

Electronic Supplementary Information for

**Ultrafast photophysics of the cyan fluorescent protein
chromophore in solution**

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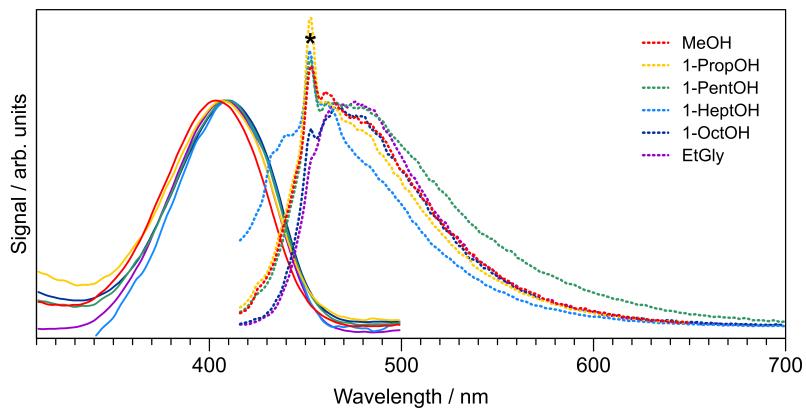


Fig. S1 Absorption (solid lines) and emission (dotted lines) spectra for neutral cyan at room temperature. The emission spectra were recorded following excitation at 400 nm. Starred peaks (*) in emission spectra are Raman scattering artefacts. Spectral maxima are summarised in Table S1.

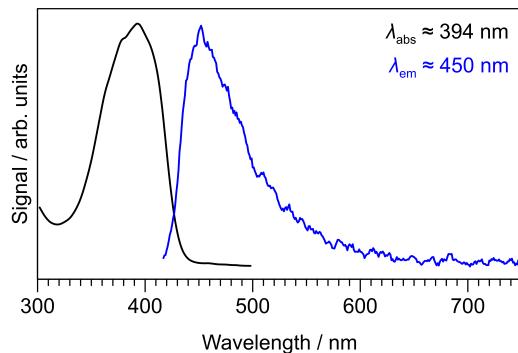


Fig. S2 Absorption (black) and fluorescence emission (blue) spectra for neutral cyan at room temperature in 2-methyltetrahydrofuran, which is a non-protic solvent. The emission spectrum was recorded following excitation at 400 nm.

Table S1 Absorption (λ_{abs}) and emission λ_{em} maxima (and associated Stokes shift ($\Delta\tilde{\nu}$)) of cyan in various solvents, with the corresponding viscosity (η) and polarity (ϵ). Values for viscosity and polarity were taken from the CRC Handbook of Chemistry and Physics, 85th Edition.

Solvent	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}$	$\Delta\tilde{\nu} / \text{cm}^{-1}$	η / cP	ϵ
2-methyltetrahydrofuran	394	450	3158	0.46	7.52
methanol	403	460	3075	0.54	33.0
ethanol	405	459	2905	1.07	25.3
1-propanol	406	460	2891	1.95	20.8
1-pentanol	409	465	2945	3.62	15.1
1-heptanol	410	458	2556	5.81	11.8
1-octanol	410	268	3023	7.29	10.3
ethylene glycol	408	470	3233	16.1	41.4

