-H2 soaked in different solvents for 24 h at room temperature.
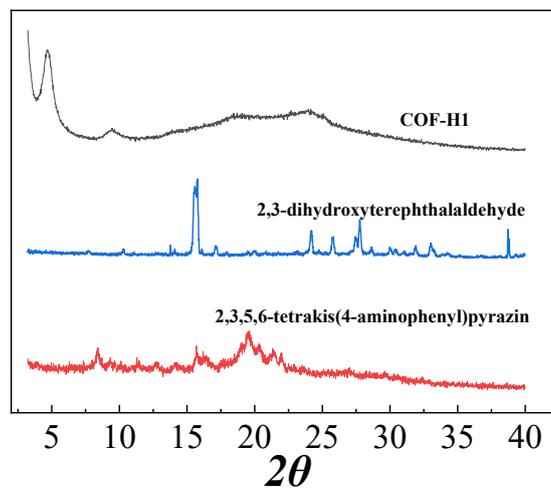
Fig. S9 XRD patterns of COF-H1 and its precursor.
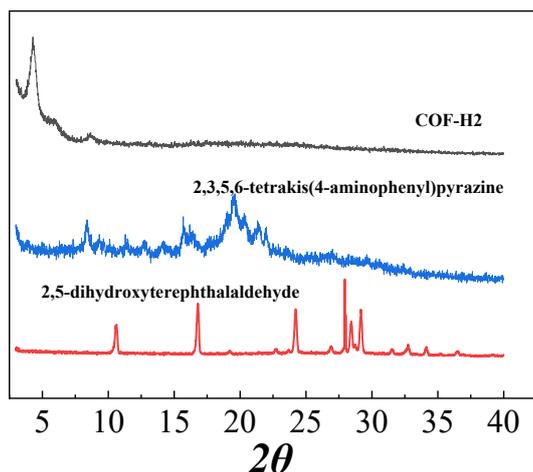
Fig. S10 XRD patterns of COF-H2 and its precursor.

6 CO$_2$ adsorption heat curves
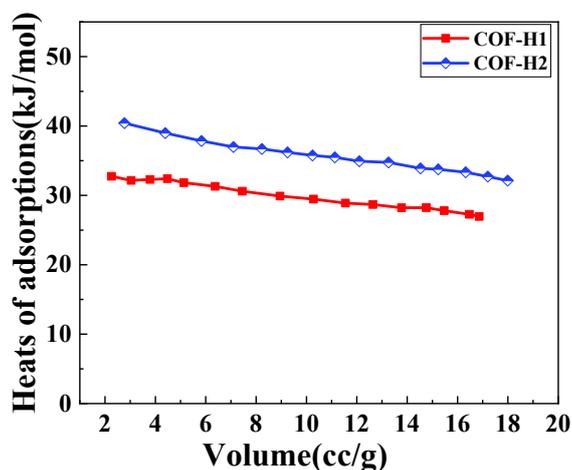
Fig. S11 Adsorption heat curves of COF-H1 and COF-H2 to CO$_2$.

7 standard curves of 4 dyes

RhB (1.0 mg) was dissolved in 100 mL of water to prepare 100 mg L^{-1} RhB solution, which was diluted with distilled water to prepare 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mg L^{-1} RhB standard solutions, respectively. Afterward the UV-Vis spectra of the different RhB standard solutions were collected (the left of Fig. S12a). As shown in Fig. S12a, the absorbance at the maximum adsorption wavelength increases with the increasing of RhB concentration. According to this, the linear relationship (the right of Fig. S12a) between the RhB concentration and the absorbance is obtained by fitting and matches the standard equation inserted in Fig. S12a.

Similar to the above, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mg L^{-1} MB, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 24.0 and 28.0 mg L^{-1} CR, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 mg L^{-1} GV standard solutions were prepared. The UV-Vis spectra of the different standard solutions were also gathered (the left of Fig. S12b-d). Analogously to RhB, the linear relationships and standard equations of MB, CR, and GV were established in turn (Fig. S12b-d). The following equilibrium concentration of the dye adsorption was calculated by the fitted standard equation.

