



Selective and efficient tripodal receptors for competitive solvent extraction and bulk liquid membrane transport of Hg^{2+}

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ABSTRACT

A series of tripodal receptors that are different from each other in their end groups were synthesized. The extraction ability and the transport rate of these receptors were evaluated for transition metal ions (Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Hg^{2+}). The receptor bearing pyridyl nitrogens extracted Hg^{2+} from a buffered aqueous medium containing a mixture of metal ions and transported it into an organic phase with a complete selectivity over the other metal ions. This receptor was effectively used for transporting Hg^{2+} from aqueous buffered source phase to aqueous receiving phase through a chloroform membrane.

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1. Introduction

Toxic heavy metals such as mercury, chromium, lead, nickel and cadmium can cause serious problems to the aqueous environment as well as to animals and humans [1–13]. Therefore, treatment of waste water prior to discharge is essential. Solvent extraction [12] and membrane transport [13,14] of metal ions have drawn considerable attention over other conventional techniques for removal of metal ions from waste water. The solvent extraction can be performed from the laboratory level to the industrial scale, and it is very attractive because of its high selectivity. The metal ion transport is an advanced form of solvent extraction that involves a continuous process of metal extraction and metal decomplexation [15]. Among the various types of membranes that have been used for the metal transport, bulk liquid membranes have mainly been used at laboratory scale [16,17]. The major factors influencing the efficiency of the method are the carrier (or receptor) used in the organic phase and pH of a source and/or receiving phase [18–20]. For a receptor to be an effective candidate, its structural features must be complementary with those of the guest.

Among transition metal ions, Hg^{2+} is known for its toxicity. A matter of great concern is its presence in water, where Hg^{2+} is transformed into methyl mercury which has higher toxicity than its state of ion [21]. Thus, the consumption of mercury-contaminated fish by human leads to serious health problems. Therefore, designing the

receptors that can remove Hg^{2+} from water is a research area of great interest. The mixed donor receptors afford an organized and interesting assembly to optimize the selective removal of a particular metal ion [22–24]. We herein present the design and properties of mixed donor receptors that can be used for selective removal of Hg^{2+} from water.

2. Experimental

2.1. Instruments

The ^1H and ^{13}C NMR spectra were performed on a Bruker 400 NMR spectrometer which operated at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei and are internally referenced to residual protio solvent signals. Chemical shifts are reported in parts per million (ppm). FAB mass spectrum and high resolution mass spectra (HRMS) were obtained on a JEOL JMS-AX 505WA mass spectrometer. The measurements of metals were performed on a PerkinElmer AAnalyst 700 spectrometer equipped with a PerkinElmer Lumina hollow cathode lamp and a deuterium background corrector, at respective wavelength using an air-acetylene flame. The instrument was used under conditions suggested by the manufacturer. An Accumet AB15 Fisher Scientific pH meter was used to adjust the pH of the solutions.

2.2. Reagents and solutions

All organic solvents were of HPLC grade. Unless otherwise specified, chemicals were purchased from chemical suppliers and

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used without further purification. 2-Aminoethanol, *N,N*-dimethyl-ethane-1,2-diamine and 2-amino methyl pyridine were purchased from Aldrich Chemicals. 2,2',2''-(2,2',2''-Nitrilotris(ethane-2,1-diyl)tris(oxy))tribenzaldehyde (**1**) was prepared according to the method described previously [25]. Doubly distilled, deionized water was used throughout. The standard solutions of Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Hg²⁺ were prepared by dissolving Fe(NO₃)₃·9H₂O (Duksan, Korea), Ni(NO₃)₂·6H₂O (Washihata, Japan), Cu(NO₃)₂·3H₂O (Duksan, Korea), Zn(NO₃)₂·6H₂O (Duksan, Korea) and Hg(NO₃)₂·H₂O (Aldrich) in water, respectively. Working solutions were prepared by appropriate dilution of the stock solution with water. The buffer was prepared at pH 4.6 by mixing an appropriate amount of 2.0 M sodium acetate (NaC₂H₃O₂·3H₂O, Aldrich) and 2.0 M glacial acetic acid (C₂H₄O₂, Oriental, Korea)