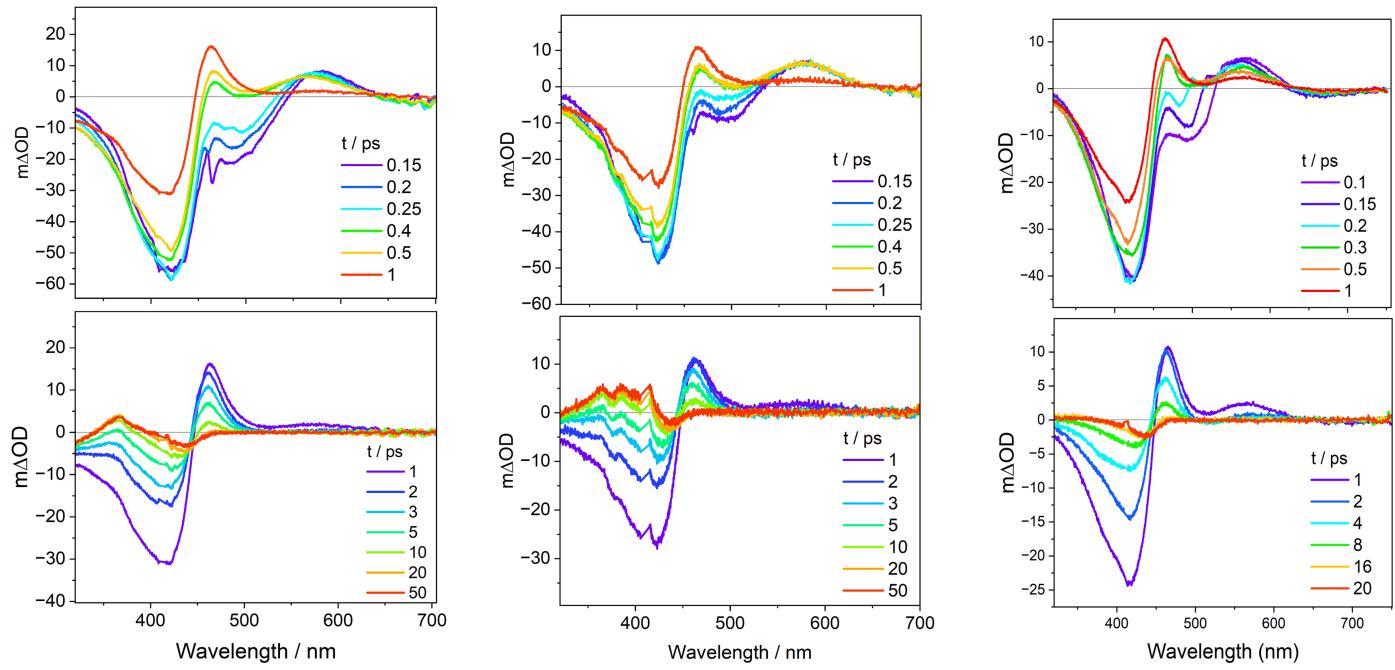


Fig. S3 TA difference spectra for cyan in: (left) butanol, (middle) heptanol, and (right) ethylene glycol. In all cases, TA band D is on the red edge of the ground state bleach. TA spectra were recorded with ≈ 400 nm pump light.

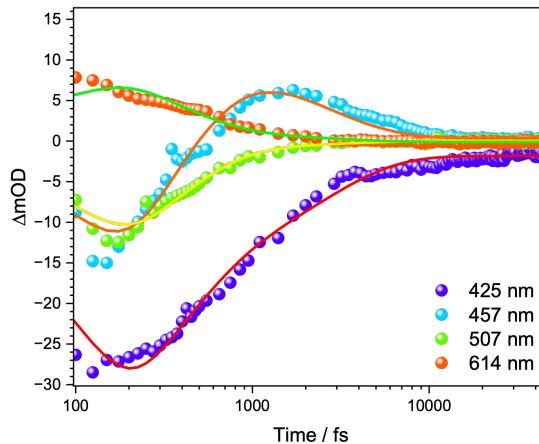
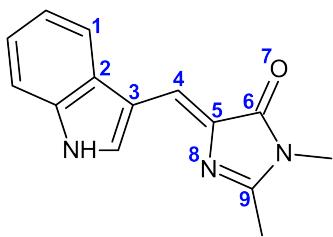


Fig. S4 Experimental (points) and kinetics model from a global fit (traces) for TA spectra of cyan in ethanol at four selected wavelengths corresponding to band features.

Table S2 Bond lengths (r in Å) and angles (θ in °) of cyan at its S_0 , S_1 , and conical intersection (CI) relaxed optimised geometries from MRSF-TDDFT calculations.

	S_0	S_1	CI
$\text{r}(3-4)$	1.432	1.360	1.354
$\text{r}(4-5)$	1.351	1.445	1.443
$\text{r}(5-6)$	1.471	1.410	1.399
$\text{r}(6-7)$	1.208	1.237	1.244
$\theta(3-4-5)$	127.58	123.55	123.75
$\theta(1-2-3-4)$	0.04	1.51	4.77
$\theta(4-5-8-9)$	179.92	174.15	163.98



