Novel Bicyclic Fluorescent Calix[4]arene-based Sensors for Toxic Metals

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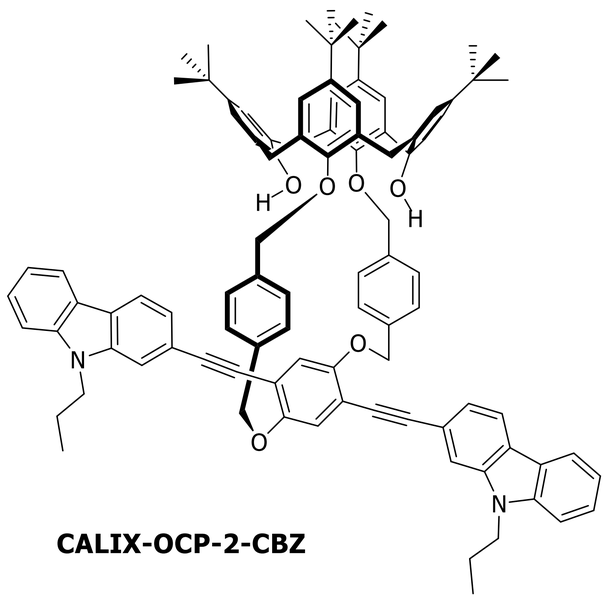
OVERVIEW

Calix[4]arene has been widely exploited as the basic molecular framework for many fluorescent chemosensors in the construction of selective binding sites given its structural rigidity (particularly important when the recognition and reporting events are to be undertaken in fluid phase), various conformations, and facile introduction of fluorophores. Exploring the inherent capabilities of certain fluorescent calixarene scaffolds for establishing strong host:guest interactions, several sensing materials have been recently developed by us [1].

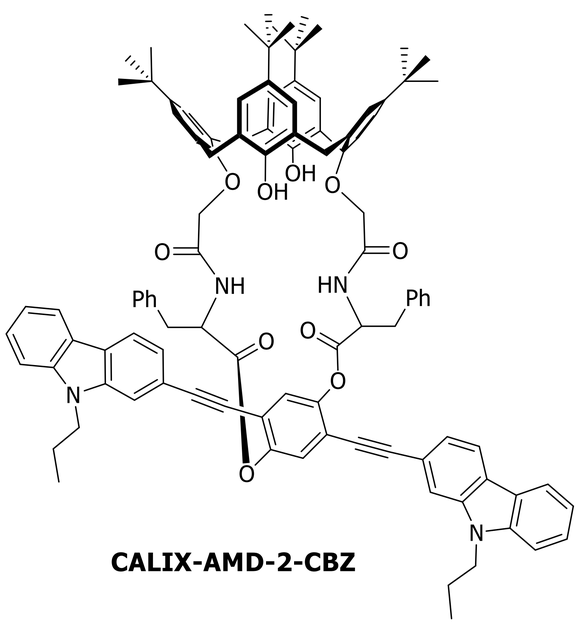
In the same line of research new bicyclic calix[4]arene-based fluorescent chemosensors containing amides as coordination sites (ionophore) and carbazole segments as fluorescent signaling moieties (**CALIX-AMD-CBZ**) are being developed and that are expected to have high ability toward the detection of metallic cations in solution. However its complex synthesis and characterization has led to the use of a similar compound based on narrow rim 1,3-oxacyclophane tethered calix[4]arene derivatives integrating the same fluorescent segments (**CALIX-OCP-2-CBZ**) [2] as fluorophore in the present communication.

Herein we report the most significant photophysical properties and sensory capabilities of **CALIX-OCP-2-CBZ** towards divalent ions (Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}) by fluorescence spectroscopy in fluid phase.

RESULTS AND DISCUSSION



CALIX-OCP-2-CBZ



CALIX-AMD-2-CBZ

Fig. 1. Bicyclic Fluorescent Calix[4]arene-based Sensors.

PHOTOPHYSICAL PROPERTIES

The photophysical properties of **CALIX-OCP-2-CBZ** are shown in Figure 2.

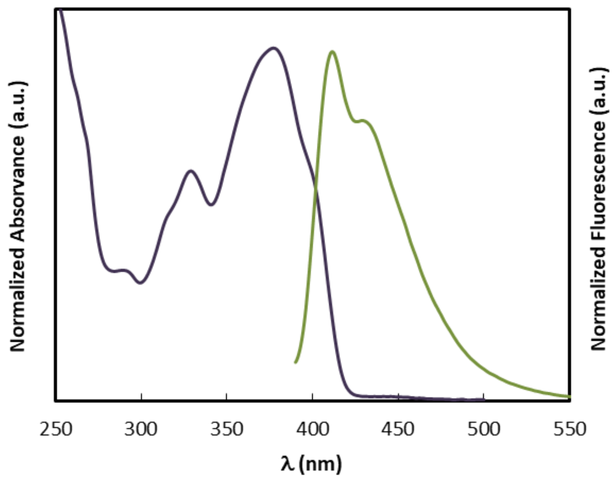


Fig. 2. Normalized absorption and fluorescence spectra in CH_3CN of **CALIX-OCP-2-CBZ** (λ_{exc} = 380 nm).

CALIX-OCP-2-CBZ is a deep-blue emitter, displaying high fluorescence quantum yield (Φ_F = 1.0 in $CHCl_3$) in fluid phase. Under conditions of continuous irradiation (λ_{exc} = 380 nm) no noticeable photodegradation occurs.

