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Ultrafast dynamics of fluorescent dyes embedded in aromatic micelles

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[Introduction]

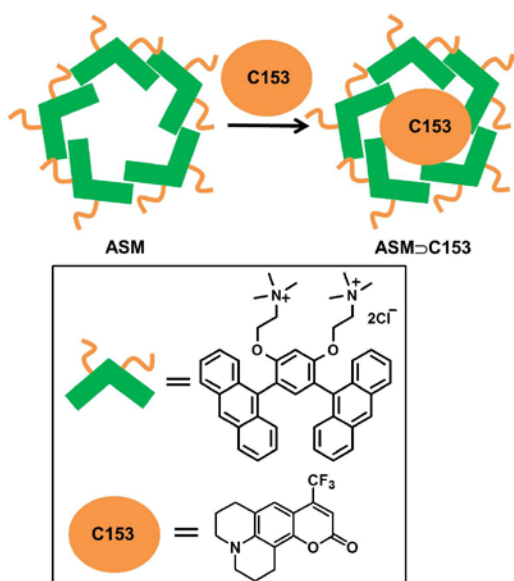


Fig. 1. Encapsulation of Coumarin 153 (C153) in the anthracene-shelled micelle (ASM) aggregate to form the ASM⊃C153 complex.

A recently-synthesized, anthracene-embedded amphiphile forms micelle-like structures with diameters of ~ 2 nm in water. These anthracene-shelled micelles (ASM) can encapsulate and thereby solubilize hydrophobic molecules, as shown in Fig. 1.¹ Because of the tight packing of the host and guest, the entire assembly can be regarded as an aggregate. In order to understand the photophysical properties of this molecular assembly and the association between host and guest, we employ ultrafast time-resolved fluorescence and absorption spectroscopies to probe its excited-state

dynamics. Based on the favorable spectral positions of its absorption and emission bands, Coumarin 153 (C153) was chosen as the guest molecule, forming the complex ASM⊃C153.

[Results]

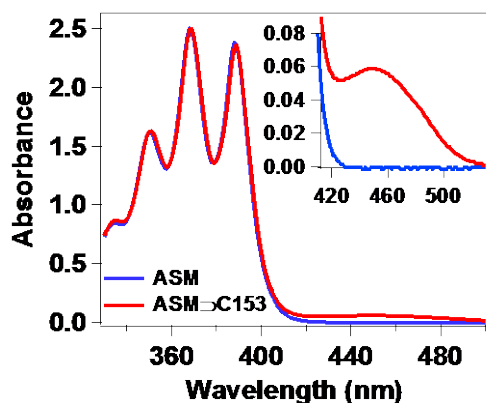


Fig. 2. Steady-state absorption spectra of ASM and ASM⊃C153. Inset: C153 region.

The absorption spectra of ASM and ASM⊃C153 are shown in Fig. 2. The spectrum of ASM⊃C153 is characterized by an ASM-like feature at short wavelengths and an additional, small band around 450 nm that is assignable to C153. Since C153 is insoluble in water, this long-wavelength feature is attributable to encapsulated C153. That the spectral features are easily associated with each molecule suggests that ground state host-guest interaction is weak.

Figure 3a shows femtosecond time-resolved fluorescence spectra obtained following 435 nm excitation into the band associated with encapsulated C153. Due to the weak host-guest interaction in the ground state, the time-resolved fluorescence spectrum obtained immediately after photoexcitation represents a primarily locally excited (LE) state with C153 character. On the time scale of a hundred picoseconds, the time-resolved fluorescence spectra exhibit a red-shift and a *ca.* 70% drop in intensity. This indicates that the initially-excited state having the LE character is relaxed on the time-scale of several 10s of picoseconds.

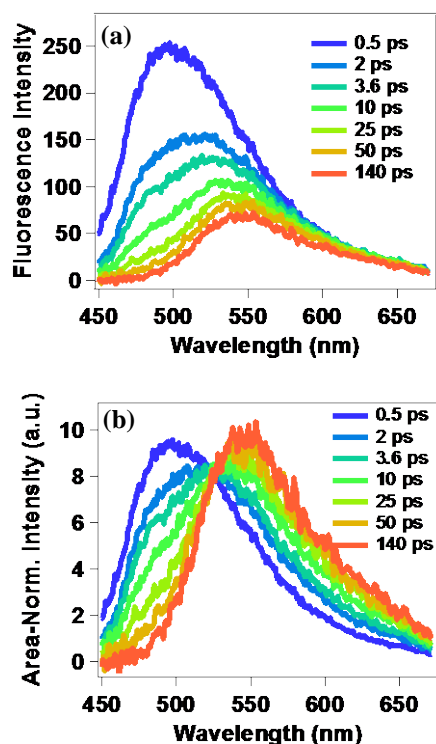


Fig. 3. (a) Time-resolved fluorescence spectra of ASM⊃C153 excited at 435 nm. (b) Area-normalized spectra.

Figure 3b shows the time-resolved fluorescence spectra after normalization by their areas. The spectra reveal a clear isosbestic point (Fig. 3b), indicating that the observed spectral shift arises from an interconversion between two distinct states.² A possible assignment for the lower energy state is an exciplex formed between the C153 and ASM. Unlike the electronic relaxation processes of simple molecules in solution, which typically show single-exponential decays, the electronic relaxation from the LE state to the exciplex state in ASM⊃C153 is a non-exponential process occurring on the time-scale of several 10s of picoseconds.

To explain this phenomenon, we assume that the complex, ASM⊃C153, can be assembled into many different conformations in the ground state. Then, photoexcitation generates the LE states in complexes having many different conformations of ASM and C153. The conformations of the exciplex likely differ from those found in the ground state, so a conformational change must precede exciplex formation. It is highly likely that the time constant for the conformational change depends on the initial conformation. Since there are many conformations in the ground state, the rates of these changes should span a wide range of time scales. Thus, the conformational heterogeneity of the ASM⊃C153 assembly explains the non-exponential relaxation from locally excited state to exciplex.

[References]

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- ² Koti, A. S. R.; Krishna, M. M. G.; Periasamy, N. *J. Phys. Chem. A* **2001**, *105*, 1767.