Synthesis and characterization of new soluble phthalocyanines containing macrocycle units

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A soluble metal-free phthalocyanine 5 and its metal complexes (Zn, Ni, Co and Cu) 6, 7, 8 and 9 containing eight 16-membered tetrathiamonoaza macrocycles on peripheral substituent positions have been synthesized. The metal-free phthalocyanine 5 was synthesized from 4,5-bis[2-(1,4,10,13-tetraaza-7-clohexadecan-7-yl)ethoxy]phthalonitrile 4. The metal complexes 6, 7, 8 and 9 were prepared by a tetramerization reaction of the phthalonitrile derivative 4 with appropriate materials. Copper(II) phthalocyanine 9 was prepared by the reaction of 4,5-bis[2-(1,4,10,13-tetraaza-7-clohexadecan-7-yl)ethoxy]yl]2,1-dibromobenzene 3 with excess CuCN and dry quinoline. Liquid–liquid extraction of several heavy metal ions such as Ag+, Hg2+, Pb2+, Cd2+, Cu2+ and Zn2+ with compound 9 was also tested using picrate as the anion of the ion pair. The extraction avidity of 5 for Ag+ was found to be highest in the liquid–liquid phase extraction experiments. The new compounds were characterized by a combination of elemental analysis, UV–Vis, FT-IR, NMR and mass spectral data.

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1. Introduction

Supramolecular materials can be designed and created from simple molecular building blocks by self-assembly and self-organization using non-covalent interactions [1]. Phthalocyanines [2] have been employed extensively as subunits for the construction of functional materials since they exhibit special optical and electronic properties and self-organizing abilities to form columnar mesophases, Langmuir–Blodgett (LB) multilayers and aggregates in solution, or in the solid state [3]. The main forces that drive these self-assembly processes are the π–π stacking interactions between the aromatic rings. The introduction of either or both long aliphatic hydrocarbon chains or/and macrocyclic substituents at the periphery of the rigid phthalocyanine core can improve the organization properties of these molecules by exploiting either their mesogenic behavior [4] or the ability of their macrocyclic subunits to form complexes with different ions [5,6]. By contrast, hydrogen-bonding interactions have hardly been employed at all to self-assemble phthalocyanine molecules [7].

The solubility and ion-binding ability of phthalocyanines containing homo- and hetero-crowns are receiving considerable attention in view of their effect on the aggregation of the molecules [5,6]. It has been demonstrated that phthalocyanines substituted with four 15-crown–5 analogs are capable forming ion channels that allow the migration of alkali or alkaline earth ions [8]. Phthalocyanines with long alkyl or alkoxy groups as well as with crown ethers are also reported to form a new type of liquid crystals, namely the discotic mesophase [9].

Alkyl substitution increases the solubility of phthalocyanines, and the effect of bulky substituents is shown to be higher than that of smaller ones, e.g. methyl [10]. Substitution of a phthalocyanine with eight ethoxy hetero-crown moieties, therefore, is expected to enhance the solubility and improve the intermolecular stacking. In this work we report the synthesis and properties of new heterocrowns and their phthalocyanines with eight ethoxy-tetraazamoaza macrocycles. In addition, the extraction capability of assorted heavy metal ions with the metal-free phthalocyanine 5 is tested.

2. Experimental

2.1. Materials

Starting reagents were either purchased from Aldrich or, unless noted otherwise, prepared in the manner described in previous papers. We prepared 1,7,10,14-tetraaza-4-clohexadecane (2) [11] and 1,2-bis(2-idoethoxy)-4,5-dibromobenzene (1) [12] using literature procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques. Pentan-1-ol was distilled from sodium. All other reagents and solvents were of.

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reagent grade quality from commercial suppliers and were dried before use as described in the literature [13]. Silica gel (70–230 mesh) and Merck 90 active neutral alumina were used in the separation and purification of compounds by column chromatography with the indicated eluents.

