

UiO-66-(SH)₂ as stable, selective and regenerable adsorbent for the removal of mercury from water under environmentally-relevant conditions

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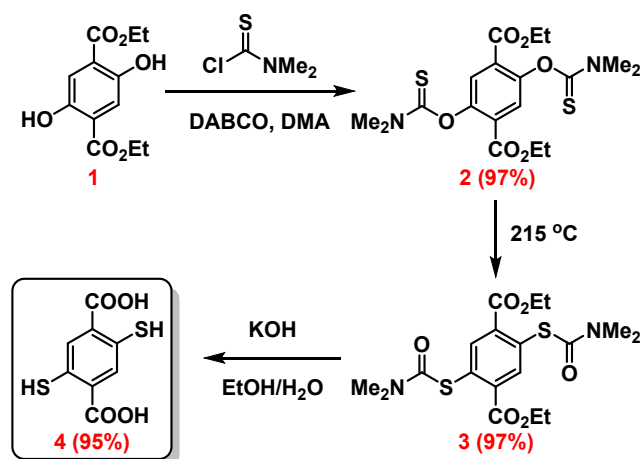
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A. Synthesis of 2,5-dimercaptoterephthalic acid ($H_2BDC-2,5-SH$)



Scheme 1 Synthesis route for $H_2BDC-2,5-SH$ **4**.

2,5-dihydroxyterephthalic acid diethyl ester **1** (5 g, 19.7 mmol, 1 eq) was mixed with DABCO (9 g, 80.2 mmol, 4.1 eq) in a Schlenk flask under argon, and anhydrous DMA (50 mL) was added. The mixture was cooled down to 0 °C in an ice bath. Afterwards, a solution of dimethylcarbamoyl chloride (9.5 g, 88.3 mmol, 4.5 eq) dissolved in anhydrous DMA (25 mL) was added dropwise to the mixture, also under argon. The sample was stirred at room temperature for 16 hours. The offwhite precipitate was filtered and washed extensively with water (250 mL). The residue was dried under vacuum to obtain the desired product **2** (8.2 g, 97%). 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.73 (s, 2H), 4.30 (q, $J = 7.1$ Hz, 4H), 3.46 (s, 6H), 3.40 (s, 6H), 1.33 (t, $J = 7.1$ Hz, 6H).

Compound **2** (1.5 g, 2.3 mmol) was heated in a Schlenk tube at 215 °C for 20 minutes. After cooling to room temperature, pale brown crystals were formed to quantitatively give the desired product compound **3** (1.46 g, 97%). This was used in the next step without further purification. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.11 (s, 2H), 4.34 (q, $J = 7.1$ Hz, 4H), 3.11 (s, 6H), 3.02 (s, 6H), 1.37 (t, $J = 7.1$ Hz, 6H).

In a 250-mL flask, compound **3** (7.5 g, 17.5 mmol) was dissolved in degassed 1.3 M KOH in ethanol/water (1:1, 230 mL), and refluxed under argon for three hours. Hereafter, the sample was cooled in an ice bath, and was acidified to pH 1 using concentrated HCl. The yellow precipitate was extracted with ethyl acetate for five times. The combined organic layer was dried with $MgSO_4$, and concentrated in vacuum to give 2,5-dimercaptoterephthalic acid **4** as a yellow powder (3.8 g, 95%). 1H NMR (300 MHz, CD_3OD) δ (ppm) 8.03 (s, 2H).

Spectral data are identical to those reported in literature.¹ All the NMR spectra can be found in Figure S1 to S3.

