Supporting Information:

Structural interrogation of a Cucurbit[7]uril-Ferrocene host-guest complex in the solid state: a Raman spectroscopy study

*Yuan Chen, Agnieszka Klimczak, Elena Galoppini, Jenny V. Lockard**

Department of Chemistry, Rutgers University, 73 Warren St., Newark, NJ 07102

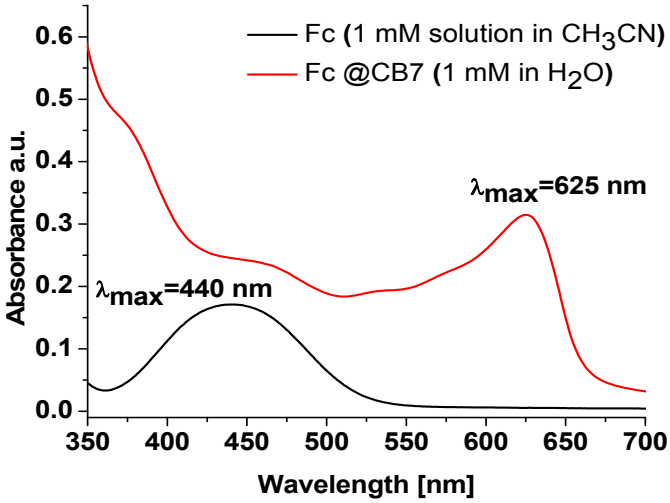

Figure S 1. UV-Vis spectra of Fc and Fc@CB7 solutions in aerated conditions. The 625 nm peak in the Fc@CB7 spectrum indicates Fc/Fc+ oxidation in the presence of dissolved oxygen.

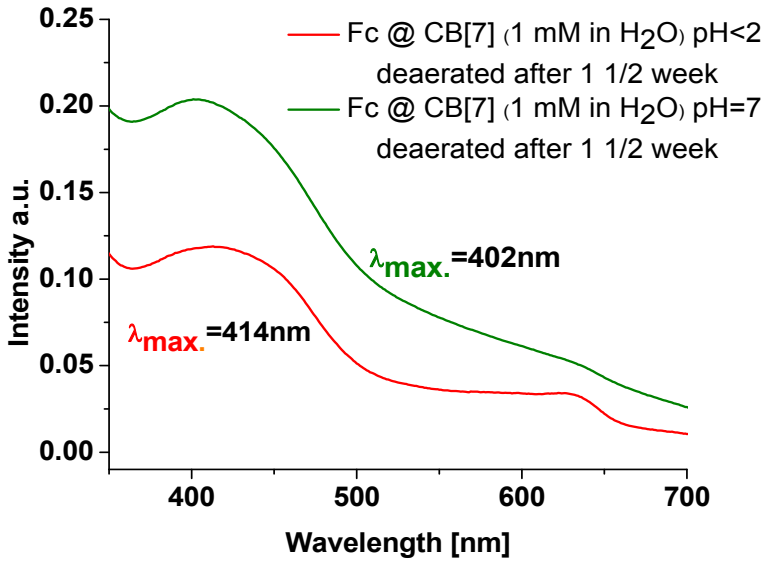

Figure S 2. UV-Vis spectra of Fc@CB7 complexes in deaerated (pH<2 and pH 7) H_2O after 10 days.

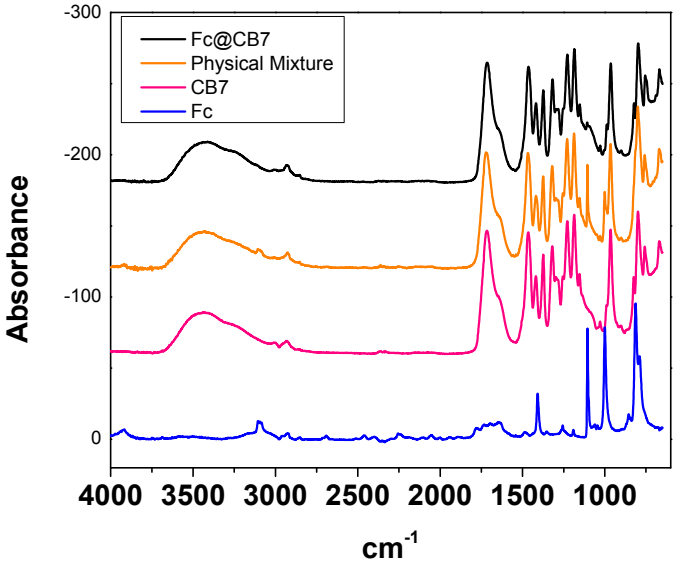

Figure S 3. FTIR-ATR spectrum of Fc@CB7 compared with those of Fc, CB7, and 1:1physical mixture of Fc and CB7.

