Unusual partner radical trimer formation in a host complex of cucurbit[8]uril, ruthenium(II) *tris*-bipyridine linked phenol and methylviologen

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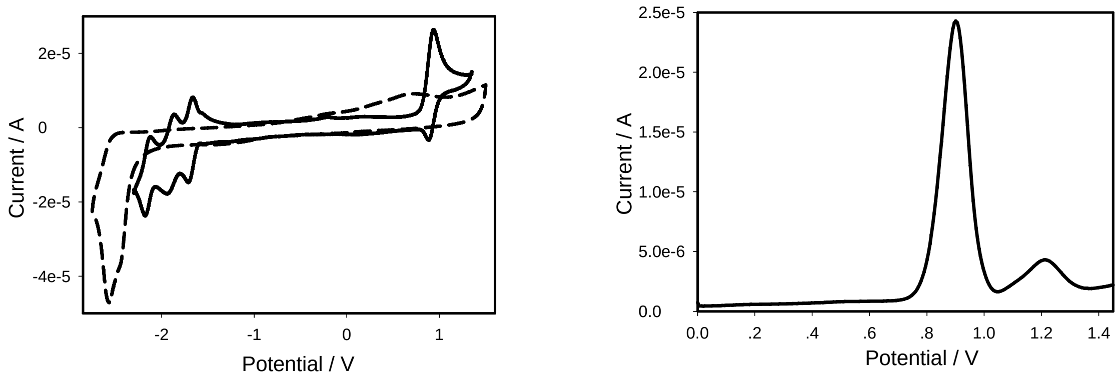
Supporting information

Synthesis

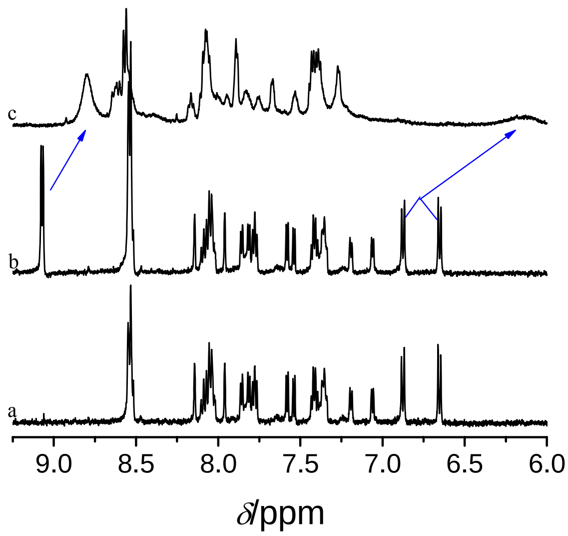
4-(Chloromethyl)phenyl acetate. This compound was prepared according to a literature procedure [Taylor L. D., Grasshoff J. M., Pluhar M. *J. Org. Chem.* 1978, **43**, 1197]. ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.31 (s, 3H, CH_3COOPh-), 4.57 (s, 2H, -$PhCH_2Cl$), 7.10 (d, *J* = 8.8 Hz, 2H, Ph-H), 7.40 (d, *J* = 8.8 Hz, 2H, Ph-H).

4-(ethyl-phenol)-4′-methyl-2,2′-bipyridine. To a solution of 4,4′-dimethyl-2,2′-bipyridine (2.5 g, 13.5 mmol) in THF (50 mL) was added a solution of freshly prepared LDA (2 mL of diisopropylamine, 8.1 mL of 1.6 M n-butyllithium in 10 mL of THF maintained at 0 °C) in drop wise under N_2 at 0 °C, the resulting dark brown solution was stirred for 1h, 4-(Chloromethyl)phenyl acetate (20 mmol, 3.69 g) was added quickly, then the ice bath was removed and the solution was allowed to warm to room temperature. After 3 h, the reaction was quenched by the addition of 100 mL of phosphate buffer (pH = 7.0). The solution was extracted with 3 × 50 mL of CH_2Cl_2, the combined CH_2Cl_2 layers were dried (Na_2SO_4) and evaporated to a yellow residual oil. The crude product was purified by column chromatography on silica gel, eluting first with CH_2Cl_2, followed by 10% acetone/CH_2Cl_2, yielded 3.1 g of the desired compound (82.5%). ^{1}H NMR ($CDCl_3$, ppm) δ 2.37 (s, 3H, CH_3), 2.75-2.84 (m, 4H, CH_2), 6.73-6.75 (d, *J* = 8.4 Hz, 2H, Ph-H), 6.89-6.92 (d, J = 8.4 Hz, 2H, Ph-H), 7.03-7.05 (dd, J = 4.8 Hz, 1.2 Hz, 1H, bpy-H), 7.12-7.13 (dd, J = 4.8 Hz, 1H, bpy-H), 8.18 (s, 2H, bpy-H), 8.49-8.53 (m, 2H, bpy-H).

