

Supporting Information

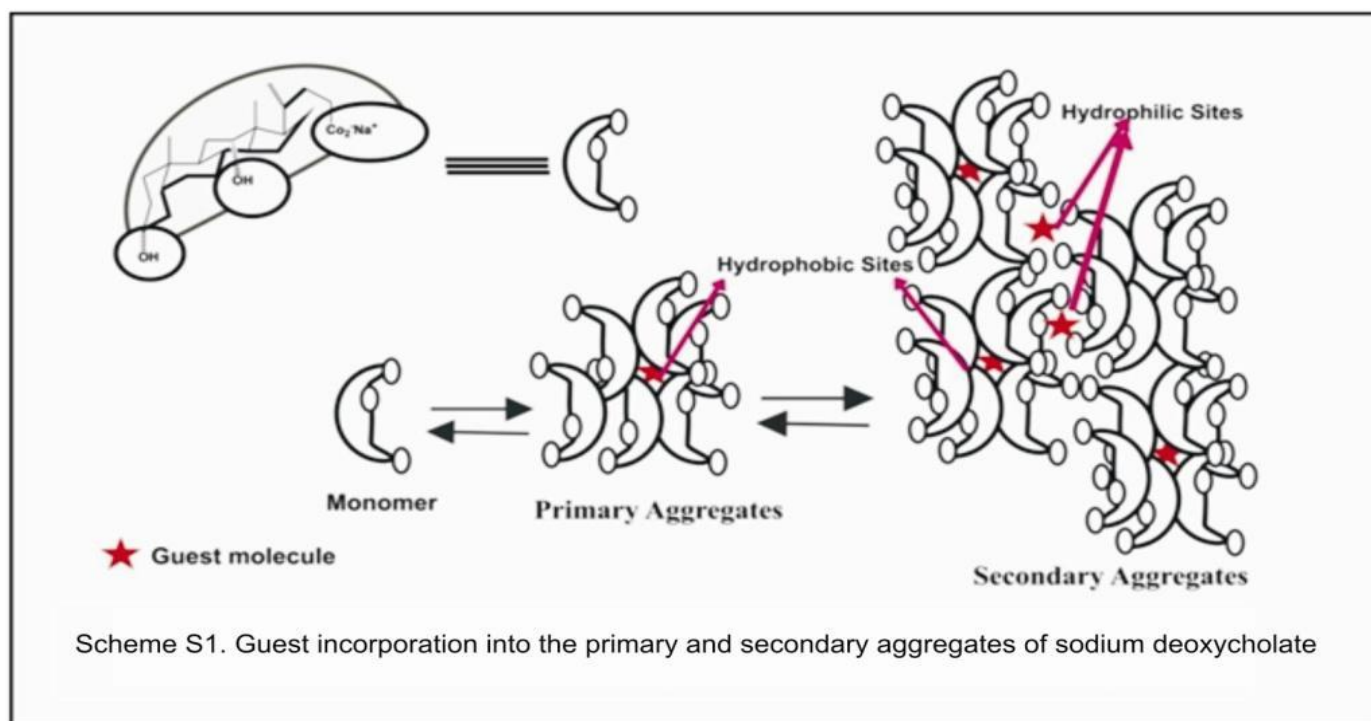
Modulation of the Aggregation Properties of Sodium Deoxycholate in Presence of Hydrophilic Imidazolium Based Ionic Liquid: Water Dynamics study to probe the structural alteration of the aggregates

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1. Instrumentation:

1.1 Transmission Electron Microscopy (TEM) measurements: TEM measurements of Deoxycholate aggregates in presence of different concentration of [bmim]-BF₄ were carried out with analytical TEM (FEI. TECNAIG220S-TWIN) instruments operating at 200 KV. TEM

samples were prepared by blotting a carbon coated (50 nm carbon film) Cu grid (300 mesh, electron microscopy science) with a drop of solution and the samples were allowed to dry for overnight.

1.2. Scanning Electron Microscopy (SEM) measurements: For SEM measurements, the sample cast film on an aluminum foil was first air-dried at room temperature and then stored in desiccators before measurement. A layer of gold was sputtered on top and the sample was examined on ZEISS EVO 60 Scanning Electron Microscope (with oxford EDS detector) operating at 10 kV.

