Which probes can report intrinsic dynamic heterogeneity of a glass forming liquid?

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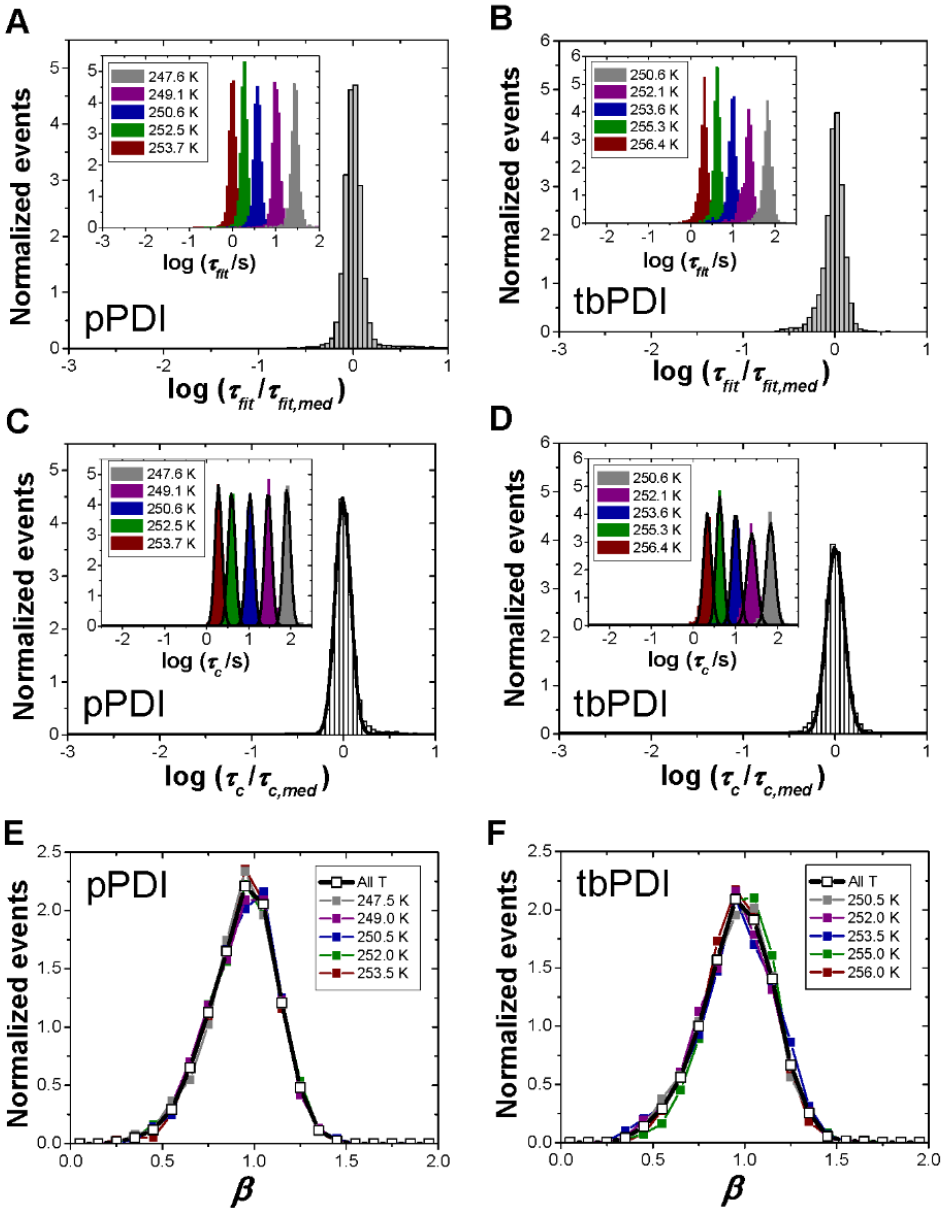

Fig. S1. Single molecule (left) pPDI and (right) tbPDI rotational relaxation data in *o*-terphenyl used also in Figs. 1 and 2 and detailed in Tables S1 and S2. Trajectory lengths are 264 $\tau_{fit,con}$ and 227 $\tau_{fit,con}$ for pPDI and tbPDI, respectively. (**A**, **B**) temperature-combined τ_{fit} histograms; insets are τ_{fit} distributions for each temperature interrogated. (**C**, **D**) temperature-combined τ_c histograms; insets are τ_c distributions for each temperature interrogated. Lines are Gaussian fits to the data and the temperature-combined FWHM for pPDI is 0.20 while that for tbPDI is 0.23. (**E**, **F**) β distributions for each measured temperature. Lines are guides to the eye.

