Direct Observation of Dynamic Crossover in Fragile Molecular Glass Formers with 2D IR Vibrational Echo Spectroscopy

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Supplemental Material

Section S1. Polarization Dependence of the CLS

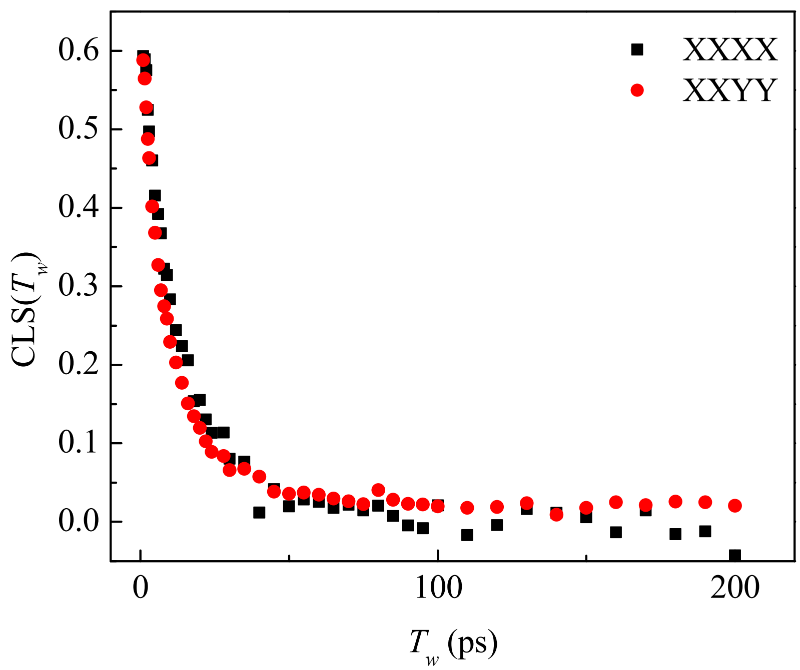

Figure S1. CLS of 5 mol % PhSeCN in BZP at 325 K in the $\langle XXXX \rangle$ and $\langle XXYY \rangle$ polarization schemes. The similarity of the two within experimental error shows that rotation of the probe has negligible impact on the measured spectral diffusion.

Section S2. FFCF Parameters (Kubo Multiexponential Model)

Values of the FFCF fit to the Kubo Model (Equation 4 in the main text). Δ_i are standard deviations of the i^{th} component of the inhomogeneous part of the absorption lineshape. Δ_T is the FWHM of the total inhomogeneous component, given by $\Delta_T = 2.35\sqrt{\sum_i \Delta_i^2}$. Γ is the total homogeneous linewidth (FWHM). T_2 is the dephasing time associated with Γ. Values in parentheses were held constant for fitting remaining values to insure fit convergence.

Table SI. FFCF Parameters for 5 mol % PhSeCN in BZP

T (K)	Δ_1 (cm^{-1})	τ_1 (ps)	Δ_2 (cm^{-1})	τ_2 (ps)	Δ_3 (cm^{-1})	τ_3 (ps)	Δ_T (cm^{-1})	Γ (cm^{-1})	T_2 (ps)
345	2.8 ± 0.3	4.7 ± 0.8	2.0 ± 0.4	17 ± 6	--	--	8.2 ± 0.3	2.9 ± 0.6	3.6 ± 0.8
335	2.7 ± 0.2	4.6 ± 0.7	2.4 ± 0.2	17 ± 2	--	--	8.5 ± 0.2	2.5 ± 0.4	4.2 ± 0.6
325	2.7 ± 0.3	6.0 ± 1.0	2.4 ± 0.3	23 ± 6	--	--	8.5 ± 0.1	2.3 ± 0.6	4.5 ± 1.1
315	2.1 ± 0.1	3.1 ± 0.6	3.0 ± 0.1	24 ± 2	--	--	8.5 ± 0.1	2.3 ± 0.2	4.5 ± 0.4
300	2.4 ± 0.1	5.3 ± 0.3	2.7 ± 0.1	44 ± 3	--	--	8.5 ± 0.1	2.2 ± 0.1	4.7 ± 0.3
295	2.2 ± 0.1	5.7 ± 0.7	2.7 ± 0.1	47 ± 3	--	--	8.2 ± 0.1	2.2 ± 0.1	4.8 ± 0.3
288	2.0 ± 0.1	6.3 ± 0.4	2.9 ± 0.1	53 ± 2	--	--	8.2 ± 0.1	2.3 ± 0.1	4.6 ± 0.3
275	2.1 ± 0.1	7.8 ± 1.0	1.7 ± 0.2	52 ± 18	2.5 ± 0.1	210 ± 20	8.6 ± 0.1	1.7 ± 0.4	6.1 ± 1.4
270	2.0 ± 0.1	6.6 ± 0.4	2.1 ± 0.1	59 ± 9	2.4 ± 0.1	351 ± 34	8.8 ± 0.1	1.4 ± 0.2	7.4 ± 1.2
265	2.0 ± 0.1	8.4 ± 0.5	1.9 ± 0.1	77 ± 13	2.6 ± 0.1	490 ± 37	8.9 ± 0.1	1.3 ± 0.2	8.0 ± 1.4
260	1.9 ± 0.1	6.7 ± 0.6	1.9 ± 0.1	85 ± 17	2.6 ± 0.1	1280 ± 290	8.7 ± 0.1	1.5 ± 0.2	6.8 ± 0.9
254	1.8 ± 0.1	9.8 ± 0.7	2.3 ± 0.1	310 ± 140	2.9 ± 0.1	2890 ± 2770	9.6 ± 0.1	0.4 ± 0.2	30 ± 17
248	1.6 ± 0.1	9.1 ± 1.8	1.7 ± 0.2	360 ± 120	3.4 ± 0.2	(10000)	9.7 ± 0.1	0.2 ± 0.2	48 ± 58

