Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Femtosecond to nanosecond studies of octupolar molecules and their quadrupolar and dipolar analogues

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Table S1. Quantum Yield (Φ), lifetime (τ), radiative lifetime (τ_{rad}), excited state decay rate (k), radiative decay rate (k_{rad}) and non-radiative decay rate (k_{nrad}) of **1T** and **2T** in various solvents.

Compound	Solvent	Φ	τ (ns)	τ_{rad} (ns)	k (10^9 s^{-1})	k_{rad} (10^9 s^{-1})	k_{nrad} (10^9 s^{-1})
1T	n-Hexane	0.91	1.09	1.20	0.92	0.83	0.09
	Toluene	0.88	1.27	1.44	0.79	0.69	0.10
	Chloroform	0.78	1.60	2.05	0.62	0.49	0.13
	Tetrahydrofuran	0.67	1.78	2.66	0.56	0.37	0.19
	Acetone	0.54	2.41	4.46	0.41	0.22	0.19
	Acetonitrile	0.44	2.86	6.50	0.35	0.15	0.20
2T	n-Hexane	0.46	1.40	3.04	0.71	0.33	0.38
	Toluene	0.69	1.65	2.39	0.61	0.42	0.19
	Chloroform	0.53	1.97	3.72	0.51	0.27	0.24
	Tetrahydrofuran	0.50	2.41	4.82	0.41	0.21	0.20
	Acetone[a]	0.31					
	Acetonitrile[a]	0.20					

[a] In Acetone and Acetonitrile, **2T** exhibits bi-exponential dynamics and therefore, the parameters τ_{rad}, k , k_{rad} and k_{nrad} are not calculated.

Table S2. Fitting parameters of the TCSPC fluorescence dynamics of **1L, 1Q, 2L**, and **2Q** in various solvents.

Compound	Solvent	A_1	τ_1 (ns)	A_2	τ_2 (ns)
1L	*n*-Hexane			1	1.09
	Toluene			1	1.79
	Chloroform			1	2.48
	Tetrahydrofuran			1	2.68
	Acetone			1	3.34
	Acetonitrile			1	3.36
1Q	*n*-Hexane			1	1.12
	Toluene			1	1.28
	Chloroform			1	1.73
	Tetrahydrofuran			1	1.91
	Acetone			1	2.69
	Acetonitrile			1	2.96
2L	*n*-Hexane			1	1.33
	Toluene			1	1.52
	Chloroform			1	1.98
	Tetrahydrofuran			1	2.15
	Acetone			1	2.64
	Acetonitrile			1	2.96
2Q	*n*-Hexane			1	1.36
	Toluene			1	1.60
	Chloroform			1	2.10
	Tetrahydrofuran			1	2.35
	Acetone			1	2.03
	Acetonitrile	0.97	1.13	0.03	2.86

Table S3. Fitting parameters of the fs dynamics of the compounds in TOL and THF. τ_3 is determined by the TCSPC measurements and is a fixed parameter in the fitting.

