Porous Coordination/covalent Hybridized Polymers Constructed from Pyridine-Zinc Coordinated Compound and Their CO₂ Capture Ability and Selective Responsive Properties

Experimental section

Materials

4-Vinylpyridine was purchased from Aladdin (China). Dichorol-zinc (ZnCl₂) were purchased from West Long chemical co. LTD (China). The remaining chemicals and solvents were purchased from Chengdu Kelong Chemical Co. Ltd (China). All of the chemicals were used as received without further purification

Synthesis of di(4-vinylpyridine)-dichloro-zinc (C₇NH₈ZnCl₂, ZnVP₂) coordinated compound

4-Vinylpyridine (3.09 g, 29.4 mmol) was added dropwise in a solution of $ZnCl_2$ (2.0 g, 14.7 mmol)/ethanol (200 mL). The resulting solution was let stand overnight. The precipitated crystals were washed with ethanol and centrifuged. The centrifugation was repeated three times, and the resulting powder was dried in vacuum at 40 °C.

Synthesis of poly (ZnVP₂)

In a single-neck reaction flask, $ZnVP_2$ (1.5 g) and dioxane (75 mL) were added, and the solution was evacuated three times under a nitrogen atmosphere. Once $ZnVP_2$ was completely dissolved, the temperature was raised to 70 °C. The reaction was allowed to proceed for 12 h. The solution was centrifuged, affording white powders. The powders were repeatedly centrifuged in THF and ethanol for three times. The solid product was then dried under vacuum at 50 °C.

Measurements

¹³C NMR spectra were recorded using an Avance III 400 MHz spectrometer at room temperature. Fourier transform infrared (FTIR) measurements in the frequency range 400–4000 cm⁻¹ were conducted using a Nicolet FTIR 5700 spectrophotometer at room temperature, and the sample films were prepared by casting solution on KBr plates. Thermogravimetric (TG) analyses were performed using a simultaneous SDT Q160 thermal analyzer from TA Instruments (USA) in the temperature range from room temperature to 800 °C at a heating rate of 10 °C/min under N₂ atmosphere. Highresolution mass spectra were recorded using a Thermo Scientific LTQ Orbitrap XL used for ESI. N₂ adsorption–desorption isotherms were measured using a Micromeritics NOVA 3000 system at 77 K. The samples were degassed at 100 °C for 1 h before analysis. X-ray diffraction spectra were recorded using an X Pert pro X-ray diffractometer (PANalytical B.V.) equipped with copper K α radiation in the 2θ range 3–80°. Scanning electron microscopy was performed using a high-resolution scanning microscope model Ultra 55. (Carl Zeiss AG). Fluorescence spectra were measured using a spectrofluorometer model F-4600 (Hitachi, Japan). Transmission electron microscopy (TEM) images were tested by using a Libra 200 Ultra-high resolution field emission transmission electron microscope system (Carl Zeiss irts) and the acceleration voltage was 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were tested by using a PHI 5700 ESCA System spectrometer with Al-Kα radiation, and the binding energies were calibrated using the C1s peak at 284.9 eV. Atomic force microscopy (AFM) was performed using BRUKER Dimension icon Atomic Force Microscope.



Figure S1. HR-MS spectrum of ZnVP₂.



Figure S2. ¹³C NMR spectra of ZnVP₂ and poly(ZnVP₂).



Figure S3. FTIR spectra of $ZnVP_2$ and $poly(ZnVP_2)$.



Figure S4. XRD spectra of ZnVP₂ and poly(ZnVP₂).



Figure S5. TGA curve of poly(ZnVP₂).



Figure S6. a) SEM image and EDS spectrum of ZnVP₂; b) SEM image and EDS spectrum of poly (ZnVP₂); c) TEM image of poly (ZnVP₂); d) AFM image of surface of poly (ZnVP₂); e) AFM image of cross-section of poly (ZnVP₂).



Figure S7. Fluorescence spectra of $ZnVP_2$ and $poly(ZnVP_2)$.



Figure S8. Pore size distribution for poly(ZnVP₂).



