#### **Supporting Information**

Solvation, Rotational Relaxation and Fluorescence Correlation Spectroscopic Study on Ionic Liquid-in-Oil Microemulsions Containing Triple-Chain Surface Active Ionic Liquids (SAILs)

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## **1. Sample Preparation**

Synthesis of SAIL, i.e., [BHD][AOT] has been described in our earlier publication.<sup>1</sup> It was characterized by 1H, 13C, and DEPT NMR studies. The synthesized [BHD][AOT] was dried up at 70 °C for 2 days. Also, the RTILs used in this study ([P<sub>13</sub>][Tf<sub>2</sub>N] and [N<sub>3111</sub>][TF<sub>2</sub>N]) were dried in oven for 2 days at the same temperature before use. The microemulsions were prepared by mixing appropriate weight fractions of RTILs ( $[P_{13}][Tf_2N]$  or  $[N_{3111}][Tf_2N]$ ), [BHD][AOT] and IPM. The molar ratio of RTILs and [BHD][AOT] (R=RTILs/[BHD][AOT]) were varied from 0.30 to 0.61 throughout all the experiments. The final concentration of [BHD][AOT] was kept at 150 mM. The RTILs ( $[P_{13}][Tf_2N]$  and  $[N_{3111}][Tf_2N]$ ) were used to form the pool of the microemulsion, IPM was used as an organic solvent and our synthesized SAIL ([BHD][AOT]) acted AOT-derived surfactant. Both the microemulsion as an systems, i.e.,

 $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$  and  $[N3_{111}][Tf_2N]/[BHD][AOT]/[IPM]$ , were characterized by DLS and phase behaviour studies. These results have been discussed in our earlier publication.<sup>1</sup>

# 2. General Theory of FCS:

In FCS, laser and confocal microscopy are used to produce a very small volume (in the order of femtolitres (fL)) inside the sample for observation. Diffusion of fluorescent molecules in and out of that observation volume leads to fluctuations in fluorescence intensity. These fluctuations are time-correlated to get a normalized autocorrelation function  $G(\tau)$ :<sup>2</sup>

Where  $\langle F(t) \rangle$  is the average fluorescence intensity, and  $\delta F(t)$  and  $\delta F(t + \tau)$  are the amounts of fluctuations in intensity around the mean value at time *t* and  $t + \tau$ , respectively, and are given by  $\delta F(t) = F(t) - \langle F(t) \rangle$  .....(2)  $\delta F(t + \tau) = F(t + \tau) - \langle F(t) \rangle$  .....(3)

The correlation functions were fitted to the following equation<sup>3</sup>

$$G(\tau) = 1 + \frac{1}{N} \sum_{i=1}^{n} \frac{\alpha_{i}}{\left(1 + \frac{\tau}{\tau_{i}}\right) \left(1 + \frac{\tau}{\omega^{2} \tau_{i}}\right)^{\frac{1}{2}}} \dots (4)$$

where,  $\alpha_i$  denotes the fraction of the molecules having a diffusion time of  $\tau_i$  and N is the average number of fluorescent molecules in the confocal volume.  $\omega$  is the structural parameter of the observation volume and is given by  $\omega = \omega_z / \omega_{xy}$ , where  $\omega_z$  and  $\omega_{xy}$  are the longitudinal and transverse radii, respectively, of the confocal volume. The structural parameter of the excitation volume was calibrated using a solution of R6G in water having known diffusion coefficient ( $D_t = 4.14 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ ).<sup>4,5</sup> The excitation volume is estimated to be 1.76 fL. The  $D_t$  value was calculated using the following equation (equation 5) using the  $\tau_i$  value obtained from the fit to equation 4.

