Imidazole and 1-Methylimidazole Hydrogen Bonding and Non-Hydrogen Bonding Liquid Dynamics: Ultrafast IR Experiments

Jae Yoon Shin[†], Yong-Lei Wang[‡], Steven A. Yamada, Samantha T. Hung, and
Michael D. Fayer*
Department of Chemistry,
Stanford University, Stanford, CA 94305
*Phone: (650) 723-4446; Email: fayer@stanford.edu

[†]Current address: Institute for Sustainability and Energy
Northwestern, Northwestern University, Evanston, IL 60208

[‡]Current address: Department of Materials and Environmental Chemistry
Arrhenius Laboratory, Stockholm University, SE-106 91, Sweden

1. Comparison of Population Decay Data between Imidazole (IM) and Deuterated Imidazole (IM-d$_4$)
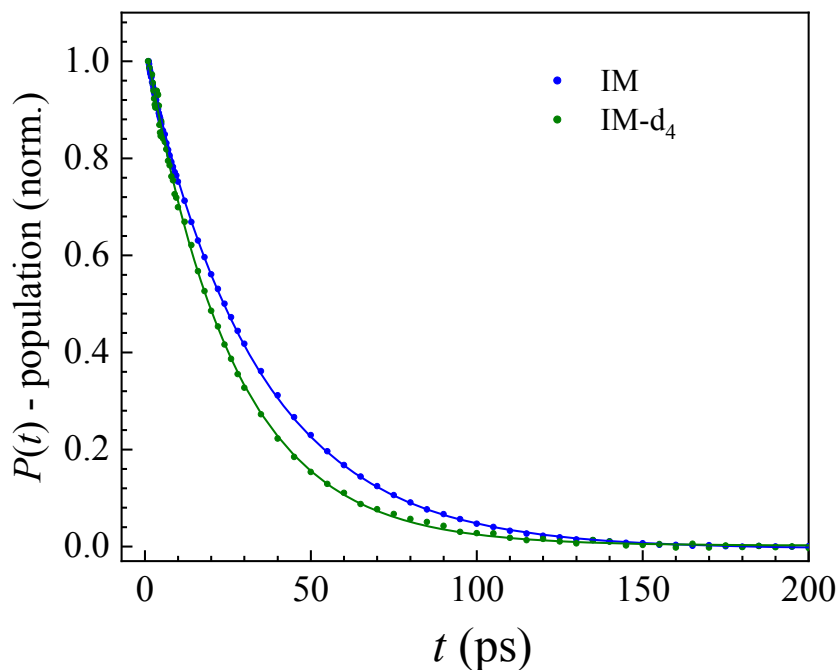
Figure S1. Population decay curves of SeCN$^-$ measured in IM and IM-d$_4$. The single exponential lifetime decreases in IM-d$_4$ to 26.1 ± 0.1 ps vs. 33.5 ± 0.2 ps in IM.