Table SII. FFCF Parameters for 2 mol % FlSeCN in BZP

T (K)	Δ_1 (cm^{-1})	τ_1 (ps)	Δ_2 (cm^{-1})	τ_2 (ps)	Δ_3 (cm^{-1})	τ_3 (ps)	Δ_T (cm^{-1})	Γ (cm^{-1})	T_2 (ps)
345	2.4 ± 0.2	5.3 ± 0.5	2.6 ± 0.2	21 ± 4	--	--	8.4 ± 0.2	2.4 ± 0.3	4.5 ± 0.6
325	2.5 ± 0.1	5.2 ± 0.9	2.4 ± 0.2	27 ± 4	--	--	8.0 ± 0.2	2.8 ± 0.3	3.8 ± 0.4
315	2.6 ± 0.1	7.1 ± 0.8	2.3 ± 0.1	49 ± 6	--	--	8.2 ± 0.1	2.3 ± 0.1	4.5 ± 0.3
300	2.3 ± 0.1	6.6 ± 0.8	2.8 ± 0.1	64 ± 4	--	--	8.5 ± 0.1	1.9 ± 0.1	5.6 ± 0.3
288	2.2 ± 0.1	8.0 ± 0.8	2.7 ± 0.1	115 ± 7	--	--	8.3 ± 0.1	1.8 ± 0.2	5.8 ± 0.2
277	1.8 ± 0.1	6.3 ± 1.0	1.9 ± 0.1	79 ± 17	2.6 ± 0.1	361 ± 16	8.5 ± 0.2	1.3 ± 0.4	7.9 ± 1.4
270	1.5 ± 0.1	6.3 ± 0.9	1.6 ± 0.1	70 ± 15	2.8 ± 0.1	593 ± 18	8.7 ± 0.1	1.7 ± 0.2	6.1 ± 0.9
265	1.8 ± 0.1	5.6 ± 1.3	1.4 ± 0.1	97 ± 30	2.8 ± 0.1	841 ± 31	8.4 ± 0.1	1.5 ± 0.2	7.0 ± 1.2

