METAL ION RECOGNITION-INDUCED BY CALIX[4]ARENE-CARBAZOLE-CONTAINING POLYMERS

Patrícia D. Barata,[1,2*] Alexandra I. Costa,[1,2] Carina B. Fialho,[1] José V. Prata[1,2]

[1]Laboratório de Química Orgânica, Área Departamental de Engenharia Química, ISEL, IPL, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; [2]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal. *pbarata@deq.isel.ipl.pt

SUMMARY

Sensing and recognition of ions and neutral molecules via synthetic receptors are of current interest in supramolecular chemistry because of their significant importance in several areas, such as chemistry, biology and environment. Compared with small molecules, polymers-based sensors displayed several important advantages like signal amplification. In this way, the incorporation of molecular receptors such as calixarenes with conjugated polymer backbones is expected to enhance the signaling events related to a host–guest interaction. The preorganized binding sites, easy derivatization and flexible three-dimensional steric structures make calixarenes ideal construction platforms for molecular design to generate fluorescent receptors. The use of calixarenes as supramolecular scaffolds for this type of architectures has been explored and the sensing abilities of resultant polymers toward metal and molecular ions established.[1,2]

Based on the high sensitivity shown by the non-polymeric analogue **CALIX-OCP-CBZ** (not shown),[3] to toxic metal cations, we decide two extend the sensing study to polymer materials. Herein, we report the preliminary results of the chemosensing ability of a new bicyclic calix[4]arene-carbazole-polymer (**CALIX-OCP-PPE-CBZ**) towards the detection of toxic metals in fluid phase (Figure 1).

RESULTS AND DISCUSSION

- Solution quenching experiments were carried out by titration of diluted solutions of the polymers with increasing amounts of toxic metals as perchlorates salts ($Cu(ClO_4)_2$ and $Hg(ClO_4)_2$; $1.24x10^{-6}$ - $2.88x10^{-5}$ M). The extent of the developed interactions between the polymers and the toxic metals were quantified by the Stern-Volmer approach.
- Figure 2 illustrates the quenching curves, Stern-Volmer plot and Job plot obtained for complex formation between **CALIX-OCP-PPE-2,7-CBZ** and Cu(II). Under conditions of continuous irradiation (λ_{exc} = 380 nm) no noticeable photodegradation occurs.

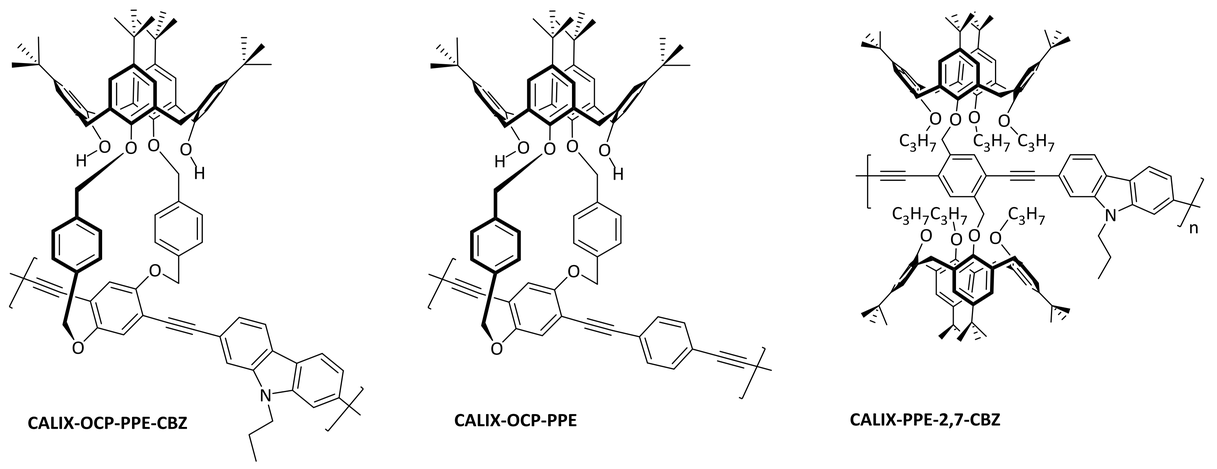

Figure 1. Calix[4]arene-PPE polymers based sensors structures.