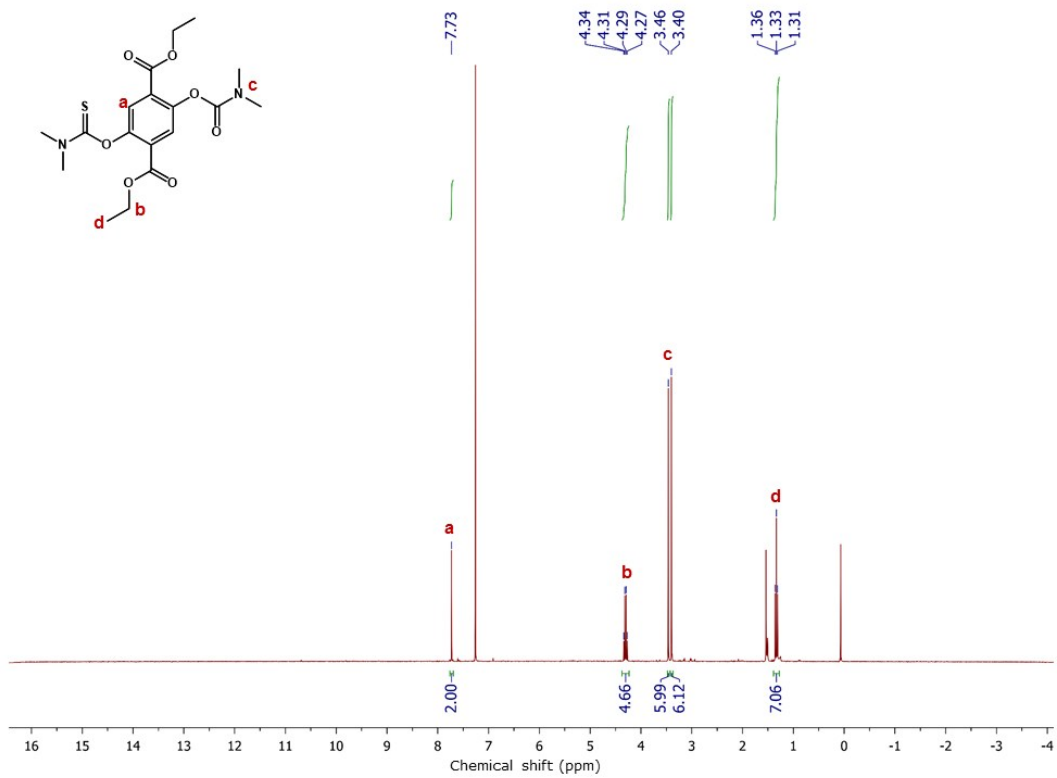


Fig. S1 ¹H NMR of compound 1.

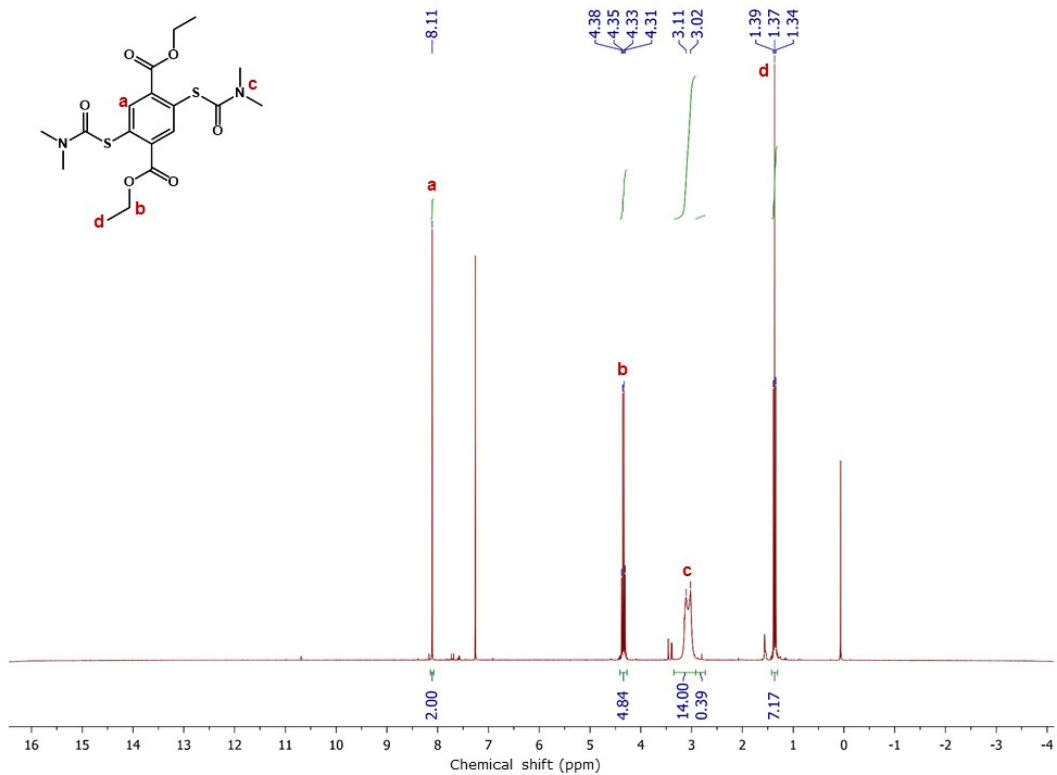


Fig. S2 ¹H NMR of compound 2.

