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Synthesis of supramolecular polymers with calix[4]arene and β -cyclodextrin and their application in heavy metal ion absorption†

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Two categories of supramolecular polymer monomers were produced by introducing the ureidopyrimidone quadruple-hydrogen bonding assemblies on the calix[4]arene and the β -cyclodextrin host units. The adsorption capacity of these supramolecular polymers for different metal ions was investigated by static adsorption. The results showed that at pH = 6 and when the adsorption equilibrium was reached, the supramolecular polymer with calixarene and β -cyclodextrin as the main body adsorbed up to 99% of Pb^{2+} and Cd^{2+} , respectively. Also, the supramolecular polymer connected with six carbon chains on β -cyclodextrin had better recognition of Cd^{2+} and Pb^{2+} , and the highest adsorption rate reached 99%. Industrial adsorbent materials from such supramolecular polymers will provide more options for water pollution control, especially for heavy metal ions.

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1. Introduction

Macrocyclic molecules, including calixarene,^{1–4} cyclodextrin,^{5–8} crown ether,^{9–12} pillar arene,^{13–16} cyclic peptides,^{17–20} *etc.* have been used in various fields, such as host/guest recognition,^{21–25} selective adsorption separation,^{26–30} water pollution control,^{31–34} optical sensing detection^{35–39} and heterogeneous catalysis,^{40–43} owing to their guest binding properties. Non-covalent bonds bind together the supramolecular polymers to form novel self-assembled structures.^{44–48} Among the non-covalent bonds are hydrogen, ligand, host-guest, and donor-acceptor interactions. They have many repeating unit structures compared to the conventional high molecular polymers. Therefore, if a supramolecular polymer is made into an adsorbent material, the polymeric material will be characterized by efficient and rapid adsorption of heavy metal ions.

Hydrogen bonding is one of the weak interaction forces in supramolecular chemistry and molecular assembly. Its formation is directional and selective, mainly when using multiple hydrogen bonds. We can obtain very stable structural systems, which will increase the degree of polymerization of supramolecular polymers. For example, Meijer's group^{49–53} discovered a quadruple hydrogen bonding system with a very high binding

constant in 1997. After being introduced into the supramolecular system, the degree of polymerization of supramolecular polymers significantly increased.

Calixarene^{54–58} and cyclodextrin,^{59–63} as the host units of supramolecular polymers, have the advantages of high efficiency, high speed, and high selectivity in the adsorption of heavy metal ions, especially the adsorption of highly toxic heavy metal ions. However, traditional polymers can only efficiently adsorb a single specific heavy metal ion, which cannot be carried out according to the characteristics of heavy metals in water. The incorporation of urea-pyrimidinone (UPy) containing quadruple hydrogen bonds into the supramolecular structure can introduce the property of quadruple hydrogen bonding into the supramolecular polymer, and the prepared supramolecular polymer can be self-repairing. From the reaction synthesis process perspective, it is highly feasible to introduce UPy's quadruple hydrogen bonds into the calixarenes and cyclodextrin structures. Therefore, two types of supramolecular monomers have been designed in this paper. Firstly, urea-pyrimidinone linked by three carbon chain on *p-tert*-butylcalix[4]arene (BC4PUPy); urea-pyrimidinone linked by six carbon chains on *p-tert*-butylcalix[4]arene (BC4HUPy); urea-pyrimidinone linked by three carbon chains on calix[4]arenes (C4PUPy); urea-pyrimidinone linked by six carbon chains on calix[4]arenes (C4HUPy). Secondly, urea-pyrimidinone was with three carbon chains on β -cyclodextrin (β -CDPUPy); urea-pyrimidinone was with four carbon chains on β -cyclodextrin (β -CDBUPy); urea-pyrimidinone linked with six carbon chains on β -cyclodextrin (β -CDHUPy). The synthetic supramolecular polymer names and related parameters are shown in Table 1 as below.

