Probing optical recognition of metal ions with employment of cationic dye-calix[4]arene supramolecular complexes

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Dedicated to Professor Richard A. Bartsch

DOI: http://dx.doi.org/10.3998/ark.5550190.0011.711

Abstract
Optical sensing of metal ions using calixarenes with covalently attached chromophores (fluorophores) has attracted considerable attention of researchers. However, the alternative approach involving host-guest complexes of calixarenes with dyes in metal recognition has been scarcely explored. In this work, addition of different metal cations to the aqueous solutions for solvent extraction of a cationic dye *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide by calix[4]arenes containing lower-rim proton-ionizable groups was found to produce significant effect on the absorption and fluorescence spectra of the organic phases. The observed spectral changes are attributed to co-extraction of the two substrates via formation of supramolecular complexes dye-calixarene-metal cation.

Keywords: Optical recognition, metal ions, calix[4]arenes, cationic dyes, fluorescence, absorption

Introduction

Selective recognition of metal ions, especially hazardous and toxic ones, is of immense importance to many areas of science, technology and ecology. During the last decade, optical sensing of metal ions based on their complexation with various macrocyclic receptors containing covalently attached chromophore (fluorophore) moieties received significant attention of researchers.[1] Among those, calixarene-based photometric reagents showed a lot of promise.[2] For example, fluorogenic calix[4]arene derivatives with dansyl units incorporated in the pendent proton-ionizable groups were found to provide selective and efficient optical recognition of such

heavy toxic metal ions as Hg^{2+},[3a,3b] Pb^{2+},[3c,3d] Cs^{+} and Tl^{+}.[3b,3e] However, this methodology has definite limitations. Thus, it requires synthetic efforts for covalent immobilization of a dye fragment to the metal receptor. Also, the amplitude of spectral changes induced by ion coordination, which determines sensitivity of the method, depends significantly on the structural factors (the chromophore attachment site, tether identity and length, etc.).

To avoid these complications, instead of covalent attachment, an optical probe may be assembled with an ion-selective receptor by means of intermolecular forces, including hydrogen bonding, π-π and hydrophobic interactions. Such an approach is attractive since not only it eliminates extra steps in synthesis, but it also allows for employment of combinatorial method: variation of dyes with the same ligand (or *vice versa*) may create libraries of ion-sensitive ensembles.[4] Functionalized calixarenes - macrocyclic receptors containing pendent functional groups on the π-electron-rich aromatic metacyclophane framework – are capable of various intermolecular interactions, which determines their propensities for "hosting" both metal cations[5] and organic molecular and ionic species, in particular, dyes.[6] This makes calixarenes appropriate ligands for exploring this alternative approach to sensing of metal ions.

Metal cation interaction with a supramolecular ensemble of the receptor and dye may be expected to proceed via different mechanisms. One of the possible ways is competitive complexation where the dye plays the role of an auxiliary substrate. Formerly, this idea was successfully implemented by Shinkai and others in the development of competitive assays for recognition of N-alkylammonium cations, *e.g.*, acetylcholine and cationic surfactants, by host-guest complexes of water-soluble p-sulfonatocalixarenes and resorcinarenes with cationic dyes.[7] The authors demonstrated that an analyte cation can displace the cationic dye from the calixarene cavity once the geometry and coordination modes of the two competing species are similar. The reaction is accompanied by significant changes in the fluorescence (absorption) spectrum of the optical probe. (Similar approach was utilized in selective recognition of various anions by ensembles of chelators with anionic dyes).[8] At the same time, only limited information is available for such competitive optical sensing of spherical metal cations with involvement of host-guest complexes of calixarenes with dyes. Thus, Nau et al. found that in complexation with a calix[4]arene containing four upper-rim sulfonate groups, different metal ions can displace encapsulated in the host cavity 2,3-diazabicyclo[2.2.2]oct-2-ene, which produces a sharp increase of this molecule fluorescence.[9] Such a reaction may be presented schematically as shown in Figure 1.

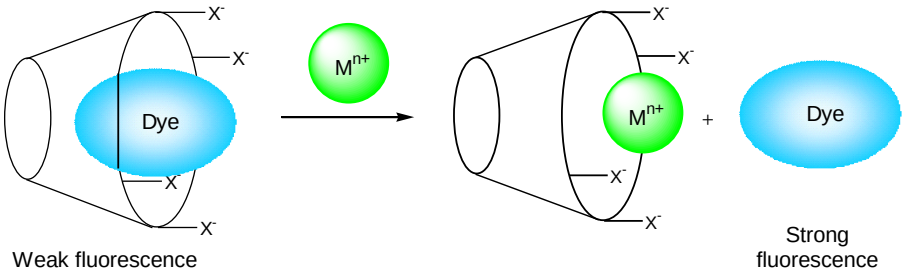

Figure 1. Schematic presentation of the reaction for a competitive assay fluorescent dye-calixarene for optical recognition of metal ions (shown for an upper-rim functionalized calixarene).

