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Electronic Supplementary Information

Selective Prototropism of Lumichrome in Cationic Micelles and Reverse Micelles: A Photophysical Perspective

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Note S1.

Preparation of BHDC Micelles and Reverse Micelles containing LC

BHDC micelles containing LC were prepared by mixing aliquots of a concentrated stock solution of BHDC in water, with an aqueous solution of the dye.

For preparing the reverse micellar solutions containing the dye, LC was first dissolved in a concentrated solution of BHDC in benzene by continuous stirring. A calculated amount of this stock was mixed with another measured amount of BHDC/benzene solution having same BHDC concentration as the previous stock solution but without containing the dye. This was followed by the addition of requisite amounts of benzene and/or water to obtain a final BHDC concentration of 0.27 M, and the desired w_0 value.

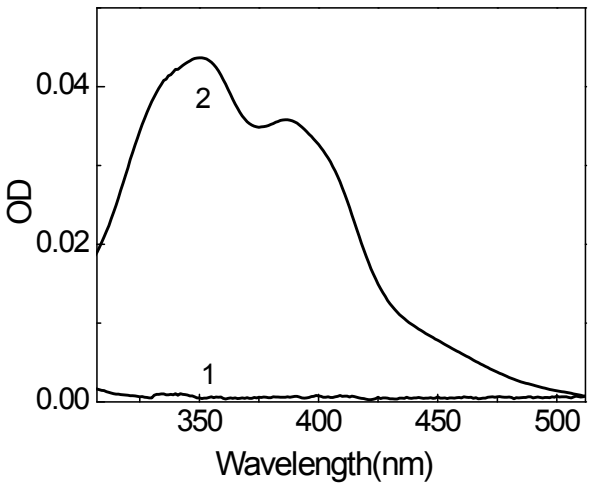

Fig. S1. Absorption spectrum of BHDC micelles (4 mM) without LC (1) and with 6 μM LC (2).

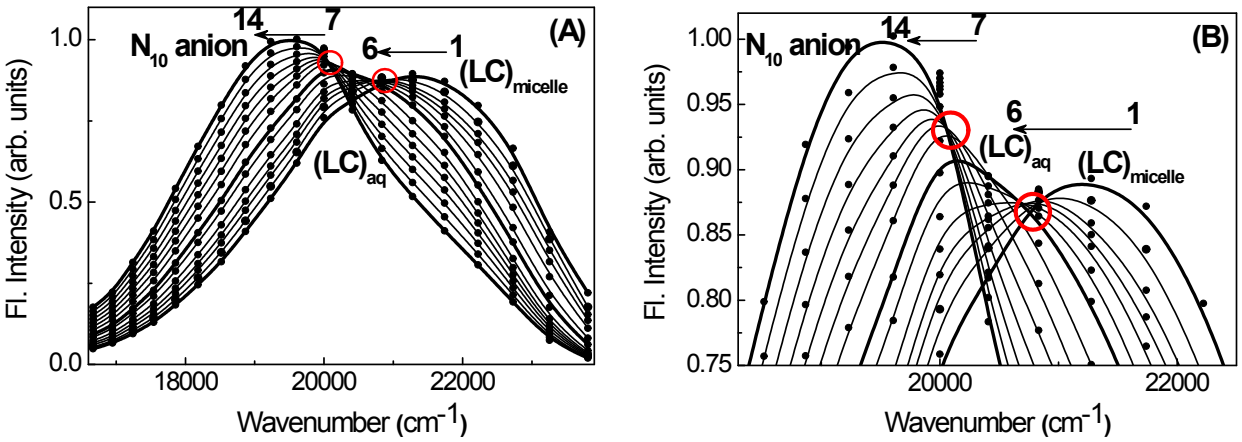

Fig. S2. (A) TRANES for LC in BHDC micelles (4 mM) at 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2, 3, 4, 5, 6, 7, 8 and 9 ns. Excitation wavelength: 374 nm (This figure is the same as Fig. 6C in manuscript). (B) Enlarged view of (A) showing the two isoemissive points.

