Electronic Supplementary Information

Amino-based Covalent Organic Frameworks for a Wide Range of Functional Modification

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Section S1. Materials and methods

Benzene-1,3,5-Tricarbadehyde (TFB) (97%), 4-Cyanobenzaldehyde (≥98%), 4-(Trifluoromethyl) PhenylIsothiocyanate(≥98%), 4-CyanobenzoylChloride (≥98%) were purchased from Adamas Reagent, Ltd. p-chloronitrobenzene (CP) was purchased from Shanghai Chemical Reagent Co., Ltd. Dimethyl aminoterephthalate (99%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. 2,5-diethoxybenzene-1,4-dicarbohydrazide (97%) was purchased from Zhengzhou Alfa Chemical Co. Ltd. Sodium hydrogen carbonate(KOH) (AR) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Sodium hydrogen carbonate(NaHCO\textsubscript{3})(99.5%) was purchased from Tianjin Tianli Chemical Reagent Co. Ltd. Organic solvents such as acetic acid (99.7+%), tetrahydrofuran (THF) (≥99%, AR), anhydrous MeOH (≥99.5%), N,N-dimethylformamide (DMF) (≥99.5%), acetone (≥99.5%) were purchased from commercially and used without further purification.

Power X-ray diffraction (PXRD) data were obtained with an X’ Pert3 powder diffractometer at 40 kV and 40 mA with Cu Kradiation from 2θ = 2° to 40° in 0.05° increment. Fourier transform infrared (FT-IR) of the samples were collected on a Spectrum 400 spectrometer (Perkin-Elmer). All samples were ground into a powder with KBr and pelletized before the measurements. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASiQwin Quantachrome instrument. The samples were treated at 150 °C for 8 h before measurements. Specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Pore size distribution data were calculated based on the nonlocal density functional theory (NLDFT) model. Field emission scanning electron microscopy (FE-SEM) observations were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0 kV. In order to analyze the thermal properties of the materials, thermogravimetric analysis (TGA) data were obtained on a STA449C under N\textsubscript{2} atmosphere from 50°C to 800°C along with a ramp rate of 10°C min\textsuperscript{-1}. 
Synthesis of 2-amino-1,4- dicarbohydrazide (2)

In a 100 mL round-bottom flask, a solution of 1.0g (4.7mmol) Dimethyl aminoterephthalate in 20 mL of methanol was mixed with 7.5mL of hydrazine hydrate. After refluxing the solution over night, a pale yellow precipitate appeared. The crude product was filtered and recrystallized from ethanol twice and further dried for 24 hours at 50 °C to afford the desired compound as a pale yellow powder (0.5 g, 50% yield).

Synthesis of \([\text{NH}_2]_{50\%}\text{COF-HNU13}\)

32.4 mg (0.20 mmol) of TFB (1), 31.4 mg (0.15 mmol) of 2-amino-1,4-dicarbohydrazide (2), 42.3mg (0.15 mmol) of 2,5-diethoxybenzene-1,4-dicarbohydrazide (3), dioxane(2mL), 1,3,5-Trimethylbenzene (6mL) were charged into a glass tube, after dispersing evenly, add 6M acetic acid(0.8mL), followed by the degassing procedure using freeze-pump-thaw cycles for three times. The glass vial was then flame-sealed and the mixture was allowed to react at 120°C for 3 days. After being collected by filtration, the precipitate was washed with ethanol, tetrahydrofuran, and acetone. Finally, the solid was dried at under vacuum at 60°C for 12 h to obtain \([\text{NH}_2]_{50\%}\text{COF-HNU13}\) as a yellow powder (yield: 95.0 %).

Synthesis of \([\text{R1}]_{50\%}\text{COF-HNU13}\)

20mg \([\text{NH}_2]_{50\%}\text{COF-HNU13}\), 60.8mg (0.4mmol) 4-Methylmercaptobenzaldehyde and EtOH (2mL) were added into a glass tube. After the slurry was sonicated for 5 min, 3M acetic acid (0.1 mL) was added. Then, the mixture was degassed and stirred at 80°C for 12 hours. Upon cooling, the resulting precipitate was collected by filtration and washed with water and ethanol. Finally, the solid was dried at under vacuum at 60 °C as a yellow powder (yield: 96%).