Compound/Solvent	Wavelength (nm)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
1L/Toluene	415			-0.07	4.5	0.91	1790
	430			-0.14		0.91	
	460			-0.24		0.97	
	490			-0.38		0.99	
1Q/Toluene	415			-0.20	3.0	0.94	1280
	430			-0.15		0.97	
	460			-0.20		0.98	
	490			-0.32		0.96	
1T/Toluene	415			-0.13	2.7	0.82	1270
	430			-0.13		0.86	
	460			-0.18		0.86	
	490			-0.28		0.85	
1L/THF	440	-0.26	0.45	0.63	2.5	0.30	2680
	470	-0.51		0.35		0.77	
	500	-0.28		-0.36		0.91	
	530	-0.40		-0.64		0.90	
1Q/THF	430	0.12	0.51	0.70	2.5	0.33	1910
	460	-0.41		0.28		0.84	
	490	-0.31		-0.31		0.96	
	520	-0.10		-0.57		1.00	
1T/THF	430	0.09	0.48	0.62	2.6	0.40	1780
	460	-0.43		0.25		0.86	
	490	-0.23		-0.33		0.96	
	520	-0.10		-0.63		0.90	
2L/Toluene	435			0.35	4.8	0.59	1520
	455			0.06		0.89	
	485			-0.21		0.94	
	515			-0.32		0.92	
2Q/Toluene	445			0.43	4.2	0.58	1600
	465			0.06		0.93	
	495			-0.08		0.96	
	525			-0.22		0.96	
2T/Toluene	445			0.36	2.6	0.51	1650
	465			0.05		0.80	
	495			-0.12		0.93	
	525			-0.20		0.93	
2L/THF	435	0.93	0.66	0.23	2.8	0.06	2150
	465	0.32		0.49		0.35	
	495	-0.24		0.20		0.81	
	525	-0.34		-0.24		0.89	
	555	-0.27		-0.50		0.86	
2Q/THF	445	0.87	0.65	0.28	2.6	0.09	2350
	475	0.16		0.57		0.38	
	505	-0.29		0.41		0.70	
	535	-0.42		-0.03		0.88	
	565	-0.53		-0.26		0.82	
2T/THF	445	0.62	0.77	0.33	3.4	0.18	2410
	475	0.08		0.48		0.47	
	505	-0.29		0.34		0.74	
	535	-0.45		-0.02		0.91	
	565	-0.68		-0.23		1.00	

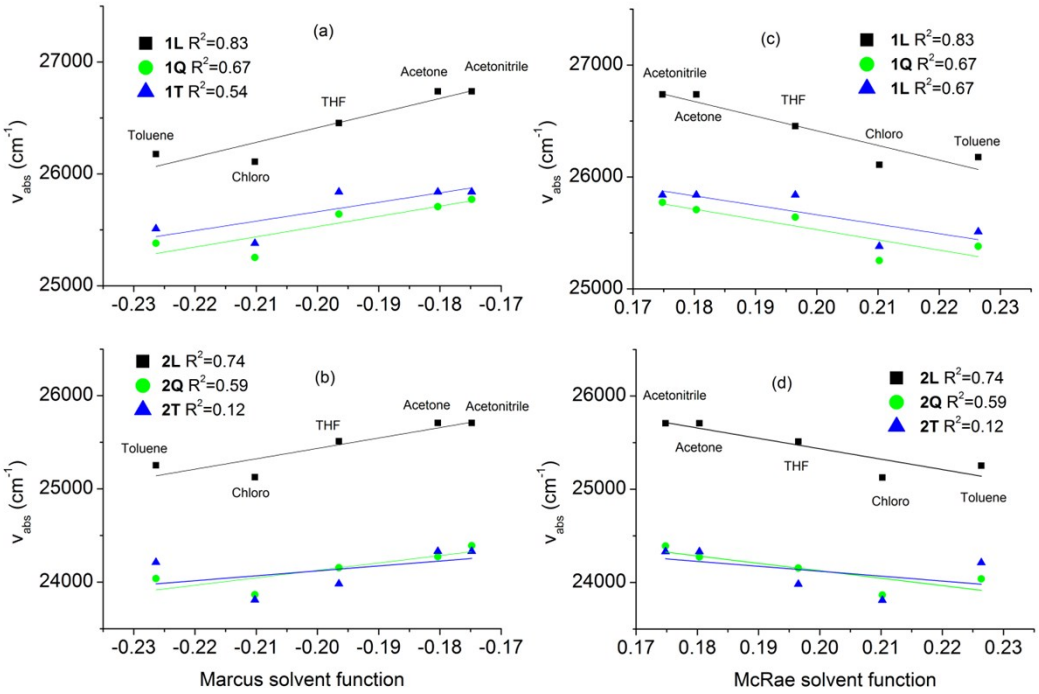

Figure S1. Plot of the solvent shift of absorption of the compounds in series **1** and **2** as a function of the Marcus solvent function $(1-n^2)/(2n^2+1)$ (a) and the McRae solvent function $(n^2-1)/(2n^2+1)$.

