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Synthesis of calix[4]arene-based dipodal receptors: Competitive solvent extraction and liquid bulk membrane transport for selective recovery of Cu²⁺

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A series of new *p*-*tert*-butylcalix[4]arene-based dipodal receptors are synthesised in high yields. The calix[4]arene units of all the receptors have been found to be present in cone conformation. To optimise the good extraction ability and high transport rate, we synthesised the receptors that differ from each other in their end groups. These receptors extract Cu²⁺ ion selectively from the buffered aqueous medium containing a mixture of metal ions. The receptor bearing four sp³ nitrogens has by far the greater ability to extract Cu²⁺ than the other receptors. All these receptors were effectively used for Cu²⁺ ion transport from the aqueous buffered source phase to the aqueous receiving phase.

Keywords: calix[4]arene; solvent extraction; bulk membrane transport; Cu²⁺ selective

Introduction

The selective removal of metal ions from industrial wastewater is required not only for safe disposal of wastewater but also for reuse of metal ions (1). Although various chemical techniques have been employed for metal ion separation, solvent extraction (2) and membrane transport (3) are particularly attractive methods because of their high selectivity. The efficiency of these methods depend upon the carrier (or receptor) used in the organic phase and pH of the source and/or receiving phase (4). The position and nature of donor groups present in a receptor determine the metal-binding affinity of that receptor. The modified calix[4]arene derivatives having additional binding sites at the lower rim enhance the binding ability of the parent calixarene (5). Such polytopic receptors employ the organising ability of the calix[4]arene platform to bring various binding subunits together in a single molecule (6). Thus, the donor receptors mixed in this way afford an organised and interesting assembly to optimise the selective removal of a particular metal ion. A number of receptors based on calix[4]arenes have been reported to have selectivity for alkali metals, alkaline earth metals, lanthanides, and transition metal ions (7). Amongst soft transition metal ions, Cu²⁺ is the third abundant (after Fe²⁺ and Zn²⁺) essential transition metal ion in the human body, and it plays an important role in various biological systems (8). When a human is exposed to Cu²⁺ levels above 1.3 mg/l for a short period of time, it will cause stomach and intestinal problems. Long-term exposure to Cu²⁺ leads to kidney and liver damage (8).

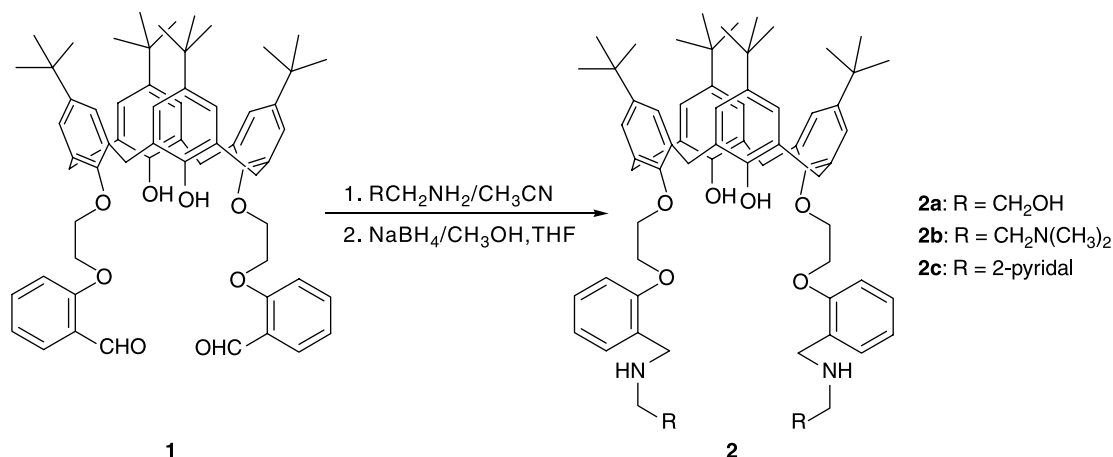
Industrial utilisation of Cu²⁺ results in its ponderous discharge in the industrial waste material. Such industrial discharges not only damage the environment but also lead to substantial monetary loss. Thus, the selective removal of Cu²⁺ from industrial waste material is required not only for safe disposal of the industrial waste but also for reuse of the metal ion.