2.3. Synthesis of 2,2',2''-(2,2',2''-(2,2',2''-nitrilotris(ethane-2,1-diyl)tris(oxy))tris(benzene-2,1-diyl))tris(methylene)tris(azanediy)triethanol (**2a**)

A solution of trialdehyde **1** (46.1 mg, 0.1 mmol) and 2-aminoethanol (27.5 mg, 0.45 mmol) in CH₃CN (10 mL) was stirred at room temperature for 1 h. Upon completion of the reaction, the solvent was evaporated in vacuo. The residue was treated with NaBH₄ (388 mg, 10 mmol) in MeOH/THF (1:1) at room temperature for 3 h. The solvent was removed in vacuo, and water was added to the residue. After neutralization with 1.0 M HCl, the aqueous phase was extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the residue was purified by recrystallization from a CH₃CN/MeOH solvent mixture affording the product (54 mg, 90%). ¹H NMR (CDCl₃, 400 MHz) δ 2.71 (t, 6H, CH₂, *J* = 5.2 Hz), 3.33 (t, 6H, CH₂, *J* = 5.6 Hz), 3.65 (t, 6H, CH₂, *J* = 5.2 Hz), 3.86 (s, 6H, CH₂), 4.22 (t, 6H, CH₂, *J* = 5.6 Hz), 5.26 (broad, 3H, NH), 6.95 (d, 3H, Ar, *J* = 8.4 Hz), 7.00 (t, 3H, Ar, *J* = 7.2 Hz), 7.21–7.33 (m, 6H, Ar). ¹³C NMR (CDCl₃, 100 MHz) δ 49.1 (CH₂), 50.5 (CH₂), 54.4 (CH₂), 60.3 (CH₂), 66.6 (CH₂), 111.2 (Ar), 120.7 (Ar), 127.1 (Ar), 128.7 (Ar), 130.6 (Ar), 156.8 (Ar). HRMS (FAB): *m/z* = 597.3652 (Calcd. for C₃₃H₄₉N₄O₆ (M + H⁺), *m/z* = 597.3652).

2.4. Synthesis of N¹-(2-(2-(bis(2-(2-((2-(dimethylamino)ethylamino)methyl)phenoxy)ethyl)amino)ethoxy)benzyl)-N²,N²-dimethylethane-1,2-diamine (**2b**)

This compound was prepared by the same method used for the synthesis of **2a** with *N,N*-dimethyl-ethane-1,2-diamine (39.6 mg, 0.45 mmol) instead of 2-aminoethanol affording the product (60 mg, 88%). ¹H NMR (CDCl₃, 400 MHz) δ 2.07 (s, 18H, CH₃), 2.31 (t, 6H, CH₂, *J* = 6.0 Hz), 2.56 (t, 6H, CH₂, *J* = 6.0 Hz), 3.12 (t, 6H, CH₂, *J* = 5.2 Hz), 3.72 (s, 6H, CH₂), 4.07 (t, 6H, CH₂, *J* = 5.2 Hz), 5.14 (broad, 3H, NH), 6.77 (d, 3H, Ar, *J* = 8.4 Hz), 6.83 (t, 3H, Ar, *J* = 7.2 Hz), 7.01–7.14 (m, 12H, Ar). ¹³C NMR (CDCl₃, 100 MHz) δ 34.1 (CH₂), 45.5 (CH₂), 61.0 (CH₂), 62.5 (CH₂), 66.6 (CH₂), 111.0 (Ar), 125.4 (Ar), 129.2 (Ar), 130.0 (Ar), 149.3 (Ar), 156.6 (Ar). HRMS (FAB): *m/z* = 678.5071 (Calcd. for C₃₉H₆₄N₇O₃ (M + H⁺), *m/z* = 678.5070).

