

## **Inclusion of electrochemically active guests by novel oxacalixarene hosts**

David Sobransingh, Mahender B. Dewal, Jacob Hiller, Mark D. Smith and Linda S. Shimizu\*

*Department of Chemistry and Biochemistry, University of South Carolina, Columbia,  
South Carolina 29208*

### SUPPORTING INFORMATION

#### **Characterization and Binding Studies**

A variety of methods were used to characterize the hosts and study the interaction of host and guest including:

##### **UV-visible spectroscopy**

UV-visible methods were not useful because of the significant overlap of host and guest bands. Additionally, high epsilon values caused the UV-visible spectral data to be unusable at concentrations required for binding as all bands were off scale.

##### **NMR**

<sup>1</sup>H and <sup>13</sup>C NMR studies were performed on a 300 MHz Mercury Varian NMR spectrometer. Although a series of solvents were surveyed, binding was best in CD<sub>2</sub>Cl<sub>2</sub> as the low polarity and solubility provided optimum conditions for binding and voltammetric experiments.

Pulse gradient spin echo (PGSE) NMR diffusion experiments were performed on a 400 MHz Bruker NMR spectrometer and used to verify the absence of large assemblies of host in solution.

##### **Cyclic Voltammetry**

Voltammetric experiments were carried out on a BAS CV50 (Bioanalytical Systems, West Lafayette, IN). Cyclic voltammetric experiments were run in a single compartment cell fitted with a glassy carbon working electrode (0.071 cm<sup>2</sup>), a Pt counter electrode, and a reference electrode made of Ag/AgCl.

##### **X-Ray Structure Determination**

X-ray diffraction intensity data from crystals were measured at 150(1) K on a Bruker SMART APEX diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). Raw area detector data frame integration was performed with SAINT+.

## Estimation of Association Constants<sup>1</sup>

Association constants were estimated using the following equations

$$K_{red}/K_{ox} = \exp(nF\Delta E_{1/2}/RT) \quad (1)$$

$$E_{1/2(\text{complex})} = E_{1/2}^0(\text{free}) + RT/F \ln(1 + K_{ox}[H]) \quad (2)$$

Where,

$K$  = association constant

$H$  = host

$E_{1/2}$  = half wave potential ferrocene/ferrocenium in presence of host

$E_{1/2}^0$  = half wave potential of free ferrocene/ferrocenium redox couple

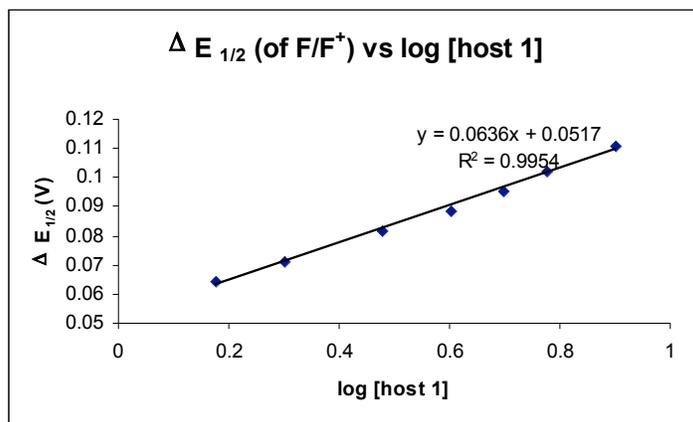
When  $K[H] \gg 1$ , Equation (1) can be rearranged to give

$$\Delta E_{1/2} = 2.303 RT/F \log [H] + 2.303 RT/F \log K \quad (2)$$

Where  $\Delta E_{1/2} = E_{1/2} - E_{1/2}^0$

When the assumption  $K[H] \gg 1$  is true, a plot of  $\Delta E_{1/2}$  vs.  $\log [H]$  gives a straight line with slope  $2.303 RT/F$  and intercept  $2.303 RT/F \log K$

A sample calculation for the  $1 \bullet F^+$  complex is shown below



Intercept =  $2.303 RT/F \log K = 0.0517$   
 $\Rightarrow K = 7.4 \text{ m}^3 \text{ mol}^{-1} = 7400 \text{ M}^{-1}$  for  $1 \bullet F^+$

<sup>1</sup>(a) N. Gupta and H. Linschitz, *J. Am. Chem. Soc.* 1997, **119**, 6384. (b) J.-M. Savéant, *J. Phys. Chem. B* 2001, **105**, 8995. (c) M. Gómez, C. Z. Gómez-Castro, I. I. Padilla-Martínez, F. J. Martínez-Martínez, and F. J. González, *J. Electroanal. Chem.* 2004, **567**, 269