An alternative mechanism of optical sensing of metal ions using receptors with non-covalently bound dyes consists of formation of three-component supramolecular structures dye-receptor-targeted cation. In particular, assembly of copper-selective chelators with different fluorescent probes and Cu^{2+} achieved in the presence of surfactants, in micelles, allowed for sensing microconcentrations of this metal ion.[10] However, formation of such ternary complexes with participation of calixarenes has not been reported previously, to the best of our knowledge.
It should be mentioned that overall, the possibilities of employment of supramolecular ensembles calixarene-dye in optical recognition of metal ions have been scarcely explored. The reported studies[9] were limited to the calixarene derivative containing metal binding sites on the upper (wider) rim which also serves the gate for an optical probe entering the ligand aromatic cavity. Competition between a metal cation and dye for coordination with the ligand (Figure 1) is the only sensing mechanism expected for such system. In contrast, use of lower rim-functionalized calixarenes that offer separate binding sites for the two substrates (aromatic cavity for a dye and donor groups on the narrow rim for a metal ion) may provide more options. In complexation with different metal ions, such ionophores tend to adopt particular conformations. Conformational organization of the calixarene by a metal ion may shape the ligand cavity inappropriately for inclusion of the optical probe. This would encourage competition between the metal and dye for complexation with the receptor. Alternatively, encapsulation of a dye in the calixarene cavity may preorganize the ligand in the conformation conducive to metal cation coordination with the lower-rim donor groups. As a result, a ternary complex dye-calixarene-metal ion will be formed.

In this paper, we present a study of complex formation of calix[4]arene derivatives **1**-**4**[11] containing pendent donor groups on the lower rim with a stilbene cationic dye, *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide **5**, and assessment of applicability of these supramolecular ensembles for optical recognition of various metal cations in aqueous solutions by means of solvent extraction. Proton-ionizable ligands used herein, structural analogs **1**[11a] and **2**[11b] with two and **3**[11c] with one lower-rim *N*-(trifluoromethylsulfonyl)carboxamide group, developed by Bartsch and co-workers, are known for their extraction propensities towards alkali

metal cations (AMC), Pb^{2+}, Hg^{2+} and other metal ions.[11a,11b,12-14] The ability of dye **5** to form host-guest complexes with calix[n]arenes was reported earlier by the Shinkai research group.[7c]

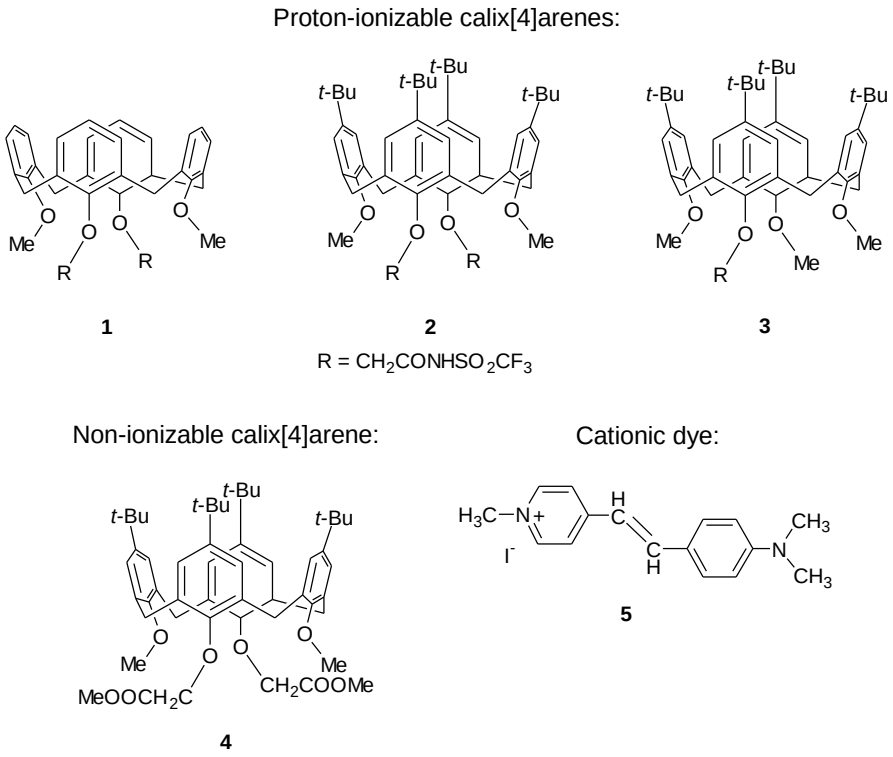

Figure 2. Calix[4]arenes **1**-**4** and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide dye, **5**.

