# Highly Selective and Sensitive Detection of Toxic Metals by Fluorescent Bicyclic Calix[4]arene-based Sensors

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## SUMMARY

Development of fast and portable chemosensors for trace detection of toxic metals, in particular those which are mostly present in the environment due to natural phenomenon and human activities (*e.g.* cadmium, mercury and lead), is a challenging area of current research.[1]

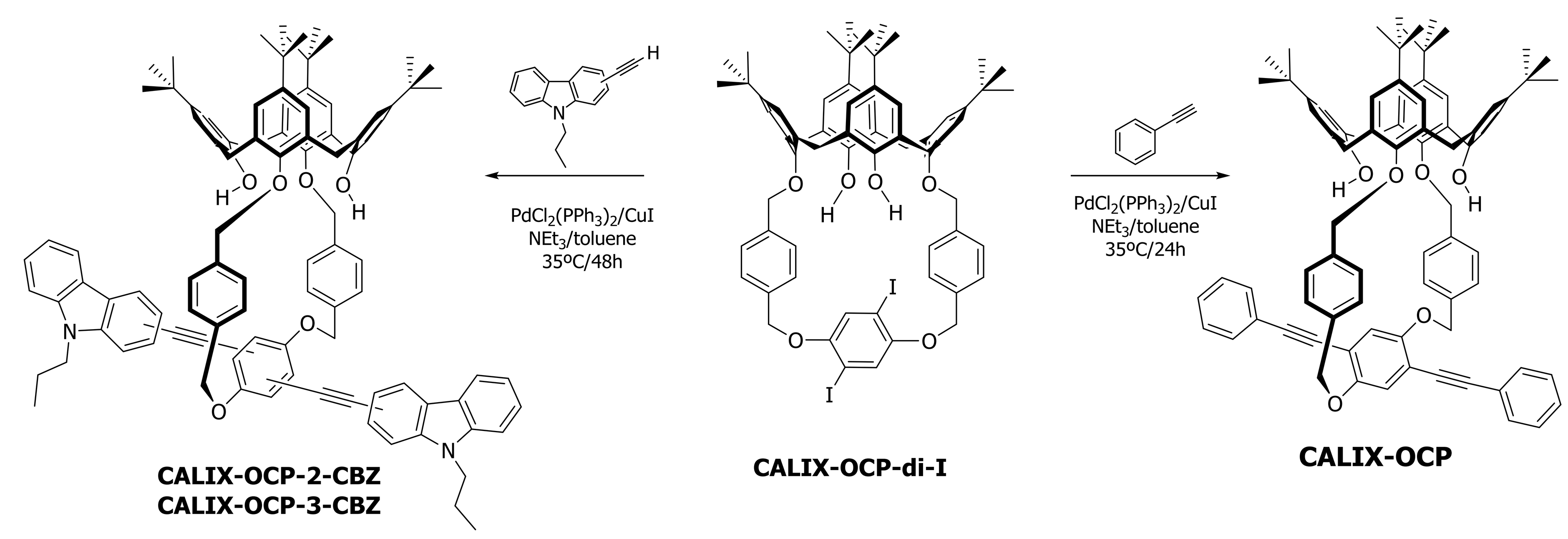
Calixarenes are one of the most widespread scaffolds in host-guest chemistry because of their rigid structures, which make them perfect candidates for complexation studies with ions and neutral molecules. Metal ions commonly bind at the lower rim of the calixarene moiety. Host-guest interaction can be enhanced by proper choice of additional binding sites containing nitrogen, oxygen, sulfur or a combination of them, and specifically designed calixarene architectures. Exploring the inherent capabilities of certain fluorescent calixarene-based compounds for establishing strong host:guest interactions, several sensing materials have been developed and tested by us towards the detection of neutral molecular species.[2]

We report in this communication the chemosensing ability of **CALIX-OCP-CBZ** and **CALIX-OCP** (Scheme 1) towards the detection of toxic metals, either by using the sensing element in fluid phase or solid state.

