

Synthesis and Selective Au(III) Adsorption of Ureido Polymers Containing Large Repeating Rings

Yunkai Sun,* Yaqian Ding, Wenwen Zhou, Xiaofeng Wang, Chunhong Tan,* Yoshimasa Matsumura, Bungo Ochiai, and Quanli Chu*



Cite This: *ACS Omega* 2021, 6, 28004–28011



Read Online

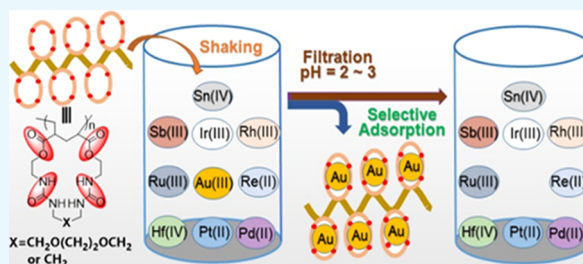
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Two polymers (polyBAUEE and polyBAUP) containing 25- and 20-membered rings are synthesized by the cyclopolymerization of bifunctional monomers 1,2-bis(acryloyloxyethyl-ureidoethoxyl)ethane (BAUEE) and 1,3-bis(acryloyloxyethylureido)propane (BAUP) and studied for the adsorption of precious metal ions. PolyBAUEE and polyBAUP selectively adsorb Au(III) with the adsorption efficiencies above 99.0% after adsorption equilibrium. PolyBAUEE adsorbed faster than polyBAUP, and the Au(III) adsorption is selective in the presence of nine interfering metal ions with similar concentrations (ca. 1 mg/L) in an aqueous solution including Pd(II) and Pt(II). The maximum Au(III) adsorption capacities of polyBAUEE and polyBAUP are 37.6 and 31.8 mg/g, respectively. Au(III) is reduced to Au(0) nanoparticles during the adsorption process. The selective adsorption behavior depends on the controlling regioselective recognition of the ring structure and the ureido groups.



1. INTRODUCTION

Heavy metal ion pollution in water has caused serious ecological problems, and how to deal with water pollution is a hot issue.^{1,2} A lot of methods are studied to remove heavy metal ions from the wastewater. Among the techniques, various functional polymers are used as adsorbents for heavy metal ions, which are to be scavenged due to the preciousness or toxicity.^{3–13} Polymers containing macrocyclic rings have attracted significant attention because of their unique properties to capture specific heavy metal ions,^{1–7} such as cadmium, lead, mercury, copper, silver metal ions, and so forth. To tune the ability of binding metal ions, proper designs of the functional groups and the ring's size are necessary, as for crown ethers,^{14,15} porphyrin,^{16,17} and cyclodextrins.^{18,19} Polymers containing large rings can be synthesized by (1) cyclopolymerization,^{20–24} (2) polymerization of monomers with macrocyclic structures,²⁵ and (3) modification of polymers using large-ring molecules.^{26,27} In all cases, the simple and efficient introduction of macrocyclic structures remains a challenge. Cyclopolymerization offers polymers with cyclic repeating units via an alternating intramolecular–intermolecular chain propagation.^{20–24} Despite the advantage in facileness, typical cyclopolymerization requires highly diluted concentrations to avoid cross-linking, which tend to limit the yield of the product.

In order to solve the limitation of macrocyclic polymer synthesis, our group^{22–24} developed polymers containing 19-membered ring units through efficient cyclopolymerization of bis(meth)acrylates with constrained conformation by the cyclic

structures and hydrogen bonds giving the polymers in excellent yields. Specifically, polyTBAUCH, the recently developed polymers containing ureido groups prepared by the polymerization of *trans*-1,2-bis(acryloyloxyethylureido)cyclohexane (TBAUCH), can selectively capture Ag⁺ with an excellent efficiency even in the presence of interfering 19 metal ions.²⁵ The excellent Ag⁺ selectivity of polyTBAUCH relies on the unique character of the ureido ligands having tuneable selectivity only with lighter elements. Additionally, polymers bearing 18-crown-6 groups can selectively capture K⁺, 15-crown-5 groups can selectively capture Na⁺, which depend on the O atoms and ring size.^{14,15} Therefore, cyclic molecules consisting of ureido groups attained selective adsorption of heavy metal ions^{28,29} and nitro-substituted compounds.^{30,31} The selectivity depends on the size and functional groups, and different designs of the cyclic structures will enable selective capture of other industrially important precious metals.

2. EXPERIMENTAL SECTION

Materials. Dichloromethane was dried over anhydrous magnesium sulfate and filtrated. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried over CaH₂ and

Received: July 21, 2021

Accepted: October 8, 2021

Published: October 18, 2021



distilled under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Water was deionized on a Nomura Micro Science MINIPURE TW-300RU instrument. Other reagents were used as received.

Preparation of Monomers and Polymers. Monomers were synthesized easily by a one-step reaction of acryloyloxyethylisocyanate (AOI) and 1,2-diaminoethoxyethane in a similar manner with other bis(ureido) derivatives prepared from 2-methacryloyloxyethyl isocyanate (MOI).³²

Synthesis of 1,2-Bis(acryloyloxyethyl ureido ethoxy)ethane (BAUEE). A solution of 1,2-diaminoethoxyethane (1.480 g, 10.0 mmol) in anhydrous dichloromethane (20.0 mL) was added dropwise to a stirred solution of AOI (2.820 g, 20.0 mmol) in anhydrous dichloromethane (30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 2 h under a stream of nitrogen. Then, the solution was concentrated by reducing pressure, and a white solid appeared overnight. The solid was washed with *n*-hexane (3 × 10 mL). The white solid was dried under high vacuum. Yield: 93.5%, mp = 70–71 °C. Anal. Calcd. for C₁₈H₃₀N₄O₈: C, 50.23; H, 7.03; N, 13.02; O, 29.73. Found: C, 50.18; H, 7.05; N, 13.00; O, 29.78. ¹H NMR (400 MHz, CDCl₃, δ in ppm): 3.33–3.35 (4H, m, –CONH–CH₂–), 3.47–3.60 (12H, m, –CH₂CH₂NH–, –OCH₂CH₂O–), 4.22–4.25 (4H, t, *J* = 5.6 Hz, –COOCH₂CH₂NH–), 5.56 (2H, br, –NHCO–), 5.71 (2H, br, –CONH–), 5.86 (2H, dd, *J* = 10.4, 1.2 Hz, CHH=CH–), 6.12 (2H, dd, *J* = 10.4, 17.2 Hz, CH₂=CH–), 6.41–6.45 (2H, dd, *J* = 17.2, 1.6 Hz, CHH=CH–). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 39.4 (–COOCH₂CH₂NH–), 40.5 (–CONHCH₂–), 64.2 (–COOCH₂CH₂NH–), 70.3 (–CH₂OCH₂CH₂OCH₂–), 70.7 (–OCH₂CH₂O–), 128.2 (CH₂=CH–), 131.4 (CH₂=CH–), 158.9 (–NHC(=O)NH–), 166.4 (CH₂=CHC(=O)–).