Table S1. Temperature dependence (264 $\tau_{fit,con}$ trajectory length dataset) of pPDI in *o*-terphenyl

	247.6 K	249.1 K	250.6 K	252.5 K	253.7 K	Combined
Number of molecules	1152	1052	1371	1280	1545	6400
Median τ_c (sec)	82.01	29.78	10.79	4.02	1.93	1
Median τ_{fit} (sec)	77.49	27.68	10.29	3.78	1.84	1
Median β	0.95	0.95	0.96	0.95	0.95	0.95
Median trajectory length (τ_{fit})	253	228	247	244	259	264
Median frame rate (frames/τ_{fit})	18.4	19.2	18.4	18.9	18.4	18.6
FWHM (τ_c distribution)	0.20	0.20	0.21	0.20	0.19	0.20
β_{QE}	0.93	0.94	0.94	0.93	0.94	0.93

Table S2. Temperature dependence (227 $\tau_{fit,con}$ trajectory length dataset) of tbPDI in *o*-terphenyl

	250.6 K	252.1 K	253.6 K	255.3 K	256.4 K	Combined
Number of molecules	1417	1302	1080	1019	1235	6053
Median τ_c (sec)	68.22	24.02	10.10	4.21	2.09	1
Median τ_{fit} (sec)	65.26	23.10	9.66	4.14	2.04	1
Median β	0.97	0.95	0.97	0.99	0.96	0.97
Median trajectory length (τ_{fit})	200	224	209	241	217	227
Median frame rate (frames/τ_{fit})	20.6	19.3	20.8	20.7	20.6	20.3
FWHM (τ_c distribution)	0.24	0.25	0.22	0.20	0.22	0.23
β_{QE}	0.95	0.95	0.97	0.98	0.95	0.96

Table S3. Trajectory length dependence of pPDI and tbPDI in *o*-terphenyl

	pPDI						tbPDI	
Median trajectory ($\tau_{fit,con}$)	91	141	215	264	668	838	227	366
Temperature (K)	251.8	251.9	251.9	multiple (Table S1)	251.5	251.8	multiple (Table S2)	254.8
Number of molecules	2250	2055	1924	6400	1695	1233	6053	1235
Median τ_c (sec)	5.69	4.37	3.52	1	3.71	3.90	1	4.48
Median τ_{fit} (sec)	5.15	3.89	3.24	1	3.37	3.66	1	4.21
Median β	0.97	0.91	0.93	0.95	0.85	0.89	0.97	0.91
Median frame rate (frames/τ_{fit})	25.8	19.4	16.2	18.6	16.9	18.3	20.3	21.1
FWHM (τ_c distribution)	0.47	0.34	0.24	0.20	0.16	0.14	0.23	0.08
β_{QE}	0.90	0.89	0.91	0.93	0.85	0.88	0.96	0.95

Simulations of Homogeneous Rotational Diffusion

Simulations of three-dimensional homogeneous rotational diffusion were carried out so that effects of finite trajectory length on measured β distribution (independent of dynamic heterogeneity) could be assessed. Simulated probe molecules were set to have a diffusion constant, D_r, by rotating a unit vector ϕ through an angle chosen from a Rayleigh distribution of width $\sqrt{2}D_r$. From the simulated trajectories, x-, y-, and z-components of the dipole orientation were used to calculate orthogonal intensities. For this calculation, wide-field excitation and detection with an NA = 0.75 objective, analogous to our experimental microscope configuration, were assumed. As in the experiments, linear dichroism was calculated from the two orthogonal intensities. For consistency with experimental data, 30% Gaussian noise was added relative to the mean signal. The diffusion constant was chosen such that $\tau_{fit} = 100$, and each trajectory length simulated consisted of 500 molecules. For each simulated probe, an autocorrelation was computed and fit to a stretched exponential, and all data analysis was performed as for experimental data.