2.5. Synthesis of tris(2-(2-((pyridin-2-ylmethylamino)methyl)phenoxy)ethyl)amine (**2c**)

This compound was prepared by the same method used for the synthesis of **2a** with 2-amino methyl pyridine (48.6 mg, 0.45 mmol) instead of 2-aminoethanol affording the product (99 mg, 88%). ¹H NMR (CDCl₃, 400 MHz) δ 3.15 (t, 6H, CH₂, *J* = 6.0 Hz), 3.87 (s, 6H, CH₂), 3.89 (s, 6H, CH₂), 4.08 (t, 6H, CH₂, *J* = 6.0 Hz), 6.80 (d, 3H, Ar, *J* = 8.0 Hz), 6.91 (t, 3H, Ar, *J* = 7.2 Hz), 7.09 (t, 3H, Ar, *J* = 6.4 Hz), 7.16–7.20 (m, 6H, Ar), 7.55 (t, 3H, Ar, *J* = 6.4 Hz), 8.49 (d, 3H, Ar, *J* = 6.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 45.5 (CH₂), 61.0 (CH₂), 62.5 (CH₂), 66.6 (CH₂), 120.7 (Ar), 125.4 (Ar), 128.1 (Ar), 129.1 (Ar), 130.0

(Ar), 142.4 (Ar), 147.7 (Ar), 149.3 (Ar), 156.6 (Ar). HRMS (FAB): *m/z* = 738.4132 (Calcd. for C₄₅H₅₂N₇O₃ (M + H⁺), *m/z* = 738.4132).

2.6. Competitive solvent extraction (%E)

An aqueous buffered solution containing 1.0 × 10⁻³ M (2 mL) metal salts, which was buffered (CH₃CO₂H–CH₃CO₂Na) at pH 4.6, was extracted with a chloroform solution containing a receptor (1.0 × 10⁻³ M, 2.0 mL) at 25 °C. A blank analysis was also performed simultaneously with the same aqueous solution containing metal salts (1.0 × 10⁻³ M, 2.0 mL) and 2.0 mL of neat chloroform. After extraction, the residual concentration of the metal ions in the aqueous phase and also in the blank experiment was determined by an atomic absorption spectrometer. The percent extraction (%E) of metal salts was determined by the formula %E = (C₁ – C₂)/C₁ × 100, where C₁ is the concentration of a metal salt in the aqueous buffer solution in the blank analysis, and C₂ is the concentration of a metal salt remaining in the aqueous solution after extraction. The average values of triplicate runs are reported.

2.7. Decomplexation of metal ion (%D)

The chloroform layer (2.0 mL) of the competitive solvent extraction experiment separated from the aqueous layer was shaken (5 min) with 2.0 mL of 0.1 M HCl at 25 °C. The concentration of metal salts in 0.1 M HCl was determined by an atomic absorption spectrometer. The percent decomplexation (%D) of metal salts was determined by the formula %D = C₃/C₁ × 100, where C₁ is the concentration of a metal salt in the aqueous buffered solution in a blank analysis of competitive solvent extraction experiment, and C₃ is the concentration of a metal salt released to 0.1 M HCl. The average values of triplicate runs are reported.

2.8. Bulk membrane transport studies

Hg²⁺ transport experiments employing **2c** as an ionophore were carried out by stirring the organic phase of bulk liquid membrane cell at a constant slow speed (at 150 rpm) so that the interfaces between the organic membrane and two aqueous phases remained flat and well defined. The aqueous source phase (4.0 mL) containing 5 × 10⁻³ M of Hg²⁺ at pH 4.6 and the receiving phase (8.0 mL) containing 0.1 M HCl were separated by the chloroform layer (25 mL) containing 1.0 × 10⁻³ M of **2c**. An aliquot of both aqueous phases of the system was taken after a regular time interval of 3 h for 12 h, and then the last sample was taken after 24 h. The atomic absorption spectroscopy was used to determine the amount of metal ions. The average values of triplicate runs are quoted. For this experiment the transport cell devised by Lamb et al. was used [26].