2.2. Measurements

Melting points were determined with an electrothermal apparatus and were uncorrected. Routine 1H, 13C NMR and IR spectra were recorded on a Varian XL-200 spectrometer and a Perkin–Elmer Spectrum One spectrometer with the samples in KBr pellets, respectively. UV–Vis spectra were recorded on a model Shimadzu 1601 UV–Vis spectrometer using cells of 10 mm pathlength at room temperature. Mass spectra were measured on Micromass Quatro LC/ULTIMA LC–MS/MS spectrometers. The elemental analyses of the compounds were determined on a CHNS-932 LECO instrument. The metal contents of the metallophthalocyanines were determined with a Unicam 929 AA spectrophotometer in solutions prepared by decomposition of the metallophthalocyanines in conc. sulfuric acid and conc. nitric acid solution followed by digestion in conc. hydrochloric acid solution and deionized water.

2.3. Synthesis

2.3.1. Synthesis of 4,5-bis[{2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl}oxy]-1,2-dibromobenzene (3)

Compound 2 (5.96 g, 20 mmol) was dissolved in 300 mL of dry acetonitrile containing anhydrous Cs2CO3 (9.78 g, 30 mmol) and anhydrous NaI (0.45 g, 3 mmol), and purged under an argon atmosphere. The reaction mixture was refluxed at 100 °C for 3 h, at the same temperature. After adding 200 mL of NH3 (25%) into the reaction mixture, oxygen gas was passed through the solution for 48 h. Then it was washed with water until the filtrate was neutral, and dried in vacuo. The crude product was placed in a Soxhlet extractor and extracted with chloroform for 3 days. The extract was evaporated to dryness under reduced pressure and dissolved in 25 mL of dry methanol and then placed inside the refrigerator at −18 °C for several hours. Light brown crystals were filtered off and dried in vacuo. Yield: 2.72 g (44%), m.p. = 226–227 °C. Anal. Calc. C34H54N4O2S8 (807.31): C, 50.58; H, 6.74; N, 6.94; S, 31.77; Found: C, 50.93; H, 6.41; N, 7.23; S, 31.60%. IR (KBr): νmax (cm−1) = 3049 (C–H aromatic), 2920–2849 (CH2), 2234 (C≡N), 1596–1506 (aromatic C=C), 1255 (Ar–O–C), 1100, 960, 750, 685. 1H NMR (ppm, CDCl3): δ = 7.78 (s, 2H, ArH), 4.25 (t, 4H, ArOCH2), 3.14–2.87 (m, 12H, CH2CH2), 2.10–1.96 (m, 4H, CH2–CH2–CH2–). 13C NMR (ppm, CDCl3): δmax = 151.8 (ArCO), 118.4 (ArCH), 114.9 (C=≡N), 109.6 (ArCO), 53.6 (CH2NCH2), 51.4 (NCH2CH2O–Ar), 32.7–32.4 (–N–CH2–CH2–S–CH2–), 31.3–30.9 (–S–CH2–CH2–S–CH2–), 28.7 (CH2–CH2–CH2–). MS (ES positive) m/z: 807.4 [M]+.

2.3.4. Synthesis of phthalocyaninate zinc(II) (6)

Compound 4 (0.81 g, 1 mmol), Zn(OAc)2·2H2O (55 mg, 0.25 mmol) and 1.5 mL of dry quinoline were placed in a Schlenk tube under an argon atmosphere. The reaction mixture was heated gently to 90 °C for 1 h and then it was heated and stirred at 150 °C for 4 h. After cooling to room temperature, 10 mL of methanol/diethyl ether (1:1, v/v) was added and stirred for 45 min. The dark green metal-free phthalocyanine derivative was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.936 g (49%), m.p. > 300 °C. Anal. Calc. C34H42Zn2N4O2S8 (810.32): C, 50.55; H, 6.80; N, 6.94; S, 31.75; Found: C, 50.87; H, 6.47; N, 6.65; S, 31.98%. IR (KBr): νmax (cm−1) = 3394 (N–H), 3066 (Ar–H), 2917–2849 (CH2), 1634 (C=C–H), 1544–1508 (C=C), 1380, 1224–1201 (Ar–O–C), 1121, 1048–1017 (CH2–O), 946, 658. 1H NMR (ppm, DMSO-d6): δmax = 8.17 (s, 8H, ArH), 4.10 (t, 16H, ArOCH2), 3.92–2.93 (m, 48H, CH2O–Ar), 2.90–2.69 (m, 128H, CH2SCH2), 1.98–1.67 (m, 16H, CH2–CH2–CH2–). MS (ES positive) m/z: 3231.4 [M]+.

