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

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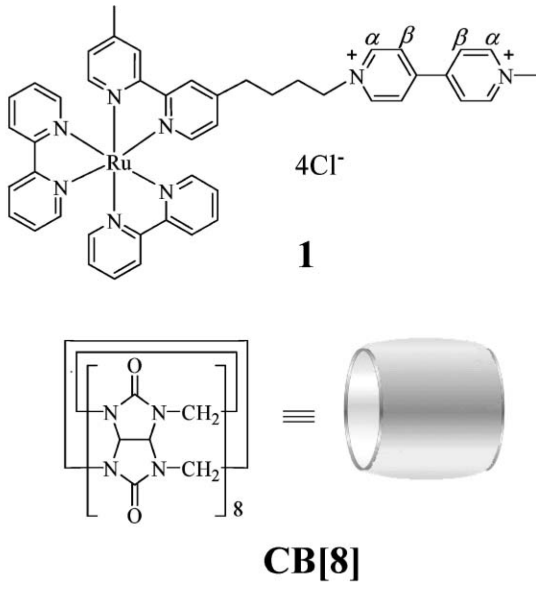
A stable 1 : 1 inclusion complex of Ru(bpy)$_3$–MV^{2+} with cucurbit[8]uril (CB[8]) is formed in aqueous solution; upon light irradiation, a long lived (τ ~ 2 μs) charge-separated state Ru^{3+}–MV$^{+\cdot}$–CB[8] is observed.

Methylviologen (*N*,*N*-dimethyl-4,4-bipyridinium, MV^{2+}) is a common electron acceptor in studies of electron transfer (ET) reactions, especially in combination with photosensitizers such as ruthenium polypyridine complexes.[1] Photochemical and photophysical studies of these types of multi-component molecular and supramolecular system are very useful for understanding the fundamental photoinduced ET processes in photosynthesis, and consequently for creating similar charge-separated states in artificial systems for solar energy conversion.[2] MV^{2+} and its derivatives are also widely used for constructing molecular machines such as rotaxanes *etc*.[3] The inclusion of MV^{2+} into the cavity of cucurbit[8]uril (CB[8], Scheme 1) has been studied extensively in recent years.[4] It has been demonstrated that CB[8] can bind both MV^{2+} and methylviologen radical (MV$^{+\cdot}$). Two MV$^{+\cdot}$ radicals can form a dimer (MV$^{+\cdot}$)$_2$ inside the CB[8] cavity, and the association constant of the dimer with CB[8] is 2 × 10^7 M^{-1}, *ca.* 10^5 times larger than that of MV$^{+\cdot}$ alone in aqueous solution.[4] The very high binding constant of the MV$^{+\cdot}$ dimer with CB[8] can be used for the design and synthesis of new types of molecular machines and devices. For example, a functional unit or multi-functional units can be linked to MV^{2+} to assemble a molecular device together with CB[8]. To the best of our knowledge, no work has been reported on the photochemical interaction between CB[8] and MV^{2+}, which is covalently linked to a redox-active component. Here, we report the formation of a 1 : 1 inclusion complex of CB[8] with a molecular dyad **1**, consisting of a Ru(bpy)$_3$ complex covalently linked to a MV^{2+} *via* a four carbon chain. When this supramolecular system is irradiated with visible light, a photoinduced ET process occurs and a long lived (τ ~ 2 μs) charge-separated state can be observed in aqueous solution.



Scheme 1 The structures of Ru–MV^{2+} (**1**) and CB[8].

Molecular dyad **1** was synthesized in accordance with a literature procedure[5] and fully characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). To make it soluble in water, chloride ions were introduced into this dyad by ion exchange column chromatography. The formation of a 1 : 1 inclusion complex of molecular dyad **1** and CB[8] was clearly observed by ^{1}H NMR spectroscopy when equivalent amounts of **1** and CB[8] were dissolved in D$_2$O. Examination of the ^{1}H NMR spectrum of **1** alone shows that the four β-protons of the viologen moiety in **1**, in the presence of CB[8], are upfield-shifted from 8.54 to 7.95 (two protons) and 7.83 (two protons) ppm. Two α-protons are upfield-shifted from 9.13 to 8.90 ppm, and the other two α-protons are upfield-shifted from 9.07 to 8.66 ppm. This result shows that the whole viologen moiety is inserted into the cavity of CB[8], forming a stable 1 : 1 inclusion complex. The α-methylene proton of the viologen, which is overlapped by H$_2$O before the inclusion, undergoes an upfield shift to 4.57 ppm. The methyl proton is downfield-shifted from 4.51 to 4.55 ppm. No chemical shift changes could be observed for the other protons on the butyl chain, meaning that the butyl chain is not inserted into the cavity of CB[8]. The protons at the 3- and 3′-positions of the substituted bipyridine ring undergo a downfield shift from 8.38 to 8.45 and 8.63 ppm, the proton at the 6-position undergoes a downfield shift from 7.68 to 7.87 ppm, and the proton at the 5-position undergoes a downfield shift from 7.23 to 7.27 ppm. Small upfield and