2. Comparisons of Bi- and Triexponential fits to the Anisotropy Decays
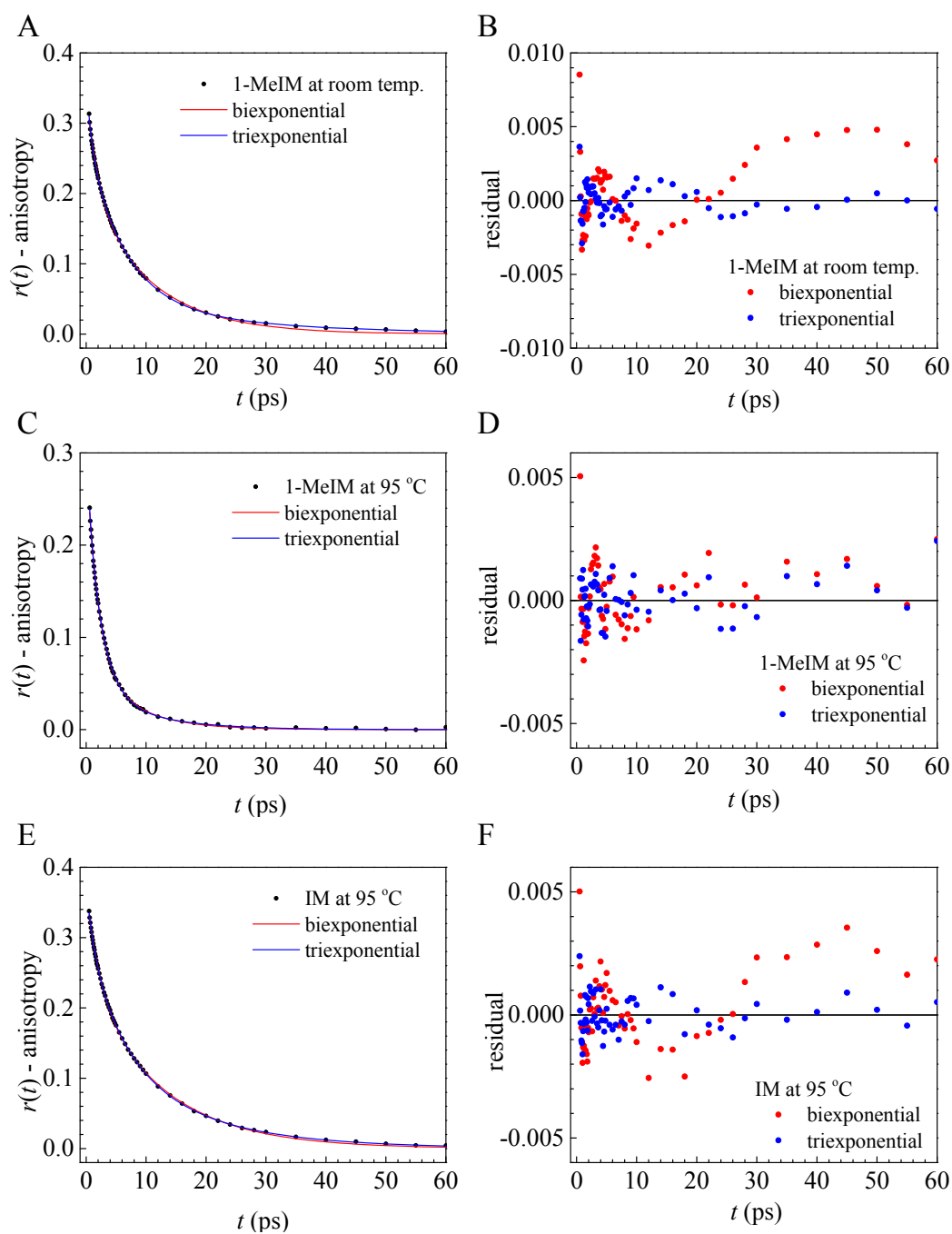
Figure S2. Bi- and triexponential fits to the anisotropy decays of 1-MeIM (A and C) and IM (E) samples. The residuals of fits are shown in (B), (D), and (F).

