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

Supplementary information

Cyano-tryptophans as dual infrared and fluorescence spectroscopic labels to assess structural dynamics in proteins

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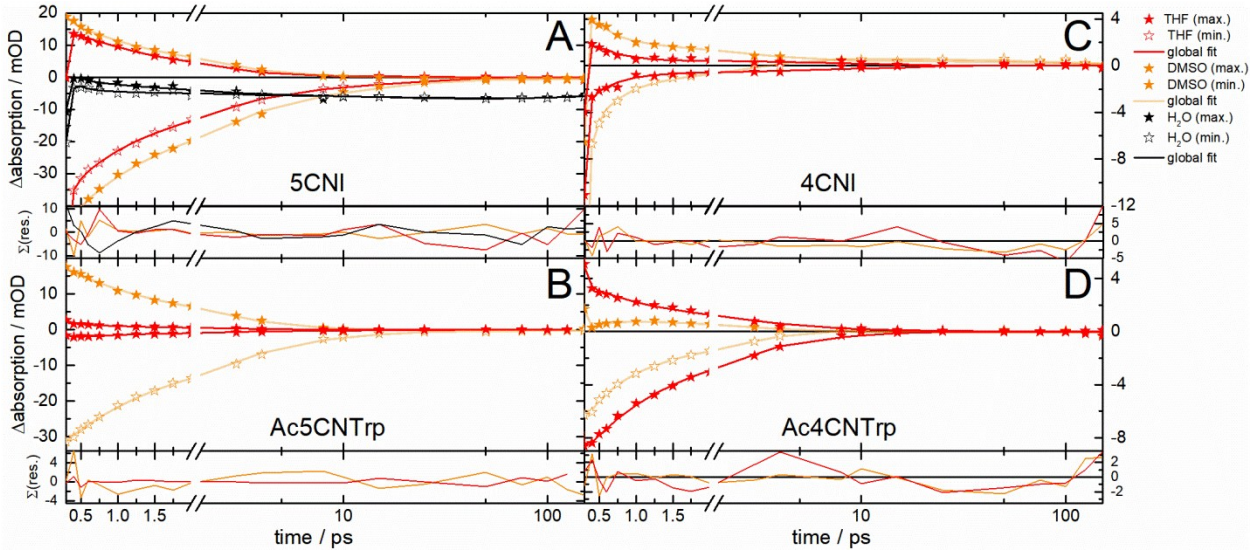

Figure S1. Ultrafast time-resolved infrared data. The raw data and their (global) fits are shown. The stars represent the collected data points of the maximum and minimum difference signal, the continuous lines the fits. The time axis is linear up to 2 ps, logarithmic thereafter. The small panel under each main panel shows the residuals of the fits, i.e. the sum of (data-fit) for all collected time traces.

