Two-dimensional ultrafast vibrational spectroscopy of azides in ionic liquids reveals solute-specific solvation

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Table of Contents

Supplementary Information

S1. Materials: All reagents, except 2-azidoethanol, were either purchased from Sigma-Aldrich or Fisher Scientific and used as received. 2-azidoethanol was kindly gifted by X. Liu group (A. Sasmal), University of Pittsburgh, USA. Ionic liquids were obtained from Ioli-tec. The model ionic liquid, $[BMIM][BF_4]$ was extracted with methylene chloride, rotovapped and dried under high vacuum at $80^{\circ}C$ before use. $[EMIM][BF_4]$ and $[BMIM][PF_6]$ were also dried under high vacuum before use. In all our experiments, the water content of ionic liquids was similar and determined through the "free water" bands at 3640 and 3560 cm^{-1}. The peak absorbance of this OH stretching region for every solution was converted to concentration using molar extinction of water 100 $M^{-1}cm^{-1}$.[1] This number was divided by the density of the ionic liquid as given in the literature to determine the water content. Analysis of test samples used for 2D-IR measurements show that the water concentration ranged approximately between 300 to 600 ppm. An example of the "free water" bands for the ionic liquid $[BMIM][BF_4]$ with an inorganic azide (sodium azide) and an organic azide (3-azido propylamine) is shown below to demonstrate the similarity in water content across different kinds of azides.

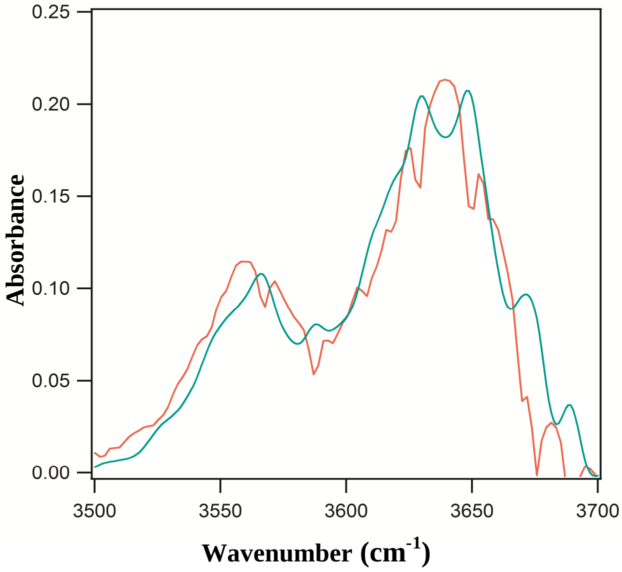


Figure S1. FTIR of OH stretching-band of water in $[BMIM][BF_4]$. The red spectrum is representative of inorganic azide (sodium azide) whereas the green spectrum represents an organic azide (3-azido propylamine) . Notice that the water content in similar in both solutions.

[1] L. Cammarata,S. G. Kazarian, P. A. Salter and T. Welton *Phys. Chem. Chem. Phys*., 2001, **3**, 5192-5200

Supplementary Information

S2. FTIR of organic and inorganic azides in [BMIM][BF$_4$], D$_2$O and THF: FTIR studies in ionic liquids and D$_2$O were performed using a Thermo Nicolet 6700 spectrometer equipped with MCT detector. FTIR spectra were collected over 32 scans with resolution of 2 cm^{-1} at regions of 4000–400 cm^{-1}. Background subtraction was done with the respective solvents. Analysis of the spectra was done with OMNIC software (Thermo Nicolet).

