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Electronic Supporting Information

Amine-functionalized metal-organic framework as a sensing platform for DNA detection

Hao-Tian Zhang,[a] Jian-Wei Zhang,[ab] Gang Huang,[a] Zi-Yi Du[b] and Hai-Long Jiang*[a]

[a]*Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*

[b]*College of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou 341000, P.R. China*

*To whom correspondence should be addressed.

E-mail: jianglab@ustc.edu.cn

Tel: +86-551-63607861; Fax: +86-551-63607861

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Section 1 Materials and Instrumentation

All commercial chemicals were used without further purification unless otherwise mentioned. $ZrCl_4$ (Aladdin Industrial Inc., 98%), H_2N-H_2BDC (Sigma-Aldrich, 99%), H_2BDC (TCI, GR), DMF (Sinopharm Chemical Reagent Co., Ltd., AR), KCl (Energy Chemical, 99.8%), NaCl (Sinopharm Chemical Reagent Co., Ltd., AR), $MgCl_2$ (Aladdin Industrial Inc., CP), Tris (Aladdin Industrial Inc., UP) were used as received. The DNA sequences listed as follows were purchased from Sangon Biotech (Shanghai) Co., Ltd.:

[1] P_{HIV} (fluorescence fluorophore labeled single-stranded DNA):

5’-FAM-AGT CAG TGT GGA AAA TCT CTA GC-3’

[2] T_1 (target DNA to P_{HIV}):

5’-GCT AGA GAT TTT CCA CAC TGA CT-3’

[3] T_2 (single-base mismatched DNA to P_{HIV}):

5’-GCT AGA GAT TGT CCA CAC TGA CT-3’

[4] T_3 (mismatched DNA to P_{HIV}):

5’-TTT TTT TTT TTT TTT TTT TTT TT-3’

De-ionized water with the specific resistance of 18.25 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). X-ray powder diffraction patterns (XRD) of the product were obtained on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). Fluorescent emission spectra were done on a LS-55 fluorescence spectrometer made by PerkinElmer. Infrared absorption spectrums were done on a Nicolet 6700 Fourier Transform Infrared Spectroscopy made by Thermo Fisher Scientific Inc. Zeta potential measurements were done on a Delsa NanoCparticle analyzer made by Beckman Coulter, Inc. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at different temperatures. UiO-66-NH_2 was activated at 80 °C for 1 h, then at elevated temperature of 150 °C for 2 h. The activated sample was again evacuated by heating at 150 °C under a dynamic vacuum for 2 h by using the “outgas” function of the surface area analyzer prior to gas adsorption/desorption measurement.

Section 2 Experimental Section

2.1 Preparation of UiO-66-NH_2

The UiO-66-NH_2 was synthesized according to the reported approaches with modifications,[1] a mixture of $ZrCl_4$ (75 mg, 0.32 mmol) and 2-amino-1,4-benzene-dicarboxylic acid (NH_2-BDC) (58 mg, 0.32 mmol) was dissolved in N,N-dimethylformamide (DMF, 9 mL) at room temperature in a Teflon reactor (20 mL). The resulting mixture was placed in a preheated oven at 80 °C for 12 h and then held at 100 °C for 24 h. After cooling down to room temperature, the resulting solid was centrifuged and magnetically stirred with absolute ethanol for 3 days at room temperature. The resulting yellow powder were centrifuged, then dried under vacuum at ambient temperature.

2.2 Preparation of UiO-66

The UiO-66 was synthesized as follows, a mixture of $ZrCl_4$ (264.5 mg, 1.13 mmol) and 1,4-benzene-dicarboxylic acid (H_2BDC, 188.5 mg, 1.13 mmol) was dissolved in DMF (15 mL) at room temperature in a 20 mL vial. The solution was placed into a Teflon reactor (20 mL) at 120 °C for 24 h. The resulting white powder was centrifuged, then washed by DMF for three times and diethylether for the last time. The product was dried at room temperature in air.

2.3 Preparation of Buffer solution

The DNA solution was prepared with 20 mM Tris-HCl buffer, containing 100 mM

NaCl, 5 mM KCl and 5 mM $MgCl_2$ (pH = 7.42). Typically, the tris was first dissolved, and NaOH was then added to obtain the desired pH value. After the addition of NaCl, KCl and $MgCl_2$, the pH value of the buffer solution was finally re-examined.

2.4 Preparation of MOF-P_{HIV} composite

Firstly, 2 mg MOF was dispersed in 1 mL buffer by sonication, and P_{HIV} was dispersed in buffer at the concentration of 5 μM. Then, 1900 μL buffer, 20 μL P_{HIV} and 20 μL MOF were mixed together and shaken for 75 minutes at room temperature.