50 mg of activated COF-H1 was dispersed in 50 mL of water to prepare 1 mg mL^{-1} COF-H1 stock solution in a volumetric flask. Subsequently 1 mg mL^{-1} COF-H2 stock solution was prepared in the same way.
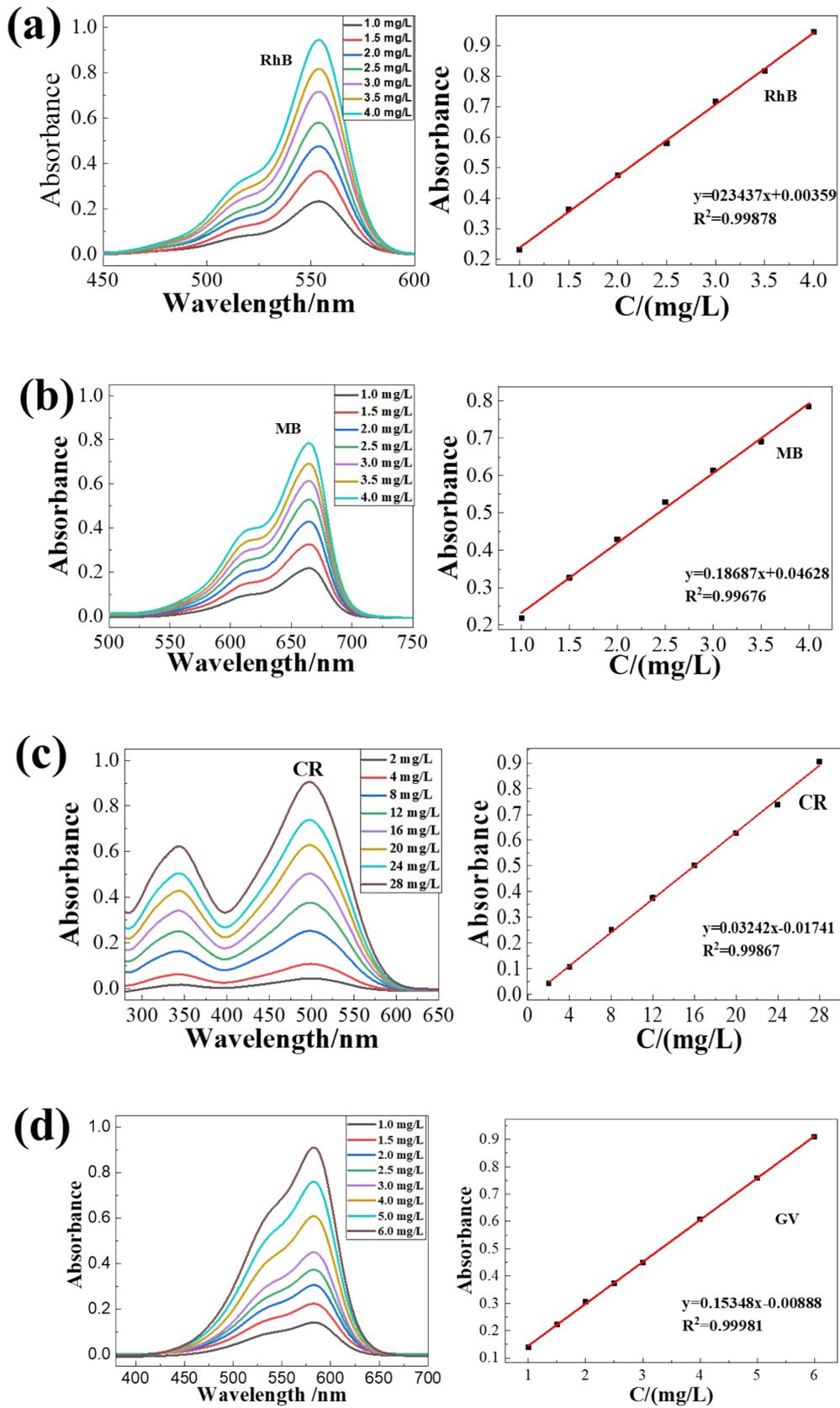
Fig. S12 UV-Vis spectra and standard curves of four target dyes.

8 Dye removal rate graphs

To six 2 mL of 4 mg L^{-1} RhB solutions were added 50, 100, 200, 400, 800, and 1000 μL of 1 mg L^{-1} COF-H1 (COF-H2) dispersion respectively, which were all diluted to 3 mL with water. Similarly, starting with 2 mL of 4 mg L^{-1} MB (24 mg L^{-1} CR and 6 mg L^{-1} GV) solutions, six 3 mL aqueous solutions of MB (CR and GV) and COF-H1 (COF-H2) were prepared separately. On the basis of the foregoing, the dye removal rates of the two COFs relate to the dye concentration before and after adsorption equilibrium in the equation 1, which correspond to absorbance at the maximum absorption wavelength. In order to obtain the relationship between the absorbance and dye concentration, all supernatants from the above solutions of 5 minutes of ultrasound were subjected to UV-Vis spectroscopy (Fig. S13 and S14). As shown in the right of Fig. S13a-d and Fig. S14a-d, according to the spectral data and equation 1, the dye removal rate curves of the two COFs were fitted. The insets of Fig. S13 and Fig. S14 are the color change contrasts of the dye residues along with the volume increase of the two COFs solution.

