

## **Atypical Energetic and Kinetic Course of Excited State Intramolecular Proton Transfer (ESIPT) in Room Temperature Protic Ionic Liquids**

*Arpan Manna,<sup>1</sup> Mhejabeen Sayed,<sup>2</sup> Anil Kumar<sup>1</sup> and Haridas Pal<sup>2,\*</sup>*

<sup>1</sup>Physical and Material Chemistry Division, National Chemical Laboratory, H. J. Bhabha Road, Pune-411 008, India, and <sup>2</sup>Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

E-mail: hpal@barc.gov.in; Tel: 91-22-2559 5396; Fax: 91-22-2550 5151 & 2551 9613

=====

### **Contents:**

- S1. Synthesis and characterization of the protic ionic liquids (PILs)
- S2. TCSPC measurements and the correction of the observed fluorescence decays of 18DHAQ for inherent emissions of the PILs.
- S3. Ultrafast Fluorescence Studies using Up-Conversion Measurements.

=====

### **S1. Synthesis and characterization of the protic ionic liquids (PILs)**

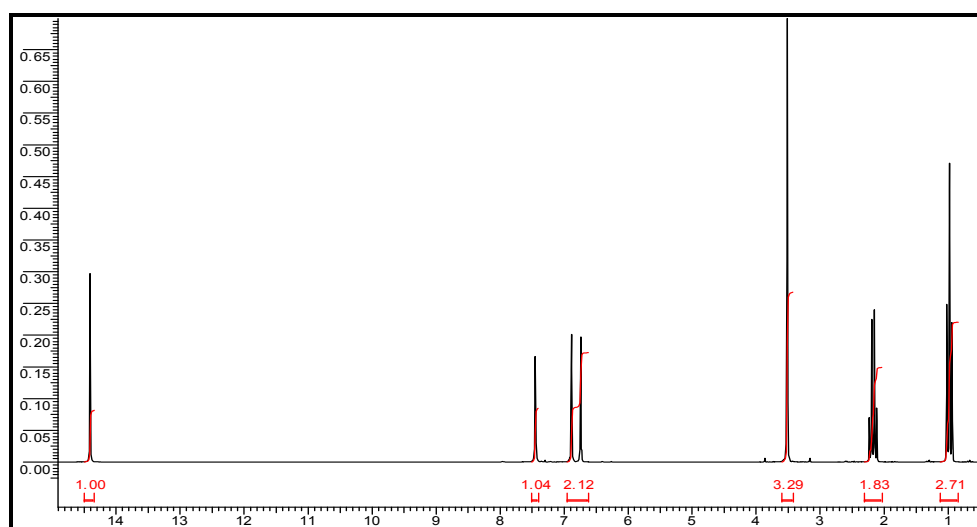
1-Methylimidazole was procured from Sigma-Aldrich, USA, and was distilled in the laboratory prior to use. Acetic acid was obtained from Sigma-Aldrich and formic acid, propanoic acid and sulfuric acid were procured from E. Merck, Mumbai, India. All the acid samples were used as received from the respective sources.

Following the single step atom economic reaction condition<sup>1-3</sup> the protic ionic liquids (PILs) were synthesized by adding equimolar quantities of the appropriate Bronsted acid in a drop wise fashion to the Bronsted base, 1-Methylimidazolium (HmIm), taken in a round bottom flask. During this addition, the round bottom flask containing the Bronsted base was placed in an ice bath. After addition of the acid to the base, the reaction mixture was stirred for 6 hrs vigorously. Thereafter the volatile impurities were removed from the product by using a rotary evaporator under reduced pressure. Traces of water were removed by keeping the prepared PILs under high vacuum for 12