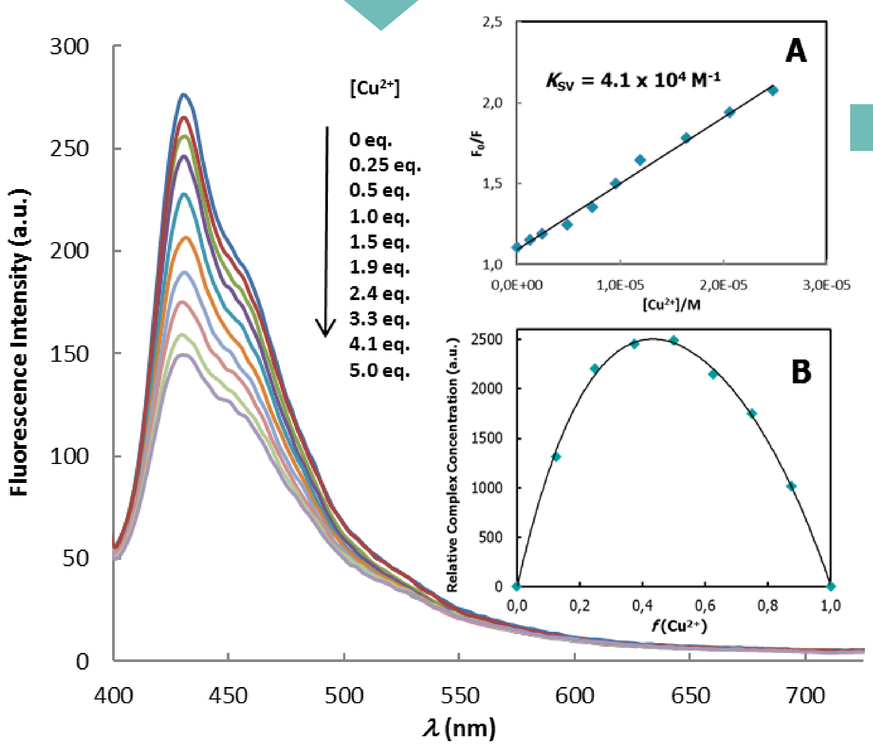

Figure 2. Photoluminescence quenching spectra of **CALIX-OCP-PPE-2,7-CBZ** ($5.0x10^{-6}$ M in CH_3CN) with $Cu(ClO_4)_2$. Inset **A.** Stern-Volmer plot; **B.** Job plot for complex formation (at constant 1.0×10^{-5} M total concentration) (λ_{exc} = 380 nm).

- **CALIX-OCP-PPE-2,7-CBZ** presents a sensitivity response to Cu^{2+} with a K_{sv} value of $4.1x10^4$ M^{-1} and a detection limit of 224 nM, which is in the same range of its homologous compound lacking of polymeric system (results present in a poster communication at this conference).
- This result was quite surprising since it would be expected that the greater extent of conjugation present in the polymer, and the probable signal amplification that would result, would give rise to higher sensory values.
- Detection response for Pb(II) was also performed (Figure 3), however, no substantial fluorescence variations were observed which confers a high specificity of **CALIX-OCP-PPE-2,7-CBZ** toward Cu(II).

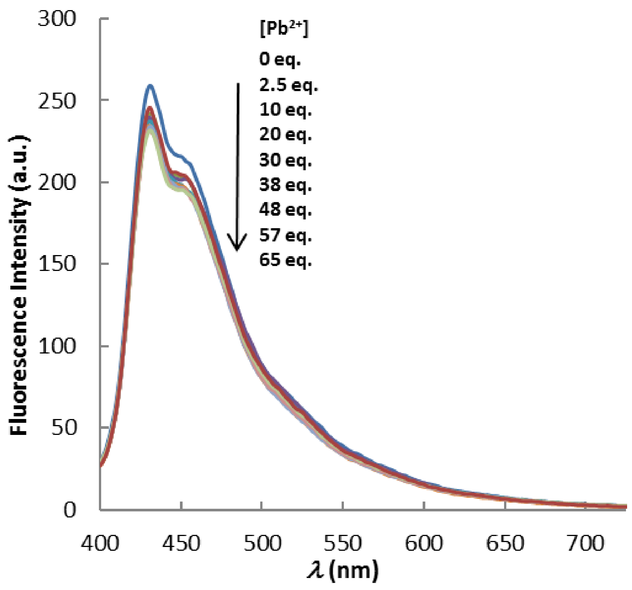

Figure 3. Photoluminescence quenching spectra of **CALIX-OCP-PPE-2,7-CBZ** ($5.0x10^{-6}$ M in CH_3CN) with $Pb(ClO_4)_2$; λ_{exc} = 380 nm.

- No quenching response was found for **CALIX-OCP-PPE** in the presence of Cu(II), evidencing the significant role of the carbazole units in the complexation process;
- The absence of solubility in acetonitrile exhibited by **CALIX-PPE-2,7-CBZ** did not allow the evaluation of its sensorial capacity in this solvent against the metals under study.

CONCLUSIONS

A new bicyclic calix[4]arene-carbazole-PPE polymer was described for the first time to act as potential chemical sensing agent for the detection of toxic metals, showing particular selectivity toward copper. However it seems that the polymeric structure does not improve the sensitivity in the detection event. Further studies with other analytes/solvents and the evaluation of its sensing abilities are in progress and will be presented elsewhere.

REFERENCES

[1] a) Kim, H. N., Ren, W. X., Kim, J. S., Yoon, J. *Chem. Soc. Rev.* **2012**, 41, 3210-3244; b) Ma, J., Song, M., Boussouar, I., Tian, D., Li, H. *Supramol. Chem*. **2015**, 27, 444-452. [2] Wosnick, J.H., Swager, T.M. *Chem. Commun*. **2004**, 2744-2745. [3] Costa, A. I., Fialho, C. B., Barata, P. D. Prata, J. V. Novel Bicyclic Fluorescent Calix[4]arene-based Sensors for Toxic Metals, 2nd International Caparica Conference on Pollutant Toxic Ions and Molecules, November 2017, Monte de Caparica, Portugal.

ACKNOWLEDGMENTS

Acknowledgements: We thank IPL (Project IPL/2016/NoSeMeTox/ISEL) and FCT/MCTES (UID/QUI/00616/2013) for financial support.

March 2018