The dye removal rate equation[2] is given below.

$$E（100\%） = \frac{C_0 - C_e}{C_0} * 100\% \qquad (1)$$

C_0: initial concentration of the dye solution (mg L^{-1});
C_e: concentration of the dye at adsorption equilibrium (mg L^{-1}).

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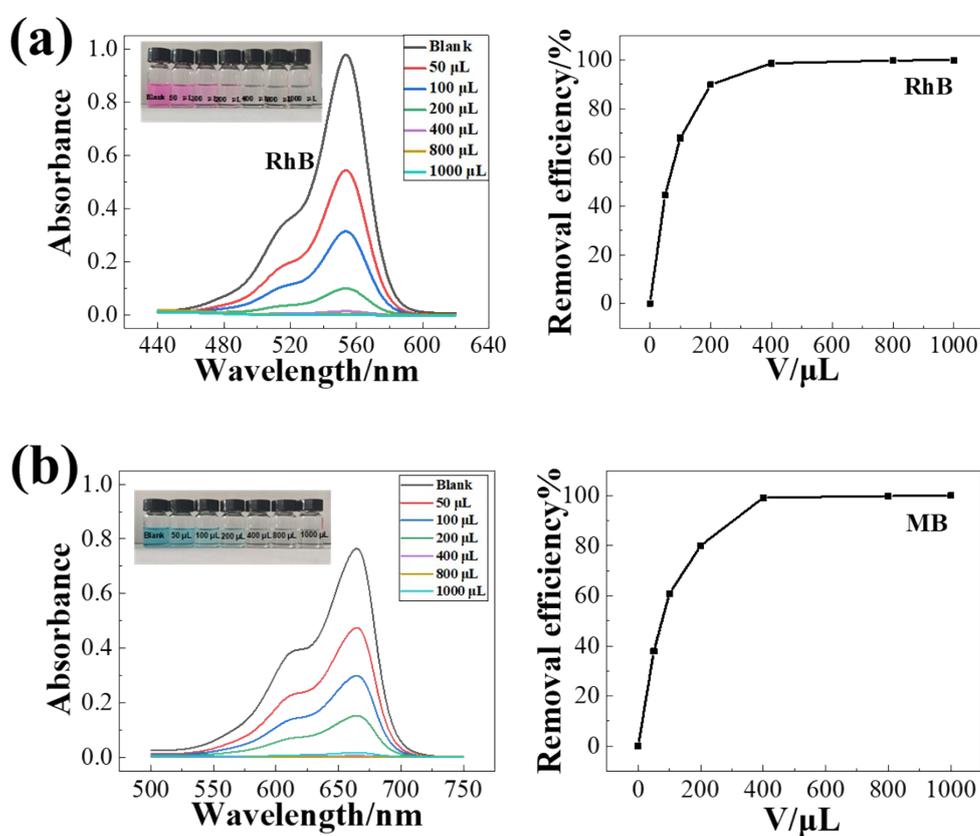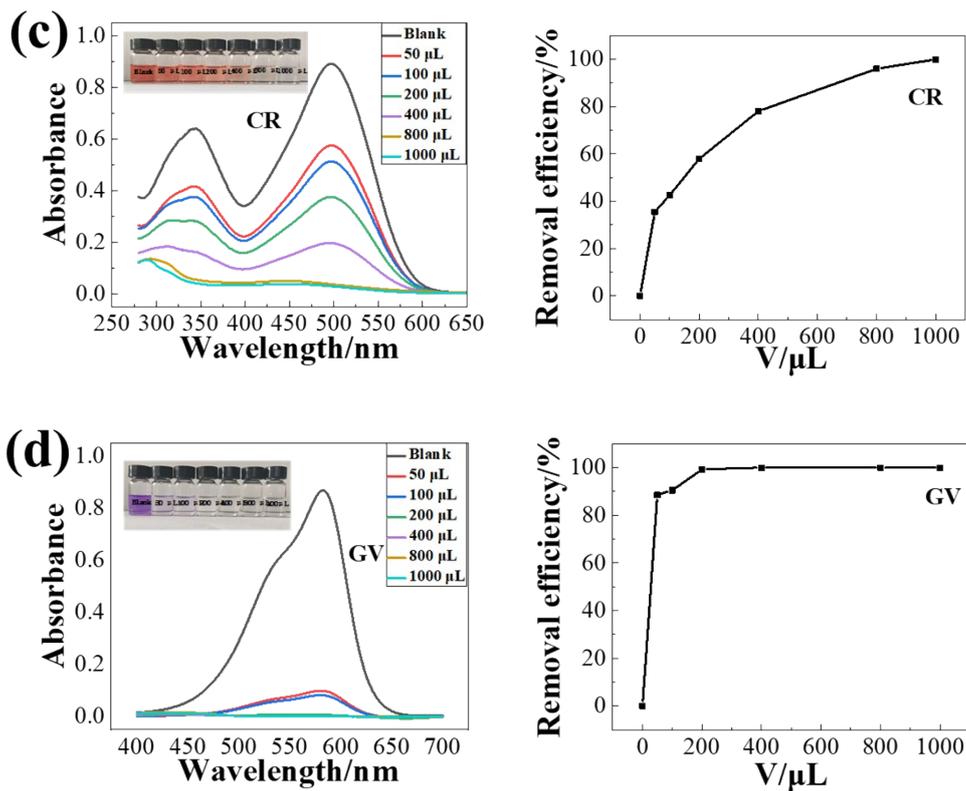
