PAPER

Dithiocarbamate-modified cellulose-based sorbents with high storage stability for selective removal of arsenite and hazardous heavy metals†

Futo Morita,‡[a] Keisuke Nakakubo, [iD] ‡[a] Koki Yunoshita,‡[a] Masaru Endo, [iD] [ab] Foni B. Biswas, [iD] [ac] Tatsuya Nishimura, [iD] [a] Asami S. Mashio, [iD] [a] Hiroshi Hasegawa, [iD] *[a] Tsuyoshi Taniguchi [iD] *[a] and Katsuhiro Maeda [iD] *[ad]

A series of cellulose derivatives bearing dialkyl dithiocarbamate (DTC) groups were synthesized. Their ability of sorption of arsenite (As(III)) and heavy metals and their storage stability in the solid state were investigated. Among them, DTC-modified cellulose derived from L-proline showed the highest sorption capacity for As(III) and heavy metals to selectively remove them from aqueous media. It also showed exellent storage stability in air at 40 °C.

Introduction

Compounds having a dithiocarbamate (DTC) group work as good chelating agents to capture heavy metals because the DTC group is a soft Lewis base that has strong affinity toward soft Lewis acids such as heavy metals to form stable complexes according to the HSAB rule.[1,2] Several small organic molecules having a DTC group, such as sodium diethyldithiocarbamate, have been industrially used as sorbents for the removal of hazardous heavy metals from aqueous or organic media.[3,4] Such small molecule-based sorbents are readily available, but further treatment is often required for the efficient removal of the resultant complexes from aqueous media due to the difficulty in precipitation of the heavy metal complexes.[5] Polymer-based sorbents carrying a DTC group are potential materials for the removal of heavy metals from aqueous media because they can work as heterogeneous sorbents for solid–liquid extraction and can be easily recovered from water.[6] However, typical polymer-based sorbents are synthesized from petroleum-based chemical materials, and the production of a large amount of waste acid solutions poses serious problem for the environment.[7]

Cellulose is the world's most abundant natural polymeric raw material with a fascinating structure and properties.[8] This polysaccharide is capable of being chemically modified through the hydroxyl groups in order to develop eco-friendly and cost-effective biosorbents for wastewater treatment. Recently, our group synthesized a DTC-modified cellulose material **1** with excellent ability as a selective sorbent for highly toxic arsenite, which is an inorganic As(III) compound, from aqueous media (Fig. 1).[9,10]

It is generally believed that DTC compounds are stable in the solid state. During the course of the above study, however, we found that the sorption capacity of compound **1** for As(III) significantly decreased with time when it was stored even in the solid state under ambient conditions, probably due to decomposition of the DTC groups by moisture or oxygen. Although degradation behaviors of polymer-based sorbents having DTC groups in the solid state have not been investigated in detail, degradation might be a general problem for DTC-modified
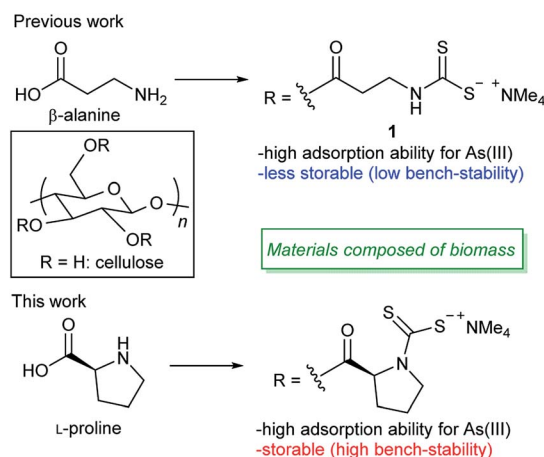
[a]Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan. E-mail: hhiroshi@se.kanazawa-u.ac.jp; tsuyoshi@p.kanazawa-u.ac.jp; maeda@se.kanazawa-u.ac.jp

