Supplementary Materials

Fluorescence detection and effective adsorption of trace Pb(II) based on nanofibrous metal-organic gel

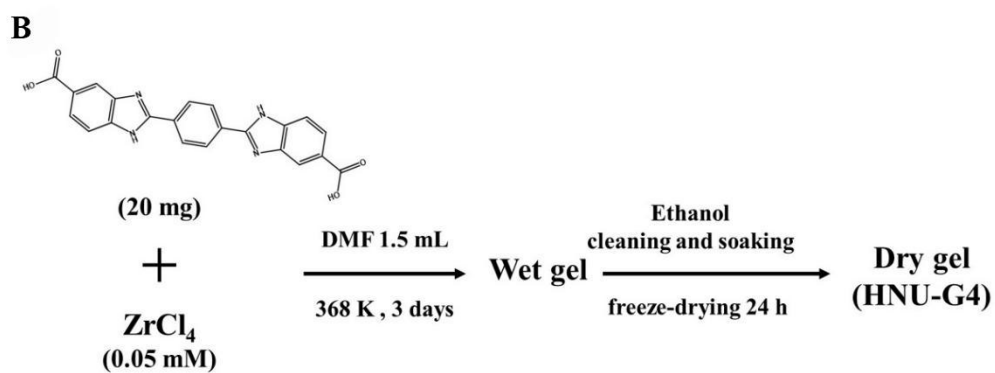**Yu Fang, Kechun Yu, Guojian Ren[*], Cong Wang, Qi Zhou, Guang Che, Meiling Li, Qinhe Pan[*]**

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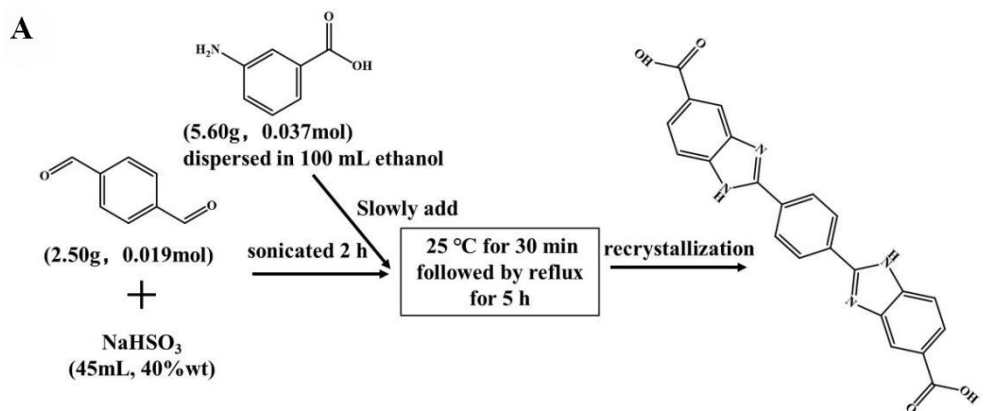[*]**Correspondence to:** Prof. Guojian Ren, Prof. Qinhe Pan, Key Laboratory of Advanced Materials of Tropical Island Resources, Ministry of Education, School of Chemistry and Chemical Engineering, Hainan University, 58 Renmin Avenue, Haikou 570228, Hainan, China. E-mail: rgj860508@163.com; panqinhe@163.com
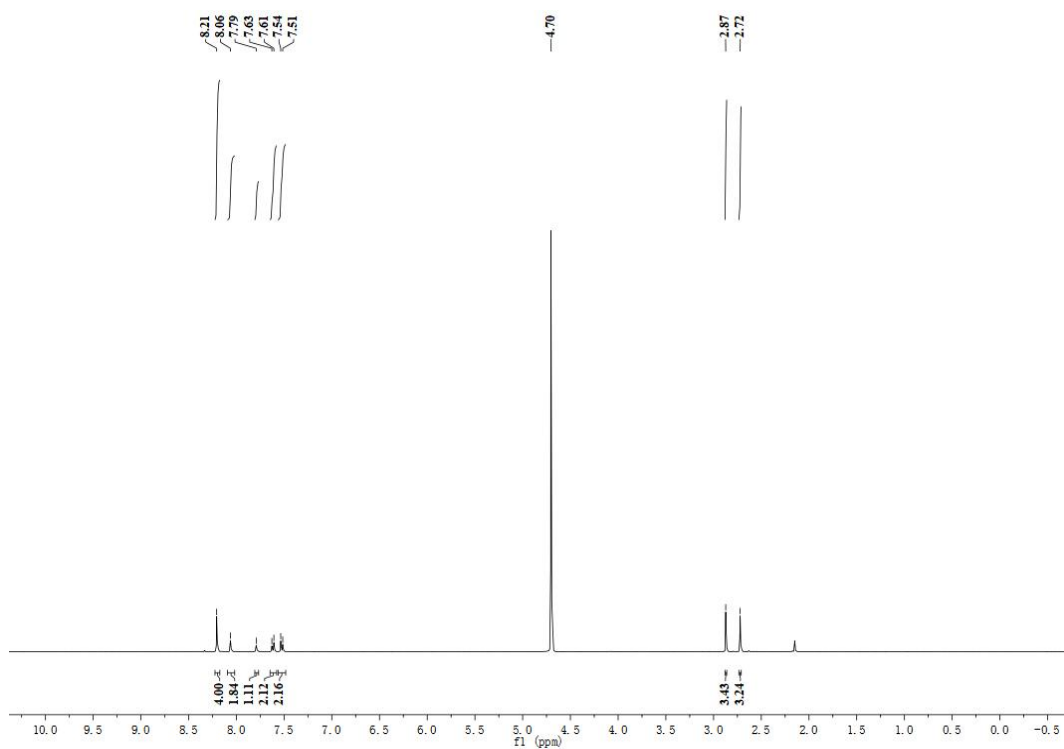
Materials and methods

