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### ACCEPTED MANUSCRIPT

# Calix[4] Based Hg(II) Ion Selective Electrodes : A Thermodynamic Protocol to Address the Selectivity versus the Hosting Capacity Paradigm in the Selection of the Carrier

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#### Abstract

A new calix[4]arene derivative, L<sub>1</sub>, and its interaction with cations has been structurally and thermodynamically characterised. The thermodynamics of cation complexation of a calix[4]pyrrole amide derivative, CPA, was also investigated. Thermodynamics is the protocol used to address the issue of selectivity vs hosting capacity of receptors in their selection for use as carrier mediated mercury (II)ion selective electrodes (ISEs). It is shown that L<sub>1</sub> has a higher affinity for Hg(II) than CPA, but the hosting capacity of the latter is greater (2 cations/unit of receptor) than that of the former (1:1 complex). Regardless of the hosting capacity of CPA, the higher affinity of L<sub>1</sub> for Hg(II) predominates when incorporated in the electrode membrane. The end result is that the sensing characteristics of the ISE for Hg(II) improve significantly when L<sub>1</sub> rather than CPA serves as a mediator carrier. The correlation found between the ISE response to cations and the difference in stability of these cations and these receptors relative to mercury (II) is discussed taking into account previous work in this area. Final conclusions are given.

**Keywords:** Thermodynamics; Ion Selective Electrodes; Mercury (II); Calix[4]arene; Supramolecular Chemistry.

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