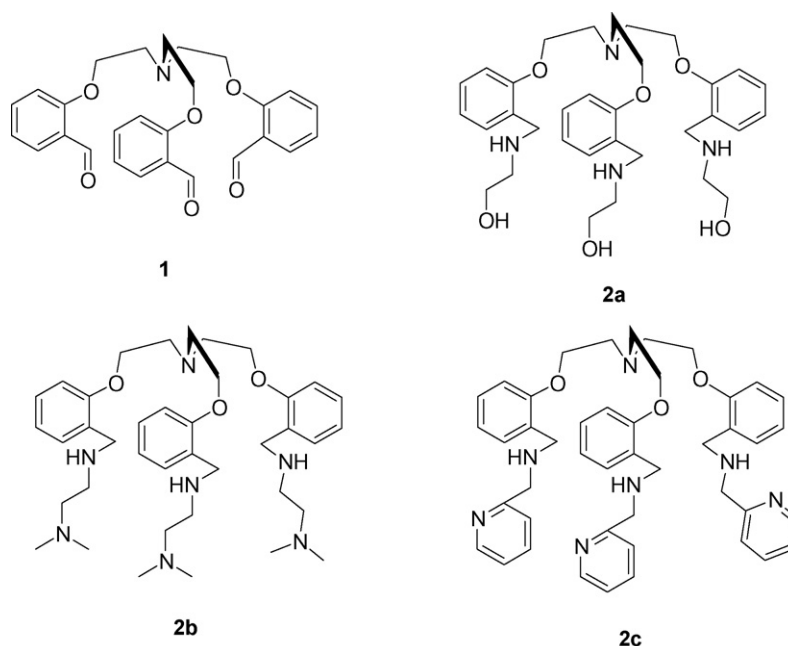
3. Results and discussion

3.1. Synthesis of receptors

We synthesized tripodal receptors **2a–c** that are different in their end groups. Tripodal aldehyde **1** was synthesized following the method described previously [25]. Receptors **2a–c** were prepared in high yields by reacting tripodal aldehyde **1** with the corresponding amines and subsequently by reducing the resultant imine derivatives with NaBH₄ (Scheme 1).

3.2. Competitive solvent extraction

The binding abilities of receptors **2a–c** for some transition metals were examined by competitive solvent extraction experiments. To determine the efficiency of competitive solvent extraction, an aqueous buffered solution containing metal salts (1.0 × 10⁻³ M) was



Scheme 1.

Table 1
Competitive solvent extraction (%E) of metal ions with receptors **2a–c**.

Receptor	Extraction (%) ^a				
	Zn ²⁺	Ni ²⁺	Cu ²⁺	Fe ³⁺	Hg ²⁺
2a	9.1 ± 0.7	7.6 ± 0.6	29.5 ± 0.4	4.5 ± 0.4	13.9 ± 0.6
2b	13.0 ± 0.5	5.4 ± 0.6	37.5 ± 0.8	8.0 ± 0.4	53.6 ± 0.8
2c	4.4 ± 0.4	5.5 ± 0.3	9.5 ± 0.6	5.3 ± 0.8	80.3 ± 1.0

^a The value following “±” is the standard deviation ($n=3$).

shaken with the host solution (2.0×10^{-3} M). The aqueous phase pH of 4.6 was maintained for correlating our receptor efficiency with the receptors already reported in the literatures [18–20]. Table 1 presents the percentage of individual metal ions extracted (%E) by receptors **2a–c** after 24 h of liquid phase contact. Under the experimental conditions, **2c** bound exclusively to Hg²⁺ among the transition metals (Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Hg²⁺) examined whereas **2a–b** were coordinated with Cu²⁺ and Hg²⁺ ions with a low selectivity. A comparison of the extraction efficiency of **2a** and **2b** for the metal ions reveals that **2b** that has softer binding sites (N(CH₃)₂) provides better results. The highest extraction efficiency of **2c** toward Hg²⁺ is attributed to the proper size of Hg²⁺ to fit the cavity that is formed by **2c**.

To utilize a system in separation chemistry, a receptor should have high extraction efficiency as well as high decomplexation efficiency towards a specific metal ion. A receptor is of no use if it binds very strongly to the metal ion and it do not undergo decomplexation by any methods. This would waste the receptor after a single use and it would be difficult to recycle the receptor. Hence, the decomplexation of metals is one of the important factors in the solvent extraction. Thus, we evaluated the decomplexation efficiency of **2a–c**.

A decomplexation experiment was carried out by extracting the organic layer of the competitive metal ion solvent extraction experiment with 0.1 M HCl. Table 2 presents a comparison of the extraction efficiency and the decomplexation efficiency of **2a–c** towards Hg²⁺. As can be observed, shaking an organic layer containing the metal–receptor (**2c**) complex with 0.1 M HCl

released a great deal of Hg²⁺. These results imply that 0.1 M HCl is acidic enough to protonate metal-coordinated amines. **2c** shows a high efficiency both in extraction and in decomplexation of Hg²⁺.

