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# Photoinduced electron transfer between a donor and an acceptor separated by a capsular wall†

**Mintu Porel,[a] Steffen Jockusch,[b] Anand Parthasarathy,[a] V. Jayathirtha Rao,[a] Nicholas J. Turro[b] and V. Ramamurthy*[a]**

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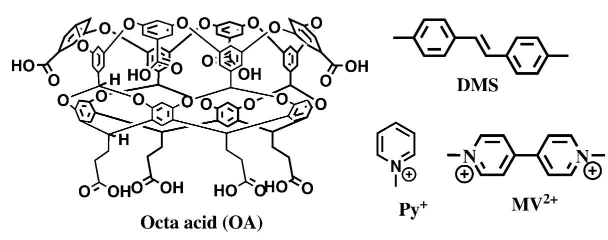
**The efficient photoinduced electron transfer from a stilbene derivative incarcerated within a negatively charged organic nanocapsule to positively charged acceptors (methyl viologen and a pyridinium salt) adsorbed outside and the back electron transfer were controlled by supramolecular effects.**

Recent establishment of spin and energy communication between two molecules, one trapped within an organic capsule and the other free in solution, led us to investigate the feasibility of electron transfer between such molecules.[1] The electron donor used in this study, 4,4′-dimethyl stilbene (DMS), is enclosed within a capsule made of two octa acid (OA) molecules and the electron acceptors explored are *N*-methyl pyridinium iodide ($Py^+$) and 4,4′-dimethyl viologen chloride ($MV^{2+}$) (Scheme 1). The choice of the pair was made based on well-established literature reports that photoinduced electron transfer between stilbene and the above electron acceptors is exothermic and occurs in solution.[2] Based on excitation energy and oxidation potential of DMS and reduction potentials of $Py^+$ and $MV^{2+}$ the electron transfer in both systems is expected to be exothermic ($\sim$1.3 eV in the case of $MV^{2+}$ and $\sim$0.5 eV in the case of $Py^+$).[3] In this report we present results demonstrating (1) that the electron transfer between excited DMS and the above cationic acceptors takes place despite their separation by the atoms of the capsular wall and (2) the control of the back electron transfer process by judicious choice of electron acceptors.




**Scheme 1** Structures of host and guest molecules; counter anions of $Py^+$ and $MV^{2+}$ are $I^-$ and $Cl^-$ respectively.

[a] *Department of Chemistry, University of Miami, Coral Gables, Florida 33124, USA*
[b] *Department of Chemistry, Columbia University, New York, New York 10027, USA*

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We have established previously that DMS formed a 1 : 2 (guest to host) complex with OA in aqueous borate buffer solution (pH $\sim$9.0).[4] In Fig. S1 in the ESI† $^1$H NMR spectra of free DMS, $Py^+$ and $MV^{2+}$ and DMS@$OA_2$ alone (one molecule of guest included within two molecules of host OA) and in the presence of $Py^+$ and $MV^{2+}$ are provided. Based on the large upfield shift of $^1$H NMR signals of the 4-methyl group of DMS and the corresponding small shifts of the methyl group(s) of $Py^+$ and $MV^{2+}$ in the presence and absence of OA we concluded that DMS is encapsulated inside the OA host and $Py^+$ and $MV^{2+}$ are located outside the capsule. The DOSY spectra presented in Fig. S2 and S3 in ESI† indicated reduced mobility of the cationic guests $Py^+$ and $MV^{2+}$ in the presence of DMS@$OA_2$. For example, the diffusion constant for $Py^+$ in the presence of OA was reduced to $4.8 \times 10^{-10}$ m$^2$ s$^{-1}$ from that in water ($8.9 \times 10^{-10}$ m$^2$ s$^{-1}$). Guest $MV^{2+}$ had an identical diffusion constant ($1.2 \times 10^{-10}$ m$^2$ s$^{-1}$) to that of DMS@$OA_2$ suggesting that DMS, OA and $MV^{2+}$ move together in aqueous solution. Based on DOSY data we conclude that the cationic acceptors $Py^+$ and $MV^{2+}$ remain closely associated with DMS@$OA_2$ due to electrostatic interaction between their cationic pyridyl parts and the carboxylate anion groups of OA. Apparently, $Py^+$ is not associated to the capsule as strongly as $MV^{2+}$. The preferential intracapsular location of the neutral stilbene and cationic guests in proximity of the exterior walls of OA is consistent with our previous observations with cationic and neutral nitroxides.[1a–d]

