Supporting Information:

## Nano-Confined Charged Layer Defy the Principle of Electrostatic Interaction

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Materials and Methods

Chloride salt of Thioflavin-T (ThT, see scheme S1 for molecular structure) was purchased from Sigma, USA. ThT was re-crystallized twice from methanol solution. The purity of the re-crystallized ThT was checked through NMR spectra [1]. AOT was obtained from Sigma and purified by boiling its methanolic solution with activated charcoal. Charcoal was removed by hot filtration and AOT was recovered by removing methanol under vacuum. Because of the hygroscopic nature of AOT, its water content was determined through the Karl-Fischer titration method. The sample had a [water]/[AOT] molar ratio of 0.67 very similar to the value reported earlier [2, 3]. BHDC was purchased from sigma and was used as received. Benzene was purchased from Spectrochem (India) and was freshly distilled before use. Nano pure water (conductivity less than 0.1 μS cm^{-1}), from Millipore Milli Q system, was used for all sample preparations. The surfactant concentration was kept at 0.2 mol dm^{-3} throughout the present study. Water was systematically added to the surfactant solution in benzene to prepare the RM with appropriate w_o value. Concentration of ThT was kept very low (~10μM) so that the possibility of having more than one ThT molecule per RM is negligible.

Scheme- S1: Chemical structure of ThT, BHDC, and AOT
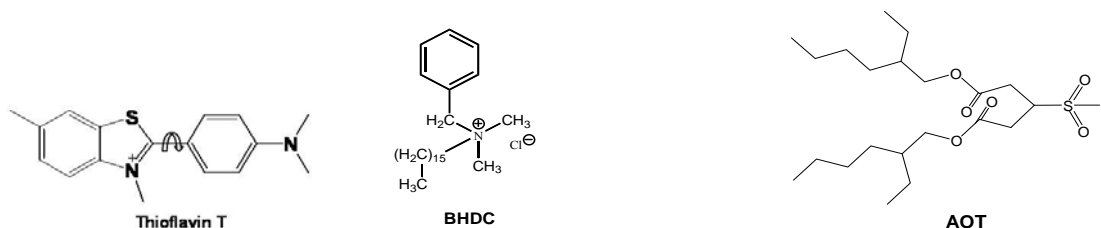
Time-resolved fluorescence measurements were carried out using a femtosecond fluorescence upconversion instrument (FOG 100, CDP Inc. Russia). Briefly, a second harmonic laser pulse (410 nm, 50 fs, 88 MHz) of a Ti-Sapphire oscillator was used for the sample excitation. Fluorescence from the sample was collected using two parabolic mirrors and focused onto a 0.5 mm BBO crystal. The residual fundamental laser beam was mixed with the fluorescence beam in the BBO crystal to generate the sum

frequency light, which was detected by a PMT based photon counter after passing through a double monochromator. The instrument response function (IRF) of the present instrument was independently measured through the cross correlation of the excitation and the fundamental laser pulse. The IRF was found to have a Gaussian intensity profile with FWHM of 220 fs.

The decay traces at each wavelength were collected at least for two times to see the reproducibility of the measurements. Sample was taken into a rotating cell of optical path length of 0.4 mm, to avoid the photodecomposition of the sample. At the monitoring wavelength of the fluorescence decay, the contribution of the scattering light (Raman scattering) from the medium was checked by placing a sample cell filled with the RM only. The contribution of such scattering at the monitoring wavelength was negligible compared to the sample intensity. All the measured fluorescence decays were fitted with a multi- exponential function using the standard convolute-and-compare nonlinear least square procedure [4].

Steady-state fluorescence measurements were carried out using a Hitachi spectro fluorimeter (model F-4500). All the samples were excited with 410 nm light. Spectrum of standard quinine sulfate solution was recorded and compared with the standard spectrum given in the unit of photon/nm [5], to get the wavelength dependent correction factors for the instrumental sensitivity. These correction factors were used to correct the observed fluorescence spectra for the sample.

Radius of the central water pool for the BHDC/benzene RMs were calculated from the experimental value reported in the literature [6, 7]. It is shown in the literature that the radius of the water pool in BHDC/benzene RM varies linearly with the w_0 ([water]/[surfactant]) value as shown in the figure S1. The values of water pool radius for the w_0 value used in our experiment were obtained from the linear fitting (solid line in figure S1) of the experimental value reported in the literature [6, 7]. The radius of the water pool in the AOT/benzene RM were taken for those measured in toluene solvent [8]. It is shown by Keh et al. that the water pool size at the centre of the AOT RM are similar when toluene and benzene are used as non-polar media [9]. It is to be noted that the AOT RM in benzene solvent is reported to be stable only up to w_0=10 [10].
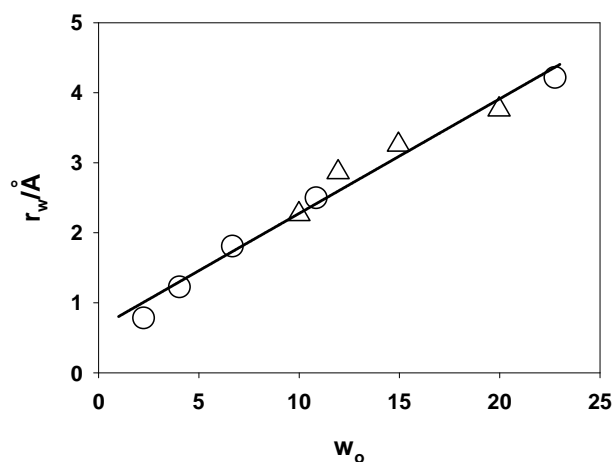
Fig. S1. Variation in the water pool radius (r_w) of BHDC/benzene RM with the w_0. The round symbol is from ref 6 and the triangle symbol from ref 7. The solid line is the linear fit to the data points.

The overall nonradiative rate constant (k_{nr}), which is a measure of ultrafast bond twisting process in the excited state of the ThT, is calculated using following relation,[11]

$$k_{nr} = \frac{1-\phi}{\tau_f} \qquad (8)$$

where τ_f and ϕ are the average lifetime and emission quantum yield, respectively, of the dye. The variation in the total non-radiative rate constant, k_{nr}, with the central water pool size for BHDC and AOT RMs is shown in the figure S2.
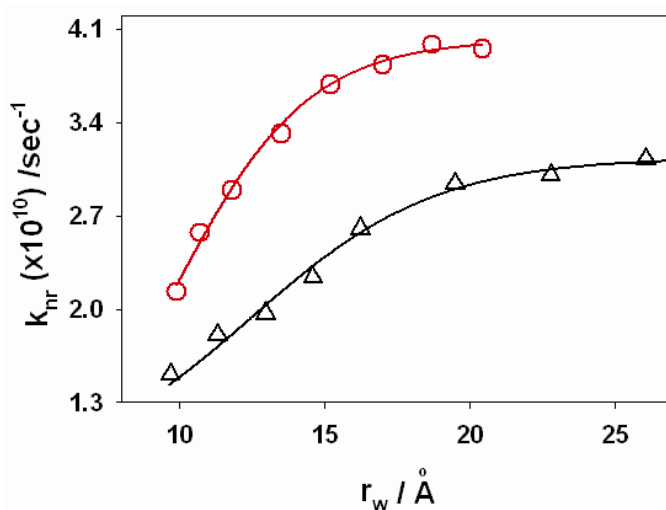

Fig. S2. Variation in the rate of bond twisting process in the excited ThT molecule with the size of the central water pool in AOT (○) and BHDC (Δ) RMs.

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