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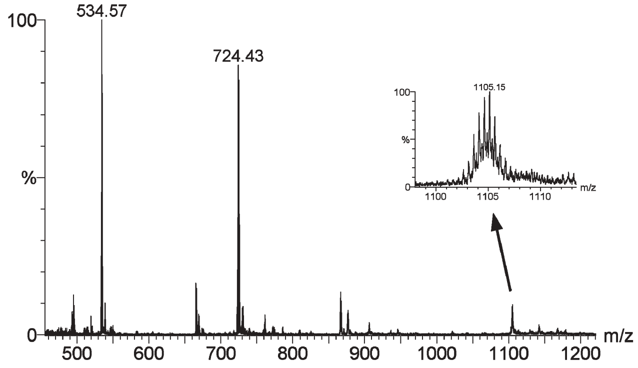
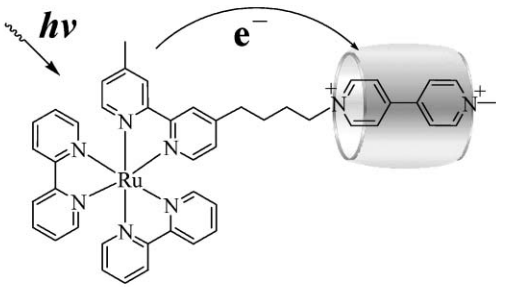


Fig. 1 ESI-MS spectrum of the 1 : 1 inclusion complex of molecular dyad **1** and CB[8].

downfield shifts for the protons on the unsubstituted bipyridine rings can also be observed. The formation of the 1 : 1 inclusion complex between **1** and CB[8] has been further confirmed by ESI-MS. When equivalent amounts of **1** and CB[8] were dissolved in water, the ESI-MS spectrum (Fig. 1) gave a doubly-charged peak at *m/z* 1105.15 (calculated for $[\mathbf{1} + \mathrm{CB[8]} - 2\mathrm{Cl}^{-}]^{2+}$, 1104.98), a triply-charged peak at *m/z* 724.43 (calculated for $[\mathbf{1} + \mathrm{CB[8]} - 3\mathrm{Cl}^{-}]^{3+}$, 724.84) and a quadruply-charged peak at *m/z* 534.57 (calculated for $[\mathbf{1} + \mathrm{CB[8]} - 4\mathrm{Cl}^{-}]^{4+}$, 534.76). Both NMR and ESI-MS results provide strong evidence for the formation of a stable 1 : 1 host–guest complex between **1** and CB[8].

The stoichiometry of the binding of molecular dyad **1** with CB[8] is further verified by UV-vis absorption titration measurements (Fig. 2). The data can be easily fitted to a 1 : 1 binding model with a binding constant of 3×10^5 L mol^{-1}.

The redox properties of molecular dyad **1** before and after inclusion in CB[8] were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a 0.1 M phosphate buffered (pH 7.0) aqueous solution using Ag/AgCl as a reference electrode. For molecular dyad **1** alone, one peak potential at −0.60 V, corresponding to the reduction of MV^{2+} to MV$^{+\cdot}$, and one peak potential at 0.99 V, related to the oxidation of Ru^{2+} to Ru^{3+}, were detected. With the addition of one equivalent of CB[8], the peak potential related to the redox couple MV^{2+}/MV$^{+\cdot}$ appeared at −0.50 V and the oxidation process Ru^{2+}/Ru^{3+} was observed at 0.95 V. This result shows that the MV^{2+} moiety in **1** was more easily reduced when it was inserted into the cavity of CB[8], while the formation of a 1 : 1 inclusion complex had less influence on the oxidation potential of the Ru(bpy)$_3$ moiety.



Scheme 2 The structure of the 1 : 1 inclusion complex of Ru–MV^{2+} and CB[8], and photo-induced intramolecular electron transfer.

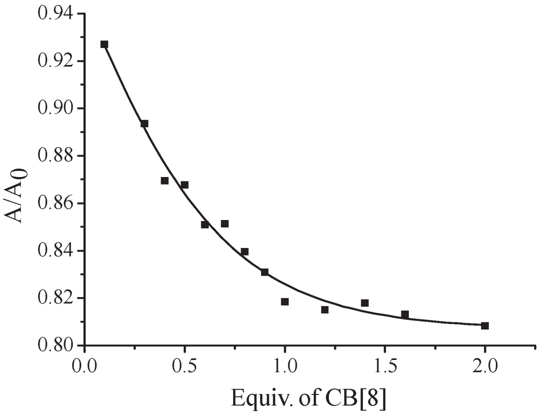


Fig. 2 The dependence of the absorbance of 5 μM molecular dyad **1** in aqueous solution at 285 nm on the increasing number of equivalents of CB[8].