3. Viscosity Measurements

The viscosities of 1-Methylimidazole (1-MeIM) and Imidazole (IM) were measured using a rheometer (ARES-G2, TA Instruments) at Soft & Hybrid Materials Facility (SMF), Stanford. The measurements used a stainless steel cone plate with a diameter of 40 mm and an angle of 2° (0.0349 rad). To prevent the contamination of liquid with atmospheric water during the measurements, the rheometer was sealed with an inflatable polyethylene glove bag and purged with dry N_2 gas. All the sample preparations and measurements were performed inside the purged glove bag. The viscosities were recorded at a shear rate ranging from 300 s^{-1} to 1000 s^{-1} as displayed in Figure S3. The viscosities of both 1-MeIM and IM monotonically increase with the shear rate. Since the literature viscosity value of 1-MeIM at 25°C matches the measured value at the shear rate of 304 s^{-1},[1] the viscosity values at this shear rate were used in this study: 1.72 cP and 0.73 cP for 1-MeIM at 25°C and 95°C and 2.28 cP for IM at 95°C.
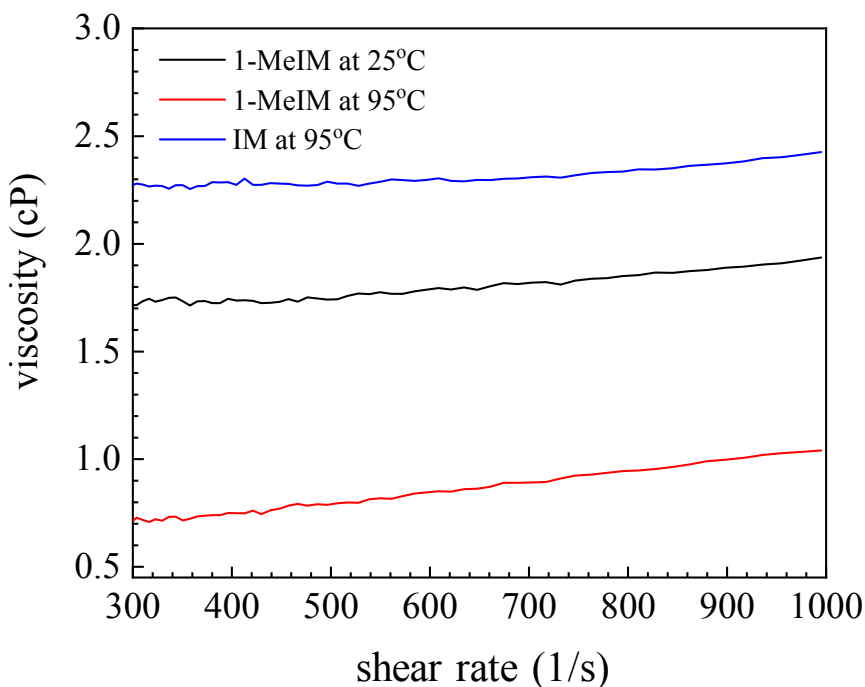
Figure S3. Viscosities of 1-MeIM and IM measured as a function of shear rate.

4. The First-order Stark Effect RISD Theory

Recent studies of polarization selective 2D IR experiments on various systems have shown that the probe molecules' orientational relaxation can contribute to spectral diffusion.[2-3] Orientational relaxation will contribute to spectral diffusion if it occurs on similar time scales as the spectral diffusion caused by structural evolution of the sample, and if the sample produces electric fields at the vibrational probe that evolve on a comparable or slower time scale than the reorientation.[2-3] In this regime, the reorientation of the SeCN$^-$ probe induces a change in its interaction with the electric field through the first order Stark effect and thus, the vibrational frequency changes. The contribution of RISD differs in the two experimental polarization configurations, parallel ($\langle XXXX \rangle$) and perpendicular ($\langle XXYY \rangle$).

The total spectral diffusion is the result of RISD and the structural spectral diffusion, SSD. For the first-order Stark effect coupling, the total FFCF is the product of the two contributions,

$$C_{tot}^i(t) = F_{SSD}(t)R_i(t), \tag{S1}$$

where $F_{SSD}(t)$ is the structural contribution from fluctuations in the liquid structure and $R_i(t)$ is the RISD contribution with i = parallel or perpendicular.[2-3] The RISD contribution is given by

$$R_{para}(t) = \frac{3}{25}\left[\frac{11C_1(t)+4C_3(t)}{1+0.8C_2(t)}\right] \tag{S2}$$

for the parallel configuration and

$$R_{perp}(t) = \frac{3}{25}\left[\frac{7C_1(t)-2C_3(t)}{1-0.4C_2(t)}\right] \tag{S3}$$

for the perpendicular configuration. In addition, the isotropic decay curve can be obtained by adding the parallel 2D spectrum to twice the perpendicular 2D spectrum ($\langle XXXX \rangle + 2\langle XXYY \rangle$) at each T_w, and obtaining the CLS from these combined spectra. The isotropic RISD factor is given by

$$R_{iso}(t) = C_1(t) \tag{S4}$$

The $C_1(t)$, $C_2(t)$, and $C_3(t)$ are the first, second, and third order Legendre polynomial orientational correlation functions, respectively.[2-3] $C_2(t)$ is obtained from the anisotropy measurements. From $C_2(t)$, $C_1(t)$ and $C_3(t)$ are calculated.[3] In using Equation S1 to S3 to