Results and discussion

Calix[4]arene-based dipodal receptors were synthesised as shown in Scheme 1. The calix[4]arene-based dipodal aldehyde **1** was prepared by the literature method (9). The final receptors were prepared in high yields by the reactions of dipodal aldehydes **1** with various types of amines and a subsequent reduction of imine linkages with NaBH₄. Spectroscopic data were fully interpreted and found to be in accordance with the formula of receptors. The conformation of these compounds was derived from the signals of the bridging methylene protons in ¹H NMR (10). A pair of doublets at around 3.20–3.29 and 4.22–4.31 ppm in ¹H NMR with *J* = 12–13 Hz and signals around 32 ppm in ¹³C NMR for ArCH₂Ar show that the calix[4]arenes exist in a cone conformation in all. The –CH₃ protons of *t*-butyl groups appeared as two sharp singlets in all of them.

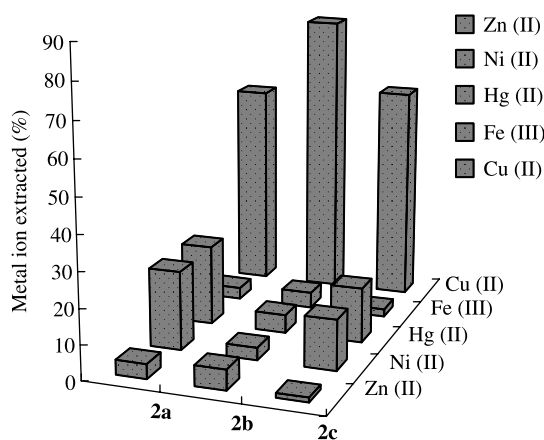
To evaluate a particular metal-binding ability of receptors **2a–c**, a competitive solvent extraction experiment was performed. In a typical experiment of competitive solvent extraction, an aqueous buffered solution containing metal salts (1.0 mM) was shaken

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Scheme 1.

with the host solution (2.0 mM). In these experiments the pH of the aqueous phase was maintained at pH = 4.6 (this value of pH was selected so as to correlate these experimental conditions with the literature experiments) (4). The concentrations of metal salts left in aqueous phase after extraction and also in blank analysis were determined by atomic absorption spectroscopy, and these values were taken as a measure to determine the percentage of metal ion extracted by the receptor. Figure 1 represents the average percent of metal ions extracted (%E) by the receptor **2a–c** in three independent determinations. Figure 1 clearly shows that the complexation ability of all the receptors is higher towards Cu²⁺ than for any other metal ions. Among these, the receptor bearing four sp³ nitrogens, **2b**, has a greater ability to extract Cu²⁺ than the receptor **2a** that has two sp³ nitrogens and two oxygen donors. Receptor, **2b**, also has a greater ability to extract Cu²⁺ than receptor **2c** that has two sp³ nitrogens along with two sp² nitrogen donors. This means that the four sp³

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

nitrogens provide a favourable combination of donor sets to bind with Cu²⁺.

The extraction experiment helps to determine the efficiencies of a receptor to complex metal ions at the interface of aqueous source phase and organic layer. However, a higher extraction ability of any receptor alone does not warrant its use for applications in separation chemistry. If a receptor forms a very strong complex with a particular metal ion and yet the decomplexation of metal ions from the receptor is not possible, then the receptor is of no use because it will be wasted after a single use. Thus, the metal decomplexation from a receptor is also important. For the determination of decomplexation of metal from the receptors **2a–c**, a decomplexation experiment was performed by extracting the organic layer of the competitive metal ion solvent in an extraction experiment with hydrochloric acid (pH = 1). The data are expressed as the average of Cu²⁺ ion decomplexation from the receptor in three different independent determinations. The concentration of metal salt released to the acidic aqueous phase was determined by atomic absorption spectroscopy.

A comparison of extraction ability and ease of decomplexation is represented in Figure 2. Figure 2 shows that the decomplexation ability of all the receptors for Cu²⁺ is approximately the same. A good deal of extracted metal ions were released when the organic layer containing the metal–receptor complex was shaken with the hydrochloric acid (pH = 1) because the high acidity (pH = 1.0) of the water is sufficient to protonate metal-coordinated amines. Hence, metal ions are leased at a high rate.

