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Ultrafast Photoinduced Electron Transfer between an Incarcerated Donor and a Free Acceptor in Aqueous Solution

Mintu Porel,[†] Chi-Hung Chuang,[‡] Clemens Burda,*[,‡] and Vaidhyanathan Ramamurthy*[,†]

[†]Department of Chemistry, University of Miami, Coral Gables, Florida 33124, United States

[‡]Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United States

Supporting Information

ABSTRACT: Supramolecular photoinduced electron transfer dynamics between coumarin 153 (C153) and 4,4′-dimethyl viologen dichloride (MV^{2+}) across the molecular barrier of a host molecule, octa acid (OA), has been investigated with femtosecond time resolution. The ultrafast electron transfer from C153 to MV^{2+} followed excitation with 150 fs laser pulses at a wavelength of 390 nm despite the fact that C153 was incarcerated within an OA_2 capsule. As a result, the photoexcited coumarin did not show any of the typical relaxation dynamics that is usually observed in free solution. Instead, the excited electron was transferred across the molecular wall of the capsuleplex within 20 ps. Likewise, the lifetime of the charge transfer state was short (724 ps), and electron back-transfer reestablished the ground state of the system within 1 ns, showing strong electronic coupling among the excited electron donor, host, and acceptor. When the donor was encapsulated into the host molecule, the electron transfer process showed significantly accelerated dynamics and essentially no solvent relaxation compared with that in free solution. The study was also extended to *N*-methylpyridinium iodide as the acceptor with similar results.

Supramolecular assemblies provide unique opportunities to examine and manipulate the excited- and ground-state processes of encapsulated small organic molecules and reactive intermediates.[1,2] Hemicarceplexes were used in the past to examine the fundamental aspects of the electron transfer process.[3−5] We recently established the feasibility of electron transfer between a molecule trapped within a closed organic capsule and another molecule free in solution.[6] Even though a number of key features regarding photoinduced electron transfer in supramolecular assemblies were elucidated, some relevant important questions, such as the rates of the electron transfer in the absence of solvation dynamics and the resulting recombination rates, remained to be answered. Using nanosecond laser flash photolysis, we were not able to measure electron transfer dynamics occurring on the picosecond time scale or faster. To elucidate the electron transfer process in the above supramolecular assembly fully, we switched from nanosecond to femtosecond laser spectroscopy. Femtosecond transient absorption measurements enabled us to monitor the rates of both electron transfer and recombination between the incarcerated donor and free acceptor. Comparison of the electron transfer rates in solution and in the supramolecular assembly demonstrated the advantage of using an appropriate host molecule between the donor and acceptor. In this report, we describe the photoinduced ultrafast electron transfer from coumarin 153 (C153; Figure 1) encapsulated within an organic capsule to 4,4′-dimethyl viologen dichloride (MV^{2+}; Figure 1) and *N*-methylpyridinium iodide (Py^+; Figure 1) present free in water. The electron transfer occurs despite the lack of solvent reorganization around the donor within the capsule and the physical separation by the molecular wall of the host, octa acid[7] (OA; Figure 1).

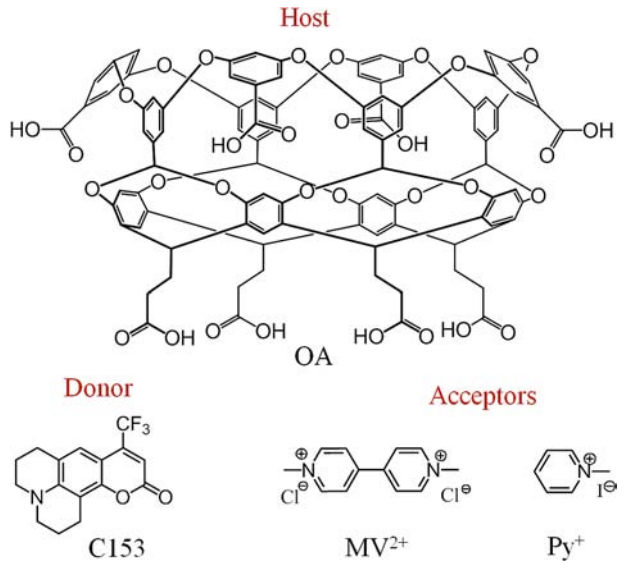

Figure 1. Structure of the molecules examined in this study: octa acid (OA), coumarin 153 (C153), 4,4′-dimethyl viologen dichloride (MV^{2+}), and *N*-methylpyridinium iodide (Py^+). Two OA units form a capsule that encapsulates C153 and forms an organic microenvironment within the aqueous solution.