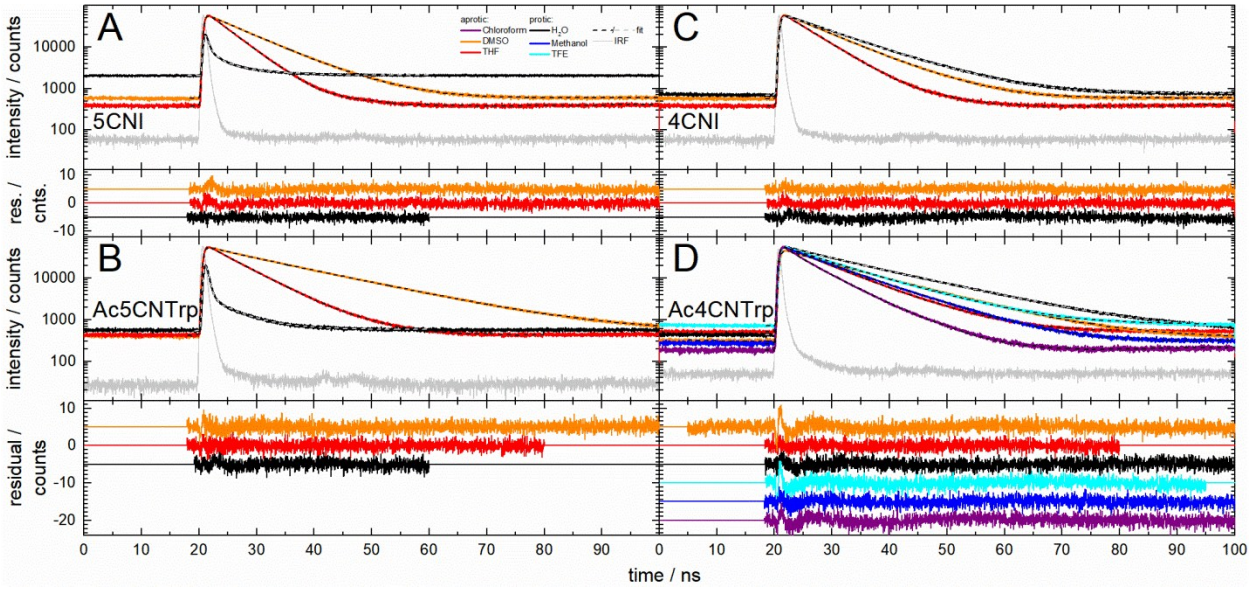

Figure S2. Raw data from the measurements shown in Figure 6. In addition, the corresponding residuals to the multi-exponential fits are shown (see Table 3 for the corresponding lifetimes).

Table S1. Extension of table 1 with errors of the frequencies and widths, determined with lorentzian fits of the measured data.

Compound		5CNI		Ac5CNTrp		4CNI				Ac4CNTrp	
Solvent	Dielectric constant ε[37]	ν_c / cm^{-1}	fwhm / cm^{-1}	ν_c / cm^{-1}	fwhm / cm^{-1}	ν_c peak 1 / cm^{-1}	fwhm / cm^{-1}	ν_c peak 2 / cm^{-1}	fwhm / cm^{-1}	ν_c / cm^{-1}	fwhm / cm^{-1}
Aprotic											
PCE	2.27	2226.49 (0.05)	9.1 (0.2)	2218.8 (0.3)	11.8 (0.8)	2218.1 (0.2)	12.5 (0.6)	2232.55 (0.08)	9.8 (0.3)		
Chloroform	4.81	2224.40 (0.07)	11.9 (0.3)	2218.67 (0.08)	15.1 (0.04)	2216.8 (0.2)	11.1 (0.4)	2231.9 (0.1)	12.1 (0.4)	2218.30 (0.07)	9.8 (0.3)
THF	7.52	2220.64 (0.03)[a]	7.88 (0.09)	2220.16 (0.03)[b]	7.5 (0.1)	2215.27 (0.07)[c]	9.0 (0.3)	2229.55 (0.08)[c]	10.4 (0.3)	2216.46 (0.04)	6.6 (0.2)
DCM	8.93	2223.26 (0.07)	11.5 (0.3)	2218.91 (0.07)	14.9 (0.3)	2216.7 (0.3)[c]	13.0 (0.7)	2230.5 (0.2)[c]	11.6 (0.6)	2218.20 (0.05)	10.5 (0.2)
Acetonitrile	36.64	2221.14 (0.06)	10.0 (0.2)	2221.55 (0.04)	9.0 (0.2)	2215.3 (0.1)	8.6 (0.4)	2230.3 (0.2)	13.8 (0.4)	2217.39 (0.08)	9.5 (0.4)
DMF	38.25	2218.11 (0.03)	8.33 (0.09)			2213.97 (0.07)[c]	9.6 (0.2)	2229.1 (0.2)[c]	11.2 (0.5)		
DMSO	47.24	2217.18 (0.03)	9.2 (0.2)	2216.96 (0.04)	8.9 (0.2)	2213.60 (0.08)[c]	10.5 (0.3)	2229.1 (0.2)[c]	11.8 (0.6)	2214.27 (0.05)	7.4 (0.2)
Protic											
HFIP	16.70	2224.6 (0.6)/2242.5 (0.2)	26 (2) /20.9 (0.5)			2223.1 (0.5)	25 (2)	2246.0 (0.2)	14.2 (0.4)		
TFE	27.68	2232.3 (0.2)	23.0 (0.5)			2220.0 (0.2)[c]	13.2 (0.6)	2239.77 (0.09)[c]	15.3 (0.4)	2224.88 (0.09)	13.0 (0.3)
Methanol	33.0	2224.28 (0.07)	13.3 (0.3)			2217.30 (0.09)[c]	10.2 (0.3)	2233.32 (0.09)[c]	12.1 (0.3)	2219.47 (0.06)	8.6 (0.2)
H_2O	80.2	2223.9(0.1)[a]	12.7 (0.4)	2225.80 (0.05)[b]	13.4(0.2)	2218.9 (0.2)	12.4 (0.5)	2235.1 (0.2)	11.9 (0.5)	2221.13 (0.07)	11.6 (0.3)

Table S2. Reproduction of Table 3, compared to literature data of similar compounds. The numbering of the references corresponds to those given in the main paper. The fluorescence properties are determined at given excitation and emission wavelengths. The quantum yield (QY) and lifetimes are compared to literature values (data in a single row represents data from the same reference). The listed lifetimes are determined via fit to a sum of exponentials, with the standard deviation given in brackets, the fractional intensity of each component in percent, the intensity weighted average lifetime,and the goodness-of-fit parameter χ^2. All lifetimes collected in this work are marked with an asterix (∗) at the χ^2 value.