## RESULTS AND DISCUSSION

### SYNTHESIS AND CHARACTERIZATION

The bicyclic calix[4]arene-based sensors were synthesized from **CALIX-OCP-di-I**[2d] by a Sonogashira-Hagihara cross-coupling reaction with catalytic amounts of $PdCl_2(PPh_3)_2$/CuI in toluene/$NEt_3$ at 35ºC and ethynyl carbazoles with two different substitution patterns (2- or 3-) (**CALIX-OCP-2-CBZ**; 67%; **CALIX-OCP-3-CBZ**; 61%)[2e] or phenylacetylene (**CALIX-OCP**; 66%).[2d] The compounds were characterized by FT-IR, $^1H/^{13}C$ NMR and elemental analysis. Their photophysical properties were studied by UV-Vis and fluorescence spectroscopy. All compounds exhibiting high quantum yields of fluorescence and a great stability toward photobleaching.[2d-e]




**Scheme 1.** Synthesis of bicyclic calix[4]arene-based sensors.

### SENSORIAL STUDIES

#### Detection of Metals in Solution

Solution quenching experiments were carried out by titration of diluted solutions of the fluorophores with known amounts of perchlorate salts of metals. The extent of the developed interactions between the sensors and the metals were quantified by the Stern-Volmer approach. Figure 1 depicts the quenching curves, Stern-Volmer plot and Job plot for complex formation between **CALIX-OCP-3-CBZ** and $Cu^{2+}$.

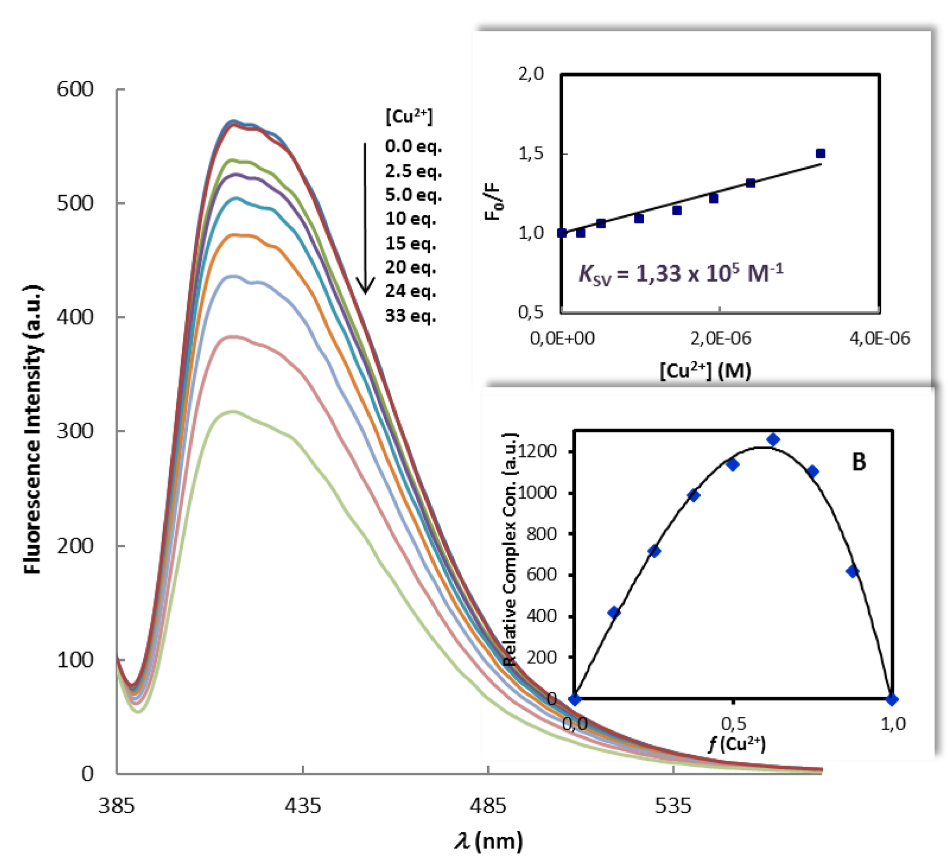



**Fig. 1.** Photoluminescence quenching spectra of **CALIX-OCP-3-CBZ** ($1.0 \times 10^{-7}$ M in $CH_3CN$) with $Cu(ClO_4)_2$. Inset **A)** Stern-Volmer plot; **B)** Job plot for complex formation (at constant $7.5 \times 10^{-6}$ M total concentration) ($\lambda_{exc}$ = 380 nm).