S4

obtain the SSD, there are no adjustable parameters in the RISD term. The SSD can be obtained by fitting the SSD parameters to either the parallel or perpendicular CLS decay. The SSD is modeled as a sum of exponentials.
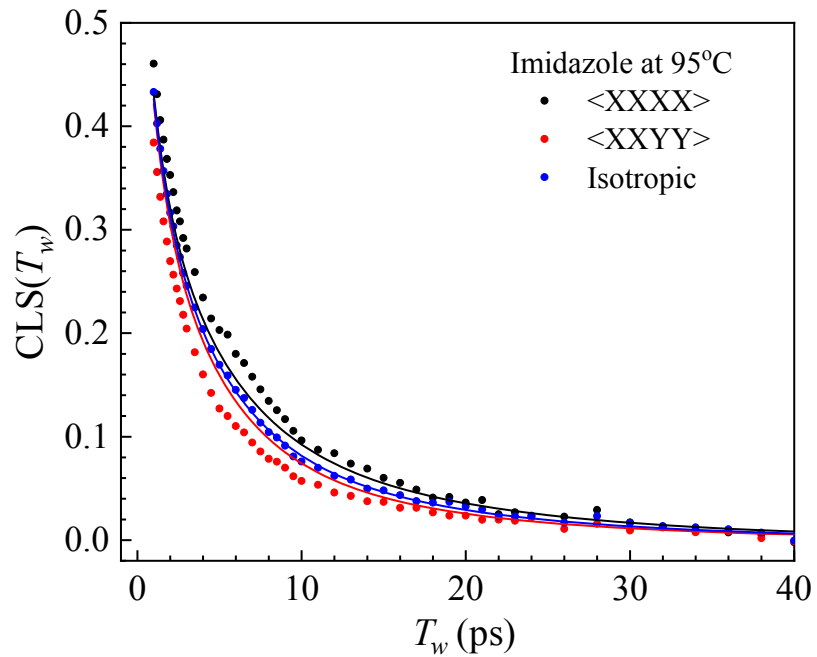
5. The CLS Decay Curves with the RISD Fits
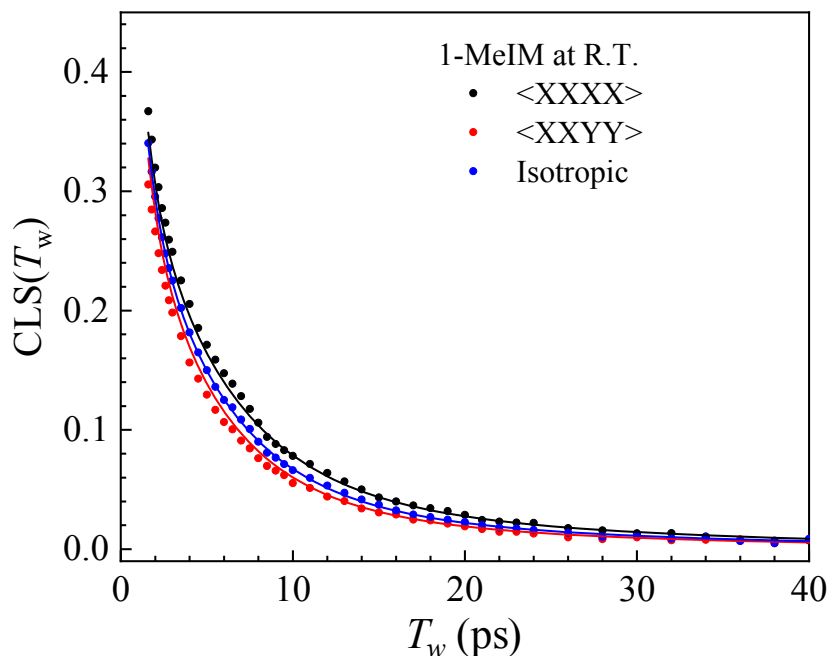
Figure S4. 2D IR CLS decay data of SeCN⁻ in 1-MeIM from the parallel ($\langle XXXX \rangle$) and perpendicular ($\langle XXYY \rangle$) polarization configurations at room temperature. The isotropic CLS was obtained from the isotropic 2D IR spectra reconstructed with the two polarization data ($\langle XXXX \rangle + 2\langle XXYY \rangle$). The solid lines are the simultaneous RISD fits to three CLS curves.
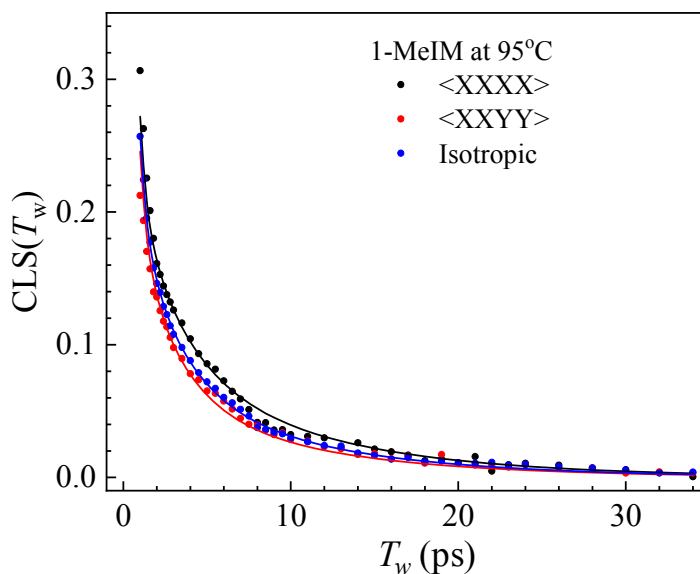
Figure S5. 2D IR CLS decay data of SeCN⁻ in 1-MeIM from the parallel ($\langle XXXX \rangle$) and perpendicular ($\langle XXYY \rangle$) polarization configurations at 95°C. The isotropic CLS was obtained from the isotropic 2D IR spectra reconstructed with the two polarization data ($\langle XXXX \rangle + 2\langle XXYY \rangle$). The solid lines are the simultaneous RISD fits to three CLS curves.

