Cu(II) DETECTION BY FLUORESCENT CALIX[4]ARENE-OXACYCLOPHANE ARCHITECTURES

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OUTLINE

Calixarenes are cyclic oligomers widely investigated due to their ability to recognize and differentiate neutral and ionic guests through the formation of inclusion complexes [1]. Various topologies of fluorescent sensors for metal cation recognition based on calixarene-derived molecular receptors have been developed [2]. Copper(II), lead(II) and mercury(II) ions are ubiquitous in nature, either associated to important physiological processes [3] or representing environmental hazards and health issues [4], making their sensitive and selective detection highly desirable.

In this communication we report the results of the sensing ability of calix[4]arene-oxacyclophane (Calix-OCP) receptor, either wired-in-series in arylene-*alt*-ethynylene conjugated polymers [5] or standing alone as a sole molecular probe (Fig. 1) [6], toward metal ions in solution.

RESULTS AND DISCUSSION

Synthesis

The fluorescent sensors (Fig. 1) were synthesized by a Pd-catalysed Sonogashira-Hagihara methodology and were isolated in good yields [5,6].

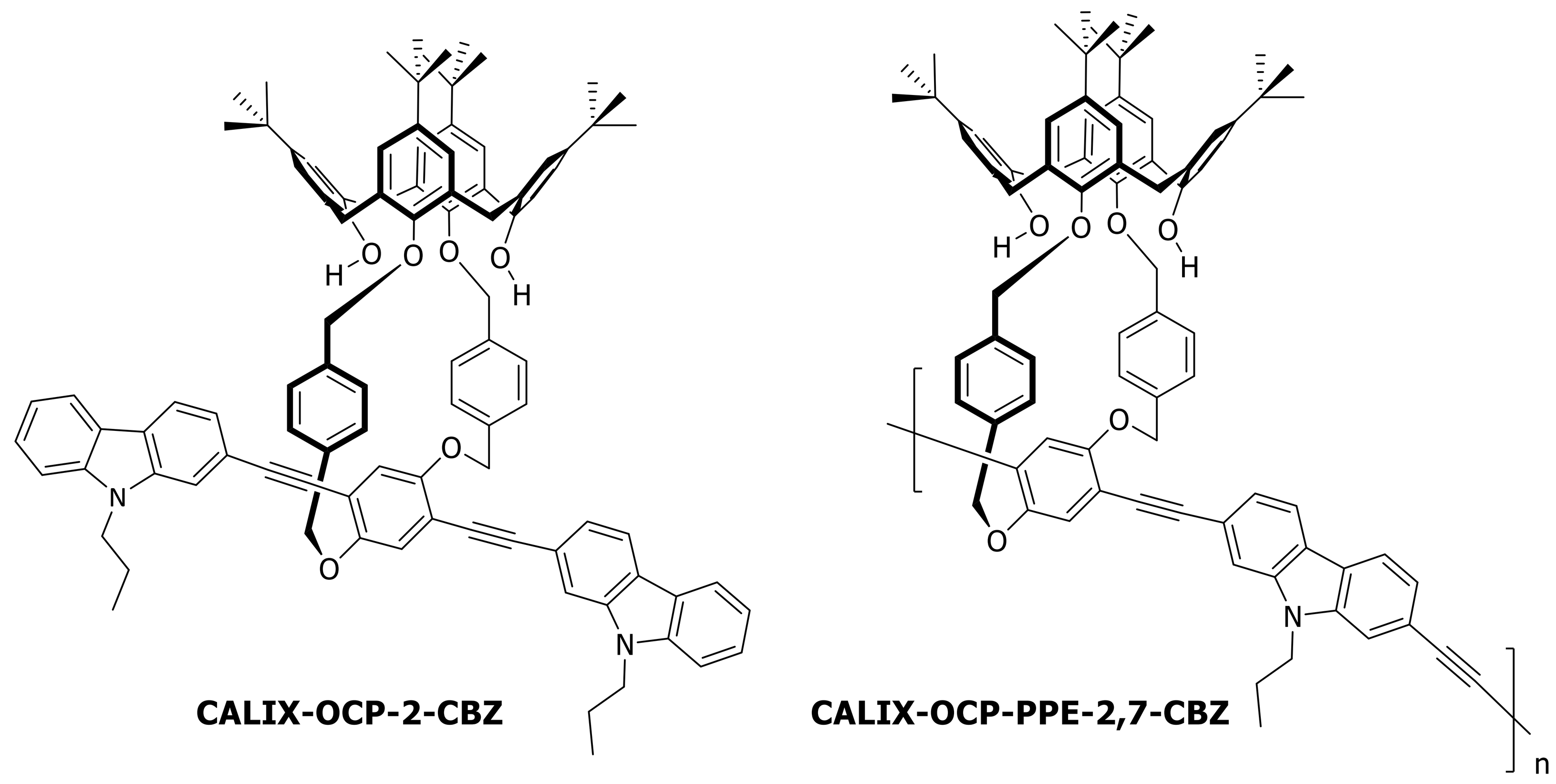

Figure 1. Molecular structures of Calix-OCP sensors.

Sensing Metal Cations

The quenching experiments were carried out by fluorimetric titrations of CH_3CN solutions of **Calix-OCP-2-CBZ** and **Calix-OCP-PPE-2,7-CBZ** using metal cations as perchlorates salts. The fluorescent sensors revealed excellent photostability under the conditions used in sensorial experiments (λ_{exc} = 380 nm). **Calix-OCP-PPE-2,7-CBZ** and **Calix-OCP-2-CBZ** showed relevant response for Cu(II) detection (Table 1). Titration experiments with Pb(II) and Hg(II) do not reveal any significant quenching.

Table 1. Association constants (K_a) and free energy changes (ΔG) for the inclusion complexation with Cu(II).

Host	K_a / M^{-1}	ΔG / kJ/mol
Calix-OCP-PPE-2,7-CBZ	8.52×10^4	-28.1
Calix-OCP-2-CBZ	6.62×10^4	-27.5

The **Calix-OCP-PPE-2,7-CBZ** is strongly quenched (44%) upon contact with 5 equivalent of Cu(II) (Fig. 2 (A)) and the excellent curve-fitting plot (Fig. 2 (B)) confirms the 1:1 stoichiometry of complex. The stoichiometry of the complex was also assessed by the continuous variation method (Job's method) (Fig. 3).