Compound	Solvent	QY	Exc. / nm, Em. / nm	Lifetimes(error)/ns \ fractional intensity/%			*Intensity weighted average lifetime (error) / ns*	χ^2
				τ_1	τ_2	τ_3		
5CNI	THF	0.11	310, >320			4.08 (0.01)\100	4.08 (0.01)	1.14∗
		0.11[20]	270, 360			4.4\100	4.4	1.15
	DMSO	0.16	310, >320			7.15 (0.02)\100	7.15 (0.02)	1.20∗
		0.16[20]	270, 360			7.1\100	7.1	1.18
	H_2O	<0.01	310, >320	0.240 (0.003)\32	1.83 (0.04)\24	6.6 (0.2)\43	3.39 (0.1)	1.01∗
		0.005[20]	270, 360		0.1\91	0.3\9	0.1	1.19
Ac5CNTrp	THF	0.09	310, >320		2.02 (0.01)\4	5.99 (0.02)\96	5.81 (0.02)	1.16∗
	DMSO	0.23	310, >320		3.5 (0.3)\2	14.60 (0.03)\98	14.35 (0.04)	1.16∗
	H_2O	<0.01	310, >320		0.340(0.003)\57	5.25 (0.07)\43	2.47 (0.04)	1.22∗
5CNTrp	THF	0.12[20]	270, 360		2.5\18	5.9\82	5.3	1.07
	DMSO	0.24[20]	270, 360		2.1\21	16.5\79	13.5	1.06
	H_2O	0.01[20]	270, 360		0.4\91	1.6\9	0.5	0.97
4CNI	THF	0.48	310, >320			5.00 (0.01)\100	5.00 (0.01)	1.09∗
			270,>300[5]			5.3\100	5.3	
	DMSO	0.56	310, >320			7.40 (0.02)\100	7.40 (0.02)	1.11∗
			270,>300[5]			7.1\100	7.1	
	H_2O	0.85[5]	270, 270			9.1\100	9.1	
		0.59	310, >320			8.90 (0.02)\100	8.90 (0.02)	1.28∗
		0.78[5]	270, 325					
			270,>300[5]			0.3\100	0.3	
Ac4CNTrp	Chloroform	0.45	310, >320		2.08 (0.05)\5	6.19 (0.02)\95	5.63 (0.03)	1.14∗
	THF	0.44	310, >320		2.60 (0.09)\5	7.89 (0.02)\95	7.64 (0.03)	1.09∗
	DMSO	0.58	310, >320		2.13 (0.09)\6	10.17 (0.03)\94	9.65 (0.04)	1.24∗
	TFE	0.76	310, >320		2,6 (0.1)\5	10.03 (0.02)\95	9.65 (0.02)	1.47∗
	Methanol	0.55	310, >320		2.8 (0.2)\13	9.00 (0,02)\87	8.68 (0.02)	1.21∗
	H_2O	0.76	310, >320		4.4 (0.3)\4	13.90 (0.03)\96	13.5 (0.04)	1.15∗
4CNTrp	H_2O	0.88[5]	270, 325		1.9\5	13.7\95	13.1	
Trp	H_2O	0.13[8]	280					
			295, 320[7]		0.3\16	2.9\84	2.5	1.23

Table S3. Literature parameters describing the solvent in the Kamlet-Taft model.[39]

solvent	α	β	π*
Aprotic			
PCE	0	0	0.28
Chloroform	0.44	0	0.58
THF	0	0.55	0.58
DCM	0.3	0	0.82
Acetonitrile	0.19	0.31	0.75
DMF	0	0.69	0.88
DMSO	0	0.76	1
Protic			
HFIP	1.96	0	0.65
TFE	1.51	0	0.73
Methanol	0.93	0.62	0.6
H_2O	1.17	0.18	1.09

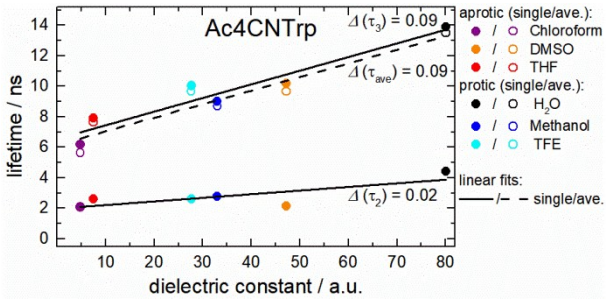

Figure S3. Reproduction of Figure 7, including the intensity-averaged lifetimes (open symbols) and their corresponding fit (dashed line).