[b]Daicel Corporation, 1239 Shinzaike, Aboshi-ku, Himeji, Hyogo 671-1283, Japan

[c]Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh

[d]Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

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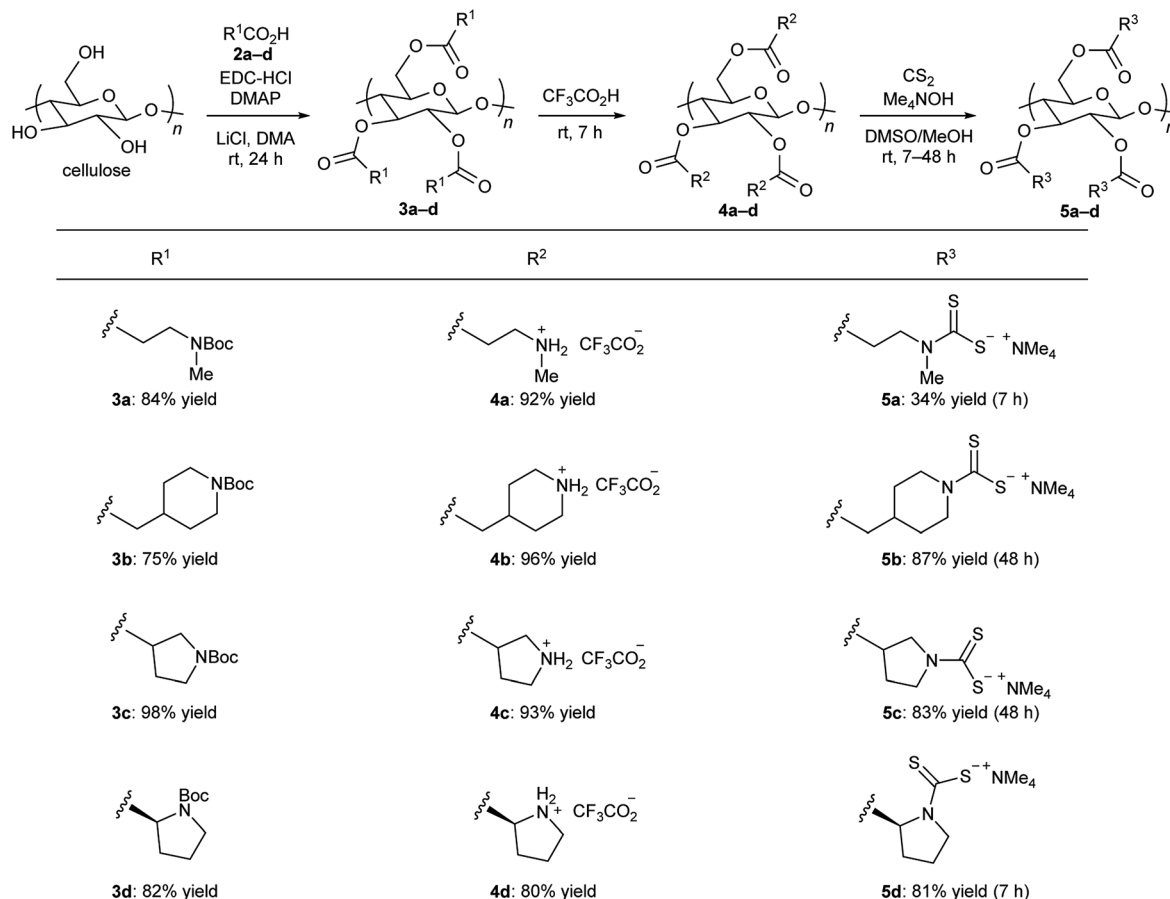
‡ These authors contributed equally.

Fig. 1 DTC-modified cellulose-based sorbents for the selective removal of As(III).

Fig. 2 Synthesis of DTC-modified cellulose derivatives **5a–d**.

polymer-based sorbents. This drawback would greatly limit the applicability of the material because manufacturing and transport of materials with poor storage stability are problematic.

We therefore decided to develop DTC-modified cellulose materials with good storage stability that are capable of efficiently removing toxic As(III) and heavy metals from aqueous media. Since monoalkyl DTC compounds (R–NH–C(=S)S⁻; R = alkyl group) have several competitive decomposition pathways based on the N–H group,[11] they do not have sufficient stability

compared with the stability of dialkyl DTC compounds. In this study, we synthesized a series of dialkyl DTC-modified (–R^1–N (R^2)–C(=S)S⁻; R^1 and R^2 = alkyl group) cellulose materials and evaluated their ability for sorption of As(III) and other heavy metals as well as their storage stability. As a result, we identified a novel biopolymer material derived from cellulose and L-proline as a potential sorbent with excellent storage stability for selective sorption of As(III) and other heavy metals (Fig. 1).

