### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>Figure 3.1.</strong> Steady state absorption and fluorescence spectra of AP (dotted lines) and C153 (solid lines) in neat MOEMPLFAP at 298 K. $\lambda_{\text{exc.}} = 375$ nm. All spectra are normalized at the corresponding peak maximum. Inset shows the absorption spectrum of neat MOEMPLFAP.</td>
<td>87</td>
</tr>
<tr>
<td>2.</td>
<td><strong>Figure 3.2.</strong> Time-resolved fluorescence decay behavior of AP in neat MOEMPLFAP at 298K. $\lambda_{\text{exc.}} = 375$ nm. The IRF and decay profiles at different monitoring wavelength are shown in the same figure.</td>
<td>88</td>
</tr>
<tr>
<td>3.</td>
<td><strong>Figure 3.3.</strong> Time-resolved emission spectra (TRES) of (a) C153 and (b) AP in neat MOEMPLFAP at 303K. $\lambda_{\text{exc.}} = 375$ nm.</td>
<td>88</td>
</tr>
<tr>
<td>4.</td>
<td><strong>Figure 3.4.</strong> Decay of the spectral shift correlation function, $C(t)$, of (a) AP and (b) C153 in MOEMPLFAP at (i) 293 K (ii) 298 K and (iii) 303 K. $\lambda_{\text{exc.}} = 375$ nm. In both cases, solid lines denote the bi-exponential fit to the data points.</td>
<td>89</td>
</tr>
<tr>
<td>5.</td>
<td><strong>Figure 3.5.</strong> Plot of average solvation time vs. bulk viscosity of MOEMPLFAP at $\lambda_{\text{exc.}} = 375$ nm.</td>
<td>90</td>
</tr>
<tr>
<td>6.</td>
<td><strong>Figure 3.6.</strong> Viscosity dependence of average solvation time of C153 and AP in different room temperature ionic liquids. The data points shown in the plot are collected from the reference 113 and the present study. The solid line represents the linear fit to all the data points except that for AP in MOEMPLFAP.</td>
<td>91</td>
</tr>
</tbody>
</table>
7. **Figure 3.7.** Decay of time-resolved anisotropy (r(t)) of AP in neat MOEMPLFAP at $\lambda_{\text{exc.}} = 375$ nm at different temperatures.

8. **Figure 3.8.** Structures of solute molecules and the solvent shell; (a) AP and RTIL and (b) C153 and RTIL

9. **Figure 3.9.** Optimized Structures of (a) neat MOEMPLFAP, (b) MOEMPLFAP-AP and (c) MOEMPLFAP-C153.

10. **Figure 3.10.** Steady state absorption and emission spectra of C153 in neat RTILs at 298 K. All spectra are normalized at the corresponding peak maximum. Emission spectra for different ILs are also shown at the bottom at $\lambda_{\text{exc.}} = 405$ nm.

11. **Figure 3.11.** TRES of C153 in EMIMBSU at different time span at 293K. The time intervals are indicated by the corresponding symbols. All spectra are normalized at their corresponding peak maximum.

12. **Figure 3.12.** Plot of FWHM, obtained from several time-resolved emission spectra of C153 in EMIMBSU, at different time span at 293K.

13. **Figure 3.13.** (a) Bi-exponential fits of the spectral correlation function, $C(t)$, of C153 in different RTILs at 293 K. (b) stretched exponential fits of $C(t)$ of C153 in different ILs at 293 K.

14. **Figure 3.14.** (i) Variation of average solvation times with respect to the viscosity of different RTILs at 298 K. The solid line represents linear fit to the data. Data for 1-ethyl-3-methylimidazolium ethylsulfate (EMIMESU) is taken from
reference 135. (ii) Plot of weighted solvation time-components vs. bulk viscosity of ILs at 293 K. The symbol represents data points and solid line represents linear fit to the data. (a) EMIMBSU, (b) EMIMHSU and (c) EMIMOSU.

15. **Figure 4.1.** Time-resolved fluorescence anisotropy decay profiles of C153 in 1-ethyl-3-methylimidazolium alkylsulfates. Long and short decay profiles are at 293K and 313K respectively. Solid lines represent the bi-exponential fit to the data points.

16. **Figure 4.2.** Plots for $\ln(\eta)$ versus $1/T$ for all four 1-ethyl-3-methylimidazolium alkylsulfates. The line passing to the data points are drawn as visual aid.