***K* for the 1•F complex was estimated using<sup>2</sup>**

$$K_{red}/K_{ox} = \exp(nF\Delta E_{1/2}/RT)$$

$$\Delta E_{1/2} = -0.114 \text{ V}$$

$$\Rightarrow K_{ox}/K_{red} = 85$$

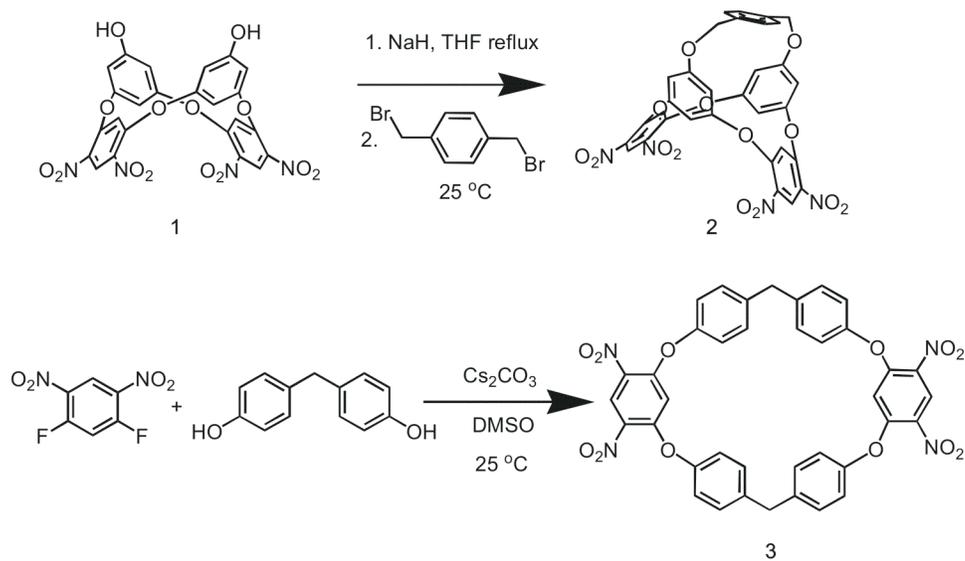
$$K = 87 \text{ M}^{-1} \text{ for } \mathbf{1}\bullet\mathbf{F}$$

---

<sup>2</sup> (a) A. E. Kaifer and M. Gómez-Kaifer, *Supramolecular Electrochemistry*; Wiley-VCH: Weinheim, Germany, 2000. (b) C. Bourgel, A. S. F. Boyd, G. Cooke, H. A. de Cremiers, F. M. A. Duclairoir and V. M. Rotello, *Chem. Commun.* 2001, 1954.

## Synthesis

Host **1** was synthesized according to the procedure reported by Katz and coworkers<sup>3</sup>



**Scheme S1.** Synthesis of hosts **2** and **3**

<sup>3</sup> (a) J. L. Katz, M. B. Feldman and R. R. Conry, *Org. Lett.* 2005, **7**, 91.

## Synthesis and Characterization of **2**

**2** was synthesized by refluxing 200 mg of **1** with 24 mg of NaH in THF for 45 minutes followed by addition of 91 mg of *p*-xylylene dibromide and stirring at room temperature for 24 hours. The reaction was quenched using 1N HCl and extracted using CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was concentrated under vacuum and purified by flash chromatography using 7:3 hexanes: ethyl acetate, to afford **2** in 40% yield. <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>): δ 8.82 (s, 2H), 7.48 (s, 4H), 6.99(d, 4H), 6.61 (3, 2H), 5.66 (s, 2H), 5.45 (s, 4H); <sup>13</sup>C NMR (75 MHz, acetone-*d*<sub>6</sub>): δ 161.15, 156.39, 154.77, 136.30, 132.40, 129.54, 125.54, 110.47, 107.42, 104.48, 69.94. ESI (-) MS *m/z* 681 (M-H)<sup>-</sup>, 727 (M+HCOO)<sup>-</sup>; TLC R<sub>f</sub> = 0.39 (7:3 hexanes: ethyl acetate).