Experimental Section.

General. ^{1}H-NMR (499.896 MHz) spectra were collected on a Varian IN0VA 500 NMR spectrometer at room temperature in D_2O. Chemical shifts were reported in ppm (δ) relative to the central line of the solvent (δ_{D2O}=4.82 ppm). Acetone, methanol (HPLC grade), ferrocene, glycoluril, formaldehyde (37% solution in water), α–cyano-4-hydroxy-cinnamic acid (CHCA) were used as received. Spectrophotometric grade solvents were used for the spectroscopic and spectrometric measurements. Attenuated Total Reflectance Infrared (FT-IR-ATR) spectra were recorded at room temperature on a Thermo Scientific Nicolet 6700 Spectrometer, with 100 numbers of scans and a resolution of 4 cm^{-1}. High resolution mass spectra (MALDI) were obtained on the departmental mass facility (Bruker Daltonics Apex-Qe series, Fourier Transform Mass Spectrometer) using CHCA as the matrix. The complex was mixed with a solution of the matrix in CH_2Cl_2/$CHCl_3$. The mixture was deposited on the plate and allowed to dry in the air at room temperature prior to the measurement. UV-Vis absorption spectra were acquired at ambient temperature on a Varian Cary-500 spectrophotometer.

Synthesis of Cucurbit[7]uril. CB7 was synthesized following a procedure published by Nau and coworkers,[S1] and separation of CB7 from the CBn homologues and the product purification were adapted from procedures described by Kim and coworkers.[S2, S3] The pure product was dried under vacuum at 140 ^oC for 48 h. The spectral data were consistent with those reported in literature:[S2, S4- S7] ^{1}H-NMR (D_2O): δ = 4.27-4.30 ppm (d, 14 H, J = 15.5, CH_2), 5.58 ppm (s, 14 H, CH), 5.82-5.85 ppm (d, J = 15.4, 14 H, CH_2); FT-IR-ATR: ~ 3432 (N-H), 2925 (C-H), 1721 (C=O), 1634 (C=C), 1468 (C-N), 1373, 1320, 1219, 1185, 965, 800 cm^{-1}, MALDI *m/z* calcd for $[(C_6H_6N_4O_2)_7 + Na]^+$: 1185.3327; found: 1185.3334. calcd for $[(C_6H_6N_4O_2)_7 + K]^+$:

1201.3067; found: 1201.3066. Aqueous solutions of CB7 (as synthesized) are acidic and the pH was adjusted to pH 7 prior to the freeze-pump-thaw procedure described below, because we observed that ferrocenium formation was slower in neutral solution (See Figure S2).

Formation of Fc@CB7 Complex. The formation of the ferrocene@CB7 complex in deaerated conditions was done in a quartz cuvette for freeze-pump-thaw equipped with a stirring-bar. The aqueous solution of CB7 (3 ml of a 1 mM solution, pH 7) was added to a quartz cuvette charged with ferrocene (0.6 mg, 0.003 mmol) and deaerated by several freeze-pump-thaw cycles, followed by sonication. The resulting solution, maintained under vacuum in the sealed cuvette, was stirred overnight in the dark. UV-Vis spectra, collected immediately after formation of the complex and after one and a half week showed little change. The evaporation of the aqueous solution of the Fc@CB7 complex was done by quickly transferring under nitrogen the solution into a round bottom flask and by evaporating water in high vacuum. The solid complex was then used for spectroscopic measurements.

Raman Spectroscopy. Solid State CB7, and Ferrocene samples were prepared Raman measurements by grinding with ~80 wt% KNO_3 as an internal frequency standard and then pressed into pellets. Raman spectra were collected using 785 nm diode laser (Innovative Photonic Solutions) excitation (~25 mW), a Trivista triple monochromator and a 1340 x 100 pixel Spec-10 liquid nitrogen-cooled CCD detector (Princeton Instruments). With 150 μm entrance slit width, the spectral resolution was < 5 cm^{-1}. Data were collected on spinning samples when possible to minimize photodecomposition or thermal damage. Due to a reduced amount of sample, The Fc@CB7 complex was pressed with KNO_3 in a smaller sample holder that did not allow spinning. However, no evidence of photodecomposition or thermal damage was detected

upon laser irradiation throughout the experiment. Raman peak frequencies were determined from the average of two spectra, each obtained from separate sample batches.

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