17. **Figure 4.3.** log-log plots of average rotational relaxation time of C153 vs. $\eta/T$ in different 1-ethyl-3-methylimidazolium alkylsulfates with slip and stick boundary condition parameters. Symbols denote the experimental data points.

18. **Figure 4.4.** log-log plots of average rotational relaxation time of C153 vs. $\eta/T$ in different 1-ethyl-3-methylimidazolium alkylsulfates with boundary condition parameters obtained from DKS and GW model. Symbols denote the experimental data points. Solid and dotted lines represents the boundary condition for GW and DKS model respectively (red=EMIMESU, green = EMIMBSU, blue=EMIMHSU, cyan=EMIMOSU).
19. **Figure 4.5.** Anisotropy decay profiles of AP in the four 1-ethyl-3-methylimidazolium alkylsulfates. Long and short decay profiles are at 293 K and 313 K respectively. Solid lines represent the single exponential fit to data points.

20. **Figure 4.6.** log-log plots of average rotational relaxation time of AP vs. \( \eta/T \) in different 1-ethyl-3-methylimidazolium alkylsulfates with slip and stick boundary condition parameters. Symbols denote the experimental data points.

21. **Figure 4.7.** Proton NMR spectra for IL (EMIMESU), AP and AP with IL in DMSO-\( d_6 \).

22. **Figure 4.8.** Time-resolved fluorescence anisotropy decay profiles of C153 in different 1-ethyl-3-methylimidazolium cation containing RTILs at different temperatures. Symbols denote experimental data points and solid lines passing to the experimental data points represent the bi-exponential fit to the data points.

23. **Figure 4.9.** Plots of \( \ln(\eta) \) versus \( I/T \) for all four 1-ethyl-3-methylimidazolium cation contain RTILs.

24. **Figure 4.10.** Plots for \( \tau_r \) vs. \( \eta/T \) for C153 in 1-ethyl-3-methylimidazolium cation containing RTILs. Computed data are with slip, stick boundary conditions and experimentally measured data are shown by symbol.

25. **Figure 4.11.** Time-resolved fluorescence anisotropy decays of AP in different 1-ethyl-3-methylimidazolium cation containing RTILs at different temperatures. The smooth lines passing...
to the experimental data points are fitted ones

26. **Figure 4.12.** log-log plots for $\tau$ vs. $\eta/T$ for AP in different 1-ethyl-3-methylimidazolium cation containing RTILs. Computed data are with slip, stick boundary conditions and experimentally measured data are shown by symbol.

27. **Figure 5.1.** Optimized geometry of neat MOEMPLFAP.

28. **Figure 5.2.** (a) Absorption spectra of neat RTIL and C153 in neat RTIL, RTIL-toluene mixture and (b) steady state fluorescence spectra for (i) C153 in RTIL-toluene mixture, (ii) C153 in RTIL and (iii) neat RTIL.

29. **Figure 5.3.** Time-resolved emission spectra (TRES) of C153 in RTIL-toluene mixture at different time intervals at 293 K. $\lambda_{exc} = 405$ nm.

30. **Figure 5.4.** Decay of solvent correlation function $C(t)$ of C153 in RTIL and RTIL-toluene mixture at 293K. In each case solid lines represent the (a) bi-exponential and (b) stretched exponential fit to the experimental data points, where $\chi^2$ are the goodness of fit parameters and $R^2$ are the correlation coefficient values. $\lambda_{exc} = 405$ nm.

31. **Figure 5.5.** Absorption and emission spectra of C153 in BMIMTFA. Emission spectrum of neat RTIL is also shown in the same figure.

32. **Figure 5.6.** Absorption spectra of ANF and C153 in BMIMTFA. Spectra are normalized at their corresponding peak maxima.
33. **Figure 5.7.** Emission maxima (cm$^{-1}$) vs. $\lambda_{\text{exc}}$ (nm) plots of ANF RTIL-cosolvent systems at room temperature.

34. **Figure 5.8.** Fluorescence decay profile of C153 in BMIMTFA-H$_2$O system at different monitoring wavelength. The monitoring wavelengths are shown by the corresponding symbol in the same figure. Instrument response function (IRF) of the TCSPC technique is also given in the figure. Symbols denote the experimental data points and solid lines are fit to the data points.

35. **Figure 5.9.** Time-resolved emission spectra (TRES) of C153 in BMIMTFA-H$_2$O system at different time span. Symbols denote the experimental data points and solid lines represent the log normal fit to the data points.