Synthesis of 1,3-Bis(acryloyloxyethyl ureido)propane (BAUP). A solution of 1,3-diaminopropane (0.740 g, 10.0 mmol) in anhydrous dichloromethane (20.0 mL) was added dropwise to a stirred solution of AOI (2.820 g, 20.0 mmol) in anhydrous dichloromethane (30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 2 h under a stream of nitrogen, and a white solid appeared. Then, the solid was collected by suction filtration and washed with dichloromethane (3 × 10 mL). The white solid was dried under high vacuum. Yield: 96.3% (3.44 g), mp = 133–134 °C. Anal. Calcd. for C₁₅H₂₄N₄O₆: C, 50.55; H, 6.79; N, 15.72; O, 26.94. Found: C, 50.50; H, 6.83; N, 15.77; O, 26.90. ¹H NMR (400 MHz, DMSO, δ in ppm): 1.39–1.46 (2H, m, –CH₂CH₂CH₂–), 2.95–3.00 (4H, m, –COOCH₂CH₂NH–), 3.24–3.28 (4H, m, –CONH–CH₂–), 4.07 (4H, t, *J* = 5.6 Hz, –COOCH₂CH₂NH–), 5.94–5.97 (4H, m, –NHCONH–, CHH=CH–), 6.05 (2H, t, *J* = 6.0 Hz, –NHCONH–), 6.17 (2H, dd, *J* = 10.4 and 17.2 Hz, CH₂=CH–), 6.35 (2H, dd, *J* = 17.2 and 1.2 Hz, CHH=CH–). ¹³C NMR (100 MHz, DMSO, δ in ppm): 31.5 (–CH₂CH₂CH₂–), 37.2 (–COOCH₂CH₂NH–), 38.8 (–CONHCH₂CH₂CH₂–), 64.1 (–COOCH₂CH₂NH–), 128.8 (CH₂=CH–), 132.2 (CH₂=CH–), 158.3 (–NHC(=O)NH–), 166.0 (CH₂=CHC(=O)–).

Synthesis of 2-[3-[2-(Dimethylamino)ethyl]ureido]ethyl Acrylate (DMUEA). DMUEA was synthesized with the reaction of AOI and *N,N*-dimethylethane-1,2-diamine by the analogous synthetic method of BAUP. After the reaction, volatile substances were removed by decompression and a colorless

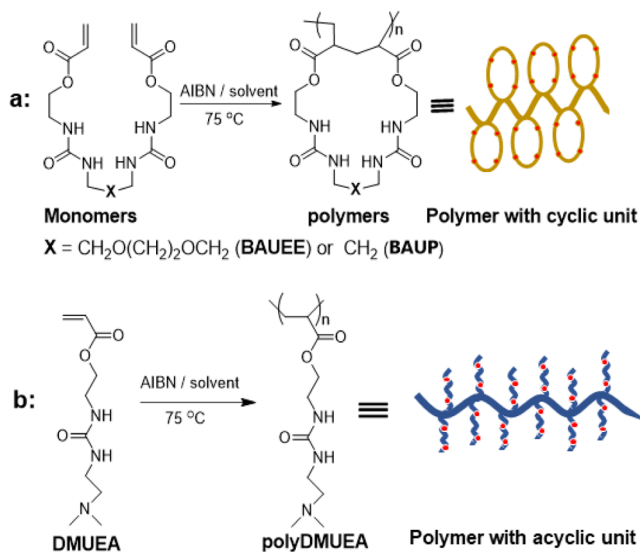
oily product was given. Yield: 95.6% (3.64 g). Anal. Calcd. for C₁₀H₁₉N₃O₃: C, 52.39; H, 8.35; N, 18.33; O, 20.93; Found: C, 52.35; H, 8.37; N, 18.37; O, 20.91. ¹H NMR (400 MHz, CDCl₃, δ in ppm): 2.22 (6H, s, –CH₃), 3.40 [2H, t, *J* = 5.6 Hz, (CH₃)₃NCH₂–], 3.21–3.25 (2H, m, –NHCH₂CH₂O–), 3.47–3.51 [2H, m, (CH₃)₃NCH₂CH₂–], 4.22–4.25 (2H, m, –COOCH₂–), 5.18 (H, br, –NHCONH–), 5.57 (1H, br, –NHCONH–), 5.85 (1H, dd, *J* = 10.4, 1.2 Hz, CHH=CH–), 6.14 (1H, dd, *J* = 17.4 and 10.2 Hz, CH₂=CH–), 6.42 (1H, dd, *J* = 1.2, 17.2 Hz, CHH=CH–). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 38.3 (–CONHCH₂–), 39.5 (–CH₂NHCONH–), 45.3 (–CH₃), 59.2 ((CH₃)₂NCH₂–), 64.3 (–COOCH₂–), 128.2 (CH₂=CH–), 131.3 (CH₂=CH–), 158.7 (–NHC(=O)NH–), 166.4 (CH₂=CHC(=O)–).

Free Radical Polymerization of the Monomer (Typical Procedure). A monomer (500 μmol), AIBN (10 μmol), and DMF (5.0 mL) were placed in a glass tube. The polymerization was conducted at 75 °C for 20 h under N₂ atmosphere. After the reaction, the mixture was poured into an excess amount of tetrahydrofuran. The precipitate was collected by filtration and dried in vacuo at 80 °C overnight.

3. RESULTS AND DISCUSSION

Two polymers consisting of larger 25- and 20-membered repeating units with two ureido groups (Scheme 1) were

Scheme 1. (a) Cyclopolymerization of BAUEE and BAUP and (b) Polymerization of DMUEA



developed, which efficiently adsorb Au(III) from aqueous solutions. These polymers were synthesized by the cyclopolymerization of bifunctional monomers, 1,2-bis(acryloyloxyethylureidoethoxy)ethane (BAUEE) and 1,3-bis(acryloyloxyethylureido)propane (BAUP), respectively. In order to compare, an acyclic polymer, polyDMUEA, was also synthesized by the similar method.