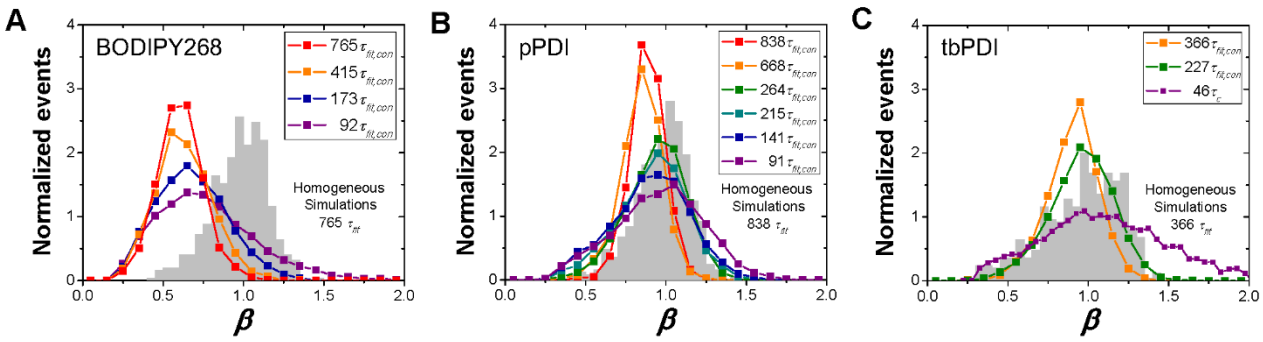

Fig. S2. Distributions of single molecule β values with varying median trajectory length for (**A**) BODIPY268, (**B**) pPDI, and (**C**) tbPDI probes in *o*-terphenyl, also shown in Fig. 3 in the main text. Trajectory lengths are expressed in terms of $\tau_{fit,con}$, which is the median τ_{fit} value of the longest trajectory length data set, where the τ_{fit} value has converged and shows no additional trajectory length dependence. Distributions are normalized by the area under the curve. Grey histograms are results from simulations described above of length (**A**) 765 τ_{fit}, (**B**) 838 τ_{fit}, and (**C**) 366 τ_{fit}.

Inverse Laplace Transform (ILT) – built Distribution Construction

As described in the Supporting Material of Reference 1, an inverse Laplace transform of a stretched exponential function can be mathematically written as, $e^{-(t/\tau_{fit})^{\beta}} = \int_{-\infty}^{\infty} P(\log\tau;\tau_{fit},\beta)\cdot e^{-t/\tau} d\log\tau$, which states that a stretched exponential function is a sum of exponential functions with $P(\log\tau;\tau_{fit},\beta)$ being the normalized probability density function of exponential relaxation times.

When written in reduced rates, $s = \lambda/\lambda_0 = \tau_{fit}/\tau$, the inverse Laplace transform of a stretched exponential function converts to $e^{-(\lambda_0\cdot t)^{\beta}} = \int_0^{\infty} P(s,\beta)\cdot e^{-s\cdot\lambda_0\cdot t} ds$, and various numerical expressions for the probability density function can be found in the literature, including expressions such as $P(s,\beta) = \frac{1}{\pi}\int_0^{\infty} e^{-u^{\beta}\cdot\cos(\pi\beta/2)}\cdot\cos\left[su - u^{\beta}\cdot\sin(\pi\beta/2)\right] du$ and $P(s,\beta) = \frac{1}{\pi}\int_0^{\infty} e^{-su}\cdot e^{-u^{\beta}\cdot\cos(\pi\beta)}\cdot\sin\left[u^{\beta}\cdot\sin(\pi\beta)\right] du$.[2,3] From these expressions, the normalized probability density function on a logarithm scale,

$P(\log\tau;\tau_{fit},\beta) = P(s,\beta)\cdot s\cdot\ln 10$, can be generated for any τ_{fit} and β values.

In practice, both numerical expressions for $P(s,\beta)$ suffer from convergence problems at high and low reduced rates, which makes it difficult to compute distributions directly from the measured τ_{fit} and β values. Instead, we built a set of reference distributions for $\tau_{fit} = 1$ and β ranging from 0.20 to 0.99 in 0.01 steps and used these reference distributions to approximate the distribution for any given τ_{fit} and β value. A set of reference distributions without convergence problems were built using an iterative process[4] of correcting generated $P(\log\tau; \tau_{fit}, \beta)$ distributions and fitting stretched exponential functions constructed by the corrected distributions until the reconstructed stretched exponential functions produced fitted β values that were within 0.3% error relative to the original β values.

ILT-built distributions were constructed from this set of reference ILT distributions by using actual experimental sets of fitted τ_{fit} and β values from single molecule ACFs. For a given experimental data set of single molecule ACFs, the fitted set of τ_{fit} and β values was obtained and from the fitted β value, a reference distribution was chosen from the reference ILT distribution and shifted in time by the fitted τ_{fit} value. This process was repeated for all single molecule ACFs, and the distributions were added and normalized by the area under the distribution to produce the *ILT-built* distribution for each data set.

References

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