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## OVERVIEW

- Chemical sensors have been playing a crucial role in analytical chemistry, bio-medicinal science and environmental chemistry.
- Chemosensors offer an accurate and low-cost finding of anions, cations, enzymes and toxic metal ions with high selectivity and sensitivity. In this regard, many organic compounds have been synthesized and are being used as successful chemosensors, however calixarenes offer distinct advantages in terms of selectivity and the easy incorporation of a fluorophore into the structure [1,2].
- Cation complexing ligands containing calix[4]arene have been used to obtain more selective metal ions receptors.
- Herein, we report fluorescent calix[4]arene-based sensors with different molecular architecture [3] and their potentialities to address the detection of toxic metals (Figure 1). Using fluorescence as the signal transduction technique, experiments have shown that **CALIX-OCP-2-CBZs** are the most sensitive to Cu (II).

## RESULTS

- Fluorescence quenching in fluid phase of bicyclic calix[4]arene carbazole conjugates (**CALIX-OCP-2-CBZ**) and arylenethynylene trimer bearing bis-calix[4]arene units (**CALIX-2-CBZ**) ( $1.0 \times 10^{-7}$  M) with increasing amounts of toxic metals as perchlorates salts ( $\text{Cu}(\text{ClO}_4)_2$  and  $\text{Hg}(\text{ClO}_4)_2$ ;  $2.49 \times 10^{-7}$ – $7.26 \times 10^{-6}$  M) was evaluated (Figure 1 and 2).

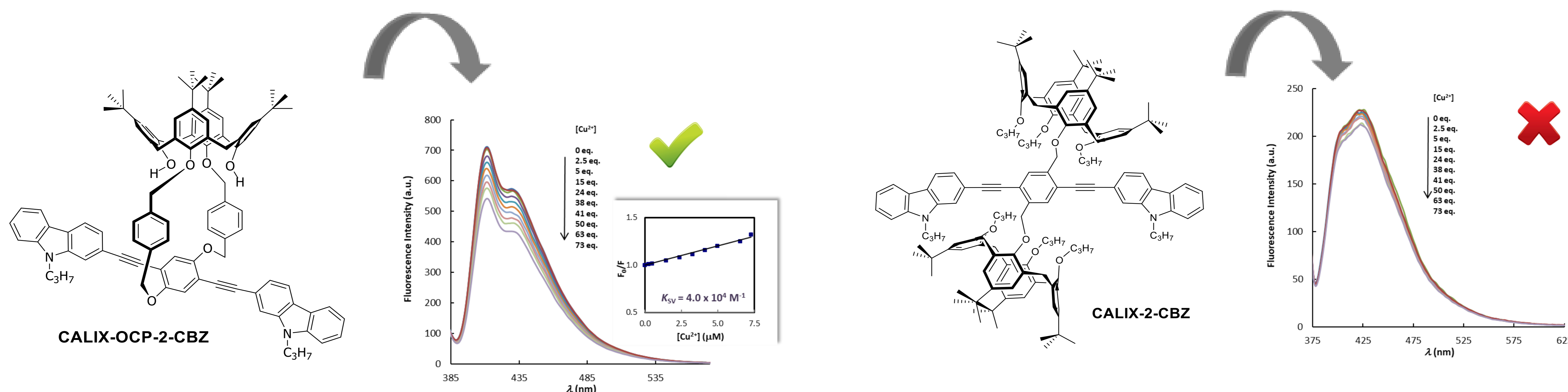


Figure 1: Calix[4]arene-based sensors (**CALIX-OCP-2-CBZ** and **CALIX-2-CBZ**) and fluorescence quenching response in  $\text{CH}_3\text{CN}$  upon the addition of  $\text{Cu}(\text{ClO}_4)_2$  ( $\lambda_{\text{exc}} = 380$  nm and  $\lambda_{\text{exc}} = 360$  nm, respectively).

- Experimental results revealed that **CALIX-OCP-2-CBZ** shows a better efficiency and affinity for copper by Stern-Volmer approach ( $K_{\text{sv}} = 4.0 \times 10^4 \text{ M}^{-1}$ ).
- Negligible responses were detected with a previously disclosure architecture (a double-cavity calix[4]arene derivative integrating *p*-phenyleneethynylene segments - **CALIX-OCP**, not shown) and **CALIX-2-CBZ**. Based on these results, other experiments were also conducted with their counterparts polymeric fluorescent materials (not shown), expecting to observe a signal amplification effect in the sensory event. The results are available in another poster communication at this conference.