As depicted in Figure 2, **CALIX-OCP-3-CBZ** presents the higher sensitivity response to $Cu^{2+}$ ($K_{sv}$=1.33x10$^5$ M$^{-1}$) compared with its homologous **CALIX-OCP-2-CBZ** ($K_{sv}$=3.37x10$^4$ M$^{-1}$) which reveals a rather selective behavior of **CALIX-OCP-CBZs** toward this metal cation. The comparison of the results with an analogous compound lacking the carbazole unit (**CALIX-OCP**) (Scheme 1) and a model compound without the calixarene unit (**TBP-3-CBZ**; not shown)[2c] revealed the importance of the nitrogen atoms of carbazole unit and the calixarene macrocycle in the complexation event, respectively.

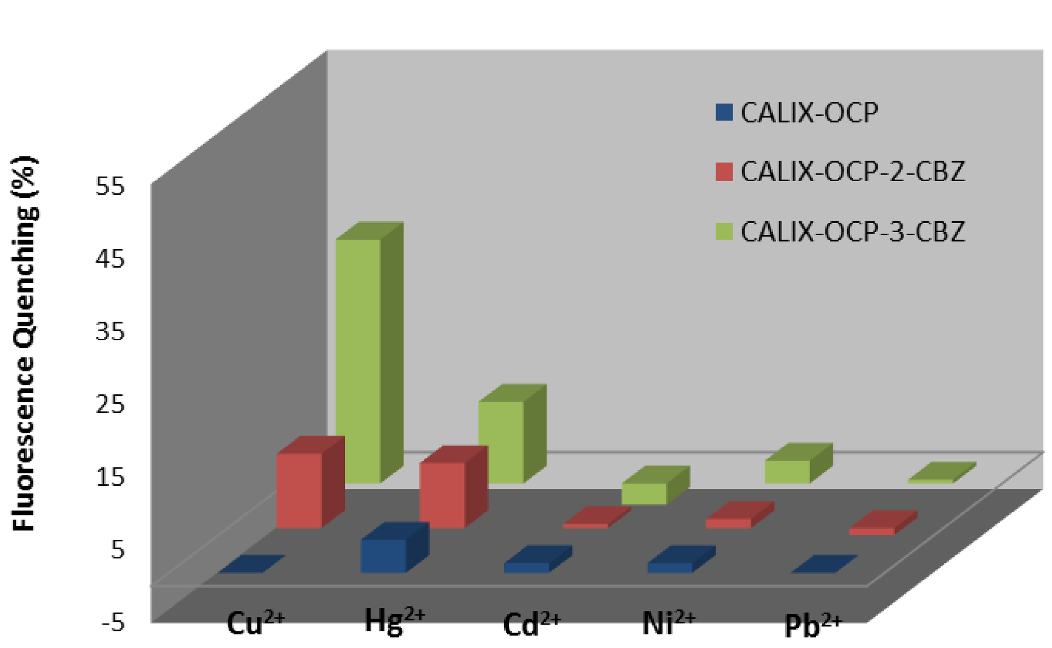



**Fig. 2.** Comparative fluorescence quenching of several fluorophores ($1.0 \times 10^{-7}$ M in $CH_3CN$) towards different metal cations (33 eq.).

Detection response to other metals (Pb(II), Ni(II) and Cd(II)) were also performed, however, no substantial fluorescence variations were observed. The limit of detection (LOD) for $Cu^{2+}$ were determined as 65 nM (**CALIX-OCP-3-CBZ**) and 196 nM (**CALIX-OCP-2-CBZ**), respectively, a promising result as compared with other reported sensors for toxic metals.[3]

#### Detection of Metals in Solid Phase

The solid-state chemosensing ability of **CALIX-OCP-2-CBZ** and **CALIX-OCP-3-CBZ** in pure water (ultrapure water by Merck Millipore®) spiked with $Cu^{2+}$ was evaluated using thin films. The films showed a significant stability toward photobleaching under the same conditions of the quenching experiments. Furthermore, the films are firmly adhered to the quartz surface even if they are kept in aqueous phase for prolonged times. This behavior is of utmost importance in the development of sensor devices.

In the concentration range evaluated (see Fig. 3), the sensor response to metal show a linear behavior. Therefore the sensibility to this cation was assessed at higher concentrations (up to *ca.* 19.8 μM). Fig. 3 compares the results of the fluorescence quenching efficiencies of **CALIX-OCP-2-CBZ** and **CALIX-OCP-3-CBZ** with $Cu(ClO_4)_2$ in pure water. In the presence of Hg(II), the response of both sensors were negligible.