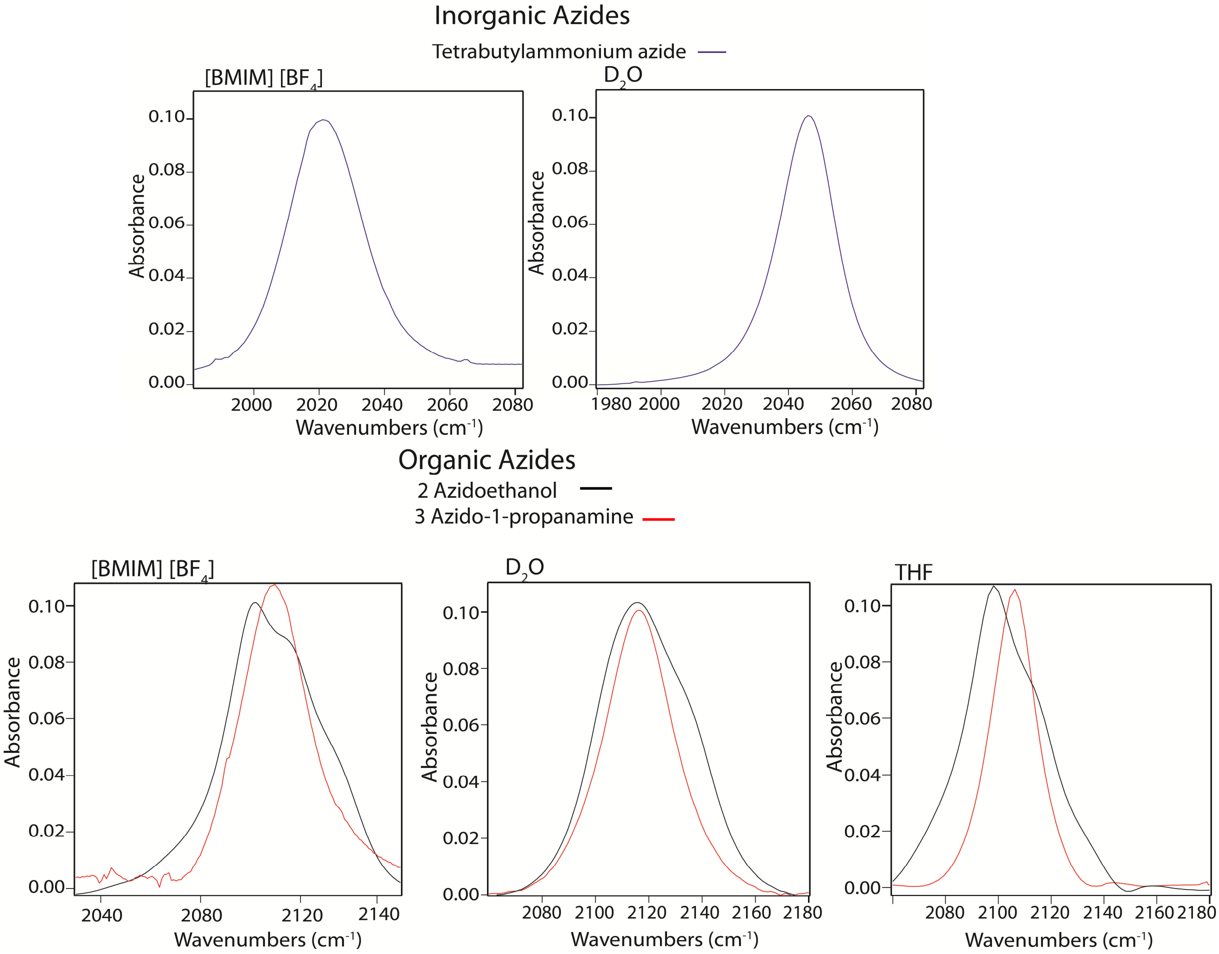


Figure S2. FTIR of inorganic and organic azides in [BMIM][BF$_4$], D$_2$O and THF.

Table S2. FTIR characteristics of azides in [BMIM][BF$_4$], D$_2$O and THF.

	[BMIM][BF$_4$]		D$_2$O		THF	
Sample	***Peak Position (cm^{-1})***	***FWHM (cm^{-1})***	***Peak position (cm^{-1})***	***FWHM (cm^{-1})***	***Peak position (cm^{-1})***	***FWHM (cm^{-1})***
Sodium Azide	2012	17	2042	13	-	
Tetrabutylammonium azide	2021	19	2046	14	2014	22
3′-Azido-3′-deoxythymidine	2118	21	2118	23	2096	17
2-Azidoethanol	2115*	32	2115*	31	2098*	18
3-Azido-1-propanamine	2111	19	2111	21	2106	16

***** Multiple peaks

Supplementary Information

S3. Two-dimensional Spectroscopy: A commercial Ti:sapphire at 800 nm with ~120 fs pulse duration and a repetition rate of 5 kHz was focused onto a home-built optical parametric amplifier (OPA). The OPA generated ∼2 μJ tunable mid-IR pulses of sub 100 fs duration, centered between 2120-2000 cm^{-1},with a bandwidth of 250 cm^{-1}. For the 2D measurements, we used a Fourier transform 2D-IR setup in the pump−probe geometry. The data acquisition was performed with a fast-scanning routine without phase ambiguity. Further details can be found in elsewhere[2]. A liquid sample holder made of CaF_2 windows separated by a 25 μm spacer was used to interrogate the IL sample which contained an approximately 30 mM concentration of the probe.