We also investigated the recovery and reuse of **2c** for Hg²⁺ extraction from the aqueous buffered phase. After extraction of Hg²⁺ from the aqueous buffered phase with **2c**, the organic phase was treated with 0.1 M HCl for decomplexation. Before reuse of **2c**, it was neutralized with a base. Fig. 1 presents the results which show no significant decrease in extraction efficiency of Hg²⁺ after five runs.

3.3. Transport of Hg²⁺

We conducted metal transport experiments across a bulk chloroform membrane (water/chloroform/water). The chloroform membrane phase contained receptors **2a–c** at 1.0×10^{-3} M, respectively. The concentration of Hg²⁺ in the buffered source phase (pH

Table 2
Comparison of Hg²⁺ extraction (%E) and decomplexation (%D) efficiency of receptors **2a–c**.

Receptor	Decomplexation of Hg ²⁺ (%) ^a	Extraction of Hg ²⁺ (%) ^a
2a	10.9 ± 0.8	13.9 ± 0.4
2b	12.2 ± 0.5	53.6 ± 0.4
2c	78.8 ± 0.6	80.3 ± 0.9

^a The value following “±” is the standard deviation ($n=3$).

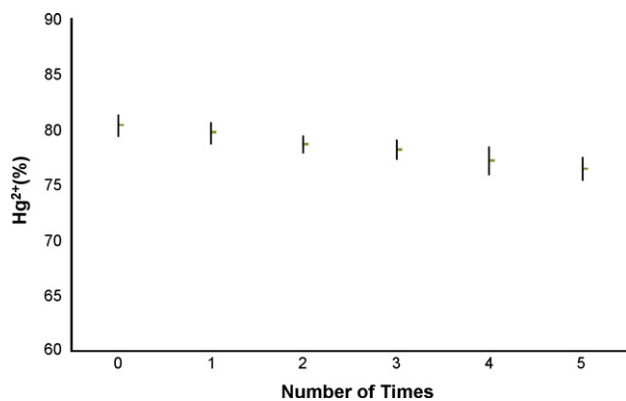


Fig. 1. Reuse of receptor **2c** for extracting Hg²⁺.

4.6) was 5.0×10^{-3} M. 0.1 M HCl was used for the receiving phase. The concentration of Hg²⁺ was monitored in both aqueous compartments with atomic absorption spectroscopy as a function of time. An aliquot of both aqueous phases of the system was taken after an interval of 3 h for 12 h and then after a total of 24 h (Fig. 2). **2a** was very poor in the efficiency of extraction and release of Hg²⁺. In the case of **2b**, the extraction of Hg²⁺ was efficient whereas the release of Hg²⁺ was poor. During the course of transport experiment, some suspension in the organic layer of the transport cell appeared, indicating that **2b** precipitated out of the organic layer upon complexation with Hg²⁺. A good carrier must be soluble in the organic medium both in its free form and in its complexed form. No such precipitation was observed during the transport experiment of **2c**. The solubility of **2c** in the organic phase might be attributed to the presence of pyridine moiety in **2c**. In the case of **2c**, the transport rate was very fast for 6 h, and most Hg²⁺ was transported within next 6 h (after a total of 12 h).

Finally, the mode of binding between **2c** and Hg²⁺ was established by ¹H NMR titration (Fig. 3). Upon addition of Hg²⁺ to a solution of **2c**, the signals in the ¹H NMR spectrum shifted drastically. Although every proton showed significant shift, the shift in the proton signals of pyridine at 8.49 ppm was more distinct and prominent. The shifts showed that pyridine rings play an important role in the binding of Hg²⁺. Two singlet signals of -NCH₂ at 3.87 and 3.89 ppm also shifted upfield. This confirms that the secondary amines also coordinate with Hg²⁺. These concurrent shifts of aromatic protons of pyridine and -CH₂- adjacent to the secondary amines led us to conclude that Hg²⁺ might be bound into the cavity defined by three nitrogen donors of pyridine and three nitrogen donors of the secondary amines.