Fig. S13 The UV-Vis spectra of dyes before and after adsorption equilibriums (left) and dye removal rate curves (right) under different COF-H1 solution volumes ((a) RhB, (b) MB, (c) CR and (d) GV).
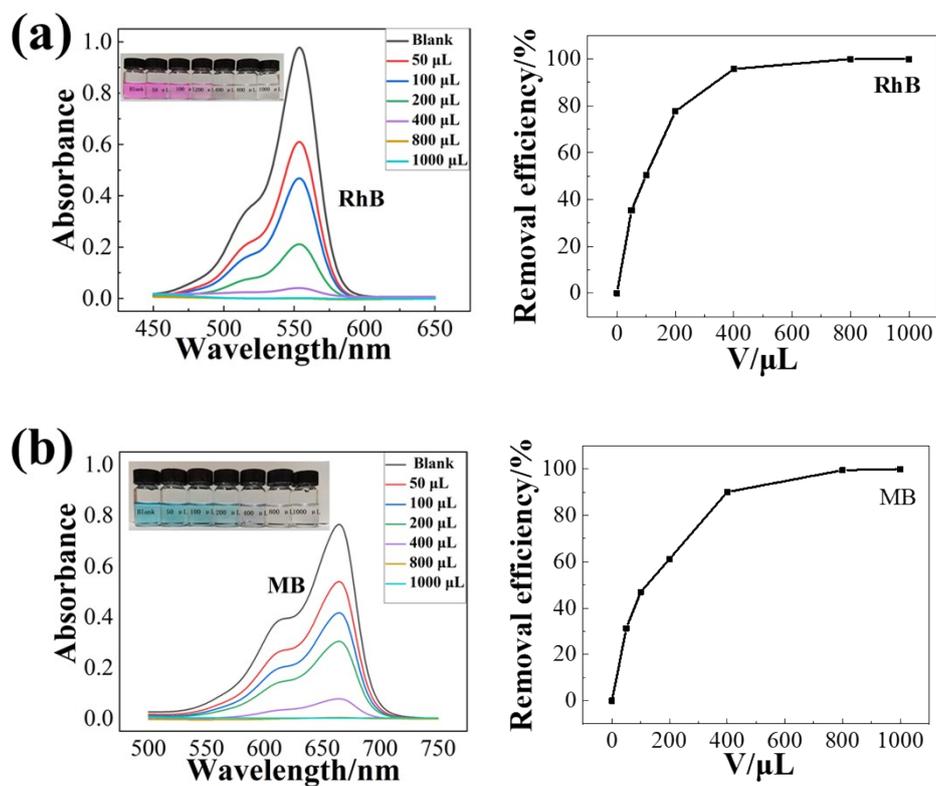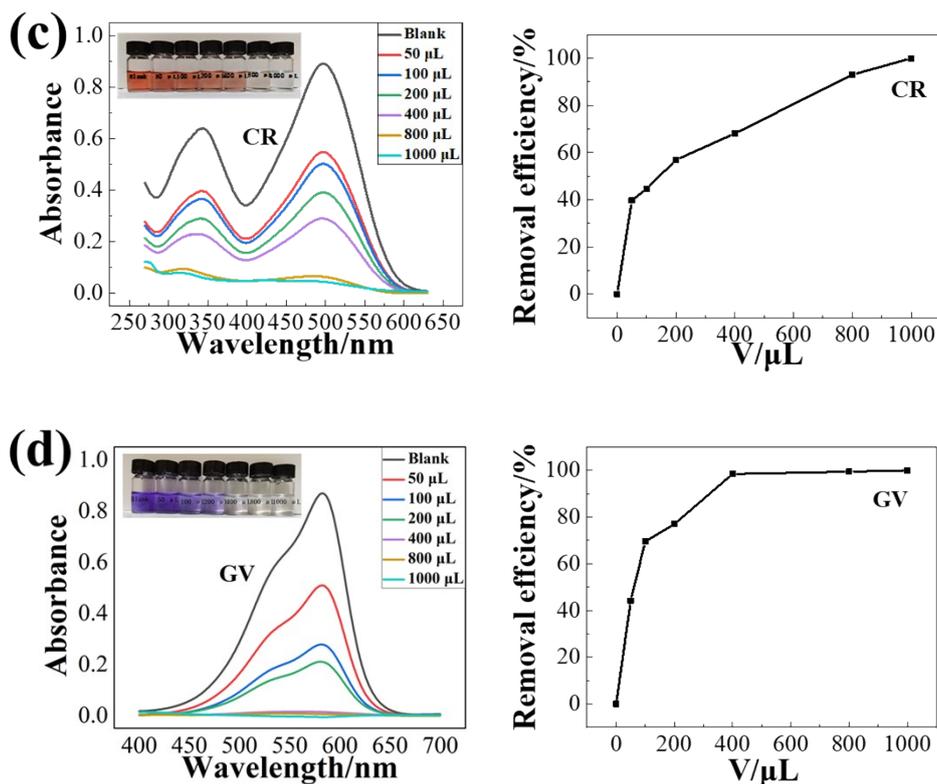
Fig. S14 The UV-Vis spectra of dyes before and after adsorption equilibriums (left) and dye removal rate curves (right) under different COF-H2 solution volumes ((a) RhB, (b) MB, (c) CR and (d) GV.

