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Short Communication

Voltammetric study of inclusion of *p*-sulfonated thiacalix[*n*]arenes ($n = 4, 6$) toward ferrocenyl guests in aqueous solutions

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Abstract

Inclusion behavior of negatively charged host molecules, thiacalix[4]arene-*p*-tetrasulfonate (TC4AS) and [6]arene-*p*-hexasulfonate (TC6AS), toward (ferrocenylmethyl)trimethylammonium ($FcCH_2NMe_3^+$), hydroxymethylferrocene ($FcCH_2OH$), ferrocenecarboxylic acid (FcCOOH), and 1,1′-ferrocenedicarboxylic acid ($Fc(COOH)_2$) was studied in aqueous solutions (pH 7.0) with cyclic voltammetry. Upon increasing the concentration of TC4AS to 4-fold of each guest, the anodic peak current density ($j_{p,a}$) decreased, suggesting inclusion of the ferrocenyl guests in TC4AS. Also oxidation half-wave potential ($E_{1/2}$) of $FcCH_2NMe_3^+$, $FcCH_2OH$, and FcCOOH was shifted to cathodic direction, showing preferential inclusion of the oxidative state. Inclusion of neutral guests such as $FcCH_2OH$ and Fc^+COO^- implies that hydrophobic interaction between TC4AS and the guests is the chief driving force for formation of host–guest assembly. The decrease of $E_{1/2}$ for each guest was in the order: $FcCH_2NMe_3^+ > FcCH_2OH > FcCOOH$, suggesting that electrostatic interaction controls the preference toward oxidative form of the guest. Dicarboxylic $Fc(COOH)_2$ showed decrease of $j_{p,a}$ but increase of $E_{1/2}$ upon inclusion, suggesting TC4AS preferred reduced form $Fc(COOH)_2$ to oxidized form $Fc^+(COO^-)_2$. TC6AS behaved similarly to TC4AS but with larger decrease in of $E_{1/2}$ and $j_{p,a}$. The larger shift of $E_{1/2}$ for inclusion of FcCOOH, the oxidative form of which is also neutral (Fc^+COO^-), than that attained with TC4AS endorses main role of hydrophobic interaction between TC*n*AS ($n = 4, 6$) and ferrocenyl guest molecules. Having the most preferential electrostatic interaction, kinetically stable complex was formed between TC6AS and $FcCH_2NMe_3^+$.

Keywords: Thiacalixarene; Ferrocene derivatives; Inclusion; Host–guest interaction; Hydrophobic interaction

1. Introduction

Direct control of host–guest inclusion by electrochemical potential as an external stimulus can lead to electrochemical switching self-assembles and devices [1–3]. A key to realize such switching systems is a host molecule capable of differentiating oxidative and reductive states of a guest, which can be conveniently measured by shift of redox potential of the guest. For instance, one of the authors first studied inclusion of β-cyclodextrin toward ferrocenecarboxylate ($FcCOO^-$ [4]) with cyclic voltammetry to show preferential inclusion of $FcCOO^-$ over Fc^+COO^- [5]. Kaifer et al. carried out voltammetric study of inclusion of calix[6]arene-*p*-hexasulfonate (C6AS) toward variety of ferrocenyl guests to reveal that a large fraction of the free energy change upon inclusion is due to nonelectrostatic interactions [6]. Furthermore, inclusion behavior of hexamethyl ether of C6AS revealed decisive role of preorganization of host in inclusion [7]. Thus electrochemical study of host–guest inclusion has afforded insight into interaction between host and guest with varying redox states.

In the last decade, we have studied functions of thiacalix[*n*]arenes such as complexation with metal ions and inclusion toward guest molecules [8]. Examples for the latter are inclusion of thiacalix[4]arene-*p*-tetrasulfonate

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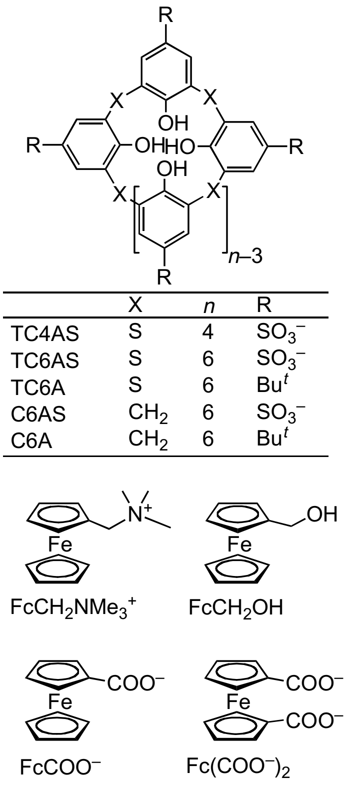


	X	n	R
TC4AS	S	4	SO_3^-
TC6AS	S	6	SO_3^-
TC6A	S	6	Bu^t
C6AS	CH_2	6	SO_3^-
C6A	CH_2	6	Bu^t

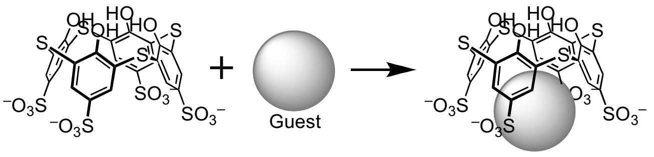
Scheme 1. Calixarenes and hosts.