1.3. Fluorescence Lifetime Imaging Microscopy (FLIM): Fluorescence Lifetime imaging of aggregated structure of bile salts in presence of [bmim]-BF₄ at different experimental conditions were taken using the DCS 120 confocal laser scanning FLIM system (Becker & Hickl DCS-120) equipped with an inverted optical microscope of Zeiss. Detection of fluorescence lifetime was achieved with a polarized dual channel confocal scanning instrument (Becker & Hickl DCS-120) attached to an output port of the microscope and controlled by a galvo-drive unit (Becker & Hickl GDA- 120). The DCS-120 is equipped with a polarizing beam splitter and two single photon avalanche photodiode (SPAD) detectors for the acquisition of fluorescence lifetime images. Polarized fluorescence transients used in the generation of images presented in this work are acquired using time correlated single photon counting detection electronics (Becker & Hickl). This system is characterized by an instrument response function of less than 100 ps fwhm (full width half maximum). A 50 µl of the sample solution was placed on a slide and it was allowed to equilibrate for about 15 minutes before the images were taken and the sample was allowed to dry in high vacuum for 2 days and then the images were taken with the dry sample.

1.4. NMR measurements: NMR measurements were recorded using a Bruker 400 MHz NMR spectrometer. All NMR measurements were carried out in D₂O (Aldrich, 99.6 atom % D) solvent as the chemical shift reference for mode locking.

1.5. Viscosity measurements: Viscosity of the aggregates in presence of different wt% of [bmim]-BF₄ was measured using a Brookfield DV-II+ Pro (Viscometer) at 25⁰C. Temperature was maintained constant by circulating water through the cell holder using JEIOTECH Thermostat (RW-0525G).

Rheology measurements were performed on a MCR 102 (Anton Paar) rheometer, and parallel plate geometry was used for the measurement. The gap between the parallel plates was maintained at 100 μm and an amplitude sweep experiment was performed at constant oscillation frequency of 1.00 Hz at 298K.

1.6. Zeta Potential (ξ) Measurements: Malvern Nano ZS instrument with 4mW He-Ne laser ($\lambda = 632 \text{ nm}$) was used to determine the zeta potential of the aggregated structure of NaDC with increasing concentration of [bmim]-BF₄ at 298K.

1.7. Steady states and Time Resolved measurements:

The steady state absorption and emission spectra were recorded on Shimadzu (model no UV-2450) spectrophotometer and Spex-fluorolog-3 spectrofluorimeter (model FL3-11), respectively. For the steady state experiments, Pyrene was excited at 336 nm and C-153 was excited at 375, 408 and 440 nm. The time resolved spectra were recorded with a TCSPC setup. The detail of the timeresolved setup is described elsewhere.^{1*} Briefly, picosecond laser diode (IBH, Nanoled) at 408 nm and 440 nm were used to excite the sample and to collect the signals at a magic angle (54.7⁰) Hamamatsu microchannel plate photomultiplier tube (3809U) were used. The instrument response function (IRF) of our setup was 100 ps. For anisotropy measurements, we have used the same set up and the procedure of collection of anisotropy decays which are described in our earlier publications.³⁷ To analyze the decays and the anisotropy data, IBH DAS, version 6, decay analysis software was used. All the decays were fitted with biexponential functions, because χ^2 was closer to 1, which indicates a good fit.

Table S1. Emission Maxima of Coumarin-153 in 20 mM NaDC aggregate with different amount of [bmim]-BF₄ at different Excitation Wavelengths.

System	$\lambda_{\text{abs}}^{\text{max}}$	$\lambda_{\text{emi}}^{\text{max}}$		
		$\lambda_{\text{ex}} = 375 \text{ nm}$	$\lambda_{\text{ex}} = 408 \text{ nm}$	$\lambda_{\text{ex}} = 440 \text{ nm}$
20 mM NaDC	426 nm	Broad spectrum	470 nm, 522 nm	531 nm
20 mM NaDC + 1.68 wt% [bmim]-BF ₄	425 nm	Broad spectrum	470 nm, 520 nm	527 nm
20 mM NaDC + 5.56 wt% [bmim]-BF ₄	427 nm	521 nm (single peak)	524 nm (single peak)	531 nm
20 mM NaDC + 11.2 wt% [bmim]-BF ₄	430 nm	527 nm (single peak)	531 nm (single peak)	534 nm

