

## Supporting Information

# Highly selective and efficient chelating fiber functionalized by bis(2-pyridylmethyl)amino group for heavy metal ions

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## 1. Reagents

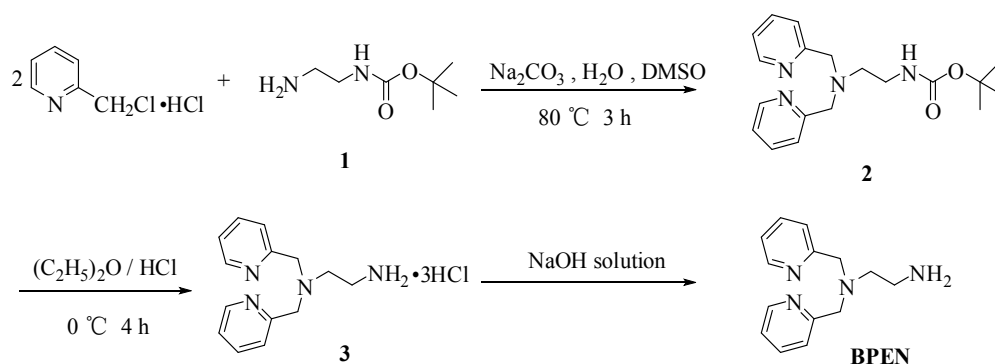
Commercially available PANF with lengths of about 10 cm and diameter of  $20 \pm 0.5 \mu\text{m}$  (from the Fushun Petrochemical Corporation of China) was used, it was prepared through the copolymerization of acrylonitrile (93.4 wt%), methyl acrylate (6.1 wt%) and trace sodium styrene sulfonate (0.5 wt%). 2-chloromethylpyridine hydrochloride, di-tert-butyl dicarbonate, ethylenediamine and the other reagents were analytical grade and used without further purification. The water was deionized. Standard solutions of metal ions were prepared by dissolving the appropriate quantities of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , respectively, in 50 mL of deionized water, which was then diluted to 100 mL. The standard solutions were diluted to the desired concentrations with deionized water prior to use and their pH values were adjusted with 0.1 mol/L NaOH or 0.1 mol/L  $\text{HNO}_3$ .

## 2. Apparatus and instruments

The FTIR spectra were obtained with an AVATAR360 FTIR spectrometer (Thermo Nicolet). An ICP-9000 (N+M) inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Jarrell-Ash) and an iCE3300 atomic absorption spectrometer (AAS, Thermo Fisher Scientific) were employed to determine the concentrations of metal ions. The pH values were adjusted by a Model PHS-3C pH meter. The Elemental analyses (EA) were performed on a vario micro cube (Elementar). A scanning electron microscope (SEM) (Hitachi, model S-4800) was used to characterize the surface of the modified fibers. The X-ray powder

diffraction spectra were recorded with a D/MAX-2500 X-ray diffractometer (Rigaku Corporation). Analysis of the X-ray photoelectron spectra (XPS) was performed on PH1600 spectrometer (PERKIN ELMZR).  $^1\text{H}$  NMR spectra were recorded on an AVANCE III instrument (Bruker, 600 MHz) using TMS as an internal standard. All photos in this article were recorded by a Canon PowerShot SX700 HS digital camera.

### 3. Synthesis of *N,N*-bis(2-pyridylmethyl)ethylenediamine (BPEN)



**Scheme 1.** The route for synthesis of BPEN.

*N*-(2-aminoethyl)carbamate tert-butyl ester (**1**) was prepared according to a literature procedure<sup>1</sup> (light yellow oil, 85%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.13 (s, 1H), 3.17 (q, 2H), 2.80 (t, 2H), 1.45 (s, 9H), 1.29 (s, 2H).