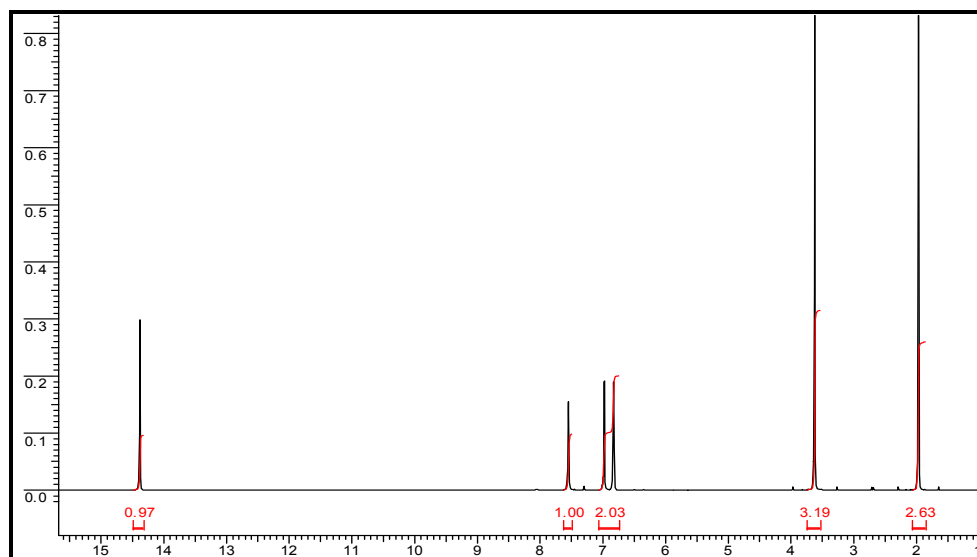
hours. The PILs synthesized and used in this work are, [HmIm]propanoate, [HmIm]acetate, [HmIm]formate, and [HmIm]bisulphate, where the abbreviation [HmIm] refers to the 1-Methylimidazolium cation.

The  $^1\text{H}$  NMR spectra were recorded to characterize the PILs synthesized and used in this work. These measurements were carried out using a 200 MHz and 400 MHz (as per suitable for the samples) NMR spectrometer from Bruker India Pvt. Ltd. The NMR spectra thus obtained for different PIL solvents used in this work are shown in the following panels of Figure S1.

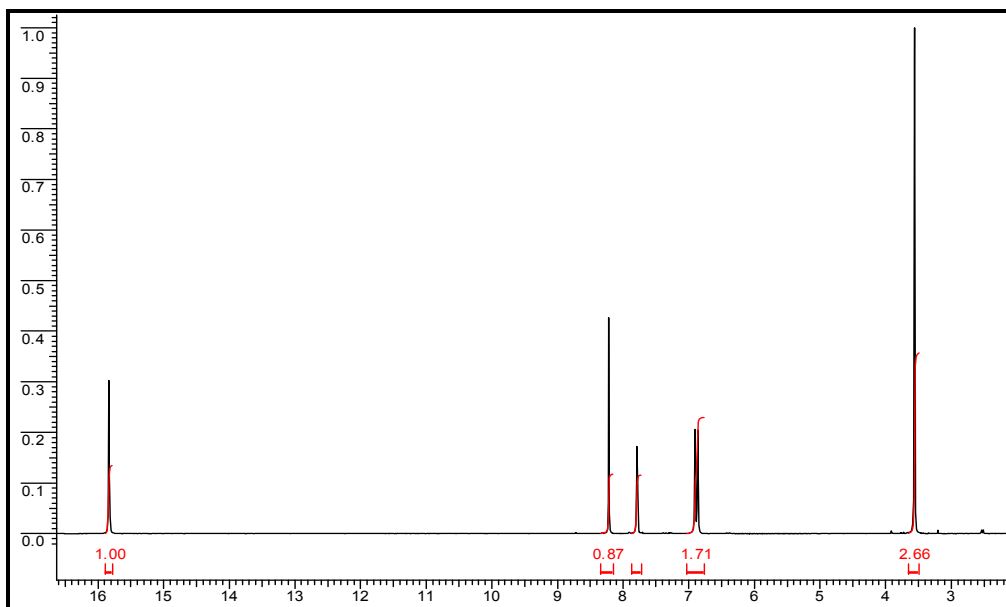
**(A) The  $^1\text{H}$  NMR spectra of [HmIm]propanoate in  $\text{CDCl}_3$  at 200 MHz**