Table SIII. FFCF Parameters for 5 mol % PhSeCN in OTP

T (K)	Δ_1 (cm^{-1})	τ_1 (ps)	Δ_2 (cm^{-1})	τ_2 (ps)	Δ_3 (cm^{-1})	τ_3 (ps)	Δ_T (cm^{-1})	Γ (cm^{-1})	T_2 (ps)
365	2.7 ± 0.2	5.4 ± 0.3	1.4 ± 0.2	25 ± 5	--	--	7.2 ± 0.5	2.8 ± 0.3	3.8 ± 0.5
355	2.9 ± 0.2	6.9 ± 0.3	1.4 ± 0.3	31 ± 4	--	--	7.7 ± 0.3	2.1 ± 0.5	5.1 ± 1.3
345	2.2 ± 0.1	4.7 ± 0.5	2.1 ± 0.1	37 ± 3	--	--	7.1 ± 0.1	2.8 ± 0.2	3.8 ± 0.3
335	2.2 ± 0.1	6.1 ± 0.8	2.0 ± 0.1	49 ± 5	--	--	7.1 ± 0.1	2.7 ± 0.2	3.9 ± 0.2
325	2.6 ± 0.1	7.5 ± 0.5	1.9 ± 0.1	89 ± 11	--	--	7.6 ± 0.1	2.1 ± 0.1	5.1 ± 0.2
315	2.2 ± 0.1	7.3 ± 0.8	1.4 ± 0.4	84 ± 52	1.8 ± 0.4	278 ± 72	7.6 ± 0.1	2.1 ± 0.9	5.1 ± 2.1
310	2.0 ± 0.1	6.8 ± 0.5	1.7 ± 0.1	87 ± 11	1.8 ± 0.1	618 ± 90	7.5 ± 0.1	2.2 ± 0.1	4.8 ± 0.3
305	1.9 ± 0.1	6.3 ± 0.5	1.4 ± 0.1	74 ± 7	2.4 ± 0.1	912 ± 50	7.8 ± 0.1	1.6 ± 0.1	6.4 ± 0.3
300	1.9 ± 0.1	6.9 ± 0.6	1.5 ± 0.1	72 ± 7	2.5 ± 0.1	2150 ± 170	8.2 ± 0.1	1.4 ± 0.1	7.8 ± 0.5
295	1.9 ± 0.1	8.4 ± 0.5	1.5 ± 0.1	143 ± 26	2.2 ± 0.1	2380 ± 1150	7.7 ± 0.1	2.1 ± 0.1	5.1 ± 0.3
290	1.9 ± 0.1	6.3 ± 0.5	1.5 ± 0.1	150 ± 22	2.6 ± 0.1	(10000)	8.4 ± 0.1	1.1 ± 0.1	9.9 ± 1.1
280	1.8 ± 0.1	8.1 ± 0.4	1.4 ± 0.1	346 ± 39	2.8 ± 0.1	--	8.5 ± 0.1	0.9 ± 0.1	11.9 ± 0.7
270	1.7 ± 0.1	10.4 ± 0.5	1.1 ± 0.1	476 ± 156	3.5 ± 0.1	--	9.4 ± 0.1	0.5 ± 0.1	19.6 ± 4.4
260	1.6 ± 0.1	8.4 ± 0.4	1.5 ± 0.1	967 ± 138	3.4 ± 0.1	--	9.6 ± 0.1	0.3 ± 0.1	31.4 ± 12.3

Section S3. FFCF Parameters (Exponential + Stretched Exponential Model)

Fits using the alternative exponential plus stretched exponential model (Equation 5) for datasets that were fit as a triexponential in the Kubo model. Fits are to the normalized FFCF. $\langle \tau_2 \rangle$ was calculated from the fit using Equation 6. Values in parentheses were held constant for fitting to insure fit convergence.

Table SIV. Exponential + Stretched Exponential Parameters for 5 mol % PhSeCN in BZP

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	β	$\langle \tau_2 \rangle$ (ps)
275	0.23 ± 0.02	8.0 ± 0.8	0.55 ± 0.03	131 ± 9	0.75 ± 0.04	213 ± 25
270	0.15 ± 0.02	7.2 ± 0.4	0.65 ± 0.02	151 ± 9	0.64 ± 0.03	332 ± 35
265	0.15 ± 0.01	8.2 ± 0.4	0.67 ± 0.02	247 ± 9	0.62 ± 0.02	566 ± 40
260	0.15 ± 0.02	7.8 ± 0.8	0.64 ± 0.02	533 ± 30	0.59 ± 0.04	1370 ± 180
254	0.15 ± 0.01	8.8 ± 0.7	0.81 ± 0.01	1182 ± 39	0.67 ± 0.04	2350 ± 220
248	0.16 ± 0.01	9.1 ± 2.1	0.82 ± 0.01	7410 ± 1150	(0.70)	13700 ± 2100

Table SV. Exponential + Stretched Exponential Parameters for 2 mol % FlSeCN in BZP

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	β	$\langle \tau_2 \rangle$ (ps)
277	0.16 ± 0.02	8.2 ± 1.5	0.64 ± 0.02	240 ± 13	0.87 ± 0.04	257 ± 26
270	0.18 ± 0.01	7.6 ± 0.9	0.63 ± 0.02	409 ± 18	0.73 ± 0.03	498 ± 42
265	0.18 ± 0.02	6.1 ± 1.2	0.61 ± 0.01	636 ± 22	0.74 ± 0.03	765 ± 57