The receptor **2b** was tested for its reuse for extracting Cu²⁺ from the buffered aqueous phase. First, metal ions were extracted from the buffered aqueous phase and then decomplexed with 0.1 M HCl. Before reuse, the receptor was neutralised with a base. As the results show in

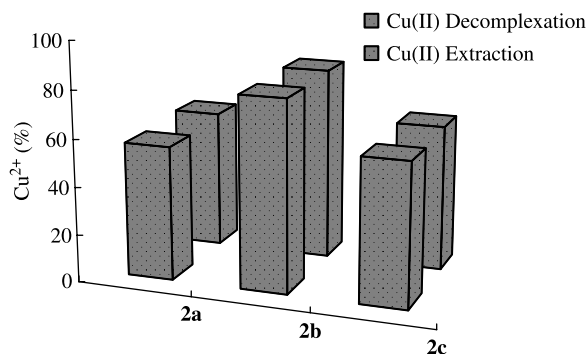


Figure 2. Comparison of Cu^{2+} extraction (%E) and decomplexation (%D) efficiencies of the receptors **2a–c**.

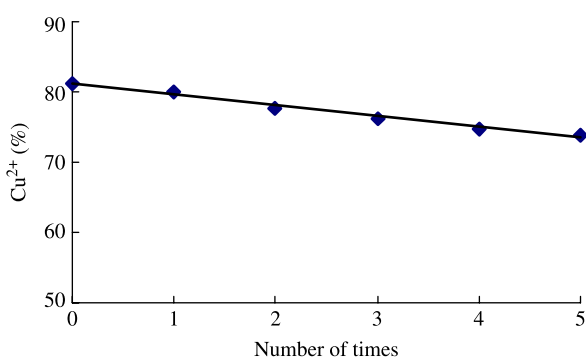


Figure 3. Reuse of receptor **2b** for the extraction of Cu^{2+} .

Figure 3, the receptor **2b** can be reused effectively for the extraction of Cu^{2+} and even after five times of reuse, the extraction efficiency of receptor **2b** did not suffer much.

Transport experiment involves complexation at the surface of the source aqueous phase and the organic layer, while decomplexation occurs at the other surface of the organic layer and the receiving aqueous phase. Hence, transport experiment is a continuous process of metal extraction and metal decomplexation. A slow decrease in the concentration of metal ions in the source aqueous phase signifies the inability of a receptor to extract ions from the aqueous phase. On the other hand, a

slow increase in the concentration of ions in the receiving aqueous phase reflects a problem in the decomplexation of metal ions. We examined the transport ability of receptors **2a–c** by taking a carrier in the chloroform layer and metal ions in the aqueous buffer phase (source phase). In these transport experiments, the concentration of the carrier in the membrane and of the metal ions in the buffer source phase (pH = 4.6) was 1 mM and 5 mM, respectively. Hydrochloric acid (pH = 1) was used for the receiving phase. The concentration of Cu^{2+} was monitored in both aqueous compartments (i.e. both in the source phase and in the receiving phase) with atomic absorption spectroscopy. To compare the receptor properly, it is necessary to find out the time dependence of metal level in all three phases. Therefore, the metal ion transported was monitored as a function of time, i.e. each reading was taken after a time interval of 2 h for 12 h and then after 24 h. This makes it possible to estimate the rate of transport of Cu^{2+} ion and also the time required to complete the experiment (Figure 4). The data show the average transport rate of two independent experiments and conclude that transport rate is very fast for 4 h and then after next 4 h (i.e. after total 8 h) most of Cu^{2+} are transported. The maximum transport of Cu^{2+} was observed with **2b**. This means that among the present set of receptors, the better extractant acts as a better transporter of Cu^{2+} .

To establish the role of calix[4]arene part of receptor **2b**, we synthesised the compound **3** as shown in Scheme 2. The compound **3** resembles the single pod of receptor **2b**. The 2 mM concentration of compound **3** was taken for the transport experiment of metal ions (2 mM concentration of compound **3** has the same number of binding sites as that of 1 mM concentration of **2b**). The results of Cu^{2+} ion transport experiment with compound **3** are shown in Figure 5.

