Supporting Information

A Direct Observation of Solvation Dynamics in Aqueous Reverse Micellar System Containing Silver Nanoparticle in the Reverse Micellar Core.

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Experimental Section:

TEM measurements were performed using a (JEOL) JEM-2100 instrument operating at 200keV. Samples for TEM were prepared by blotting a carbon coated (50 nm carbon film) Cu grid (300 mesh, Electron Microscopy Science), with a drop of the Ag-micro emulsion and allowed to dry. Histograms are constructed manually by measuring the individual particle diameter with the help of Image-J software. The absorption and fluorescence spectra were measured using a Shimadzu (model no. UV-1601) spectrophotometer and a Spex-Fluorolog-3 (model no. FL3-11) spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the instrument. For steady-state experiments, all samples were excited at 440 nm (to avoid the contribution of the n-heptane part). The setup for time-resolved fluorescence measurements was described in detail in our earlier publication [Chakrabarty, D.; Chakraborty, A.; Seth, D.; Hazra, P.; Sarkar, N. Chem. Phys. Lett. **2004**, 397, 469.] Briefly, the samples were excited at 408 nm using a picosecond diode laser (IBH), and the signals were collected at magic angle (54.7°) polarization using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is ~90 ps. The same setup

was used for anisotropy measurements. For the anisotropy decays, we used a motorized polarizer in the emission side. The emission intensities at parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) polarizations were collected alternatively until a certain peak difference between parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) decays were reached. The peak differences depended on the tail matching of the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) decays. The analysis of the time-resolved data and anisotropy decays were done using IBH DAS, version 6, decay analysis software. All experiments were carried out at 298 K. The same software was also used to analyze the anisotropy data. We had to use 408 nm picosecond diode laser for time resolved study due to the unavailability of picosecond diode laser in the range of 440 nm. For dynamic light scattering (DLS) measurements, we used a Malvern Nano ZS instrument employing a 4mW He-Ne laser (λ=632.8 nm) and equipped with a thermostated sample chamber. All experiments were carried out at 173° scattering angle at 298 K.

Anisotropy measurements:

Time resolved fluorescence anisotropy, r(t) was calculated using the following equation

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)}$$

Where G is the correction factor for the detector sensitivity to the polarization direction of the emission. $I_{\parallel}$(t) and $I_{\perp}$(t) are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively.

Time Resolved Studies:

We have observed a dynamic Stoke's shift in the emission spectra of C-153 in both systems. In both condition, fluorescence transient of C-153 is dependent on the emission wavelength. At the red edge of the emission spectra, we have observed a decay profile that consists of a clear rise followed by usual decay, and at the blue end of the emission, a faster decay is observed, which is shown in Figure 2A and 2B. All decay profiles were best fitted by a biexponential function. The time-resolved emission spectra (TRES) were constructed using the procedure of Fleming and Maroncelli [Maroncelli, M.; Fleming, G. R. *J.Chem.Phys.***1987**,*86*,6221]. The TRES at a given timet, S(λ;t), is obtained by the fitted decays D(t;λ), by relative normalization to the steady state spectrum $S_0(\lambda)$, as follows

$$S(\lambda;t) = D(t;\lambda)\frac{S_0(\lambda)}{\int_0^\infty D(t;\lambda)dt}$$

Each time-resolved emission spectrum was fitted by the "log-normal line shape function", which is defined as

$$g(v) = g_0 \exp\left[-\ln 2\left(\frac{\ln[1+2b(v-v_P)/\Delta]}{b}\right)^2\right]$$

where g_0, b, ν_p, and Δ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. TRES of C-153 in normal water/AOT/n-heptane reverse micelle and reverse micelle containing silver nanoparticle are given in figure 3 and figure 4 respectively.