The polymerization of BAUEE (0.10 M) was conducted in the presence of AIBN (Table 1). The low concentration of 0.10 M was chosen to limit the rate of intermolecular propagation and to avoid cross-linking before cyclization. The polymerization proceeded homogeneously regardless of the [M]₀/[AIBN] ratios during the polymerization periods (runs

Table 1. Cyclopolymerization of BAUEE and BAUP^{a,c}

run	monomer	[M] ₀ /[AIBN] ₀	temp. (°C)	sol. (M)	yield (%) ^b	M _n ^c (10 ³)	M _w /M _n ^c
1	BAUEE	30/1	75	0.10	75	6.7	2.4
2	BAUEE	50/1	75	0.10	80	7.1	2.0
3	BAUEE	100/1	75	0.10	83	7.2	1.9
4	BAUEE	50/1	65	0.10	78	5.6	1.9
5	BAUEE	50/1	85	0.10	80	6.4	2.1
6	BAUEE	50/1	75	0.05	66	5.5	1.6
7	BAUEE	50/1	75	0.15	90	8.6	1.8
8	BAUEE	50/1	75	0.25	96	crosslinked polymer	
9	BAUP	50/1	75	0.10	81	7.1	1.5
10	DMUEA	50/1	75	0.15	93	8.3	1.2

^aConditions: 20 h, DMF, and N₂ protection. ^bIsolated yield after precipitation with tetrahydrofuran. ^cEstimated by SEC (DMF containing 10 mM LiBr, polystyrene standard). M_n, number-average molecular weight; M_w, weight-average molecular weight; and M_w/M_n, polydispersity index.

1–3). PolyBAUEE (content of ureido = 27.0%), soluble in DMF and dimethylsulfoxide (DMSO), was obtained in high yields. Insoluble polymers were not produced.

The polymerization of BAUEE was also conducted under various concentrations (runs 2, 6–8). The yield of polyBAUEE obtained at 0.05 M is obviously lower than those obtained at 0.10 and 0.15 M (runs 2 and 7). With the increase of concentration, M_n became larger. The polymerization at 0.25 M afforded an insoluble product (run 8), whose infrared (IR) spectrum is identical to that of the soluble polymer, suggesting that the cross-linking reaction occurred by the increased probability of the intermolecular propagation. The effect of temperature was investigated in the range of 65–85 °C, applying a [M]₀/[AIBN] ratio of 50/1 and a concentration of 0.10 M (runs 2, 4, and 5). The polymerization at 75 °C resulted in the highest M_n and narrowest M_w/M_n and was found to be a suitable temperature for this cyclopolymerization. PolyBAUP (content of ureido = 32.6%) was also synthesized by a similar method using BAUP (Scheme 1a; run 9). The polymerization behavior of BAUP was almost identical to that of BAUEE. The polymerization of 2-{3-[2-(dimethylamino)ethyl]ureido}ethyl acrylate (DMUEA), a mono-acrylate analogue of BAUEE and BAUP, was also carried out, and the corresponding polymer with acyclic units (polyDMUEA, content of ureido = 25.3%) was obtained in an excellent yield (92.6%) (Scheme 1b; run 10).

¹H NMR Characterization. Figure 1 shows the ¹H NMR spectra of BAUEE, polyBAUEE, and deuterium-exchanged polyBAUEE. The spectrum of polyBAUEE (Figure 1b) indicates the signals agreeable to the expected structure, namely, signals of the methylene protons in the side chains, a broad signal of the ureido protons, and a broad signal at 1.50–2.50 ppm assignable to the methyne and methylene groups of the main chain formed by cyclopolymerization. Very small signals assignable to the residual vinyl groups were also observable at 5.84–5.87, 6.10–6.17, and 6.41–6.45 ppm, as observed in the spectrum of BAUEE. The residual content of the vinyl group is below 0.8% according to the deuterium-exchanged spectrum of polyBAUEE (Figure 1c). The ¹³C NMR and IR spectra (Figures S4 and S18 in the Supporting Information) also agree well with the expected structure. This observation supports that the free radical polymerization of BAUEE proceeds in an excellent cyclization efficiency. PolyBAUP could also be characterized in a similar manner (Figure S1), and the content of the residual vinyl group is below 0.7% (Figure S16).

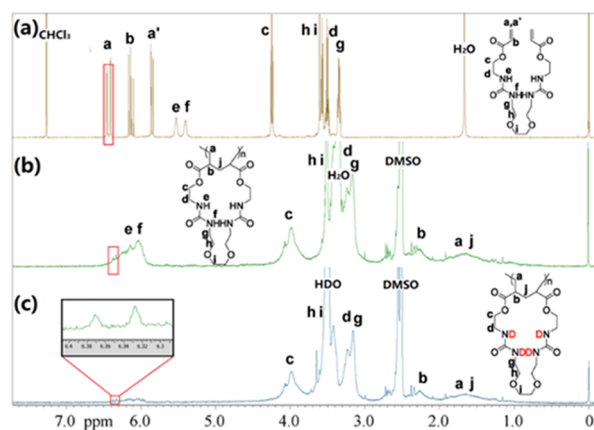


Figure 1. ¹H NMR spectra of (a) BAUEE (400 MHz, CDCl₃), (b) polyBAUEE obtained in run 2 (Table 1), and (c) deuterium-exchanged polyBAUEE (400 MHz, DMSO-*d*₆).

Adsorption of Single Metal Ions. PolyBAUEE, polyBAUEP, and polyDMUEA (500 mg/L) were examined for the adsorption of Au(III), Pd(II), and Pt(II) in their aqueous single metal ion solution (pH = 2, ca. 1100 μg/L) (Figure 2a–c). The concentration of Au(III) was decreased below 5 μg/L in the presence of polyBAUEE and polyBAUP, respectively, while the concentrations of Pd(II) and Pt(II) were decreased less than that of Au(III). The adsorption efficiencies of Au(III) on both polyBAUEE and polyBAUP exceeded 99.5% after adsorption equilibria (8 h and 28 h for polyBAUEE and polyBAUP, respectively, as described later), while the adsorption efficiencies of Pd(II) and Pt(II) stayed 30–40%. The maximum Au(III) adsorption capacities of polyBAUEE and polyBAUP were 37.6 and 31.8 mg/g, respectively (Supporting Information, eq S2). PolyBAUEE and polyBAUP can be reused three times with adsorption efficiency >75%. By contrast, polyDMUEA did not adsorb Au(III), Pd(II), and Pt(II), as can be confirmed by the ignorable decrease in the concentrations. The adsorption with contact time is shown in Figure 2d. The interactions result in an increase in the uptake of Au(III) ions onto polyBAUEE until the adsorption equilibrium is reached at 8 h. However, the adsorption equilibrium of Au(III) ions onto polyBAUP is 28 h. The faster adsorption by polyBAUEE originates from the larger ring structure and hydrophilic linker structure (more oxygen atoms and ureido groups) (Figures 2d, 1, and S1).