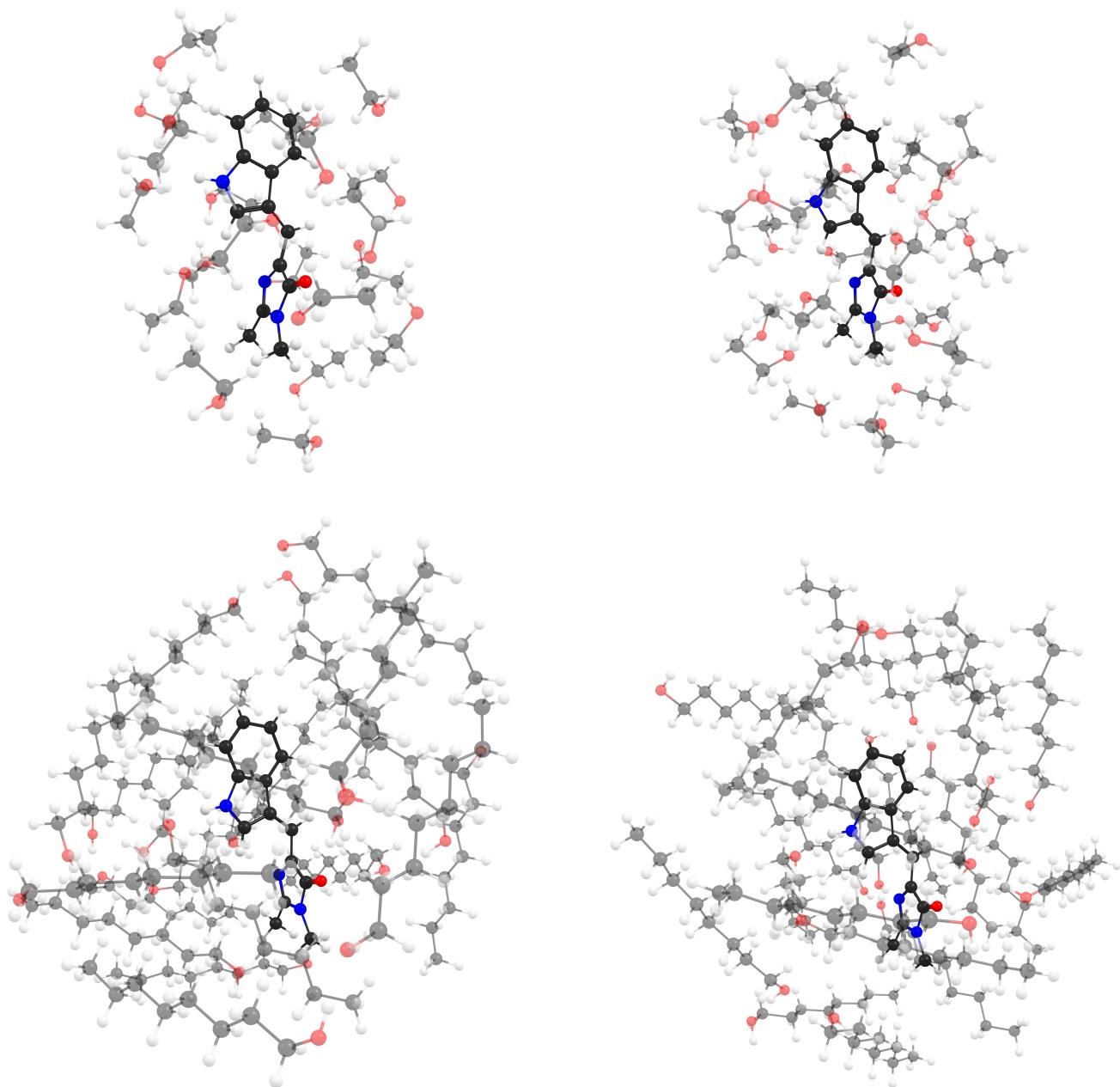


Fig. S5 Cyan in the S_1 state optimised geometry solvated with 20 (upper) ethanol and (lower) octanol molecules. (left) Solvent molecules were optimised based on the electronic structure (charge distribution) for the S_0 state. (right) Solvation optimised used the S_0 electronic structure with partial charges (equivalent to charge density for the S_1 state from MRSF-TDDFT) placed on each of the two ring systems to approximately account for prompt solvent reorientation due to the change in charge distribution on the S_1 state.