[2] J. Helbing and P. Hamm.*J. Opt. Soc. Am. B* 2011,**28**, 171.

Supplementary Information

S4. Example fits of 2D-IR spectra with ellipticity and centerline slope routines: In the first row of the figure, we show the experimental 2D-IR data along with the centerline (in red) of sodium azide in D_2O. The second row shows the data fitted to two-dimensional gaussian in line with the ellipticity method. As the waiting time increases, the 2D-line shapes become circular due to spectral diffusion. Such changes in the 2D-shapes cause the slope of the centerline and the ellipticities to vary. The decay of these numerical quantities is the measure of the FFCF, which connects the observables to the underlying dynamics.

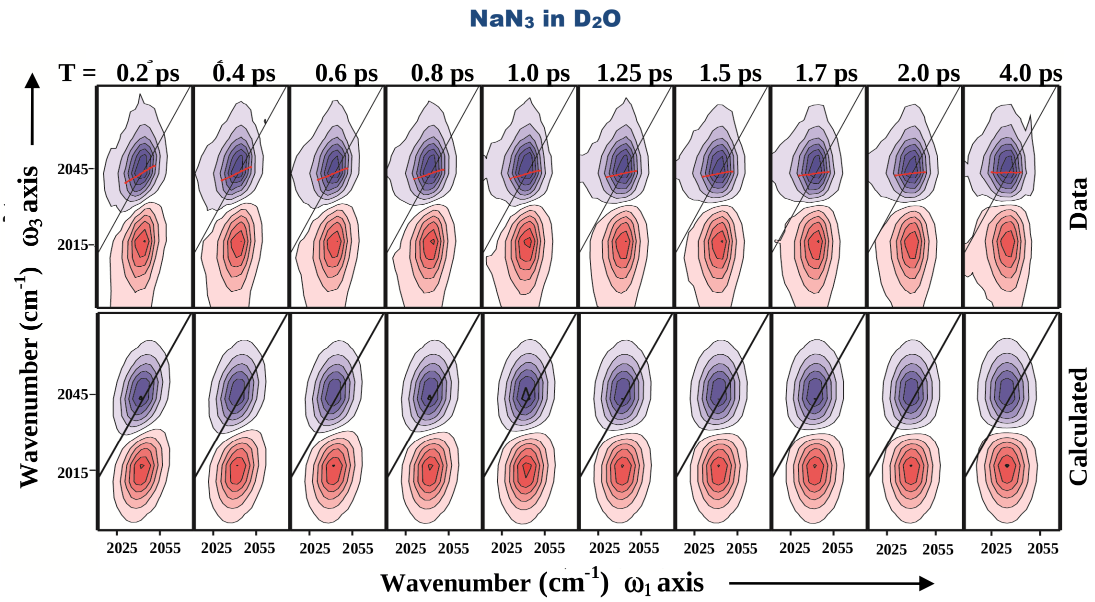
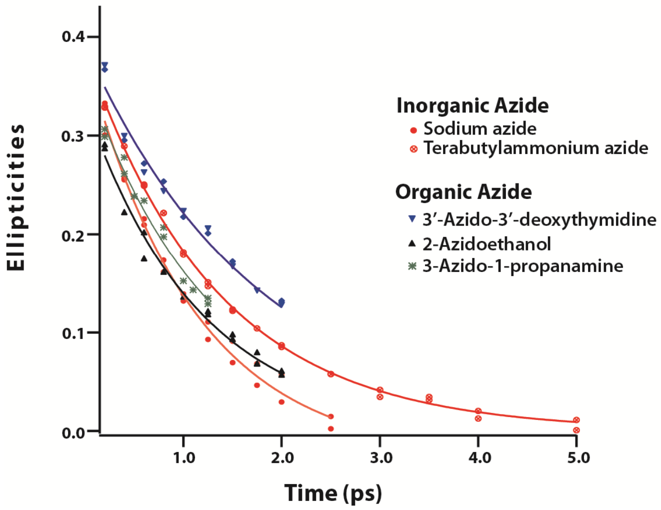


Figure S4. The top plot shows 2D-IR spectra of sodium azide analyzed by centerline slope method. The thin redlines shows the changes in slope with the waiting time,T. The bottom plot is the calculated 2D-gaussian profile from the 2D-IR data showing the change of ellipticity with time.