Figure S9. a) Photographs of fluorescence emission change (under UV lamp with λ_{ex} =312 nm) of poly(ZnVP₂) with CuSO₄ aqueous solution of different concentrations; b) Linear concentration range of Cu²⁺ for poly (ZnVP₂) in water (λ_{ex} = 312 nm). The F₀ and F represent the fluorescence emission intensities of poly (ZnVP₂) in the absence and in the presence of Cu²⁺, respectively. The detection limit for Cu²⁺ in aqueous solution was determined as 76.6 ppb using the equation LOD = 3 × S.D./k, where k represents the slope of the curve equation, and S.D. is the standard deviation for F₀ (the fluorescence intensity of poly (ZnVP₂) in the absence of Cu²⁺).



Figure S10. Fluorescence spectra of poly(CuVP₂) and poly (ZnVP₂).



Figure S11. a) Photographs of fluorescence emission change (under UV lamp of 312 nm) of $poly(ZnVP_2)$ in DMF in the presence of different metal ions; b) Quenching efficiency of $poly(ZnVP_2)$ in DMF in the presence of different metal ions.



Figure S12. Fluorescence response of $poly(ZnVP_2)$ in different solvents under UV lamp of λ_{ex} =365 nm.

Kinetics of Cu²⁺ Adsorption.

The amount of adsorbed uranium at the equilibrium was calculated from the difference of the Cu^{2+} concentration in the aqueous before and after the adsorption according to the equation (1):

$$q = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

where q (mg/g) is the amount of U adsorbed on adsorbent; $C_0 \text{ (mg/L)}$ and $C_e \text{ (mg/L)}$ are the initial and equilibrium concentrations of uranium in the solutions, respectively; m (g) is the mass of sorbent; and V(L) is the volume of aqueous solution.

For research of kinetics of adsorption, the adsorption isotherm is used to fit the pseudo-second-order rate equation (2).

$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{t}{q_{e}}$$
(2)

R² is regression coefficient. k_2 (g·mg^{-1.} min⁻¹) denotes the adsorption rate constants of the pseudo-second-order adsorption. q_t is theamounts of adsorption uranium adsorbed (mg/g) at the given time of "t", q_e is the maximum adsorption capacity (mg/g).

To estimated the type of adsorption, the adsorption isotherm is used to fit the Langmuir or Freundlich equations.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_l q_m}$$
(3)
$$lnq_e = lnk_f + \frac{1}{n} lnC_e$$
(4)

Where q_e is the amount adsorbed at equilibrium $(mg \cdot g^{-1})$ and C_e is the equilibrium concentration $(mg \cdot L^{-1})$. q_m is the maximum amount or the saturated adsorption amount $(mg \cdot g^{-1})$. k_1 is an equilibrium constant related to the binding strength $(L \cdot mg^{-1})$. n and k_f are Freundlich constants which are indicators of the adsorption capacity and adsorption intensity, respectively.



Figure S13. The adsorption kinetics of Cu^{2+} on poly (ZnVP₂) and fitting it by pseudo second order (R^2 =0.998). C₀=100 ppm, m_{adsorbent}=10 mg, and T=298K.



Figure S14. a) Adsorption isotherms of Cu^{2+} on poly (ZnVP₂) m _{adsorbent} = 10 mg, t = 24 h and T = 298 K; b) Fitting the adsorption isotherm of poly (ZnVP₂) by Langmuir equations (R^2 =0.987).



Figure S15. a) FTIR and b) XPS spectra of $poly(ZnVP_2)$ and that after uptake of Cu^{2+} (poly(ZnVP_2)-Cu).

Polymers -	Uptake of metal ions (mg/g)		
	Cu	Ni	Со
Poly (ZnVP ₂)	54.55	4.60	×
Poly (CuVP ₂)		18.63	×
Poly (DVB-ZnVP ₂)	50.63	0.85	×
Poly (DVB-VP)	4.13	×	×
Poly (DVB-VP)-Zn	10.54	6.04	×

Table S1. Uptake for different metal ions by different polymers

 $* \times$ represents that no uptake of metal ions is measured.

Poly(ZnVP₂): poly(di(4-vinylpyridine)-dichorol-zinc)

Poly (CuVP2): poly (di(4-vinylpyridine)-dichorol-copper)

Poly (DVB-VP): copolymer of 4-vinylpyridine with divinylbenzene

Poly (DVB-VP)-Zn: the polymer which was obtained by post-coordination of poly (DVB-VP) with Zn^{2+} .

Poly (DVB-ZnVP₂): copolymer of di(4-vinylpyridine)-dichorol-zinc with divinylbenzene.