# Sulfur-rich Covalent Triazine Polymer Nanospheres for

# **Environmental Mercury Removal and Detection**

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### **Section A** Experimental Materials

Cyanuricchloride (CC, 98%) was purchased from TCI (Tokyo, Japan). Diphenylsulfane (DPS, 99% and AlCl<sub>3</sub> were supplied from Aladdin Industrial Corporation (Shanghai, China). Chloroform,1,2-dichloroethane,o-dichlorobenzene (99%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), and purified by reduced pressure distillation and stored with molecular sieves (4 Å).

#### **Section B** Measurements

- 1.FT-IR spectra were collected on a Thermo Nicolet Nexus 380 Fourier transform infrared (FT-IR) using the KBr pellet technique.
- 2.Solid-state <sup>13</sup>C cross polarization magic angle spinning (<sup>13</sup>C CP/MAS) NMR spectra were obtained on a Bruker Avance III 400 NMR spectrometer. The spectra were obtained by using a contact time of 2.0 ms and a relaxation delay of 10.0 s.
- 3.Elemental analysis (CHN) of the polymers was performed on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesyteme GmbH.
- 4. Thermal gravimetric analysis (TGA) measurements were examined using Mettler TGA/SDTA851 thermogravimetric analysis instrument from 100 to 800°C at a heating rate of 10°C/min under N<sub>2</sub>.
- 5.Powder X-ray diffraction (PXRD) data were collected over the 2θ range of 5~60° on a CPS120 Ineldiffractometer equipped with Ni-filtered Cu Ka radiation (40 kV, 100 mA) at room temperature with a scan speed of 5° min<sup>-1</sup>.
- 6.SEM was recorded using a FEI SIRION200 microscope with at accelerating voltage of 10 kV. Before measurement, the sample was prepared by drop-casting THF suspension onto mica substrate and then coated with gold.
- 7.High resolution transmission electron microscopy (TEM) images were collected in a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. Prior to TEM measurement, the samples were ultrasonically dispersed in ethanol and dropped onto a copper grid coated with a carbon film.
- 8. The surface areas and pore size distributions were performed at a Micromeritics

ASAP 2020 sorption analyzer by nitrogen adsorption and desorption at77K, and the pore parameters including BET specific surface area, pore size and pore volume could be evaluated from obtained adsorption-desorption isotherms. By using the non-local density functional theory (NLDFT) model, the pore volume and pore size distribution of NOP-28@2 were derived from the sorption curve. While for others samples, pore size distributions were derived from the N2 adsorption isotherms using the BJH method. Before each measurement, the samples were degassed for 8 h at 180 °C under vacuum.

- 9. Fluorescence spectra were conducted on F-4600FL Spectrophotometer, and the investigated samples were ultrasonically dispersed in ethanol.
- 10. Inductively Coupled Plasma Mass (ICP-MS) were performed with PerkinElmer Optima 5300 DV. The X-ray photoelectron spectra (XPS) were collected over a Thermo ESCALAB 250 spectrometer with an Al- Kα X-ray source, and the binding energies were calibrated using C1s peak at 284.9 eV.
- 11. UV–Vis absorption of sample solutions in alcohol was measured in a 1 cm quartz cell using a Shimadzu UV-2550 UV–Vis spectrophotometer.

#### **Section C** General procedure for the preparation of NOP-28

A typical synthesis for NOP-28@2 was given as an example. To a mixture of cyanuric chloride (CC, 20 mmol) and anhydrous AlCl<sub>3</sub> (66 mmol) in 30 mL of CHCl<sub>3</sub>,diphenylsulfane (DPS, 30 mmol) was injected into the flask at 25°C,and then the mixture was heated to reflux and stirred for 24 h under N<sub>2</sub>. The resulting reaction mixture was filtered, and then the filter cake was further purified using Soxhlet extraction with methanol for 24 h and then with tetrahydrofuran and acetone for another 24 h. Finally, the desired polymer was collected as gray brown solids and dried in a vacuum oven at 80°C for 24 h. Yield: 84%.

The polymerization parameters including reaction temperature and medium and catalyst type were optimized and listed in Tab. S1.

	Tablor			erres	
Samples	Monomers <sup>a</sup>	Solvents	Catalyst <sup>b</sup>	Ccc <sup>c</sup>	Yield
				(mol/L)	(%)
NOP-28@1	CC:DPS	Chloroform	AICI <sub>3</sub>	0.1	62.1
NOP-28@2	CC:DPS	o-dichlorobenzene	AICI <sub>3</sub>	0.1	82.6
NOP-28@3	CC:DPS	chlorobenzene	AICI <sub>3</sub>	0.1	78.7
NOP-28@4	CC:DPS	o-dichlorobenzene	FeCl <sub>3</sub>	0.1	91.5
NOP-28@5	CC:DPS	<i>o</i> -dichlorobenzene	CH₃SO₃	0.1	95.4

Tab.S1 The reaction conditions of NOP-28 series

<sup>a</sup>The molar ratio of CC verse DPS is 2:3; b The content of catalyst against cyanuric chloride keeps at 3.3:1; <sup>c</sup>The molar content of cyanuricchloride verse solvent medium.