Supplementary Information

S5. Analysis of 2D-IR data of azides in D_2O and [BMIM][BF_4] with the ellipticity method: In order to verify the trend we observe by CLS method, we analyzed our data with 2D-elllipticity method following Lazonder routine[3]. The decay patterns obtained from ellipticities were fitted to a single exponential in a similar way as the CLS decays in the main text. The decay profiles and the correlation timescales are given below.



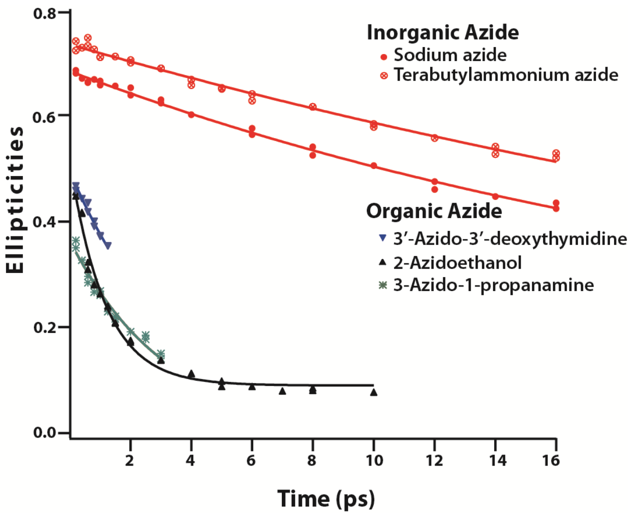


Figure S5. Ellipticity decays obtained from 2D-IR spectra clearly show striking difference in dynamics between inorganic solutes and organic solutes in [BMIM][BF_4]. In contrast, both kinds of azides sample the environment on similar timescales in D_2O.

Table S5: FFCF decay of azides in D_2O & [BMIM][BF_4]

Sample	**D_2O** τ**ellip(ps)**	**BMIM BF_4** τ**ellip(ps)**
Sodium Azide	**1.1 ± 0.1**	**33 ± 2**
Tetrabutylammonium azide	**1.3 ± 0.2**	**44 ± 6**
3′-Azido-3′-deoxythymidine	**1.2 ± 0.1**	**3.8 ± 0.4**
2-Azidoethanol	**1.2 ± 0.2**	**2.4 ± 0.1**
3-Azido-1-propanamine	**1.8 ± 0.1**	**3.2 ± 0.3**

τellip : Correlation decay times as obtained from ellipticity method by fitting an exponentially decaying function

[3] K. Lazonder, M. S. Pshenichnikov and D. A. Wiersma, *Opt. Lett.*, 2006, **31**, 3354–3356.

Supplementary Information

S6. Solvation dynamics of azides in THF: We studied the dynamics of organic and inorganic azides in the aprotic liquid, THF, by 2D-IR under same conditions as we used for studying ionic liquids. As sodium azide is poorly soluble in THF, we used tetrabutylammonium azide for this study. Our results suggest that the spectral diffusion of both kinds of azides in this non-aqueous solvent is comparable and ranges between 4-8 ps. However, the homogeneous component is smaller for organic azides. The results of 2D-IR analysis, both by centerline slope and ellipticities, are given below along with their decay parameters.