Results and discussion

We began our study with the design and synthesis of four new DTC-modified cellulose compounds **5a–d** (Fig. 2). First, commercially available microcrystalline cellulose was converted to the corresponding cellulose esters **3a–d** by condensation between acyclic and cyclic N-protected amino acid derivatives **2a–d** in the presence of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC-HCl) and 4-(N,N-dimethyla-mino)pyridine (DMAP). Compounds **3a–d** were readily soluble in organic solvents, and ^{1}H NMR and elemental analyses of **3a–d** indicated that the degree of substitution (DS) was almost 3. Next, the *tert*-butoxycarbonyl group of **3a–d** was removed by treatment with trifluoroacetic acid (TFA) to give secondary ammonium salts **4a–d**. Finally, treatment of **4a–d** with CS$_2$ and tetramethylammonium hydroxide provided the corresponding

Table 1 Sorption capacity of **1** and **5a–d** for As(III)

| Entry | Sorbent | Amounts of adsorbed As(III) (μmol g^{-1})^a | |
		As is	After 2 weeks^b
1	**1**	595.3 ± 5.1	66.5 ± 6.2 (−89%)
2	**5a**	480.6 ± 20.9	430.2 ± 7.6 (−11%)
3	**5b**	332.1 ± 2.6	184.0 ± 2.4 (−45%)
4	**5c**	489.5 ± 40.9	464.8 ± 1.5 (−5%)
5	**5d**	618.8 ± 17.6	595.2 ± 11.7 (−4%)

^{a} Conditions: [As(III)] = 2 mmol L^{-1} at pH 3. ^{b} Under air at 40 °C. Percentage values in parentheses show a rate of decrease in the sorption capacity.
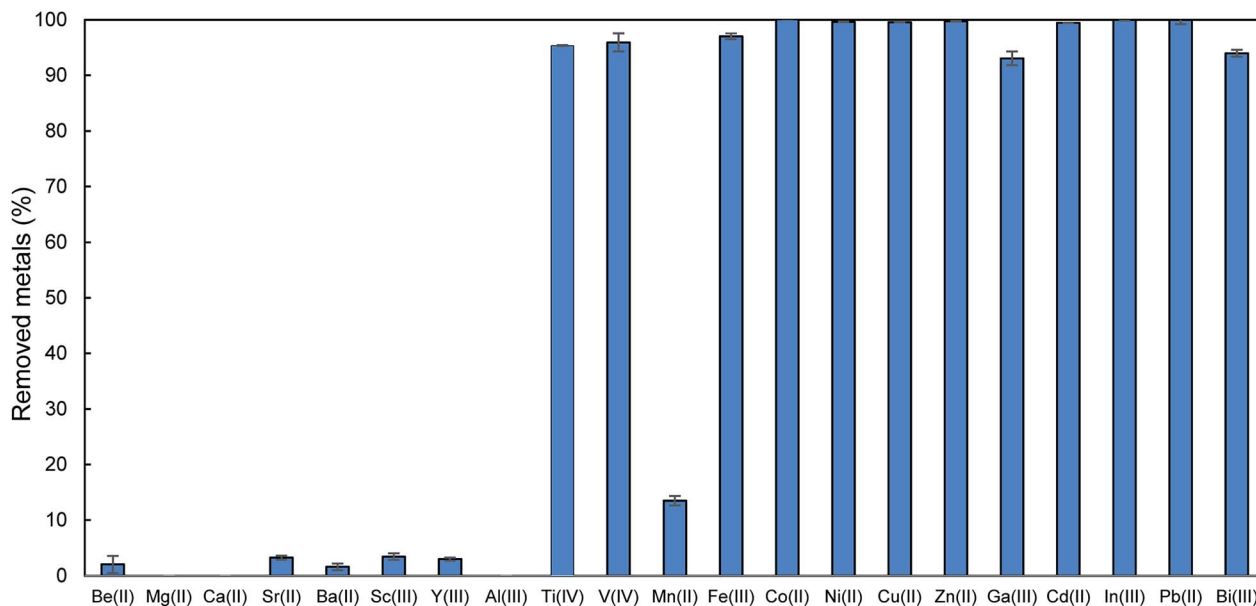
Fig. 3 Removal percentages of metals from 5 mg L^{-1} multi metal solution at pH 3 using **5d**.

dialkyl DTC-modified cellulose compounds **5a–d** as white powders in good yields.§ Since compounds **5a–d** were slightly soluble in water or acetic acid, ^{1}H NMR analysis of these compounds could be performed unlike in our previous study.[9] Although ^{1}H NMR spectra of **5a–d** showed rather broadened signals, they clearly indicated the existence of each side chain and tetramethylammonium cation (see ESI†). IR spectra of **5a–d** showed a typical and strong band at around 1730–1740 cm^{-1} based on C=O stretching of ester groups. The spectra also displayed characteristic bands at around 1375–1485 cm^{-1} and 1155–1185 cm^{-1}, which correspond to N–C(S) and C=S stretching of DTC groups, respectively. The N–C(S) vibration characteristically shifted to a lower value in the order of acyclic **5a** (1485 cm^{-1}) > 6-membered cyclic **5b** (1410 cm^{-1}) > 5-membered cyclic **5c** (1384 cm^{-1}) and **5d** (1375 cm^{-1}) (see ESI†).