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Table 1 The related parameters of title supramolecular polymers

Target materials	Host unit	Alkyl chain
BC4PUPy	<i>tert</i> -Butylcalix[4]arene	Propyl
BC4HUPy	<i>tert</i> -Butylcalix[4]arene	Hexyl
C4PUPy	Calix[4]arene	Propanyl
C4HUPy	Calix[4]arene	Hexanyl
β -CDPUPy	β -Cyclodextrin	Methyl
β -CDBUPy	β -Cyclodextrin	Ethyl
β -CDHUPy	β -Cyclodextrin	Butyl

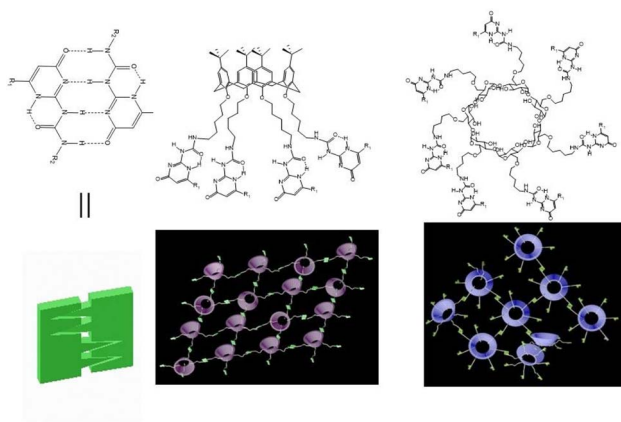


Fig. 1 The chemical structure of the formation of the quadruple-hydrogen bonding assemblies in UPy and the supramolecular polymers dominated by β -cyclodextrin and calix[4]arene.

As shown in Fig. 1, two types of supramolecular monomer polymers have unique adsorption capabilities and can be used to absorb heavy metal ions.

2. Results and discussion

2.1 Design and synthesis

Through the study of related literature, we have found that the derivatives with cyclodextrin and calixarene as host structures are similar to their unmodified host structures in the inclusion interaction of guest ions or molecules. So, the properties of urea-pyrimidinone linked by polycarbonate chain on calix[4]arenes are determined by the properties of calix[4]arenes. The properties of the β -cyclodextrin determine the properties of urea-pyrimidinone linked by polycarbonate chain on β -cyclodextrin. Therefore, by changing their substituents, cyclodextrin, and calixarene derivatives can regulate their selectivity to guest ions or molecules. The structure of cyclodextrin and calixarene derivatives can be regulated by changing the type of cyclodextrin and calixarene, the size of the central hole, and the type, position, and number of substituents among the supramolecular polymers assembled by hydrogen bonds. Two advantages can be obtained by introducing urea-pyrimidinone (UPy) into the supramolecular host. First, the supramolecular polymer with cyclodextrin and calixarene as the host units can be adjusted by the solvent method; second, by changing the position of UPy, the amount and the type of substituents are used to regulate the

solubility of supramolecular polymers, which makes the supramolecular polymers have more abundant technological properties. At the same time, they also enhance the selectivity of different heavy metal ions and the adsorption effect of heavy metal ions.

2.2 Determination of heavy metal ion adsorption properties

The 20 mg of the newly synthesized supramolecular polymer was added to the conical flask containing 25 mL of metal ion water solution, shaking in a water bath and shaker at a rate of 150 rpm. The temperature was 20 °C. At the end of time, the conical flask was removed. A centrifuge separated the solution at 10 000 rpm. An atomic absorption spectrophotometer then detected the supernatant. The concentration of heavy metal ions in the sample was measured. The PhSJ-3F pH meter produced by Shanghai Precision Scientific Instrument Co., Ltd is used for pH measurement. The concentration of heavy metal ions is measured using the Shimadzu AA6300 atomic absorption spectrophotometer. SHZ-03 high precision air water bath constant temperature shaker produced by Shanghai Kangxin Instrument Equipment Co., Ltd is used for shock treatment of supramolecular polymer adsorption of heavy metal ions. Hunan Xingke Scientific Instrument Co., Ltd produced a TGL-16G table high-speed centrifuge for solid-liquid separation after the adsorption of clear liquid. Ultra-pure water is prepared by MO6-226 mole elemental ultra-pure water machine produced by Moler Biotechnology Co., Ltd. The adsorption effect of the adsorbent on the heavy metal ion was obtained based on the calculation. The formula is as follows:⁶⁴

$$E = \frac{C_0 - C}{C_0} \times 100$$

E represents the adsorption percentage of heavy metal ions by the adsorbent. C_0 represents the concentration of heavy metal ions in the solution, mg L^{-1} . C denotes the concentration of heavy metals in the solution after adsorption treatment, mg L^{-1} .

The main content of this paper is to investigate the inclusion adsorption of five heavy metal ions (Pb^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+}) by supramolecular polymers after self-assembly into supramolecular polymers. The selection of (Pb^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , and Cu^{2+}) as the targets of our study was driven by their environmental significance and toxicity, with their ionic radii informing our understanding of their unique interactions and behaviors at the molecular level and their ionic radii as shown in Table 2.