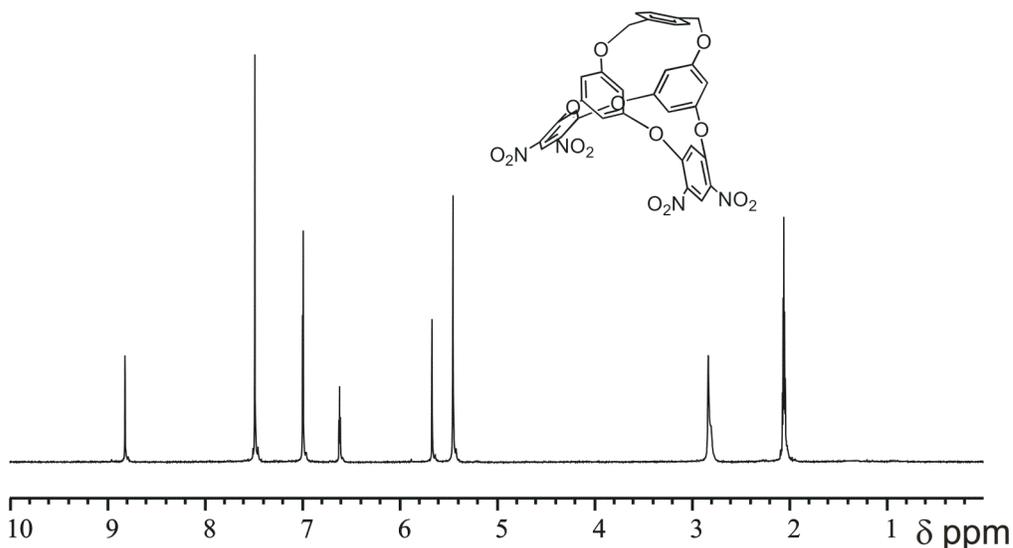


Figure S1 <sup>1</sup>H NMR (300 MHz) of host **2** in acetone-*d*<sub>6</sub>

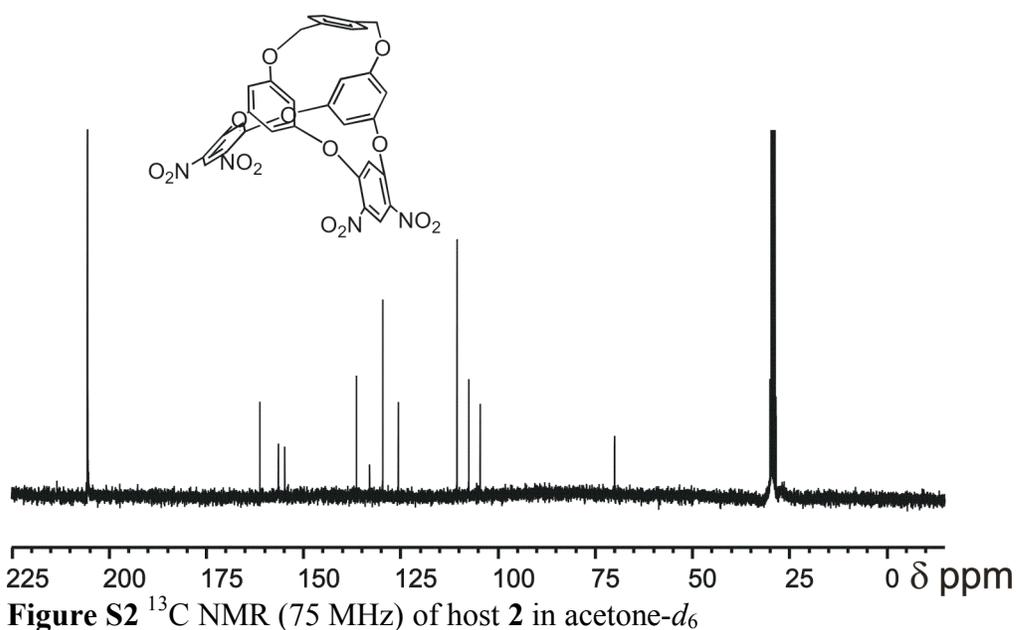
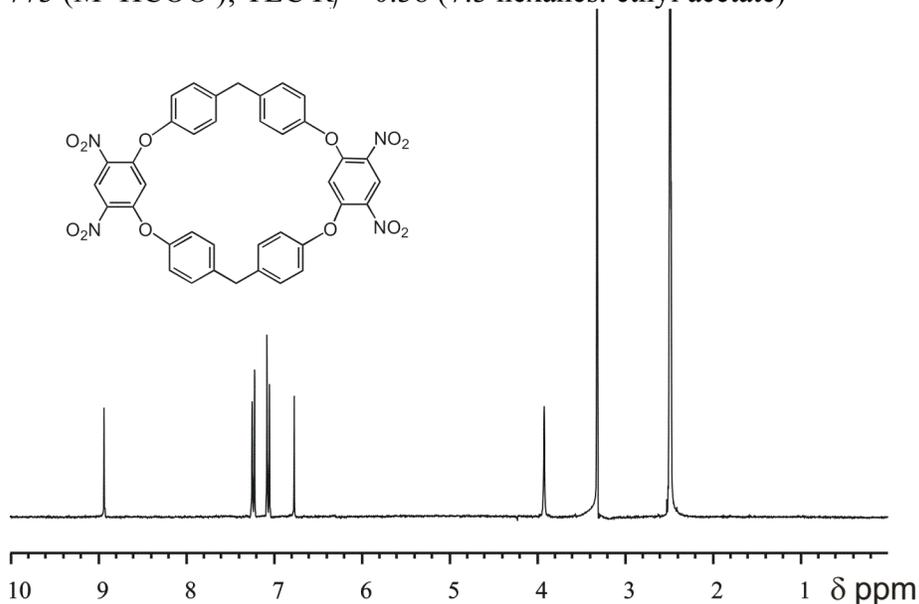