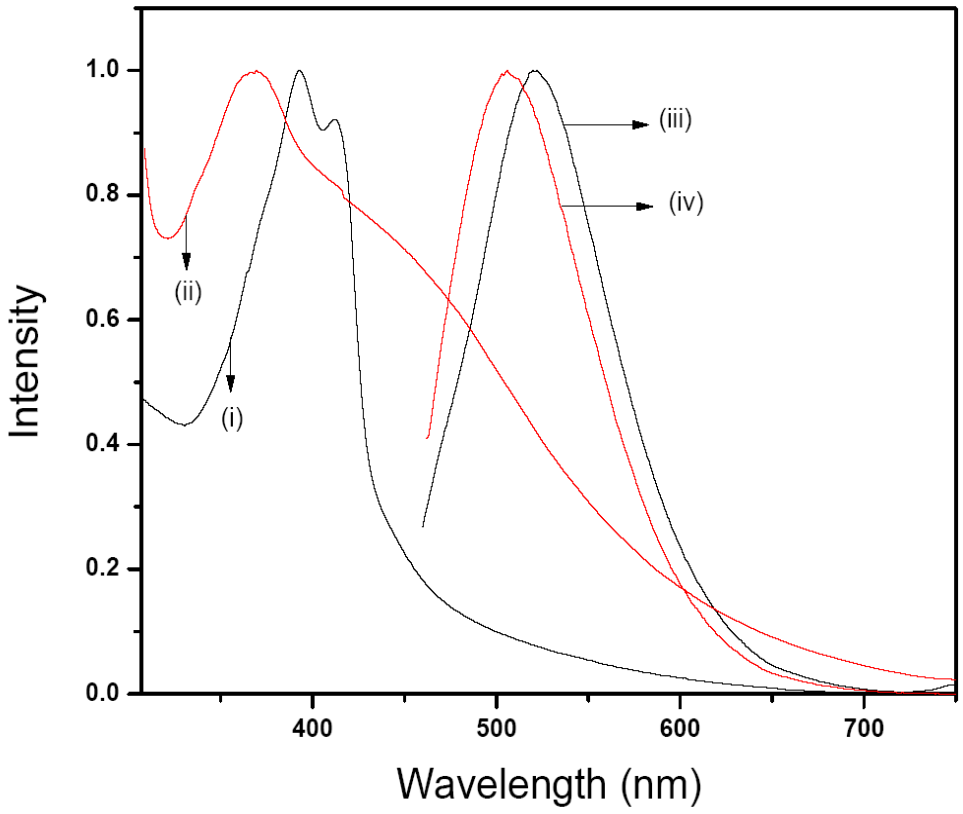

Figure 1. All the spectra are recorded at w_0=4. (i) Absorption spectra of C-153 in normal water/AOT/n-heptane system. (ii) Absorption spectra of C-153 in water/AOT/n-heptane

system in presence of silver nanoparticle. (iii) Fluorescence spectra of C-153 in normal water/AOT/n-heptane system. (iv) Fluorescence spectra of C-153 in water/AOT/n-heptane system in presence of silver nanoparticle.

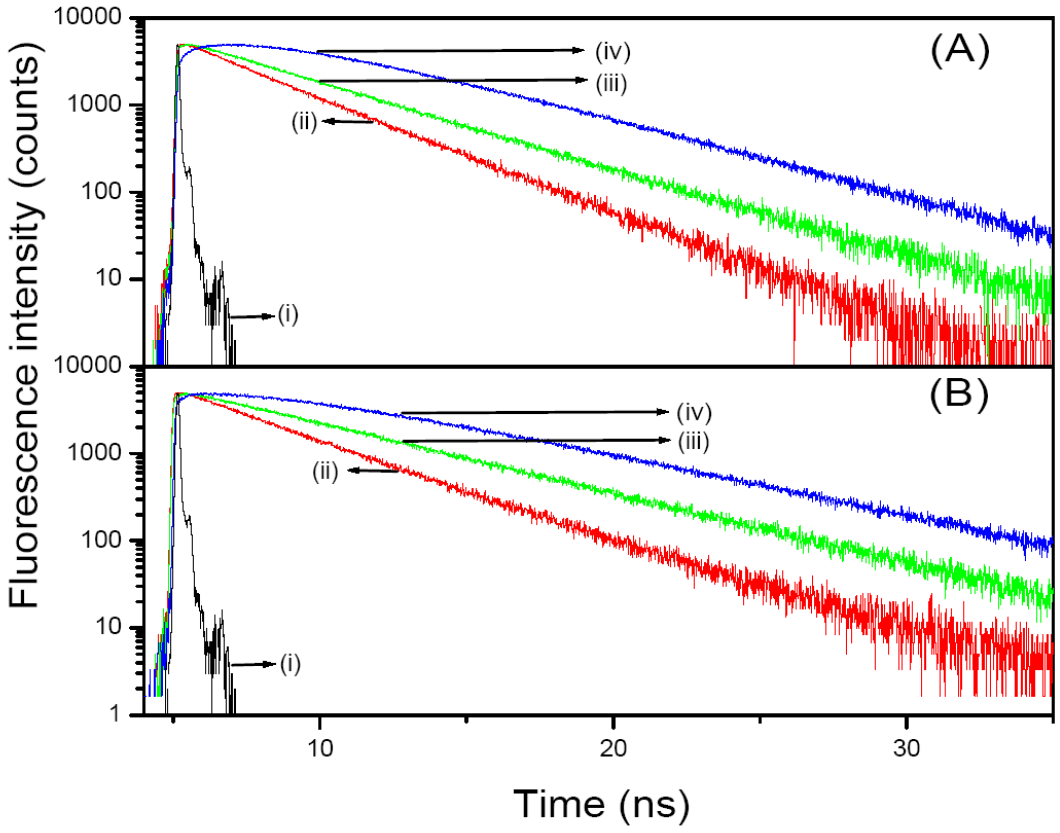

Figure 2. Panel (A) shows the fluorescence decay of C-153 in normal water/AOT/n-heptane system at w_0=4 (i) instrument response function (ii) 465 nm (iii) 510 nm and (iv) 600 nm. Panel (B) represent the same things but in presence of nanoparticle.