Results and Discussion

In the earlier study,[7c] cationic dye **5** in aqueous solution was found to form an inclusion complex with water-soluble *p*-sulfonatocalix[4]arene. However, no data on binding of **5** with lower rim-functionalized calix[4]arenes in organic solutions have been reported. In this work, investigation of complex formation of ionophores **1**-**4** with dye **5** and subsequent probing of metal ion recognition using the calixarene-dye assemblies was carried out in a solvent extraction system water-chloroform.

Study of calixarene-dye complex formation

In the absence of calixarene ligands, cationic dye **5** is very weakly extracted from aqueous solutions into $CHCl_3$. The UV-Vis spectrum of **5** in $CHCl_3$ shows an absorption maximum at 500 nm (Figure 3). In the presence of proton-ionizable calixarenes **1** and **2** in $CHCl_3$, the distribution of **5** into the organic phase was found to increase dramatically. The calixarene-dye complexation

produced significant changes in the UV-Vis spectrum of **5** in $CHCl_3$ (Figure 3): the absorption band of the dye exhibited hypsochromic shift to 487 and 475 nm with **1** and **2**, respectively. Extraction of **5** by **1** and **2** was observed to enhance with increasing concentrations of the ligands in the organic phase, which could be monitored spectrophotometrically by increasing absorbance at the appropriate wavelength, as shown in Figure 4.

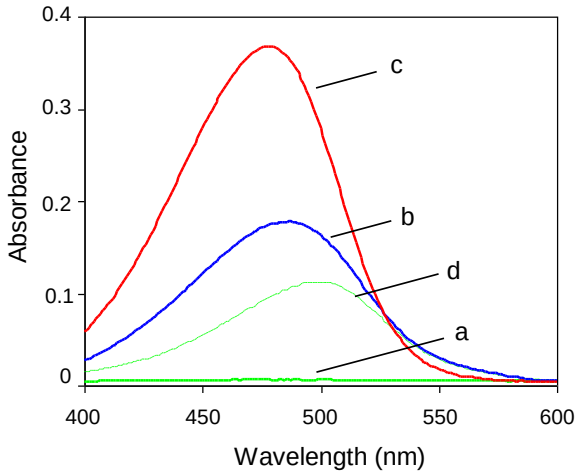

Figure 3. Absorption spectra of the $CHCl_3$ phases after extraction of **5** from 1.0×10^{-5} M aqueous solution (pH 6, dil. HNO_3) in the absence of ligands (a) and in the presence of 1.0×10^{-4} M calixarenes **1** (b) and **2** (c). Spectrum d is for the $CHCl_3$ extract of higher-concentration, 1.0×10^{-4} M aqueous **5** in the absence of ligands (shown to indicate position of the absorption maximum for uncomplexed **5** in $CHCl_3$).

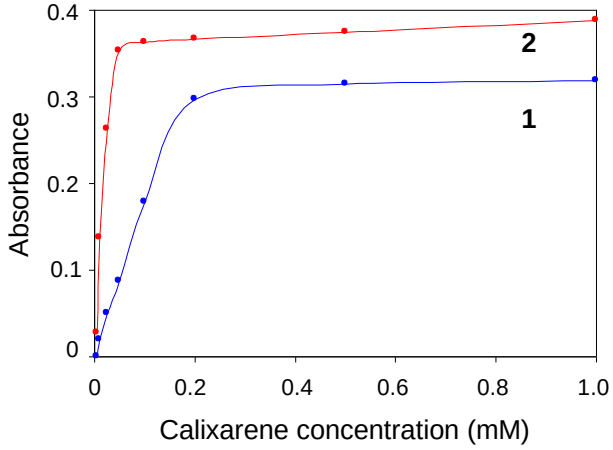

Figure 4. Changes in absorbance observed upon extraction of **5** into $CHCl_3$ by proton-ionizable calixarenes **1** (λ_{max} = 487 nm) and **2** (λ_{max} = 475 nm) as a function of the host concentration. Aqueous phase: 1.0×10^{-5} M **5**, pH 6.

For comparison purposes, a mono-ionizable analog of **2**, ligand **3** with one pendent N-(trifluoromethylsulfonyl)carboxamide group on the lower rim of *t*-Bu-substituted calix[4]arene moiety was involved in the extraction studies of **5** under otherwise identical conditions. From the measurement of absorbance of **5** in the aqueous phase before and after extraction into $CHCl_3$ by di-ionizable **2** (H_2L) and mono-ionizable **3** (HL), the dye loadings of the ligands were calculated. It was found that with equal (5.0×10^{-5} M) formal concentrations of aqueous **5** and ligand in the organic phase, the dye loadings of the calixarenes were 97.3 and 95.7% for **2** and **3**, respectively. Upon doubling the concentration of **5** in the aqueous phase with unchanged ligand concentrations in $CHCl_3$, the dye loadings for both **2** and **3** increased to nearly 100%, but none of them exceeded this value (which might be observed for di-ionizable **2** in the case of binding of more than one equivalent of the dye). Hence, this fact is in favor of predominant 1:1 complex formation between **5** and the calixarenes. This complex stoichiometry is in agreement with the data published for interaction of **5** with *p*-sulfonatocalix[4]arene.[7c]