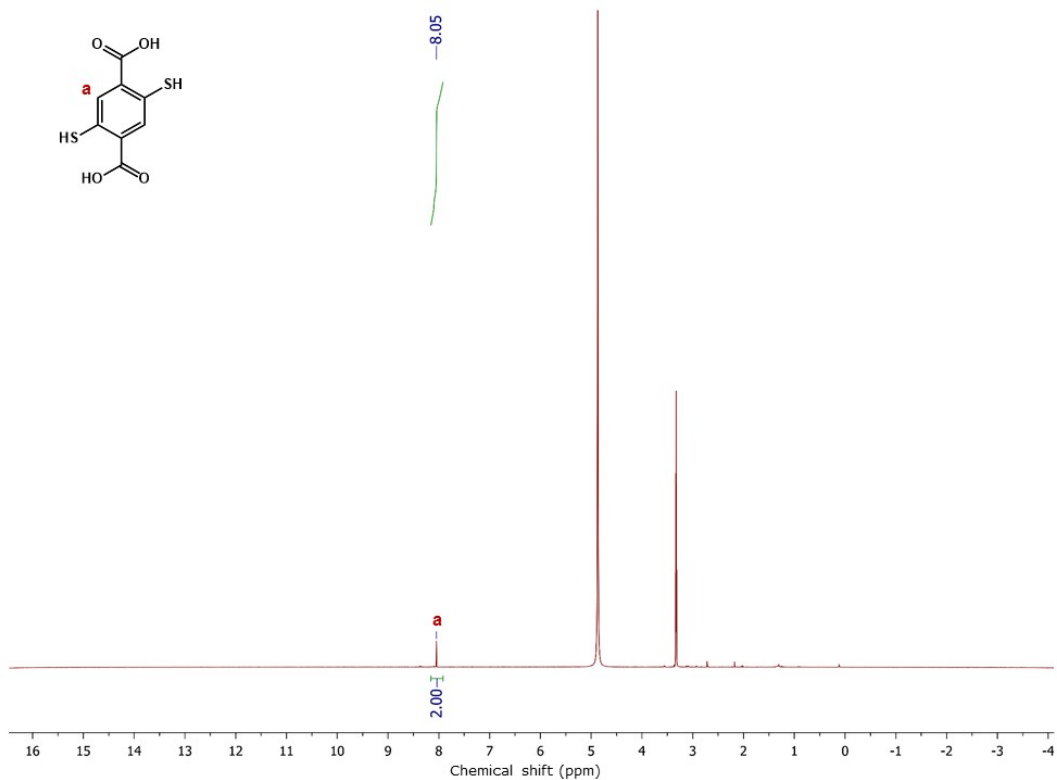


Fig. S3 ¹H NMR of compound 3.

B. X-ray powder diffraction (XRPD)

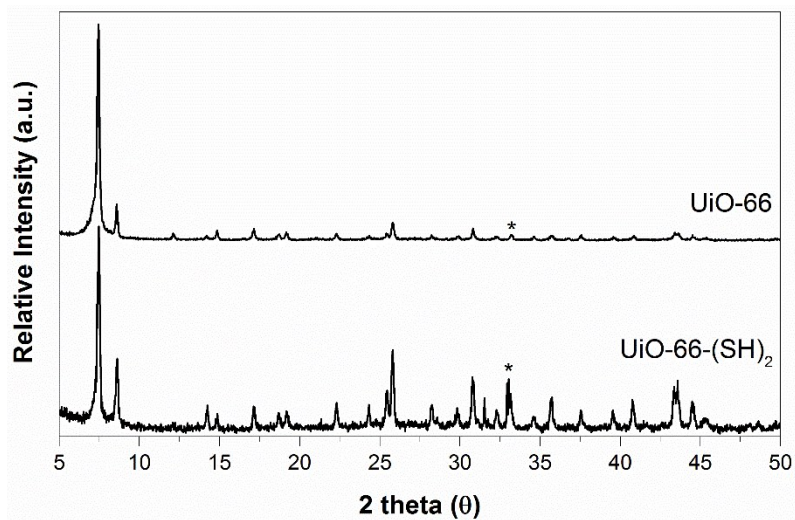


Fig. S4 XRPD patterns of UiO-66 and UiO-66-(SH)₂ samples. The diffraction peak denoted by * corresponds to the background of the sample holder at an angle of 32.9°.