### 3. Instrumentation

The absorption and fluorescence spectra were recorded using Shimadzu (model no. UV-2450) spectrophotometer and Hitachi (model no. F-7000) spectrofluorimeter, respectively. The excitation of all the samples was done at 375 nm for steady-state experiments. The detailed setup for the time-resolved experiments has been described elsewhere.<sup>6</sup> In short, a picosecond laser diode (IBH, Nanoled) was used for the excitation of samples at 375 nm, and a Hamamatsu microchannel plate photomultiplier tube (3809U) was used for the collection of signals at the magic angle of 54.7°; the instrument response was 100 ps. IBH DAS, version 6 software was used for decay analysis. The biexponential fitting of all the long as well as short wavelength decays was done considering  $\chi^2$  close to 1 that indicates a good fit. A motorized polarizer was used in the emission side for the measurement of anisotropy decays. The emission intensities at parallel and perpendicular polarizations were collected alternately, until a certain peak difference was reached. The analysis of the data was done using IBH DAS, version 6 decay analysis software.

Viscosities of the microemulsion were determined using a Brookfield DV-II+ Pro (Viscometer) at 25°C. Temperature was maintained constant by circulating water through the cell holder using JEIOTECH Thermostat (RW-0525G).

The detailed of the FCS setup is given in our earlier publication.<sup>7</sup> Briefly, FCS experiments were carried out using a DCS-120 (Complete laser scanning confocal FLIM microscope by Becker & Hickl GmbH) system that involves excitation by picosecond diode lasers which are connected to inverted microscopes of Zeiss, equipped with a  $40 \times$  water-immersion objective (NA 1.2). Samples were excited with a 488 nm diode laser kept in CW mode (20 mW). The fluorescence signal was separated from the excitation line using long-pass filters (498 nm) and collected using two HMP-100-40 GaAsP hybrid detectors. Microscope correction collar and height were adjusted manually for the correction of the refractive-index mismatch between the immersion solution and experimental environment.<sup>8</sup> The pinhole diameter was properly adjusted at 0.5  $\mu$ m, and the number of molecules was maintained between 5 and 10 in the confocal volume by adjusting the concentration.

Systems	<i>a</i> <sub>fast</sub>	<i>a</i> <sub>slow</sub>	$ au_{fast}(ns)$	$ au_{ m slow}( m ns)$	<\u03c0_{rot}> (ns)*
IPM	1.00	0.00	0.34	-	0.34
[BHD][AOT]/[IPM]	1.00	0.00	0.52	-	0.52
$[P_{13}][Tf_2N]$	0.16	0.84	0.45	3.42	2.94
$[N_{3111}][Tf_2N]$	0.18	0.82	0.44	3.82	3.21

Table S1. Anisotropy Decay Parameters of C-480 in neat IPM, [BHD][AOT] / IPM and neat IL.

\* Error in experimental data of  $\pm 5\%$ 



**Figure S1.** Normalize absorption spectra of C-480 in (a)  $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$ , (b)  $[N_{3111}][Tf_2N]/[BHD][AOT]/[IPM]$  microemulsions with variation of R values (0.30 to 0.76) at 298 K



**Figure S2.** Normalize Emission spectra of C-480 in (a)  $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$ , (b)  $[N_{3111}][Tf_2N]/[BHD][AOT]/[IPM]$  microemulsions with variation of R values (0.30 to 0.76) at 298 K.



Figure S3. Time Resolved Fluorescence Anisotropy Decays of C480 in (a) IPM and [BHD][AOT] / IPM and (b) in neat IL.



Figure S4. Residuals of the fitted anisotropy decays of C-480 in (a) [N<sub>3111</sub>][Tf<sub>2</sub>N]/[BHD][AOT]/IPM and (b) [P<sub>13</sub>][Tf<sub>2</sub>N] /[BHD][AOT]/IPM microemulsions.



Figure S5. (a) Decays of solvent response function, C(t) and (b) Time Resolved Emission Spectra (TRES) of C-480 in [BHD][AOT]/ IPM (at R = 0.00)



Figure S6. Fitted FCS Traces of DCM in neat ILS and IPM and [BHD][AOT]/IPM (R=0.00)

### **References:**

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