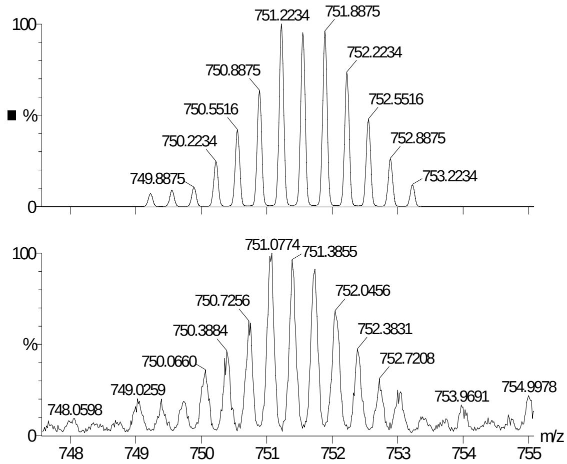
[Ru(bpy)$_2$(4-(4-ethyl-phenol)-4′-methyl-2,2′-bipyridine)](Cl)$_2$ (**1**). Compounds 4-(4-ethyl-phenol)-4′-methyl-2,2′-bipyridine (87 mg, 0.3 mmol) and *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O (141 mg, 0.27 mmol) were added to the solution of 40 ml of 50% ethanol/water (v/v). The reaction flask was wrapped with aluminum foil and refluxed under N_2 atmosphere for 4 h, an orange brown solution was obtained. After removing the solvent by rotary evaporation, the crude product was purified by column chromatography on silica gel (eluent CH_3CN/H_2O/saturated aqueous KNO_3, 10/2/1, v/v/v). Excess KNO_3 and the solvent were removed; the residue was re-dissolved in water and precipitated with a saturated solution of NH_4PF_6. The precipitate was filtered and dried in vacuum to afford the compound as PF_6^- salt. ^{1}H NMR (400 MHz, CD_3CN), δ 2.51 (s, 3H, CH_3), 2.87 (t, J = 6.8 Hz, 2H, CH_2), 3.03 (t, 2H, J = 6.8 Hz, CH_2), 6.66-6.68 (d, J = 8.4 Hz, 2H, Ph-H), 6.83-6.85 (d, J = 8.4 Hz, 2H, Ph-H), 7.07-7.09 (m, 1H, bpy′-H), 7.20-7.22 (m, 1H, bpy′-H), 7.35-7.39 (m, 2H, bpy-H), 7.42-7.46 (m, 2H, bpy-H), 7.48-7.52 (m, 2H, bpy′-H), 7.66-7.76 (m, 4H, bpy-H), 8.00-8.09 (m, 4H, bpy-H), 8.29 (s, 1H, bpy′-H), 8.37 (s, 1H, bpy′-H), 8.56-8.60 (m, 4H, bpy-H). ESI-MS (*m*/*z* (%)): 849.0 (30) $[M\text{-}PF_6^-]^+$, 352.0 (100) $[M\text{-}2PF_6^-]^{2+}$; HRMS (ESI, *m/z*): $[M\text{-}PF_6^-]^+$ calcd for $C_{39}H_{34}F_6N_6OPRu$, 848.7616; found, 848.7651, $[M\text{-}2PF_6^-]^{2+}$ calcd for $C_{39}H_{34}N_6ORu$, 351.8984, found, 351.8995. Because CB[8] is completely insoluble in organic solvents, so the PF_6^- salt was metathesized to the chloride salt for aqueous solution by using tetra-*n*-butylammonium chloride (Bu_4NCl) dissolved in a minimal amount (< 10 ml) of acetone.



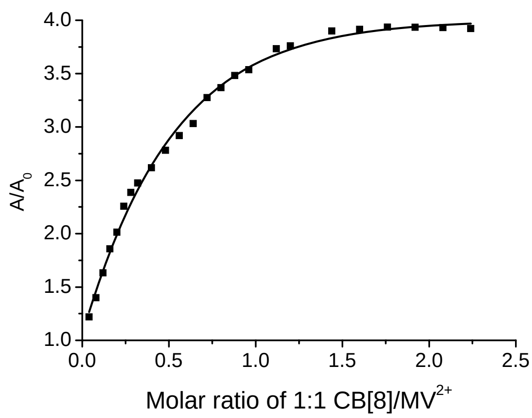
S1. Cyclic voltammograms of the Ru(bpy)$_3$ complex (left, solid line), phenol-bipyridine ligand (left, dashed line) and DPV of the Ru Complex **1** (right) in CH_3CN. Electrolyte: 0.1 M N(n-C_4H_9)$_4$$PF_6$; Scan rate: v = 100 mV s^{-1}.