The adsorption equilibrium time of heavy metal ions by supramolecular polymers was studied at pH = 6. The results showed that the adsorption of Zn^{2+} by the supramolecular polymer formed by the self-assembly of β -CDBUPy reached

Table 2 The ionic radii of chosen heavy metal ions

Ion	Pb^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}
Radii (pm)	119	95	70	74	73



Table 3 The highest adsorption rate of heavy metal ions

Polymer	Pb ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺	Cu ²⁺
BC4PUPy	99%	4%	19%	21%	5%
BC4HUPy	99%	3%	20%	23%	8%
C4PUPy	99%	3%	13%	17%	6%
C4HUPy	99%	5%	35%	19%	13%
(-CDPUPy)	14%	99%	2%	7%	4%
(-CDBUPy)	13%	99%	6%	17%	10%
(-CDHUPy)	99%	99%	25%	22%	20%

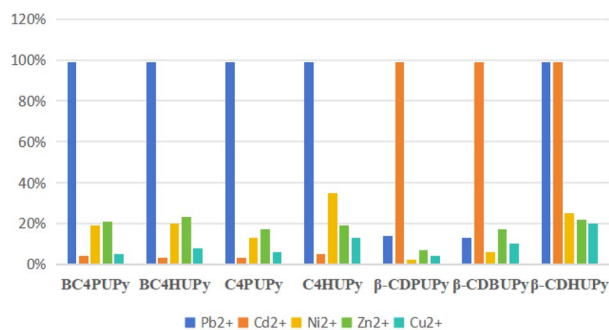


Fig. 2 Maximum adsorption rate of 5 metal ions by title polymers.

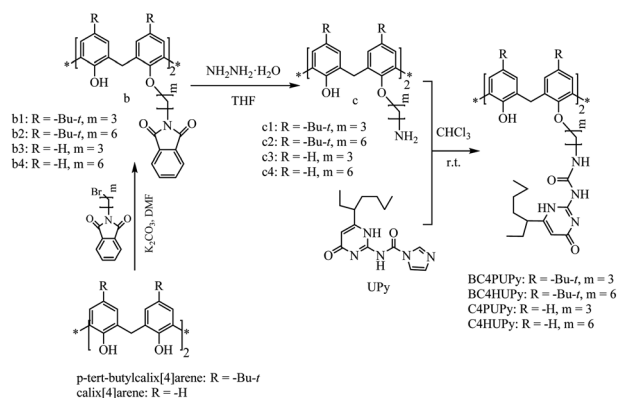
equilibrium after 6 h. The adsorption of Ni²⁺ by supramolecular polymers formed by β-CDHUPy self-assembly reached equilibrium after 6 h. Other supramolecular polymers reached equilibrium in 2 h. Before reaching the adsorption equilibrium, the adsorption capacity of various supramolecular polymers for heavy metal ions increased with the adsorption time. When the adsorption equilibrium is reached, the adsorption rate remains almost unchanged.

At the same adsorption time (6 h), the adsorption effects of the supramolecular polymer on heavy metal ion solution were investigated at pH = 2, 4, and 6, respectively. The results showed that the adsorption capacity of heavy metal ions enhanced with the increase of pH from 2 to 6 (as shown in ESI Section II†). The highest adsorption rate and the best adsorption effect were observed at pH = 6.

The supramolecular polymers achieved an impressive maximum adsorption rate of 99% for Pb²⁺ and Cd²⁺, underscoring their remarkable selectivity. Notably, BC4HUPy, BC4HUPy, C4PUPy, C4HUPy were the standout performers in Pb²⁺ adsorption, while β-CDPUPy and β-CDBUPy demonstrated strong Cd²⁺ adsorption. β-CDHUPy exhibited good adsorption capacity for both ions. The highest adsorption rate is shown in Table 3.

The maximum adsorption rates of different metal ions by supramolecular polymers are shown in Fig. 2.

By studying the pH value and adsorption time of heavy Metal solution, it can be found that the adsorption rate of calixarene-based supramolecular polymeric monomers on Pb²⁺ are 99% after their respective self-assembly and the adsorption of Cd²⁺, Ni²⁺, Zn²⁺ and Cu²⁺ is not apparent. This result may be related to the structure of supramolecular polymers. The cavity's size



Scheme 1 Synthetic routes of the polymer monomers with calixarenes as the host unit.

after the supramolecular polymer's formation is compatible with Pb²⁺, whose ionic radius is 0.119 nm, so it has a high rate of inclusion junction adsorption for lead ions. In contrast, the ionic radius of Cd²⁺, Ni²⁺, Zn²⁺, and Cu²⁺ is lower than the requirement of cavity adsorption, and desorption is evident. Therefore, the inclusion junction adsorption of Cd²⁺, Ni²⁺, Zn²⁺, and Cu²⁺ is not good.