2.3.5. Synthesis of phthalocyaninate nickel(II) (7)

A mixture of compound 4 (0.81 g, 1 mmol), Ni(OAc)2·4H2O (75 mg, 0.30 mmol) and DBU (152 mg, 1 mmol) was refluxed under
an argon atmosphere in pentan-1-ol (20 mL) for 24 h. The cooled suspension was poured into MeOH (60 mL) and the precipitate was centrifuged, washed with EtOAc, EtOH, H₂O and diethyl ether, and dried in vacuo. Further purification was carried out using column chromatography, silica gel, CHCl₃/MeOH, (90:1 v/v). Yield: 0.83 g (47%), m.p. > 300 °C. Anal. Calc. for C₁₇₆H₂₁₆N₁₆O₈S₄Ni: C, 49.68; H, 6.62; N, 6.82; S, 31.20; Ni, 1.79. Found: C, 49.87; H, 6.45; N, 6.58; S, 31.49; Ni, 1.93%. IR (KBr): 3077–2870 and 1640 cm⁻¹. 1H NMR (ppm, DMSO-d₆): δ = 7.93 (s, 8H, ArH), 10.40 (16H, ArOCH₂), 2.30–2.84 (m, 48H, NCH₂H₂), 2.67, 2.82 and 3.19 (s, 8H, ArNH). MS (ES positive) m/z: 3289.1 [M⁺]⁺.

2.3.6. Synthesis of phthalocyaninato cobalt(II) (8)

A mixture of compound 4 (0.81 g, 1 mmol), urea (105.6 mg, 1.76 mmol), Cu(OAc)₂·4H₂O (0.75 mg, 0.30 mmol), a catalytic amount of (NH₄)₂MoO₄ (40 mg) and quinoline (2 mL) was kept at 200–210 °C under an argon atmosphere for 6 h. The mixture was poured into CH₂CN (40 mL) and the precipitate was filtered off after 1 h stirring. The crude product was washed sequentially with EtOAc, EtOH, H₂O and acetone, and dried in vacuo. The cobalt(II) phthalocyanine was purified by column chromatography, neutral alumina, CHCl₃/MeOH, (100:1 v/v). Yield: 0.39 g (47%), m.p. > 300 °C. Anal. Calc. for C₁₇₆H₂₁₆N₁₆O₈S₄Co: C, 49.46; H, 6.79; N, 7.07; S, 31.46; Co, 1.58%. IR (KBr): v max (cm⁻¹) = 3050 (Ar–H), 2975–2889 (CH₂), 1625 (C=O), 1600–1575 (C=O), 1440 (C–H), 1365, 1244–1228 (Ar–O–C), 1120–1025 (CH₂–O), 960, 845, 656. 1H NMR (ppm, DMSO-d₆): δ = 7.96 (s, 8H, ArH), 10.42 (16H, ArOCH₂), 2.35–2.90 (m, 48H, NCH₂H₂), 2.87–2.69 (m, 128H, ArCH₂), 2.10–1.82 (m, 16 H, CH₂CH₂CH₂), UV/Vis (pyridine) λ max (log ε) = 695 (4.77), 640 (4.02), 606 (3.38), 369 (4.41), 322 (4.84). MS (ES positive) m/z: 3284.1 [M⁺]⁺.