Based on the analysis of the source phase and the receiving phase of the transport cell containing compound **3**, it can be concluded that the host is capable of extracting metal ions, but the release of metal ions is poor. We also observed some suspension in the organic layer of transport cell, indicating that receptor **3** precipitated out of the organic layer upon complexation

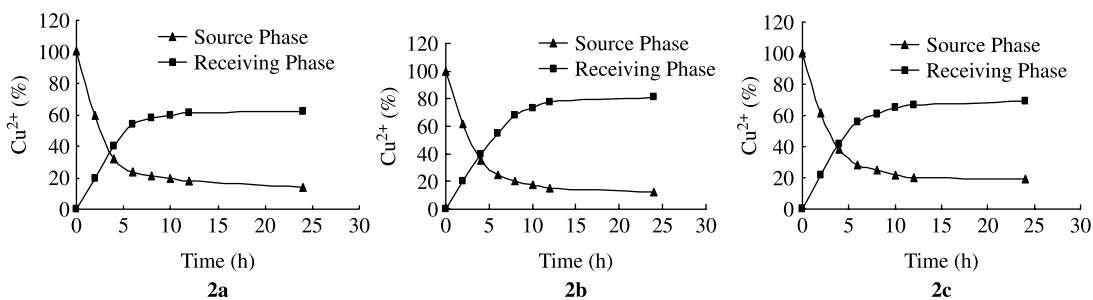
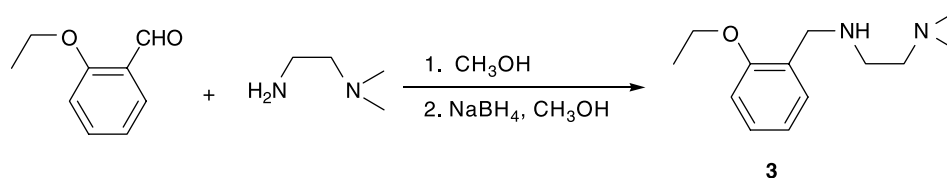


Figure 4. Transport rate of Cu^{2+} as a function of time.



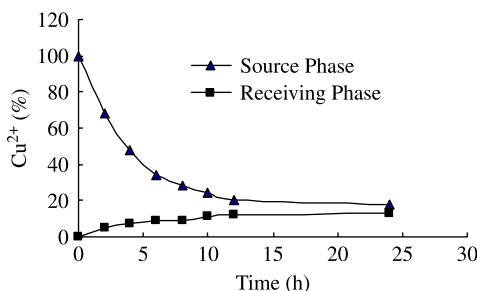
Scheme 2.

with metal ion. 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 **2b**, which has the same type of binding sites as that of compound **3**. With other receptors (**2a** and **2c**) we did not find any precipitates in the organic phase upon metal ion complexation. Consequently, the presence of calix[4]arene unit in the designs of a receptor is responsible for imparting organic solubility of metal complexes in all these cases.

The structure of complex formed between receptor **2b** and Cu^{2+} was determined by energy minimisation studies with MacroModel v 9.0 using Merck molecular force field (MMFFs) (Figure 6) (11). The structure reveals the binding of Cu^{2+} in the cavity of receptor **2b** is through two nitrogens and one oxygen of one pod and via only one oxygen of the other pod. Thus, two oxygens and two nitrogens combine to provide a square planar coordination sphere to Cu^{2+} , and hence the complex exhibits 1:1 stoichiometry.

Conclusion

In conclusion, a new set of *p-tert*-calix[4]arene-based receptors are synthesised in cone conformation. The receptor **2b** bearing four sp^3 nitrogens has a greater ability to extract Cu^{2+} than the receptor **2a** that has two sp^3 and two oxygen donors. Receptor **2b** also has a greater ability to extract Cu^{2+} than **2c** that has two sp^3 nitrogens along with two sp^2 nitrogen donors. Receptor **2b** was successfully reused to extract Cu^{2+} from the buffered aqueous phase, and despite being reused five times the extraction efficiency of receptor **2b** remained

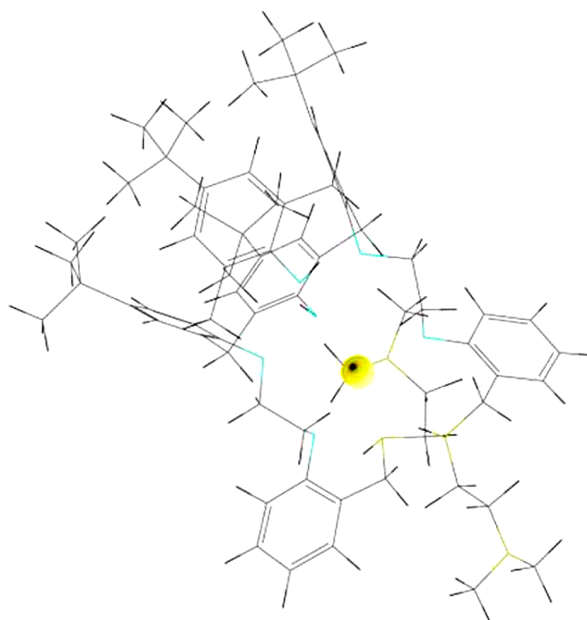
Figure 5. Cu^{2+} ion transport rate of receptor **3**.

almost the same. Though all these receptors have the ability to transport Cu^{2+} ion from the aqueous buffered source phase to the aqueous receiving phase, the best results are obtained with receptor **2b**. Thus, the better extractant acts as a better transporter of Cu^{2+} .