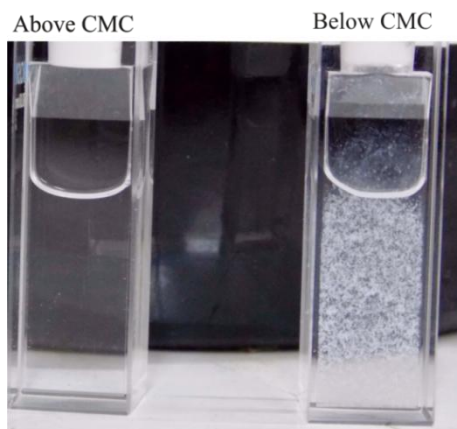


Figure S1: Image of NaDC solution in 5.68 wt% [bmim]-BF₄, above and below CMC

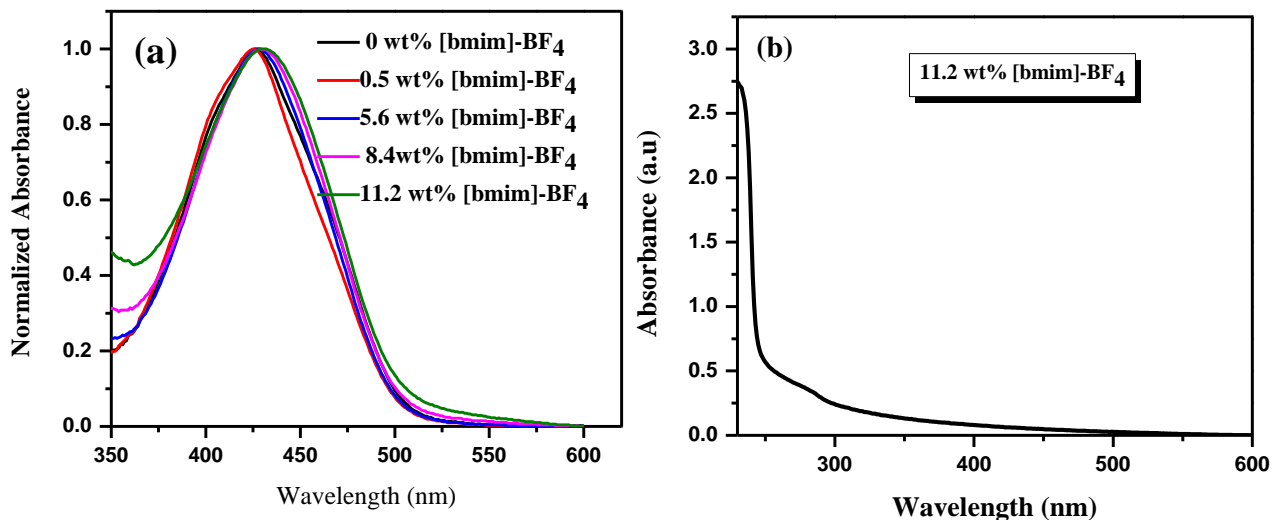


Figure S2: (a) Normalized UV-Vis spectra of Coumarin-153 in 20 mM NaDC solution with increasing concentration of [bmim]-BF₄ and (b) the absorption spectra of 11.2 wt% [bmim]-BF₄