A solution of  $\text{Na}_2\text{CO}_3$  (4.24 g, 40 mmol) in  $\text{H}_2\text{O}$  (30 mL) was added to neutralize the 2-chloromethylpyridine hydrochloride (6.04 g, 40 mmol), then compound **1** (3.2 g, 20 mmol), DMSO (10 mL) and  $\text{Na}_2\text{CO}_3$  (2.12 g, 20 mmol) was added and stirred at  $80\text{ }^\circ\text{C}$  for 3 h. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was separated and washed with saturated solution of NaCl, then the solvent was removed, and the residue was purified by column chromatograph (silica gel,  $\text{EtOAc}/\text{MeOH} = 1/1$  v/v), affording *N*-(2-(bis(2-

pyridylmethylamino)ethyl)carbamic acid tert-butyl ester (**2**) as a light yellow viscous oil (5.30 g, 77%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.55 (d, 2H), 7.65 (t, 2H), 7.42 (d, 2H), 7.17 (m, 2H), 5.86 (s, 1H), 3.87 (s, 4H), 3.24 (t, 2H), 2.71 (t, 2H), 1.45 (s, 9H).

A solution of **2** (5.23 g, 15.4 mmol) in 60 mL of ethyl ether was saturated with hydrogen chloride and stirred at 0 °C for 4 h. The solvent was removed under reduced pressure to give BPEN·3HCl (**3**) as a light yellow solid. The solid was then dissolved in an aqueous solution of sodium hydroxide and extracted with CH<sub>2</sub>Cl<sub>2</sub>, then the solvent was immediately removed under vacuum to give *N,N*-bis(2-pyridylmethyl)ethylenediamine (BPEN) as a yellow oil (3.52 g, 94%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.53 (d, 2H), 7.64 (m, 2H), 7.49 (d, 2H), 7.15 (m, 2H), 3.85 (s, 4H), 2.81 (t, 2H), 2.67 (t, 2H).

#### 4. Weight gain and functionality of BPEN-PANF

The modification extent was calculated by weight gain:

$$\text{weight gain} = \frac{(w - w_0)}{w_0} \times 100\% \quad (1)$$

where  $w$  and  $w_0$  are the weights of BPEN-PANF and PANF (g), respectively.

The functionality (mmol/g) can also be used to illustrate the extent of modification which is given with the equation below:

$$f = 1000 \times \frac{(w - w_0)}{M \times w} \times 100\% \quad (2)$$

where  $M$  is the increased formula weight (the weight of bis(2-pyridylmethyl)ethyl + O + H, *i.e.* 243) after BPEN moiety was introduced into the fiber.

## 5. Chelating capacities of BPEN-PANF for metal ions

**Table S1.** The data of chelating capacities of BPEN-PANF.

ions	Pb <sup>2+</sup>	Hg <sup>2+</sup>	Cd <sup>2+</sup>	Ag <sup>+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Cr <sup>3+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	Mg <sup>2+</sup>
$q_e^a$ (mmol/g)	1.08	1.06	0.7	1.01	0.73	1.11	0.81	0.65	0.81	0.22	0.20	0.37

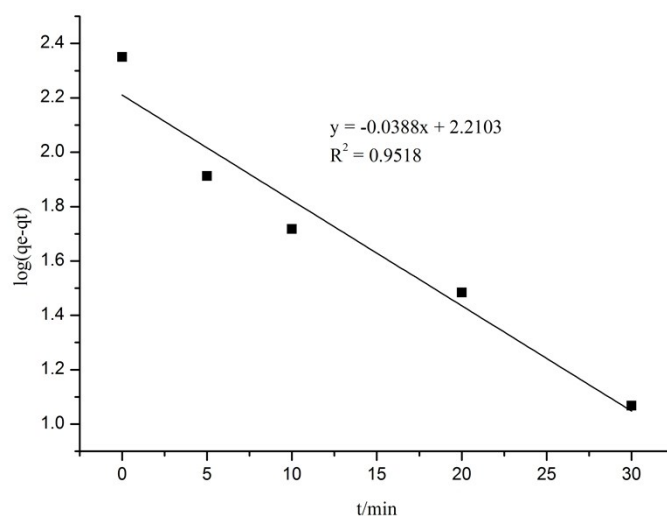
<sup>a</sup>. The chelating capacity  $q_e$  was obtained by means of soaking the fiber into 50 mL relevant metal ions solution with the concentration of  $10^{-3}$  mol/L about 120 min.