Effect of pH. Effect of pH on adsorption of Au(III) onto polyBAUEE and polyBAUP was studied by preparing 20 mg/L

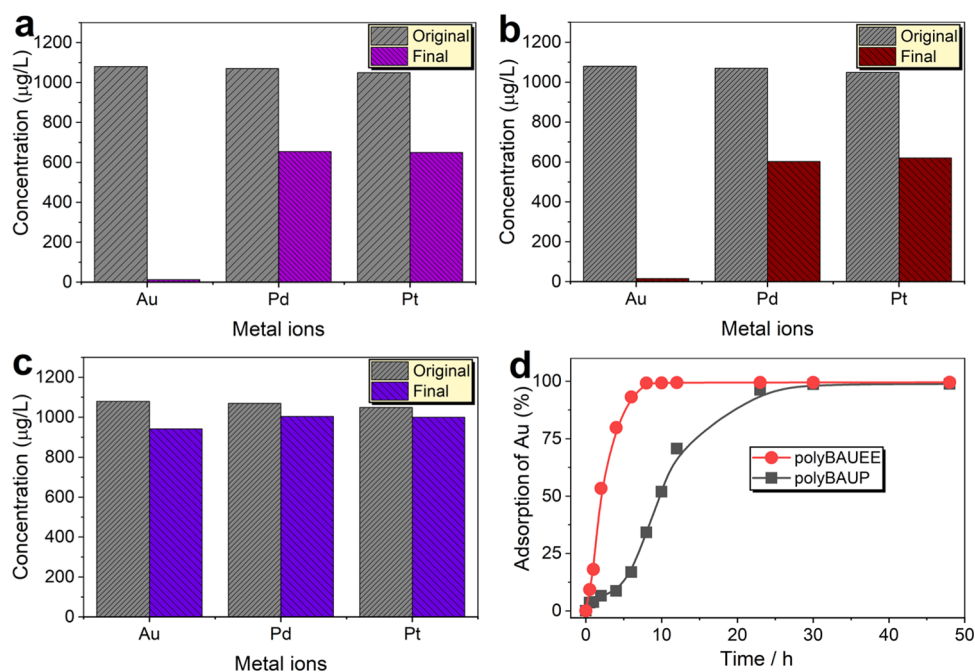


Figure 2. Adsorption of single metal ions by (a) polyBAUEE, (b) polyBAUP, and (c) polyDMUEA; (d) time course of adsorption of Au(III) on polyBAUEE and polyBAUP in HAuCl_4 aqueous; conditions: $[\text{M}^{3+}]_0 = 1.1 \text{ mg/L}$, $C_{\text{polymer}} = 500 \text{ mg/L}$, $\text{pH} = 2$, $25 \text{ }^\circ\text{C}$, and 28 h.

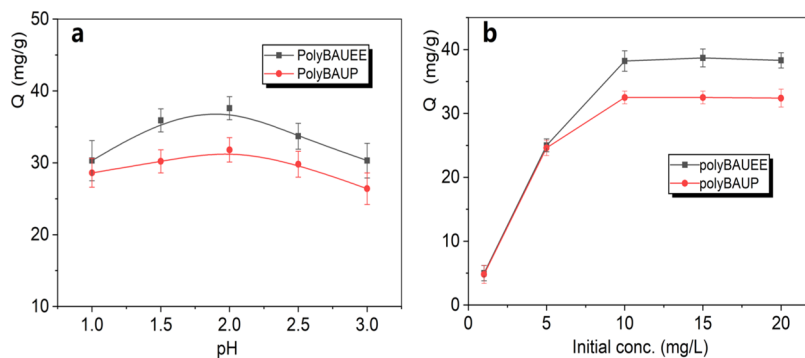


Figure 3. Effect of (a) pH [conditions: $C_0 = 20 \text{ mg/L}$, $C_{\text{polymer}} = 200 \text{ mg/L}$, $25 \text{ }^\circ\text{C}$, 8 h (polyBAUEE), and 28 h (polyBAUP)] and (b) initial concentration on the adsorption of Au(III) ions on polymers [conditions: $C_{\text{polymer}} = 200 \text{ mg/L}$, $\text{pH} = 2$, $25 \text{ }^\circ\text{C}$, 8 h (polyBAUEE), and 28 h (polyBAUP)].

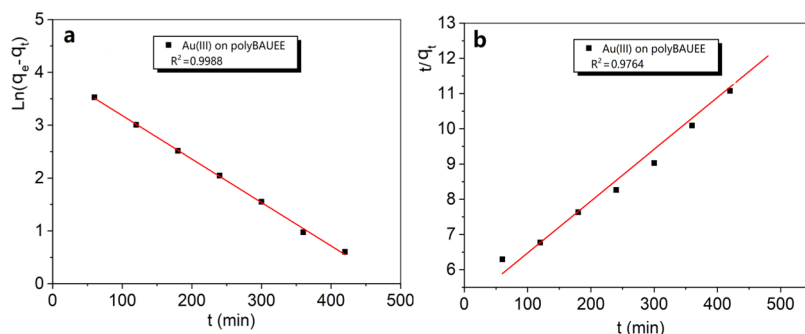


Figure 4. Plots of (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.