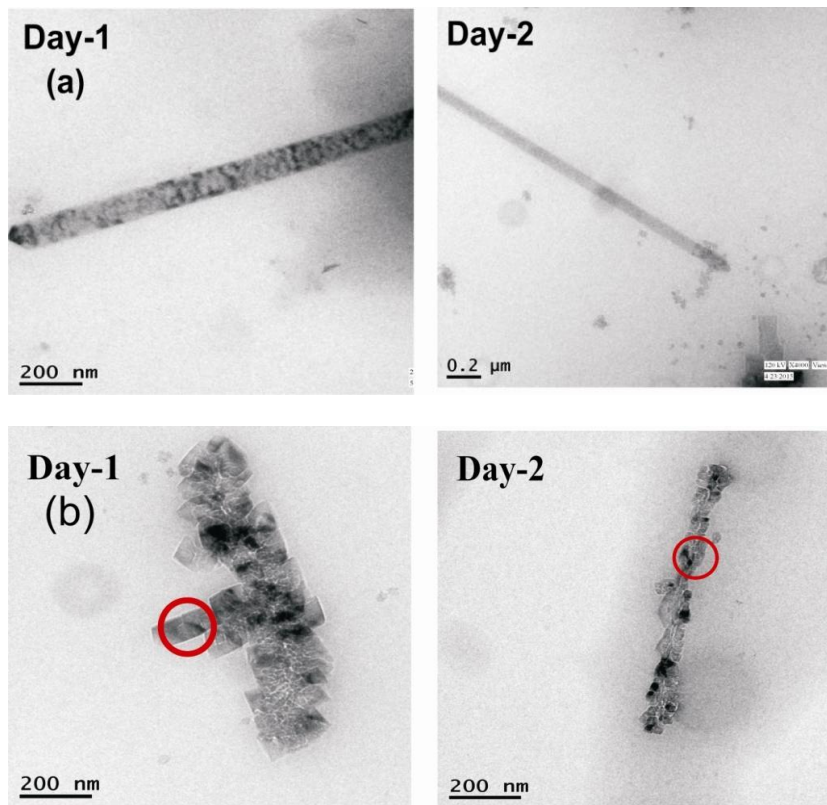


Figure S3. TEM images of 20 mM NaDC in presence of (a) 1.12 wt% and (b) 11.2 wt% [bmim]-BF₄ in two different days. The structural features do not change for the samples dried on different days.

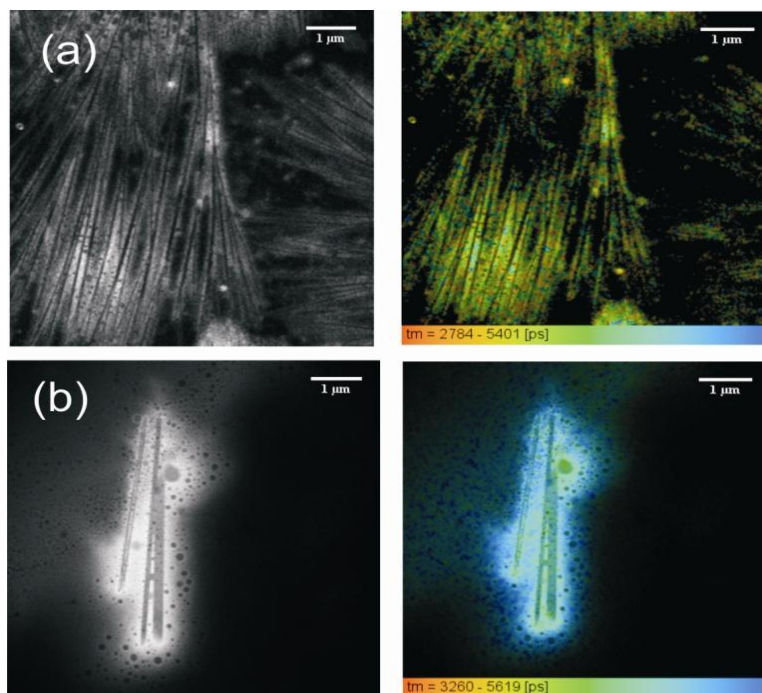


Figure S4. Fluorescence Lifetime Images of 20 mM NaDC in presence of 3 wt% [bmim]-BF₄. Images are taken in both gray mode and FLIM mode. Figure (a) was taken with dry sample and figure (b) was taken in solution phase. (The scale length of the images are 1 μ m)

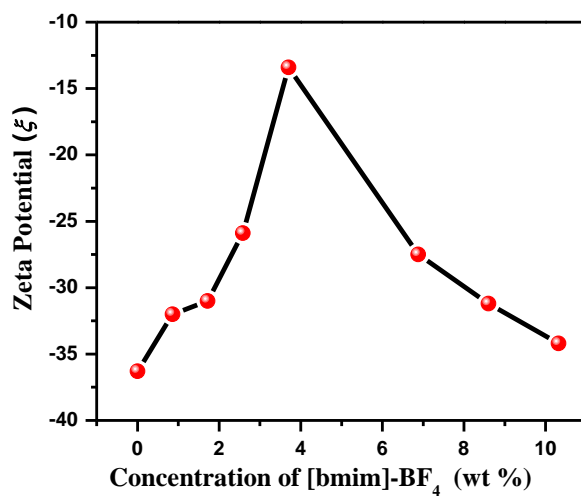


Figure S5. Zeta potential (ξ) of 20 mM NaDC in presence of different concentration of [bmim]-BF₄