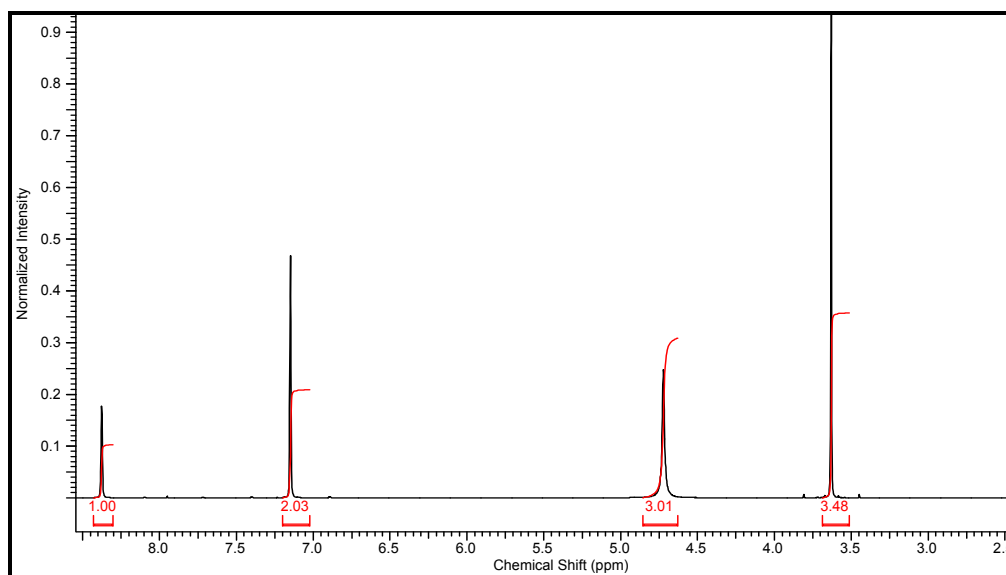
**(B) The  $^1\text{H}$  NMR spectra of [HmIm]acetate in  $\text{CDCl}_3$  at 200 MHz**



**(C) The  $^1\text{H}$  NMR spectra of [HmIm]formate in  $\text{CDCl}_3$  at 200 MHz**



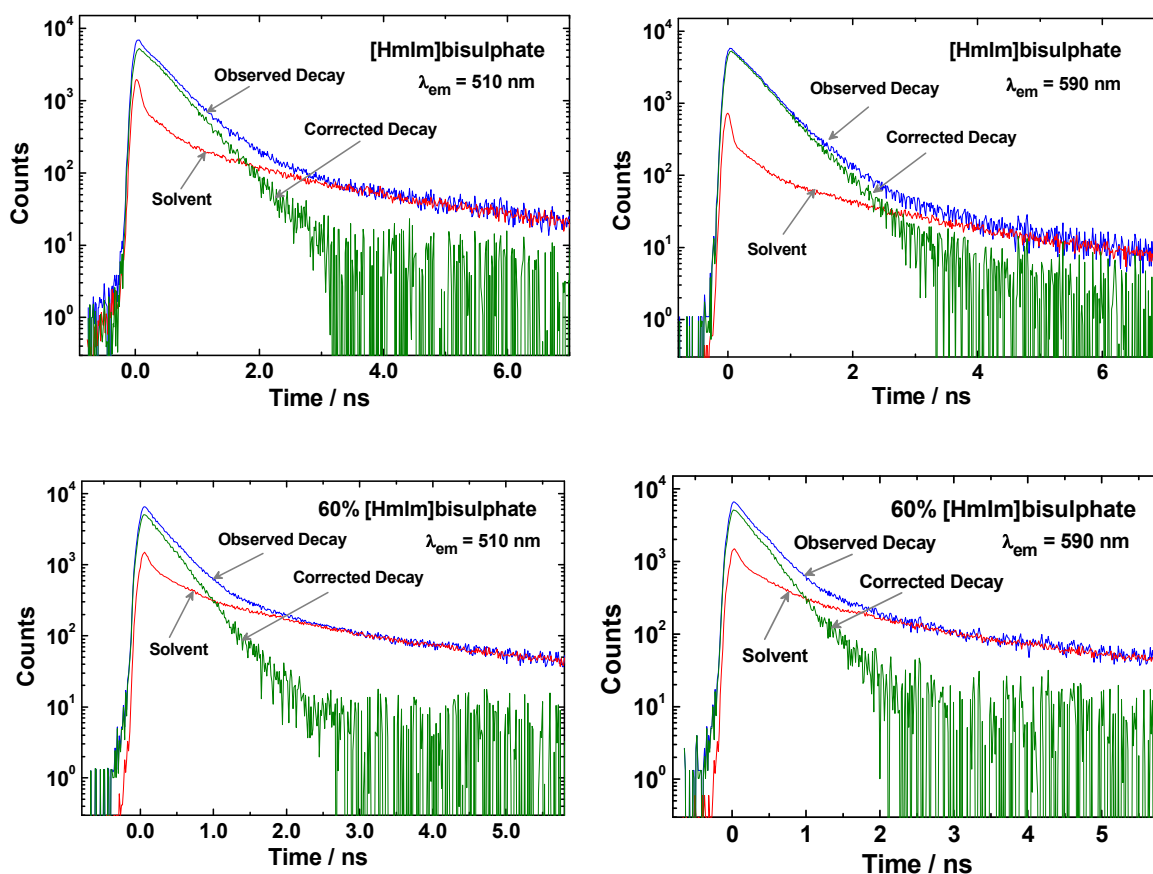
**(D) The  $^1\text{H}$  NMR spectra of [HmIm]bisulphate in  $\text{DMSO-d}_6$  at 400 MHz**

