Supporting Information

Ultrafast Excited-State Proton Transfer in 4-nitrocatechol: Implications for the Photochemistry of Nitrophenols

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Table S1. Vertical excitation energies (VEEs) from time-dependent density functional theory calculations for the ground state of 4NC at the TD-PBE0/6-311+G* level of theory

State	Total energy / au	VEE / eV	VEE / nm	Oscillator Strength (f)
With C-PCM for 2-propanol				
		Singlets		
S_1	-586.5985057	3.5706	347.2	2.017×10^{-1}
S_2	-586.5832187	3.9866	311.0	1.733×10^{-7}
S_3	-586.5770892	4.1534	298.5	1.764×10^{-1}
S_4	-586.5589382	4.6473	266.8	4.039×10^{-4}
S_5	-586.5316219	5.3906	230.0	1.296×10^{-1}
S_6	-586.5134661	5.8846	210.7	8.828×10^{-5}
S_7	-586.5009861	6.2242	199.2	1.416×10^{-1}
S_8	-586.5004953	6.2376	198.8	8.360×10^{-2}
S_9	-586.4883026	6.5694	188.7	2.329×10^{-2}
S_{10}	-586.4878781	6.5809	188.4	1.212×10^{-4}
		Triplets		
T_1	-586.6355414	2.5628	483.8	0
T_2	-586.6166768	3.0761	403.0	0
T_3	-586.6033993	3.4374	360.7	0
T_4	-586.6021297	3.4720	357.1	0
T_5	-586.5809496	4.0483	306.3	0
T_6	-586.5780085	4.1283	300.3	0
T_7	-586.5625706	4.5484	272.6	0
T_8	-586.5395633	5.1745	239.6	0
T_9	-586.5183137	5.7527	215.5	0
T_{10}	-586.5115932	5.9356	208.9	0
With C-PCM for water				
		Singlets		
S_1	-586.6002712	3.5514	349.1	1.930×10^{-1}
S_2	-586.5842646	3.9870	311.0	3.437×10^{-7}
S_3	-586.5787231	4.1378	299.6	1.806×10^{-1}
S_4	-586.5596949	4.6556	266.3	4.449×10^{-4}
S_5	-586.5325425	5.3944	229.8	1.275×10^{-1}
S_6	-586.5138969	5.9018	210.1	8.273×10^{-5}
S_7	-586.5016864	6.2340	198.9	1.573×10^{-1}
S_8	-586.5012615	6.2456	198.5	5.789×10^{-2}
S_9	-586.4900420	6.5509	189.3	2.355×10^{-2}
S_{10}	-586.4892628	6.5721	188.6	1.211×10^{-4}
		Triplets		
T_1	-586.6374488	2.5398	488.1	0
T_2	-586.6175373	3.0816	402.3	0
T_3	-586.6043871	3.4394	360.5	0
T_4	-586.6038340	3.4545	358.9	0
T_5	-586.5821313	4.0450	306.5	0
T_6	-586.5787212	4.1378	299.6	0
T_7	-586.5636022	4.5492	272.5	0
T_8	-586.5409596	5.1654	240.0	0
T_9	-586.5187663	5.7693	214.9	0
T_{10}	-586.5133978	5.9154	209.6	0

Table S2. Relative energies from S_1, T_1, and T_3 based on ground-state vertical excitation energies in 4NC

	$S_1 \rightarrow S_n$		$T_1 \rightarrow T_n$		$T_3 \rightarrow T_n$
$\mathbf{S}_n$	**ΔVEE / nm**	$\mathbf{T}_n$	**ΔVEE / nm**	$\mathbf{T}_n$	**ΔVEE / nm**
S_5	681.2	T_5	834.6	T_8	713.7
S_6	535.8	T_6	792.0	T_9	535.5
S_7	467.2	T_7	624.4	T_{10}	496.3
S_8	464.9	T_8	474.7	T_{11}	442.5
S_9	413.4	T_9	388.7	T_{12}	403.7
S_{10}	411.9	T_{10}	367.6	T_{13}	401.4
S_{11}	401.2			T_{14}	389.4
S_{12}	394.4			T_{15}	363.4
S_{13}	393.7				
S_{14}	374.6				

