Solvent effect on the singlet excited state dynamics of 5-fluorouracil in acetonitrile as compared to water

Supplementary information

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Additional experimental results

Steady-state absorption and fluorescence spectra are shown on a wavenumber scale in Figure S1. Steady-state spectra were converted to wavenumber scale and normalized before being fitted with a simplified lognormal function[1] to evaluate the position peak frequency.

This lognormal function is given by:

$$\varepsilon(\nu) = \varepsilon_0 \, exp\left(- \beta^2 \left[ln \frac{\nu - a}{b} \right]^2 \right) \qquad \text{(S1)}$$

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Fluorescence spectra were scaled by a λ^2 factor prior to fitting. Resulting fits are also shown in Figure S1. Stokes shifts were calculated as the difference between the peak frequencies of the absorption and fluorescence spectra.

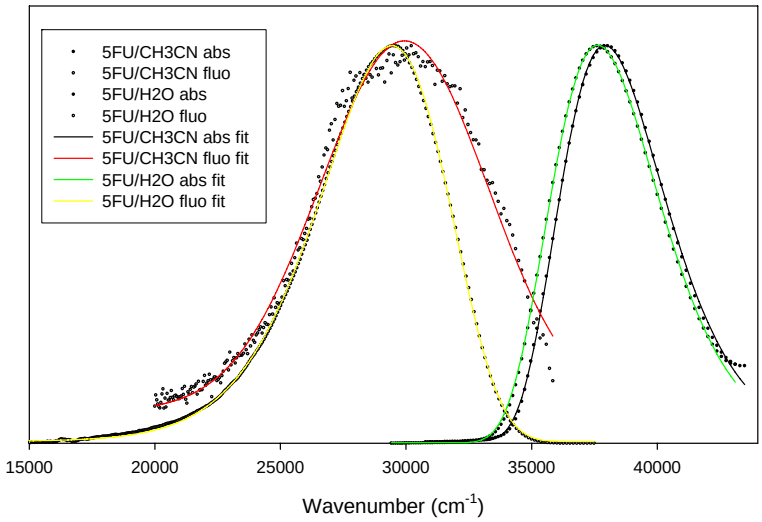

Figure S1. Steady-state absorption and fluorescence spectra of 5-fluorouracil in room-temperature H_2O and CH_3CN on a vavenumber scale with corresponding lognormal fits.

Total fluorescence decays *I(t)* shown below in Figure S2 were constructed from the parallel and perpendicular signals ($I_{par}(t)$ and $I_{perp}(t)$) according to the equation

$$I(t) = I_{par}(t) + 2I_{perp}(t) \qquad \text{(S2)}$$

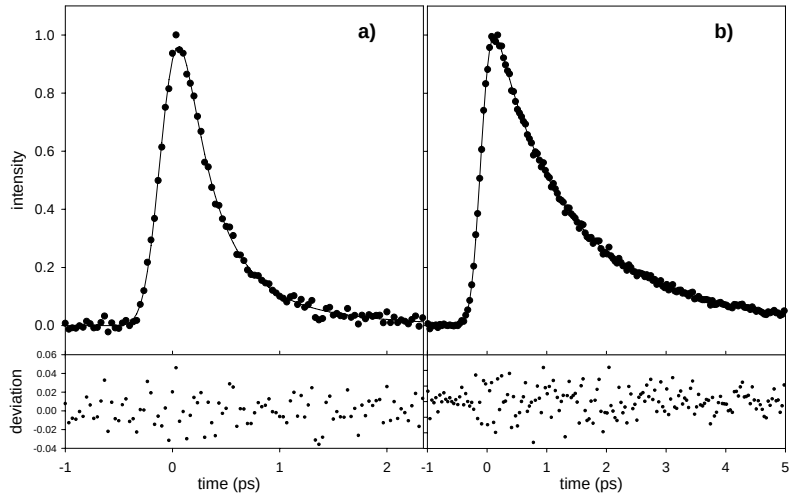

Figure S2. Fluorescence decays recorded at 330 nm after excitation at 267 nm of 5-fluorouracil in room-temperature a) acetonitrile and b) aqueous solutions (~2.5×10^{-3} mol/dm^{-3}). Note that a linear scale is used, contrary to Figure 2 in the article. Also indicated are bi-exponential fits (solid lines).