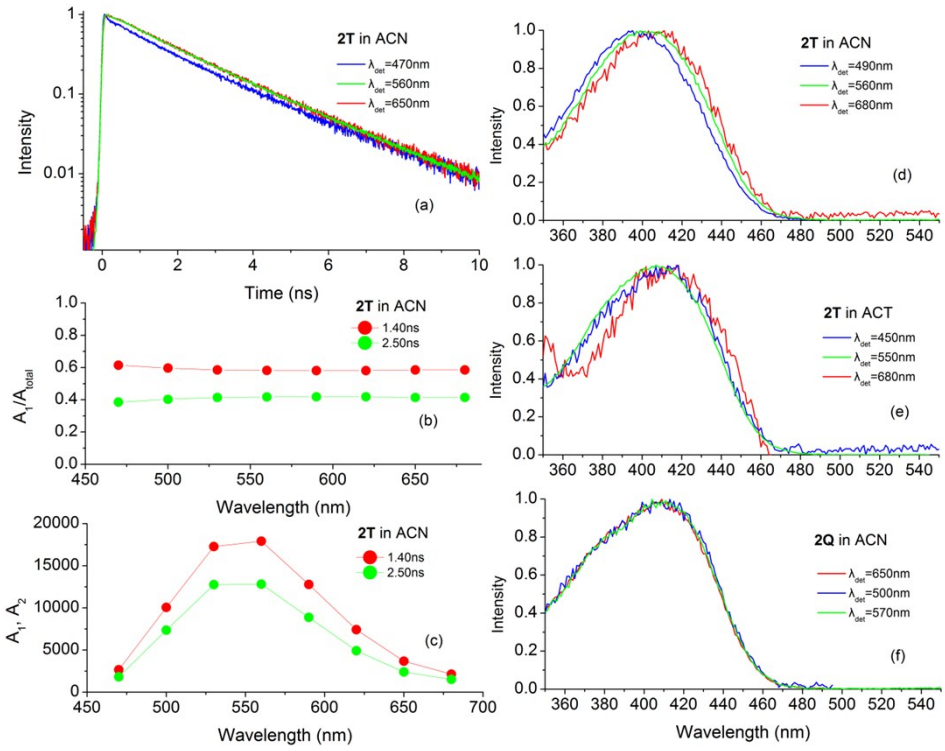

Figure S2. TCSPC decays of **2T** in ACN at various detection wavelengths (a), normalized and non-normalized pre-exponential factors obtained after global fitting analysis, as a function of emission wavelength (b) and (c), excitation spectra of **2T** in ACN (d) and ACT (e) and of **2Q** in ACN (f).