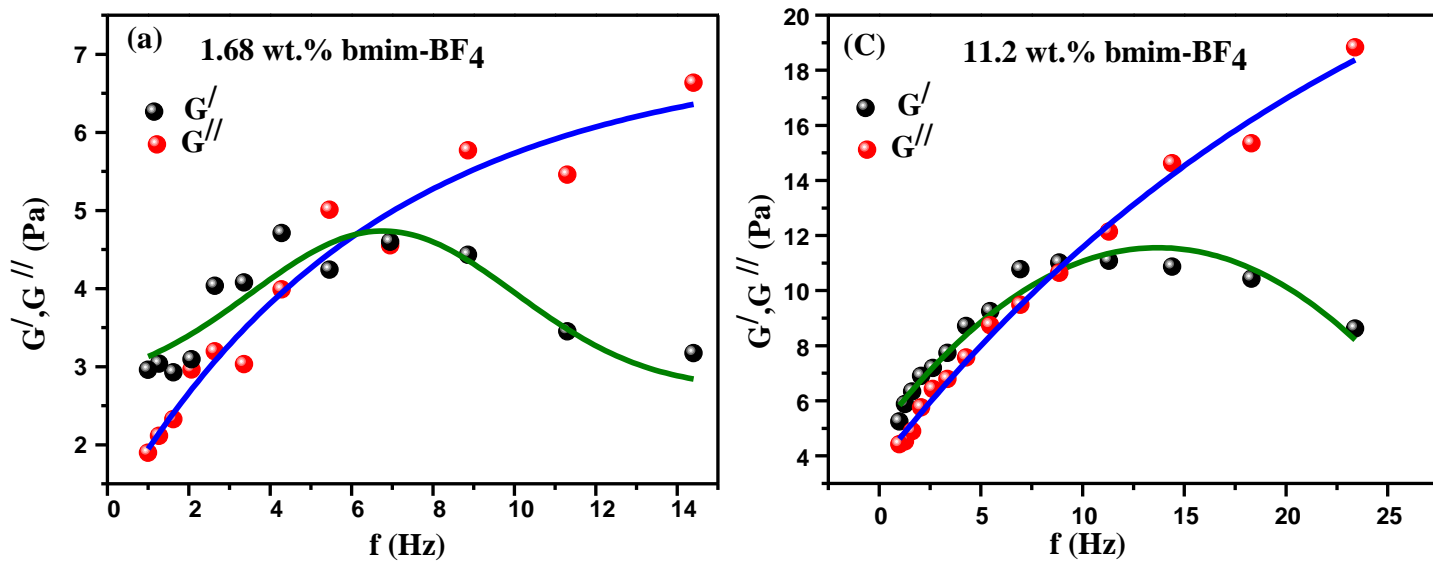


Figure S6. Variation of G' , G'' as a function of frequency for the viscous solution with 20 mM NaDC and different concentration of [bmim]-BF₄