After the self-assembly of supramolecular polymerized monomers, the adsorption rates of β-cyclodextrin-based supramolecular polymer adsorbs 99% of Cd²⁺ in all cases, and the adsorption rates on Zn²⁺, Ni²⁺, and Cu²⁺ are insignificant. After the formation of the supramolecular polymer, the size of the cavity is compatible with Cd²⁺ with a radius of 0.095 nm, so the adsorption rate of Cd²⁺ is higher, and the cavity of the supramolecular polymer is larger than the size of Ni²⁺, Zn²⁺ and Cu²⁺. The adsorption is poor as it is shed after adsorption. Conversely, the adsorption rate of supermolecular polymers formed by the self-assembly of β-CDPUPy and β-CDBUPy on Pb²⁺ is 15% or less. In contrast, the adsorption rate of supramolecular polymers formed by β-CDHUPy on Pb²⁺ is 99%.

We speculate that the possible mechanism is due to after the self-assembly of polymers with β-CDPUPy and β-CDBUPy, the cavity is enlarged, but it is still smaller than the size of Pb²⁺, so it is impossible to adsorb Pb²⁺. However, when β-CDHUPy forms a polymer, the cavity becomes more extensive and adapts to the size of Pb²⁺; at the same time, the polymer forms a simple network structure, so the inclusion effect is obviously enhanced, and Pb²⁺ can be adsorbed well. Under encapsulation, Pb²⁺ cannot easily fall off, so it has a superior adsorption effect on Pb²⁺ (Scheme 1).

3. Experimental section

3.1 Apparatus and reagents

Commercially available reagents were used without further purification unless otherwise stated. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker spectrometer at 500 MHz using TMS as an internal standard. The β-keto acid ester, urea pyrimidine ketone derivatives, and UPy were prepared by literature procedures.⁵²



3.2 General synthesis of the polymer monomers with calixarenes as the host unit

3.2.1 Synthesis of intermediate b. With the protection of nitrogen, 1.0 mol calix[4]arene derivatives, 4.0 mmol *N*-bromoalkylphthalimide, 0.55 g K_2CO_3 (4.0 mmol) (baked in an oven at 130 °C for 6 h), and 20 mL anhydrous DMF are added to a 100 mL single-mouth flask, and the reaction is warmed to 65 °C for 2 days. The reaction is stopped when the reaction time is reached and cools to room temperature. The reaction solution is added to 100 mL of water, and a white turbid substance is immediately formed, extracted with 30 mL of chloroform three times. The organic phase is further treated with 30 mL of 5% NaOH solution and water (20 mL \times 3). The solution is washed with saturated brine and dried with anhydrous magnesium sulfate. The solvent is evaporated to give intermediate **b1** to **b4**.

b1: (0.54 g, 54%), 1H NMR ($CDCl_3$, ppm): δ = 7.76 (m, Ar-H, 4H), 7.62 (m, Ar-H, 4H), 7.07 (s, Ar-H, 8H), 6.82 (s, Ar-H, 8H), 4.35 (m, O-CH₂-C, 4H), 4.15 (m, -CH₂, 8H), 3.35 (m, N-CH₂-C, 4H), 2.47 (m, -CH₂, 4H), 1.30 (s, -C(CH₃)₃, 36H).

b2: (0.49 g, 45%). 1H NMR (500 MHz, $CDCl_3$): δ = 7.70 (m, Ar-H, 4H), 7.41 (m, Ar-H, 4H), 7.05 (s, Ar-H, H), 6.79 (s, Ar-H, 8H), 3.99–3.96 (m, O-CH₂-C, 4H), 3.73–3.65 (m, N-CH₂-C, 4H), 3.31 (dd, -CH₂, 8H), 2.05–1.65 (m, O-C-CH₂-C, 4H), 1.55–1.44 (m, N-C-CH₂-C, 4H), 1.33 (s, -C(CH₃)₃, 36H), 0.88 (m, -CH₂, 8H).

b3: (0.49 g, 51%), 1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (m, 4H), 7.70 (m, 4H), 7.22–6.26 (m, 12H), 4.02 (m, 4H), 3.9–3.4 (m, 8H), 3.04 (d, 4H), 2.22 (m, 4H).

b4: (0.49 g, 56%), 1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (m, 4H), 7.67 (m, 4H), 7.16–6.18 (m, 12H), 4.09 (dd, 8H), 3.74–3.49 (m, 8H), 1.56–0.89 (m, 16H).