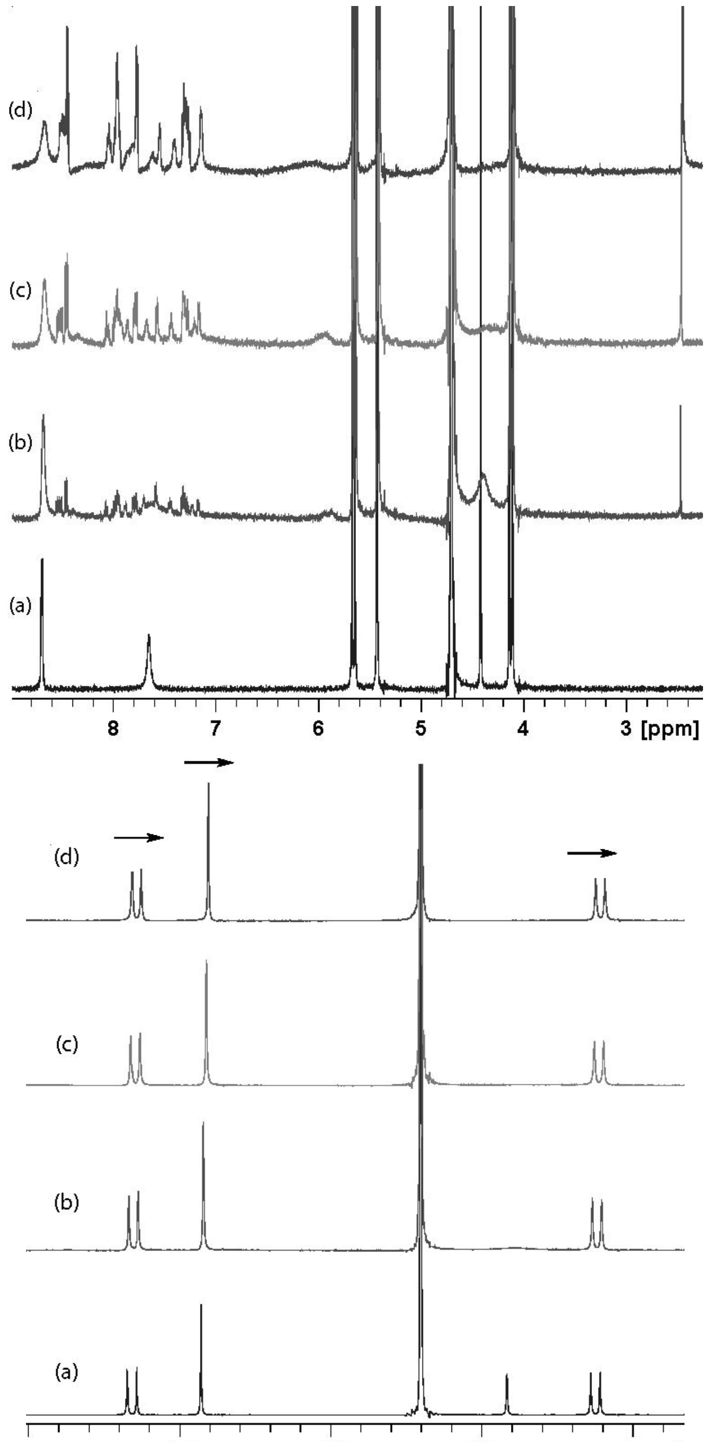
S2. ^{1}H NMR spectra (500 MHz, D_2O) of complex **1** only (a), addition of 1 equiv of MV^{2+} (b), addition of 1 equiv of CB[8] (c).



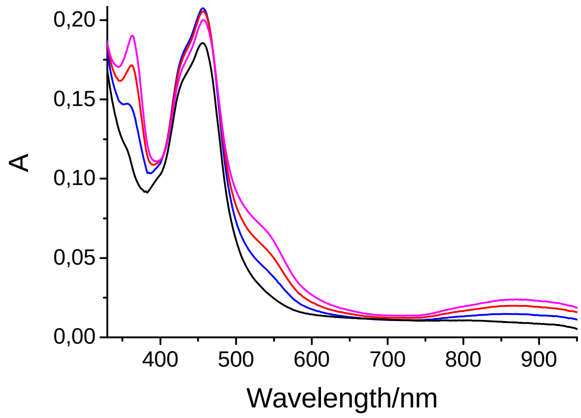
S3. Part of the MS spectrum for the 1:1:1 inclusion complex (bottom) and simulation (top).