On the basis of the oxidation potential of C153 (0.89 eV), the energy of its S_1 excited state (>2.7 eV), and the reduction potential of MV^{2+} (−0.69 eV), the electron transfer from C153 to MV^{2+} is expected to be exergonic.[8] However, while the effect of solvation on C153 in solution has been studied in great detail in the past,[9−11] the question of lack of solvation following

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excitation and the resulting dynamics of a possible electron transfer remained to be investigated in a host−guest assembly. Ultrafast photoinduced electron transfer from OA_2-incarcerated C153 to free MV^{2+} was studied by exciting C153 with femtosecond laser pulses [λ_{ex} = 390 nm, pulse width = 150 fs; see Figure S2 in the Supporting Information (SI)]. For this study, it was important to ensure that the excited C153 remained inside the OA_2 capsule and did not escape into the aqueous solution within the excited state lifetime. One way to monitor this was to examine the solvation dynamics in solution as well as within the OA_2 capsule using C153 as the solvation probe. The solvation dynamics in solution (30% acetonitrile in water) was demonstrated by the wavelength-dependent fluorescence decay of C153 with the well-known red shift (Figure 2a).[9] The absence of any red shift in the fluorescence at

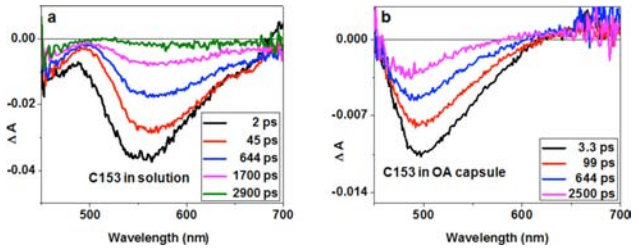

Figure 2. Femtosecond time-resolved laser-induced fluorescence spectra (λ_{ex} = 390 nm, pulse width = 150 fs) of C153 (a) in 30% acetonitrile in water with [C153] = 5×10^{-4} M and (b) within the OA_2 capsule, where [C153] = 6×10^{-5} M and [OA] = 4×10^{-4} M in 10 mM sodium tetraborate buffer. No solvent relaxation of the excited state of C153 was observed within the OA_2 complex.

500 nm for C153 within the OA_2 capsule (Figure 2b) suggested that the microenvironment of excited C153 was restricted to the hydrophobic (benzene-like)[12] interior of the OA_2 capsule. In fact, a slight blue shift, the origin of which is unclear at this stage, was noticed. These results suggested that C153 remained within the capsule for the entire duration of its excited state lifetime. Hence, OA provided an ideal environment for studying the electron transfer processes across the molecular wall in the absence of any solvent relaxation. The fluorescence lifetime of C153 within the OA_2 capsule was slightly longer than in solution (Figures S3a and S4a), implying a lack of excited state quenching by the medium.

We previously established that C153 forms a strong 2:1 host:guest complex with OA in aqueous borate buffer solution (pH ≈ 9.0) and that MV^{2+} remains strongly associated with C153@OA_2 as a result of Coulombic attraction between its cationic pyridyl parts and the carboxylate anion groups of OA.[13] ^{1}H NMR titration and diffusion-ordered spectroscopy (DOSY) spectra (see the SI) suggested that there were no free C153 molecules in solution and that MV^{2+} remained associated with the capsule (Figures S5 and S6). The interaction between OA_2-incarcerated photoexcited C153 and free MV^{2+} was probed by the quenching of the C153 fluorescence upon addition of MV^{2+} to a solution of C153@OA_2 (Figures S7 and S8). The origin of the quenching became clearer from the transient spectra of the intermediates of C153@OA_2 in the presence of MV^{2+} recorded by femtosecond pump−probe spectroscopy. The femtosecond transient absorption measurements were conducted using a Clark MXR 2001 femtosecond laser system producing 780 nm pulses from a regenerative amplifier. The laser pulse train was split to generate a white-light continuum probe pulse in a sapphire crystal and a 390 nm pump pulse using second harmonic generation. The excitation laser fluence of ∼5 mJ/cm^2 per pulse was carefully controlled. All of the femtosecond laser experiments were carried out in a 2 mm quartz cuvette at room temperature. The time resolution of the instrument was determined to be ∼150 fs via a pump−probe cross-correlation analysis.[14,15]