Materials and methods

General

All the solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. Thin layer chromatography (TLC) was performed on glass sheets pre-coated with silica gel (Kieselgel 60 PF254, Merck). The ^1H - and ^{13}C -NMR spectra were performed in CDCl_3 with tetramethylsilane (TMS) as an internal reference on a Bruker 400 NMR spectrometer which operated at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei. The chemical shifts were reported as δ values (ppm) relative to TMS. Fast-atom bombardment (FAB) mass spectrum and high-resolution mass spectra

Figure 6. Energy minimised structure of the complex formed between receptor **2b** and Cu^{2+} obtained by MacroModel calculation.

(HRMS) were obtained on a JEOL JMS-AX 505WA mass spectrometer.

Compound 2a

A solution of dialdehyde **1** (47.2 mg, 0.05 mmol) and ethanolamine (9.0 mg, 0.15 mmol) in CH₃CN was stirred at room temperature for 1 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the solvent was evaporated, and the crude product was dissolved in a methanol and tetrahydrofuran (THF) solvent mixture. The imine linkages of the product were reduced with an excess of NaBH₄ (194 mg, 5 mmol). The reaction mixture was stirred for 3 h. The solvent was evaporated, and water was poured into the content of the reaction mixture. After neutralisation with 1 M HCl, the organic material was extracted with dichloromethane (3 × 50 ml). The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the residue was recrystallised from the acetonitrile methanol solvent mixture to obtain semisolid pure material (43 mg, 83%): ¹H NMR (CDCl₃, 400 MHz) δ 1.03 (s, 18H, CH₃), 1.16 (s, 18H, CH₃), 2.72 (t, 4H, CH₂, *J* = 5.2 Hz), 3.29 (d, 4H, ArCH₂Ar, *J* = 12.8 Hz), 3.49 (t, 4H, CH₂, *J* = 5.2 Hz), 4.22–4.29 (m, 12H, CH₂, ArCH₂Ar), 4.59 (s, 4H, CH₂), 6.61 (d, 2H, Ar, *J* = 8.0 Hz), 6.85 (t, 2H, Ar, *J* = 5.2 Hz), 6.91 (s, 4H, Ar), 6.94 (s, 4H, Ar), 7.10 (t, 2H, Ar, *J* = 8.0 Hz), 7.24 (d, 2H, Ar, *J* = 8.0 Hz), 8.58 (broad, 2H, -NH); ¹³C NMR (CDCl₃, 100 MHz) δ 31.1 (CH₃), 31.5 (CH₃), 32.02 (ArCH₂Ar), 33.8 (Me₃C), 34.1 (Me₃C), 43.6 (CH₂), 60.9 (CH₂), 63.6 (CH₂), 66.6 (CH₂), 74.6 (CH₂), 110.9 (Ar), 120.7 (Ar), 125.4 (Ar), 125.9 (Ar), 128.1 (Ar), 129.2 (Ar), 130.0 (Ar), 130.2 (Ar), 133.4 (Ar), 142.4 (Ar), 147.7 (Ar), 149.3 (Ar), 149.4 (Ar), 156.6 (Ar); HRMS (FAB) calculated for C₆₆H₈₇N₂O₈ (M + H⁺): 1035.6462, found: 1035.6462.