Figure S6. 2D IR CLS decay data of SeCN⁻ in imidazole from the parallel ($\langle XXXX \rangle$) and perpendicular ($\langle XXYY \rangle$) polarization configurations at 95°C. The isotropic CLS was obtained from the isotropic 2D IR spectra reconstructed with the two polarization data ($\langle XXXX \rangle + 2\langle XXYY \rangle$). The solid lines are the simultaneous RISD fits to three CLS curves.
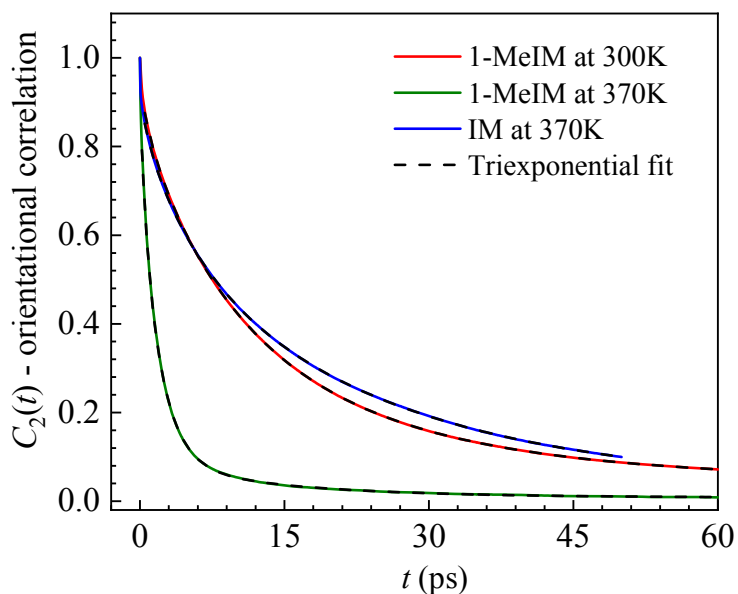
6. Comparisons of Bi- and Triexponential fits to the CLS Decays
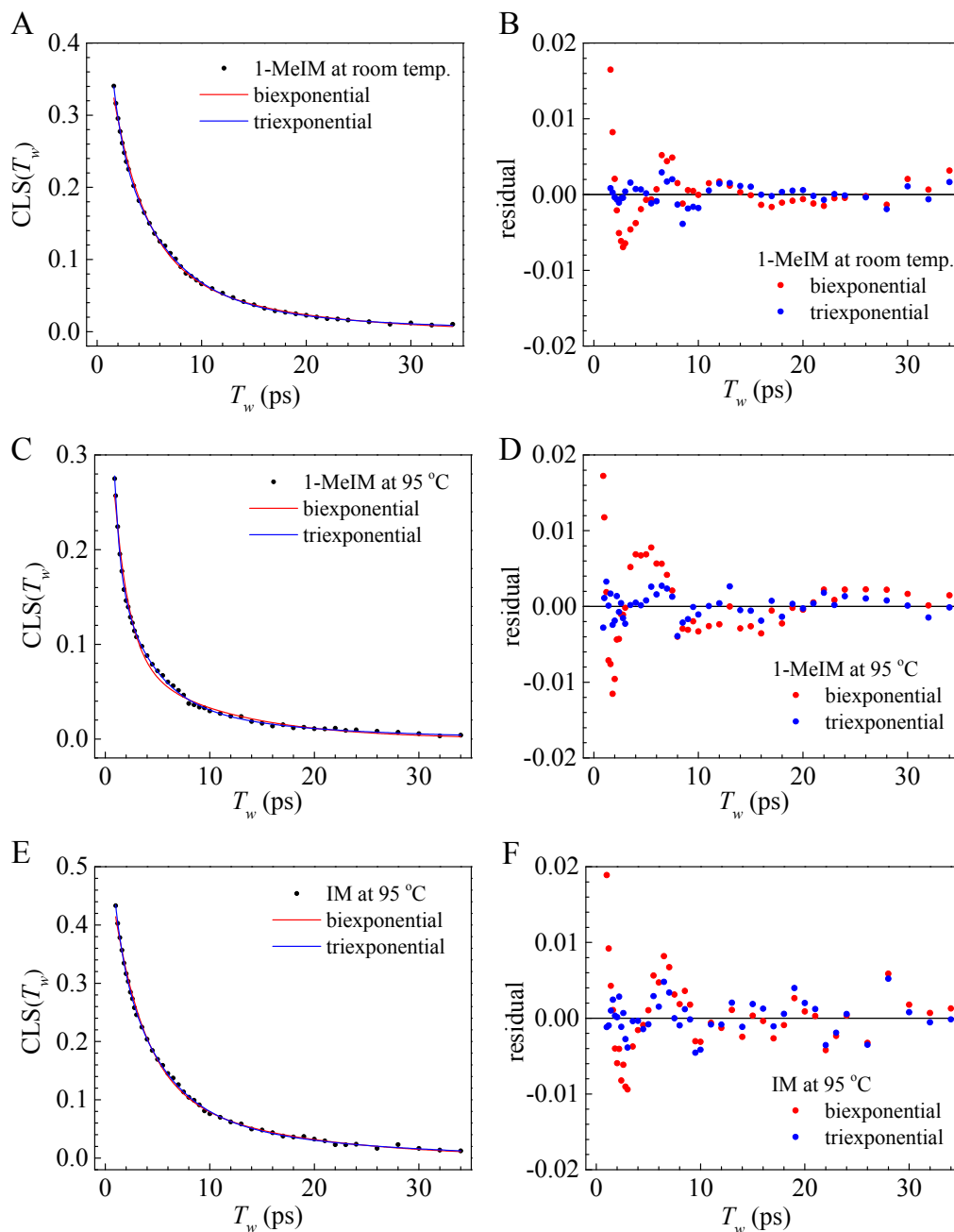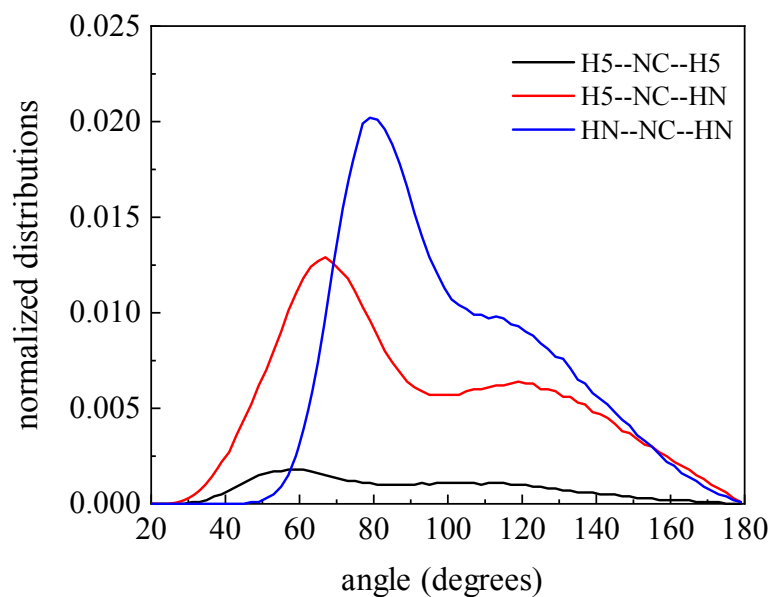