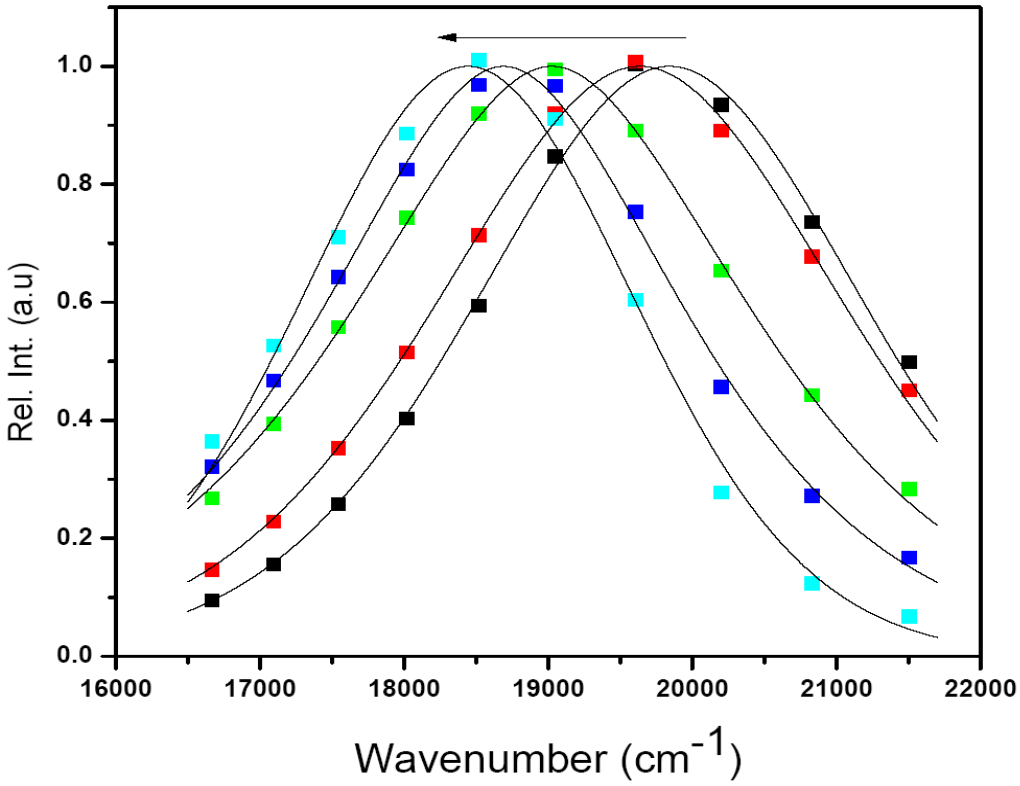

Figure 3. Time-resolved emission spectra (TRES) of C-153 in water/AOT/n-heptane reverse micellar system at w_0=4. (i) 0 ns (black) (ii) 1 ns (red) (iii) 5 ns (green) (iv) 10ns (blue) (v) 20 ns (cyan).