The reagents used were not further purified and used directly after commercial purchase. Metal ion solutions [Pb(II), Ca(II), Co(II), Zn(II), Mg(II), Ni(II), K(I), Na(I)] are prepared with nitrates, all of which are purchased from Guangzhou Chemical Reagent Factory. $ZrCl_4$, terephthalaldehyde and 3,4-diaminobenzoic acid was purchased from Macklin. $NaHSO_3$ was purchased from Aladdin. Purchase $Pb(NO_3)_2$ from Guangzhou Chemical Reagent Factory, and the wastewater was obtained from Baishamen Sewage Treatment Plant in Haikou City.

2,2'-(1,4-phenylene)bis(1H-benzo[d]imidazole-5-carboxylic acid) (H_2L_1) was synthesized via terephthalaldehyde and 3,4-diaminobenzoic acid. Powder X-ray diffraction (PXRD) patterns were performed on a Rigaku Miniflex 600 X-ray diffractometer at room temperature. The morphology of HNU-G4 was observed by a Hitachi S3000 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed on a Rigaku Thermal plus EVO2 TG-DTA 8122 instrument. Photoluminescence (PL) measurements were performed using an RF-6000 spectrofluorometer at room temperature. X-ray photoelectron spectroscopy (XPS) data were collected using a Saimofei Escalab 250Xi-ray photoelectron spectrometer equipped with an Al Ka X-ray source. Infrared spectra (IR) were acquired in the 4,000-400 cm^{-1} range on a Brooktensor-27 infrared spectrometer using a KBr wafer. The adsorption experiments were carried out on a SHZ-C digital constant temperature water bath oscillator. The concentration of Pb(II) was measured by TAS-990 Super AFG atomic absorption spectrometer. Elemental analysis was performed on an Agilent ICP-OES 730. The zeta potentials were tested on the UK Zetasizer Pro Blue Label. Data for nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR) were collected at 400 MHz using a Bruker ADVANCE III spectrometer.

A

(5.60g, 0.037mol)
dispersed in 100 mL ethanol

Slowly add

(2.50g, 0.019mol)

sonicated 2 h

25 °C for 30 min
followed by reflux
for 5 h

recrystallization

NaHSO₃
(45mL, 40%wt)

B

(20 mg)

+

ZrCl₄
(0.05 mM)

DMF 1.5 mL

368 K , 3 days

Wet gel

Ethanol
cleaning and soaking

freeze-drying 24 h

Dry gel
(HNU-G4)

Supplementary Figure 1. (A)The synthesis route of H_2L_1; (B) The synthesis route of HNU-G4.