2.3.7. Synthesis of phthalocyaninato copper(II) (9)

A mixture of 3 (0.915 g, 1 mmol), CuCN (0.269 g, 3 mmol) and quinoline (2.5 mL) was heated under argon at 215 °C for 24 h. At the end of this period, the mixture was cooled to room temperature and 30 mL of ethanol was added to this mixture, was centrifuged, washed with EtOAc, EtOH, H₂O and diethyl ether, and the crude product was heated in vacuo dried. The crude product was heated in 44% yield after purification. The LC/ES mass spectrum of compound 5 in chloroform. Then equal volumes of both the metal picate solutions and compound solution were added into plastic bottles, closed and then mechanically shaken for 5 h by a shaker at 25 ± 1 °C. Finally we took the aqueous phase and measured the absorbance at the maximum wavelength of each metal picate solution. For each combination of host and metal picate, the picate extraction was conducted on three different samples and the average value of percent picate extracted, with a standard deviation, was calculated. The picate extraction results are presented in Table 1. In the absence of host, a blank experiment, no metal ion picate extraction was detected. The extractability was determined by using the equation below:

\[
E(\%) = \frac{[A_{\text{before}} - A_{\text{after}}]}{A_{\text{before}}} \times 100
\]

where A before is the absorbance in the absence of ligand and A after denotes the absorbance in the aqueous solution phase after extraction.

### Table 1

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Extractability of the metal-free phthalocyanine 5 (%)</th>
<th>λ max (nm) of metal picate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>93.2 ± 0.1</td>
<td>354</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>64.7 ± 0.1</td>
<td>358</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>48.4 ± 0.1</td>
<td>360</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>70.5 ± 0.1</td>
<td>362</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>43.6 ± 0.1</td>
<td>352</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>37.3 ± 0.1</td>
<td>347</td>
</tr>
</tbody>
</table>

* a Temperature 25 ± 1 °C, aqueous phase (10 mL), [picate] = 2.0 × 10⁻³ M, organic phase (chloroform, 10 mL), [extractant] = 2.0 × 10⁻³ M.

* b Average and standard deviation for three independent measurements.

### 3. Result and discussion

The synthetic routes to 3–9 are exhibited in Schemes 1 and 2. We report here the synthesis and structural properties of a series of novel metal-free and metallophthalocyanines. The dibromo derivative 3 was obtained by a substitution reaction of compound 2 and 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene 1 in the presence of anhydrous Cs₂CO₃ and anhydrous NaI in dry acetonitrile at reflux temperature for 6 days under argon. The crude product was purified by column chromatography on silica gel, chloroform:pentane:ether:methanol (6:3:1) to give 3 in 69% yield. In the 1H NMR spectrum of 3, the signals corresponding to the N–H protons in the precursor compound 2 disappeared after the macrocyclization reaction. The resonance peaks are in good agreement with the proposed structure in the 1H NMR spectrum of 3, being at δ = 4.14, 3.06–2.92 and 2.85–2.74 ppm corresponding to Ar–O–CH₂, N–CH₂ and CH₂–S–CH₂ groups respectively. In the 13C NMR spectrum, the existence of new carbon resonances at δ = 148.3, 120.1 and 114.2 ppm are also in good accord with the proposed structure. Further, the infrared data of 3 give sufficient support for the desired product formation. In the IR spectrum of compound 3, the presence of characteristic vibrations belonging to (=CH aromatic ring), (aliphatic CH₂) and (C–Br) were observed at 3056, 2977–2870 and 645 cm⁻¹, respectively. The LC/ES mass spectrum of 3, which shows a molecular ion peak at m/z = 915.1 [M⁺]⁺, confirms the proposed formula.

Substitution of the bromo groups in 3 by cyanide in a Rosen-mund-von Braun reaction using three equivalents of CuCN [14], affords the corresponding phthalonitrile 4 in 44% yield after purification by column chromatography on silica gel with chloroform:pentane:ether:ethanol (7:3:1) solvent mixture. The critical point in this route is to isolate the diyano derivative, which was...
accomplished by keeping the concentration of the reactants sufficiently low and by making use of a moderately high boiling point solvent to avoid the formation of copper phthalocyanine [15]. In the IR spectrum of 3, the signal at 645 cm\(^{-1}\) that was for the C–Br bond vanished and a new peak arose in the IR spectrum of 4 at 2234 cm\(^{-1}\), which was attributed to the dicyano groups. The rest of the spectrum is closely similar to that of the precursor dibromo derivative, including the characteristic vibrations of 3. The \(^1\)H NMR spectrum of 4 was recorded after dissolution in CDCl\(_3\) at room temperature, and exhibited the expected signals indicating the integrity of 4 in that solvent. The spectrum was almost identical with that of 3, as expected. In the proton-decoupled \(^{13}\)C NMR spectrum of compound 4, the presence
of a signal at \( \delta = 114.9 \) ppm, attributable to \( \text{C} = \text{N} \) groups, indicates that the conversion has occurred. Compound 4 displayed the expected molecular ion peak in its mass spectrum at \( m/z = 807.4 \) [M].