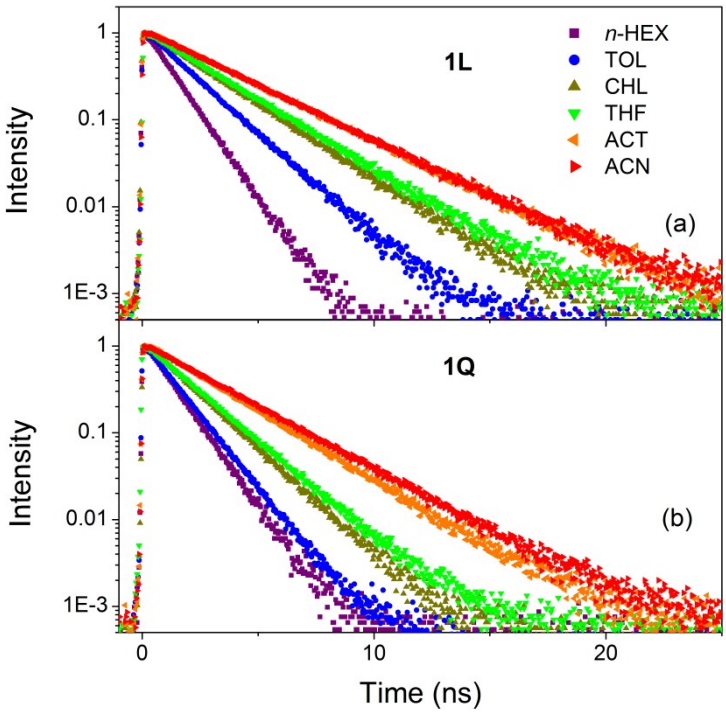

Figure S3. TCSPC fluorescence dynamics of **1L** (a) and **1Q** (b) in various solvents. Excitation at 400 nm, detection at the peaks of the fluorescence spectra.

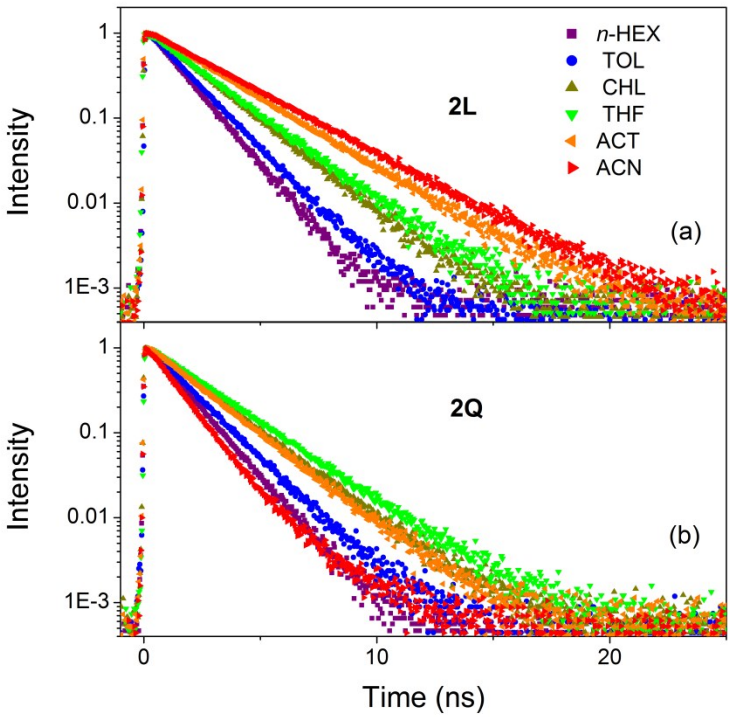

Figure S4. TCSPC fluorescence dynamics of **2L** (a) and **2Q** (b) in various solvents. Excitation at 400 nm, detection at the peaks of the fluorescence spectra.