2.5 Fluorescent measurement

The MOF-P_{HIV} composite was mixed with 60 μL target (5 μM), being incubated for 4 h at room temperature, prior to the fluorescence investigation of P_{HIV} and P_{HIV}+MOF in the presence or absence of T_1. For other experiments, the MOF-P_{HIV} composite was mixed with 60 μL target (5 μM), being incubated for 24 h at room temperature before measurements. All fluorescent measurements were carried out at room temperature. Both the excitation and emission slit widths were set to 10.0 nm. The emission spectra were collected from 500 to 650 nm under the excitation wavelength of 480 nm, and the fluorescence intensity at 518 nm is used for analysis.

Section 3 Characterizations for UiO-66-NH_2

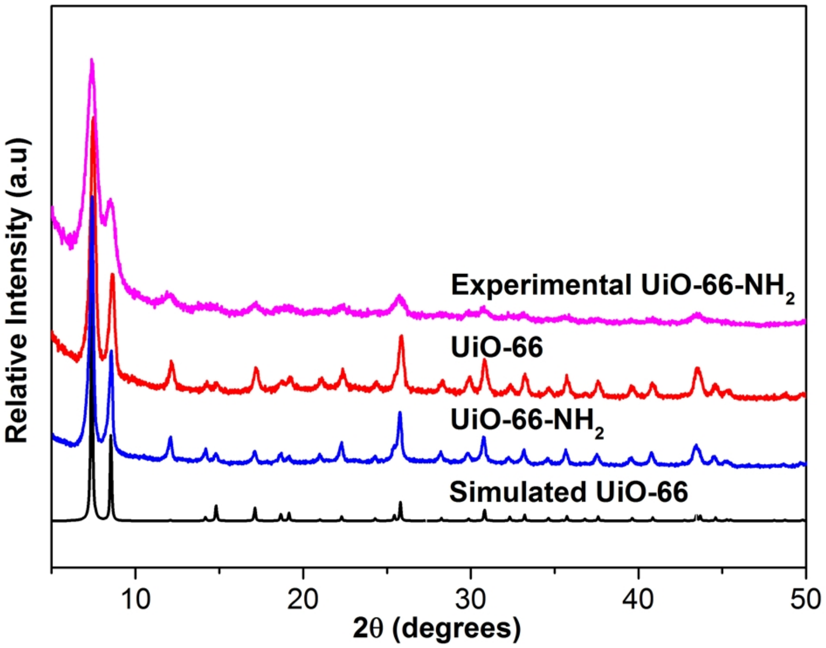

Fig. S1 Powder X-ray diffraction (XRD) profiles for simulated and experimental UiO-66, UiO-66-NH_2 and UiO-66-NH_2 dipped in DNA buffer for 24 h, demonstrating the well-retained framework of UiO-66-NH_2 during the experiment.

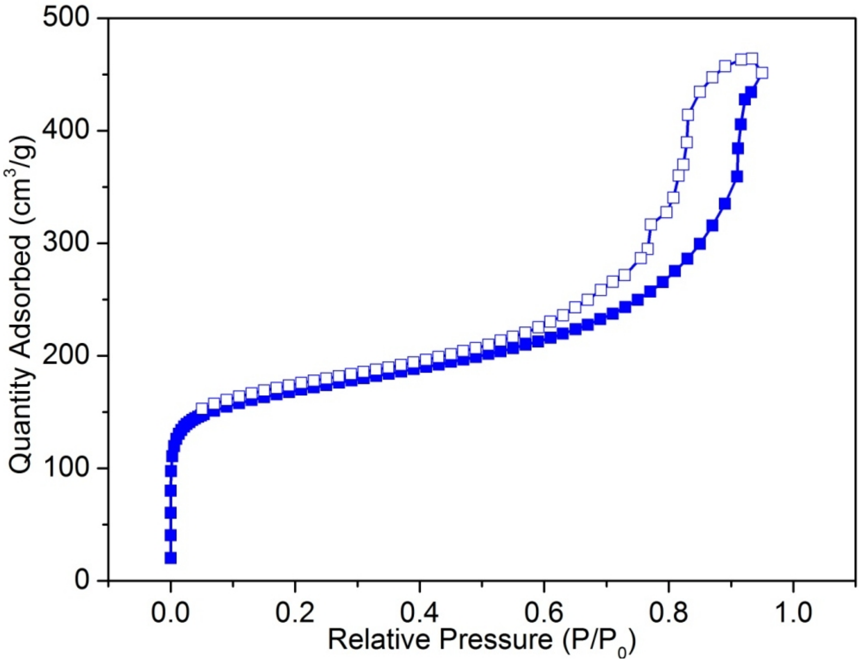

Fig. S2 N_2 adsorption (■) and desorption (□) isotherms for UiO-66-NH_2. The BET surface area and N_2 sorption isotherms are a bit different from those in the previous report.[1] The difference could be caused by the following points: 1) Although a similar synthetic approach to that in the report was employed, our reaction vessel (20 mL) is much smaller than the reported one, which allows the use of 180 mL DMF in each experiment. 2) Our activation process for UiO-66-NH_2 before N_2 sorption measurement is a bit different from that in the previous report. 3) The appearance of mesopore could be due to the interparticle voids as the small MOF particles stack together (see Figure 1D).