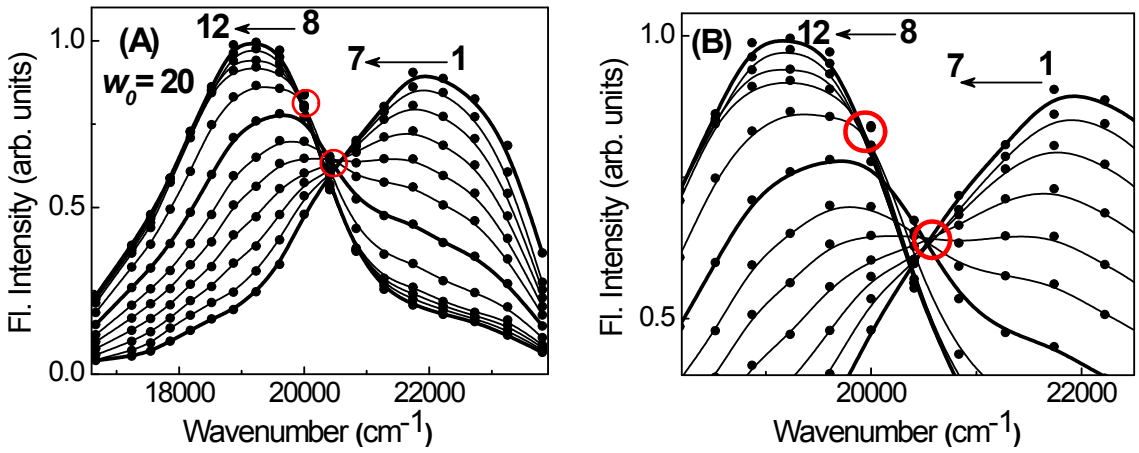

Fig. S3. (A) TRANES for LC in BHDC reverse micelles for w_0=20 at 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.5, 2, 3, 4, 5, and 6 ns. Excitation wavelength: 374 nm (This figure is the same as Fig. 11C in manuscript). (B) Enlarged view of (A) showing the two isoemissive points.

Note S2.

Fluorescence Anisotropy decay of LC in BHDC Micelles and Reverse Micelles

Time-resolved anisotropy decays of LC were measured in BHDC micelles and reverse micelles to understand the microenvironment around the dyes. The anisotropy measurements were carried out using the time-correlated single photon counting (TCSPC) instrument (Horiba Jobin Yvon, UK). The samples were excited with a vertically polarized excitation beam, and the vertically and

horizontally polarized fluorescence decays were collected with a large spatial bandwidth of ~32 nm. Using these polarized fluorescence decays, the anisotropy decay function, r(t), was constructed as follows:

$$r(t) = \frac{I_V(t) - GI_H(t)}{I_V(t) + 2GI_H(t)}$$

$I_V(t)$ and $I_H(t)$ are the vertically and horizontally polarized decays, respectively, and G is the correction factor for the polarization bias of the detection setup. The G factor was determined independently by using a horizontally polarized excitation beam and measuring the two perpendicularly polarized fluorescence decays. All anisotropy measurements were repeated twice.

The anisotropy decay of LC in water (pH 5.9) is very fast and could not be detected within the time resolution of the present TCSPC set-up. However, in the presence of BHDC micelles and reverse micelles, the anisotropy decay traces were significantly slower and could be easily monitored. The anisotropy decays, r(t), were bi-exponential in nature with average rotational correlation times $<\tau_{rot}>$ of 1.84 ns in BHDC micelles and 1.88 ns in BHDC reverse micelles with $w_0 = 40$. The long rotational correlation time of LC suggests that the dyes are bound to the micellar interfaces.

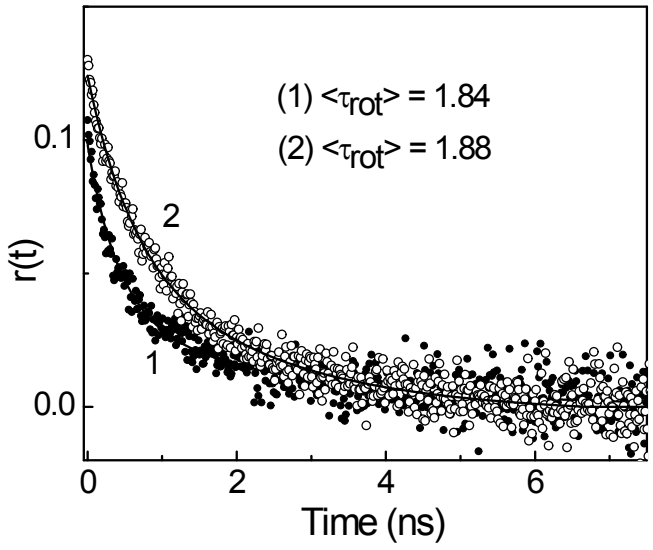

Fig. S4. Anisotropy decay traces for LC in BHDC micelles (1) and reverse micelles with $w_0 = 40$ (2) recorded at 550 nm, excitation wavelength 374 nm.