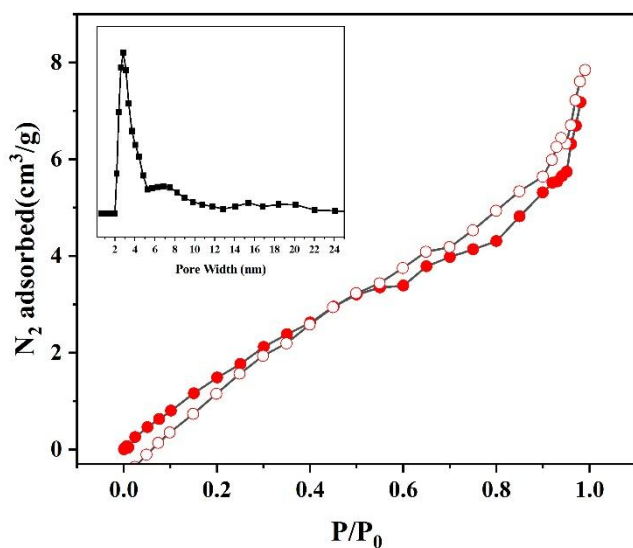**Supplementary Figure 2.** ^{1}H NMR spectrum of H_2L_1.
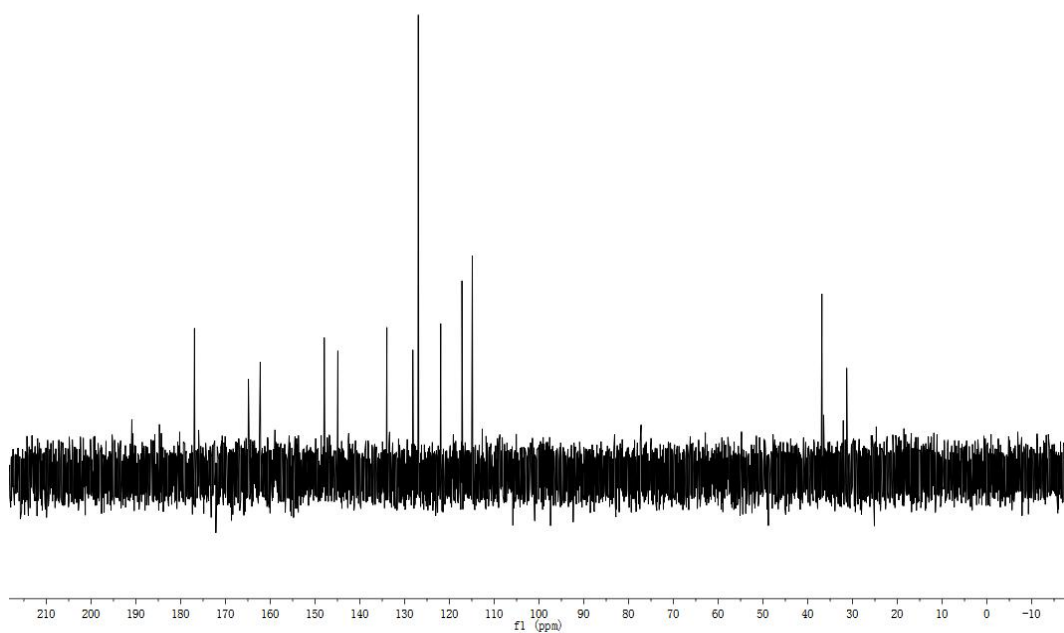
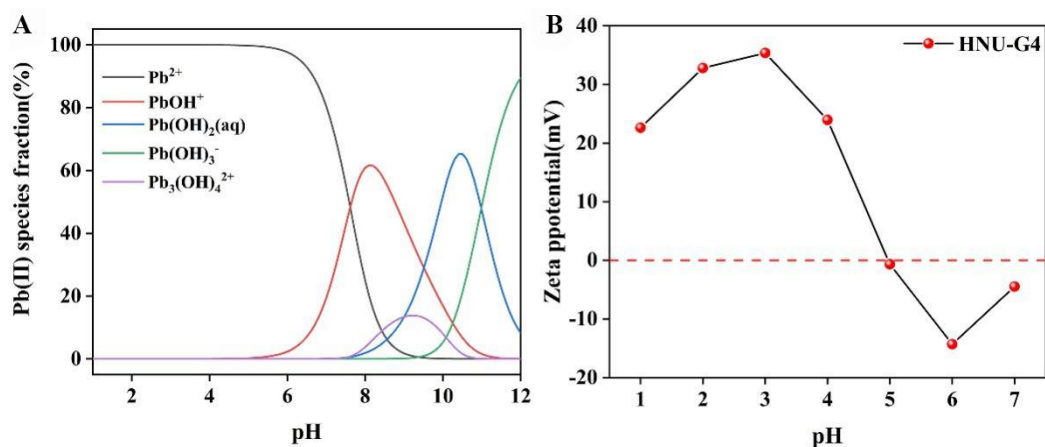**Supplementary Figure 3.** ^{13}C NMR spectrum of H_2L_1.