9 Dye uptake capacities

Similar to the experiments of the dye removal rate, to six 2 mL of 4, 6, 8, 10, 12 and 14 mg L^{-1} RhB solutions were added 100 μL of 1 mg L^{-1} COF-H1 (COF-H2) dispersion respectively, which were all diluted to 3 mL with water. Similarly, starting with 2 mL of 4, 6, 8, 10, 12 and 14 mg L^{-1} MB (14, 16, 18, 20, 22, 24 mg L^{-1} CR and 6, 8, 10, 12, 14 and 16 mg L^{-1} GV) solutions, six 3 mL aqueous solutions of MB (CR and GV) and COF-H1 (COF-H2) were prepared separately. In order to obtain the relationship between the dye absorption capacity and concentration, all supernatants from the above solutions of 5 minutes of ultrasound were subjected to UV-Vis spectroscopy (Fig. S16 and Fig. S17). According to the spectral data (Fig. S16a-d and Fig. S17a-d) and equation 2, the equilibrium adsorption capacity curves of the two COFs were fitted.

The adsorption capacity equation[3] of COFs for different dyes is given below.

$$Q = \frac{1000(C_0V_0 - C_eV_e)}{C_mV_m} \qquad (2)$$

Q: dye adsorption capacity of the COF sample (mg g^{-1});

C_0: initial concentration of the dye solution (mg L^{-1});

V_0: initial volume of the dye solution (mL);

C_e: concentration of dye solution at adsorption equilibrium (mg L^{-1});

V_e: volume of dye solution at adsorption equilibrium (mL);

C_m: initial concentration of COF dispersion (mg L^{-1});