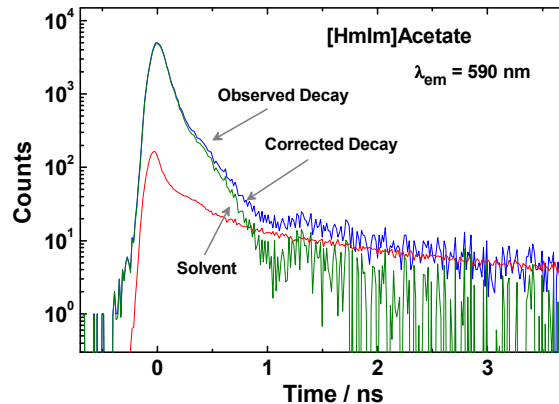
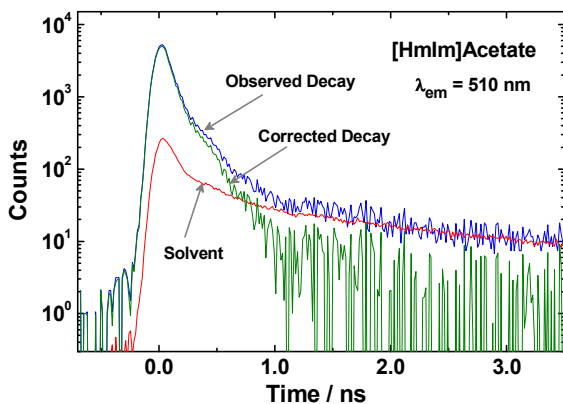
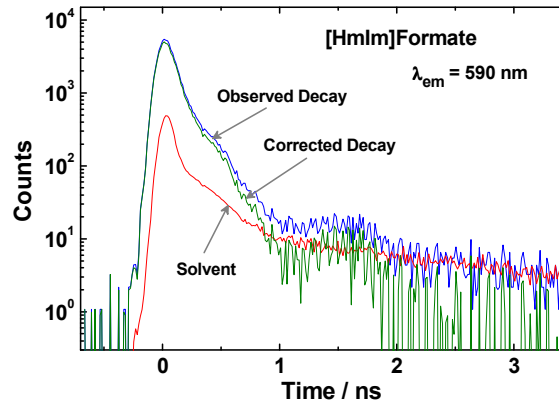
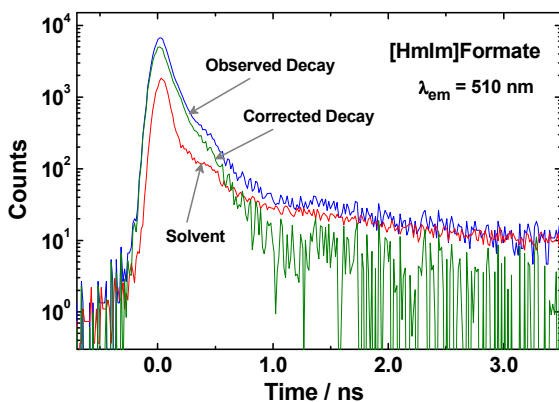
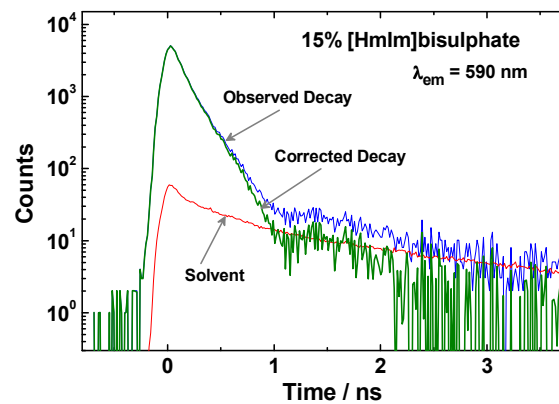
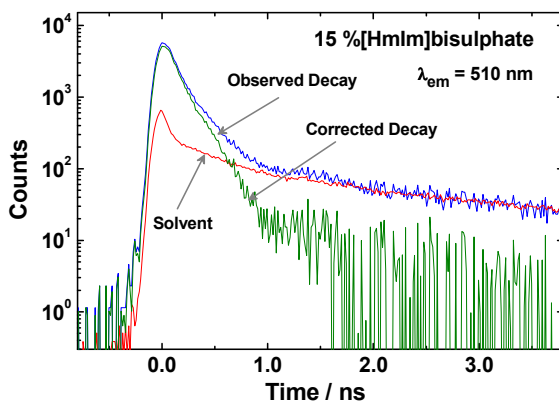
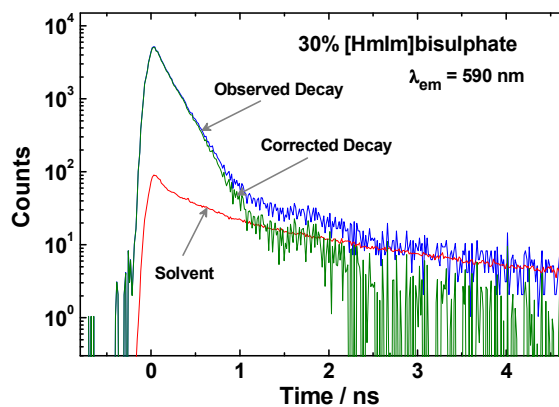
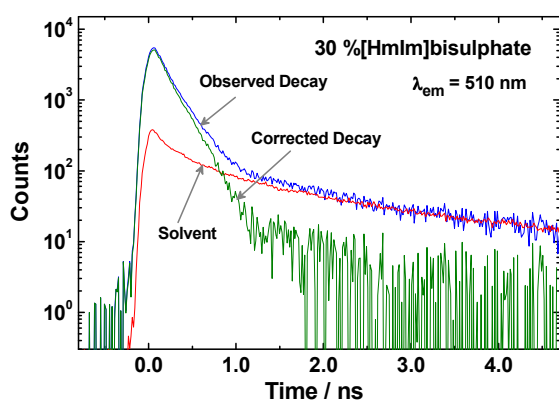