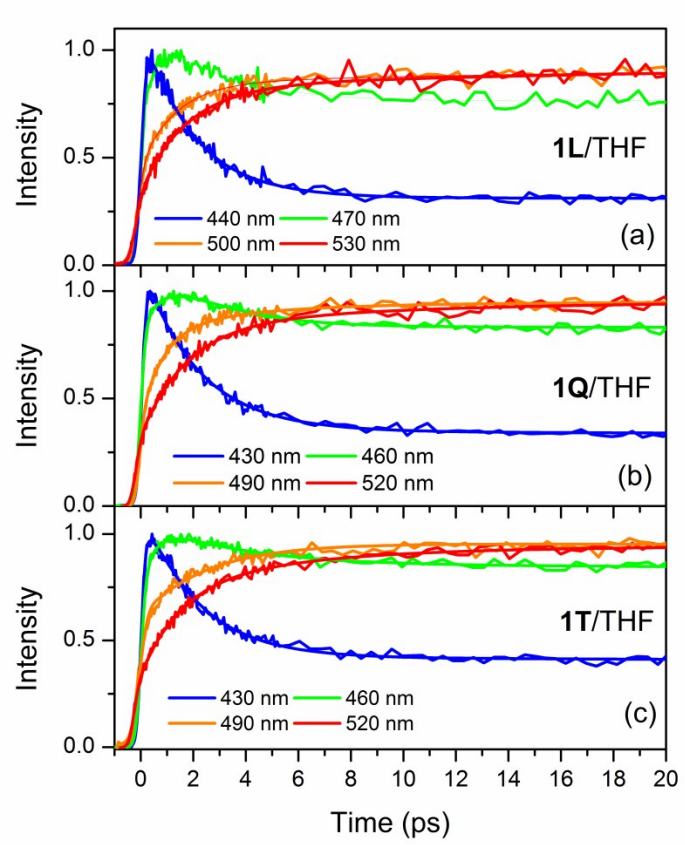

Figure S5. FU fluorescence dynamics of **1L**, **1Q** and **1T** in THF. Excitation at 400 nm, detection at various wavelengths across the fluorescence spectrum indicated in the figures.

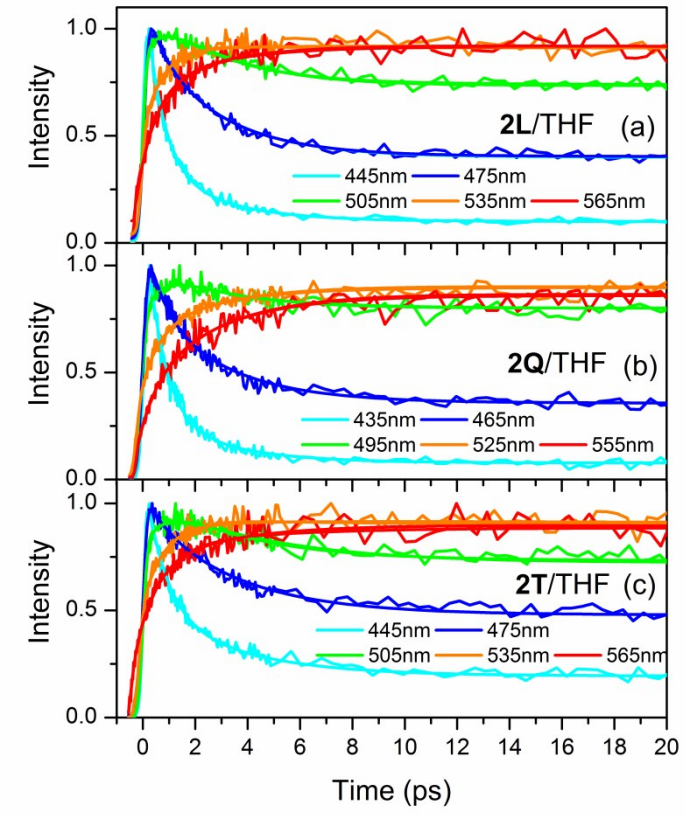

Figure S6. FU fluorescence dynamics of **2L**, **2Q**, and **2T** in THF. Excitation at 400 nm, detection at various wavelengths across the fluorescence spectrum indicated in the figures.