Table S3. Energetic quantities from TD/TDA-PBE0/6-311+G(d) excited-state geometry optimizations

$\mathbf{T}_n$	**SOC (eV)**	$\mathbf{E}_n$ **(au, @** $\mathbf{T}_n$ **min)**	$\mathbf{E}_n$ **(au, @** $\mathbf{S}_1$ **min)**	k_{ISC} **(1/s)**	$1/k_{ISC}$ **(ps)**
S_1			-586.6274087		
T_1	0.267555	-586.6442544	-586.6338723	2.40×10^{-1}	4.17×10^{12}
T_2	0.563071	-586.6342262	-586.6021542	3.57×10^{2}	2.80×10^{9}
T_3	13.70255	-586.6193243	-586.5776467	3.65×10^{7}	2.74×10^{4}

Potential Energy Surface for 4NC in Water

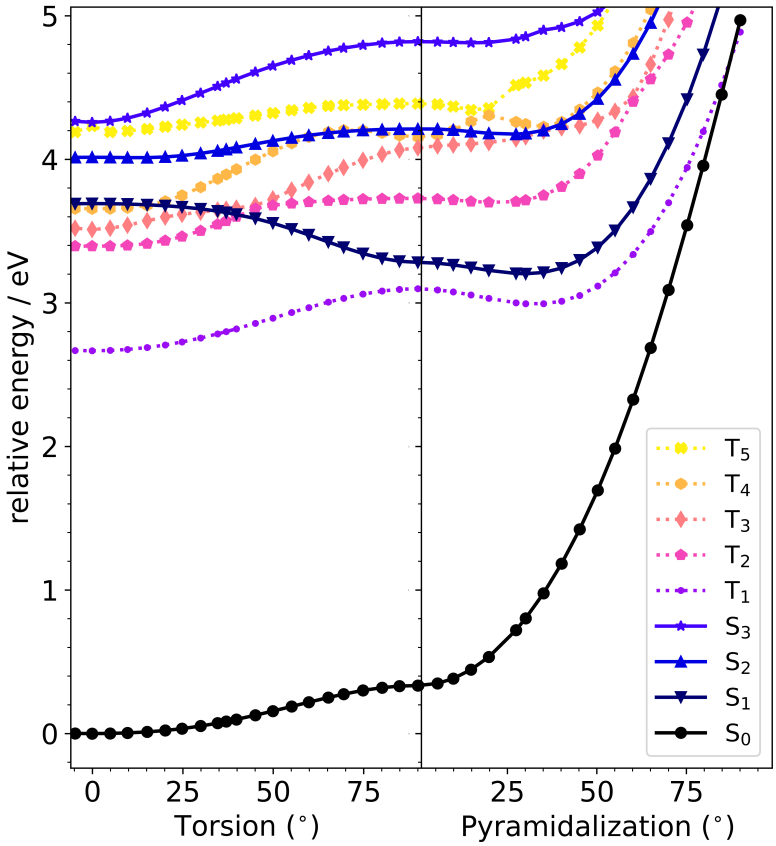

Figure S1. Effect of torsion angle and pyramidalization angle of the -NO_2 on the potential energies of excited singlets and triplets in 4NC with a C-PCM for water at TD/TDA-PBE0/6-311+G(d) level of theory.