Evidently, the principal driving force behind the reaction of the cationic dye ($\mathbf{5}^+$) and proton-ionizable calixarene (HL or H_2L) is electrostatic interaction leading to formation of complex ion pairs [$\mathbf{5}^+L^-$] or [$\mathbf{5}^+(HL)^-$], respectively (for the latter, see eqn (1) below):

$$\mathbf{5}^+(aq) + H_2L(org) \rightleftharpoons [\mathbf{5}^+(HL)^-](org) + H^+(aq) \quad (\mathbf{1})$$

At the same time, it is worth of note that di-ionizable calixarenes **1** and **2**, which have identical sets of lower-rim donor groups, but differ in the upper-rim substituents in *para*-positions of the phenol rings, demonstrate dissimilar extraction capacity towards **5**. In addition, complexes [$\mathbf{5}^+(\mathbf{1})^-$] and [$\mathbf{5}^+(\mathbf{2})^-$] in $CHCl_3$ solution show absorption maxima at different wavelengths. Obviously, not only the proton-ionizable groups, but also the calixarene moieties of **1** and **2** are involved in complex formation with the dye cation $\mathbf{5}^+$.

In order to verify engagement of calix[4]arene unit in complexation with **5**, it was desirable to eliminate the possibility of electrostatic interactions as a driving force behind this process. Hence, extraction of the dye into $CHCl_3$ was examined using a neutral ligand **4**. Since pendent ester groups of **4** are not expected to possess strong affinity for $\mathbf{5}^+$, the calixarene aromatic cavity may be the only binding site appropriate for hosting this ionic guest. Accordingly, the extraction ability of ligand **4** towards **5** should be much weaker relative to the ionizable analogs, with the reaction proceeding via formation of complex ion pairs [$\mathbf{5}^+(\mathbf{4})I^-$] in the organic phase (eqn (2)):

$$\mathbf{5}^+(aq) + I^-(aq) + \mathbf{4}(org) \rightleftharpoons [\mathbf{5}^+(\mathbf{4})I^-](org) \quad (\mathbf{2})$$

The study revealed that presence of **4** in $CHCl_3$ produces no significant changes in the absorption spectra of the aqueous and organic phases measured after the extraction of **5** as compared to the spectra after blank extraction of **5** in the absence of the host compound. This observation is consistent with a very weak extraction ability of this neutral calixarene towards the cationic dye. However, uptake of **5** by **4** in $CHCl_3$ was registered by means of a more sensitive fluorescence spectroscopy. Complex [$\mathbf{5}^+(\mathbf{4})I^-$] in the $CHCl_3$ extract, upon excitation at 480 nm, produced fluorescence emission at wavelength of 562 nm. Emission of the blank-extracted **5** and free **4** in $CHCl_3$ solution was negligible at this wavelength. The fluorescence intensity enhanced gradually with increasing concentration of the calixarene ligand in the organic

phase, as shown in Figure 5. This finding confirms involvement of the calix[4]arene moiety in complex formation of the cationic dye **5** with ligands **1**-**4**.

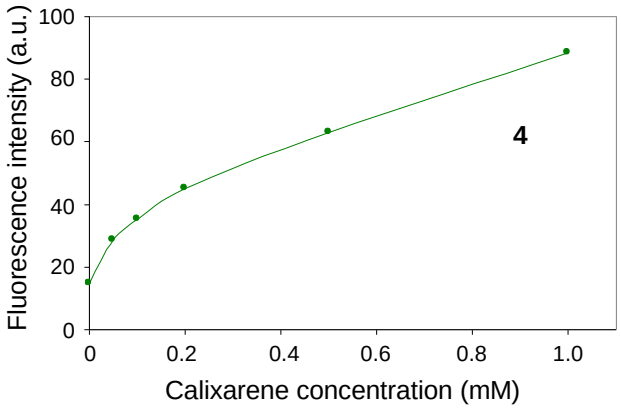

Figure 5. Changes in the fluorescence emission intensity (λ_{em} = 562 nm, λ_{ex} = 480 nm) observed upon extraction of **5** into $CHCl_3$ by calixarene **4** as a function of the host concentration. Aqueous phase: 1.0×10^{-5} M **5**, pH 6.

Shinkai and co-workers[7c] proposed a possible structure for the complex of **5** with *p*-sulfonatocalix[4]arene based on the results of its studies by UV-Vis spectrophotometry and ^{1}H NMR spectrometry. It was suggested that 1-methylpyridinium group of $\mathbf{5}^+$ is included in the aromatic cavity of the calixarene, and complex formation is controlled by both the cation-π and hydrophobic interactions of the dye and host. In agreement with this model, the structure of complex of $\mathbf{5}^+$ with a lower rim-functionalized calixarene is depicted schematically in Figure 6 (shown for di-ionizable ligands, such as **1** and **2**). Evidently, enclosure of **5** in the hydrophobic calixarene cavity is responsible for the observed in this study increase in the fluorescence quantum yield of this environment-sensitive optical probe (for similar calixarene effects, see[15]).

