Photoexcitation dynamics of p-nitroaniline and N,N-dimethyl-p-nitroaniline in 1-alkyl-3-methylimidazolium-cation based ionic liquids with different alkyl chain lengths

Yoshifumi Kimura*, Shinya Ibaraki, Ryusei Hirano, Yosuke Sugita, Yoshiro Yasaka, Masakatsu Ueno

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Corresponding Author
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FAX: +81-774-65-6801
Table S1. Relative amplitudes and time constants obtained by the coevolution fit of the transient absorption profiles of pNA at different probe wavelengths to the multi-exponential function. The value of $\tau_3$ is fixed to be 1000 ps. The errors are estimated from the residual of the fit and correlations of error matrix for each transient.

### 365 nm

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Table S2. Relative amplitudes and time constants obtained by the coevolution fit of the transient absorption profiles of DMpNA at different probe wavelengths to the multi-exponential function. The value of $\tau_3$ is fixed to be 1000 ps. The errors are estimated from the residual of the fit and correlations of error matrix for each transient.

365 nm

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<td>0.39 ± 0.29</td>
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380 nm

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<td>0.39 $\pm$ 0.01</td>
<td>0.017 $\pm$ 0.001</td>
<td>1.2 $\pm$ 0.1</td>
<td>7.4 $\pm$ 0.2</td>
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<td>C$_4$ mim$^+$</td>
<td>-1 $\pm$ 0.04</td>
<td>0.38 $\pm$ 0.01</td>
<td>0.024 $\pm$ 0.002</td>
<td>1.2 $\pm$ 0.1</td>
<td>8.2 $\pm$ 0.3</td>
</tr>
<tr>
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<td>-1 $\pm$ 0.01</td>
<td>0.40 $\pm$ 0.01</td>
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<td>-1 $\pm$ 0.01</td>
<td>0.40 $\pm$ 0.01</td>
<td>0.035 $\pm$ 0.002</td>
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<td>8.3 $\pm$ 0.3</td>
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<td>-1 $\pm$ 0.01</td>
<td>0.39 $\pm$ 0.01</td>
<td>0.038 $\pm$ 0.002</td>
<td>1.3 $\pm$ 0.1</td>
<td>8.7 $\pm$ 0.4</td>
</tr>
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<td>C$_{12}$ mim$^+$</td>
<td>-1 $\pm$ 0.02</td>
<td>0.40 $\pm$ 0.02</td>
<td>0.044 $\pm$ 0.003</td>
<td>1.3 $\pm$ 0.1</td>
<td>8.8 $\pm$ 0.6</td>
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</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
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<td>0.84 $\pm$ 0.01</td>
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<td>$A_3$</td>
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<td>----------</td>
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</tr>
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<td>C$_2$ mim$^+$</td>
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<td>0.015 ± 0.001</td>
<td>0.70 ± 0.01</td>
<td>3.9 ± 0.1</td>
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<td>-1 ± 0.01</td>
<td>0.38 ± 0.02</td>
<td>0.022 ± 0.001</td>
<td>0.77 ± 0.01</td>
<td>4.0 ± 0.1</td>
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<td>C$_6$ mim$^+$</td>
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<td>0.34 ± 0.03</td>
<td>0.025 ± 0.001</td>
<td>0.76 ± 0.01</td>
<td>4.7 ± 0.1</td>
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<td>0.029 ± 0.002</td>
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<td>4.4 ± 0.3</td>
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<td>0.32 ± 0.03</td>
<td>0.033 ± 0.006</td>
<td>0.81 ± 0.01</td>
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<td>0.045 ± 0.001</td>
<td>0.79 ± 0.01</td>
<td>4.7 ± 0.1</td>
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</tbody>
</table>
Table S3. Absorption maximum wavelength, the reaction free energy ($\Delta G$) and the solvent reorganization energy ($\lambda_S$) estimated from the absorption spectrum using eq. (3), and the ratio of the calculated back-ET rate from eq. (4) for DMpNA in different ILs.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\Delta G$ / cm$^{-1}$</th>
<th>$\lambda_S$ / cm$^{-1}$</th>
<th>$k_{\text{et}}([\text{C}_2\text{mim}][\text{NTf}<em>2])/k</em>{\text{et}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{mim}^+$</td>
<td>402.1</td>
<td>20990</td>
<td>3260</td>
<td>1.00</td>
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<td>$\text{C}_4\text{mim}^+$</td>
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<td>21120</td>
<td>3230</td>
<td>1.29</td>
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<tr>
<td>$\text{C}_6\text{mim}^+$</td>
<td>400.9</td>
<td>21240</td>
<td>3100</td>
<td>2.02</td>
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<tr>
<td>$\text{C}_8\text{mim}^+$</td>
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<td>21320</td>
<td>3060</td>
<td>2.47</td>
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<tr>
<td>$\text{C}_{10}\text{mim}^+$</td>
<td>399.8</td>
<td>21400</td>
<td>3020</td>
<td>3.04</td>
</tr>
<tr>
<td>$\text{C}_{12}\text{mim}^+$</td>
<td>399.1</td>
<td>21430</td>
<td>3030</td>
<td>3.11</td>
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</table>
Figure S1 Time profiles of the transient absorption ($\Delta$OD) of pNA at different probe wavelengths in (a) [C$_4$mim][NTf$_2$], (b) [C$_6$mim][NTf$_2$], (c) [C$_8$mim][NTf$_2$], (d) [C$_{10}$mim][NTf$_2$], and (e) [C$_{12}$mim][NTf$_2$]. The dashed lines indicate $\Delta$OD = 0. The black lines are the results of fitting by a multi-exponential function.
Figure S2. Time profiles of the transient absorption ($\Delta$OD) of DMpNA at different probe wavelengths in (a) $[\text{C}_4\text{mim}][\text{NTf}_2]$, (b) $[\text{C}_6\text{mim}][\text{NTf}_2]$, (c) $[\text{C}_8\text{mim}][\text{NTf}_2]$, (d) $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, and (e) $[\text{C}_{12}\text{mim}][\text{NTf}_2]$. The dashed lines indicate $\Delta$OD = 0. The black lines are the results of fitting by a multi-exponential function.
Figure S3. Example of the spectral simulation by eq.(3) for DMpNA in [C_{12}mim][NTf_2]. The black solid curve is the experimental absorption spectrum and the red curve is the calculated one.