The first indication of interaction between OA-trapped excited DMS and free $Py^+$ and $MV^{2+}$ came from fluorescence spectra of DMS@$OA_2$ in their presence. As illustrated in Fig. 1a and Fig. S4 (ESI†) addition of $Py^+$ or $MV^{2+}$ to a solution of DMS@$OA_2$ resulted in quenching of the fluorescence of DMS. Stern–Volmer plots that include $I_o/I$ and $\tau_o/\tau$ *vs.* concentration shown in Fig. 1b and Fig. S5 (ESI†) suggested that the quenching was entirely static for $MV^{2+}$, and mostly static for $Py^+$. Note, had the quenching been dynamic, the Stern–Volmer plots based on steady state fluorescence intensity and lifetime measurements should have fully overlapped, but this was not the case.

The origin of the quenching became clearer from the absorption spectra of the transient intermediates of DMS@$OA_2$ in the presence of $Py^+$ and $MV^{2+}$ recorded by laser flash photolysis. In both cases transient absorptions at 510 and > 700 nm were observed (Fig. 2), which were assigned to the radical cation of

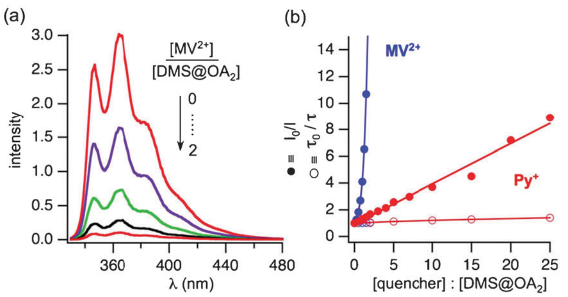



**Fig. 1** (a) Fluorescence spectra of DMS@OA$_2$ at different amounts of MV$^{2+}$. (b) Stern–Volmer plots of fluorescence quenching with Py$^+$ (red) and MV$^{2+}$ (blue) using steady-state fluorescence intensity (solid circles) and fluorescence lifetime (hollow circles); [DMS] = 1.25 × 10$^{-5}$ M, [OA] = 2.5 × 10$^{-5}$ M, $\lambda_{ex}$ = 320 nm.

DMS (DMS$^{+\bullet}$) based on previously reported transient absorption spectra of DMS$^{+\bullet}$.[2] Both absorptions showed the same decay kinetics. This suggests that the quenching is due to electron transfer from the singlet excited state of DMS to Py$^+$ and MV$^{2+}$ that are associated to the capsule. The excellent correlation observed between bleaching of DMS (observed at 320 nm) and generation of DMS$^{+\bullet}$ proved that the observed transient spectra are not artifacts.

Further support for the assignment of the observed transient at 510 nm to a radical cation was provided by the absence of quenching by dissolved oxygen (oxygen saturated solution; Fig. S6 in ESI†). Most importantly, the methyl viologen monocation radical (MV$^{+\bullet}$) spectrum (Fig. 2b)[5] provided unequivocal support for electron transfer across the capsular wall. Thus we have been able to directly identify both the products of electron transfer in the case of MV$^{2+}$, namely DMS$^{+\bullet}$ and MV$^{+\bullet}$. However, the spectrum of an *N*-methyl pyridinium radical (Py$^\bullet$ generated from Py$^+$) could not be detected because it does not possess detectable absorption at