V_m: initial volume of COF dispersion (mL).
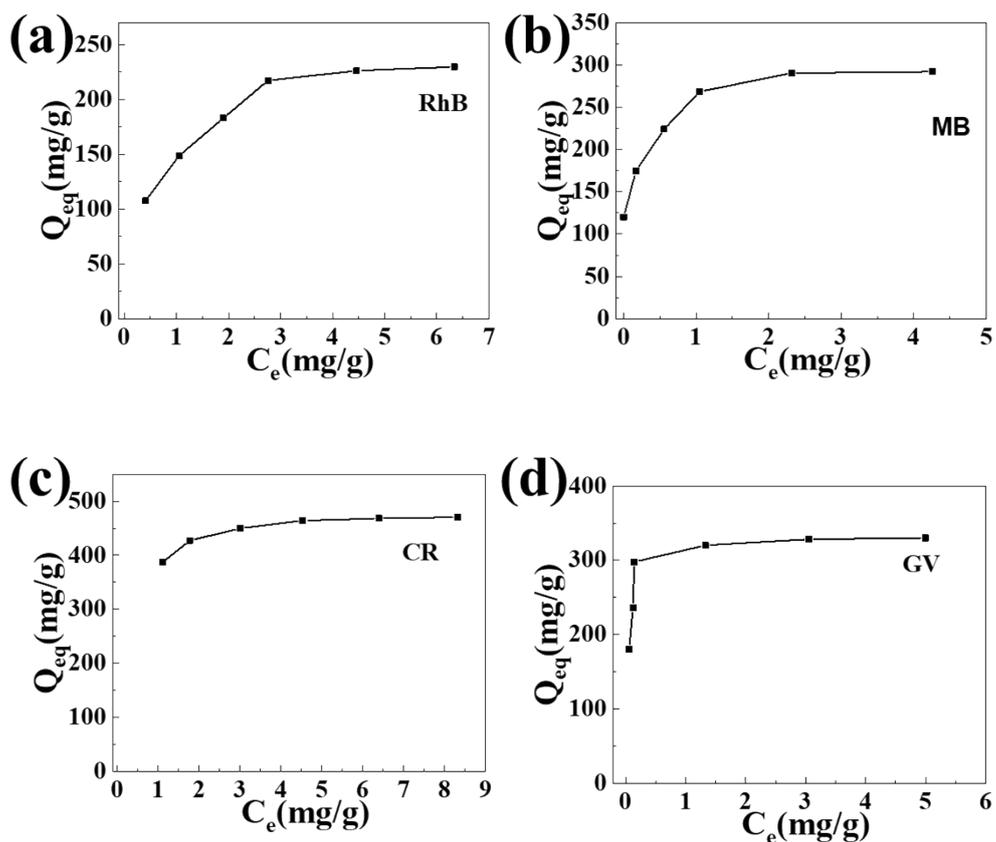
Fig. S15 The maximum adsorption capacity of COF-H1 on the dye (a) RhB, (b) MB, (c) CR and (d) GV.
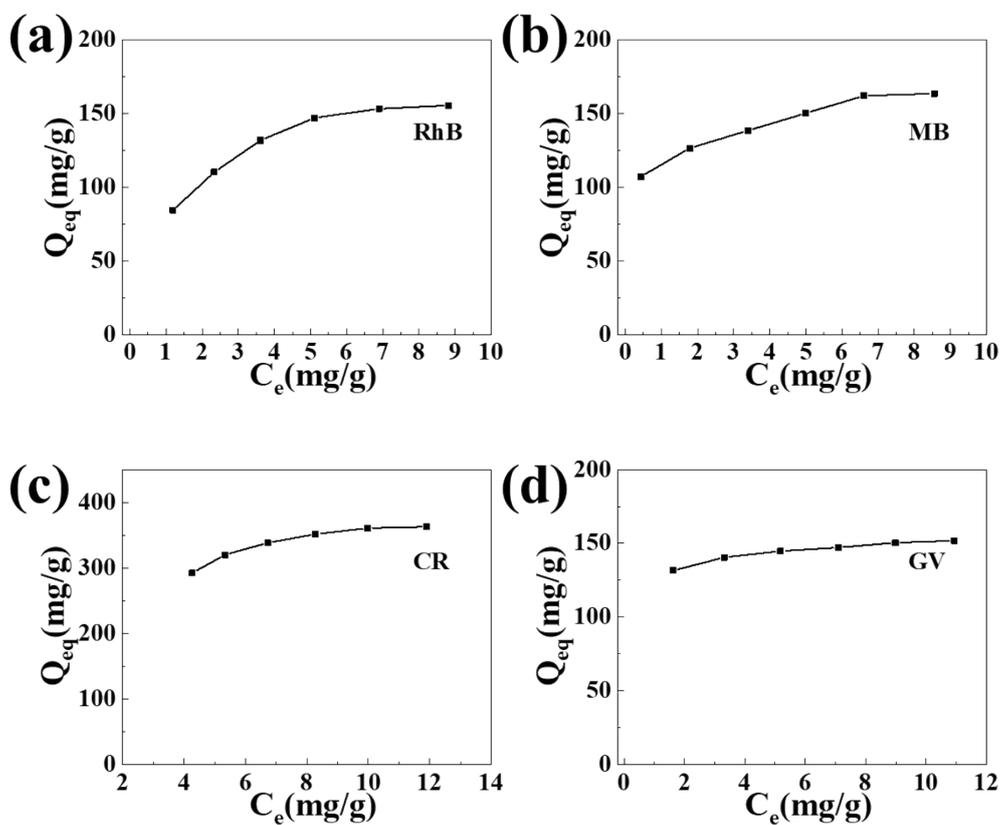
Fig. S16 The maximum adsorption capacity of COF-H2 on the dye (a) RhB, (b) MB, (c) CR and (d) GV.