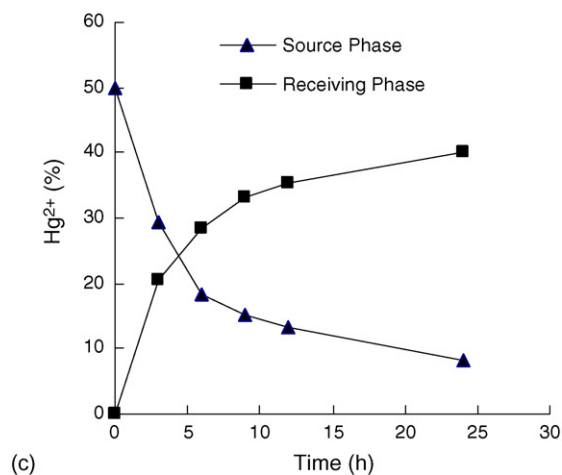
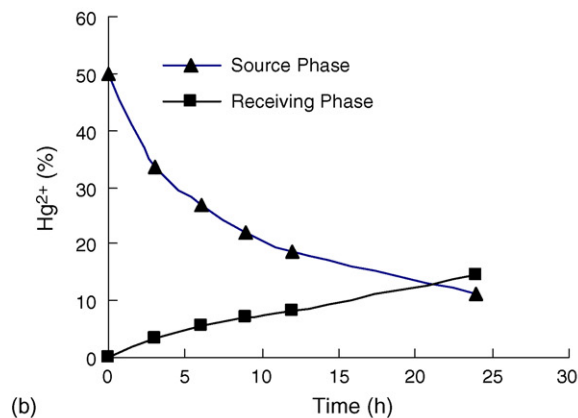
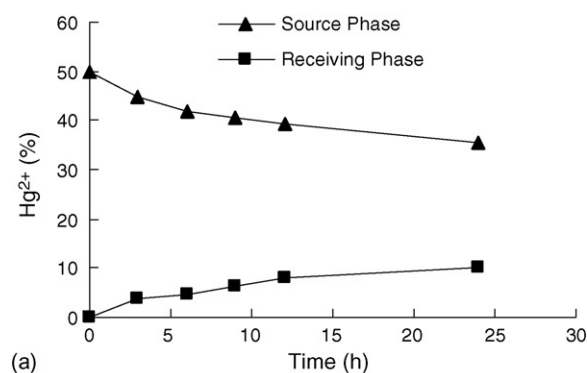


Fig. 2. Transport rate of Hg²⁺ as a function of time.

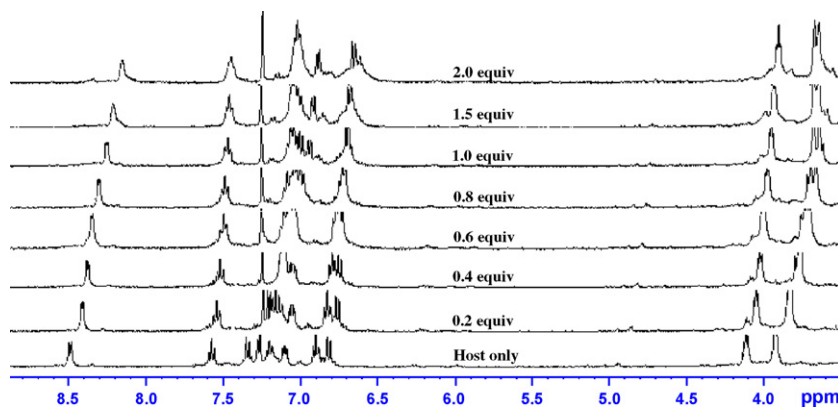


Fig. 3. Family of ¹H NMR spectra in CDCl₃ showing the shift in signals upon the binding of Hg²⁺ with receptor **2c**.

4. Conclusions

We investigated the extraction and transport efficiency of new tripodal receptors for selective removal of heavy metal ions from aqueous phases. The tripodal receptor possessing pyridyl moieties at the end of the structure provided the highest extraction and transport efficiency of Hg^{2+} among the receptors we examined. Little change in the efficiency of the receptor for transporting Hg^{2+} over consecutive cycles increases its potential applicability for selective removal of Hg^{2+} from industrial wastes.

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