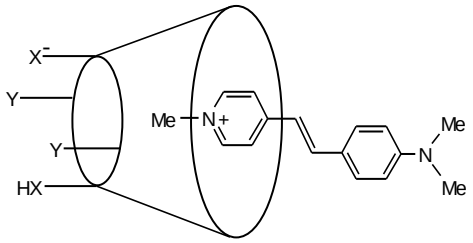

Figure 6. Suggested structure for the complex of cationic dye $\mathbf{5}^+$ with di-ionizable calix[4]arene (**1** or **2)**.

Probing optical recognition of metal ions using the calixarene-dye complexes

In order to probe for the possibility of recognition of metal ions in water using the calixarene-dye assemblies described above, solvent extraction studies of **5** from aqueous solutions containing

also alkali metal cations (AMC), Ag^+, Pb^{2+}, or Hg^{2+} into $CHCl_3$ by calixarenes **1**-**4** were carried out. The distribution of the dye into the organic phase was monitored by UV-Vis and fluorescence spectrophotometry.

Complex formation in a tri-component system dye cation ($\mathbf{5}^+$) – calixarene (L) – metal cation (M^{n+}) was expected to proceed in one of the two contrasting ways: competitive complexation of $\mathbf{5}^+$ and M^{n+} with L, which normally results in the dye displacement from its complex with calixarene by the metal ion, or assembly of a tri-component complex [$\mathbf{5}^+$-L-M^{n+}]. In accordance with the former mechanism, calixarene-facilitated transfer of the dye into the organic phase should decline in the presence of aqueous-phase metal ions. Reduced extraction must be accompanied by decrease in the absorbance/fluorescence of the organic solution after extraction. For the reaction progressing in accord with the alternative mechanism, uptake of the dye by the ligand in $CHCl_3$ should not diminish. However, if the triple complex [$\mathbf{5}^+$-L-M^{n+}] has different spectral characteristics than the dye-calixarene one, absorption (fluorescence) spectra of the organic extract may change.

The present study revealed that extraction of **5** by all of the calixarenes **1**-**4** is affected by the presence of aqueous phase metal ions, as will be illustrated below. Distribution of **5** into $CHCl_3$ was judged based on the difference in its absorbance in the aqueous solutions before and after the extraction. Interestingly, no significant decline in the dye transfer into the organic phase in the presence of metal ions was observed. At the same time, in most of the cases, addition of M^{n+} to the aqueous phase resulted in increase of organic phase absorbance and/or fluorescence, consistent with formation of tri-component complexes [$\mathbf{5}^+$-L-M^{n+}].

Proton-ionizable ionophores **1** and **2** are known to be efficient extractants of AMC from aqueous solutions into $CHCl_3$.[11a,13] In competitive complexation of five AMC, both **1** and **2** demonstrate high selectivity for Na^+. Neutral calixarenes with ester groups on the lower rim usually provide weaker binding of metal ions than the ionizable analogs.[5] Hence, **4** was expected to possess weaker extraction ability towards AMC than **1** and **2**. Nevertheless, for all three of these calixarenes, no significant changes in the absorption spectra of the organic phases were registered upon addition of 1×10^{-3} M AMC to the aqueous solutions for extraction of 1.0×10^{-5} M dye **5** (pH 6.0) by 1.0×10^{-5} M ligand. At the same time, a noticeable increase in the emission intensities of the bands was observed in the fluorescence spectra of the organic extracts of **5** with **1** and **2** (Figure 7). (Fluorescence spectrum of the organic solution after the blank extraction of **5** into $CHCl_3$ containing no calixarenes was not affected by the aqueous-phase AMC.) It is noteworthy that for both **1** and **2**, presence of Na^+ produced the largest effect on the fluorescence intensity of the calixarene-bound **5** in $CHCl_3$. In contrast to extraction of **5** by the two proton-ionizable ligands, with neutral **4**, addition of AMC to the aqueous phase caused only insignificant changes in the fluorescence spectra of the extracts (Figure 8). Apparently, such a dissimilar spectral response of the organic phases after extraction of **5** by **1**, **2** and **4** to the presence of AMC is in agreement with different metal ion complexing abilities of these ligands.