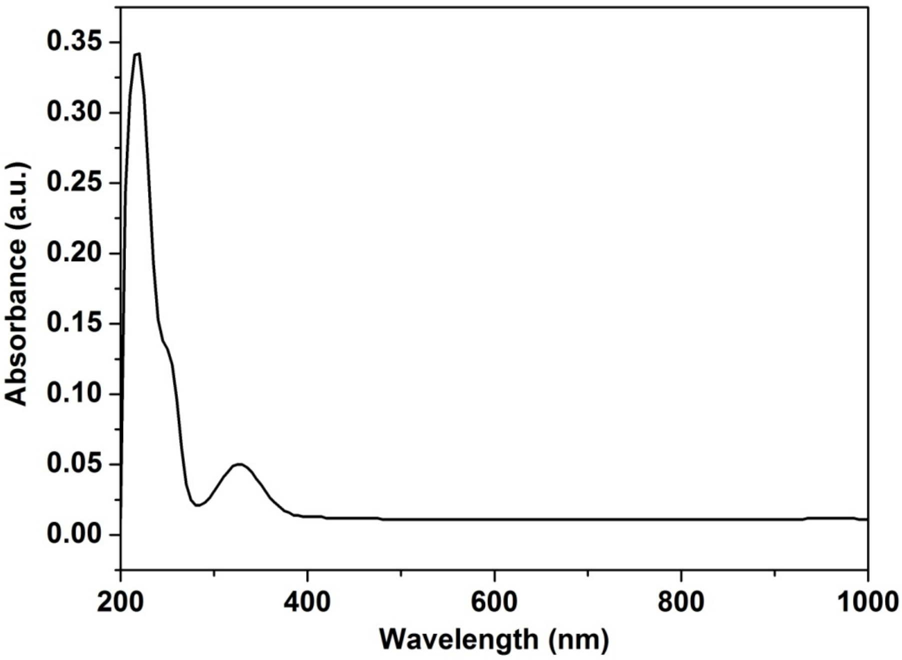

Fig. S3 The absorption spectrum of UiO-66-NH_2.

Section 4 Quenching kinetics of P_{HIV} with different amounts of UiO-66-NH$_2$

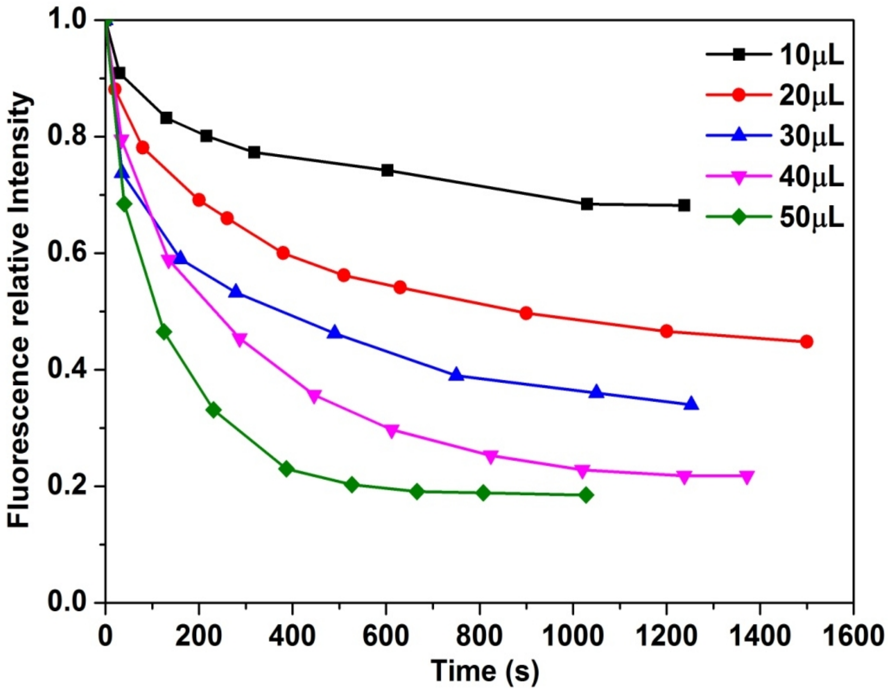

Fig. S4 Fluorescence quenching under λ_{ex} = 480 nm of P_{HIV} (50 nM) with different amounts of UiO-66-NH$_2$.