The self-condensation of the dicyano compound 4 in a high-boiling solvent, such as dry pentan-1-ol, in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a dry argon atmosphere afforded the metal-free phthalocyanine 5 in 49% yield as a dark green solid. A diagnostic feature of the formation of 5 from 4 is the disappearance of the sharp vibration of the dicyano groups at 2234 cm\(^{-1}\). A comparison of the IR spectra obtained on refluxing solvent, such as dry pentan-1-ol, in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a dry argon atmosphere afforded the metal-free phthalocyanine 5 in 49% yield as a dark green solid. A diagnostic feature of the formation of 5 from 4 is the disappearance of the sharp vibration of the dicyano groups at 2234 cm\(^{-1}\). The stretching vibrations at 3394 cm\(^{-1}\) for 5 can be attributed to the N–H bond of the inner core of the metal-free phthalocyanine. A \(^{1}H\) NMR investigation of compound 5 provided the characteristic chemical shifts for the expected structure. The inner core protons of compound 5 could also be observed at \( \delta = 3.96 \) ppm with a broad signal. In the \(^{13}C\) NMR spectrum of compound 5, all the signals are identical to those of the precursor dicyano derivative 4 except for the dicyano carbon atoms. The peak related to \( \text{C} = \text{N} \) groups in the \(^{13}C\) NMR spectrum of 4 vanished in the case of the metal-free phthalocyanine 5. Other peaks in the \(^{13}C\) NMR spectrum resembled those of the precursor compound 4. The molecular ion of 5 was observed at \( m/z = 3231.4 \) [M] and was in accord with the suggested structure.

Metallophthalocyanines 6, 7 and 8 have been prepared from the dicyano derivative 4 and the appropriate metal salts in the required solvents and catalysts under an argon atmosphere in yields of 62%, 73% and 47%, respectively. A comparison of the IR spectra obtained for 4 and 6, 7 and 8 confirmed the conversion of the \( \text{C} = \text{N} \) groups into the characteristic skeleton of phthalocyanine. In this case, the \( \text{C} = \text{N} \) band at 2234 cm\(^{-1}\) of compound 4 disappeared and \( \text{C} = \text{N} \) stretching vibrations of the inner core of the metallophthalocyanines 6, 7 and 8 appeared at 1618, 1624, 1625 cm\(^{-1}\), respectively. In the \(^{13}C\) NMR spectrum of compound 4, the presence of a signal at \( \delta = 114.9 \) ppm, attributable to the \( \text{C} = \text{N} \) groups, vanished in the case of complexes 6, 7 and 8. The \(^{13}C\) NMR and \(^{1}H\) NMR spectra of 6, 7 and 8 were almost identical with that of the metal-free phthalocyanine 5. The elemental analyses and LC/ES mass spectral data of all the metallophthalocyanines (6–8) were consistent with the proposed structures. The molecular ion clusters [M+1]\(^{+}\) for metallophthalocyanines 6, 7 and 8, at 3295.8, 3284.1, and 3289.1, respectively, were found by the ES/MS technique, together with some reasonable fragment ions.

Copper(I) phthalocyanine 9 has been synthesized directly from the dibromo derivative 3 and CuCN in a high-boiling solvent such as quinoline. The crude product was washed several times with ethanol to remove the unreacted starting material and was subsequently treated with a solution of NaCN to separate the excess CuCN. The yield of the crude product was only moderate (33%), and the purification steps were tedious and required a final chromatography on neutral alumina using chloroform:methanol (100:1) as the eluent. A comparison of the IR spectra obtained on 3 and 9 confirmed the conversion of the bromo groups into the characteristic skeleton of phthalocyanine. In this case, the C–Br band at 645 cm\(^{-1}\) disappeared and C–N stretching vibrations at 1620 cm\(^{-1}\) appeared. The mass spectrum of 9 was measured by the LC/ES MS technique and the complex displayed a peak corresponding to [M+1]\(^{+}\) at \( m/z = 3293.9 \). Elemental analysis data were also in good accord with the proposed formula.