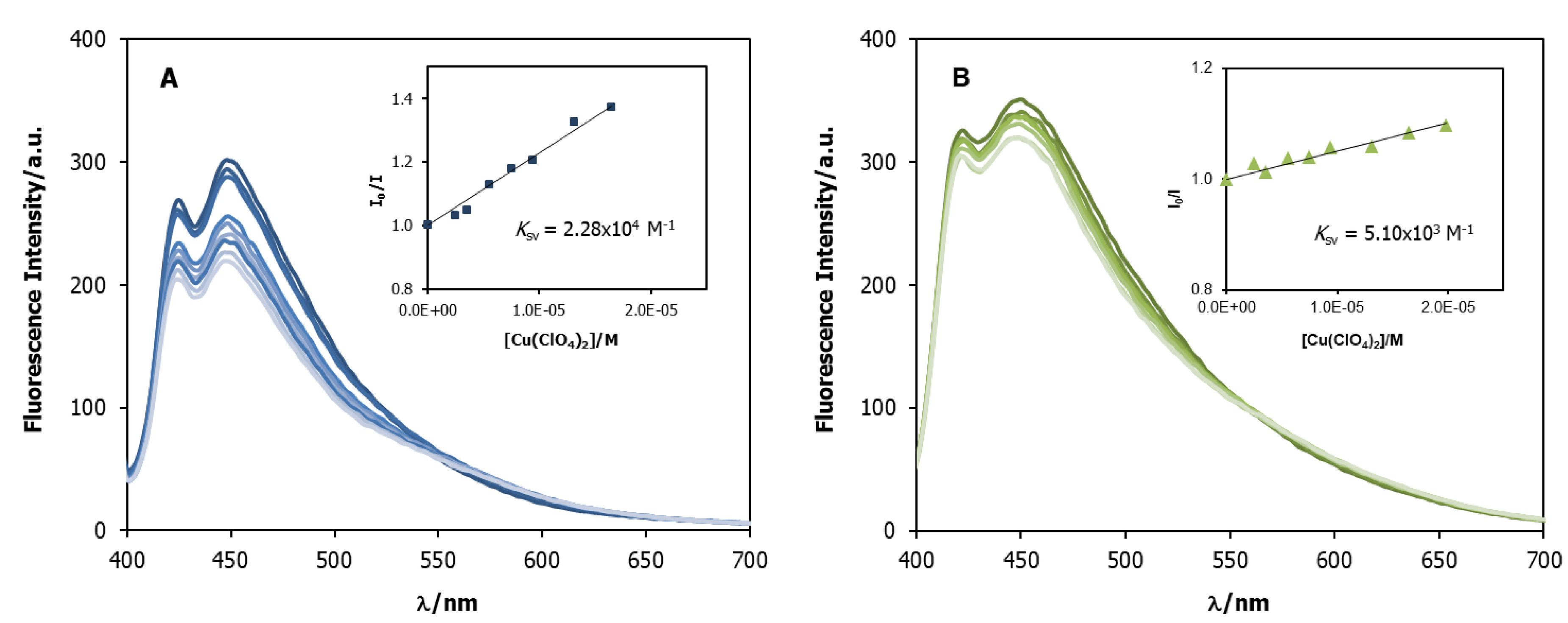



**Fig. 3.** Fluorescence emission spectra of **CALIX-OCP-2-CBZ** (**A**) and **CALIX-OCP-3-CBZ** (**B**) in the presence of different concentrations of $Cu(ClO_4)_2$ (from top to bottom: 0, 2.53, 3.56, 5.57, 7.52, 9.41, 13.1, 16.5 and 19.8 μM) in pure water. Inset: Stern-Volmer plot ($\lambda_{exc}$ = 380 nm).

## CONCLUSIONS

The evaluation of fluorescence spectra clearly showed that bicyclic calix[4]arenes (**CALIX-OCP-CBZs**) are good sensors for the selective recognition of copper in fluid phase ($CH_3CN$) when compared with other cations, revealing low detection limits. **CALIX-OCP-CBZs** were also selective for Cu(II) detection in the solid state. The influence of structural factors on the sensorial characteristics of **CALIX-OCP-CBZs** may be useful in future design of efficient metal-selective fluoroionophores.

### REFERENCES

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### ACKNOWLEDGMENTS

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