The femtosecond time-resolved transient pump−probe spectra are composed of three contributions: (i) transient absorption of the excited state species generated, (ii) laser-induced fluorescence (LIF) from the singlet excited state induced by the probe pulse, and (iii) ground-state absorption bleaching due to transient depopulation of the ground state. In our transient spectra, we observed the LIF of ^{1}C153* and the transient absorption of the radical cation formed from MV^{2+} ($MV^{+\bullet}$) (Figure 3a). These were directly confirmed by

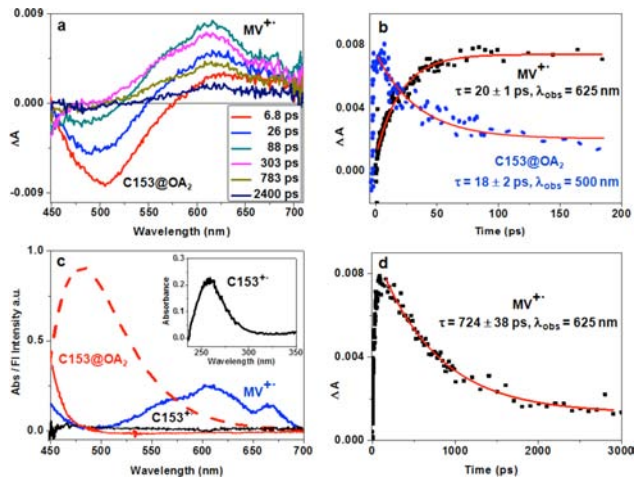

Figure 3. (a) Transient absorption spectra of the methyl viologen radical cation ($MV^{+\bullet}$) upon electron transfer from C153@OA_2 recorded at different times following excitation of C153. (b) Kinetics of the rise of $MV^{+\bullet}$ (black) and LIF of the photoexcited C153 (blue). (c) Fluorescence spectrum of C153@OA_2 (red dashed line) and absorption spectra of C153@OA_2 (red), $MV^{+\bullet}$ (blue), and $C153^{+\bullet}$ (black). The inset shows the spectroelectrochemically generated absorption spectrum of $C153^{+\bullet}$ over the wavelength range 230−350 nm. No absorption was observed beyond 300 nm. (d) Decay of $MV^{+\bullet}$. Conditions: [MV^{2+}] = 6×10^{-4} M, [C153] = 6×10^{-5} M, and [OA] = 4×10^{-4} M in 10 mM sodium tetraborate buffer; λ_{ex} = 390 nm, pulse width = 150 fs; λ_{obs} = 625 nm for the rise and decay of $MV^{+\bullet}$ and λ_{obs} = 500 nm for the LIF dynamics of C153. Forward electron transfer across the OA wall is ultrafast, and recombination occurs within 1 ns.

comparison to the steady-state fluorescence spectrum and the spectroelectrochemically observed spectrum of $MV^{+\bullet}$ shown in Figure 3c. Transient absorption in the range from 550 to 700 nm (Figure 3a) was assigned to $MV^{+\bullet}$ on the basis of the electrochemically produced $MV^{+\bullet}$ absorption spectrum and known literature information.[16] The formation of the $MV^{+\bullet}$ radical cation resulting from electron injection from C153 to MV^{2+} provided unequivocal support for electron transfer across the capsular wall. During the first few picoseconds of the experiment, the intensity of the transient absorption of $MV^{+\bullet}$ increased, indicating the accumulation of $MV^{+\bullet}$ (Figure 3a). The LIF decay of C153 was consistent with the progressive generation of $MV^{+\bullet}$ (Figure 3a). To rule out the possibility of OA acting as the electron donor in the above-described experiment, we performed the transient absorption measure-

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ments in which the *trans*-dehydrosterone@OA_2 capsuleplex was excited at 390 nm in the presence of MV^{2+}. *trans*-Dehydrosterone, which is known to form a strong 2:1 host:guest complex with OA, did not absorb at 390 nm.[7] The absence of any transient absorption in this case (Figure S9) confirmed that the aforementioned electron transfer from C153 to MV^{2+} through the OA wall was free of electron transfer from the OA host.