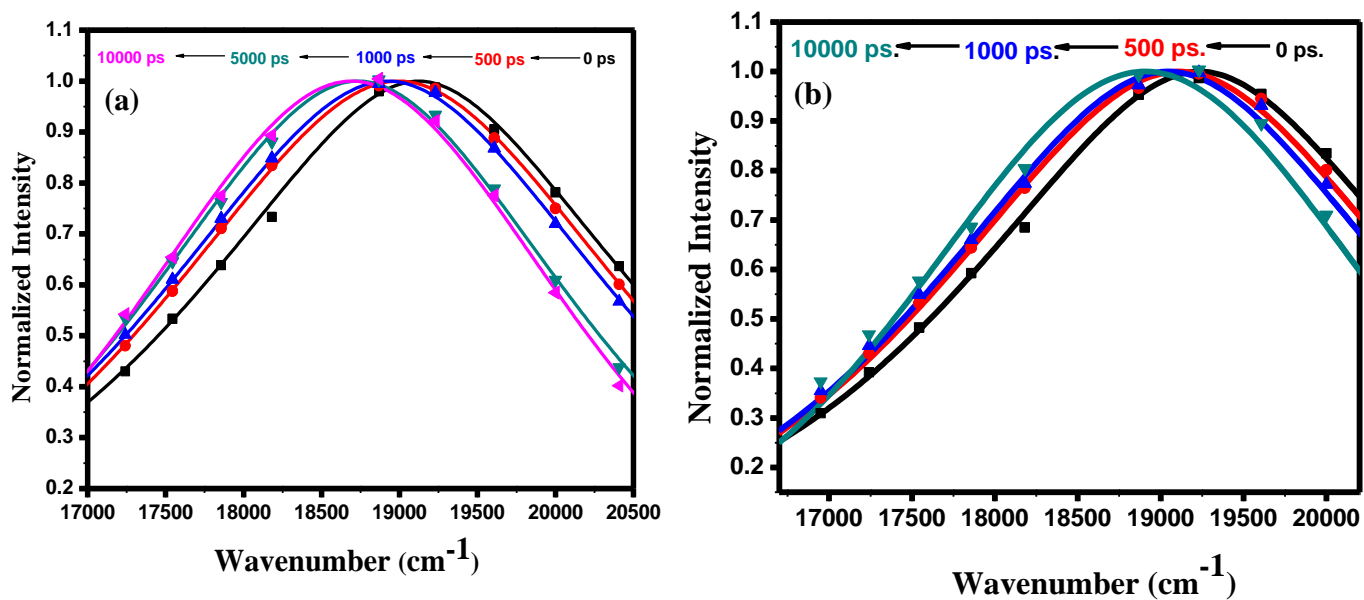


Figure S7: Time resolved emission spectra (TRES) of C-153 in 20 mM NaDC + 11.2 wt% [bmim]-BF₄ at $\lambda_{exc} = 408$ nm (a) and $\lambda_{exc} = 440$ nm.

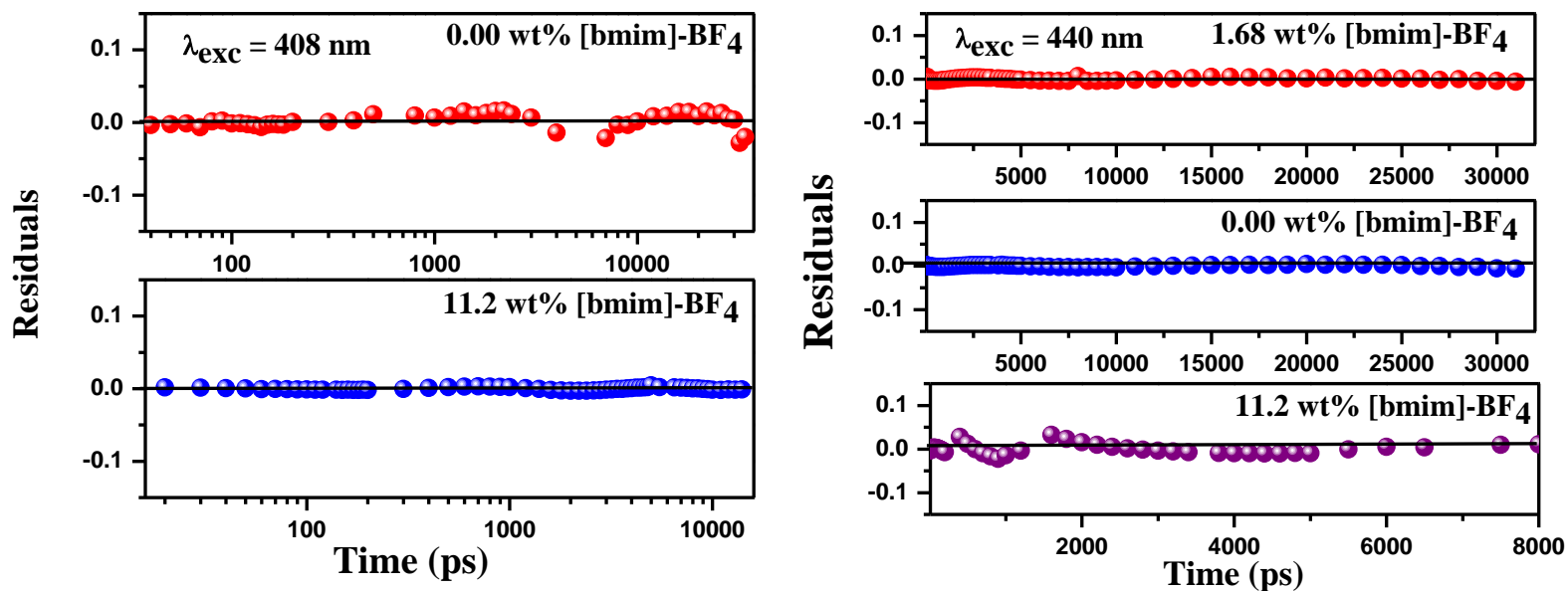


Figure S8. Residuals of the fitted curves of C-153 in 20 mM NaDC in presence of different concentration of [bmim]-BF₄

Reference:

(1*). Seth, D.; Chakrabarty, D.; Chakraborty, A.; Sarkar, N. Study of energy transfer from 7-amino coumarin donors to rhodamine 6G acceptor in non-aqueous reverse micelles. *Chem. Phys. Lett.* **2005**, *401*, 546–552.