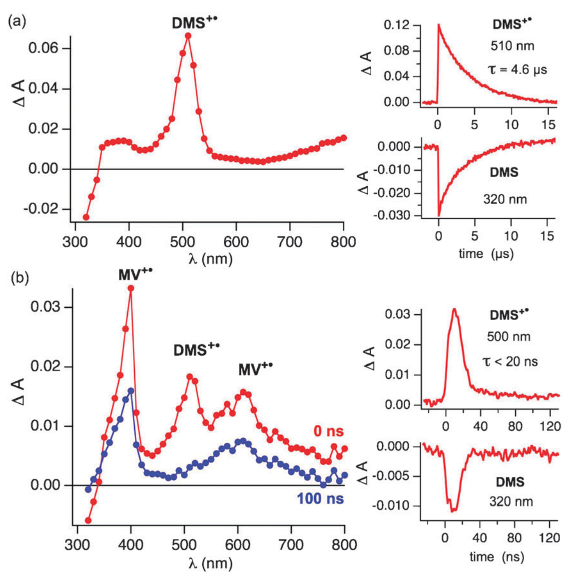



**Fig. 2** Transient absorption spectra after laser excitation of DMS@OA$_2$ in the presence of (a) Py$^+$ and (b) MV$^{2+}$; right: kinetic traces at different observation wavelengths. [DMS] = 1.25 × 10$^{-5}$ M, [OA] = 2.5 × 10$^{-5}$ M and [Py$^+$] = 31.25 × 10$^{-5}$ M and [MV$^{2+}$] = 2.5 × 10$^{-5}$ M in 10 mM sodium tetraborate buffer; laser pulse: 308 nm, pulse width: 15 ns.

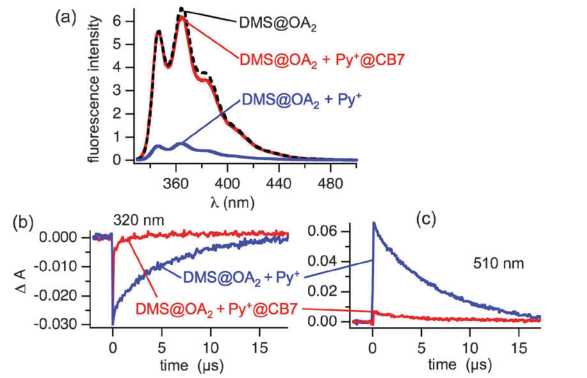
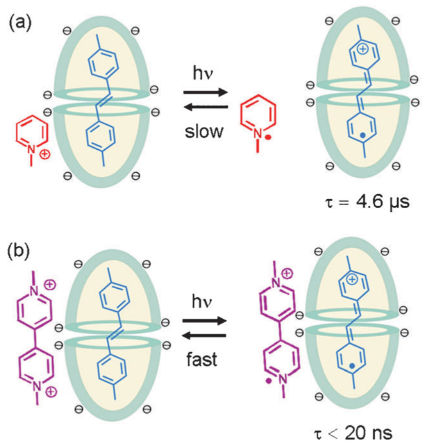



**Fig. 3** (a) Fluorescence spectra of DMS@OA$_2$ in the absence and presence of Py$^+$ and CB7 ($\lambda_{ex}$ = 320 nm); transient absorption decay traces of (b) bleaching and recovery of DMS and (c) decay of DMS$^{+\bullet}$ in the absence and presence of CB7; [DMS] = 1.25 × 10$^{-5}$ M, [OA] = 2.5 × 10$^{-5}$ M, [Py$^+$] = [CB7] = 31.25 × 10$^{-5}$ M in 10 mM sodium tetraborate buffer; laser pulse: 308 nm, pulse width: 15 ns.

350 to 800 nm.[6] Based on the above data we conclude that photoinduced electron transfer between excited DMS@OA$_2$ and Py$^+$ and MV$^{2+}$ occurs under our experimental conditions. Examination of Stern–Volmer plots shown in Fig. 1b suggests that the electron transfer is much more efficient in the case of MV$^{2+}$ compared to Py$^+$. The lower efficiency in the case of Py$^+$ is probably due to the weaker binding of Py$^+$ (+1 charge) compared to MV$^{2+}$ (+2 charge) to the negatively charged exterior walls of OA as suggested by DOSY data and/or the electron transfer process is much less exothermic than in the case of MV$^{2+}$.[3]

Support for the hypothesis that the electron transfer is indeed between a molecule within a capsule and the other adjacent to it came from experiments involving cucurbit[7]uril (CB7) as the second host molecule. As illustrated in Fig. 3 the quenched fluorescence of DMS by Py$^+$ could be fully recovered upon addition of CB7 to the solution. Consistent with this, in the presence of CB7 there was no transient absorption due to DMS$^{+\bullet}$ (510 nm) and bleaching of the DMS ground state (320 nm) did not occur. Similar observations were made with MV$^{2+}$ (Fig. S7 in ESI†). From $^1$H NMR spectra (Fig. S8 and S9 in ESI†) we inferred that both Py$^+$ and MV$^{2+}$ complexed to CB7 under our conditions. This is consistent with the known high binding constant of MV$^{2+}$ to CB7.[7] The above stated fluorescence quenching by Py$^+$ and MV$^{2+}$ and fluorescence recovery by CB7 suggested that removal of electrostatically held Py$^+$ and MV$^{2+}$ from the capsular wall inhibited the electron transfer. Given that the OA capsular assembly–disassembly occurs in the microsecond time scale,[8] this process is unlikely to play a role in the above observed electron transfer process that takes place in the sub-nanosecond time scale. Based on the above results we conclude that generation of DMS$^{+\bullet}$ is due to electron transfer from DMS inside the OA capsule to the acceptors Py$^+$ and MV$^{2+}$ that are closely associated to the external capsular wall.