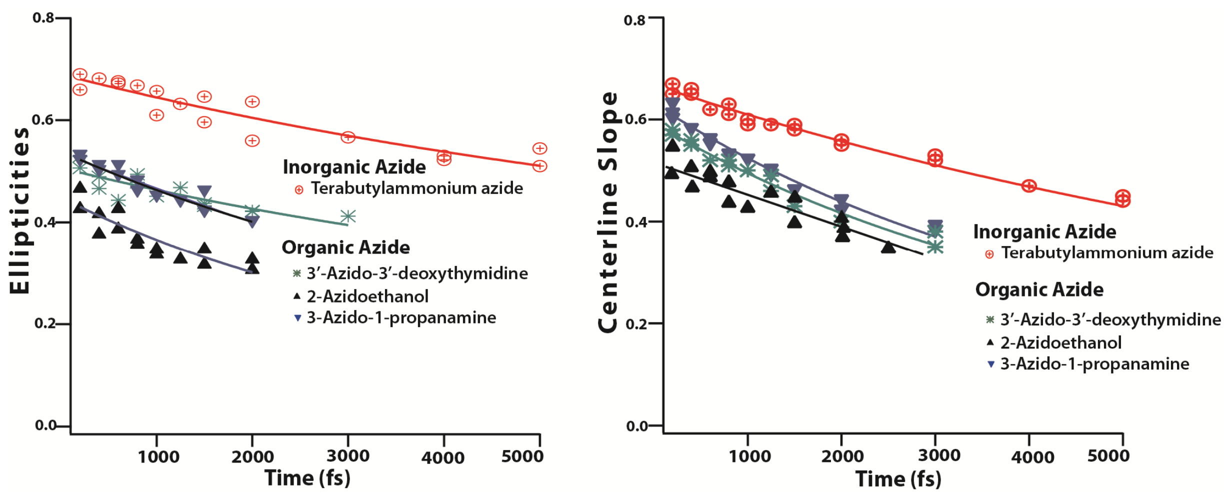


Figure S6. Ellipticity and centerline slope decay in THF shows similar trend in dynamics for both kinds of azides

Table S6. Correlation decays of azides in THF

Sample	**THF**	
	τcls(ps)	**τellip(ps)**
Tetrabutylammonium azide	**9.2 ± 0.5**	**8.4 ± 0.8**
3′-Azido-3′-deoxythymidine	**4.8 ± 0.4**	**6.5 ± 1.2**
2-Azidoethanol	**4.1 ± 0.5**	**4.6 ± 0.4**
3-Azido-1-propanamine	**6.1 ± 0.5**	**5.8 ± 0.6**

τcls & τellip : Correlation decay times as obtained from centerline slope and ellipticity methods by fitting an exponentially decaying function.

Supplementary Information

S7. Solvation dynamics of azides in [EMIM][BF$_4$]: 2D-IR data collected from organic and inorganic azides under similar conditions as with D_2O and [BMIM][BF$_4$]. The data was analyzed by 2D-elllipticity & CLS methods. Both methods show that differential solvation exist between organic and inorganic azides in this ionic media. Note that only tetrabutylammonium azide is soluble this medium. The decay of the FFCF and the correlation time thereof is given below;

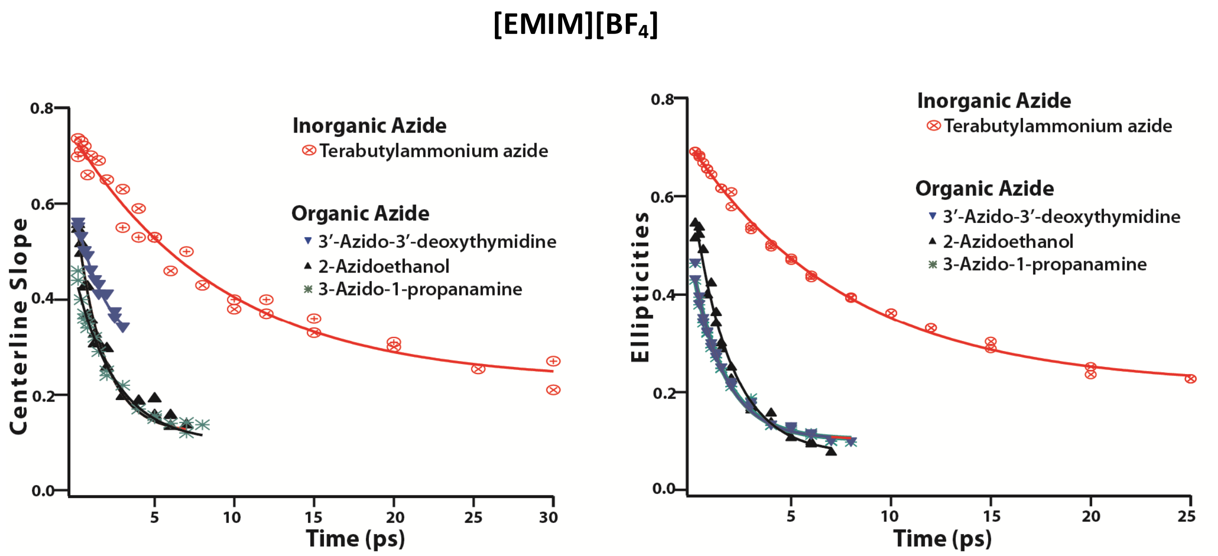


Figure S7. Centerline slope and ellipticities decays, obtained from 2D-IR data, of azides in [EMIM][BF$_4$] shows solute-specific dynamics.