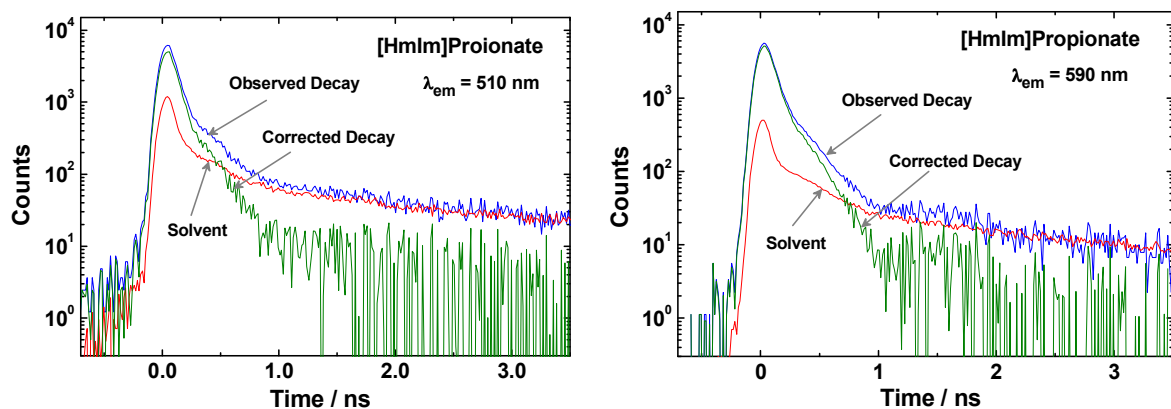
**Figure S1.** The  $^1\text{H}$  NMR spectra for the PILs used in this work are shown in this figure. The spectra in panels A-D represent the solvents [HmIm]propanoate, [HmIm]acetate, [HmIm]formate, and [HmIm]bisulphate, respectively.

