Supplementary Information

Control of the stoichiometry in host-guest complexation by redox chemistry of guests: Inclusion of methylviologen in cucurbit[8]uril

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Electrochemical experiments. The electrochemical experiments were performed with a Princeton Applied Research Model 273 multipurpose instrument interfaced to a personal computer. A glassy carbon working electrode (0.07 cm^2), a Pt counter electrode, and a saturated calomel electrode (SCE) as a reference electrode separated with a fine glass frit were utilized in a single-compartment cell. The surface of the working electrode was polished with 0.05 μm alumina/water slurry on a felt surface and rinsed with purified water prior to electrochemical experiments. The experiments were conducted in 0.075 M phosphate buffer solutions (pH = 7.0) prepared with purified water (Milli-Q, Millipore). All solutions were deoxygenated by purging with nitrogen gas and maintained under an inert atmosphere during the electrochemical experiments.

Spectroelectrochemical experiments. A spectroelectrochemical cell was assembled with a piece of glass sheet and a piece of indium tin oxide (ITO) coated glass and a spacer film (thickness 200 μm). The ball-shaped polyethylene supporters located between ITO working electrode and cell wall were used to maintain a reproducible light path length. Electrolysis of methylviologen to generate one-electron-reduced species was achieved by applying a potential (-0.8 V) to the ITO working electrode. UV-visible absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. The solution prior to electrolysis was used as a blank reference.

Estimation of apparent dimerization constant. The apparent dimerization constant (K'_D) of $MV^{+\bullet}$ in the presence of CB[8] was estimated by the reported method.[1] More specifically, the K'_D value at a given concentration of CB[8] was calculated from the monomer and dimer concentrations (eq 1), which were estimated by deconvoluting the spectrum of the radical cation into its monomer and dimer components. The concentrations of monomer were calculated by using the molar absorption coefficient at 602 nm (ε = 14,000 $M^{-1}cm^{-1}$; ref. 1). From this data, the molar absorption coefficient of $[CB[8]\text{-}(MV^+)_2]$ complex was estimated to be 16,500 $M^{-1}cm^{-1}$ at 518 nm, which is slightly smaller than that of free dimer in water (21,000 $M^{-1}cm^{-1}$; ref. 1). From the plot of K'_D vs. concentration of CB[8] (Fig. S2), the K'_D value in the presence of 1 equiv of CB[8] was estimated.

$$\text{Apparent } K_D\ (K'_D) = \frac{[\text{Dimer}]}{[\text{Monomer}]^2} = \frac{[(MV^+)_2] + [CB[8]\text{-}(MV^+)_2]}{\{\,[MV^+] + [CB[8]\text{-}(MV^+)]\,\}^2} \qquad (1)$$

Ref. 1) C. Lee, M. S. Moon and J. W. Park, *J. Incl. Phenom. Mol. Recogn.*, 1996, **26,** 219.

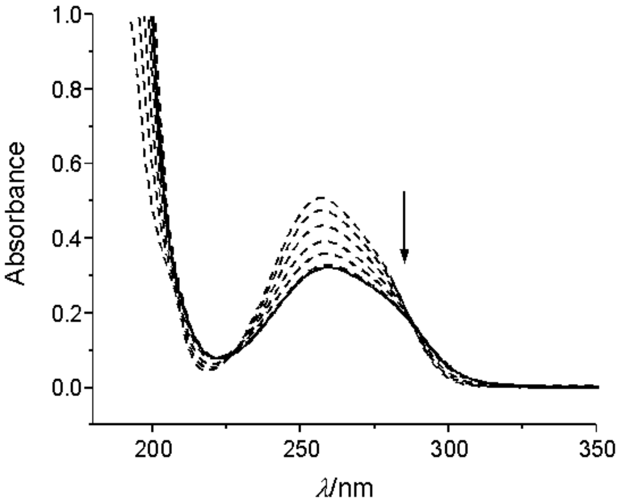

Figure S1. Changes in UV-vis spectrum of MV^{2+} during the titration with CB[8].

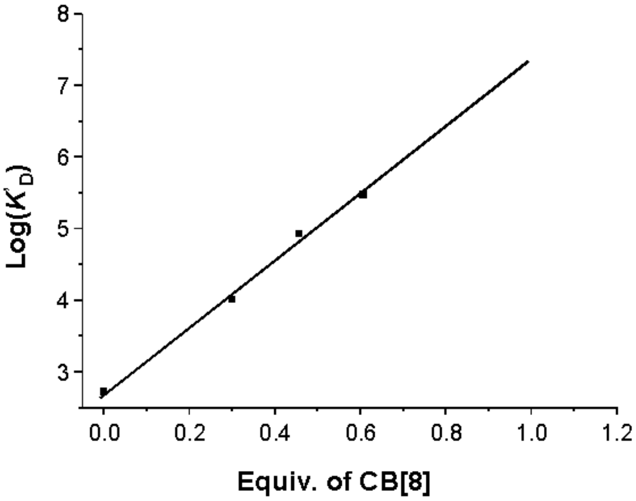

Figure S2. The plot of apparent dimerization constant (K'_D) versus concentration of CB[8].

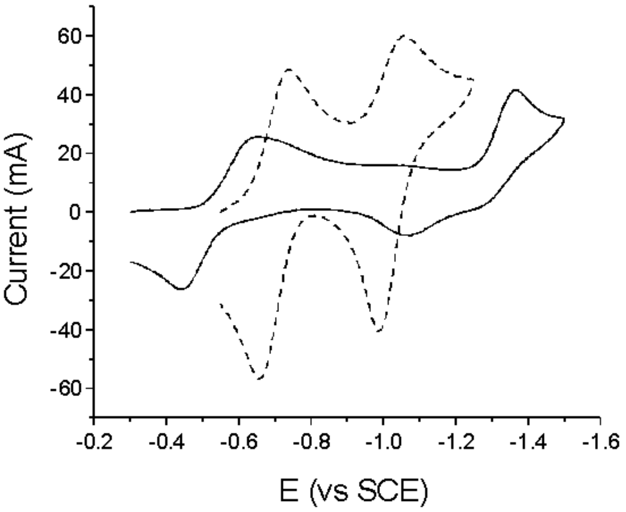

Figure S3. Cyclic voltammogram at scan rate 3.0 Vs^{-1} of MV in the absence (dashed line) and in the presence of 1 equivalent CB[8] (solid line) in pH 7.0 phosphate buffer. SCE, saturated calomel electrode.