Highly polar environment within an aromatic micelle

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[Introduction]

A synthetic, anthracene-embedded amphiphile forms unique aggregates in water. These aggregates contain a small cavity with a hydrophobic interior, which gives them a micelle-like structure. Due to their hydrophobic interior, these anthracene-shelled micelles (ASM) can encapsulate a hydrophobic chromophore in water, as depicted in Fig. 1. However, the local environment experienced by the encapsulated molecule is not known. In order to investigate this, we encapsulated the solvatochromic probe molecule, Coumarin 153 (C153) into the micelle. The absorption and fluorescence of C153 are highly sensitive to the local polarity, and can be used to describe the surroundings.

[Results]

The absorption and fluorescence spectra of C153 in various environments are presented in Fig. 2. For encapsulated C153, the excitation spectrum is used instead of absorption, because small amounts of multiply-occupied micelles were found to give additional absorption and fluorescence at short-wavelengths. This is not due to free C153, as its solubility in water is too low. The excitation maximum of encapsulated C153 (λmax = 457 nm) is red-shifted relative to that of C153 in water (λmax = 433 nm). Thus, despite being surrounded by nonpolar anthracene panels, the local polarity around C153 is greater than that of water. The fluorescence spectrum of encapsulated C153 (λmax = 541 nm) appears in a similar position to that of C153 in water (λmax = 553 nm), indicating that little reorganization of the surroundings...
occurs following photoexcitation of encapsulated C153. In fact, the fluorescence of C153 in water is more red-shifted than that of encapsulated C153, due to greater solvent reorganization.

The reorganization dynamics of the environment of encapsulated C153 were examined using its time-resolved fluorescence spectra (Fig. 3). Consistent with the small difference between the excitation and fluorescence spectra, only a small dynamic Stokes shift was observed at the red edge of the spectrum, at early times. The larger shift and intensity loss at short wavelengths are due to encapsulation of multiple chromophores in some micelles.

In addition to examining the solvation dynamics, we also examined the freedom of motion of the guest within the micelle. Since both empty micelle and encapsulated guest are fluorescent, the fluorescence anisotropy of each was used to obtain their rotational time-constants. The encapsulated guest showed a time constant of 860 ps, which is greater than the 510 ps time-constant obtained for the empty host. Since the guest cannot rotate more slowly than the host, the slower rotation of the encapsulated guest indicates that the guest and host rotate together as one unit. Interestingly, rotational diffusion of the host→guest complex is slower than that of the empty micelle. This result suggests that the host becomes larger in size when it encapsulates a guest.

[References]