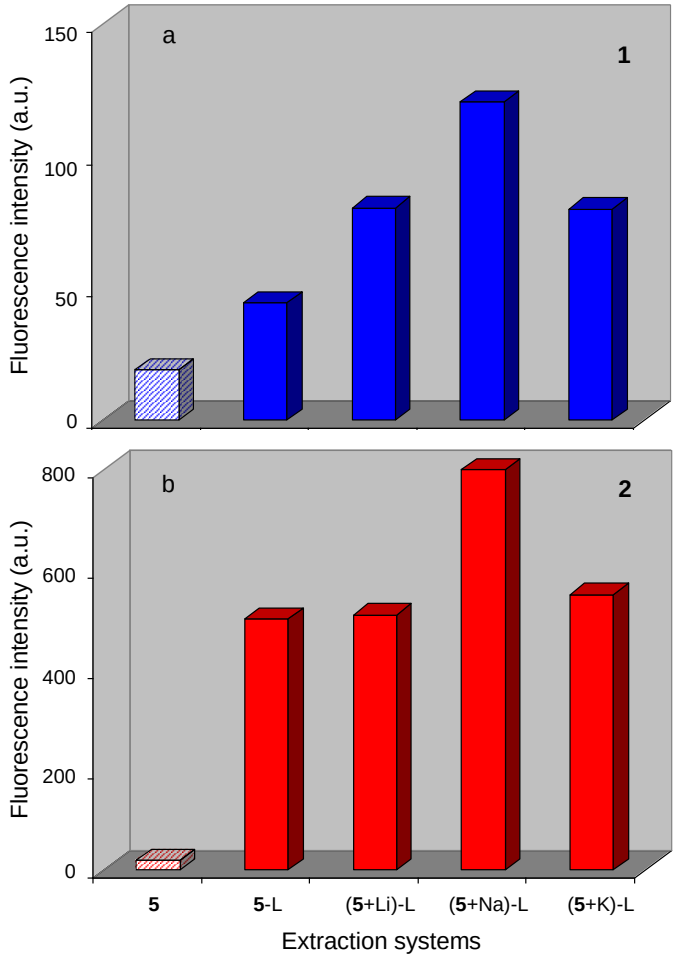

Figure 7. Fluorescence intensity of the extract of **5** into $CHCl_3$ by 1.0×10^{-5} M proton-ionizable calixarenes (a) **1** (λ_{em} = 552 nm) and (b) **2** (λ_{em} = 548 nm) in the absence and in the presence of alkali metal cations in the aqueous phase. λ_{ex} = 480 nm; aqueous phase: $C_5=1.0\times10^{-5}$ M, $C_M=1\times10^{-3}$ M, pH 6.

A much greater effect on the emission spectrum of the dye-**4** complex in $CHCl_3$ was obtained by introduction into the aqueous solutions of 1×10^{-3} M Ag^+, Pb^{2+}, and Hg^{2+}, as may be seen in Figure 8. Presence of Pb^{2+} produced the most pronounced fluorescence response in this extraction system. Yet, only small deviation in the corresponding absorption spectra were observed for this neutral calixarene.

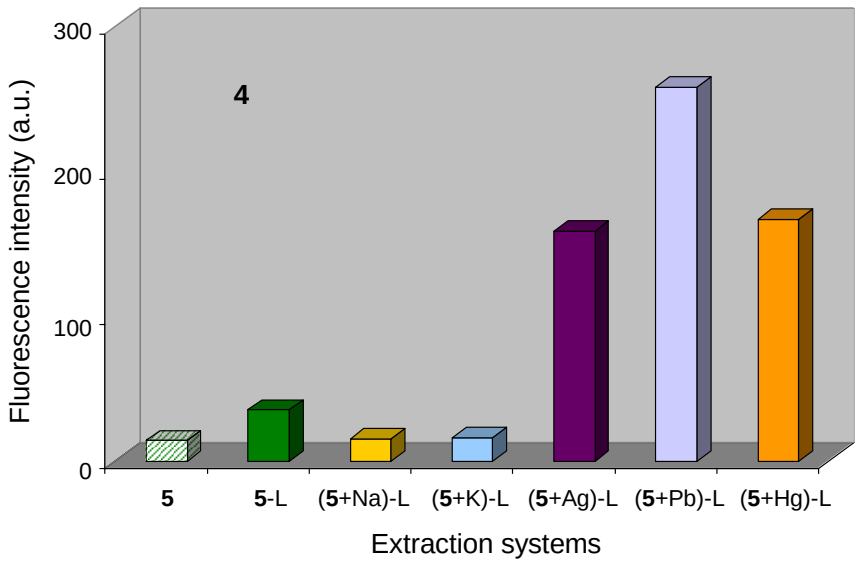

Figure 8. Fluorescence intensity (λ_{em} = 562 nm; λ_{ex} = 480 nm) of the extract of **5** into $CHCl_3$ by 1.0×10^{-5} M non-ionizable calixarene **4** in the absence and in the presence of different metal cations in the aqueous phase. Aqueous phase: $C_5=1.0\times10^{-5}$ M, $C_M=1\times10^{-3}$ M, pH 6.0.