36. **Figure 5.10.** Decay of solvent correlation function, $C(t)$ of C153 in BMIMTFA, BMIMTFA-H$_2$O, BMIMTFA-CH$_3$OH systems. Symbols denote the experimental data points and solid lines represent the bi-exponential fit to the data points.

37. **Figure 5.11.** Time-resolved fluorescence anisotropy decay of C153 in BMIMTFA, BMIMTFA-H$_2$O, BMIMTFA-CH$_3$OH systems at 293K. Symbols denote the experimental data points and solid lines represent the bi-exponential fit to the data points.

38. **Figure 5.12.** log-log plots of rotational relaxation times of C153 vs. $\eta/T$ in BMIMTFA, BMIMTFA-H$_2$O and BMIMTFA-CH$_3$OH
system with slip and stick boundary condition parameters. Dashed and dotted lines represent the slip and stick boundary condition for C153. Symbols denote the experimental data points and solid lines represent the fit to the data points respectively.

39. **Figure 5.13.** Optimized structure of BMIMTFA, BMIMTFA-H$_2$O and BMIMTFA-CH$_3$OH system calculated at the B3LYP/6-31++G (d, p) level in the gas phase.

40. **Figure 6.1.** (a) Viscosities and (b) densities of MOEMMOFAP and MOEMPLFAP RTILs as a function of temperature.

41. **Figure 6.2.** Optimized stricture of MOEMPL and MOEMMO cations at AM1 level theory.

42. **Figure 6.3.** Steady state absorption spectra of C153 in (1) MOEMPLFAP and (2) MOEMMOFAP. Spectra are normalized at the corresponding peak maximum. Symbols are denoted the excitation wavelengths ($\lambda_{\text{exc}}$).

43. **Figure 6.4.** Steady state emission spectra behavior of C153 in MOEMPILFAP and MOEMMOFAP at different excitation wavelength ($\lambda_{\text{exc}}$) at 293K. All emission spectra of C153 are normalized at the corresponding peak. Emission spectra of neat RTILs at the different excitation wavelength ($\lambda_{\text{exc}}$) are also shown in corresponding figure.

44. **Figure 6.5.** Representative emission wavelength dependent decay profile for C153 in MOEMMOFAP at 293K ($\lambda_{\text{exc}}=405$ nm). Circles denote the experimental data points and solid
line represent the fit to the data points. Instrument response function (IRF) is also shown in the same figure (dotted lines). The goodness of fit parameter values ($\chi^2$) in these two wavelengths are 1.1 and 1.01 respectively.

45. **Figure 6.6.** TRES of C153 in MOEMPLFAP at 293 K at different time span. The time intervals are indicated by the corresponding symbols. All spectra are normalized at their corresponding peak maximum. $\lambda_{exc.} = 405$ nm

46. **Figure 6.7.** Plot of full width half maxima (FWHM), obtained from several time-resolved emission spectra of C153 in MOEMMOFAP at 293 K at $\lambda_{exc.} = 405$ nm.

47. **Figure 6.8.** (a) Bi-exponential fits and (b) stretched exponential fits to spectral correlation function, $C(t)$ versus time plot of C153 in MOEMPLFAP and MOEMMOFAP at 293 K. Symbols are denoting the data points and solid lines represent the corresponding fit to the data points. $\lambda_{exc.} = 405$ nm.

48. **Figure 6.9.** log-log plots of average solvent relaxation time ($<\tau_s>$) of C153 vs. $\eta/T$ in (a) MOEMPLFAP and (b) MOEMMOFAP. Symbols denote experimental data points and solid lines are linear fit to the data.

49. **Figure 6.10.** Excitation wavelength dependence ($\lambda_{exc.}$), (a) emission peak frequency ($\nu_{em}$) for ANF and C153 and (b) full widths at half maximum (FWHM) of emission spectra of the two solutes in MOEMMOFAP.
50. **Figure 6.11.** Time-resolved fluorescence Anisotropy decay for C153 in MOEMMOFAP and MOEMPLFAP at 293K. Solid lines in the same figure represent the bi-exponential fit to the data points. Data representations are clearly explained inside the panels.

51. **Figure 6.12.** log-log plots of rotational relaxation time of C153 vs. η/T in the present RTILs with slip and stick boundary condition parameters.

52. **Figure 6.13.** log-log plots of rotational relaxation time of C153 vs. η/T in different RTILs. P⁺, N⁺ Pr⁺, Im⁺ denoted the phosphonium, ammonium, pyrrolidinium, and imidazolium cation containing RTILs which experimental data are taken from ref. 123. Experimental data for protic and aprotic solvent are taken from ref. 272.