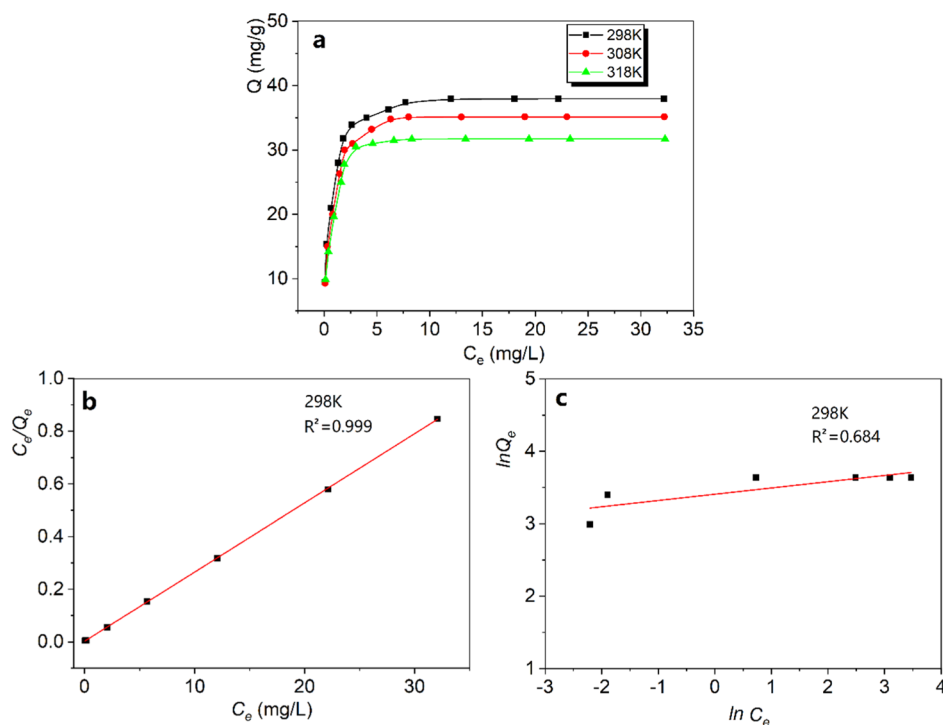
HAuCl_4 with different pH values at $25 \text{ }^\circ\text{C}$ (Figure 3a). pH has a similar effect on Au(III) adsorbing onto PolyBAUEE and polyBAUP. When pH is increased from 1 to 2, the concentration of H^+ decreases in the solution, which results in increased adsorption capacity of Au(III) ions onto the adsorption sites, attaining maximum adsorption at $\text{pH} = 2$.

When $\text{pH} > 2$, adsorption capacity decreases with the increase of pH.

Effect of the Initial Concentration of Au(III) Ions. The initial concentration of Au(III) ions plays an important role in studying the kinetics of adsorption. In order to study the effect of initial concentration of the adsorbate, different concen-

Table 2. Parameters of Kinetic Models for the Adsorption of Au(III) Ions by polyBAUEE

kinetic model	$Q_e^{exp}/(\text{mg/g})$	$Q_e^{cal}/(\text{mg/g})$	$K_1 \text{ \& } K_2/(\text{min}^{-1}) \text{ \& } (\text{g}/\text{mg}\cdot\text{min})$	R^2
pseudo first order	37.6	43.2 ± 3.56	0.0045 ± 0.0008686	0.999
pseudo second order	37.6	63.1 ± 9.25	$0.000055006 \pm 0.000025758$	0.976

**Figure 5.** Adsorption isotherms of Au(III) ions by polyBAUEE at different temperatures (a), Langmuir isotherm of adsorption (b), and Freundlich isotherm of adsorption (c).**Table 3. Coefficient of the Langmuir and Freundlich Isotherm Adsorptions of Au(III) Ions on PolyBAUEE at 298 K**

T (K)	Langmuir isotherm			Freundlich isotherm		
	$Q_m/(\text{mg/g})$	$k_L/(\text{L}/\text{mol})$	R^2	$K_F/(\text{mg/g})/(\text{mg/L})^{1/n}$	n	R^2
298	38.42 ± 0.99	2.658 ± 0.444	0.999	15 ± 0.54	1.257 ± 0.123	0.684

trations of the Au(III) ion, 1, 5, 10, 15, and 20 mg/L, were taken at 25 °C (Figure 3b). It is shown that, with higher initial concentration, the higher quantity of Au(III) ion was adsorbed by polyBAUEE and polyBAUP at equilibria. This can be attributed to the probability of the adsorbent–adsorbate interaction increasing rapidly with higher Au(III) ion concentration, which results in the increase of adsorption.

Adsorption Kinetics. Two kinetic models,^{1,2} pseudo first order (eq 1) and pseudo second order (eq 2), were used to determine the rate of adsorption of Au(III) onto polyBAUEE. The results are shown in Figure 4 and Table 2. The linear forms of the two models are given below

$$\ln(q_e - q_t) = \ln Q_e - k_1 t \quad (1)$$

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

where q_e is the actual equilibrium adsorption capacity, q_t is the adsorption capacity at time t , Q_e is the theoretical equilibrium adsorption capacity, and k_1 and k_2 are first order and second order rate constants, respectively.

On comparing the R^2 values (Table 2 and Figure 4a,b), pseudo-first-order plot with $R^2 = 0.999$ and pseudo-second-

order plot with $R^2 = 0.976$ were observed. Q_e obtained by the pseudo-first-order dynamic model is close to Q_{eexp} . Therefore, the kinetic process of the adsorption of Au(III) ions by polyBAUEE is closer to the pseudo-first-order kinetic model.

Adsorption Isotherm. Langmuir adsorption isotherm (eq 3) and Freundlich adsorption isotherm (eq 4) were used to process the experimental data. The results are shown in Figure 5 and Table 3.

$$\frac{C_e}{Q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m} \quad (3)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where Q_e is the equilibrium adsorption capacity, Q_m is the saturated adsorption capacity of Langmuir monolayer, C_e is the mass concentration of Au(III) ions in adsorption equilibrium, k_L is the Langmuir constant, and n and K_F are Freundlich constants.