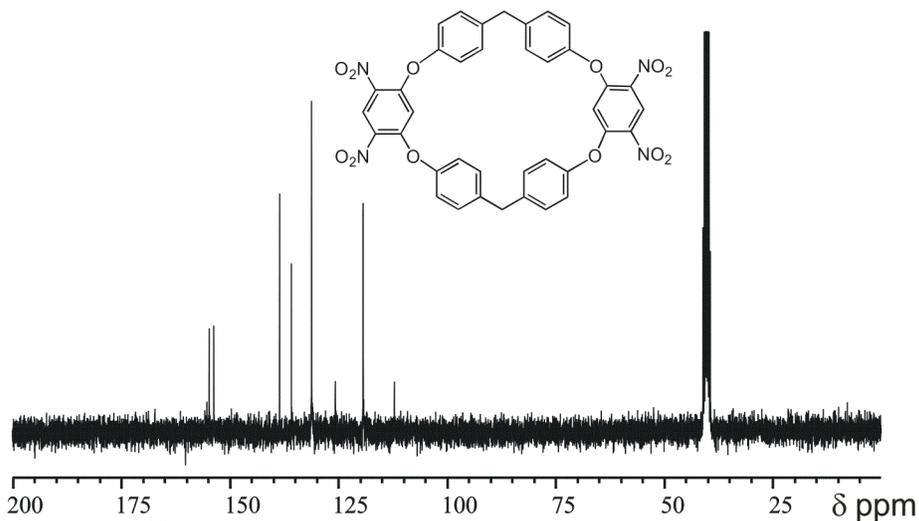
Figure S2 <sup>13</sup>C NMR (75 MHz) of host **2** in acetone-*d*<sub>6</sub>

### Synthesis and characterization of **3**

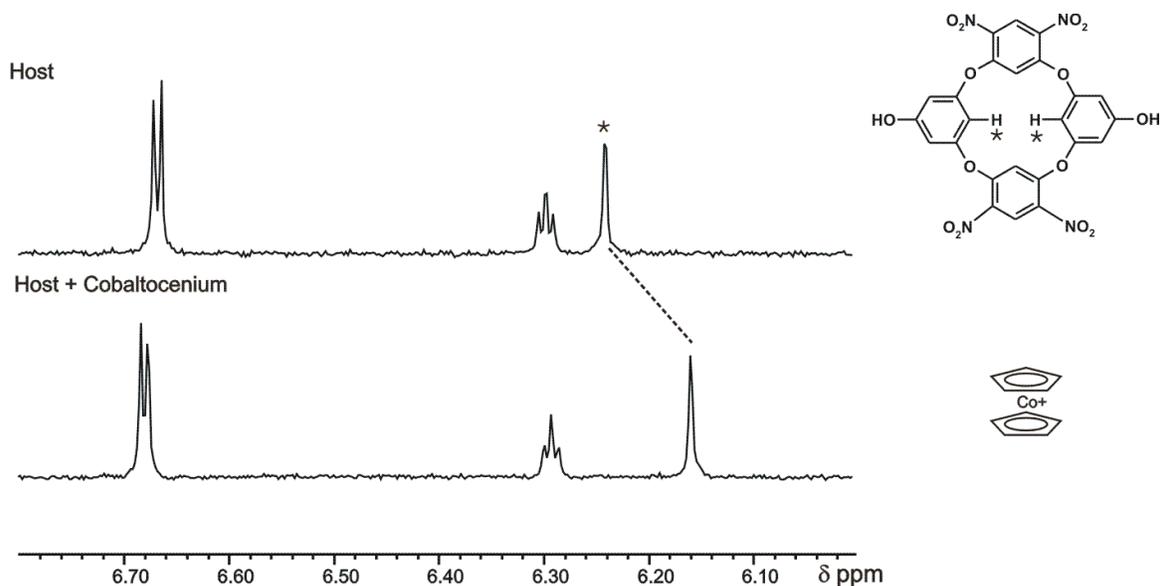
200 mg of bis(4-hydroxyphenyl)methane along with 204 mg of 1,5-difluoro-2,4-dinitrobenzene was added to a round bottom flask containing 815 mg  $\text{Cs}_2\text{CO}_3$  and 250 ml DMSO and stirred overnight. The reaction was partitioned between ethyl acetate and 1N HCl and the organic layer was washed two times. The solvents in the combined organic layers were removed under vacuum and the solid residue was recrystallized from ethyl acetate to afford pure **3** in 60% yield.  $^1\text{H}$  NMR (300 MHz in  $\text{DMSO-}d_6$ )  $\delta$  8.94 (s, 2H), 7.24 (d, 8H), 7.07 (d, 8H), 6.77 (s, 2H), 3.93 (s, 4H)  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  154.74, 153.67, 138.52, 135.81, 131.17, 119.31, 112.09 ESI (-) MS  $m/z$  727 (M-H) $^-$ , 773 (M+HCOO) $^-$ ; TLC  $R_f$  = 0.38 (7:3 hexanes: ethyl acetate)