## 6. The competitive chelating experiment

**Table S2.** The competitive chelating experiment for Pb<sup>2+</sup> and Ca<sup>2+</sup>

mixed ions	$m$ (mg)	before absorbing (mol/L)	after absorbing (mol/L)	$q$ (mmol/g)	$q_{Pb^{2+}}/q_{Ca^{2+}}$
Pb <sup>2+</sup>	9.1	$0.346 \times 10^{-3}$	$0.249 \times 10^{-3}$	0.533	24.23
Ca <sup>2+</sup>		$0.335 \times 10^{-3}$	$0.331 \times 10^{-3}$	0.022	

## 7. Absorption dynamics



**Figure S1.** First-order plot for BPEN-PANF upon Pb<sup>2+</sup>.

**Table S3.** The fitting results of BPEN-PANF-Pb by the pseudo-first order kinetic model.

t/min	0	5	10	20	30
log(q <sub>e</sub> -q <sub>t</sub> )	2.3502	1.9130	1.7179	1.4840	1.0674
first-order model	y = -0.0388x + 2.2103				
constants	k <sub>1</sub> =0.0894 min <sup>-1</sup> , R <sup>2</sup> = 0.9518				

**Table S4.** The fitting results of BPEN-PANF-Pb by the pseudo-second-order kinetic model.

t/min	0	5	10	20	30	40	50	60	120
q <sub>t</sub> /(mg/g)	0	142.1500	171.7700	193.5200	212.3200	223.9300	216.7700	216.8000	224.5000
t/q <sub>t</sub>	0	0.03517	0.05822	0.10335	0.141296	0.178627	0.230659	0.276753	0.53452
pseudo-second-order model	y = 0.0044x + 0.01								
constants	q <sub>e</sub> (theor) =227 mg/g, k <sub>2</sub> =0.0019 g · mg <sup>-1</sup> · min <sup>-1</sup> , R <sup>2</sup> = 0.9989								

## 8. Comparison of removal capacities

**Table S5.** Removal capacities of some absorbents for Pb<sup>2+</sup>.

Materials	Contact time	pH	$q_e$ (mg/g)	Reference
Volcanic tuff	25 min	5	8.8	Karatas <i>et al.</i> <sup>2</sup>
PHEMA	120 min	6	3.04	Moradi <i>et al.</i> <sup>3</sup>
Sludge-derived biochar	240 min	5	30.88	Lu <i>et al.</i> <sup>4</sup>
MSWI-BAs	two weeks	5	45.54	Chiang <i>et al.</i> <sup>5</sup>
AO-ABS	120 min	6	56.5	Masoumi <i>et al.</i> <sup>6</sup>
<i>L. perpusilla</i>	210 min	6	86.96	Tang <i>et al.</i> <sup>7</sup>
GO-PAMAM 2.0	24 h	--	124	Yuan <i>et al.</i> <sup>8</sup>
Calcite NR	30 min	4	240	Lopez Marzo <i>et al.</i> <sup>9</sup>
GO-APP	72 h	--	500.3	Qin <i>et al.</i> <sup>10</sup>
Fe <sub>3</sub> O <sub>4</sub> /PANI	4 h	--	552	Wang <i>et al.</i> <sup>11</sup>
BPEN-PANF	5 min	5	142.15	This study
	30 min	5	212.32	

## 9. Absorption isotherms

**Table S6.** The data of BPEN-PANF-Pb by the Langmuir absorption isotherm.

$c_e$ /(mg/L)	0	0.134	74.224	165.2978	523.37	934	1918.89
$q_e$ (mg/g)	0	98.0559	150.8510	226.1082	284.8885	294.7059	294.2629
$c_e/q_e$ (g/L)	0	0.0014	0.4920	0.7311	1.8165	3.1690	6.5210
constants	$q_e$ (theor) =227 mg/g, $K_l$ = 0.0358 L•g <sup>-1</sup> , $R^2$ = 0.9989						

## 10. The process of simulated sewage experiment

Excess dried sample (40 mg) of BPEN-PANF was immersed into simulated wastewater (20 mL) containing varied metal ions (the initial concentration of each metal ion was 0.5 mg/L) under pH = 5 and statically placed at room temperature for 48 h. Then the fiber was filtered out and the concentration of the solution was measured by ICP-AES.