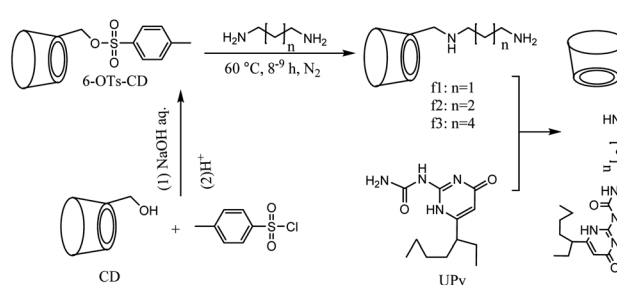
3.2.2 Synthesis of intermediate c. 0.5 mmol **b** and THF (20 mL) are added to a 50 mL three-necked flask under a nitrogen atmosphere. The mixture is heated to reflux, and then 10 mL of hydrazine hydrate is added dropwise using a dropping funnel. The reaction mixture is refluxed for 8 h. Stop heating and cool to room temperature. Separate the lower layer with a separatory funnel and take the upper layer of liquid. Evaporate the solvent with a rotary evaporator and obtain a brownish oily body extracted with 60 mL of chloroform. The chloroform phase is washed with 40% sodium hydroxide solution and 50 mL of saturated brine and dried with anhydrous Na_2SO_4 . The solvent is evaporated to give intermediate **c1** to **c4**.

c1: (0.28 g, 73.5%), 1H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 8H), 6.82 (s, 8H), 4.15 (m, 8H), 3.31 (d, 8H), 2.47 (m, 4H), 1.93 (m, 4H), 1.33 (s, 36H).

c2: (0.34 g, 80%), 1H NMR (500 MHz, $CDCl_3$): δ = 7.28 (s, 8H), 6.91 (s, 8H), 4.0 (t, 4H), 3.41 (t, 4H), 3.31 (d, 8H), 1.91 (m, 4H), 1.45 (m, 16H), 1.29 (s, 36H).

c3: (0.11 g, 41.5%), 1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (m, 4H), 7.70 (m, 4H), 7.22–6.26 (m, 12H), 4.02 (m, 4H), 3.9–3.4 (m, 4H), 3.04 (d, 8H), 2.22 (m, 4H).

c4: (0.095 g, 31%), 1H NMR (500 MHz, $CDCl_3$): δ = 11.45 (s, 2H), 9.71 (s, 2H), 8.55 (s, 2H), 7.23–7.06 (m, 8H), 5.73 (s, 2H), 4.20–4.14 (m, 8H), 3.66–3.43 (m, 8H), 3.32 (m, 4H), 2.21 (s, 2H), 2.08 (m, 8H), 1.5 (m, 8H), 0.88–0.72 (m, 12H) ppm.



Scheme 2 Synthetic routes of the polymer monomers with β -cyclodextrin as the host unit.

3.2.3 Synthesis of the polymer monomers with calixarenes as the host unit. Under nitrogen protection, 0.5 mmol intermediate **c** and UPy (0.6 g, 2 mmol) is added to a 50 mL three-necked flask, and 20 mL of $CHCl_3$ (already dehydrated and dried) is added at 25 °C. Stir and avoid light for 12 h. The reaction is stopped when the reaction time is reached and cools to room temperature. $CHCl_3$ treated (50 mL) is added to the reaction solution, and the reaction solution is washed sequentially with 2 N HCl (20 mL), saturated $NaHCO_3$ (30 mL), and saturated brine (30 mL). The organic phase is dried with anhydrous Na_2SO_4 , and the solvent is evaporated. The crude product is separated by column chromatography and then precipitated in methanol to obtain the target materials as a white solid (Scheme 2).

BC4PUPy: (0.21 g, 35%), the rate of UPy substitution is 2.3 estimated from the 1H NMR data. 1H NMR (500 MHz, $CDCl_3$): δ = 13.54 (s, 2H), 11.77 (s, 2H), 10.18 (s, 2H), 7.99 (s, 2H), 6.99 (s, 4H), 6.83 (s, 4H), 5.47 (s, 2H), 4.21 (d, 8H), 3.9 (m, 8H), 3.2 (m, 4H), 2.23 (s, 2H), 2.20 (m, 8H), 1.6 (m, 8H), 1.21 (s, 36H), 0.90–0.70 (m, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.79, 171.77, 155.46, 154.64, 154.11, 150.40, 148.76, 145.91, 139.97, 131.88, 126.19, 124.56, 123.99, 104.25, 73.87, 44.10, 38.38, 33.00, 32.78, 31.38, 30.94, 30.05, 29.86, 29.33, 28.21, 25.09, 21.65, 12.96, 10.67.