Optimised equilibrium geometries from MRSF-TDDFT calculations

	S₀ minimum			S₁ minimum		
C	-1.062952255	-0.233246142	-0.001313524	C	-1.014166769	0.051378366
C	0.081044467	0.503558998	0.444418176	C	0.100528154	0.806222048
H	-0.097266429	1.461516022	0.908107218	H	-0.073779548	1.855564631
C	1.380190932	0.142140563	0.355268552	C	1.442652194	0.285540350
C	2.487166091	0.978504298	0.846273390	C	2.222026303	0.315817763
C	3.173493502	-0.950171430	-0.064875263	C	3.326285762	-0.488806540
N	1.895411198	-1.030362790	-0.191794995	N	2.146633702	-0.202296404
N	3.606634196	0.211876239	0.542220430	N	3.441371074	-0.211640721
C	4.132480796	-1.988164699	-0.518115786	C	4.437050344	-1.055257149
H	4.727162019	-2.365161600	0.311980022	H	4.763028219	-2.028949821
H	3.579222826	-2.808741023	-0.957468396	H	4.095242127	-1.172189167
H	4.822636314	-1.589114128	-1.259088559	H	5.313697263	-0.406999060
O	2.498710894	2.060851789	1.383113673	O	2.012803399	0.653089669
C	4.954653428	0.618545571	0.837517924	C	4.579548866	-0.384810897
H	5.438332957	-0.0744446407	1.521140539	H	4.875310080	-1.430169812
H	5.552131218	0.699525278	-0.066739228	H	5.435439507	0.190678476
H	4.891549165	1.592444455	1.307995308	H	4.284292959	-0.026884248
C	-1.080777534	-1.461211259	-0.612743105	C	-0.948550278	-1.321965683
H	-0.247672007	-2.085796435	-0.866404309	H	-0.063776948	-1.901811561
C	-2.443385617	0.179640416	0.108170583	C	-2.439902054	0.366650306
C	-3.224768738	-0.842817447	-0.453881098	C	-3.127470912	-0.807677185
N	-2.360236043	-1.824542226	-0.881912237	N	-2.165349531	-1.800534019
C	-4.610683378	-0.777001608	-0.517089634	C	-4.503673564	-0.901537997
C	-3.082018764	1.307353412	0.623818871	C	-3.164334561	1.509438033
C	-5.215724290	0.348937504	0.000231205	C	-5.208838948	0.251527029
C	-4.457520494	1.381620232	0.565492843	C	-4.547418018	1.438596418
H	-5.191997467	-1.573675124	-0.953277128	H	-5.008970229	-1.822129015
H	-6.289517263	0.435732400	-0.031310699	H	-6.285503930	0.228982259
H	-4.961236371	2.248416188	0.961414551	H	-5.125139632	2.318276597
H	-2.511983934	2.110812292	1.062165179	H	-2.665940711	2.433341615
H	-2.629942849	-2.679078297	-1.324127534	H	-2.379957751	-2.743499240
						0.767663768

Optimised CI geometry from MRSF-TDDFT calculations

Conical intersection

C	-1.022565425	0.046793102	0.012010413
C	0.106639014	0.777875128	-0.125143151
H	-0.054005264	1.836444300	-0.327563689
C	1.434475014	0.225191065	-0.005949843
C	2.217545123	0.259637442	1.148595546
C	3.327409481	-0.478008416	-0.693015991
N	2.141993771	-0.207666465	-1.128024010
N	3.442707581	-0.236203649	0.655899859
C	4.446290827	-0.998938819	-1.521172409
H	4.796983239	-1.975426608	-1.183978273
H	4.100115366	-1.096235930	-2.544165007
H	5.309269665	-0.332238252	-1.514502195
O	2.016411271	0.567984368	2.337158384
C	4.590243102	-0.399128162	1.496500328
H	4.945145169	-1.428849670	1.504320908
H	5.413809671	0.244903536	1.190943881
H	4.275464997	-0.121347544	2.496306295
C	-0.961234757	-1.327113560	0.392114065
H	-0.072447883	-1.897333138	0.567271028
C	-2.447223982	0.370262331	-0.066798555
C	-3.136876273	-0.794573218	0.262754516
N	-2.170288273	-1.789337533	0.541410688
C	-4.510937949	-0.890468488	0.290878533
C	-3.169364316	1.507456683	-0.388331528
C	-5.215772688	0.258002477	-0.033064106
C	-4.553252803	1.436825024	-0.366369984
H	-5.016085955	-1.805967521	0.549675922
H	-6.292248283	0.236548901	-0.027505623
H	-5.130163603	2.312070824	-0.612951278
H	-2.670605004	2.425083892	-0.650165676
H	-2.388294264	-2.728297060	0.822047924