Figure 5b,c shows the fitting curves of the Langmuir adsorption isotherm equation and Freundlich adsorption isotherm equation, respectively, and the specific parameter results are shown in Table 3. The Langmuir adsorption

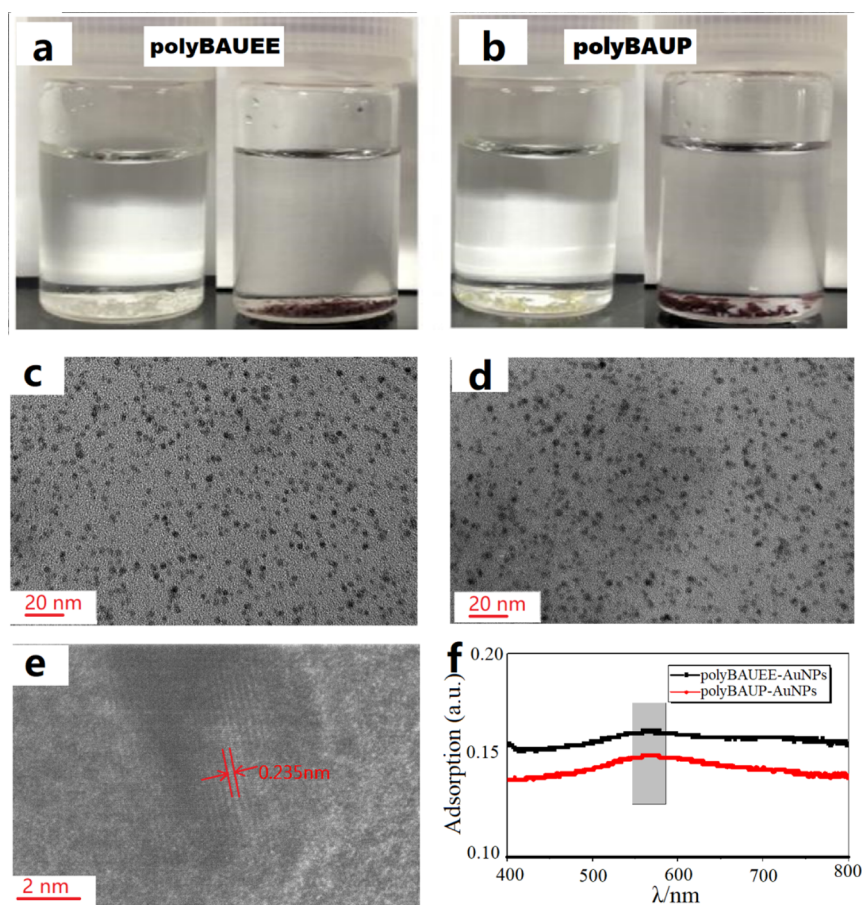


Figure 6. Optical images of (a) polyBAUEE (left) and that after adsorption of Au(III) for 8 h (right); (b) polyBAUP (left) and that after adsorption of Au(III) for 28 h (right); TEM images of (c) polyBAUEE-Au and (d) polyBAUP-Au; (e) HRTEM images of polyBAUEE-Au; and (f) DR spectra of polyBAUEE-Au and polyBAUP-Au showing SPR bands of AuNPs. PolyBAUEE-Au and polyBAUP-Au were carried out in HAuCl_4 aq. (c_0 Au(III) = 1 mg/L, pH = 2) at 25 °C.

isotherm equation was used to fit the experimental data, and the correlation coefficient ($R^2 > 0.999$) showed a good fit. However, when the Freundlich adsorption isotherm equation was used to fit the experimental data, the correlation coefficient ($R^2 = 0.684$) was very low. Therefore, the adsorption isotherm of polyBAUEE for Au(III) ion conforms to the Langmuir isotherm model, showing a single layer adsorption.

As shown in Figure 6a,b, the color of the polymers changed from white to purple (Figure S6), which is characteristic of gold nanoparticles (AuNPs), after adsorption of Au(III) from HAuCl_4 solution. The formation of AuNPs during the adsorption process probably originated from the spontaneous reduction of Au(III) as reported in various systems^{33–35} due to the high susceptibility of reduction of Au(III). The TEM images of the polymers after adsorption of Au(III) show evenly distributed and nanosized black spots assignable to AuNPs with the diameters of 2–5 nm (Figure 6c,d). High-resolution transmission electron microscopy (HRTEM) and diffuse reflectance (DR) spectroscopy revealed the formation of AuNPs. The HRTEM image shows a characteristic spacing of 0.235 nm for the (111) lattice fringe of face-to-face cubic gold (Figure 6e). The DR spectra show broad peaks with peak tops at 550–570 nm, agreeing well with the surface plasmon resonance of AuNPs^{33,35} (Figure 6f).

Selective Adsorption of Au(III). The selectivity of adsorption of Au(III) by faster polyBAUEE was examined in the presence of multiple ions (Figure 7a). The aqueous

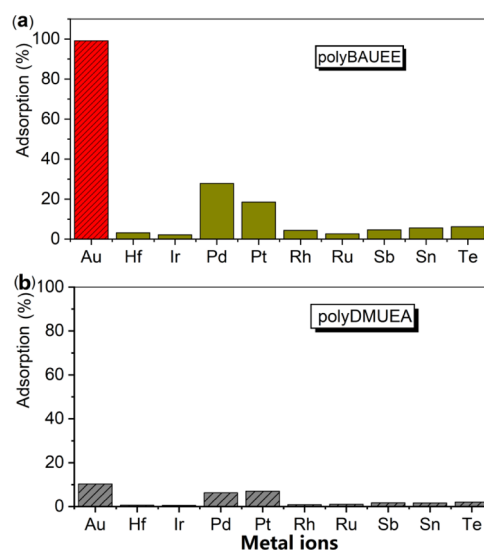


Figure 7. Adsorption of metal ions from a multi-ion solution by (a) polyBAUEE (8 h) and (b) polyDMUEA (8 h) under the conditions of $C_{\text{polymer}} = 500$ mg/L, pH = 2, and 25 °C.

solution of the multiple metal ions used for this adsorption study was prepared by diluting a multielement calibration standard solution containing Au(III), and the concentrations of the metal ions were adjusted to approximately 1 mg/L. The

10 ions included were Au(III), Hf(IV), Ir(III), Pd(II), Pt(II), Rh(III), Ru(III), Sb(III), Sn(IV), and Te(II). Disposable plastic bottles were used as containers to avoid contamination with trace elements possibly drained out from glassware. PolyBAUEE (500 mg/L) was placed in the multi-ion solution (pH = 2) at 25 °C. The color of the polymer was changed to purple during the adsorption. The adsorption efficiency of Au on polyBAUEE reached 99.6% after shaking for 8 h. The adsorption efficiencies of the other nine metal ions were significantly low, while the adsorptions of softer Pd(II) and Pt(II) are slightly higher than those of the others. By contrast, polyDMUEA, an acyclic analogue consisting of identical structures, negligibly adsorbed the examined ions (Figure 7b), which indicates that the adsorption of gold ions on the acyclic polymer with ureido and ester groups is weak. The selective affinity of polyBAUEE to Au(III) is attributed to the cooperative coordination of the four carbonyl groups in the ureido and ester groups aligned in the rings suitable for the specific recognition of Au(III). Calculation by the density functional theory (B3LYP/6-31G(d) + SDD) supports the acceptable structure of the complex including Au(III) in the ring of a model compound (Figures S9 and S11; Tables S3 and S6).

