

Highly polar environment within an aromatic micelle

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[Introduction]

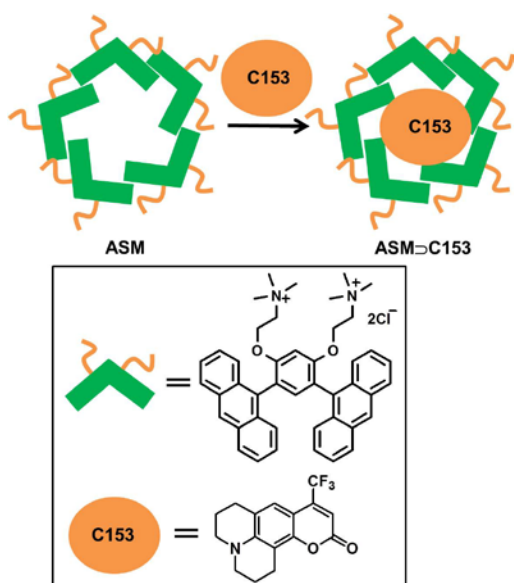


Fig. 1. Encapsulation of Coumarin 153 (**C153**) in ASM aggregate to form the **ASM⊃C153** complex.

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. 1.¹ 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** ($\lambda_{\text{max}} = 457 \text{ nm}$) is red-shifted relative to that of **C153** in water ($\lambda_{\text{max}} = 433 \text{ nm}$). 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** ($\lambda_{\text{max}} = 541 \text{ nm}$) appears in a similar position to that of **C153** in water ($\lambda_{\text{max}} = 553 \text{ nm}$), indicating that little reorganization of the surroundings

occurs following photoexcitation of encapsulated **C153**. In fact, the fluorescence of **C153** in

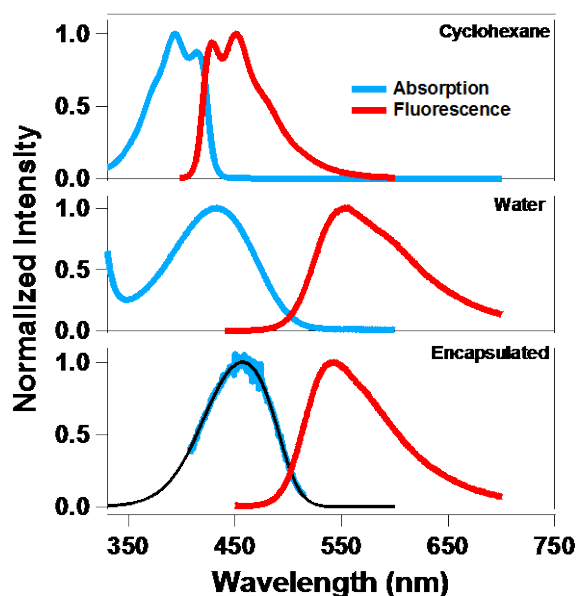


Fig. 2. Excitation and fluorescence spectra of **C153** in various solvents and encapsulated in ASM, after subtraction of the ASM contribution). The black line is a fitted line.

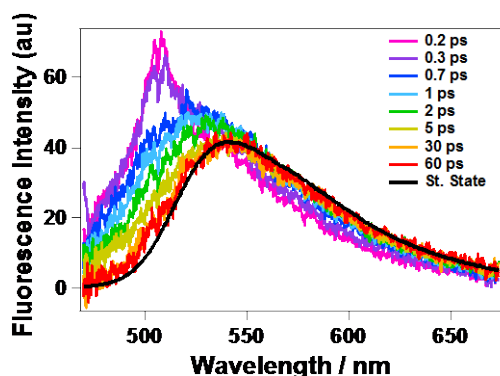


Fig. 3. Fluorescence upconversion showing very little dynamic Stokes shift for encapsulated **C153**.

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]

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

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