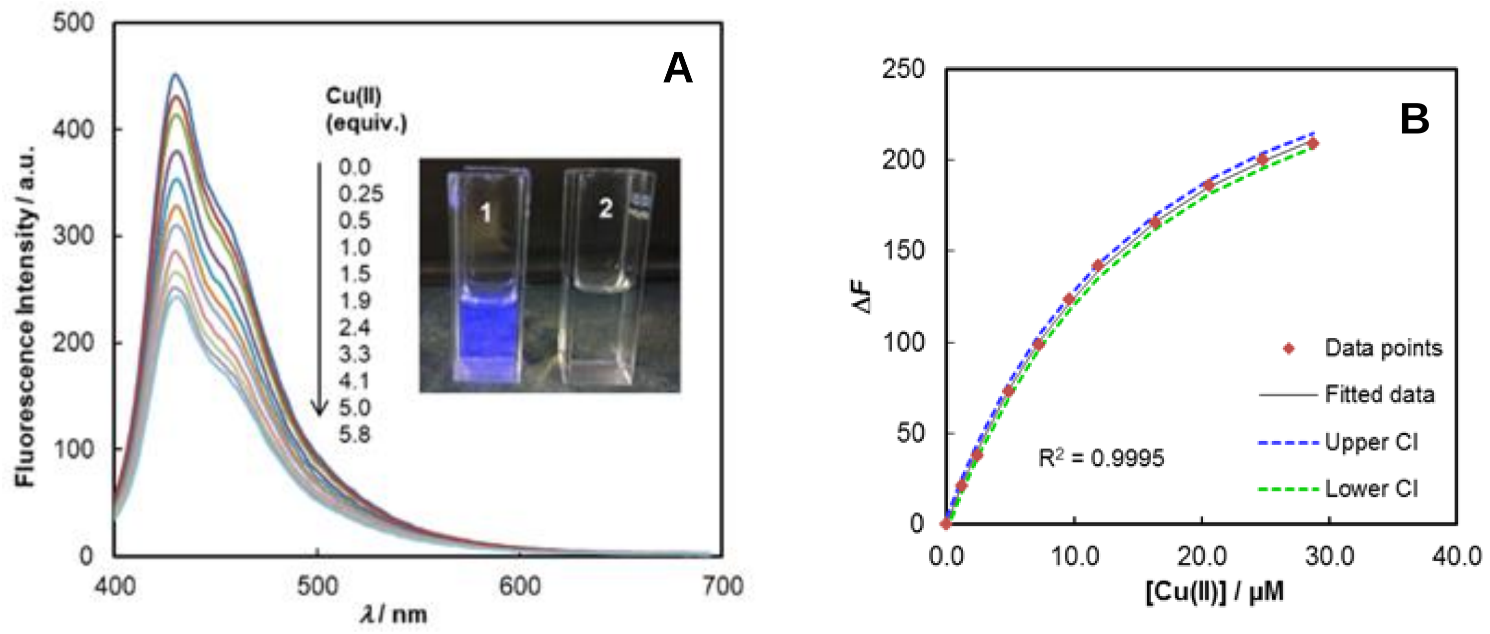

Figure 2. (**A**) Emission spectra of **Calix-OCP-PPE-2,7-CBZ** (5.0×10^{-6} M in CH3CN) upon addition of increasing amounts (0.25-5.8 equiv.) of $Cu(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: photo of polymer fluorescence under UV irradiation (366 nm) before (1) and after (2) $Cu(ClO_4)_2$ addition (5 equiv.); (**B**) Binding isotherm with fitted curve and confidence intervals.

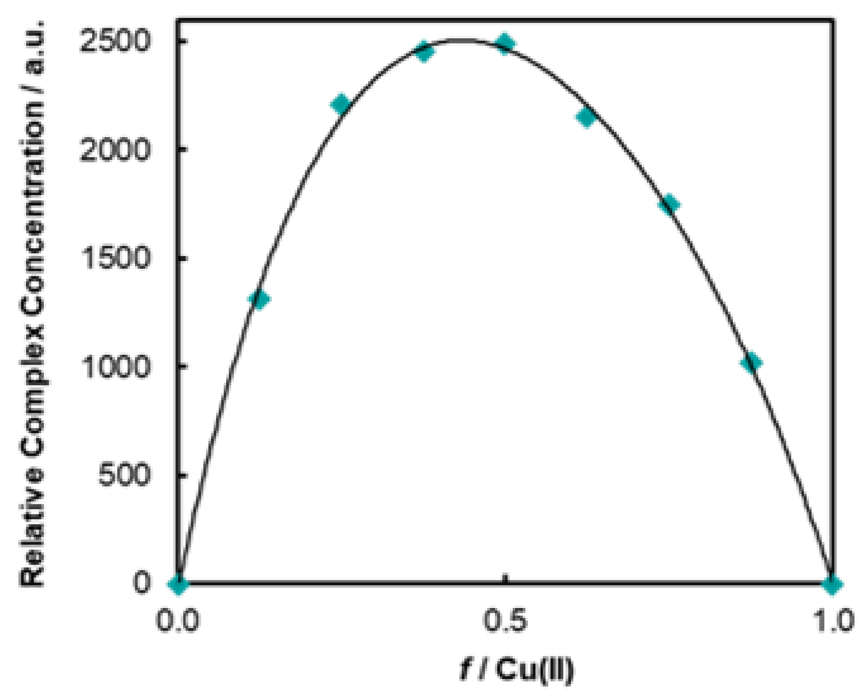

Figure 3. Job plot for complex formation between polymer and Cu(II) in CH_3CN (at constant 1.0×10^{-5} M total concentration) as obtained from changes in fluorescence (λ_{exc} = 380 nm).

CONCLUSIONS

Results showed that calix[4]arene-oxacyclophane molecular receptors are excellent platforms for the recognition of Cu(II) and display remarkable high sensitivity and selectivity toward this cation. Evaluation of the behavior of Calix-OCP-Cu(II)/Cu(I) inclusion complexes as potential redox-active centers in biomimetic chemistry field is now progressing.

REFERENCES: [1] Gutsche, C.D. Calixarenes - An Introduction, 2nd ed. in Monographs in Supramolecular Chemistry; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, U. K., 2008; [2] Valeur, B.; Leray, I. Coord. Chem. Rev. 2000, 205, 3-40. [3] Malmström, B.G.; Leckner, J. Curr. Opin. Chem. Biol. 1998, 2, 286-292. [4] Desai, V.; Kaler, S.G. Am. J. Clin. Nutr. 2008, 88, 855S-858S. [5] Costa, A.I.; Barata, P.B.; Fialho, C.F.; Prata, J.V. Molecules 2020, 25, 2456.[6] Prata, J.V.; Barata, P.D.; Pescitelli, G. Pure Appl. Chem. 2014, 86, 1819-1828.

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