## 11. Chelating result of BPEN-PANF for metal ions in simulated wastewater.

**Table S7.** Chelating result of BPEN-PANF for metal ions in simulated wastewater.

Metal ions	Pb <sup>2+</sup>	Hg <sup>2+</sup>	Cd <sup>2+</sup>	Ag <sup>+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Cr <sup>3+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	Mg <sup>2+</sup>
Before absorbing (mg/L)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
After absorbing (mg/L)	0.00476	0.04491	0.01374	0.02914	0.03634	0.03368	0.00852	0.01354	0.06821	0.35935	0.10522	0.41369
removal efficiency (%)	99.01	91.02	97.25	94.17	92.73	93.26	98.29	97.29	86.36	28.13	78.96	17.26

## 12. Atomic percent and element content of BPEN-PANF by XPS before and after absorption of Pb<sup>2+</sup>

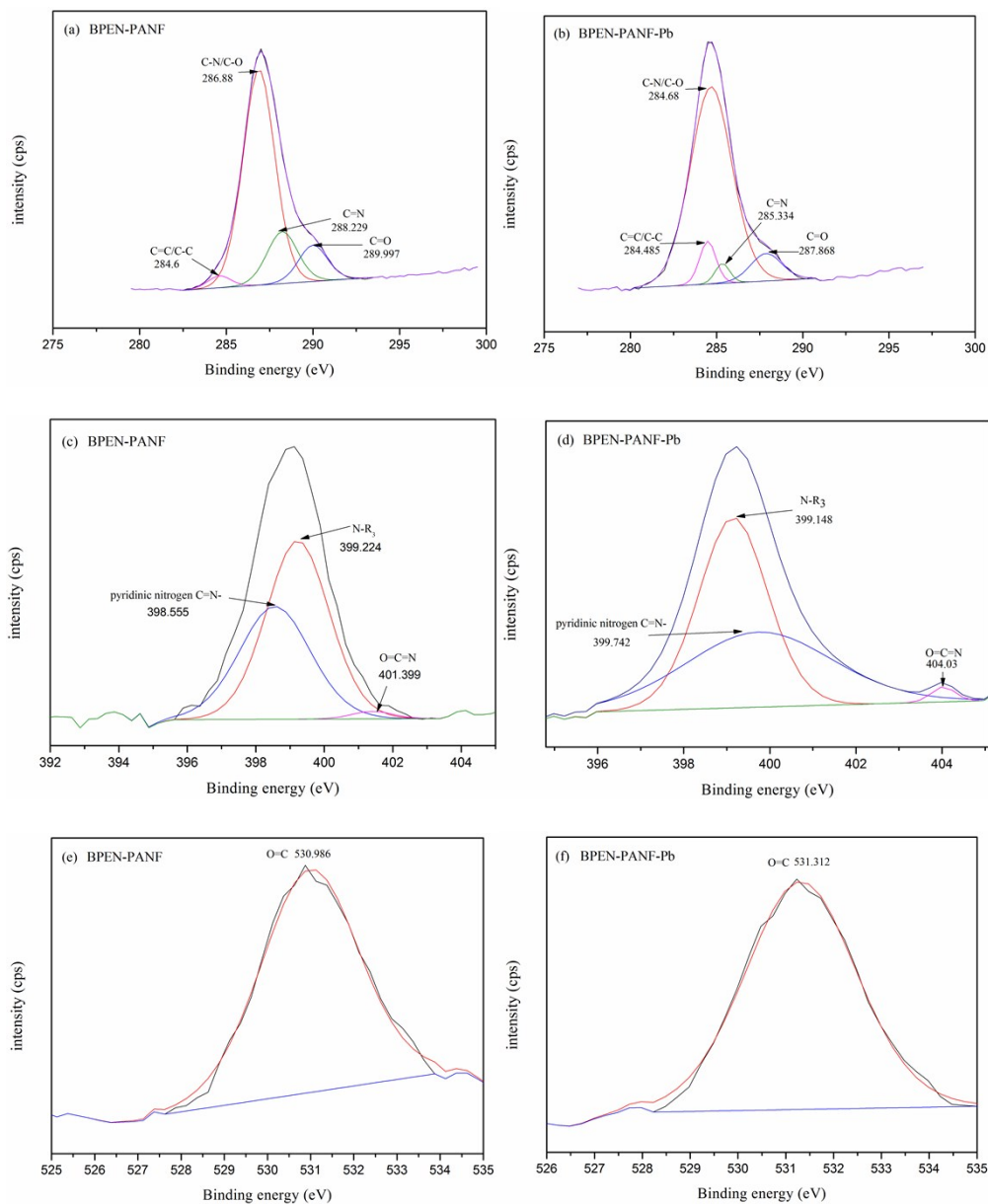
**Table S8.** Atomic percent and element content of BPEN-PANF before and after absorption of Pb<sup>2+</sup>.