BC4HUPy: (0.21 g, 33%), the rate of UPy substitution is 2.5 estimated from the 1H NMR data. 1H NMR (500 MHz, $CDCl_3$): δ = 13.18 (s, 2H), 11.83 (s, 2H), 10.16 (s, 2H), 7.62 (s, 2H), 6.96 (s, 4H), 6.75 (s, 4H), 5.73 (s, 2H), 4.20 (d, 8H), 3.89 (m, 8H), 2.2–2.0 (m, 16H), 1.59–1.44 (m, 16H), 1.20 (s, 36H), 0.89–0.70 (m, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.77, 172.08, 171.96, 155.73, 154.15, 153.94, 149.83, 149.78, 149.14, 145.63, 140.19, 131.80, 126.83, 124.50, 124.43, 124.01, 105.23, 105.04, 44.32, 44.19, 39.14, 39.07, 32.92, 32.78, 31.87, 31.68, 30.86, 30.69, 30.05, 29.83, 29.33, 28.99, 28.29, 26.00, 25.59, 25.40, 24.76, 24.57, 21.76, 21.53, 21.47, 12.87, 10.68.

C4PUPy: (0.37 g, 75%), the rate of UPy substitution is 2.2 estimated from the 1H NMR data. 1H NMR (500 MHz, $CDCl_3$): δ = 11.45 (s, 2H), 9.71 (s, 2H), 8.55 (s, 2H), 7.23–7.06 (m, 8H), 5.73 (s, 2H), 4.20–4.14 (m, 8H), 3.66–3.43 (m, 8H), 3.32 (m, 4H), 2.21 (s, 2H), 2.08 (m, 8H), 1.5 (m, 8H), 0.88–0.72 (m, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.93, 172.91, 156.63, 155.81, 155.25, 151.61, 149.89, 147.08, 141.11, 133.02, 127.57, 125.71, 125.13, 105.39, 75.05, 45.24, 39.52, 34.15, 33.92, 31.86, 29.36, 26.24, 22.80, 14.11, 11.82.



C4HUPy: (0.32 g, 60%), the rate of UPy substitution is 2.3 estimated from the ^1H NMR data. ^1H NMR (500 MHz, CDCl_3): $\delta = 11.45$ (s, 2H), 9.72 (s, 2H), 8.39 (s, 2H), 7.23–7.05 (m, 8H), 5.73 (s, 2H), 4.21–4.0 (m, 8H), 3.66–3.43 (m, 8H), 3.33 (m, 4H), 2.22–2.08 (m, 10H), 1.20–1.17 (m, 8H), 0.81–0.72 (m, 12H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 206.90, 173.22, 173.09, 156.85, 155.06, 150.96, 150.91, 150.27, 146.76, 141.32, 132.93, 127.95, 125.63, 125.56, 125.14, 106.17, 76.77, 76.61, 45.44, 45.32, 40.27, 40.20, 34.05, 33.90, 31.99, 31.82, 30.46, 30.11, 29.42, 27.13, 26.72, 26.53, 25.89, 25.70, 22.66, 22.60, 14.00, 11.81$.

3.3 General synthesis of the polymer monomers with β -cyclodextrin as the host unit

3.3.1 Synthesis of intermediate 6-OTs-CD. Add 10 g of β -cyclodextrin (8.8 mmol) to a 500 mL single-necked flask with 100 mL of double distilled water and stir magnetically at room temperature for 2 h. The solution is emulsified by adding 20 mL of 50% NaOH solution dropwise with a dropping funnel and stirring for 30 min. Add 20 mL of 50% NaOH solution drop by drop with a dropping funnel, and continue stirring for 30 min. 1.5 g of *p*-toluenesulfonyl chloride (TsCl) is weighed and dissolved in 30 mL of acetonitrile and then ultrasonicated in an ultrasonic apparatus to dissolve *p*-toluenesulfonyl chloride completely. The solution is added to the reaction dropwise with a constant pressure burette funnel and stirred at 10 °C for three h. The unreacted *p*-toluenesulfonyl chloride is filtered out by filtration. The filtrate is adjusted to a pH value of about 7 with 2 mol L^{-1} hydrochloric acid and stored at a low temperature below 5 °C for 12 h. A large amount of white precipitate is produced, and a white solid is obtained by filtration under reduced pressure. The product is recrystallized twice with 100 mL of double distilled water and dried in a vacuum oven at 60 °C for 12 h. The final product 6-OTs-CD is obtained with a yield of 20.0%. ^1H NMR (500 MHz, DMSO): $\delta = 8.75$ (d, 2H, Ar-H), 7.75 (d, 2H, Ar-H), 5.75 (s, 14H, 2- and 3-OH), 4.70 (s, 7H, H-1 of CD), 4.5–4.1 (m, 1H, 6-OH), 3.75–3.25 (m, 42H, H-2, 3, 4, 5, 6 of CD), 2.40 (s, 3H, $-\text{CH}_3$).