Compound 2b

Compound **2b** was prepared by the same procedure that was adopted for the synthesis of compound **2a**, except that compound **1** (0.05 mmol, 47.2 mg) was chosen along with *N,N*-dimethylethylamine (0.15 mmol, 13.2 mg). The final purification by recrystallisation from the acetonitrile methanol solvent mixture afforded a semisolid product (47.8 mg, 88%): ¹H NMR (CDCl₃, 400 MHz) δ 1.05 (s, 18H, CH₃), 1.17 (s, 18H, CH₃), 2.15 (s, 12H, NCH₃), 2.64 (t, 4H, CH₂, *J* = 6.4 Hz), 2.69 (t, 4H, NCH₂, *J* = 6.4 Hz), 3.30 (d, 4H, ArCH₂Ar, *J* = 12.8 Hz), 4.23–4.31 (m, 12H, CH₂, ArCH₂Ar), 4.60 (s, 4H, CH₂), 6.62 (d, 2H, Ar, *J* = 8.0 Hz), 6.90 (t, 2H, Ar, *J* = 6.8), 6.93 (s, 4H, Ar), 6.96 (s, 4H, Ar), 7.10 (t, 2H, Ar, *J* = 8.0 Hz), 7.25 (d, 2H, Ar, *J* = 8.0 Hz), 8.60 (broad, 2H, NH); ¹³C NMR (CDCl₃, 100 MHz) δ 31.1 (CH₃), 31.6 (CH₃),

32.02 (ArCH₂Ar), 33.8 (Me₃C), 34.1 (Me₃C), 45.5 (CH₃), 61.0 (CH₂), 62.5 (CH₂), 65.1 (CH₂), 66.6 (CH₂), 74.6 (CH₂), 111.0 (Ar), 120.7 (Ar), 125.4 (Ar), 125.9 (Ar), 128.1 (Ar), 129.2 (Ar), 130.0 (Ar), 130.2 (Ar), 133.4 (Ar), 142.4 (Ar), 147.7 (Ar), 149.3 (Ar), 149.4 (Ar), 156.6 (Ar); HRMS (FAB) calculated for C₇₀H₉₇N₄O₆ (M + H⁺): 1089.7408, found: 1089.7408.

Compound 2c

A solution of dialdehyde **1** (47.2 mg, 0.05 mmol) and 2-(aminomethyl) pyridine (16.2 mg, 0.15 mmol) in CH₃CN was stirred at room temperature for 2 h. The progress of the reaction was monitored by TLC. When aldehyde was all consumed, one half of the solvent was evaporated, and the reaction mixture was kept in the refrigerator. A white-coloured material was separated on cooling. This was filtered, recrystallised from acetonitrile and dried under vacuum. The imine linkages of this product were reduced with an excess of NaBH₄ (388 mg, 10 mmol). The reaction mixture was stirred for 3 h. The solvent was evaporated and water was poured into the content of reaction mixture. After neutralizing with 1M HCl, the organic material was extracted with dichloromethane (3 × 50 ml). The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the residue that was purified by recrystallisation from acetonitrile methanol solvent mixture afforded the semisolid product (50.2 mg, 89%): ¹H NMR (CDCl₃, 400 MHz) δ 0.96 (s, 18H, CH₃), 1.13 (s, 18H, CH₃), 3.20 (d, 4H, ArCH₂Ar, *J* = 12.8 Hz), 4.24–4.28 (m, 16H, ArCH₂Ar, CH₂), 4.58 (s, 4H, CH₂), 6.79 (d, 2H, Ar, *J* = 8.0 Hz), 6.83 (s, 4H, Ar), 6.89 (s, 4H, Ar), 6.91 (t, 2H, Ar, *J* = 8.0 Hz), 7.04 (t, 2H, Ar, *J* = 6.0 Hz), 7.08 (d, 2H, Ar, *J* = 7.6 Hz), 7.28 (t, 2H, Ar, *J* = 8.0 Hz), 4.48 (t, 2H, Ar, *J* = 8.0 Hz), 7.72 (s, 2H, -OH), 8.01 (d, 2H, Ar, *J* = 7.6 Hz), 8.45 (d, 2H, Ar), 8.95 (broad, 2H, NH); ¹³C NMR (CDCl₃, 100 MHz) δ 30.8 (CH₃), 31.1 (CH₃), 31.6 (ArCH₂Ar), 33.8 (Me₃C), 34.1 (Me₃C), 61.0 (CH₂), 65.1 (CH₂), 66.6 (CH₂), 74.6 (CH₂), 111.0 (Ar), 120.7 (Ar), 121.8 (Ar), 125.4 (Ar), 126.0 (Ar), 128.1 (Ar), 129.2 (Ar), 130.0 (Ar), 130.2 (Ar), 133.4 (Ar), 136.5 (Ar), 142.4 (Ar), 147.7 (Ar), 149.3 (Ar), 149.4 (Ar), 156.6 (Ar), 161.9 (Ar); HRMS (FAB) calculated for C₇₄H₈₉N₄O₆ (M + H⁺): 1129.6782, found: 1129.6782.