(TC4AS, Scheme 1) toward halomethanes [9], water-miscible organic molecules [10], and mono-substituted benzenes [11] in its cone-shaped cavity (Scheme 2). Hydrophobic interaction was found to be the main factor to determine stability of TC4AS–alkyl alcohol complex [12]. Very recently, we have succeeded in preparation of a larger analogue, thiacalix[6]arene-*p*-hexasulfonate (TC6AS), which is expected to accommodate guest molecules larger than mono-substituted benzenes. In an attempt to see inclusion ability of TC4AS and TC6AS toward large guest species and possibility of the electrochemical control, we chose ferrocenyl guests with variety of charges (from positive to negative) to monitor the change of redox behavior upon inclusion with cyclic voltammetry to unveil major role of hydrophobic interaction in inclusion of ferrocenyl guests.

2. Experimental

2.1. Equipment

Fast atom bombardment mass spectra were recorded on a JEOL JMS-SX102A spectrometer using Xe as a bombarding atom and diethanolamine as a matrix. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or CH_3CN as an external standard and D_2O as the solvent. The pHs of the solutions were measured by a Toa HM-7J with GST-5725C electrode. Cyclic voltammograms were obtained by use of a potentiostat model CS-2RA (Cypress system, Lawrence, Kansas) with a glassy carbon electrode (6.0 mm o.d. × 3.0 mm i.d., purchased from BAS) as working, a homemade Ag/AgCl (saturated) reference electrode, and a Pt wire counter electrode.



Scheme 2. Inclusion of TC4AS in the hydrophobic cavity.

2.2. Materials

Thiacalix[4]arene-*p*-tetrasulfonate (TC4AS) tetrasodium salt and *p*-*tert*-butylthiacalix[6]arene (TC6A) were prepared as reported previously [13,14]. (Ferrocenylmethyl)trimethylammonium ($FcCH_2NMe_3^+$) bromide, hydroxymethylferrocene ($FcCH_2OH$), ferrocenecarboxylic acid (FcCOOH), and 1,1′-ferrocenedicarboxylic acid ($Fc(COOH)_2$) were purchased from Tokyo Chemical Industry Co. Ltd. A stock solution of 0.010 M $FcCH_2NMe_3Br$ and 0.10 M $FcCH_2OH$, FcCOOH, and $Fc(COOH)_2$ were prepared by dissolving an appropriate amount in water (for $FcCH_2NMe_3^+$) and in DMSO (for other ferrocenyl guests). Piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) was purchased from Dojindo Laboratories, Kumamoto. The buffer solution (0.100 M) was prepared by dissolving an appropriate amount of PIPES in water, followed by adjustment of the pH (=7.0) with NaOH and made up to appropriate volume by water.

2.3. Synthesis of hexasodium 37,38,39,40,41,42-hexahydroxy-2,8,14,20,26,32-hexathiacalix[4]arene-5,11,17,23,29,35-hexasulfonate (TC6AS)

The procedure for TC4AS via direct sulfonation of TC4A [13] was slightly modified as follows. A mixture of *p*-*tert*-butylthiacalix[6]arene (TC6A) [14] (1.00 g, 0.92 mmol) and conc. H_2SO_4 (20 cm^3) was heated at 90 °C for 18 h. After cooling to ambient temperature, the mixture was filtered to recover precipitates, which was then dissolved in a small amount of water. Addition of NaCl to the solution gave purple precipitate of the crude product, which was recrystallized from water–acetone mixture to give acetone-included crystals. After filtration, the crystals were dissolved in water, which was evaporated to dryness to give acetone-free TC6AS (545 mg, 43.4%). FAB MS *m*/*z* 1355.6 (M$^-$). ^{1}H NMR (400 MHz, D_2O, DSS as ext. std.) $\delta = 7.59$ (s, 12H, ArH). ^{13}C NMR (400 MHz, D_2O, CH_3CN as ext. std.) $\delta = 118.72$, 127.03, 132.92, 153.11 (C_{Ar}).

2.4. Cyclic voltammetry

To a 10-ml volumetric flask were added appropriate amounts of 0.10 M TC*n*AS ($n = 4$ or 6), 0.10 M PIPES (pH 7.0), 1.00 M KCl as a supporting electrolyte, and