Next, we evaluated the sorption ability of the obtained dialkyl DTC-modified cellulose compounds **5a–d** for As(III) (Table 1). Our previous study showed that the monoalkyl DTC-modified cellulose **1** had high capacity for sorption of As(III) in acidic and neutral conditions (≤pH 7) because As(III) exists as a neutral form over a wide pH range (pK_{a1} = 9.2),[9] and As-containing wastewater such as mining and smelting wastewater is usually acidic.[12] Therefore, we tentatively compared the sorption capacities of compounds **5a–d** for As(III) at pH 3. Compound **5a**, which is an N-methylated analogue of **1**, showed a lower sorption capacity than **1** (Table 1, entries 1 and 2). The sorption capacity of compound **5b** having a piperidine ring was also not good (Table 1, entry 3). Compound **5c** having

a pyrrolidine ring showed better sorption capacity than **5a** or **5b**, but its sorption capacity was still lower than that of **1** (Table 1, entry 4). Finally, we found that the sorption capacity of compound **5d** having a L-proline side chain is superior to that of **1** (Table 1, entry 5). The impact of reaction time in the introduction of DTC groups to **4d** does not seem to be significant because **5d** synthesized from **4d** in a prolonged reaction time (7 h → 24 h) did not show improved sorption capacity for As(III) (503.6 ± 65.8 µmol g^{-1}).

We investigated the change in sorption capacity of compounds **1** and **5a–d** after they had been stored in air at 40 °C for 2 weeks (Table 1). The sorption capacity of compound **1** having an N–H group was significantly decreased by about 89% after 2 weeks (Table 1, entry 1), and this was consistent with the gradual degradation observed in the course of storage under ambient conditions as mentioned in the introduction section. On the other hand, the sorption capacity of N-substituted DTC derivatives **5a–d** did not decrease as much as that of compound **1** even after 2 weeks (Table 1, entries 2–5). Notably, the sorption capacity of **5c** and **5d** having a pyrrolidine moiety was hardly changed after 2 weeks (Table 1, entries 4 and 5), indicating that these sorbents are sufficiently stable to be stored for a long time under ambient conditions.¶ Consequently, **5d** having a L-proline side chain was identified as a practical DTC-modified cellulose-based sorbent with both high sorption capacity and excellent storage stability. These good properties of **5d** might be due to the high nucleophilicity of a pyrrolidine moiety, which could strongly ligate CS$_2$.[13,14] However, it is unclear why the sorption capacity of **5d** is different.

Finally, we preliminary tested the efficiency of compound **5d** for the removal of other metal ions using aqueous solutions

§ An appropriate caution (*e.g.*, the use of safety glass and glove) should be paid for the use of potentially toxic reagents such as DMAP and Me$_4$NOH. In addition, the use of hazardous CS$_2$ as a reagent is unavoidable for the synthesis of DTC compounds, but reacted CS$_2$ is essentially incorporated to the material as a stable DTC group.

¶ After exposing the materials to air at 40 °C for 2 weeks, the IR spectrum of **1** greatly changed whereas those of **5d** hardly changed (Fig. S1 and S2†).

containing 21 representative metal ions together with As(III) as shown in Fig. 3. Compound **5d** adsorbed heavy metals, including V(IV), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Cd(II), In(III), Pb(II) and Bi(III), with high efficiency.[1,9] In contrast, compound **5d** hardly adsorbed alkaline earth metal ions, which are hard metals. This trend is very similar to that of **1** and is consistent with the HSAB rule.[2] Exceptionally, Ti(IV), which is a hard acid, was efficiently adsorbed by **5d**, and this might be because Ti(IV) could form a stable multidentate complex with DTC groups like other heavy metals.[15] Thus, **5d** is a potential sorbent for the selective and efficient removal of As(III) and other hazardous heavy metals from natural water or wastewater with high concentrations of hard metal ions such as alkaline earth metal ions.