10 The cyclic reproducibility of COF-H1 (COF-H2)

The dye-absorbed samples of COF-1 (COF-2) were collected and washed with ethanol and water (V/V = 1/1) through two ultrasonic-centrifugal cycles to remove the loaded dyes before the reproducibility experiments of the adsorbent COFs were performed. To 2 mL of 4 mg L^{-1} RhB (4 mg L^{-1} MB, 28 mg L^{-1} CR and 6 mg L^{-1} GV) solution was added 400 μL of 1 mg L^{-1} COF-H1 (COF-H2) dispersion, which was diluted to 3 mL with water. after adsorbed by ultrasonic for 5 min, centrifuged, the supernatant was taken to test the ultraviolet spectrum. Similar to the experiments of the dye removal rate, all reproducible results are shown in Fig. 17S.
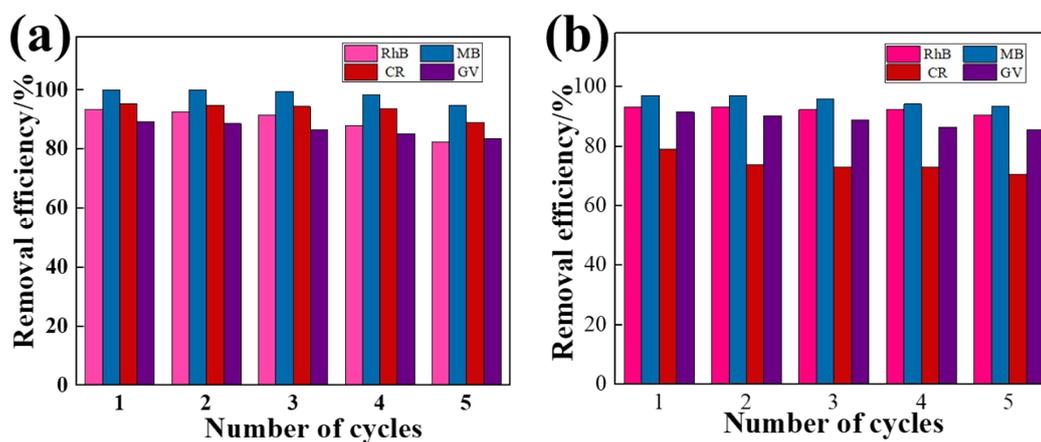
Fig. S17 Reusability of (a) COF-H1and (b) COF-H2 for the adsorption of RhB, MB, CR and GV.

11 NMR and MS spectra of 2,3,5,6-tetrakis (4-aminophenyl) pyrazine
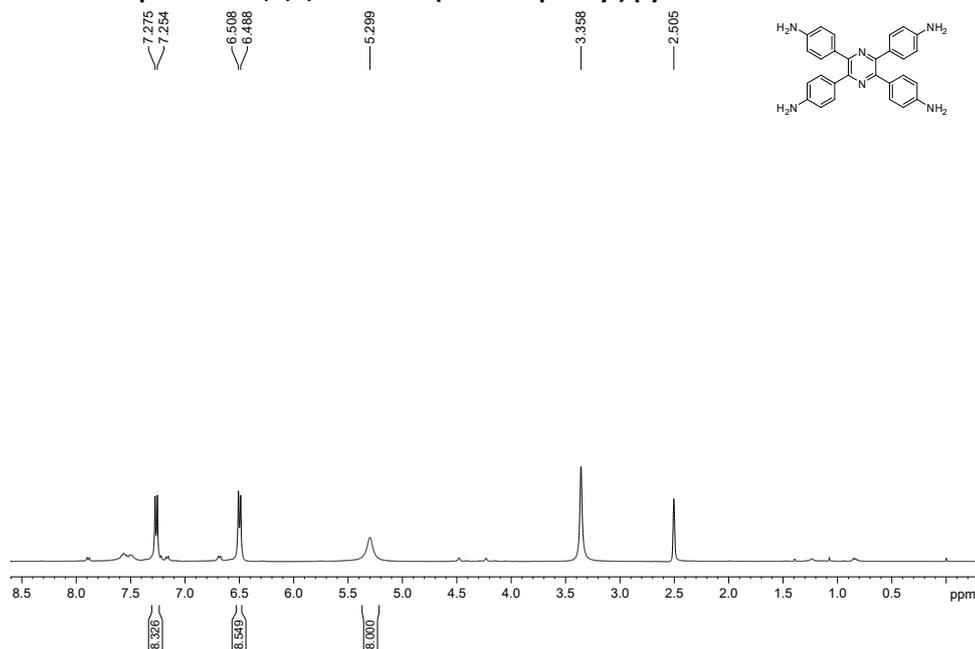
Fig. S18 ^{1}H NMR spectrum of 2,3,5,6-tetrakis (4-aminophenyl) pyrazine.