Synthesis of \([\text{R2}]_{50\%}\text{COF-HNU13}\)

20mg \([\text{NH}_2]_{50\%}\text{COF-HNU13}\), 81.3 mg (0.4 mmol) 4-(trifluoromethyl)phenyl
isothiocyanate and DMF (2 mL) were added into a glass tube. Then, the mixture was heated at 40°C for 3 hours under stirring. Upon cooling, the resulting precipitate was collected by filtration and washed with water and ethanol. Finally, the solid was dried at under vacuum at 60 °C as a yellow powder (yield: 97 %).

Synthesis of [R3]_{50%} COF-HNU13

20mg [NH$_2$]$_{50%}$COF-HNU13, 52.5mg (0.4mmol) 4-cyanobenzoyl chloride and 1/1 (v/v) mixture of THF/NaHCO$_3$ (aq) were added into a glass tube under ambient conditions. Then, the mixture was stirred for 3 hours. The resulting precipitate was collected by filtration and washed with water and ethanol. Finally, the solid was dried at under vacuum at 60 °C as a yellow powder (yield: 97 %).

Synthesis of [R4]_{50%} COF-HNU13

20mg [NH$_2$]$_{50%}$COF-HNU13, 63.0 mg (0.4mmol) p-chloronitro-benzene, 70 mg (1.25 mmol) KOH and DMF (5 mL) were added into a glass tube. Then, the mixture was heated at 50°C for 12 hours under stirring. Upon cooling, the resulting precipitate was collected by filtration and washed with water and ethanol. Finally, the solid was dried at under vacuum at 60 °C as a yellow powder (yield: 93 %).
Section S2. Figures S1-13

**Figure S1** FT-IR spectra of the $[\text{NH}_2]_{0\%}\text{COF-HNU13}$ and $[\text{NH}_2]_{50\%}\text{COF-HNU13}$.

**Figure S2** SEM images of the $[\text{NH}_2]_{50\%}\text{COF-HNU13}$. 
Figure S3 Nitrogen sorption isotherms of [NH$_2$]$_{50\%}$COF-HNU13 and [R1]$_{50\%}$COF-HNU13 at 77 K.

Figure S4 (a) NLDFT pore size distributions of [NH$_2$]$_{50\%}$COF-HNU13 and [R1]$_{50\%}$COF-HNU13, (b) NLDFT pore size distributions of [R2]$_{50\%}$COF-HNU13, [R3]$_{50\%}$COF-HNU13 and [R4]$_{50\%}$COF-HNU13.
Figure S5 TGA curves of [NH$_2$]$_{50\%}$COF-HNU13.

Figure S6 SEM images of [R1]$_{50\%}$COF-HNU13.

Figure S7 SEM-EDS mapping images of [R1]$_{50\%}$COF-HNU13.
Figure S8 N\textsubscript{2} sorption isotherm at 77 K of \([R2]\)\textsubscript{50\%}\text{COF-HNU13}, \([R3]\)\textsubscript{50\%}\text{COF-HNU13} and \([R4]\)\textsubscript{50\%}\text{COF-HNU13}, respectively.

Figure S9 SEM images of the \([R2]\)\textsubscript{50\%}\text{COF-HNU13}.

Figure S10 SEM images of the \([R3]\)\textsubscript{50\%}\text{COF-HNU13}.
Figure S11 SEM images of the [R4]_{50\%} COF-HNU13.

Figure S12 (a) High-resolution N 1s XPS spectra of [NH2]_{50\%} COF-HNU13, (b) High-resolution F 1s XPS spectra of [R2]_{50\%} COF-HNU13, (c) High-resolution N 1s XPS spectra of [R3]_{50\%} COF-HNU13, (d) High-resolution Cl 2p XPS spectra of [R4]_{50\%} COF-HNU13.
Figure S13 (a) [$\text{NH}_2$]$_{50\%}$COF-HNU13 absorption spectrum of ofloxacin, and (b) [R2]$_{50\%}$COF-HNU13 absorption spectrum of ofloxacin.

Figure S14 $^1$H NMR spectrum of the product of the model reaction between benzaldehyde (2 mmol) and 2-amino-1,4- dicarbohydrazide (1 mmol). $^1$H NMR spectrum of the product showed that the aldehyde selectively reacted with hydrazine.