Section 5 Fluorescence spectra of P_{HIV} in different UiO-66 systems

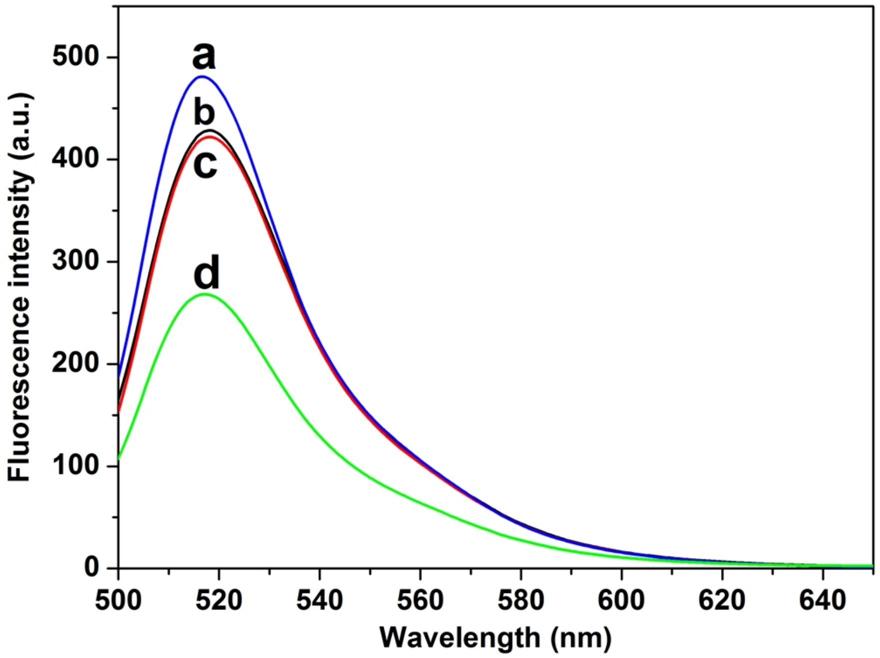

Fig. S5 Fluorescence spectra of P_{HIV} (50 nM) in different UiO-66 systems (λ_{ex} = 480 nm): (a) P_{HIV}; (b) P_{HIV}+UiO-66+T_1 (150 nM); (c) P_{HIV}+UiO-66+T_2 (150 nM); (d) P_{HIV}+UiO-66.

Section 6 The Infrared (IR) absorption spectrum of MOF-P_{HIV} composite

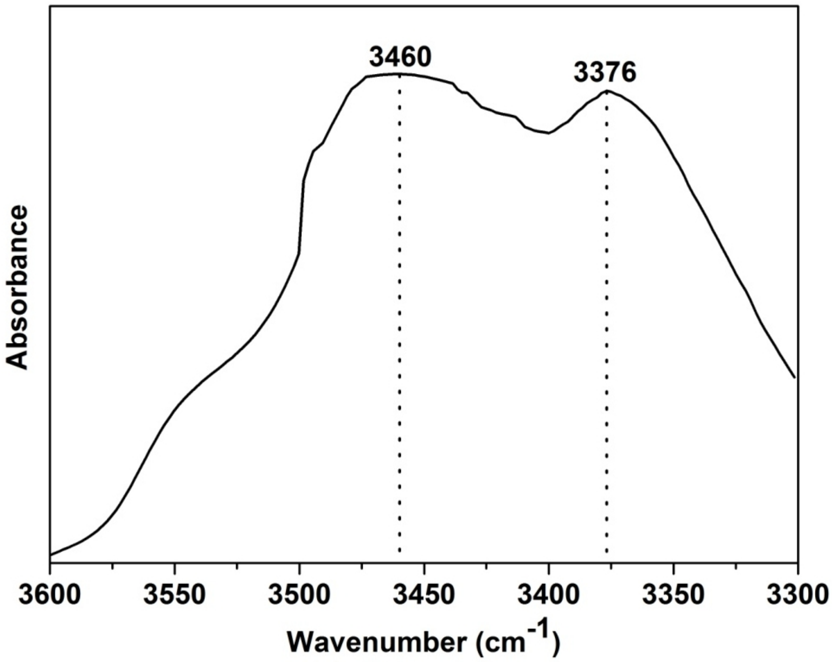

Fig. S6 The Infrared (IR) absorption spectrum of MOF-P_{HIV} composite, MOF represents UiO-66-NH_2.

Reference

1 M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632.