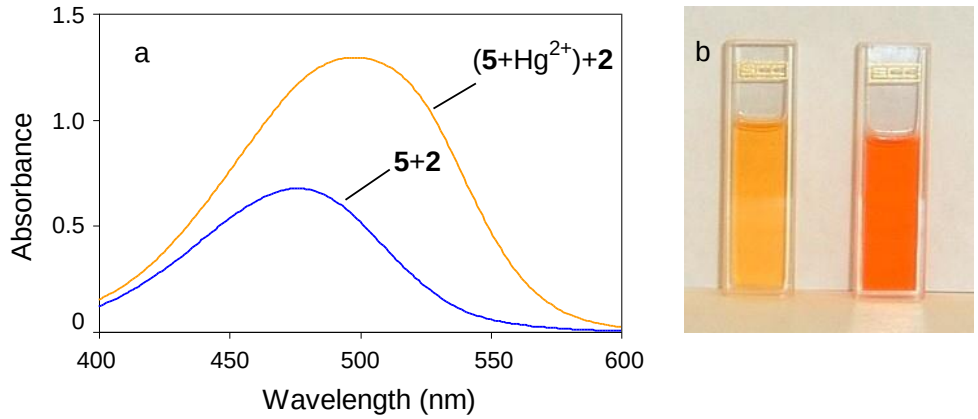

Figure 9. Extraction of **5** into $CHCl_3$ by calixarene **2** in the absence and in the presence of aqueous-phase Hg^{2+}: (a) absorption spectra of the organic phases; (b) organic extract of **5** by **2** in the absence (left) and in the presence of Hg^{2+} (right). C_5= $C_2=1.0\times10^{-4}$ M; $C_{Hg}=2\times10^{-5}$ M; pH 6 (acetate buffer).

On the other hand, for the extraction of **5** by proton-ionizable ionophores **1**-**3**, addition of Hg^{2+} and, especially, Pb^{2+} resulted in quite sizeable changes in the UV-Vis spectra of the organic phases. (Upon the blank extraction of **5** from aqueous solutions containing metal salts into $CHCl_3$, only small changes in the absorption spectrum of the dye were observed.) Thus, the absorption bands for the dye-calixarene complexes in $CHCl_3$ in the presence of these metal ions

demonstrated noticeable bathochromic shifts accompanied by the absorbance enhancement (shown in Figure 9 for extraction of **5** from the aqueous solution containing Hg^{2+} by ligand **2** in $CHCl_3$). Unfortunately, studies of heavy metal ion recognition with employment of the dye-**1** ensemble were hampered by limited solubility of the metal-containing complexes in $CHCl_3$. However, with *t*-Bu-substituted calixarenes **2** and **3** as extractants, increasing amounts of Pb^{2+} added to the aqueous solution of **5** yielded gradual enhancement of the absorption band of [$\mathbf{5}^+$-L-M^{n+}] complex observed at 516 nm. As illustrated in Figure 10, for the micro-levels of lead in the aqueous phase, the dependence of the absorbance changes (ΔA) on the formal concentration of Pb^{2+} (C_{Pb}) in these systems is linear and might be used as a calibration plot for quantification of this metal ion. Further investigation of metal ion recognition using supramolecular ensembles **5**-calixarene is in progress.

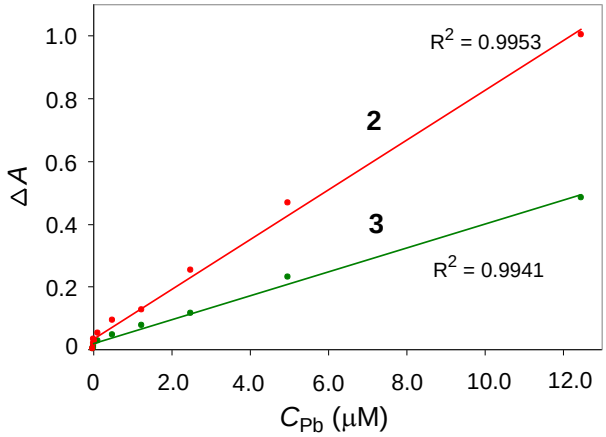

Figure 10. Change in the absorbance (Δ*A*) of the organic phase at λ = 516 nm observed upon extraction of 5.0×10^{-5} M **5** from aqueous solutions containing varying amounts of Pb^{2+} (pH 6.0, acetate buffer) into $CHCl_3$ by 5.0×10^{-5} M calixarenes **2** and **3** as a function of the formal lead ion concentration (C_{Pb}).