**Supplementary Figure 4.** Wet gel optical photo of HNU-G4.
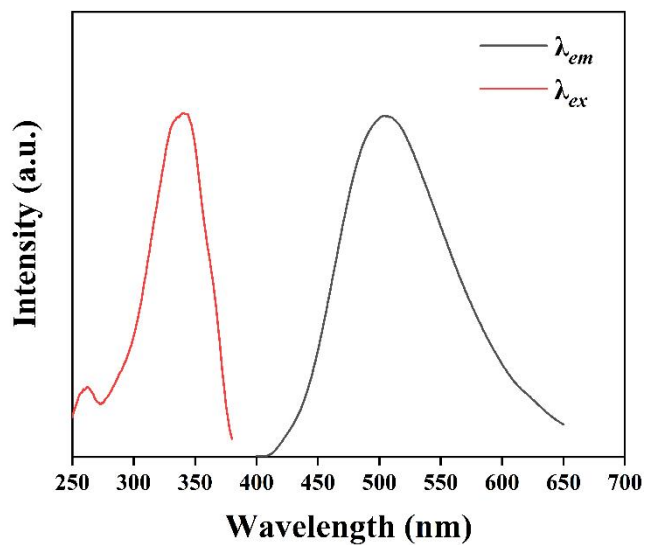
Supplementary Figure 5. N₂ adsorption/desorption isotherms measured at 77 K for HNU-G4, the illustration shows the aperture distribution.