3.3.2 Synthesis of intermediate f. Under nitrogen protection, 2.0–2.5 g of 6-OTs- β -CD and 15 mL of 1,3-alkyl diamine is added in a 100 mL single-mouth flask. The reaction is warmed to 70 °C, and reacts for 8 h. The reaction is stopped when the reaction time is reached and cools to room temperature. A vacuum distillation apparatus is set up, and excess unreacted 1,3-propane diamine is distilled off to obtain a yellow impurity. Add a small amount of hot water to dissolve the yellow debris. A large amount of anhydrous ethanol is added to produce a sizeable white precipitate. Stir for 20 min and let stand. A white solid can be obtained by filtration, the target crude product. Purification method: Sephadex C-25 ion column was used for impurity removal by eluting with 0.05, 0.15, and 0.3 mol L^{-1} sodium chloride solution. The sample is collected and purified. The purified sample is washed with a Sephadex G-25 gel column to offer **f1–f3**.

f1: yield 70%, ^1H NMR (500 MHz, DMSO-d_6): $\delta = 4.80$ –4.75 (m, 7H, H-1 of CD), 3.70–3.50 (m, 28H, H-3,5,6 of CD), 3.45–3.40 (m, 14H, H-2,4 of CD), 3.40–3.30 (t, 1H, H-6 of CD), 2.90–2.80 (t,

2H, C- CH_2 -N), 2.70–2.55 (t, 2H, C- CH_2 -N), 1.55–1.45 (m, 2H, C- CH_2 -C).

f2: yield 55%, ^1H NMR (500 MHz, DMSO-d_6): $\delta = 5.03$ –4.98 (m, 7H, H-1 of CD), 4.02–3.98 (t, 1H, H-6' of CD), 3.92–3.71 (m, 28H, H-3,5,6 of CD), 3.60–3.49 (m, 14H, H-2, 4 of CD), 3.45–3.39 (t, 1H, H-6' of CD), 2.96–2.93 (t, 2H, C- CH_2 -N), 2.89–2.84 (t, 2H, C- CH_2 -N), 1.68–1.61 (m, 4H, C- CH_2 -C).

f3: yield 65%, ^1H NMR (500 MHz, DMSO-d_6): $\delta = 4.85$ –4.75 (m, 7H, H-1 of CD), 4.60–4.25 (s, 1H, H-6' of CD), 3.75–3.50 (m, 28H, H-3,5,6 of CD), 3.45–3.20 (m, 14H, H-2,4 of CD), 2.90–2.80 (t, 2H, C- CH_2 -N), 2.75–2.55 (t, 2H, C- CH_2 -N), 1.45–1.0 (m, 8H, C- CH_2 -C).

3.3.3 Synthesis of the polymer monomers with β -cyclodextrin as the host unit. Try to avoid light reactions. Under nitrogen protection, add intermediate **f1** (0.6 g, 0.5 mmol), UPy (0.6 g, 2 mmol) and 20 mL DMF into a 50 mL three-necked flask. The reaction is stirred at 35 °C overnight and cooled to room temperature. Add 150 mL of acetone into a 250 mL beaker and stir vigorously. The cooled reaction solution is added dropwise to acetone, and the acetone solution gradually becomes turbid. A white solid can be obtained by filtration. Wash sequentially with 1 N HCl (20 mL), saturated NaHCO_3 (20 mL), and saturated brine (20 mL). The target materials can be obtained by vacuum drying as white solids.