C. Nitrogen adsorption

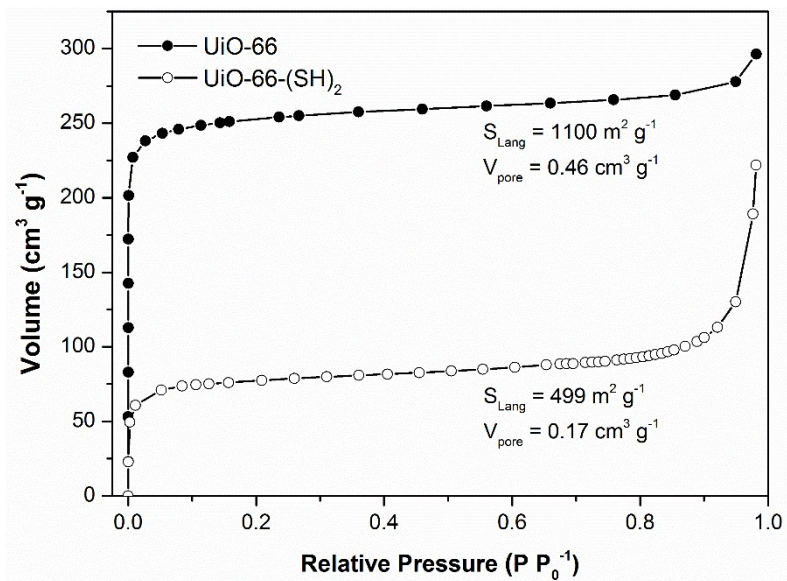


Fig. S5 Nitrogen adsorption at 77 K of thermally activated UiO-66 and UiO-66-(SH)₂ samples.

D. Adsorption experiments

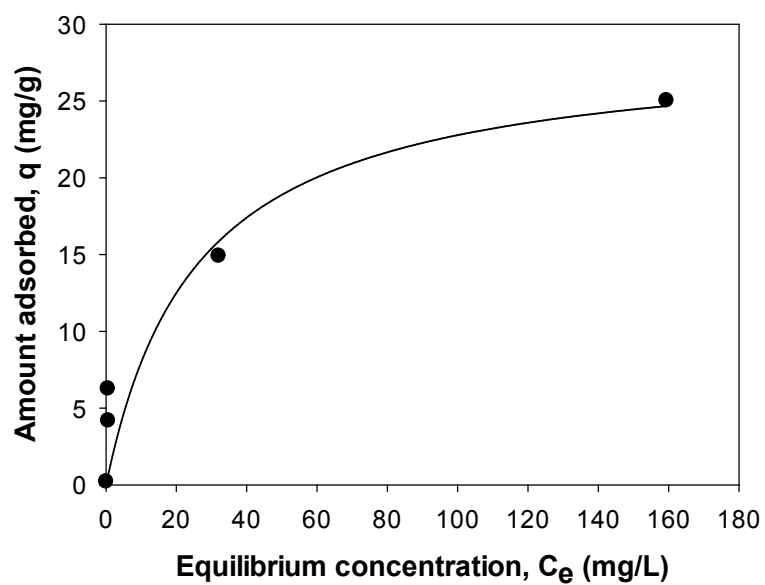


Fig. S6 Adsorption isotherm of Hg(II) on UiO-66.