**Supplementary Figure 6.** Excitation and emission spectra of HNU-G4.

Supplementary Figure 7. (A)The PXRD patterns of HNU-G4 after 12 h of immersion in aqueous solutions at pH = 1.0-7.0; (B) FT-IR spectra of HNU-G4 after soaking in aqueous solutions of different pH for 12 h.
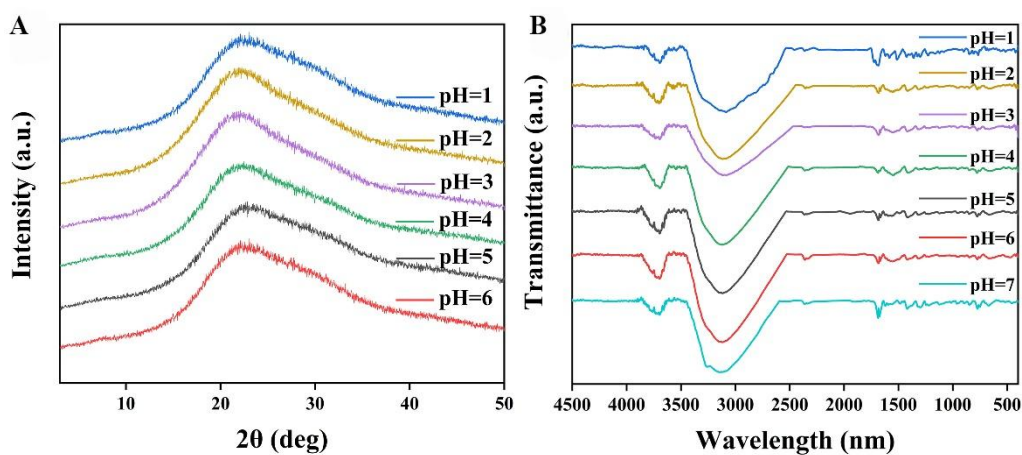
Supplementary Figure 8. (A) The existence forms of lead ions at different pH values; (B) The zeta potential of HNU-G4 at different pH values.
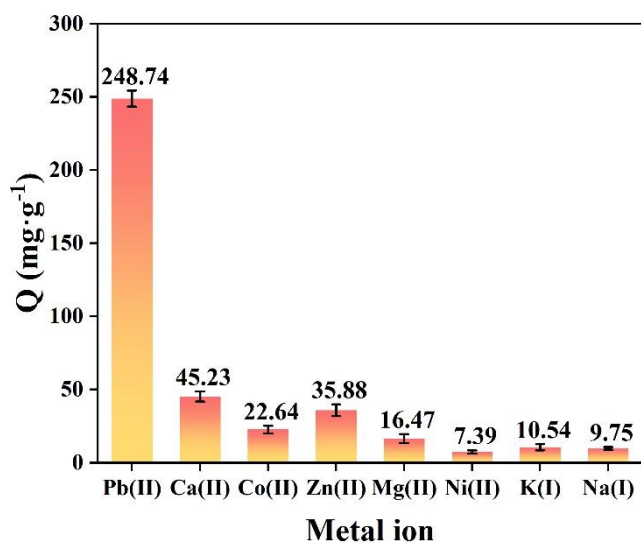
Supplementary Figure 9. Adsorption capacity of HNU-G4 for various metals in multi-component system.
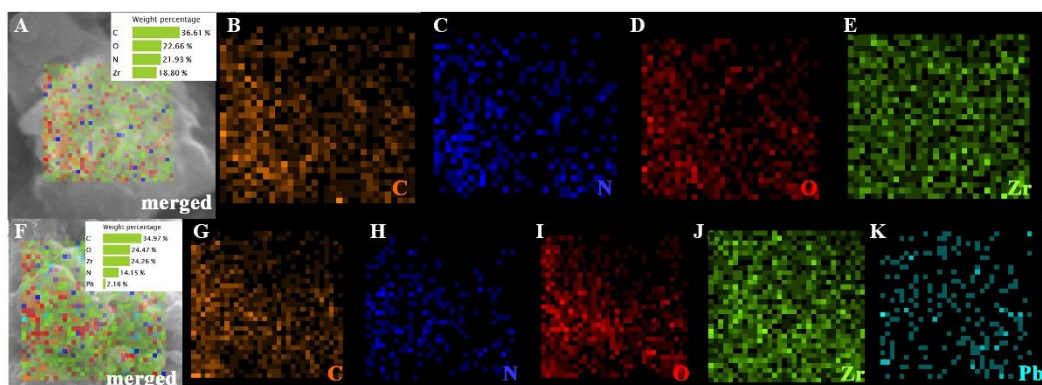
Supplementary Figure 10. Element mapping of blank gel, (A) merged; (B) C; (C) N; (D) O; (E)Zr. Element mapping after immersion in Pb (II) solution, (F) merged; (G) C; (H) N; (I) O; (J) Zr; (K) Pb.

Supplementary Table 1. Fitting parameters of adsorption kinetic model for adsorbing Pb(II).

To further explore the adsorption process, the temporal evolution of Pb(II) concentration was analyzed using the following two models, respectively.

Pseudo-first-order model：$\ln(q_e+q_t)=\ln q_e-k_1 t$

Pseudo- second-order model：$\dfrac{t}{q_t}=\dfrac{1}{k_2 q_e^2}+\dfrac{t}{q_e}$

Pseudo-first-order model			Pseudo- second-order model		
q_e (mg·g^{-1})	k_1	R^2	q_e (mg·g^{-1})	k_2	R^2
285.76	0.04681±0.00418	0.796	297.56	2.75421E-4±9.94819E-6	0.983

Supplementary Table 2. Adsorption isotherm model fitting parameters for the adsorption of Pb(II)

Langmuir			Freundlich		
q_m(mg·g^{-1})	K_L(L·mg^{-1})	R^2	K_F(mg·g^{-1})	n	R^2
466.87	0.1645±0.058	0.989	293.436±18.709	6.37052±0.84546	0.871

Supplementary Table 3. Various metal ion concentrations (ppm) before and after adsorption of HNU-G4 on reclaimed water in sewage treatment plants

Ion	Ca	Co	K	Mg
Before	38.950	0.0096	51.054	52.443
After	37.806	0.0085	50.982	52.101
Ion	Na	Ni	Pb(II)	Zn
Before	361.967	0.002218	0.001964	0.019378
After	361.732	0.002215	0.000009	0.019201