Conclusions

We have developed a new dialkyl DTC-modified biomass-based sorbent **5d** derived from cellulose and L-proline. This sorbent is a potential material for the selective removal of toxic As(III) and other heavy metals from aqueous media because it has high capacity for As(III) and other hazardous heavy metals but hardly adsorbs alkaline earth metal ions. The sorption capacity and stability was maintained even after exposure to air at 40 °C for 2 weeks, indicating its excellent storage stability for practical use. In contrast, a significant decrease in the sorption capacity for As(III) was observed for monoalkyl DTC-modified compound **1**, suggesting that monoalkyl DTC-modified polymer-based sorbents might have poor storage ability, and caution is therefore required for the practical use of such materials. The present study demonstrated development of an improved sorbent for the selective removal of As(III) and other heavy metals based on a solid molecular design with biopolymer. Studies for further improvement and practical applications of the material are ongoing in our laboratory.

Experimental

1. General remarks

1.1. For synthetic experiments. All reactions were performed in oven-dried glassware. All reagents purchased commercially were used without further purification unless otherwise noted. Dehydrated solvents were purchased from Kanto Chemical Co., Inc. Cellulose (Avicel, DP: *ca.* 200) was purchased from Merck. N-(*tert*-Butoxycarbonyl)-N-Me-β-alanine (**2a**) was prepared by methylation of commercially available N-(*tert*-butoxycarbonyl)-β-alanine with iodomethane.[16] 2-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)acetic acid (**2b**), 1-(*tert*-butoxycarbonyl)pyrrolidine-3-carboxylic acid (**2c**), (*tert*-butoxycarbonyl)-L-proline (**2d**) and tetramethylammonium hydroxide (Me₄NOH, 10% in methanol) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Lithium chloride, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), N,N-dimethyl-4-aminopyridine (DMAP), trifluoroacetic acid (TFA), and carbon disulfide were purchased from Wako Pure Chemical. DTC-modified cellulose **1** was prepared according to the procedure previously reported.[9]

¹H NMR spectra were recorded on Bruker Avance 400 and JEOL JNM-ECA 500 spectrometers at 20 °C unless otherwise noted. Chemical shifts (δ) are quoted relative to tetramethylsilane (¹H NMR, δ 0 ppm) or a solvent residual peak (D₂O: δ 4.79 ppm; CD₃CO₂D: δ 2.04 ppm) as the internal standard. Coupling constants (J) are given in Hz. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broadened). IR spectra were recorded with a JASCO Fourier Transform IR-4700 spectrophotometer. Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University or by the Research Initiative Center, Tottori University.

1.2. For batch sorption experiments. All laboratory wares were soaked in an alkaline detergent (Scat 20X-PF; Nacalai Tesque) overnight, and then rinsed with deionized water. Subsequently, they were soaked in 3 mol L⁻¹ HCl overnight, and then washed again with deionized water. As(III) standard solution (1000 mg L⁻¹), sodium hydroxide (NaOH), nitric acid (HNO₃, 60%) and acetic acid (AcOH, 99%) were purchased from Kanto Chemical. Sodium acetate (AcONa) was purchased from Nacalai Tesque. ICP multi-element standard solution IV containing 21 elements (Al, Ba, Be, Bi, Ca, Cd, Co, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Y, Zn) was purchased from GL science.

The metal concentrations were quantified with inductively coupled plasma optical emission spectrometry (ICP-OES; iCAP 6300; Thermo Fisher Scientific). For pH measurements, a pH meter (Navi F-52; Horiba Instruments) was used. In order to prepare deionized water with a resistivity of > 18.2 MΩ cm, an Arium Pro water purification system (Sartorius Stedium Biotech GmbH) was used. A natural incubator (NIB-82; Iwaki Asahi Techno Glass) was used for heating.

2. Experimental details

2.1. Synthetic experiments

2.1.1. Synthesis of 3a–d (esterification). After cellulose (1 equiv.) was dried for 2 h at 90 °C *in vacuo* (0.1 mmHg), DMA (5.4 mL mmol⁻¹) was added, and the resultant slurry was stirred for 20 h at 90 °C. LiCl (*ca.* 7–8 equiv.) was added to the slurry precooled to room temperature, and the mixture was stirred for 1 h at room temperature. **2a–d** (6 equiv.), DMAP (6 equiv.) and EDC-HCl (6 equiv.) were added to the resultant solution at 0 °C, and the mixture was stirred for 24 h at room temperature. The reaction mixture was poured into an excess amount of MeOH/H₂O (70/30–80/20, v/v) under stirring. The formed precipitate was collected by centrifugation, washed with MeOH/H₂O (80/20, v/v), and dried *in vacuo* to give **3a–d**. The product was often contaminated with small amounts of waste based on reagents used in the reaction, but those could be used for the next step without further purification. For identification, the purer product could be obtained by repeating precipitation and washing with MeOH/H₂O.