We performed merged nonlinear fitting/deconvolution process using mono- or bi-exponential impulse response model functions *i(t)* convoluted by the Gaussian instrument response function, $I(t) \propto i(t) \otimes G(t)$. Fitted curves are shown in Figure S2.

Additional computational results

Table S1. Cartesian coordinates of the PCM/TD-PBE0/6-31G(d) optimized S_0 , S_π and S_n minima, as well as the planar S_π minimum of 5-fluorouracil in CH_3CN solution. Also given are the Cartesian coordinates of the S_n/S_π conical intersection obtained by CASSCF(6/6)/6-31G(d) calculations.

Atomic numbers and Cartesian coordinates of the S_0 minimum in CH_3CN solution. PCM/PBE0/6-31G(d) geometry optimizations.

6	-0.211861	-1.507814	-0.000430
7	1.122185	-1.205626	-0.000908
6	1.614582	0.077213	0.000060
7	0.629968	1.046859	-0.000669
6	-0.748135	0.872627	-0.000120
6	-1.132684	-0.526245	-0.000110
8	2.807166	0.339463	0.001073
8	-1.522386	1.819085	0.000023
9	-2.442062	-0.793894	0.000754
1	1.815496	-1.961679	0.000983
1	0.966011	2.018401	-0.001567
1	-0.477669	-2.563384	-0.000328

Atomic numbers and Cartesian coordinates of the Sπ minimum in CH_3CN solution. PCM/TD-PBE0/6-31G(d) geometry optimizations.

7	-0.644400	1.014651	0.417518
6	0.740771	0.876365	0.093689
6	1.136454	-0.495528	0.098813
6	0.209159	-1.565893	0.176650
7	-1.069085	-1.206518	-0.146430
6	-1.567015	0.082754	-0.003141
8	1.436497	1.855296	-0.228960
9	2.415553	-0.772276	-0.132195
8	-2.750307	0.323692	-0.203541
1	-1.773469	-1.923812	-0.386360
1	-0.995224	1.979391	0.428805
1	0.417378	-2.580121	0.513635

Atomic numbers and Cartesian coordinates of the S_n minimum in CH_3CN solution. PCM/TD-PBE0/6-31G(d) geometry optimizations.

6	1.11525	-0.51496	0.00617
6	0.17152	-1.58554	0.01739
7	-1.13606	-1.19153	-0.0098
6	-1.5831	0.11881	-0.0027
7	-0.62641	1.09064	0.02741
6	0.78454	0.86808	0.00546
8	-2.78989	0.35527	-0.01312
8	1.57703	1.83401	-0.01449
9	2.39204	-0.84966	-0.00997
1	-1.88538	-1.90098	-0.02791

1	-0.95257	2.06208	0.02955
1	0.42059	-2.64041	0.02774

Atomic numbers and Cartesian coordinates of the Sπ minimum in CH_3CN solution under planarity constraint. PCM/TD-PBE0/6-31G(d) geometry optimizations.

6	-1.253648	-0.973916	0.000000
7	-1.195991	0.388590	0.000000
6	0.000000	1.171748	0.000000
6	1.172087	0.366169	0.000000
6	1.190125	-1.060516	0.000000
7	-0.043661	-1.646517	0.000000
8	-0.060917	2.419555	0.000000
9	2.344736	0.972563	0.000000
8	-2.307470	-1.608088	0.000000
1	-0.123089	-2.675479	0.000000
1	-2.089854	0.889445	0.000000
1	2.083592	-1.674189	0.000000

Atomic numbers and Cartesian coordinates of the S_n/S_π conical intersection. CASSCF(6/6)/6-31G(d) calculations.

6	1.186126	-1.092459	0.000000
7	-0.087688	-1.664901	0.000000
6	-1.298965	-0.942888	0.000000
7	-1.228751	0.405737	0.000000
6	0.000000	1.166693	0.000000
6	1.192664	0.337735	0.000000
8	-2.317851	-1.553614	0.000000
8	0.068566	2.450658	0.000000
1	-0.203572	-2.651149	0.000000
1	-2.098306	0.887152	0.000000
9	2.329707	0.920228	0.000000
1	2.064916	-1.694749	0.000000

Full references

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