## S2. TCSPC measurements and the correction of the observed fluorescence decays of 18DHAQ due to inherent emissions of the PILs

For the measured fluorescence decays of 18DHAQ dye in the PIL solvents studied, along with an unusually fast decay component, there was always a presence of a long decay tail that apparently arises due to inherent fluorescence of the ionic liquids alone.<sup>4,5</sup> Accordingly, it has been inferred that for the dye in the PIL solvents the observed decays are due to the combination of the unusually fast fluorescence decay component of 18DHAQ and the relatively long fluorescence decay components from the ionic liquids alone. Therefore, the true fluorescence decays of 18DHAQ dye in different PILs were obtained by subtracting the tail-matched decays of the ionic liquids alone from the observed decays of the dye solution at two selected wavelengths, namely 510 nm and 610 nm, corresponding to the lower wavelength emission band (LWEB) and the higher wavelength emission band (HWEB) of the dye. Different panels in Figure S2 show the observed fluorescence decays of 18DHAQ dye, tail-matched decays of the ionic liquids alone and the true (corrected) fluorescence decays of the dye obtained in ionic liquids studied at 510 nm and 610 nm emission wavelengths, as indicated in the respective panels.



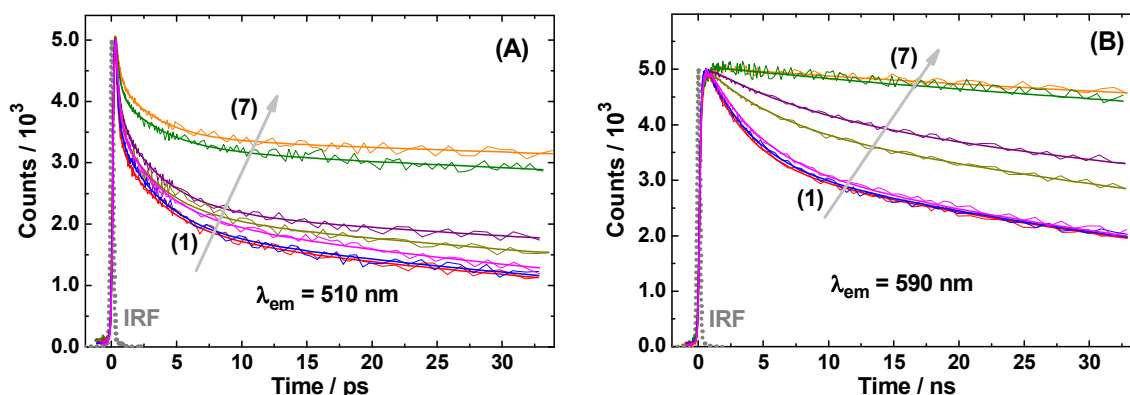




**Figure S2.** Fluorescence decays for 18DHAQ dye in different PILs and PIL mixtures (indicated in the panels) as measured at 510 nm (LWEB) and 610 nm (HWEB) using TCSPC technique. The inherent fluorescence decays for the PILs and PIL mixtures at the respective wavelengths are also shown in the respective panels. The true (corrected) fluorescence decays for the dye at 510 nm (LWEB) and 610 nm (HWEB) were obtained by the subtracting the tail-matched solvent decays from the sample decays and are also shown in the respective panels in this figure.

### S3. Ultrafast Fluorescence Studies using Up-Conversion Measurements

In the analysis of the kinetic traces from up-conversion measurements, we uniformly used a tri-exponential function and thus obtain good correlations among the estimated time constant values at the two measuring wavelengths, namely 510 nm (LWEB) and 590 nm (HWEB). To be mentioned here that in the cases of 60% [HmIm]bisulphate and neat [HmIm]bisulphate solvents, the kinetic traces recorded at 590 nm could also be fitted reasonably well using a bi-exponential