Fig. S1 Synthetic routine of NOP-28

## **Section D** Structural characterization for porous polymers



1. FTIR spectra of typical NOP-28 samples

## 2. Powdered XRD curves for typical NOP-28 networks



Fig.S3 Powdered XRD curves for typical NOP-28 networks

3.	Elemental	lanalysis	of typical	polymers
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Tab. S2 Elemental analysis data of typical polymers									
Calculated (%	) Experim	nent (%)	)						
Samples	С	Н	Ν	S	С	Н	Ν	S	
NOP-28@1	71.16	3.41	11.86	13.57	72.69	3.31	10.98	13.32	
NOP-28@2	71.86	3.41	11.86	13.57	73.89	3.87	10.04	13.20	
NOP-28@3	71.86	3.41	11.86	13.57	73.23	3.69	10.40	13.51	
NOP-28@4	71.86	3.41	11.86	13.57	73.17	3.85	10. 12	13.32	
NOP-28@5	71.86	3.41	11.86	13.57	72.87	3.14	10. 76	13.37	

## 4. Thermal stability



Fig.S4 TGA curves for typical porous polymers

### 5. Chemical stability



Fig. S5 FTIR spectra of typical NOP-28@2 after treated in aqueous HCl (3 M) and NaOH (3 M) solutions

# Section E Morphology study



Fig. S6SEM and HR-TEM images of NOP-28@1(a,b) and NOP-28@3(c,d)

# Section F Pore parameters

Samples	<b>SA</b> <sup>a</sup> BET	<b>SA</b> <sup>a</sup> Langmuir	$\mathbf{V}_{Total}{}^{b}$	<b>V</b> <sub>Micro</sub> <sup>c</sup>
	(m²/g)	(m²/g)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)
NOP-28@1	45	71	0.27	0.02
NOP-28@2	144	222	0.58	0.28
NOP-28@3	22	30	0.11	0.01
NOP-28@4	118	162	0.42	0.13
NOP-28@5	133	181	0.49	0.23

Tab. S3 BET surface area, total pore volume, micropore volume forNOP-28 series



Fig.S7 Nitrogen adsorption/desorption for typical NOP-28 polymers



Fig. S8 Pores sized distributions for NOP-28 polymers

# Section G General Procedures for the Batch adsorption experiments1. General procedures

Our batch adsorption experiments toward heavy metal ions such as Hg2+ were carried out in a series of 25 mL stuffed colorimetric tube containing HgCl<sub>2</sub> aqueous solution with different concentrations, and the tube were shaken in an air bath at a fixed temperature of 30 °C (120 rpm) for a given period. During each batch, 20 mg polymer sample was added into the solution. After reaching the adsorption equilibrium, the porous solids and liquid phase were separated by centrifugation. The porous solids were washed thoroughly with distilled water to neutral, and dried under vacuum for recyclable experiments. Hg<sup>2+</sup> concentration in the filtrate was analyzed by Inductively coupled plasma mass spectrometry (ICP-MS).

To probe pH effects on  $Hg^{2+}$  adsorption of NOP-28 porous solids, the adsorption experiments were studied in the solutions with pH value ranging from 2 to 13. The effects of contact time on adsorption were also probed in the range of 0-1440 min. For each case, the concentration of  $HgCl_2$  aqueous solution is fixed at 500 mg L<sup>-1</sup>.

Competitive adsorption experiments of  $Hg^{2+}$  with other interfering ions, including  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Pd^{2+}$ ,  $Pb^{2+}$ ,  $Cr^{3+}$ ,  $Zn^{2+}$ ,  $K^+$ ,  $Ag^+$ ,  $Na^+$ ,  $Al^{3+}$  and  $Co^{3+}$  were performed. In this set of experiments, initial concentration of each ion in the mixed solution was fixed at 20 mg L<sup>-1</sup>.

The adsorption capacity and the adsorption selectivity were separately calculated according to the equations (1) and (2):[1a]

$$Q = \frac{(C_0 - C)V}{m} \tag{1}$$

$$W = \frac{C_0 - C}{C_0} \times 100\%$$
 (2)

where Q is the sorption capacity, w is the adsorption selectivity,  $C_0$  and C are the Hg2+ concentrations before and after sorption, respectively, V is denoted as the initial volume of the Hg<sup>2+</sup> solution, and m is denoted as the weight of the porous solids.

Acid-baseresistanceand regenerative adsorption experiment. NOP-28@2 (20 mg) was charged into HCl (9 M) and NaOH (9 M) solution, respectively, to assess its acid-baseresistance. After soaking for 6 hours, the samples obtained were washed with distilled water to neutral and dried. The Hg<sup>2+</sup> adsorption experiments of the as-treated samples were conducted in the above-described optimized conditions. After sufficient sorption time, the particles were filtered from the solution, and the filtrate was then subjected to regular ICP-AES.