β -CDPUPy: yield, 0.21 g, 30%, the rate of UPy substitution is 2.2 estimated from the ^1H NMR data. ^1H NMR (500 MHz, DMSO-d_6): $\delta = 7.95$ (s, $-\text{NH}$, 3H), 5.73–5.68 (s, $-\text{CH}$, 1H), 4.83–4.81 (m, 7H, H-1 of CD), 4.46 (s, 1H, H-6' of CD), 3.65–3.55 (m, 28H, H-3,6,5 of CD), 3.37–3.35 (m, 15H, H-2, 4, 6 of CD), 2.89 (m, $-\text{CH}$, 1H), 2.73 (m, N- CH_2 -C, 2H), 1.65–1.49 (m, $-\text{CH}_2$, 4H), 1.23–1.13 (m, $-\text{CH}_2$, 8H), 0.85–0.73 (m, $-\text{CH}_3$, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 206.68, 182.21, 168.00, 154.72, 102.09, 93.10, 73.23, 72.66, 72.62, 72.17, 68.28, 60.08, 47.50, 44.84, 43.23, 32.98, 30.81, 29.13, 26.58, 22.22, 13.96, 11.82$.

β -CDBUPy: yield 0.18 g, 25%, the rate of UPy substitution is 2.0 estimated from the ^1H NMR data. ^1H NMR (500 MHz, DMSO-d_6): $\delta = 7.95$ (s, $-\text{NH}$, 3H), 5.81 (s, 1H), 4.83–4.80 (m, 7H, H-1 of CD), 4.51 (s, 1H, H-6 of CD), 3.65–3.56 (m, 28H, H-3,6,5 of CD), 3.40–3.29 (m, 15H, H-2, 4, 6 of CD), 2.88 (m, $-\text{CH}$, 1H), 2.72 (m, N- CH_2 -C, 2H), 1.51–1.48 (m, $-\text{CH}_2$, 6H), 1.21–1.23 (m, $-\text{CH}_2$, 8H), 0.85–0.73 (m, $-\text{CH}_3$, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 206.29, 171.75, 157.73, 154.55, 102.09, 96.25, 81.53, 73.06, 72.95, 72.55, 72.45, 72.00, 70.02, 68.13, 62.76, 59.91, 55.04, 49.45, 47.34, 47.31, 30.64, 28.96, 28.68, 26.41, 22.06, 21.97, 13.79, 11.65$.

β -CDHUPy: yield 0.22 g, 30%, the rate of UPy substitution is 2.1 estimated from the ^1H NMR data. ^1H NMR (500 MHz, DMSO-d_6): $\delta = 7.91$ (s, $-\text{NH}$, 3H), 5.79 (s, $-\text{CH}$, 1H), 4.88–4.74 (m, 7H, H-1 of CD), 4.60–3.90 (d, 1H, H-6 of CD), 3.90–3.50 (m, 28H, H-3, 6,5 of CD), 3.39–3.32 (m, 15H, H-2,4,6 of CD), 2.90 (m, $-\text{CH}$, 1H), 2.75 (m, N- CH_2 -C, 2H), 1.50–1.26 (m, $-\text{CH}_2$, 10H), 1.22–1.20 (m, $-\text{CH}_2$, 8H), 0.85–0.72 (m, $-\text{CH}_3$, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 205.96, 171.42, 167.45, 154.22, 101.76, 92.60, 81.16, 72.72, 72.62, 72.12, 71.67, 59.58, 54.00, 46.98, 35.3, 33.58, 32.48, 30.31, 28.62, 28.34, 26.26, 26.08, 21.72, 21.64, 13.46, 11.32$.



4. Conclusions

This proposed research designed and prepared seven supramolecular polymer monomers (BC4PUPy, BC4HUPy, C4PUPy, C4HUPy, β -CDPUPy, β -CDBUPy, β -CDHUPy). ^1H NMR and ^{13}C NMR were employed to characterize them. Their adsorption effects on heavy metal ions (Pd^{2+} , Gd^{2+} , Ni^{2+} , Zn^{2+} and Cu^{2+}) were investigated by atomic absorption method. The adsorption rate of Pb^{2+} was 99% after self-assembly of supramolecular polymeric monomers based on calix[4]arene, and the adsorption rate of Cd^{2+} was 99% after self-assembly of supramolecular polymeric monomers based on β -cyclodextrin. In addition, the adsorption rate of the supramolecular polymer formed by the self-assembly of β -CDHUPy on Pb^{2+} was 99%, which can be used for the adsorption of Pb^{2+} under special circumstances. This research will provide more excellent adsorption materials to control heavy metal pollution.

Data availability

All relevant data are within the paper.

Conflicts of interest

There are no conflicts to declare.

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