SENSORIAL STUDIES

Fluorescence titration of a solution (several solvents were tested and CH_3CN was selected for complexation experiments) of **CALIX-OCP-2-CBZ** ($1.0x10^{-7}$ M) with increasing amounts of several toxic metals as perchlorates salts ($Hg(ClO_4)_2$, $Pb(ClO_4)_2$, $Cu(ClO_4)_2$, $Ni(ClO_4)_2$ and $Cd(ClO_4)_2$; $2.49x10^{-7}$-$7.26x10^{-6}$ M) was evaluated.

The sensor exhibits relevant fluorescence sensing response toward Cu^{2+} and showed a linear relationship with K_{SV} $4.0x10^4$ M^{-1} (Fig. 3). Although Hg^{2+} also induced a similar appearance of fluorescence decrease, its turn-off efficiency is lower.

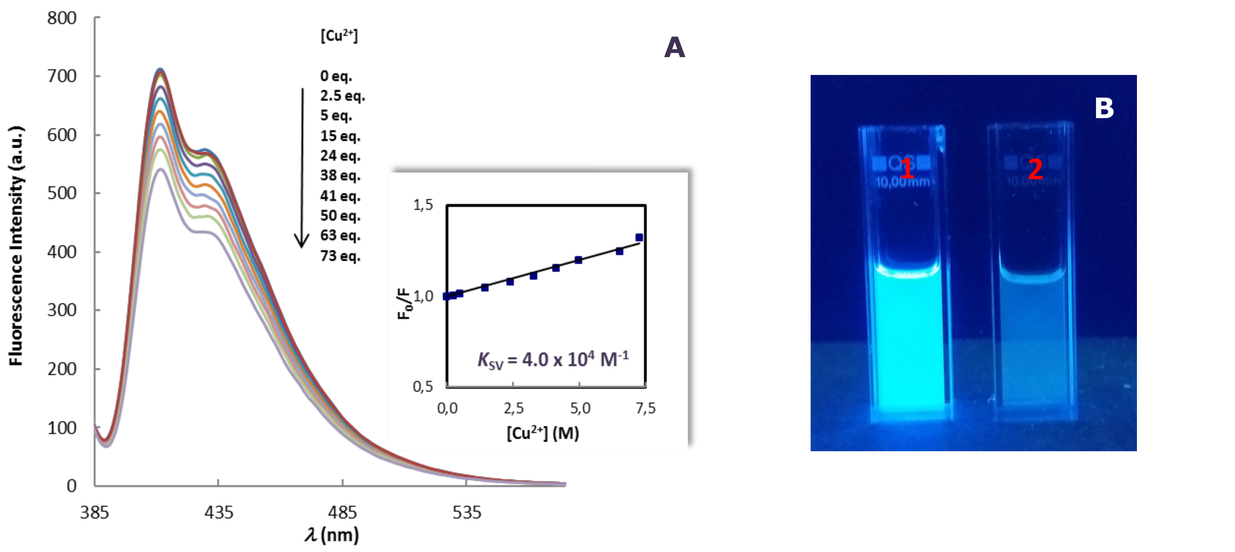
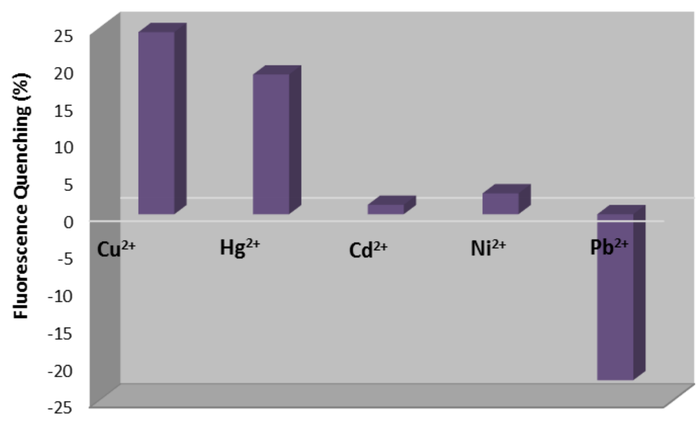


Fig. 3. A) Photoluminescence quenching spectra of **CALIX-OCP-2-CBZ** with $Cu(ClO_4)_2$. Inset: Stern-Volmer plot (λ_{exc} = 380 nm); **B)** Fluorescence changes of **CALIX-OCP-2-CBZ** solution under UV radiation (366 nm) before **(1)** and after **(2)** quenching with $Cu(ClO_4)_2$.

Detection response to other metals (Pb(II), Ni(II) and Cd(II)) were also performed, however, no substantial fluorescence variations were observed which confers a high specificity of **CALIX-OCP-2-CBZ** toward Cu(II) followed by Hg(II) (Fig. 4). The limit of detection (LOD) for Cu^{2+} and Pb^{2+} were determined as 164 nM and 233 nM, respectively, a promising result as compared with other reported sensors for toxic metals [3].

To establish whether **CALIX-OCP-2-CBZ** can selectively recognize Cu^{2+} (50 eq.) even in the presence of co-existing ions, two types of metal ions (Cd^{2+} and Ni^{2+}; 100 eq.) were evaluated.



Negligible effect on fluorescence intensity was observed which demonstrates that **CALIX-OCP-2-CBZ** makes a stable complex with Cu(II).

Fig. 4. Fluorescence quenching response for **CALIX-OCP-2-CBZ** at 414 nm in CH_3CN upon the addition of 73 eq. of various metal ions perchlorates (λ_{exc} = 380 nm).

CONCLUSIONS

Bicyclic calix[4]arene **CALIX-OCP-2-CBZ** was described for the first time with its ability to act as a chemical sensing agent for the detection of toxic metals, showing particular selectivity and sensibility toward copper. A very interesting result was also observed toward Pb^{2+} which works in a turn-on fluorescence mechanism.

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