Table S7: FFCF decay of azides in [EMIM][BF$_4$]

Sample	EMIM BF$_4$	
	τcls(ps)	τellip(ps)
Tetrabutylammonium azide	**19 ± 3**	**17 ± 3**
3′-Azido-3′-deoxythymidine	**3.3 ± 0.2**	**2.7 ± 0.6**
2-Azidoethanol	**2.0 ± 0.1**	**1.4 ± 0.1**
3-Azido-1-propanamine	**2.9 ± 0.5**	**2.6 ± 0.3**

τcls & τellip : Correlation decay times as obtained from centerline slope and ellipticity methods by fitting an exponentially decaying function.

Supplementary Information

S8. Solvation dynamics of azides in [BMIM][PF_6]: We studied the microenvironment of the aprotic ionic liquid, [BMIM][PF_6], which is similar to [BMIM][BF_4] except for the anion by 2D-IR spectroscopy. Though all the organic azides were soluble in it, unfortunately inorganic azides were found to be sparingly soluble. To improve the solubility, we mixed the inorganic azide (sodium azide) with methanol. The spectral diffusion of these azides in this non-aqueous solvent is comparable to that in [BMIM][BF_4]. The results of 2D-IR analysis, both by centerline slope and ellipticities, are given below along with their decay parameters. Note that the decay profiles, as with D_2O, [BMIM][BF_4] and [EMIM][BF_4], were fitted to a single exponential.

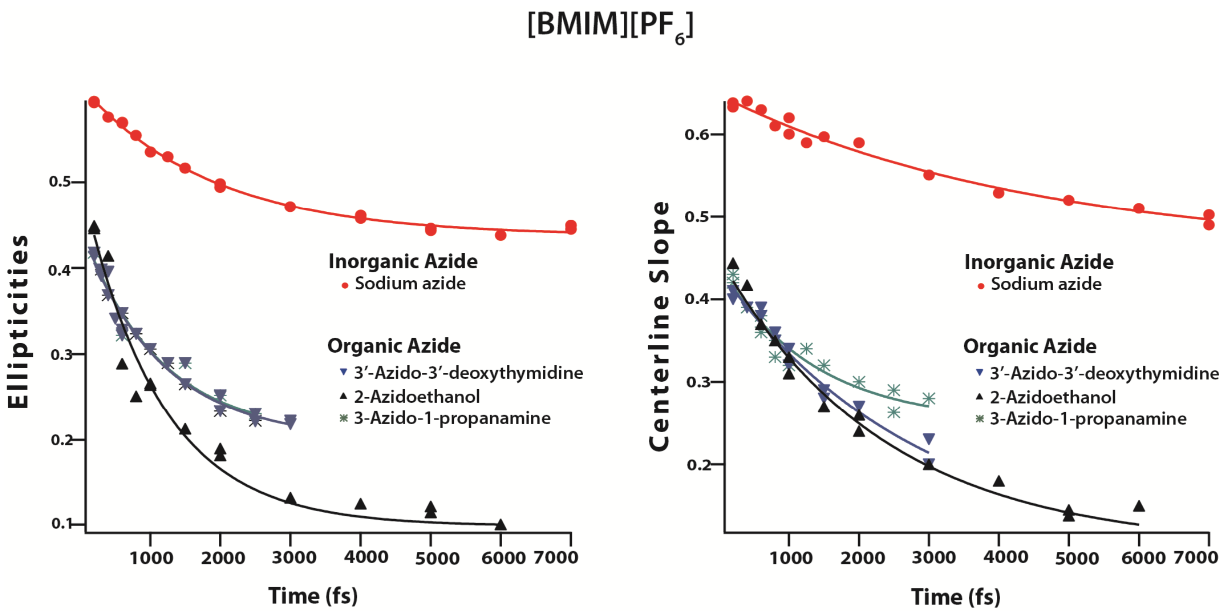


Figure S8. Ellipticity and centerline slope decay of azides in [BMIM][PF_6] shows similar trend in dynamics as observed in [BMIM][BF_4] & [EMIM][BF_4].

Table S8. Correlation decays of azides in [BMIM] [PF_6]

Sample	BMIM PF_6	
	τcls(ps)	τellip(ps)
Sodium azide*	**26 ± 4**	**21 ± 5**
3′-Azido-3′-deoxythymidine	**4.6 ± 0.5**	**3.9 ± 0.7**
2-Azidoethanol	**2.8 ± 0.3**	**2.6 ± 0.2**
3-Azido-1-propanamine	**5.1 ± 0.5**	**4.2 ± 0.6**

τcls & τellip : Correlation decay times as obtained from centerline slope and ellipticity methods by fitting an exponentially decaying function.