3a. Cellulose (301 mg, 1.86 mmol), DMA (20 mL), LiCl (642 mg, 15.1 mmol), **2a** (2.29 g, 11.3 mmol), DMAP (1.38 g, 11.3 mmol) and EDC-HCl (2.16 g, 11.3 mmol) were used for the

reaction to give **3a** (1.17 g, 84% yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, 55 °C): δ 5.05 (br, 1H), 4.73 (br, 1H), 4.55 (br, 1H), 4.48 (br, 1H), 4.07 (br, 1H), 3.33–3.70 (m, 8H), 2.82–2.87 (m, 9H), 2.43–2.56 (m, 6H), 1.43 (s, 27H); IR (KBr, cm^{-1}): 1745, 1691. Anal. calcd for C$_{33}$H$_{55}$N$_3$O$_{14}$·H$_2$O: C, 53.87; H, 7.81; N, 5.71. Found: C, 54.12; H, 7.58; N, 5.70.

3b. Cellulose (1.00 g, 6.17 mmol), DMA (31 mL), LiCl (1.96 g, 46.3 mmol), **2b** (9.00 g, 37.0 mmol), DMAP (4.52 g, 37.0 mmol) and EDC-HCl (7.09 g, 37.0 mmol) were used for the reaction to give **3b** (3.87 g, 75% yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, 55 °C): δ 5.06 (br, 1H), 4.68 (br, 1H), 4.53 (br, 1H), 4.34 (br, 1H), 3.93–4.20 (m, 7H), 3.76 (br, 1H), 3.51 (br, 1H), 2.72 (br, 6H), 2.10–2.30 (m, 6H), 1.55–1.95 (br, 9H), 1.45 (s, 27H), 1.00–1.25 (m, 6H); IR (KBr, cm^{-1}): 1747, 1691. Anal. calcd for C$_{42}$H$_{67}$N$_3$O$_{14}$: C, 60.20; H, 8.06; N, 5.01. Found: C, 59.81; H, 8.22; N, 5.04.

3c. Cellulose (253 mg, 1.56 mmol), DMA (9.4 mL), LiCl (528 mg, 12.5 mmol), **2c** (2.03 g, 9.43 mmol), DMAP (1.17 g, 9.56 mmol) and EDC-HCl (1.79 g, 9.35 mmol) were used for the reaction to give **3c** (1.15 g, 98% yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, 55 °C): δ 5.07 (br, 1H), 4.00–4.72 (m, 3H), 2.70–3.90 (m, 18H), 1.90–2.30 (m, 6H), 1.45 (s, 27H); IR (KBr, cm^{-1}): 1751, 1691. Anal. calcd for C$_{36}$H$_{55}$N$_3$O$_{14}$·0.5H$_2$O: C, 56.68; H, 7.40; N, 5.51. Found: C, 56.68; H, 7.33; N, 5.55.

3d. Cellulose (1.25 g, 7.71 mmol), DMA (42 mL), LiCl (2.60 g, 61.4 mmol), **2d** (10.0 g, 46.6 mmol), DMAP (5.72 g, 46.8 mmol) and EDC-HCl (9.00 g, 47.0 mmol) were used for the reaction to give **3d** (4.82 g, 82% yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$, 55 °C): δ 3.20–5.20 (br, 16H), 1.58–2.40 (br, 12H), 1.43 (br, 27H); IR (KBr, cm^{-1}): 1755, 1709. Anal. calcd for C$_{36}$H$_{55}$N$_3$O$_{14}$·H$_2$O: C, 56.02; H, 7.44; N, 5.44. Found: C, 55.92; H, 7.31; N, 5.45.

2.1.2. Synthesis of 4a–d (deprotection). TFA (5 mL mmol^{-1}) was added to **3a–d**, and the mixture was stirred for 7 h at room temperature. The reaction mixture was poured into an excess amount of Et$_2$O under stirring. The formed precipitate was collected by centrifugation, washed with Et$_2$O, and dried *in vacuo* to give **4a–d**.