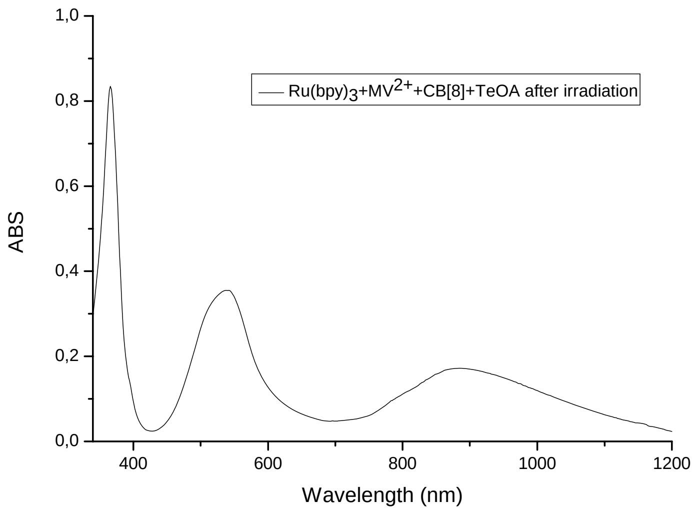
S4. The dependence of the absorbance of **1** (5 μM) in aqueous solution at 460 nm on the increasing equiv of 1:1 MV^{2+}/CB[8]



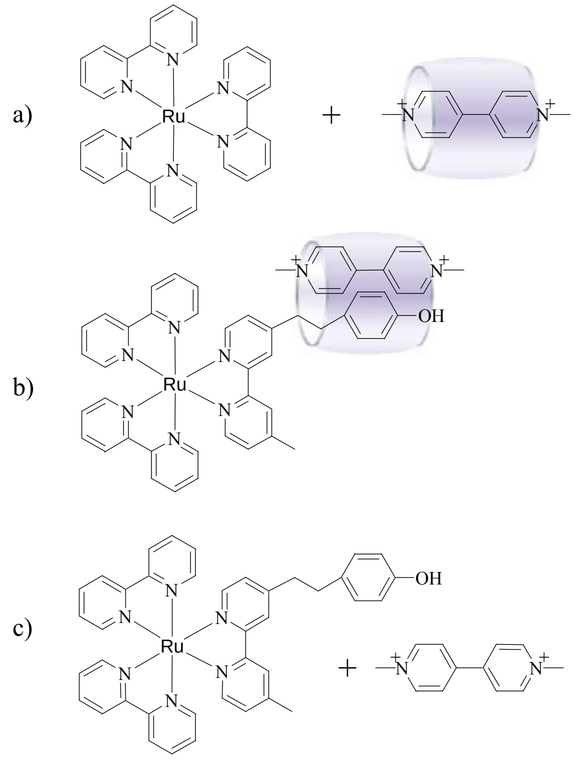
S5. [1]H NMR spectra to show (top) the dynamic inclusion of complex **1** into the MV^{2+}/CB[8] complex as 0:1.0:1.0 (a), 0.5:1.0:1.0 (b), 1.0:1.0:1.0 (c) and 2.0:1.0:1.0 (d); and (down) the focus on the shift of the CB[8] peaks showing the dynamic interaction.



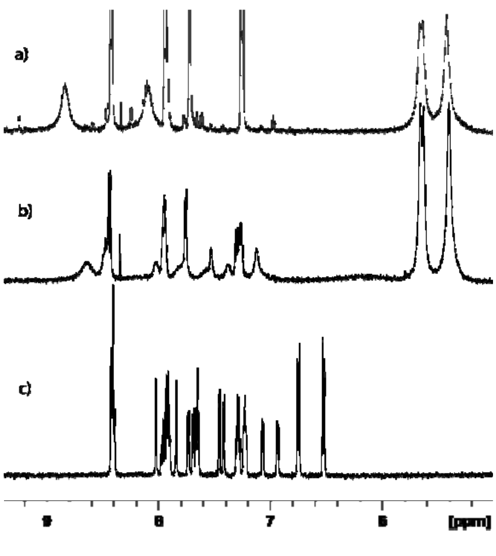
S6. Absorption spectra of complex **1** (10 μM), CB[8] (10 μM), MV^{2+} (10 μM) and 100 μM TEOA, before (black), after 20 min (blue), after 40 min (red), and after 60 min (pink) light irradiation, respectively.



S7. Normalized absorption spectra of $Ru(bpy)_3^{2+}$ (10 μM), CB[8] (10 μM), MV^{2+} (10 μM) and 100 μM TEOA after light irradiation.



S8. Composition of the three systems a), b), and c) with addition of 10 equiv TEOA and irradiated for 15 min for ^{1}H NMR measurements.



S9. ^{1}H NMR of the three systems a), b), and c) after addition of 10 equiv TEOA and irradiated for 15 min.