To probe the regenerative adsorption performance, the Hg-loaded NOP-28@2 particle was desorbed completely by extracting with HCl (6 M) solution. The desorbed sample was then washed to neutral by distilled water, dried and used for the regeneration experiments. Static Hg<sup>2+</sup> adsorption was conducted in the same optimal adsorption conditions, and then the adsorption capability was characterized quantitatively by ICP-AES.

## 2. pH effects on Hg<sup>2+</sup> removal



Fig. S9 The solution pH effects on Hg <sup>2+</sup> removal performance of NOP-28@2 after 5 minutes (Initial concentration : 25 ppm)

#### 3. Parameters of kinetics model

Mathematical	Mathematical Equation		$K_1(min^{-1})$	$\mathbb{R}^2$
model			K <sub>2</sub> (g/mg min)	
Pseudo- <sup>1</sup> st-order	$Log(Q_e-Q_t)=-0.0018t+2.39466$	659	0.00524	0.90186
Pseudo- <sup>2</sup> st-order	t/Qt=0.0015t+0.025	659	9.0*10-5	0.99979



Fig.S10Captureof Hg(II) under different pH values after 60 minutes (Initial concentration : 25

ppm)



Fig.S11 Regeneration performance of NOP-28@2 towards Hg<sup>2+</sup> adsorption

Tab. S4	BET surface	area, total pore	volume for NOP-	28@2 after regen	eration

Samples	<b>SA</b> <sup>a</sup> <sub>BET</sub> (m <sup>2</sup> /g)	$\mathbf{V}_{\text{Total}}^{b}$	<b>V</b> <sub>Micro</sub> <sup>c</sup>
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)
0	144	0.58	0.28
1	142	0.57	0.27
2	143	0.57	0.28
3	138	0.51	0.24
4	131	0.54	0.25
5	131	0.53	0.26



# 4. The binding interactions between the Hg and S atoms in NOP-28

Fig.S12 XPS spectra of NOP-28@2 before and after Hg<sup>2+</sup> adsorption

# **Section H** General procedure for the luminescent sensing experiments towards Hg(II)

#### 1. General procedure

For the sensing (sensitivity and selectivity) tests,  $30 \,\mu\text{L}$  of the stock solution of NOP-28 was diluted with 3 mL of acetonitrile in a quartz cuvette. NOP-28was readily dispersed in acetonitrile and the obtained suspension was almost transparent. The fluorescence spectra were recorded immediately after an appropriate aliquot of the stock solution of metal ions was added. Each test was repeated at least for three times to get concordant values. All the measurements, unless otherwise noted, were excited at  $\lambda_{ex} = 390$  nm and the corresponding emission wavelength was tested from  $\lambda_{em} = 350$ to 600 nm. The shape of the emission spectra was not changed upon the addition of the stock solutions of metal ions. The fluorescence titrations were carried out via gradually adding the stock solution of Hg<sup>2+</sup> in an incremental fashion. Other metal ions (2 equiv.), including Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, and Cd<sup>2+</sup>, were used to investigate the selectivity of NOP-28 toward the Hg<sup>2+</sup> detection. For the recycle tests, 30  $\mu$ L of the stock solution of NOP-28 was diluted with 3 mL of acetonitrile in a quartz cuvette, the fluorescence spectra were measured before and after the stock Hg<sup>2+</sup> solution (33.3  $\mu$ mol) was added. The stock solution of  $S^{2-}$  was further added to remove  $Hg^{2+}$  from Hg/NOP-28, and the recycled NOP-28 was reused in the next  $Hg^{2+}$  detection and removal (see Figure S15). The measured fluorescence intensities were used to assess the degree of the recovery

## 2. UV-Vis spectrum and luminescence spectrum



Fig.S13 UV-Vis spectrum and luminescence spectrum for typical polymers

Section L UV-Vis spectrum and luminescence spectrum



Fig.S14 Luminescence sensing of starting monomers towards Hg<sup>2+</sup>(5000uM)



**Figure S15.**Linear concentration range of Hg<sup>2+</sup> for NOP-28 in ethanol ( $\lambda$ ex =415 nm). The F0 and F represent the fluorescence emission intensities of NOP-28 in the absence and in the presence of Hg<sup>2+</sup>, respectively. The corresponding limit of detection (LOD) was determined as 12.0 ppb using the equation LOD = 3 × S.D./k,<sup>1</sup> where k represents the slope of the curve equation, and S.D. is the standard deviation for F<sub>0</sub>.

#### Reference

- 1. (a) Long, G. L.; Winefordner, J. D., Anal. Chem. 1983, 55, 712A;
- (b) Hussain, S.; De, S.; Iyer, P. K., ACS Appl. Mater. & Interfaces 2013, 5, 2234.