# ELECTRONIC SUPPLEMENTARY INFORMATION

## Microscopic Rigidity and Heterogeneity of Ionic Liquids Probed by Stochastic Molecular Librations of the Dissolved Nitroxides

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## 1. Influence of the nitroxide radical size

In order to test the influence of the probe size, we performed preliminary measurements in [Bmim]$PF_6$ using more bulky nitroxide N2 in a few temperature points (Figure S1). If the librational motion of the NO group was influenced to some extent by the overall mobility of the nitroxide, one would anticipate the influence of the radical size on $\langle\alpha^2\rangle\tau_c$ vs. *T*. Contrary to that, Figure S1 does not reveal any noticeable differences between $\langle\alpha^2\rangle\tau_c$ dependences obtained for N1 and N2 in the same IL. This means that the character of librations is local with respect to NO group, and is rather determined by interaction with the surrounding matrix and its properties.

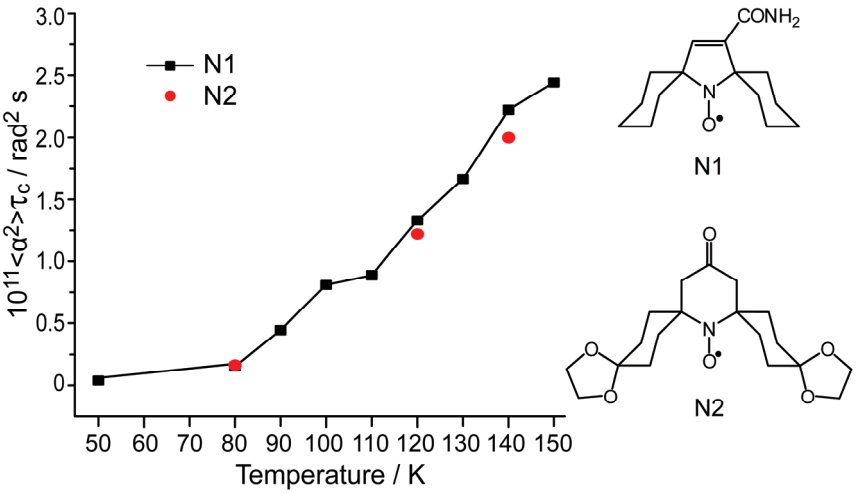


**Figure S1.** (left) Temperature dependence of the motional parameter $\langle\alpha^2\rangle\tau_c$ in [Bmim]$PF_6$ for two different nitroxide probes N1 and N2 (indicated in the plot). The solid line is shown to guide the eye. (right) Structure of the two nitroxide probes used.