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ELECTRONIC SUPPLEMENTARY INFORMATION

Stereochemistry and thermodynamics of the inclusion of aliphatic and aromatic anionic guests in a tetracationic calix[4]arene in acidic and neutral aqueous solutions

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Dedicated to Professor Julius Rebek, Jr. And Professor Javier de Mendoza on the occasion of their 65th birthdays.

Gel electrophoresis

To determine the overall charge of the host we resorted to zone electrophoresis that provides a gentle and high resolution method for the characterization of molecules based on their size, conformation, and charge. Host solutions buffered at pH 2 and the tetracationic 5,11,17,23-tetrakis(trimethylammonium)-25,26,27,28-tetrapropoxy-calix[4]arene, employed as a reference compound, have comparable mobility (Fig. S1a), indicating that the host is fully protonated (*i.e.* H_8L^{4+}) in this pH region, as also shown by the potentiometric results.

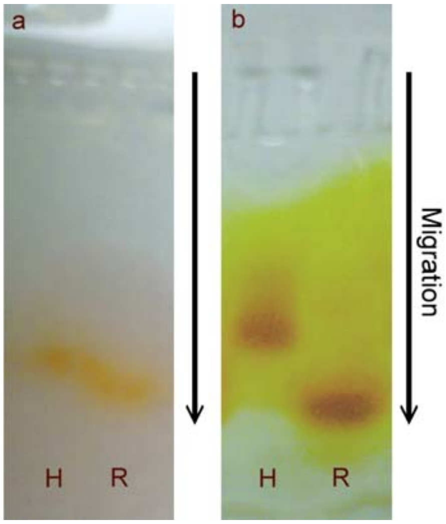

Fig. S1. Electrophoretic experiments at pH 2.0 (a) and 6.8 (b) in agarose and polyacrylamide gel, respectively. H is H_8L^{4+} and H_7L^{3+} in a and b, respectively; R is the tetracationic reference compound.

As pH increases, the hydroxyl proton is lost and the system assumes an overall charge of 3+. This is reflected by the electrophoretic experiment performed at pH 6.8; in this region the migration of the host decreases (Fig. S1b), due to the decreased net charge of the overall system. Both potentiometric and electrophoretic results lead to conclude that only the hydroxyl proton of the host is lost in neutral conditions in water and, thus, the host has a negative charge at the lower rim while the upper is fully protonated.

ESI-MS

ESI mass spectra represent chemical systems where charged host and host-guest complexes are either preformed in solution or are generated at the high-voltage conditions used in ESI. In both cases, the observation of molecular aggregates in the mass spectrum demonstrate the stability of such species in the gas phase, at least for the time-frame of mass analysis.

The positive ion electrospray of different solution of the host, shows the peak corresponding to the $[H_5L+HA]^+$ species at m/z = 689.33, m/z = 751.40 and m/z = 767.12 when, respectively, HCl, H_3PO_4 and CF_3COOH are used to adjust the pH of the final solution at 2.0. The negative analysis shows always the peak at m/z = 651.53 corresponding to the $[H_3L]^-$ specie, regardless the nature of the acid employed.

The interaction of the receptor with the anions investigated has been followed also by mass spectrometry. The mass spectra of the guest-host complexes indicate the presence of supramolecular adducts of the 1:1 type, regardless of the nature of the guest included. The formation of these adducts is confirmed by the presence of signals at m/z = 773.45, m/z = 741.45, m/z = 811.33, m/z = 777.33 attributed to the [Host-**2**]$^+$, [Host-**3**]$^+$, [Host-**4**]$^+$, [Host-**5**]$^+$ species, respectively.