4. CONCLUSIONS

In summary, we have described the design and synthesis of polymers, polyBAUEE and polyBAUP, containing 25- and 20-membered rings as repeating ring units by the cyclo-polymerization of BAUEE and BAUP derived from an isocyanate and 1,2-bis(2-aminoethoxy)ethane and 1,3-diaminopropane, respectively. These polymers showed excellently selective adsorption for Au(III), and more hydrophilic polyBAUEE adsorbed faster than polyBAUP. The adsorption of Au(III) was followed by the spontaneous reduction to Au(0) nanoparticles. The selectivity was not deteriorated in the presence of nine other interfering metal ions. The selective adsorption originates from the synergy of the ring structures and ureido groups. We believe that polymers containing macrocyclic ureido structures will explore broad applications in the complexation and recycle of noble metal ions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c03869>.

Experimental details; results of ICP–MS and SEC analyses; ¹H and ¹³C NMR spectra of monomers and polymers; Optical microscopy and SEM images of polymers and polymer-Au; IR spectra of monomers, polymers, and polymer-Au; and optimized calculation of polymer units and polymer-Au(III) by the density functional theory (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Yunkai Sun – School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China; Faculty of Engineering, Yamagata University, Yamagata 992-8510, Japan; orcid.org/0000-0001-9246-2488; Phone: +86-734-8282521; Email: sunyunkai1983@163.com

Chunhong Tan – School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China; Email: tanch2014@sina.com

Quanli Chu – State Nuclear Security Technology Center, Beijing 102401, China; Email: quanlichu@aliyun.com

Authors

Yaqian Ding – School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

Wenwen Zhou – School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

Xiaofeng Wang – School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

Yoshimasa Matsumura – Faculty of Engineering, Yamagata University, Yamagata 992-8510, Japan

Bungo Ochiai – Faculty of Engineering, Yamagata University, Yamagata 992-8510, Japan; orcid.org/0000-0002-4376-8875

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.1c03869>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the State Scholar Fund of China Scholarship Council (CSC, NO. 201802505006) and the Hunan provincial education office major project (no. 200SJY045). The authors thank Prof. Changming Nie and Yang Xiao of University of South China for their assistance with the calculation.

■ REFERENCES

- (1) Manzoor, K.; Ahmad, M.; Ahmad, S.; Ikram, S. Synthesis, Characterization, Kinetics, and Thermodynamics of EDTA-Modified Chitosan-Carboxymethyl Cellulose as Cu(II) Ion Adsorbent. *ACS Omega* **2019**, *4*, 17425–17437.
- (2) Ahmad, M.; Zhang, B.; Wang, J.; Xu, J.; Manzoor, K.; Ahmad, S.; Ikram, S. New Method for Hydrogel Synthesis from Diphenylcarbazide Chitosan for Selective Copper Removal. *Int. J. Biol. Macromol.* **2019**, *136*, 189–198.
- (3) Yuan, D.; Zhang, S.; Xiang, Z.; He, Y.; Wang, Y.; Liu, Y.; Zhao, X.; Zhou, X.; Zhang, Q. Highly Efficient Removal of Thorium in Strong HNO₃ Media Using a Novel Polymer Adsorbent Bearing a Phosphonic Acid Ligand: A Combined Experimental and Density Functional Theory Study. *ACS Appl. Mater. Interfaces* **2019**, *11*, 24512–24522.
- (4) Abney, C. W.; Mayes, R. T.; Saito, T.; Dai, S. Materials for the Recovery of Uranium from Seawater. *Chem. Rev.* **2017**, *117*, 13935–14013.
- (5) Li, Q.; Peng, Y.; Han, S.; Lan, T.; Zhang, J.; Cao, J. Synthesis of Optically Active Graft Copolymers Carrying Poly(lactide) Arms as Fluorescent Sensor for Recognition of Pyroglutamic Acid Enantiomer. *ChemistrySelect* **2020**, *5*, 6549–6555.
- (6) Gartner, T. E.; Haque, F. M.; Gomi, A. M.; Grayson, S. M.; Hore, M. J. A.; Jayaraman, A. Scaling Exponent and Effective Interactions in Linear and Cyclic Polymer Solutions: Theory, Simulations, and Experiments. *Macromolecules* **2019**, *52*, 4579–4589.