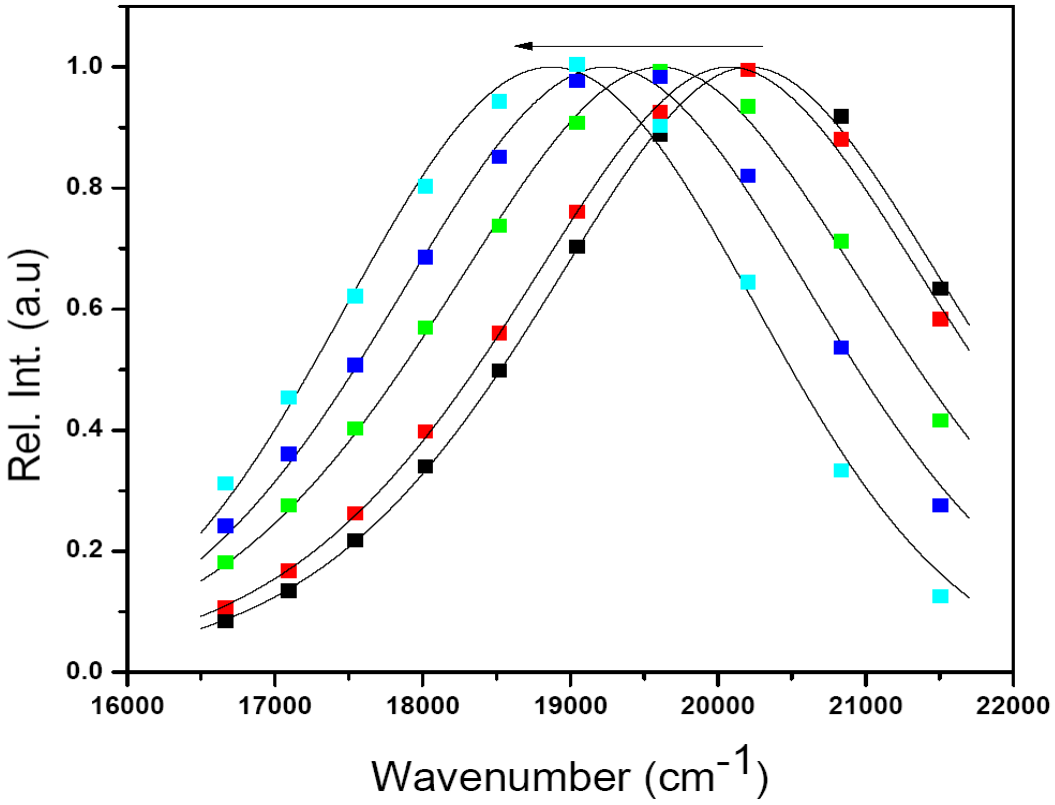

Figure 4. Time-resolved emission spectra (TRES) of C-153 in water/AOT/n-heptane reverse micellar system at w_0=4 in presence of silver nanoparticle. (i) 0 ns (black) (ii) 1 ns (red) (iii) 5 ns (green) (iv) 10ns (blue) (v) 20 ns (cyan).

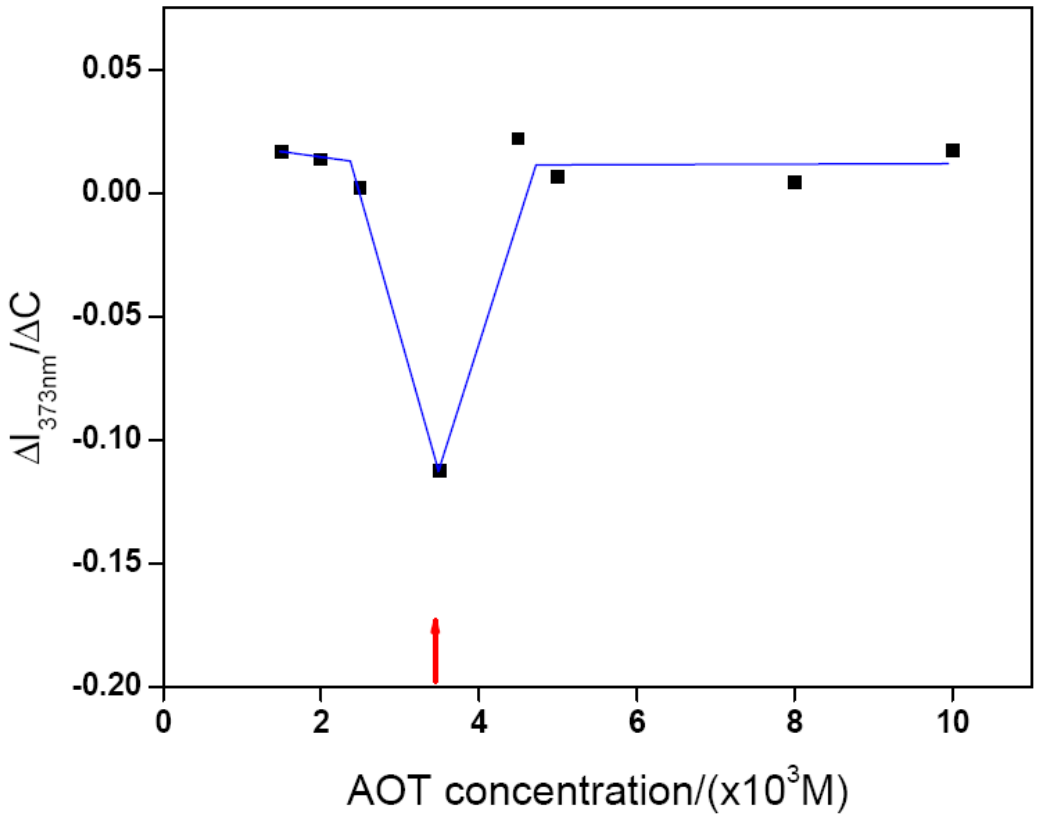

Figure 5. Plot of differential signal of fluorescence peak one (I_1, 373 nm) intensity of pyrene in AOT/n-heptane solution at various concentration of AOT. W_0=4, [pyrene]=3×10^{-7} (M), λ_{ex}=335nm.