Supporting Information

Slow water dynamics at the surface of macromolecular assemblies of different morphologies

Pramod Kumar Verma, Ranajay Saha, Rajib Kumar Mitra*, Samir Kumar Pal*

Unit for Nano Science & Technology

Department of Chemical, Biological & Macromolecular Sciences

S.N. Bose National Center for Basic Sciences

Block JD, Sector III, Salt Lake, Kolkata 700098, INDIA

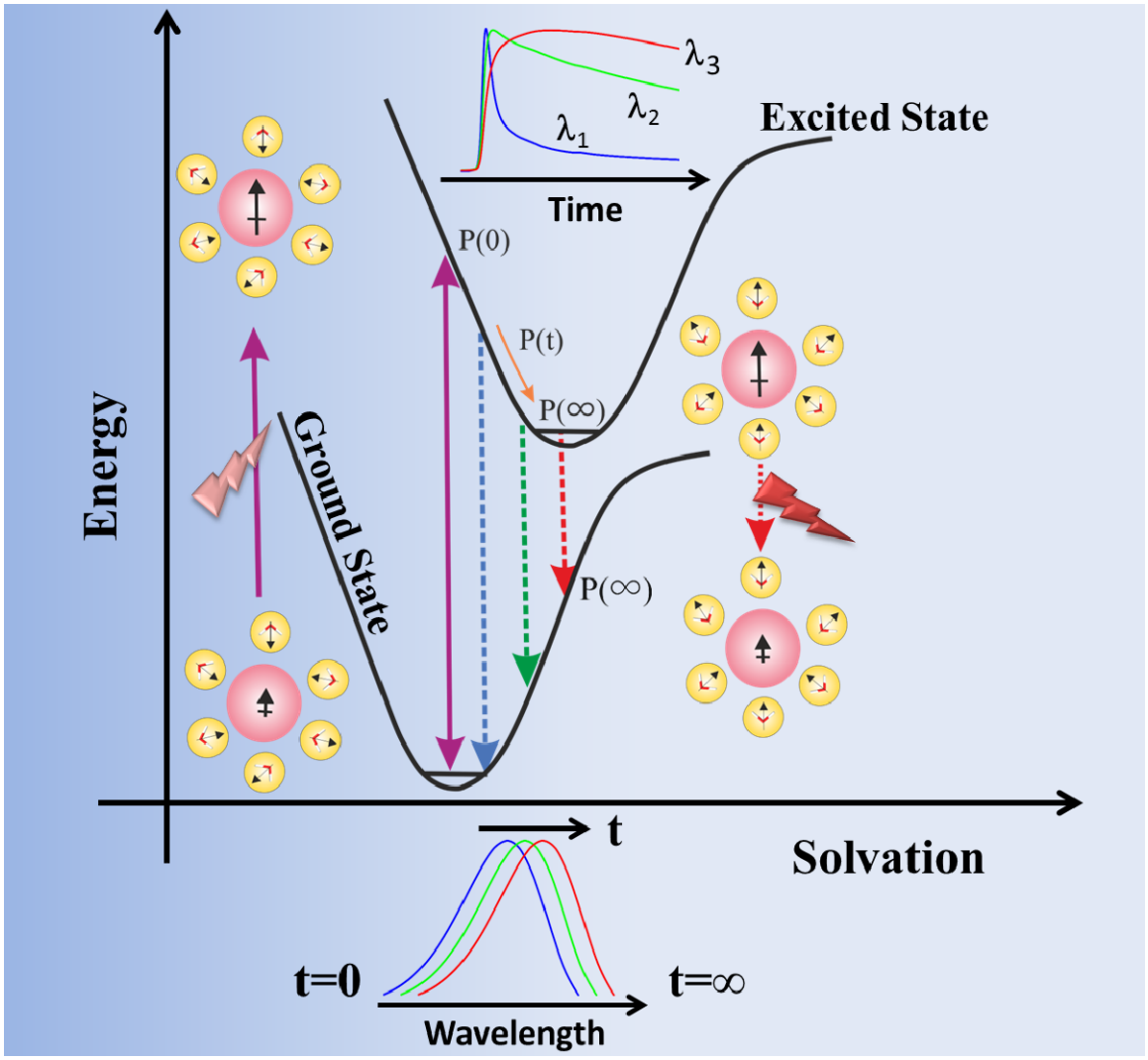
*Corresponding authors, e-mail: skpal@bose.res.in (S.K.Pal), rajib@bose.res.in (R.K.Mitra)

1. Details of the solvation dynamics.

Solvation refers to the stabilization of a solute molecule because of its interaction with the surrounding solvent molecules. Evidently, solvation is most pronounced when the solute is ionic or dipolar and the solvent is polar. The dynamics of this process, i.e., how quickly the solvent dipoles rearrange around an instantaneously created charge (electron) or dipole, is known as solvation dynamics. There are many molecules whose dipole moment is zero or very small in the ground electronic state while it is very large in the electronically excited state. Such a molecule exhibits a very prominent red shift of the absorption and the emission maximum with an increase in solvent polarity[1]. When such a solute molecule in a solution is excited by an ultrashort light pulse at time t =0, a dipole is created instantaneously. This dipole gives rise to an instantaneous electric field on the solvent molecules. Because of the interaction of the solvent permanent dipoles with the electric field, the free energy minimum of the solvent shifts to a nonzero value of the polarization. The solvent motion is critical. Since the solute is excited instantaneously (a Franck Condon transition as far the nuclear degrees of freedom are concerned), the solvent molecules at t=0 find themselves in a relatively high energy configuration. Subsequently, the solvent molecules begin to move and rearrange themselves to reach their new equilibrium positions (Figure 4, upper). With an increase in time, the solvent dipoles gradually reorient and the energy of the excited dipole decreases. Thus, with an increase in time the emission maximum shifts to lower energy, i.e., toward longer wavelength. This phenomenon is known as time dependent fluorescence Stokes shift (TDFSS)[2-6]. The nuclear motion involved can be broadly classified into rotational and translational motions.