Sample	Atomic percent (%)				
	C	N	O	Na	Pb
BPEN-PANF	73.0	9.7	15.2	2.1	0
BPEN-PANF-Pb	76.7	7.1	15.3	0	0.8
	Element content <sup>a</sup> (%)				
	C	N	O	Na	Pb
BPEN-PANF	67.3	10.4	18.6	3.7	0
BPEN-PANF-Pb	64.4	6.9	17.1	0	11.6

<sup>a</sup> The element content was calculated by atomic percent

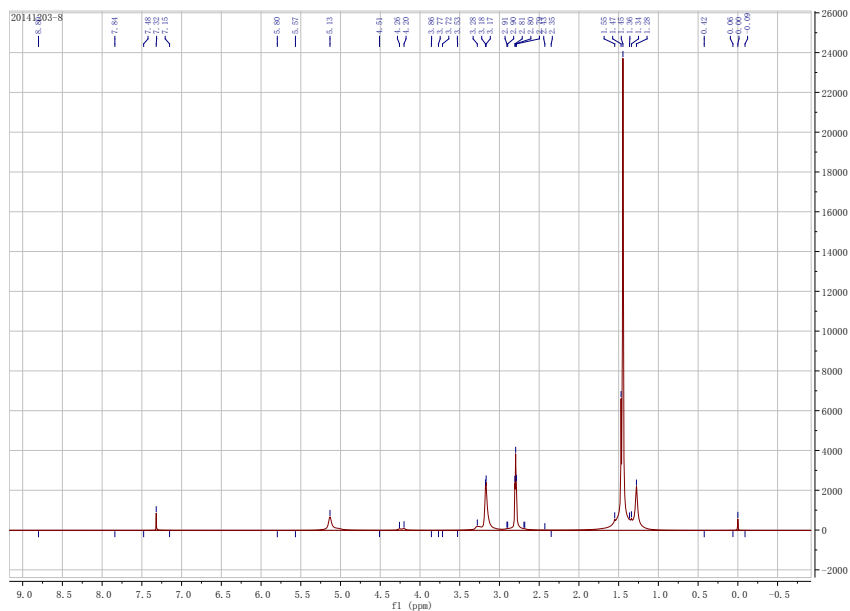


### 13. XPS spectra

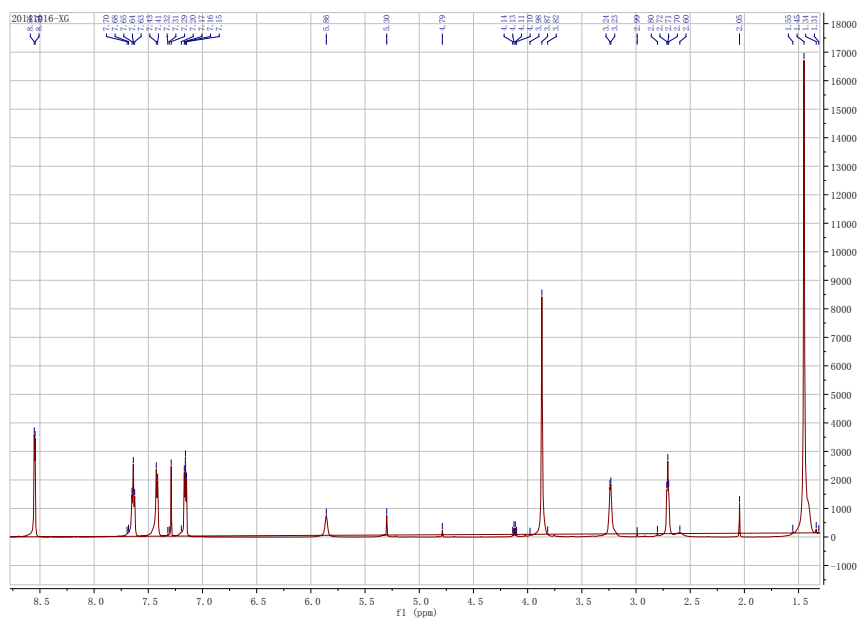


**Figure S2.** High resolution spectra of C 1s, N 1s and O 1s for BPEN-PANF before and after chelating with  $Pb^{2+}$ .

## 14. <sup>1</sup>H NMR spectra

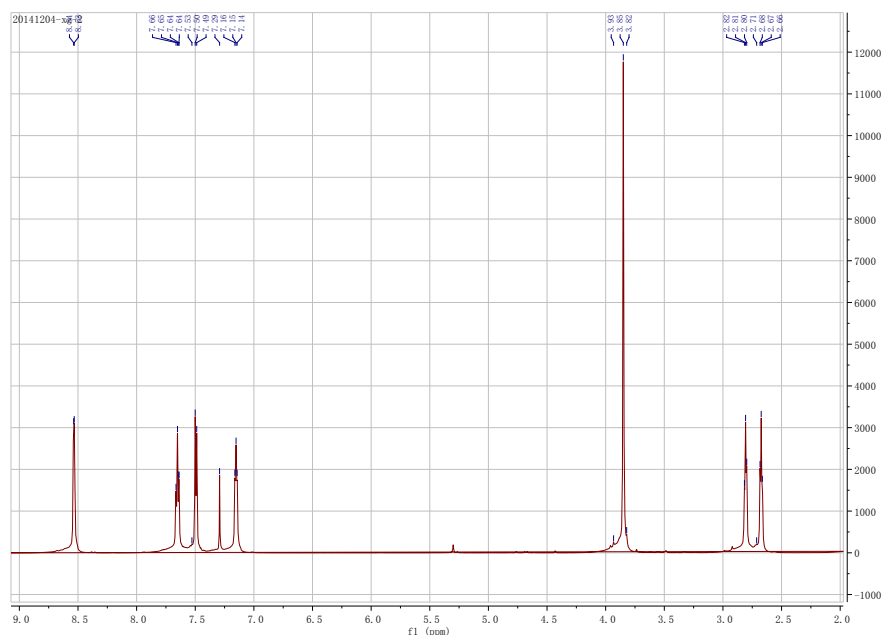


**Figure S3.** <sup>1</sup>H NMR spectra of *N*-(2-aminoethyl)carbamic acid tert-butyl ester (**1**) in CDCl<sub>3</sub>.



**Figure S4** <sup>1</sup>H NMR spectra of *N*-(2-(bis(2-pyridylmethyl)amino)ethyl)carbamic acid tert-

butyl ester (**2**) in CDCl<sub>3</sub>.



**Figure S5.** <sup>1</sup>H NMR spectra of *N,N*-bis(2-pyridylmethyl)ethylenediamine (**BPEN**) in CDCl<sub>3</sub>.

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