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Synthesis and Complexing Properties of Novel Tetraphosphonate-Calix[4] Resorcinarenes

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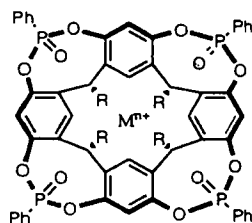
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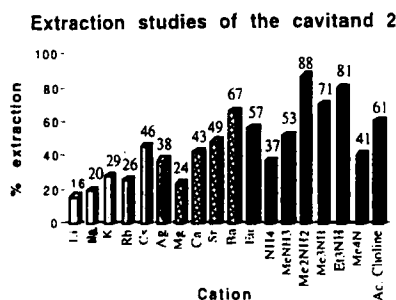
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We recently reported the synthesis of phosphorylated cavitands and their high affinity for cationic species.¹ We have thus synthesized and explored the properties of novel phosphacavitands containing four long R chain substituents at their lower rim. The amphiphilic molecule 2 could be introduced into a micelle. The compounds 3 and 4 could be used respectively as a cation carrier into Supported Liquid Membrane and as a sensor into a Self-Assembled Monolayer on gold.^{2, 3}



- 1: R = $n\text{-C}_6\text{H}_{13}$
- 2: R = $n\text{-C}_{11}\text{H}_{23}$
- 3: R = $-(\text{CH}_2)_7\text{-O-C}_6\text{H}_4\text{NO}_2$
- 4: R = $-(\text{CH}_2)_{10}\text{-S-(CH}_2)_9\text{CH}_3$



The complexing properties of ligands 1 - 4 for M^{n+} metallic cations ($n = 1-3$) and ammonium cations have been characterized by extraction experiments.⁴ We found that these cavitands are better extractants of methylammonium cations (50-90%) than metallic cations except for Cs^+ , Ba^{2+} and Eu^{3+} . The free energies of association for alkali cations are in the range 40-50 kJ/mol, with a maximum for Cs^+ .

The structural aspects (NMR and X-ray data) of the supramolecular complexes obtained with cesium and methylammonium picrates reveal that the guests are deeply encapsulated into the cavity defined by the aromatic rings and the phosphoryl moieties of the ligands.

The remarkable effect of the counterion (Cl^-) coordination has to be investigated.

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