The photoinduced long-lived charge-separated state of Ru(bpy)$_3$-methylviologen with cucurbit[8]uril in aqueous solution

Shiguo Sun, Rong Zhang, Samir Andersson, Jingxi Pan, Björn Åkermark and Licheng Sun*

$^1$H NMR spectra

Figure S1. $^1$H NMR spectra (400 MHz, D$_2$O) of complex 1 in the absence (bottom), in the presence of 0.5 equiv. (middle) and 1 equiv. (top) CB[8]. Below, a schematic illustration for the inclusion of 1 in CB[8].

Electrochemistry

For the 1:1 inclusion complex in water solution, one peak related to the redox couple MV$^{2+}$/MV$^{+•}$ appeared at -0.50 V, and the other corresponding to the oxidation process of Ru$^{2+}$/Ru$^{3+}$ was observed at 0.95 V (the peak potential was determined from DPV measurement). Because CB[8] can bind both
MV$^{2+}$ and methylviologen radical (MV$^{+\ddagger}$), which makes the MV$^{+\ddagger}$ more stable inside the CB[8] cavity than that of MV$^{+\ddagger}$ alone in aqueous solution, so the MV$^{2+}$ moiety was more easily reduced after inclusion of CB[8], due to the interaction of the formed MV$^{+\ddagger}$ radical with CB[8]. This was in agreement with the data reported in literature where MV$^{2+}$ was reduced more easily after inclusion of CB[8](see Ref. 4b).

**Figure S2.** Cyclic voltammogram of molecular dyad 1 (1×10$^{-3}$ M) in the presence of 1 equiv CB[8] in 0.1 M phosphate buffered (pH 7.0) water solution at room temperature, glassy carbon as working electrode, Ag/AgCl as reference electrode, scan rate: $v = 100$ mV s$^{-1}$

**Figure S3.** Transient absorption spectra of molecular dyad 1 alone (1×10$^{-4}$ M) in aqueous solution at room temperature, data recorded at delays of 17 ns(■), 34 ns(●), 51 ns(▲), 68 ns(♦), 100 ns(▼) following the excitation of 532 nm laser pulse)

For molecular dyad 1 alone, no transient absorptions around 400 nm and 600 nm can be observed, because the charge recombination goes very fast.