Supplementary Information for Structural origin of energetic heterogeneity in ionic liquids

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1 Simulation details

Our simulation strategy and the method to compute excitation dependent emission spectra primarily follow the previous work of ANF in a different IL, [C_4MIM^+][PF_6^-][1]. Simulations were carried out by using the software GROMACS version 4[2] under the condition of constant pressure (P=1atm), constant temperature (T=300K), and constant number of particles. Force field parameters for the ionic liquids are the same as in the previous work of Canongia Lopes and coworkers,[3]. As stated in the previous work[1], the ANF ground and excited atomic charges are obtained from an *ab initio* calculation at the (HF/6-31G*) theory level using the Gaussian program[4]. The excited-state charge distribution was estimated by computing the ground (S0) and first singlet excited-state (S1) charge difference using the ZINDO Hamiltonian with configuration interaction[5]. Parameters of ANF force field and its atomic charges at ground and excited electronic states have been listed in ref.[6]. In this work, we use an ensemble of 15 MD trajectories with their initial configurations chosen randomly. Each of these trajectories consists of one ANF molecule and 326 pairs of ions. Because of the slow dynamics nature of ionic liquids, we have done charge annealing and temperature annealing to equilibrate the ionic systems. For each trajectory, a production run with $\simeq$ 2ns duration with the ANF at its ground electronic state is followed by a production run with $\simeq$ 1ns duration with the ANF at its excited electronic state.

2 Coordination number of ions

Tab. 1 shows the coordination number of ions within 5 Åof the solute probe for each trajectory and the corresponding vertical transition energies. The order of vertical transition energy still holds when we only consider the charges within a typical simulation box of length order of 5 nm. The general trend that larger ΔE corresponds to larger value of total charges is also valid, however, variation is possible because the electrostatic interaction energy is also relevant to the distance. Typical local structures corresponding to the first and last energies in Tab. 1 is plotted in the Fig. 4 of the paper.

Table 1: Coordination number of charges within 5 Åof ANF (in unit of elementary charge, e), the corresponding averaged vertical transition energies ($\langle \Delta E(d=\infty) \rangle$ in unit of 10^4cm^{-1}), and the averaged vertical transition energies evaluated within the simulation box ($\langle \Delta E(d=5\mathrm{nm}) \rangle + c$) where $c = 0.162$ (10^4cm^{-1}) is a constant. Q_{A+}/Q_{A-} stands for contribution from positive/negative charges around the electron acceptor group. Similarly, Q_{D+}/Q_{D-} stands for that of electron donor group and $\Sigma_q = -Q_{A+} - Q_{A-} + Q_{D+} + Q_{D-}$ is the total charges within 5 Åof the solute probe.

Q_{A+}	Q_{A-}	Q_{D+}	Q_{D-}	Σ_q	$\langle \Delta E(d=\infty) \rangle$	$\langle \Delta E(d=5\mathrm{nm}) \rangle + c$
0.891	-0.456	0.680	-0.904	-0.660	2.175	2.166
0.452	-0.036	0.261	-0.345	-0.501	2.185	2.195
1.066	-0.611	0.523	-0.569	-0.501	2.194	2.193
0.869	-0.233	0.318	-0.351	-0.668	2.213	2.215
0.717	-0.290	0.462	-0.512	-0.477	2.260	2.249
0.828	-0.530	0.300	-0.431	-0.430	2.275	2.267
0.633	-0.375	0.639	-0.762	-0.381	2.286	2.284
0.962	-0.740	0.626	-0.637	-0.233	2.325	2.322
1.162	-0.933	0.748	-0.752	-0.233	2.336	2.340
1.312	-1.147	1.333	-1.292	-0.123	2.345	2.349
0.721	-0.321	0.507	-0.492	-0.384	2.369	2.367
0.965	-0.561	0.667	-0.533	-0.267	2.370	2.368
0.443	-0.312	0.134	-0.347	-0.344	2.376	2.374
0.815	-0.589	0.631	-0.575	-0.171	2.423	2.434
0.430	-0.318	0.375	-0.452	-0.188	2.454	2.461

3 Results for [C_8MIM^+][PF_6^-] system

Fig. 1 (A), (B), (C) and (D) correspond to Fig. 2 (a),(b),(c) and Fig. 3 in the paper respectively. These results of ANF in [C_8MIM^+][PF_6^-] system support our conclusion that analysis of the structural origin of energetic heterogeneity in [$C_{12}MIM^+$][PF_6^-] system is also valid for other ionic liquids.