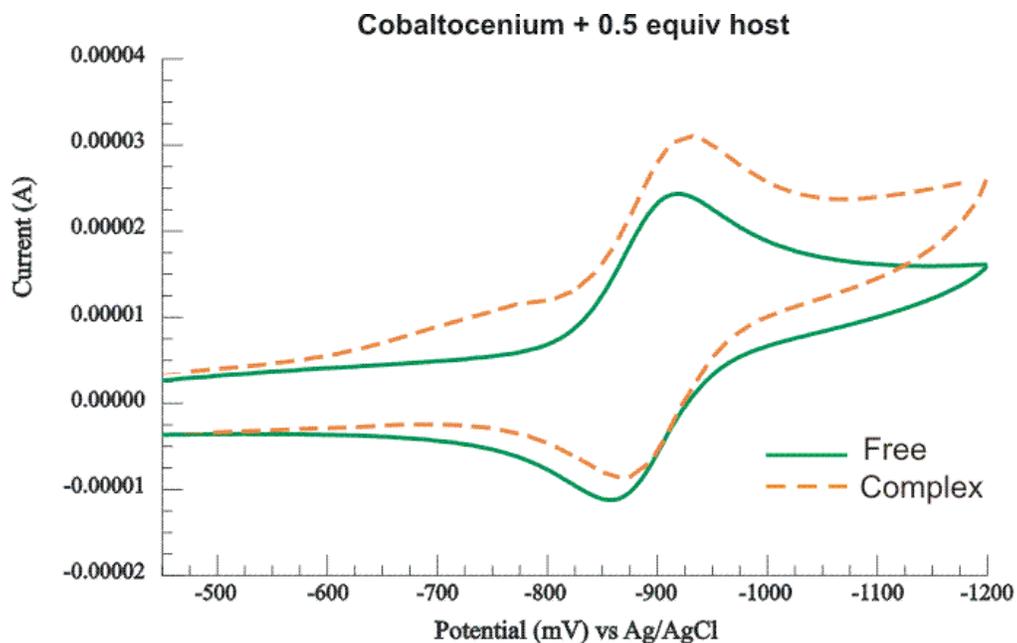
**Figure S3**  $^1\text{H}$  NMR (300 MHz) of host **3** in  $\text{DMSO-}d_6$



**Figure S4**  $^{13}\text{C}$  NMR (75 MHz) of host **3** in  $\text{DMSO-}d_6$



**Figure S5** Proton resonances of host **1** in the absence (top) and in the presence of excess cobaltocenium ( $C^+$ ) guest (bottom). Labeled proton resonance shifts upon complexation by cation- $\pi$  interactions.



**Figure S6** Cyclic voltammetric response of  $C^+$  in the absence (solid line) presence of only 0.5 equiv of host **1** (broken line). Complex is already shifted -13 mV in only 0.5 equiv. of host **1**. At higher concentrations of host **1** required to bring about binding

saturation, the reduction of the host produces precipitation and masks the response required for quantitative measurements.