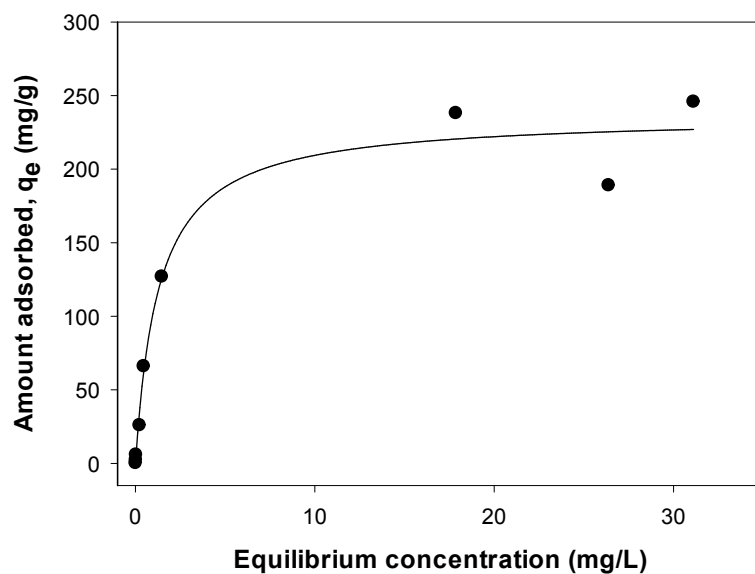


Fig. S7 Adsorption isotherm of Hg(II) on UiO-66-(SH)₂.

Table S1 Adsorption kinetic data for the removal of Hg(II).

Time (minutes)	UiO-66		UiO-66-(SH) ₂	
	C _e (μg L ⁻¹)	Removal (%)	C _e (μg L ⁻¹)	Removal (%)
10	1.17	88.7	0.85	91.8
60	0.46	95.5	0.39	96.3
240	0.39	96.2	0.11	98.9
480	0.15	98.6	0.08	99.2
1440	0.06	99.4	0.00	100.0

Table S2 Adsorption fitting parameters of Hg(II) for the evaluated kinetic models.

Isotherm parameters	UiO-66	UiO-66-(SH) ₂
<i>Lagergren's model</i>		
k ₁ (min ⁻¹)	6.18x10 ⁻³	8.64x10 ⁻³
R ²	0.5339	0.7201
<i>2nd-order model</i>		
k ₂ (L mg ⁻¹ min ⁻¹)	0.0106	0.0256
R ²	0.9859	0.9622
<i>Pseudo-2nd- order model</i>		
k ₂ (g mg ⁻¹ min ⁻¹)	111.5	96.4
R ²	0.9999	0.9999
<i>Elovich model</i>		
α	4.94x10 ⁻⁵	4.01x10 ⁻⁵
a	2.21x10 ⁻³	7.78x10 ⁻²⁸
R ²	0.8113	0.7746
<i>Intra-particle diffusion model</i>		
k _{id} (mg g ⁻¹ min ^{-1/2})	4.03x10 ⁻⁵	4x10 ⁻⁵
R ²	0.7564	0.7580

Lagergren's equation (Pseudo-1st order rate equation)

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t \quad (1)$$

where q_e is the adsorption capacity (mg g^{-1}) at equilibrium, q_t is the adsorption capacity at time t (min) and k_1 is the rate constant (min^{-1}).

Second-order rate equation

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0} \quad (2)$$

where C_0 and C_t are the initial concentration (mg L^{-1}) and concentration at time t (min), and k_2 is the rate constant ($\text{L mg}^{-1} \text{min}^{-1}$).

Pseudo-2nd-order rate equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e is the adsorption capacity (mg g^{-1}) at equilibrium, q_t is the adsorption capacity at time t (min) and k_2 is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

Elovich's equation

$$q_t = \alpha \ln(a\alpha) + \alpha \ln(t) \quad (4)$$

where q_t is the adsorption capacity at time t (min), α is the initial adsorption rate and a is the adsorption constant during any one experiment.

Intraparticle diffusion model (IPD)

$$q_t = k_i \sqrt{t} \quad (5)$$

where q_t is the adsorption capacity at time t (min) and k_i is the IPD rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$).

Table S3 Characteristics of the spiked domestic wastewater sample.

Parameter	Value	Unit
Background Hg(II) concentration	0.47	$\mu\text{g L}^{-1}$
pH	7.37 ± 0.15	-
Dissolved oxygen (DO)	10.6 ± 0.5	mg L^{-1}
Hardness	333.2 ± 54.5	$\text{mg CaCO}_3 \text{L}^{-1}$
Organic carbon (TOC)	11.2 ± 3.1	mg L^{-1}
Inorganic carbon (IC)	48.0 ± 8.1	mg L^{-1}
Total carbon (TC)	59.2 ± 11.3	mg L^{-1}
Electric conductivity (EC)	1094.0 ± 4.4	$\mu\text{S cm}^{-1}$

Reference

1. L. Vial, R. F. Ludlow, J. Leclaire, R. Pérez-Fernández and S. Otto, *J. Am. Chem. Soc.*, 2006, **128**, 10253-10257.