Our most important observation relates to the back electron transfer process to regenerate the ground states of DMS, Py$^+$ and MV$^{2+}$ (Scheme 2). As illustrated in Fig. 2, DMS$^{+\bullet}$ had lifetimes of 4.6 μs and <20 ns when generated *via* electron transfer to Py$^+$ and MV$^{2+}$, respectively. This variation in lifetimes is understandable on considering the products of




**Scheme 2** Forward and back electron transfer from DMS@$OA_2$ to (a) $Py^+$ and (b) $MV^{2+}$.

electron transfer to these acceptors; $Py^+$ upon acceptance of an electron yielded $Py^{\bullet}$ (no charge) while $MV^{2+}$ generated $MV^{+\bullet}$ (positively charged). The former is not expected to stick to the capsule while the latter with a positive charge would still be associated with the capsule. This difference would make the rates of back electron transfer to be different in these two cases. A comparison of $DMS^{+\bullet}$ decay provided in Fig. S10 (ESI†) reveals that the intensity of the signal due to $DMS^{+\bullet}$ is distinctly weaker in the case of $MV^{2+}$ than in $Py^+$. We believe that the observed weaker $DMS^{+\bullet}$ signal intensity in the presence of $MV^{2+}$ is caused by fast back electron transfer occurring in the nanosecond timescale during the laser pulse (laser pulse width 15 ns).

Balzani and co-workers, in their pioneering studies on electron transfer in supramolecular assemblies, reported that a biacetyl triplet included within a hemicarcerand is quenched by aromatic amines with rate constants in the range of $10^4$ to $10^8$ $M^{-1}$ $s^{-1}$.[9] The low rate constants were attributed to small electronic interaction between the incarcerated biacetyl acceptor and free donor amines. Due to the static nature of the quenching, we were unable to measure the exact rate constant of electron transfer. However, we believe that the quenching rate constant in our system must be higher than the fluorescence decay constant of DMS ($> 10^9$ $s^{-1}$). In our systems, the weak electronic coupling between the excited donor and the acceptor through the capsular wall is most likely compensated by the strong association of the acceptor ($Py^+$ or $MV^{2+}$) to the negatively charged external wall of the capsule (that contains the donor) through electrostatic attraction.

The final point relates to the ability of the host OA itself to act as an electron donor. Closer examination of Fig. 2b reveals that even after the complete decay of $DMS^{+\bullet}$, some amount of $MV^{+\bullet}$ is left in solution (compare the spectra at 0 and 100 ns). This suggested the possibility of OA itself acting as a donor. This was probed by exciting a solution of OA/$MV^{2+}$ (free of DMS) with laser pulses of 308 nm. As illustrated in Fig. S11 (ESI†) $MV^{+\bullet}$ is detected even in the absence of DMS. However, the signal intensity of $MV^{+\bullet}$ was weaker than when DMS is present in solution. Since DMS has a much higher absorption co-efficient than OA, we believe that the direct electron transfer between OA and $Py^+$ and $MV^{2+}$ plays only a minor role under our conditions (Fig. S12 in ESI†). However, at present we do not clearly understand why $MV^{+\bullet}$ generated *via* direct electron transfer from OA has a long lifetime. We are currently investigating this aspect in more detail.

The above observations suggest that electron transfer can occur between incarcerated and free molecules and the back electron transfer rates in photoinduced electron transfer processes can be controlled by applying supramolecular concepts. Photoinduced electron transfer between cyclodextrin, cucurbituril and hemicarcerand enclosed dyes and $TiO_2$ in the context of dye-sensitized solar cells has in fact attracted considerable interest in recent years.[10] We are currently examining the photoinduced electron transfer phenomenon of guest@$OA_2$ adsorbed on $TiO_2$ surfaces. We envision that the current study, establishing the feasibility of electron transfer across molecular walls, will lay the ground work for exploration of OA and related deep cavity cavitands as supramolecular hosts in controlling dye aggregation and the back electron transfer process in solar energy capture and release.

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