Complexation, Dimerisation and Solubilisation of Methylene Blue in the

Presence of Biamphiphilic Ionic Liquids: A Detailed Spectroscopic and

Electrochemical Study

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Figure S1 Plot showing the variation of critical micellar concentration (*cmc*) of $[C_4mim][C_{12}OSO_3]$ and $[C_6mim][C_{12}OSO_3]$ with change in concentration of MB.



Figure S2 UV-visible spectrum of MB at different concentrations.







Figure S4 Absorption Spectrum of MB (0.05mM) in the presence of increasing amounts of $[C_6 mim][C_{12}OSO_3]$.



Figure S5 Fluorescence emission spectrum of MB at different concentrations. A plot of maximum fluorescence intensity vs. the concentration of MB is shown in the inset.



Figure S6 Normalised fluorescence emission spectrum of MB (0.05mM) in the presence of increasing amounts of $[C_6mim][C_{12}OSO_3]$.



Figure S7 Plot of wavelength for maximum fluorescence emission wavelength (λ_{max}) vs. molar concentration of [C₄mim][C₁₂OSO₃] and [C₆mim][C₁₂OSO₃].



Figure S8 Cyclic Voltammogram (CV) of 0.05mM MB in 0.1M HCl at a scan rate of 0.1mVs⁻¹.



Figure S9 Cyclic Voltammograms of 0.05mM MB in the presence of increasing amounts of $[C_6 mim][C_{12}OSO_3]$ in 0.1MHCl and at a scan rate of $0.1 mVs^{-1}$.



Figure S10 Differential Pulse Voltammograms of 0.05mM MB in 0.1MHCl in the presence of increasing amounts of (**a**) [C₄mim][C₁₂OSO₃] and (**b**) [C₆mim][C₁₂OSO₃].



Figure S11 Plot of $1/\Delta A$ vs. molar concentration of $[C_4mim][C_{12}OSO_3]$ and $[C_6mim][C_{12}OSO_3]$ in region II as revealed from UV-visible measurements.



Figure S12 Exciton Model for the formation of H-type and J-type aggregates.



Figure S13 Representative spectral decomposition stratergy for deconvolution of MB absorbance spectra into Gaussian shapes.



Table S1 Comparison of concentrations C_1 (concentration for ion-pair complexation) and C_2 (critical micellar concentration) for MB + [C₄mim][C₁₂OSO₃] and MB + [C₆mim][C₁₂OSO₃] systems as determined from UV-visible absorbance and fluorescence emission spectroscopy.

System	C ₁ (mM)		C ₂ (mM)	
	UV-visible	Fluorescence	UV-visible	Fluorescence
$MB + [C_4 mim][C_{12}OSO_3]$	0.043	0.043	1.98	2.12
$MB + [C_6mim][C_{12}OSO_3]$	0.049	0.052	1.03	1.05