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Ultrafast dynamics of novel aromatic micelles encapsulating fluorescent dyes

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[Introduction]

A recently-synthesized anthracene-embedded amphiphile (AEA) was shown to aggregate into anthracene-shelled micelles (ASM), as illustrated in Figure 1.[1] These micelles can encapsulate a hydrophobic fluorescent guest (e.g. DCM) in water. Steady-state spectroscopy has shown that the chromophoric host can be photoexcited and subsequently transfer energy to the guest, resulting in emission from the latter. In this study, we examine the time-resolved fluorescence of these materials to elucidate the dynamics of this novel aromatic supramolecule.

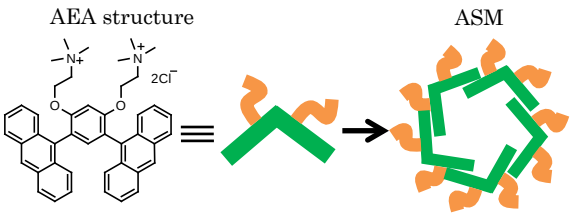

Fig. 1. Formation of ASM from AEA

[Experimental]

AEA and ASM were prepared as described previously.[1] ASM was excited using 140 fs, 400 nm pulses. 500 nm pulses were used to excite DCM in solution or within micelles. The resulting fluorescence transients were collected using a streak camera. Fluorescence anisotropy data were collected by placing a polarizer in front of the camera to alternately filter parallel and perpendicular light.

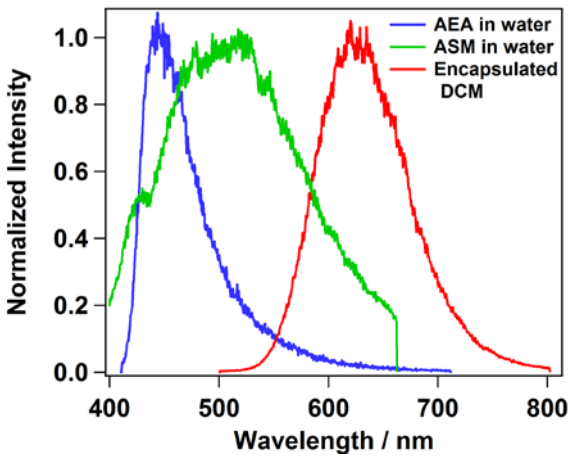

Fig. 2. Representative fluorescence spectra of AEA, ASM, and encapsulated DCM.

[Results]

Figure 2 shows the steady-state fluorescence spectra of AEA, ASM, and encapsulated DCM (i.e., ASM⊃DCM host-guest complex). A dilute solution of free AEA in water or methanol exhibits fluorescence primarily at short wavelengths, which decays monoexponentially with a time constant of 6.5 ns. A solution of empty ASM in water exhibits a bi-exponential fluorescence decay consisting of a 32-ns component, centered

at 500 nm, and 5.2 ns component, which is dominant at shorter wavelengths. The former is assigned to ASM fluorescence, and the latter is assigned to free AEA. Direct excitation of the encapsulated DCM within the ASM⊃DCM complex yields a fluorescence spectrum with a peak at 648 nm and a decay time constant of 3.6 ns.

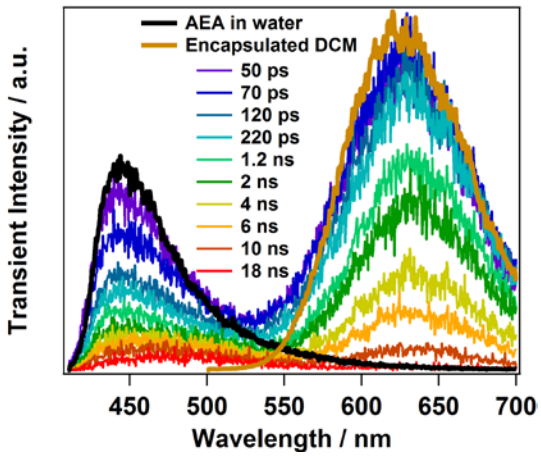

Fig. 3. Transient fluorescence decays of 400-nm-excited ASM⊃DCM. The black and brown lines represent the fluorescence of free AEA and encapsulated DCM, respectively.

Photoexcitation of the ASM⊃DCM complex at 400 nm, which primarily excites the ASM component, yields the transient fluorescence spectra shown in Figure 3. The bands with peaks at 630 and 450 nm are assignable to fluorescence from encapsulated DCM and free AEA, respectively. Fluorescence from DCM is observable even at the earliest times, indicating that energy transfer within the ASM⊃DCM complex is completed within the 25 ps time resolution of the present measurement.

The fluorescence anisotropy decays of empty ASM and encapsulated DCM were also collected to determine whether or not the guest rotates freely within the micelle. The fluorescence anisotropy of encapsulated DCM decays with a time constant of 740 ps, which is much slower than the 100 ps observed for DCM in methanol. Therefore, its motion is highly restricted in the micelle. Empty ASM shows an anisotropy decay time constant of 520 ps. Since it is very unlikely that constrained DCM rotates more slowly than its host micelle, the orientation of DCM must be completely fixed within the micelle, so that the two rotate together. Enlargement of the micelle upon encapsulation of DCM would account for the slower anisotropy decay of the complex.

[References]

[1]Kondo, K.; Suzuki, A.; Akita, M.; Yoshizawa, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2308.