function. In this cases, however, the  $\tau_1$  growth component estimated found to be unusually shorter ( $\sim 0.12$  ps) and do not correlate with  $\tau_1$  decay component ( $\sim 0.26$  ps) observed for the kinetic traces at 510 nm in the same solvent system, attributed to ultrafast ESIPT process. Additionally, with bi-exponential analysis, we effectively miss an expected  $\tau_2$  component for the 590 nm traces in 60% [HmIm]bisulphate and neat [HmIm]bisulphate solvents, a component that seems to be very important to comprehend the intricate role of solvent diffusive relaxation in modulating the relative time-dependent populations of  $N^*$  and  $T^*$  forms and accordingly the emissions intensities in the LWEB and HWEB of the dye in studied PIL solvents. Therefore, keeping uniformity with the other cases of the PILs and PIL mixtures, a tri-exponential analysis was carried out for the kinetic traces at 590 nm in 60% [HmIm]bisulphate and neat [HmIm]bisulphate solvents as well, even though a bi-exponential analysis could also apparently give good fits for the 590 nm traces in the latter solvents.



**Figure S3.** Comparison of the fluorescence kinetic traces (*for longer time span*) as measured at **(A)** the LWEB (measured at 510 nm) and **(B)** the HWEB (measured at 510 nm) of 18DHAQ dye in different PILs and PIL solvent mixtures using up-conversion technique. The traces 1 to 7 correspond to [HmIm]propanoate, [HmIm]acetate, [HmIm]formate, 15% [HmIm]bisulphate, 30% [HmIm]bisulphate, 60% [HmIm]bisulphate, and [HmIm]bisulphate (*cf.* Table 1). The instruments response functions (IRF) are also shown in the respective panels.

## References:

1. Ohno, H.; Yoshizawa, M. Ion Conductive Characteristics of Ionic Liquids Prepared by Neutralization of Alkylimidazoles. *Solid State Ionics* **2002**, *154-155*, 303-309.
2. MacFarlane, D. R.; Seddon, K. R. Ionic Liquids – Progress on the Fundamental Issues. *Aust. J. Chem.* **2007**, *60*, 3–5.
3. Xu, W.; Angell, C. A. Solvent-free Electrolytes with Aqueous Solution-like Conductivities. *Science* **2003**, *302*, 422–425.
4. Paul, A.; Mandal, P. K.; Samanta, A. On the Optical Properties of the Imidazolium Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 9148–9153.
5. Mandal, P. K.; Paul, A.; Samanta, A. Excitation Wavelength Dependent Fluorescence Behavior of the Room Temperature Ionic Liquids and Dissolved Dipolar Solutes. *J. Photochem. Photobiol. A: Chem.* **2006**, *182*, 113–120.