To confirm the mechanism of metal ion recognition by the host-guest complexes of dye **5** with calixarenes **1**-**4**, additonal studies are required. Meanwhile, based on the results from the preliminary studies presented in this paper, the following possible structure is suggested for the complex [$\mathbf{5}^+$-L-M^{n+}] (shown schematically in Figure 11). It may be assumed that the dye cation ($\mathbf{5}^+$) included in the aromatic cavity of a calixarene preorganizes the ligand in the conformation favorable for metal ion binding by the lower-rim donor groups. This interaction results in co-extraction of the dye and metal cation by the calixarene in the form of the tri-component complex. Changes in the electronic environment of the calixarene-bound $\mathbf{5}^+$ that take place due to the M^{n+} co-coordination may produce the spectral response to the metal ion recognition, as described above.

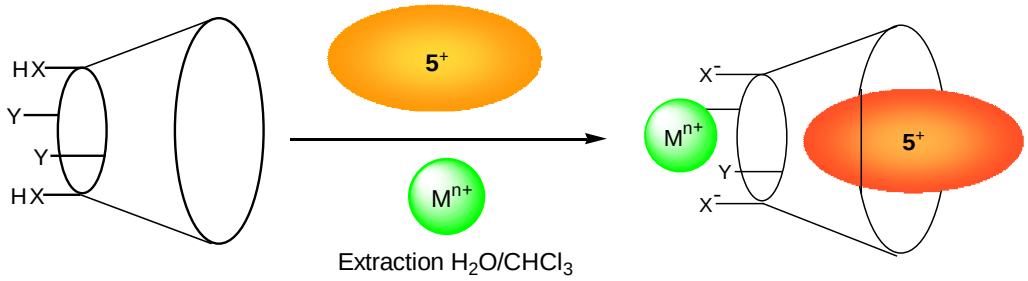

Figure 11. Schematic presentation of a reaction for optical metal ion recognition via formation of a complex [$\mathbf{5}^{+}$-L-M^{n+}] (shown for a di-ionizable calix[4]arene; inorganic anions omitted for simplicity).

Conclusions

Based on the preliminary studies presented above, employment of supramolecular complexes of lower rim-functionalized proton-ionizable calixarenes with cationic dyes (such as **5**) in optical recognition of metal ions is promising. Investigation of the mechanisms for the complexation reactions involved and structural factors that affect interactions in the systems dye-calixarene-metal ion are the subject of our ongoing research.

Experimental Section

General. Calixarenes used in this study were prepared by the earlier published procedures: **1**,[11a] **2**,[11b] **3**,[11c] and **4**.[11d] *Trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide **5** from Aldrich as well as alkali metal chlorides and Ag(I), Pb(II), and Hg(II) nitrates from different commercial suppliers, all of the highest quality available, were used as received. ACS-grade chloroform from Fisher, prior to use in the extraction experiments, was washed with deionized water. Samples for solvent extraction were shaken with a Glas-Col® Multi-Pulse Vortexer. pH was measured with a Fisher Scientific Accumet® 50 pH/ion/conductivity meter. The corrected fluorescence spectra were obtained with a Shimadzu RF-5301PC spectrofluorometer. UV-Vis spectra were registered with a Shimadzu UV-2101PC scanning spectrophotometer.

Solvent extraction of 5 by calixarenes (1-4). An aqueous solution of 1.0×10^{-5} M **5** at pH 6.0 (dil. HNO_3) was extracted by varied concentration ligand in $CHCl_3$. For the blank experiment, extraction of 1.0×10^{-5} M **5** into $CHCl_3$ was performed. The solutions were shaken with a vortexer for 15 min., centrifuged, and phases separated. Absorption spectra before and after extraction as well as absorption and fluorescence spectra of the organic extracts were measured. The

experiments were performed in triplicate runs; the reported results are mean values, with relative error not exceeding 5%.

Solvent extraction of 5 by calixarenes 1-4 in the presence of metal ions in the aqueous phase. An aqueous solution of 5.0×10^{-5} M **5** containing 1×10^{-3} M AMC (Li^+, Na^+ or K^+) chloride, Ag^+, Pb^{2+} or Hg^{2+} nitrate at pH 6.0 (dil. HNO_3 for AMC and acetate buffer for Ag^+, Pb^{2+} and Hg^{2+}) was extracted by 5.0×10^{-5} M ligand in $CHCl_3$. For the blank experiments, extraction of 1.0×10^{-5} M **5** and 1.0×10^{-5} M **5** containing 1×10^{-3} M metal salt into $CHCl_3$ were performed. The solutions were vortexed for 15 min., centrifuged, and phases separated. Absorption spectra before and after extraction as well as absorption and fluorescence spectra of the organic extracts were measured. The experiments were performed in triplicate runs; the reported results are mean values, with relative error not exceeding 5%.

For studies of the dependence of extraction of **5** on the concentration of aqueous-phase Pb^{2+}, an aqueous solution of 5.0×10^{-5} M **5** and varied concentration Pb^{2+} (pH 6.0, acetate buffer) was extracted by 5.0×10^{-5} M ligand in $CHCl_3$.

Acknowledgements

This research was supported by Howard University (Grant NF04/12) and GAANN Fellowship (N. M. B.).

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