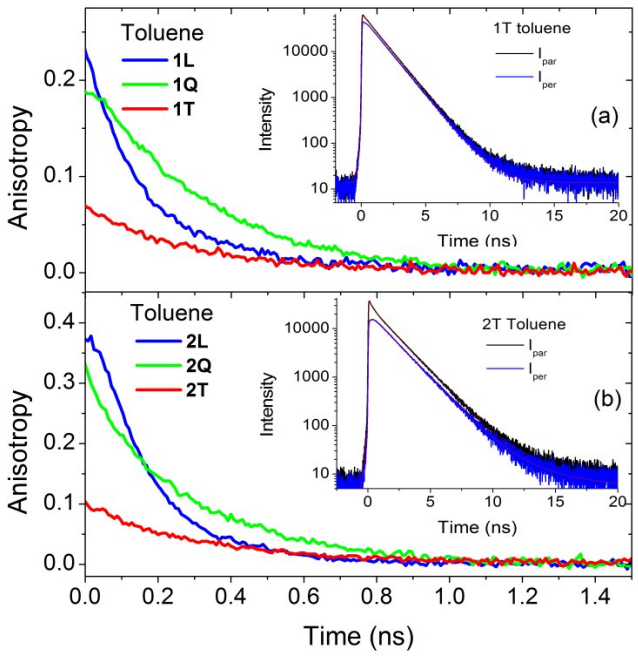

Figure S7. Time dependent anisotropy measured by means of TCSPC for the compounds in series **1** (a) and **2** (b) in toluene. The insets show the fluorescence decays and their fitting curves, with polarization parallel and perpendicular to the polarization plane of the excitation beam for **1T** (a) and **2T** (b) in TOL. Excitation 400 nm, detection at the peaks of the fluorescence spectra. The fluorescence intensity curves are shown without G-factor correction.

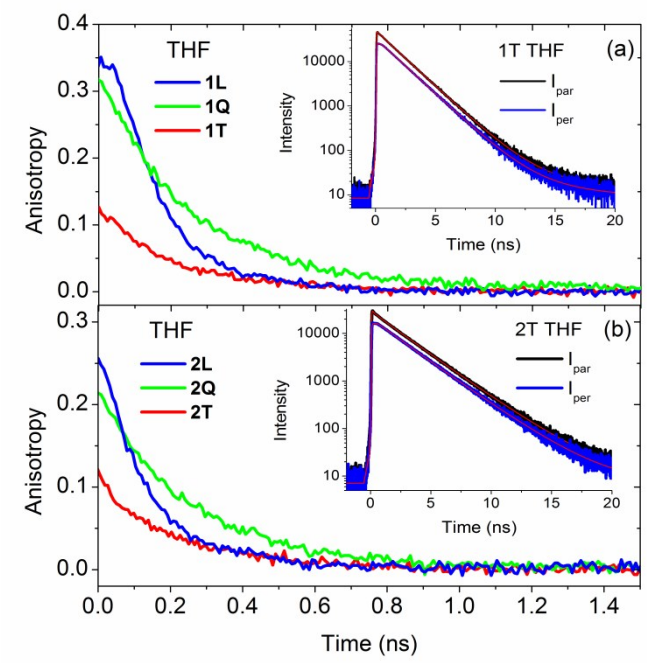

Figure S8. Time dependent anisotropy measured by means of TCSPC for the compounds in series **1** (a) and **2** (b) in THF. The insets show the fluorescence decays and their fitting curves, with polarization parallel and perpendicular to the polarization plane of the excitation beam for **1T** (a) and **2T** (b) in THF. Excitation 400 nm, detection at the peaks of the fluorescence spectra. The fluorescence intensity curves are shown without G-factor correction.