In picosecond measurement we cover mainly larger amplitude rotational and translational motions of the nearest neighbor molecules in the first solvation shell (i.e., rearrangement of

the solvent molecules that are the nearest neighbors of the probe). In the intermediate time, one gets contributions from the moderately damped rotational motions of water molecules. In a sense, with the above description one recovers the famous Onsager's "inverse snow-ball" picture of solvation[7].



Scheme S1: Schematic illustration of the potential energy surfaces involved in solvation dynamics, showing the water orientational motions along the solvation coordinate together with instantaneous polarization P. Lower inset shows the normalized spectral evolution at three delay points. Upper inset shows the position and time dependence of the population, fluorescence intensity. At early times (when the population is at λ_1), there is an ultrafast decay. At intermediate times (when the population is at λ_2) there is a slow decay as shown by the green line. At long times when the population is nearly relaxed (position λ_3, red line) we see only a rise. As solvation proceeds, the energy of the solute decreases, giving rise to a

red shift in the fluorescence spectrum. Note the instantaneous P, e.g., P(∞), on the two connected potentials.

By following the change of transients with wavelength of emission (excited-state energy), we can probe the relaxation process on the solvent coordinate of the free energy surface. The emission transients detected in the blue region (higher energy) of the emission spectrum will be characterized by decay components reflecting forces of motion. When detection is redder (lower energy), however, the decay part slows until eventually a rise is observed. The time scales of decay and rise in the blue and red regions, respectively, depend on the temporal behavior of relaxation on the solvation energy surface (Figure 4). Repeating these experiments for the entire range of energies available, we can obtain C(t) and the solvation dynamics.

2. Difference Absorption Spectra:

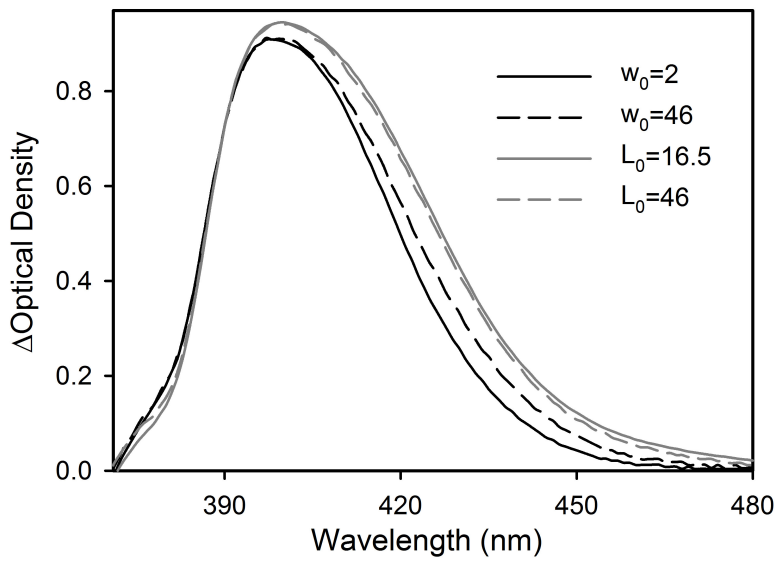


Figure S1. Difference absorption spectra of C-500 in AOT RMs and lamellar (with respect to C-500 in i-Oc) with w_0 =2 and 46 and L_0= 16.5 and 46.

The fluorophore C-500 is sparingly soluble in water and shows reasonably good solubility in isooctane. In bulk water the absorption peak (400 nm) is significantly red-shifted compared to that in isooctane (360 nm). Earlier studies[8] from our group have shown that in isooctane C-500 offers significant solubility and the absorption spectrum shows a peak at 360 nm with a shoulder at 380 nm. Upon addition of AOT, another shoulder (at 400 nm) appears in the absorption spectrum, indicating a population of the C-500 in the polar environment of the RM and lamellar. Figure S1 shows the difference absorption spectra of C-500 in AOT RM and lamellar at different w_0 and L_0 values at 298 K, in which the absorption spectrum of C-500 in i-Oc has been subtracted from that of C-500 in AOT RM and lamellar. It is evident from the figure S1b that a single absorption peak around ~400 nm, which is close to that of the probe in bulk water, is obtained for all the RM and lamellar systems. Previously we have

shown that C-500 in the AOT/isooctane mixture shows an emission peak at 430 nm with excitation wavelength at 350 nm, indicating emission from both the population of the C-500 molecules in polar and nonpolar environments. Upon excitation at 400 nm the C-500 emission is peak-shifted to 500 nm revealing the population of C-500 molecules in the polar environment only[8]. Both this fact supports the choice of 409 nm wavelength as the excitation source for the time- resolved studies as one would expect information coming only from the interphase.

References:

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