4a. TFA (7.8 mL) and **3a** (1.17 g, 1.63 mmol) were used for the reaction to give **4a** (1.08 g, 92% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O, 80 °C): δ 5.71 (br, 1H), 4.10–5.40 (m, 6H, partially overlapped with a water signal), 3.85 (br, 6H), 3.20–3.55 (m, 15H), the signal based on NH$_2$ was not observed due to H-D exchange; IR (KBr, cm^{-1}): 1750, 1681. Anal. calcd for C$_{24}$H$_{34}$-N$_3$O$_{14}$F$_9$·2H$_2$O: C, 36.23; H, 4.81; N, 5.28. Found: C, 36.32; H, 4.43; N, 5.22.

4b. TFA (8.0 mL) and **3b** (1.36 g, 1.62 mmol) were used for the reaction to give **4b** (1.37 g, 96% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 5.09 (br, 1H), 4.30–4.80 (m, 5H, partially overlapped with a water signal), 3.75 (br, 1H), 3.42 (br, 6H), 2.98 (br, 6H), 1.80–2.50 (m, 15H), 1.30–1.50 (m, 6H), the signal based on NH$_2$ was not observed due to H-D exchange; IR (KBr, cm^{-1}): 1745, 1689. Anal. calcd for C$_{33}$H$_{46}$N$_3$O$_{14}$F$_9$·2H$_2$O: C, 43.28; H, 5.50; N, 4.59. Found: C, 42.84; H, 5.07; N, 4.51.

4c. TFA (32 mL) and **3c** (4.80 g, 6.37 mmol) were used for the reaction to give **4c** (4.73 g, 93% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 5.19 (br, 1H), 3.30–3.80–4.80 (m, 6H, partially overlapped with a water signal), 3.30–3.70 (m, 12H), 1.70–2.50 (m, 9H), the signal based on NH$_2$ was not observed due to H-D exchange; IR (KBr, cm^{-1}): 1747, 1679. Anal. calcd for C$_{27}$H$_{34}$-N$_3$O$_{14}$F$_9$·H$_2$O: C, 39.86; H, 4.46; N, 5.16. Found: C, 39.49; H, 4.28; N, 5.15.

4d. TFA (32 mL) and **3d** (4.82 g, 6.40 mmol) were used for the reaction to give **4d** (4.09 g, 80% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 5.42 (br, 1H), 4.55–5.20 (m, 5H, partially overlapped with a water signal), 3.80–4.40 (m, 4H), 3.50 (br, 6H), 1.85–2.70 (m, 12H), the signal based on NH$_2$ was not observed due to H-D exchange; IR (KBr, cm^{-1}): 1755, 1678. Anal. calcd for C$_{27}$H$_{34}$N$_3$O$_{14}$F$_9$·H$_2$O: C, 39.86; H, 4.46; N, 5.16. Found: C, 39.55; H, 4.54; N, 4.97.

2.1.3. Synthesis of 5a–d (dithiocarbamation). To a solution of **4a–d** in DMSO (5 mL mmol^{-1}) was added CS$_2$ (15 equiv.) and 10% Me$_4$NOH solution in MeOH (*ca.* 6–7 equiv.) at 0 °C, and the resultant suspension was stirred at room temperature. The reaction mixture became almost homogeneous in 7–48 h. The reaction mixture was poured into an excess amount of MeOH (for **4a** and **4b**) or EtOH (for **4c** and **4d**) under stirring. The formed precipitate was collected by centrifugation, washed with MeOH (for **4a** and **4b**) or EtOH (for **4c** and **4d**), and dried *in vacuo* to give **5a–d**.

5a. **4a** (1.55 g, 2.04 mmol), DMSO (10 mL), CS$_2$ (1.84 mL, 30.5 mmol) and 10% Me$_4$NOH solution in MeOH (14 mL, 13.9 mmol) were used for the reaction (7 h) to give **5a** (605 mg, 34% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 3.90–5.50 (m, 7H, partially overlapped with a water signal), 3.45 (br, 6H), 3.18 (br, 9H), 3.16 (s, 36H); IR (KBr, cm^{-1}): 1741, 1485, 1156. The value observed by elemental analysis was significantly different from the theoretical value because the sample contained a significant amount of water or because the side chain was partially degraded by hydrolysis (for example, Anal. calcd for C$_{33}$H$_{64}$N$_6$O$_8$S$_6$: C, 45.81; H, 7.46; N, 9.71. Found: C, 41.42; H, 7.13; N, 8.14).