13
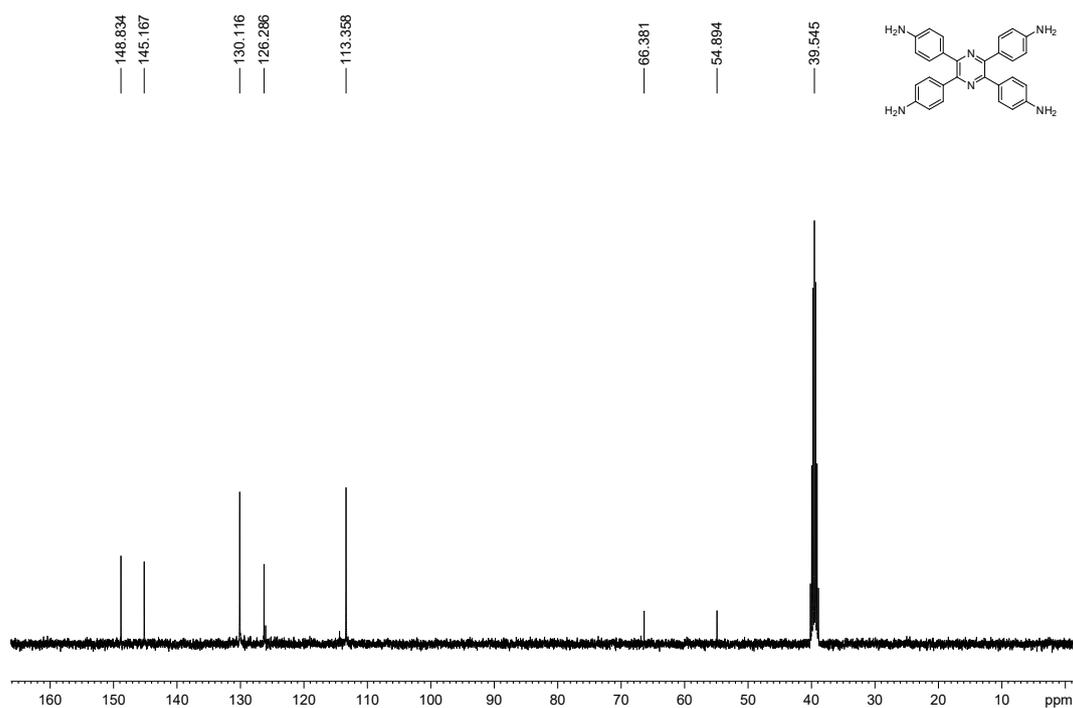
Fig. S19 ^{13}C NMR spectrum of 2,3,5,6-tetrakis (4-aminophenyl) pyrazine.

Chemical Formula: C$_{28}$H$_{25}$N$_6^+$
Exact Mass: 445.2135
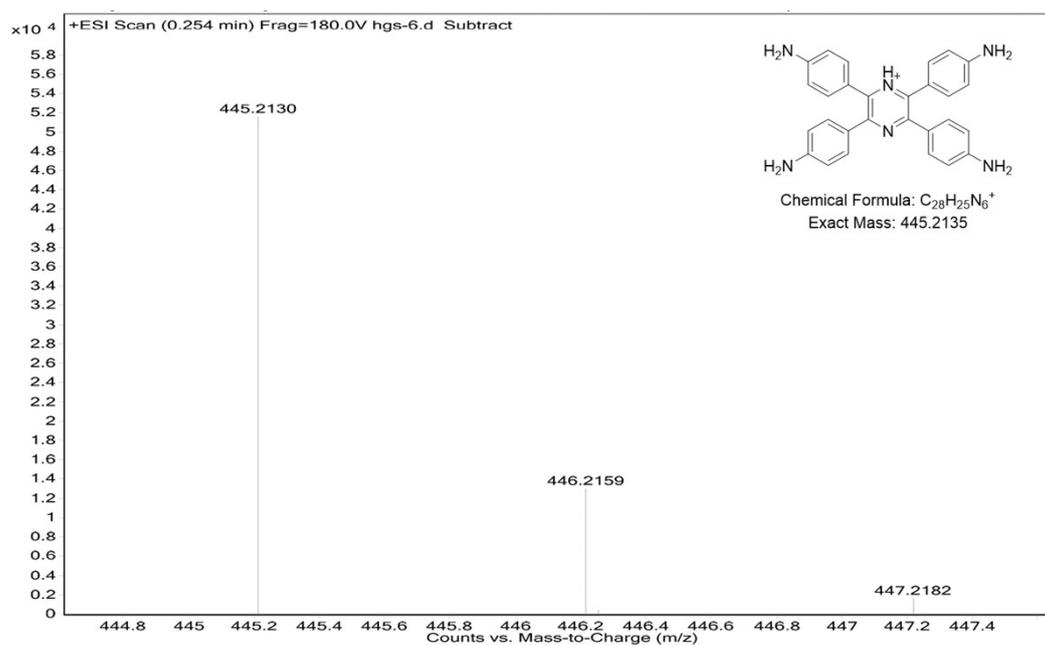
Fig. S20 High resolution mass spectrum of 2,3,5,6-tetrakis (4-aminophenyl) pyrazine.

Reference

1   G. R. Fulmer, A. J. M Miller., N. H. Sherden, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

2   S. Konavarapu, and K. Biradha, *Cryst. Growth Des.*, 2018, **19**, 362-368.

3   H. Liu, P Li, Y. Wang, H. Wang, Y. Fang, Z. Guo, Y. Huang, J. Lin, L. Hu, C. Tang, and Z. Liu, *Chemosphere*, 2022, **288**, 132520.