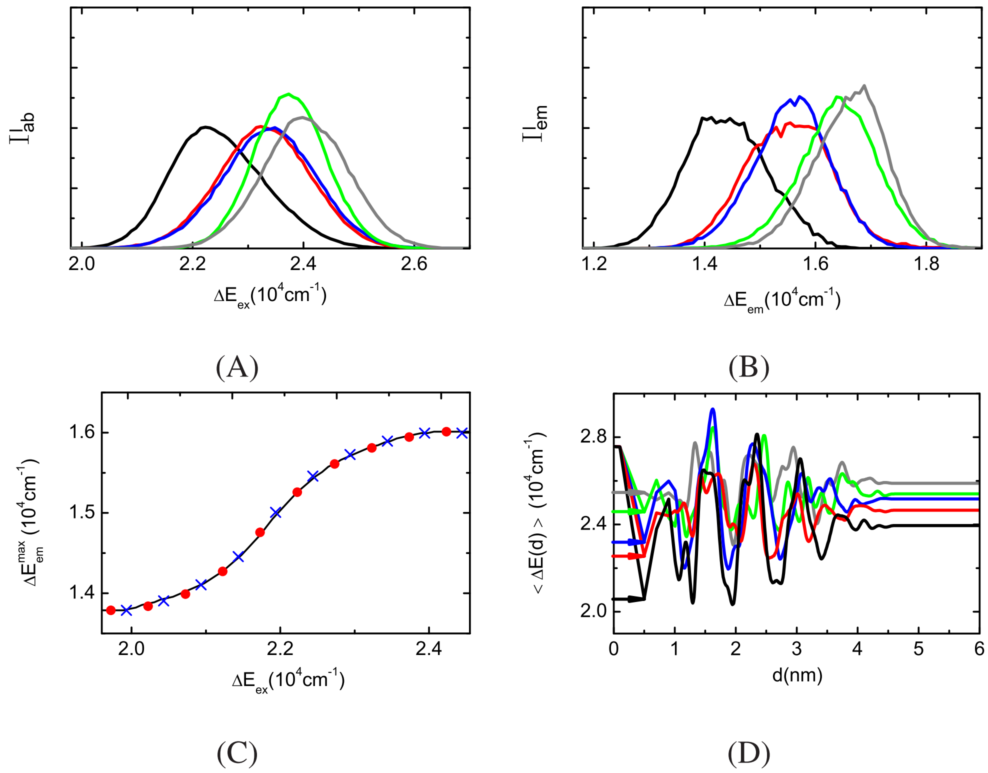

Figure 1: (A) Selected typical absorption absorption lines of ANF in [C_8MIM^+][PF_6^-] computed from 5 molecular dynamics. (B) The corresponding emission lines. (C) The overall emission maxima as a function of excitation energy. (D) Selected subensemble average of vertical transition energy as a function of distance.

References

1 Z. Hu and C. J. Margulis, Proc. Nat. Acad. Sci. USA, 2006, 103, 831
2 B. Hess, C. Kutzner, D. Van der Spoel and E. Lindahl, J. Chem. Theory Comp.,2008, 4, 435
3 J. N. A. Canongia Lopes, J. Deschamps and A. A. H. Padua, J. Phys. Chem. B, 2004, 108, 2038
4 GAUSSIAN 03 (2003) (Gaussian, Inc., Pittsburgh), Revision A.1.
5 J. Ridley, and M. Zerner, Theor. Chim. Acta, 1973, 32, 111
6 Hu, Zhonghan. ”Transport properties, optical response and slow dynamics of ionic liquids.” PhD diss., University of Iowa, 2007. http://ir.uiowa.edu/etd/160. Page 215-227, Table D10-D14.