The lifetime of the resulting charge transfer state was measured by selectively probing the $MV^{+\bullet}$. We also studied the excited-state lifetime of C153 on the picosecond time scale via LIF. An excellent correlation was observed between the time constants for the decay of the C153 LIF (τ = 18 ± 2 ps) and the formation of $MV^{+\bullet}$ (τ = 20 ± 1 ps; Figure 3b). We were also able to monitor the decay of $MV^{+\bullet}$ during the charge recombination process (Figure 3d). The recombination kinetics was very well reproduced by a single exponential with τ = 724 ± 38 ps. Interestingly, encapsulation within the host cavity increased the rates of forward electron transfer and the recombination processes.

The above observations are in sharp contrast with the stability of charge transfer intermediates produced by electron transfer from C153 to MV^{2+} in solution. We carried out femtosecond transient absorption measurements exciting C153 in the presence of MV^{2+} in 30% acetonitrile in water. Transient spectra of the C153 excited state produced by electron transfer from C153 to MV^{2+} in solution are shown in Figure 4a. The

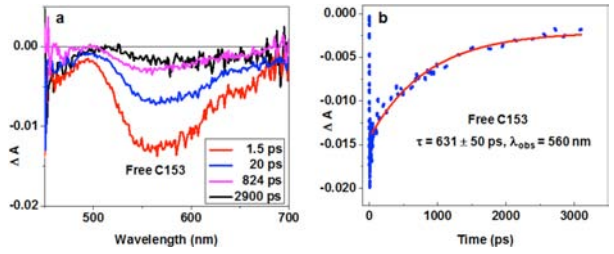

Figure 4. (a) Time-dependent transient pump–probe spectra and (b) LIF decay kinetics of C153 in the presence of MV^{2+} in 30% acetonitrile in water (no OA). Conditions: λ_{obs} = 560 nm for the decay of C153 fluorescence; [C153] = 5 × 10^{-4} M and [MV^{2+}] = 7 × 10^{-3} M; λ_{ex} = 390 nm, pulse width = 150 fs.

time constant for the electron transfer, τ = 631 ± 50 ps, was obtained from the transient spectrum of the C153 excited state at λ_{obs} = 560 nm (Figure 4b). Because of its completely diffusion-controlled nature, the electron transfer rate in solution was lower and almost identical to the recombination rate. Thus, the charge transfer intermediate ($MV^{+\bullet}$) was not sufficiently accumulated in solution, resulting in the absence of $MV^{+\bullet}$ absorption in the femtosecond transient spectra (Figure 4a).

To generalize the above-mentioned electron transfer mechanism, we studied photoinduced electron transfer from C153@OA_2 to Py^+, an acceptor that becomes neutral upon reduction (Figures S10–S13). In this system, the electron transfer from free ^{1}C153* to Py^+ (τ = 820 ± 65 ps; Figure S10) occurred on the same time scale as electron transfer from ^{1}C153* to MV^{2+}. As illustrated in Figure S11, the quenching of the fluorescence of ^{1}C153* by addition of Py^+ to the C153@OA_2 solution suggested that electron transfer occurred from incarcerated ^{1}C153* to Py^+ across the OA wall with a time constant 23 ± 1 ps. However, the spectrum of *N*-methylpyridinium radical ($Py^\bullet$) generated from Py^+ could not be detected, as it does not exhibit absorption peaks in the 450–800 nm region (see spectroelectrochemically produced absorption for $Py^\bullet$ in Figure S14c).

In summary, we have demonstrated the occurrence of photoinduced electron transfer from incarcerated C153 to free MV^{2+} across the OA wall. The lack of a red shift in the LIF of C153 suggested that the excited donor stayed within the capsule during the electron transfer process. ^{1}H NMR spectra confirmed that there were no free C153 molecules in solution. Coulombic attraction between the C153@OA_2 complex and MV^{2+} accelerated the electron transfer process in comparison with that in solution without the OA host molecule. In this molecular arrangement, the charge recombination between the donor and acceptor moieties occurred within 1 ns. We are in the process of exploring the generality of the above mechanism with the slight blue shifting in the observed femtosecond time-resolved transient spectra of encapsulated C153 and its photoinduced electron transfer across the molecular wall.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, ^{1}H NMR and DOSY spectra, fluorescence decay traces, fluorescence titration spectra, LIF spectra, transient pump–probe spectra, and spectroelectrochemically generated radical ion spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

cxb77@case.edu; murthy1@miami.edu

Notes

The authors declare no competing financial interest.

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