To investigate the effect of CB[8] on photoinduced ET and charge recombination in molecular dyad **1** (Scheme 2), transient absorption measurements on the 1 : 1 inclusion complex of **1** + CB[8] were performed in aqueous solution (Fig. 3). By following the absorption changes at 400 and 450 nm after laser irradiation at 532 nm (laser pulse: 8 ns), the formation of the MV$^{+\cdot}$ radical and Ru^{2+} ground state bleaching were observed, respectively. The follow-up spectral changes were characteristic of the formation of a charge-separated state Ru^{3+}–MV$^{+\cdot}$, indicating a photoinduced intramolecular ET from the excited state of the Ru(bpy)$_3$ moiety to the MV^{2+} moiety inserted inside the CB[8].[5,6]

The kinetic decay curve at 400 nm is fitted well by a single exponential process, with a lifetime of 2060 ns, as shown in Fig. 4. For molecular dyad **1** alone in aqueous solution, the Ru^{2+} recovery is fitted by a single exponential decay, with a lifetime of around 10 ns that is coincidental with the reported data[5b] in acetonitrile, and no absorption change at 400 nm could be detected in this ns laser system due to fast charge recombination. Thus, the long lived MV$^{+\cdot}$ radical in the 1 : 1 inclusion complex **1** + CB[8] can be explained by the effect of the CB[8] cavity, which somehow

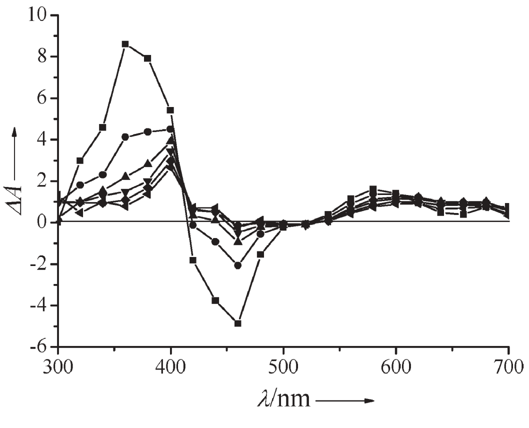


Fig. 3 Transient absorption spectra of molecular dyad **1** (1×10^{-4} M) in the presence of 1 equiv. CB[8] in aqueous solution at room temperature, with data recorded at delays of 30 (■), 360 (●), 690 (▲), 1020 (▼), 1350 (♦) and 1680 (◀) ns following excitation by a 532 nm laser pulse (Nd:YAG laser, 8 ns pulse width).

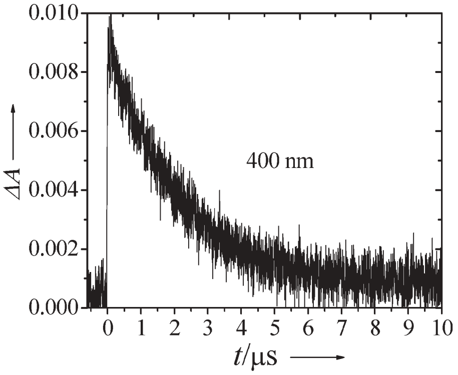


Fig. 4 The transient absorption kinetic decay at 400 nm of 1 : 1 inclusion complex of **1** + CB[8] (1×10^{-4} M) following 532 nm laser pulse excitation.

slows down the back-ET from the MV$^{+\cdot}$ to the Ru^{3+}.[5] Further insights into the reason why the CB[8] cavity can stabilize the MV$^{+\cdot}$ radical are currently being sought.

In conclusion, a molecular dyad Ru–MV^{2+} has been successfully inserted into the cavity of CB[8], forming a stable 1 : 1 inclusion complex in aqueous solution, made evident by ^{1}H NMR spectroscopy and ESI-MS. Upon light irradiation, photoinduced intramolecular ET from the excited state of the Ru(bpy)$_3$ moiety to the MV^{2+} moiety, which is inserted as a guest molecule inside the cavity of CB[8], occurred and a long-lived charge-separated state Ru^{3+}–MV$^{+\cdot}$–CB[8] was observed. The formation of a 1 : 1 inclusion complex of the photoactive ruthenium–viologen dyad **1** with CB[8] and the photoinduced long-lived charge-separated state may pave the way for the future design of more advanced systems with potential applications such as light driven molecular devices and machines.

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