5b. **4b** (507 mg, 0.576 mmol), DMSO (2.8 mL), CS$_2$ (0.52 mL, 8.61 mmol) and 10% Me$_4$NOH solution in MeOH (3.7 mL, 3.66 mmol) were used for the reaction (48 h) to give **5b** (496 mg, 87% yield) as a white solid. ^{1}H NMR (500 MHz, CD$_3$CO$_2$D): δ 3.70–5.50 (m, 7H), 3.54 (br, 6H), 3.22 (s, 36H), 3.09 (br, 6H), 1.80–2.50 (br, 15H, partially overlapped with a solvent signal), 1.40–1.70 (m, 6H); IR (KBr, cm^{-1}): 1741, 1410, 1174. The value observed by elemental analysis was significantly different from the theoretical value because the sample contained a significant amount of water or because the side chain was partially degraded by hydrolysis (for example, Anal. calcd for C$_{42}$H$_{76}$N$_6$O$_8$S$_6$: C, 51.19; H, 7.77; N, 8.53. Found: C, 47.76; H, 6.69; N, 6.43).

5c. **4c** (421 mg, 0.529 mmol), DMSO (2.7 mL), CS$_2$ (0.49 mL, 8.12 mmol) and 10% Me$_4$NOH solution in MeOH (3.7 mL, 3.66 mmol) were used for the reaction (48 h) to give **5c** (404 mg, 83% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 5.27 (br, 1H),

3.30–5.00 (m, 18H, partially overlapped with a water signal), 3.20 (s, 36H), 1.90–2.70 (br, 9H).; IR (KBr, cm^{-1}): 1740, 1384, 1165. The value observed by elemental analysis was significantly different from the theoretical value because the sample contained a significant amount of water or because the side chain was partially degraded by hydrolysis (for example, Anal. calcd for $C_{36}H_{64}N_6O_8S_6$: C, 47.97; H, 7.15; N, 9.32. Found: C, 44.32; H, 7.34; N, 8.51).

5d. 7 h: **4d** (1.00 g, 1.26 mmol), DMSO (6.3 mL), CS$_2$ (1.14 mL, 18.9 mmol) and 10% Me$_4$NOH solution in MeOH (8.7 mL, 8.61 mmol) were used for the reaction (7 h) to give **5d** (915 mg, 81% yield) as a white solid. 24 h: **4d** (504 mg, 0.633 mmol), DMSO (3.1 mL), CS$_2$ (0.57 mL, 9.44 mmol) and 10% Me$_4$NOH solution in MeOH (4.3 mL, 4.27 mmol) were used for the reaction (24 h) to give **5d** (519 mg, 91% yield) as a white solid. ^{1}H NMR (500 MHz, D$_2$O): δ 5.04 (br, 3H, partially overlapped with a water signal), 3.90 (br, 6H), 3.17 (s, 36H), 1.70–2.60 (br, 12H), signals based on the cellulose moiety (7H) were obscure due to broadening; IR (KBr, cm^{-1}): 1737, 1375, 1183. The value observed by elemental analysis was significantly different from the theoretical value because the sample contained a significant amount of water or because the side chain was partially degraded by hydrolysis (for example, Anal. calcd for $C_{36}H_{64}N_6O_8S_6$: C, 47.97; H, 7.15; N, 9.32. Found: C, 42.50; H, 7.40; N, 7.81).

2.2. Batch sorption experiments. The durability of the sorbents was investigated by comparing the sorption capacities of As(III) before and after keeping them at 40 °C for fortnight. Sorption tests were conducted in 50 mL centrifuge tubes containing 0.02 g of sorbent and 10 mL of 2 mmol L^{-1} As(III) solutions by agitating the tubes for 20 minutes at 25 °C and 200 rpm. Then, the solutions were collected by filtrating suspensions through a 0.45 μm membrane filter. Subsequently, the metal concentrations in the solutions were determined with ICP-OES. The sorption capacities of As(III) (q_e) were calculated according to the equation shown below:

$$q_e = \frac{(C_i - C_e)}{m} V \tag{1}$$

where q_e (μmol g^{-1}) represents the sorption capacity of As(III), C_i and C_e (μmol L^{-1}) refer to initial and equilibrium concentrations of As(III), m (g) is the weight of the sorbent, and V (L) is the solution volume.

The removal efficiency of various elements was examined using polymer **5d**. The solution containing 21 elements was prepared by diluting the desired amount of the ICP multielement standard solution with deionized water so that the concentrations became 5 mg L^{-1}. Then, the pH was adjusted to pH 3 using 0.1 mol L^{-1} HNO$_3$ or NaOH solution, and sorption tests were carried out according to the procedure mentioned above. The removed metal percentages (%) were calculated from the following equation:

$$\text{Removed metal}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

Conflicts of interest

Acknowledgements

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