Table SVI. Exponential + Stretched Exponential Parameters for 5 mol % PhSeCN in OTP

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	β	$\langle \tau_2 \rangle$ (ps)
315	0.33 ± 0.02	7.1 ± 0.4	0.40 ± 0.02	166 ± 11	0.79 ± 0.05	189 ± 26
310	0.19 ± 0.01	6.6 ± 0.4	0.54 ± 0.02	179 ± 14	0.48 ± 0.02	383 ± 47
305	0.28 ± 0.03	7.1 ± 0.9	0.54 ± 0.03	378 ± 46	0.68 ± 0.08	496 ± 115
300	0.24 ± 0.01	9.5 ± 0.6	0.59 ± 0.01	1300 ± 60	(0.50)	2600 ± 121
295	0.30 ± 0.02	8.1 ± 0.3	0.56 ± 0.03	1010 ± 130	0.40 ± 0.04	3430 ± 770
290	0.20 ± 0.01	7.0 ± 0.2	0.69 ± 0.01	4090 ± 490	0.47 ± 0.04	9450 ± 2000

Section S4. Synthesis of 2-Selenocyanatofluorene (FlSeCN)

2-Aminofluorene was purchased from TCI America and used as received. All other chemicals were purchased from Sigma Aldrich and used as received.

Following analogous procedures published by McCulla *et al.*[1] and the Fayer lab,[2] the amine (1.09 g, 6 mmol) was dissolved in 1 mL of warmed 30% sulfuric acid. The solution was cooled to 0 ºC with an ice bath. While under magnetic stirring, sodium nitrite (500 mg, 7.2 mmol) dissolved in 5 mL of DI water was added to the solution gradually, to keep the temperature of the reaction under 7 ºC. A saturated sodium acetate solution was added dropwise to reach a pH of ~6. Potassium selenocyanate (864 mg, 6 mmol) was added dropwise to the reaction, upon which red-brown precipitate was formed. The reaction was allowed to stir for about 1 hour. The solution was extracted with hexanes and washed twice in a separatory funnel with DI water. The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated with vacuum filtration. The solid was purified with silica column chromatography using 5% ethyl acetate in hexanes as the eluent. 2-selenocyanatofluorene was obtained as the desired product (100 mg, .37 mol, 6% yield) as a yellow powder.

FT-IR of FlSeCN in CCl_4 shows the expected narrow peak at 2158 cm^{-1} characteristic of molecular selenocyanates. ^{1}H NMR (Varian Inova 300 MHz, chloroform-*d*) δ ppm 7.87 (s, 1 H) 7.82 (m, 2 H) 7.67 (d, J = 7.8 Hz, 1 H) 7.60 (d, J = 6.6 Hz, 1 H) 7.42 (qd, J = 6.6, 2.1 Hz, 2 H) 3.96 (s, 2 H).

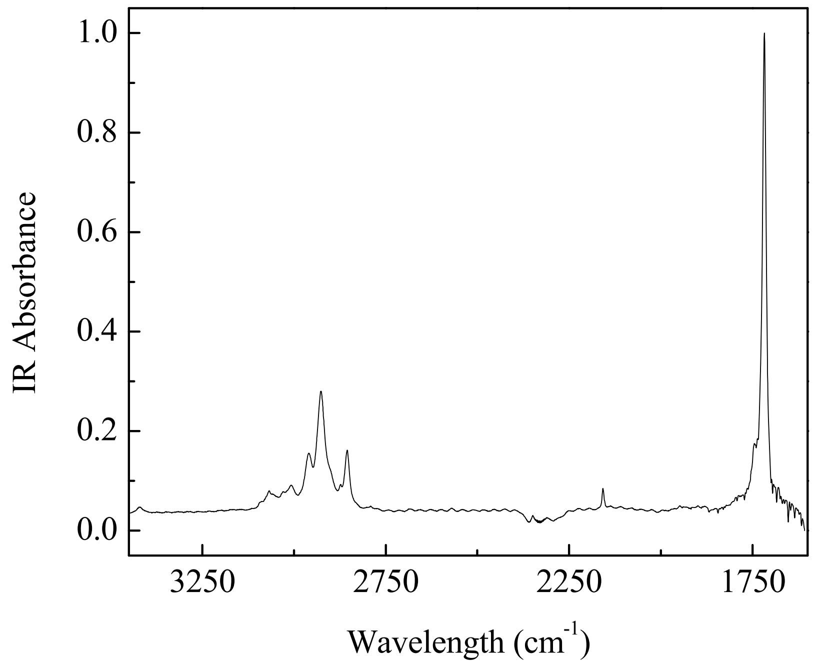

Figure S2. FT-IR of FlSeCN in CCL_4.