The electronic absorption spectrum of the metal-free phthalocyanine 5 in chloroform at room temperature is shown in Fig. 1. It displayed a split Q-band as expected and there are two strong bands in the Soret region [16]. The split Q-band, characteristic of metal-free phthalocyanines, is observed for 5 at \( \lambda_{\text{max}} = 712 \) and 672 nm with a shoulder at 649 nm, indicating monomeric species; monomeric species with \( D_{2h} \) symmetry shows two intense absorptions at around 700 nm [17]. Such split Q-band absorptions in
chloroform are due to the $\pi \rightarrow \pi^*$ transition of this fully conjugated 18 $\pi$ electron system [17d, 18]. The zinc(II) 6, nickel(II) 7, cobalt(II) 8 and copper(II) 9 phthalocyanine complexes showed the expected absorptions (Figs. 1 and 2), with the main peaks of the Q- and B-bands appearing at $\lambda_{\text{max}}$ = 694, 695, 687 nm and 292, 322, 313, 315 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with $D_{4h}$ symmetry [5b, 10], where a single band of high intensity in the visible region is observed. Upon dilution (ca. $3.5 \times 10^{-5}$ M) the absorption spectra of these compounds displayed significant changes in band positions and molar absorptivities [19]. Increasing the concentration (1 $\times$ $10^{-5}$ M to 3.5 $\times$ $10^{-5}$ M) led to aggregation, which is easily monitored by the position of the Q-band, which shifted to shorter wavelengths and showed a decrease in the molar absorption coefficient.

3.1. Solvent extraction of heavy metal cations

Polythioether crowns are well-known to bind soft cations [20] while oxygen-containing crowns are ideally suited for the ligation of hard cations [21]. The heavy metal ion-binding property of compound 5, having tetrathia-monoaza-16-crown-5 units, was estimated by solvent extraction of heavy metal picrates from the aqueous to an organic phase (Table 1). As can be seen in Table 1, the highest extraction avidity of 5 was determined as 93.2% for Ag$^+$. As expected, the obtained extraction values for Ag$^+$, Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$ were high. This is because sulfur containing ligands are especially appropriate for complexation with heavy metal cations such as Ag$^+$, Cd$^{2+}$ and Hg$^{2+}$ due to the softness of sulfur [20] and the size match between the cation and host cavity [22]. On the other hand, the metal-free phthalocyanine core has to be taken into consideration for the extraction process. There are many articles on the metal extraction properties of metal-free phthalocyanines [23] and the highest extraction affinity was determined for Ag$^+$. Although the extraction studies were not conducted under the same conditions, the extraction avidity of 5 in the case of Ag$^+$, Cd$^{2+}$ and Hg$^{2+}$ cations are somewhat higher than those of previously studied polymeric phthalocyanines which have acrylic polythio ether moieties [24]. The higher extraction avidity might be due to the macrocyclic effect. In the case of Cu(II) and Zn(II), the size of the 16-membered macrocyclic cavity of 5 is too large to accommodate the metal ion, which leads to the poorer extraction of these metals with this reagent.

4. Conclusion

In this work, we describe the synthetic procedure and characterization of new soluble phthalocyanines substituted with eight tetrathiamonoaza macrocycles through ethoxy bridges. In addition, the heavy metal cation-binding property of 5 was evaluated using a solvent extraction technique and compared to our earlier works. The extractants from our earlier works in the case of Ag$^+$, Cd$^{2+}$ and Hg$^{2+}$ cations have lower cation-binding capacities than that in this work. Picrate was used as the counter anion. The cation-binding avidity of 5 for Ag$^+$, amongst the heavy metals, was found to be the highest.

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