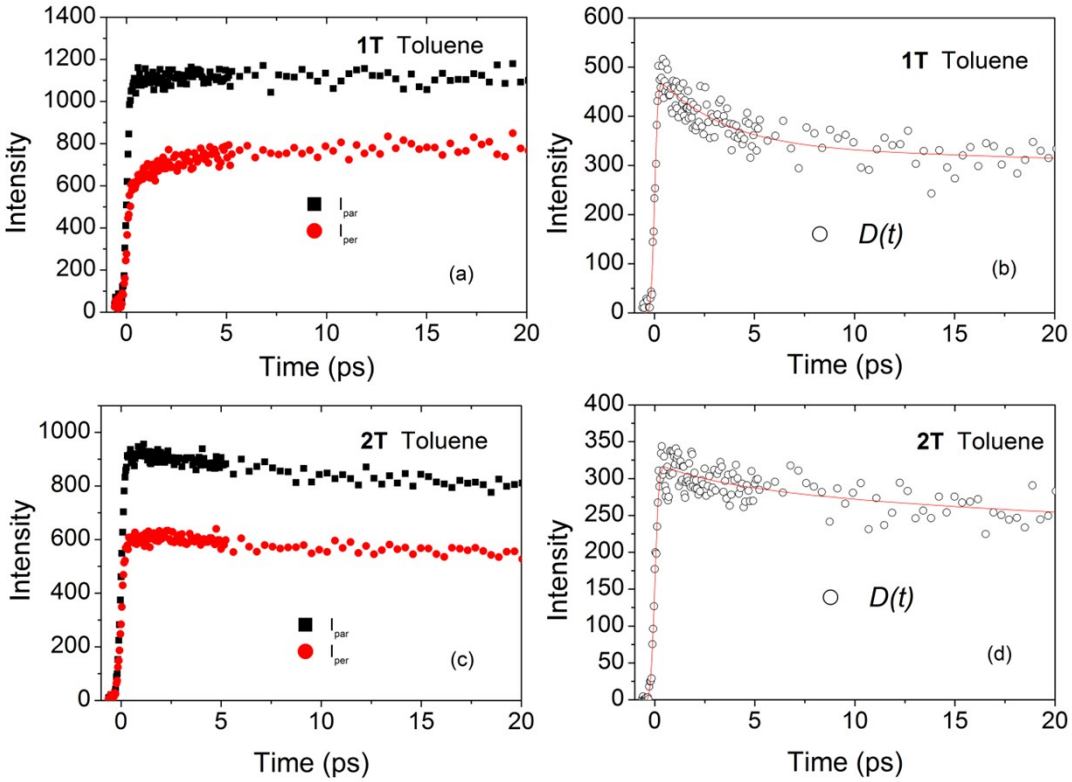

Figure S9. FU fluorescence dynamics polarized parallel and perpendicular to the polarization plane of the excitation beam for **1T** (a) and **2T** (c) in TOL. Figures (b) and (d) show the difference factor *D(t)* and its fitting curve.

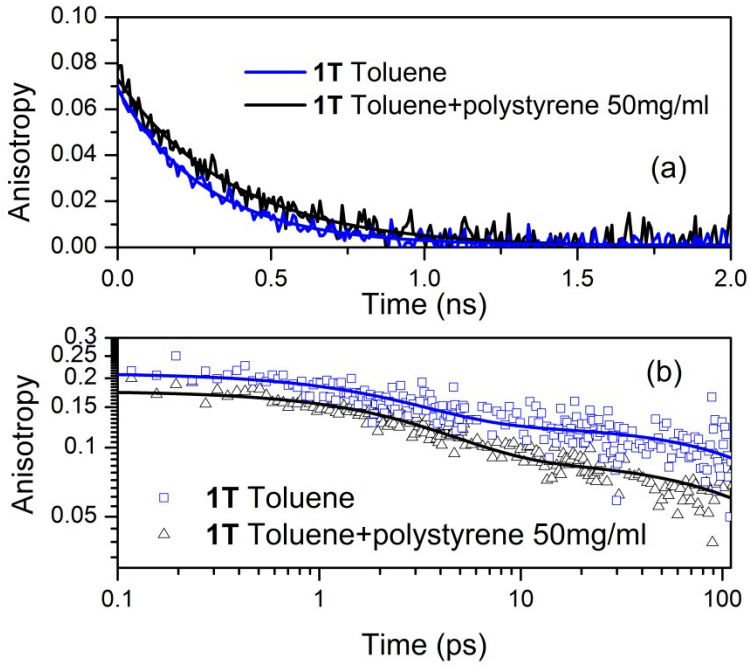

Figure S10. Time dependent anisotropy measured by means of TCSPC (a) and FU (b) for **1T** in TOL with and without polystyrene.