- (7) Shimomoto, H.; Kikuchi, M.; Aoyama, J.; Sakayoshi, D.; Itoh, T.; Ihara, E. Cyclopolymerization of Bis(diazocarbonyl) Compounds Leading to Well-Defined Polymers Essentially Consisting of Cyclic Constitutional Units. *Macromolecules* **2016**, *49*, 8459–8465.
- (8) Liu, X.; Pang, H.; Liu, X.; Li, Q.; Zhang, N.; Mao, L.; Qiu, M.; Hu, B.; Yang, H.; Wang, X. Orderly Porous Covalent Organic Frameworks-based Materials: Superior Adsorbents for Pollutants Removal from Aqueous Solutions. *Innovation* **2021**, *2*, 100076.
- (9) Ma, J.; Wang, C.; Xi, W.; Zhao, Q.; Wang, S.; Qiu, M.; Wang, J.; Wang, X. Removal of Radionuclides from Aqueous Solution by Manganese Dioxide-based Nanomaterials and Mechanism Research: A review. *ACS ES&T Engg* **2021**, *1*, 685–705.
- (10) Manzoor, K.; Ahmad, M.; Ahmad, S.; Ikram, S. Removal of Pb(II) and Cd(II) from wastewater using arginine cross-linked chitosan-carboxymethyl cellulose beads as green adsorbent. *RSC Adv.* **2019**, *9*, 7890–7902.
- (11) Kavetskyy, T.; Boev, V.; Ilcheva, V.; Kukhazh, Y.; Smutok, O.; Pan'kiv, L.; Šauša, O.; Svajdlenková, H.; Tatchev, D.; Avdeev, G.; Gericke, E.; Hoell, A.; Rostamnia, S.; Petkova, T. Structural and free volume characterization of sol-gel organic-inorganic hybrids, obtained by co-condensation of two ureasilicate stoichiometric precursors. *J. Appl. Polym. Sci.* **2021**, *138*, No. e50615.
- (12) Rostamnia, S.; Doustkhah, E.; Baghban, A.; Zeynizadeh, B. Seaweed-derived κ -carrageenan: Modified κ -carrageenan as a recyclable green catalyst in the multicomponent synthesis of aminophosphonates and polyhydroquinolines. *J. Appl. Polym. Sci.* **2016**, *133*, 43190.
- (13) Rostamnia, S.; Zeynizadeh, B.; Doustkhah, E.; Baghban, A.; Aghbash, K. O. The use of κ -Carrageenan/Fe₃O₄ nanocomposite as a nanomagnetic catalyst for clean synthesis of rhodanines. *Catal. Commun.* **2015**, *68*, 77–83.
- (14) Gokel, G. W.; Leevy, W. M.; Weber, M. E. Crown Ethers: Sensors for Ions and Molecular Scaffolds for Materials and Biological Models. *Chem. Rev.* **2004**, *104*, 2723–2750.
- (15) Smolyanitsky, A.; Paulechka, E.; Kroenlein, K. Aqueous Ion Trapping and Transport in Graphene-Embedded 18-Crown-6 Ether Pores. *ACS Nano* **2018**, *12*, 6677–6684.
- (16) Tian, J.; Zhang, W. Synthesis, Self-assembly and Applications of Functional Polymers Based on Porphyrins. *Prog. Polym. Sci.* **2019**, *95*, 65–117.
- (17) Schappacher, M.; Deffieux, A. Reversible Switching between Linear and Ring Polystyrenes Bearing Porphyrin End Groups. *J. Am. Chem. Soc.* **2011**, *133*, 1630–1633.
- (18) Prochowicz, D.; Kornowicz, A.; Lewiński, J. Interactions of Native Cyclodextrins with Metal Ions and Inorganic Nanoparticles: Fertile Landscape for Chemistry and Materials Science. *Chem. Rev.* **2017**, *117*, 13461–13501.
- (19) Alsbaiie, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. Rapid Removal of Organic Micropollutants from Water by A Porous β -cyclodextrin Polymer. *Nature* **2016**, *529*, 190–194.
- (20) Sharma, A. K.; Cornaggia, C.; Pasini, D. Controlled RAFT Cyclopolymerization of Oriented Styrenic Difunctional Monomers. *Macromol. Chem. Phys.* **2010**, *211*, 2254–2259.
- (21) Li, J.; Du, M.; Zhao, Z.; Liu, H. Cyclopolymerization of Disiloxane-Tethered Divinyl Monomers to Synthesize Chirality-Responsive Helical Polymers. *Macromolecules* **2016**, *49*, 445–454.
- (22) Ochiai, B.; Ootani, Y.; Endo, T. Controlled Cyclopolymerization through Quantitative 19-Membered Ring Formation. *J. Am. Chem. Soc.* **2008**, *130*, 10832–10833.
- (23) Ochiai, B.; Shiomi, T.; Yoshita, H. Cyclopolymerization of a bisacrylate through selective formation of a 19-membered ring. *Polym. J.* **2016**, *48*, 859–862.
- (24) Sun, Y.; Matsumura, Y.; Ochiai, B. Selective Ag⁺ Adsorption of Ureido Polymer Prepared by Cyclopolymerization Giving Large Ring Repeating Units. *ACS Appl. Polym. Mater.* **2020**, *2*, 1417–1421.
- (25) Habaue, S.; Morita, M.; Okamoto, Y. Anionic Polymerization of Macrocylic α -(Alkoxyethyl)acrylates Leading to Novel Vinyl Polymer with Crown Ether Type Side Chain. *Macromolecules* **2002**, *35*, 2432–2434.
- (26) Yan, F.; Pei, H.; Pei, Y.; Li, T.; Li, J.; He, B.; Cheng, Y.; Cui, Z.; Guo, D.; Cui, J. Preparation and Characterization of Polysulfone-graft-4'-aminobenzo-15-crown-5-ether for Lithium Isotope Separation. *Ind. Eng. Chem. Res.* **2015**, *54*, 3473–3479.
- (27) Bartolome, J. P.; Fragoso, A. Preparation of Stable Aqueous Dispersions of Carbon Nano-onions via Supramolecular Crown Ether-ammonium Interactions with Aminated Biocompatible Polymers. *J. Mol. Liq.* **2018**, *269*, 905–911.
- (28) Sajjadi, B.; Broome, J. W.; Chen, W. Y.; Mattern, D. L.; Egiebor, N. O.; Hammer, N.; Smith, C. L. Urea Functionalization of Ultrasound-treated Biochar: A Feasible Strategy for Enhancing Heavy Metal Adsorption Capacity. *Ultrason. Sonochem.* **2019**, *51*, 20–30.
- (29) Shen, J.; Chai, W.; Wang, K.; Zhang, F. Efficient Removal of Anionic Radioactive Pollutant from Water Using Ordered Urea-Functionalized Mesoporous Polymeric Nanoparticle. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22440–22448.
- (30) Tehrani, A. A.; Esrafil, L.; Abedi, S.; Morsali, A.; Carlucci, L.; Proserpio, D. M.; Wang, J.; Junk, P. C.; Liu, T. Urea Metal-Organic Frameworks for Nitro-Substituted Compounds Sensing. *Inorg. Chem.* **2017**, *56*, 1446–1454.
- (31) Seo, P. W.; Khan, N. A.; Jhung, S. H. Removal of nitroimidazole antibiotics from water by adsorption over metal-organic frameworks modified with urea or melamine. *Chem. Eng. J.* **2017**, *315*, 92–100.
- (32) Gomy, C.; Schmitzer, A. R. Rational Design of New Polymerizable Oxyanion Receptors. *J. Org. Chem.* **2006**, *71*, 3121–3125.
- (33) Selvakannan, P.; Mandal, S.; Phadtare, S.; Gole, A.; Pasricha, R.; Adyanthaya, S. D.; Sastry, M. Water-dispersible Tryptophan-protected Gold Nanoparticles Prepared by The Spontaneous Reduction of Aqueous Chloroaurate Ions by The Amino Acid. *J. Colloid Interface Sci.* **2004**, *269*, 97–102.
- (34) Iwamoto, M.; Kuroda, K.; Zaporotchenko, V.; Hayashi, S.; Faupel, F. Production of gold nanoparticles-polymer composite by quite simple method. *Eur. Phys. J. D* **2003**, *24*, 365–367.
- (35) Amendola, V.; Pilot, R.; Frascioni, M.; Maragò, O. M.; Iati, M. A. Surface Plasmon Resonance in Gold Nanoparticles: A Review. *J. Phys.: Condens. Matter.* **2017**, *29*, 203002.