Figure S7. Bi- and triexponential fits to the CLS decays of 1-MeIM (A and C) and IM (E) samples. The residuals of fits are shown in (B), (D), and (F).

7. Simulated Data

Figure S8. Calculated orientational correlation functions $C_2(t)$ of 1-MeIM and IM. The dashed lines are the triexponential fits to $C_2(t)$. The fit parameters are summarized in Table S1.

Figure S9. Calculated distributions of the angle between two IM donors forming H-bonds to the same SeCN⁻, ∠HN··N··HN, ∠H5··N··H5, and ∠HN··N··H5. The notations of H atoms are given in Fig 3B.

Table S1. Parameters from the Triexponential Fits to the Calculated Orientational Correlation Functions

sample		$A_1{}^a$	t_1 (ps)	$A_2{}^a$	t_2 (ps)	$A_3{}^a$	t_3 (ps)	offset
1-MeIM	300K	0.08	1.2	0.41	8.7	0.40	21.3	0.05
	370K	0.18	0.6	0.64	2.1	0.08	14.0	0.008
IM at 370K		0.06	0.9	0.25	5.5	0.56	23.7	0.03

^aA_i is the amplitude of each exponential.

Table S2. Triexponential SSD Parameters from the RISD Fits

Sample		$A_1{}^a$	τ_1 (ps)	$A_2{}^a$	τ_2 (ps)	$A_3{}^a$	τ_3 (ps)
1-MeIM	R.T.	0.46 ± 0.18	0.8 ± 0.2	0.36 ± 0.02	5.7 ± 0.8	0.07 ± 0.03	33 ± 13
	95°C	0.67 ± 0.34	0.5 ± 0.2	0.15 ± 0.03	3.2 ± 1.3	0.15 ± 0.03	15 ± 2
IM at 95°C		0.21 ± 0.08	1.0 ± 0.8	0.31 ± 0.08	4.6 ± 2.7	0.15 ± 0.11	20 ± 10

^aA_i is the amplitude of each exponential.

References

1. Shirota, H.; Fujisawa, T.; Fukazawa, H.; Nishikawa, K. Ultrafast Dynamics in Aprotic Molecular Liquids: A Femtosecond Raman-Induced Kerr Effect Spectroscopic Study. *Bull. Chem. Soc. Jpn.* **2009,** *82* (11), 1347-1366.

2. Kramer, P. L.; Nishida, J.; Giammanco, C. H.; Tamimi, A.; Fayer, M. D. Observation and theory of reorientation-induced spectral diffusion in polarization-selective 2D IR spectroscopy. *J. Chem. Phys.* **2015,** *142* (18), 184505.

3. Kramer, P. L.; Nishida, J.; Fayer, M. D. Separation of experimental 2D IR frequency-frequency correlation functions into structural and reorientation-induced contributions. *J. Chem. Phys.* **2015,** *143* (12), 124505.