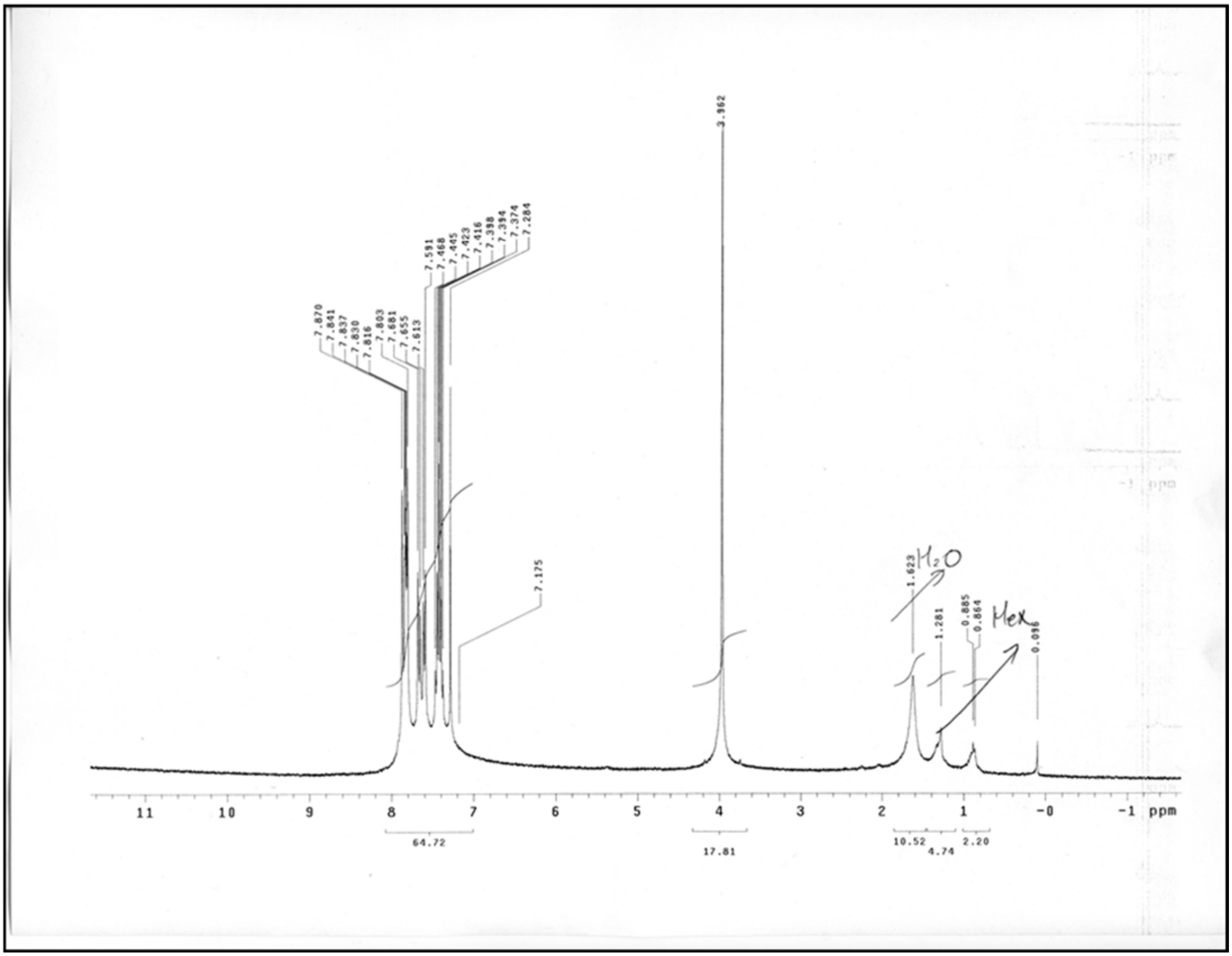

Figure S3. [1]H NMR of FlSeCN in $DCCl_3$.

References

1. R. D. McCulla and W. S. Jenks, J. Am. Chem. Soc. **126**, 16058-16065 (2004).

2. K. P. Sokolowsky, H. E. Bailey and M. D. Fayer, J. Chem. Phys. **141**, 1-12 (2014).