Compound 3

Compound **3** was prepared by the same procedure that was adopted for the synthesis of compound **2a**, except that 2-ethoxybenzaldehyde (0.2 mmol, 30.0 mg) was taken along with *N,N*-dimethylethylamine (0.3 mmol, 26.4 mg). The reduction of imine linkage was performed

in MeOH. The evaporation of the solvent afforded a viscous product (33.3 mg, 75%). ^1H NMR (CDCl_3 , 400 MHz): δ 1.45 (t, 3H, CH_3 , $J = 6.8$ Hz), 2.20 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.43 (t, 2H, CH_2 , $J = 6.0$ Hz), 2.69 (t, 2H, CH_2 , $J = 6.0$ Hz), 3.82 (s, 2H, CH_2), 4.04–4.09 (m, 2H, CH_2), 6.84–6.94 (m, 2H, Ar), 7.21–7.31 (m, 2H, Ar). ^{13}C NMR (CDCl_3 , 100 MHz): δ 14.4 (CH_3), 45.3 (CH_3), 46.3 (CH_3), 49.3 (CH_2), 54.5 (CH_2), 58.9 (CH_2), 63.1 (CH_2), 110.9 (Ar), 120.2 (Ar), 122.5 (Ar), 128.3 (Ar), 129.6 (Ar), 131.5 (Ar). HRMS (FAB): $m/z = 223.1810$ (Calcd. $m/z = 223.1810$ for $\text{M} + \text{H}^+$).

Competitive solvent extraction (%E)

The percent extraction (%E) of the metal salt extracted from the aqueous acetate buffer solution (pH = 4.63) containing metal salts (1.0×10^{-3} M, 2.0 ml) to the chloroform layer containing a receptor (1.0×10^{-3} M, 2.0 ml) was determined at 25°C. The aqueous and organic mixtures were shaken vigorously for a few minutes in the test tubes guarded with septum and the mixtures were left to stand until phase separation was completed. Similarly, the blank analysis was performed by taking metal salts (1.0×10^{-3} M, 2.0 ml) dissolved in the aqueous acetate buffer solution (pH = 4.6) and 2.0 ml of neat chloroform. The concentration of the metal salts in the aqueous buffer solution was determined after extraction and also in blank analysis by an atomic absorption spectrometer. The percent extraction (%E) of metal salts was determined by the formula $\%E = (C_1 - C_2) \times 100/C_1$, where C_1 is the concentration of metal salts in the aqueous buffer solution in blank analysis, and C_2 is the concentration of metal salts remaining in the aqueous buffer solution after the extraction. The average value of three independent determinations is reported.

Decomplexation of metal ion (%D)

The percent decomplexation (%D) of the complexed metal salts from the chloroform layer (containing complex 2.0 ml) to hydrochloric acid was determined at 25°C. The chloroform layer of a competitive solvent extraction experiment separated from the aqueous layer was selected. This organic layer was shaken with 2.0 ml of hydrochloric acid (pH = 1.0), and the solution was kept undisturbed until complete separation had occurred. The concentration of metal salts in hydrochloric acid was determined by an atomic absorption spectrometer. The percent decomplexation (%D) of metal salts was determined by the formula $\%D = (C_2/C_1) \times 100$, where C_1 is the concentration of metal salts in the aqueous buffer solution in the blank analysis of

competitive solvent extraction experiment, and C_2 is the concentration of metal salts released to 0.1 M HCl. The average value of three independent determinations is reported.

pH-dependent transport experiment

Transport experiments were carried out by stirring the organic phase of a bulk liquid membrane cell at a constantly slow speed so that the interfaces between the organic membrane and two aqueous phases remained flat and well defined. The two aqueous phases were separated by the organic phase. An aqueous source phase (4.0 ml) containing Cu^{2+} (5×10^{-3} M) in acetate buffer (pH = 4.6) and a receiving phase (8.0 ml) containing HCl (pH = 1.0) were separated by the organic layer of chloroform (25 ml) containing a carrier (1×10^{-3} M). The concentration of the carrier in the transport cell containing compound **3** was 2×10^{-3} M. The metal ion concentrations in both the aqueous phases were monitored with an atomic absorption spectrophotometer. The average value of two independent determinations is reported.

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