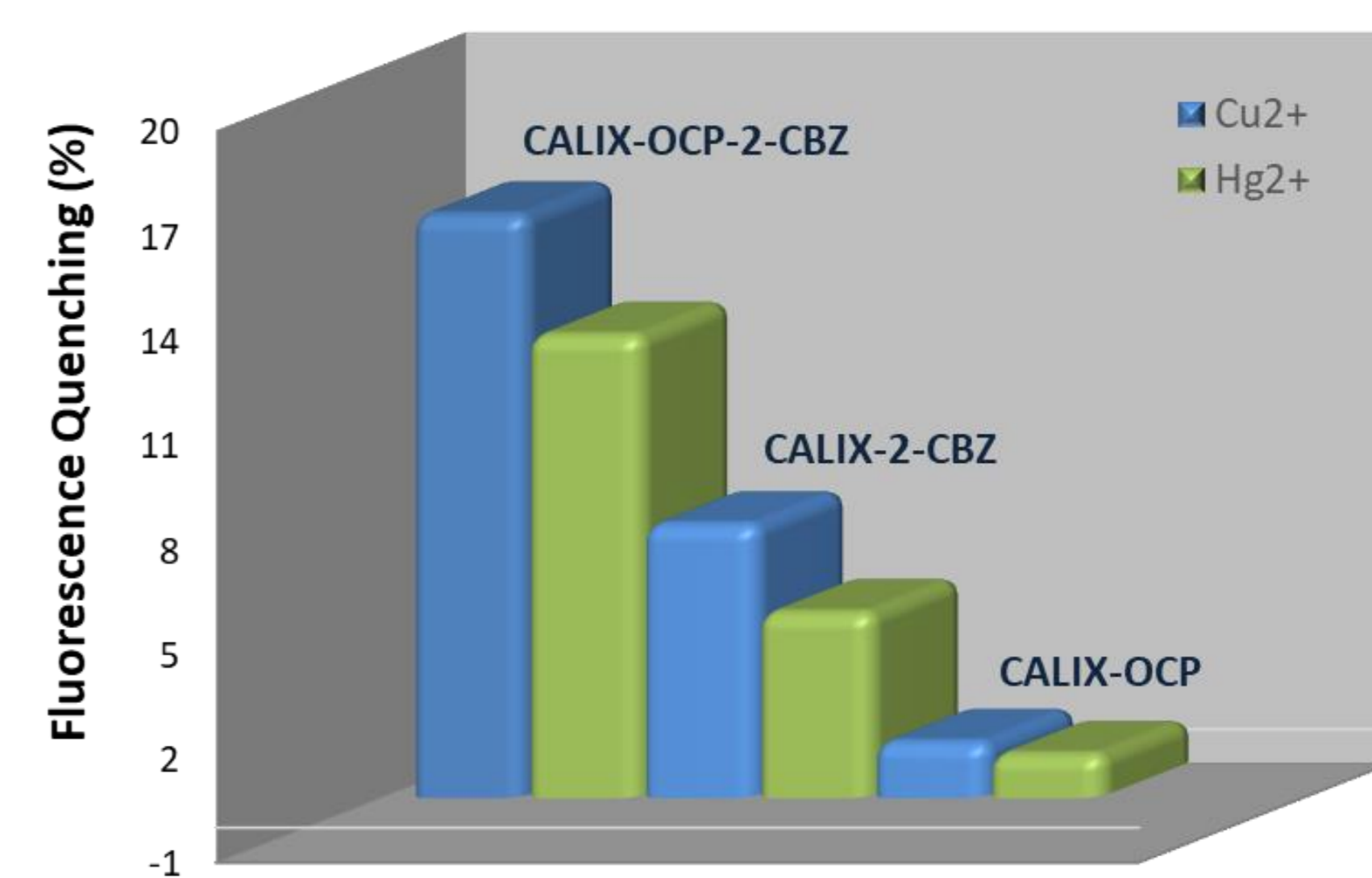


Figure 2. Fluorescence quenching response for fluorophores in  $\text{CH}_3\text{CN}$  upon the addition ca. 41 eq. of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions perchlorates.

## REMARKS

The bicyclic calix[4]arene architecture acting together with the carbazole units undoubtedly play a crucial role in the complexation of metal ions via appropriate coordination sites, such as oxygen and nitrogen donor atoms. These results demonstrate an important cooperative effect concerning the cavity shape and the carbazole units together in the complexation event. The nature and the precise site of coordination between **CALIX-OCP-2-CBZ** and several metal cations is currently under study by UV-Vis and  $^1\text{H}$ NMR.

## REFERENCES

[1] Patra, S.; Lo, R.; Chakraborty, A.; Gunupuru, R.; Maity, D.; Ganguly, B.; Paul, P. *Polyhedron* **2013**, *50*, 592-601. [2] Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780-3799. [3] a) Teixeira, C., Costa, A. I., Prata, J. V. *Tetrahedron Lett.* **2013**, *54*, 6602-6606; b) Barata, P. D., Prata, J. V., *Supramol. Chem.* **2013**, *25*, 782-797.

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