Natural Transition Orbital Analysis

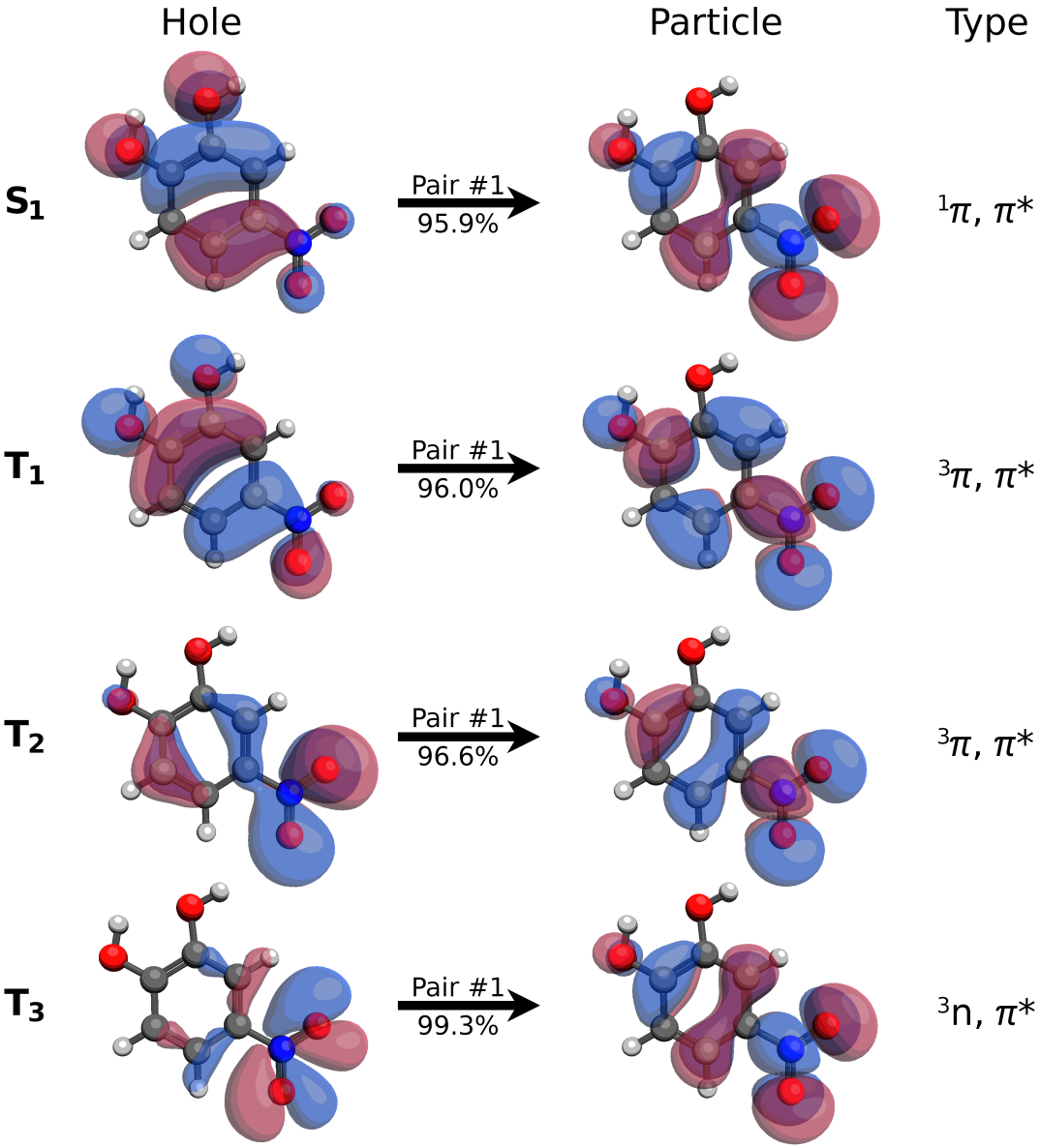

Figure S2. Natural transition orbital (NTO) pairs calculated at the TD-PBE0/6-311+G* level of theory. The transitions for S_1, T_1, and T_2 are all of $\pi\pi^*$ nature, while T_3 is the only one to exhibit $n\pi^*$. As discussed in the main text, this has positive implications toward the probability of ISC from S_1 to T_3.

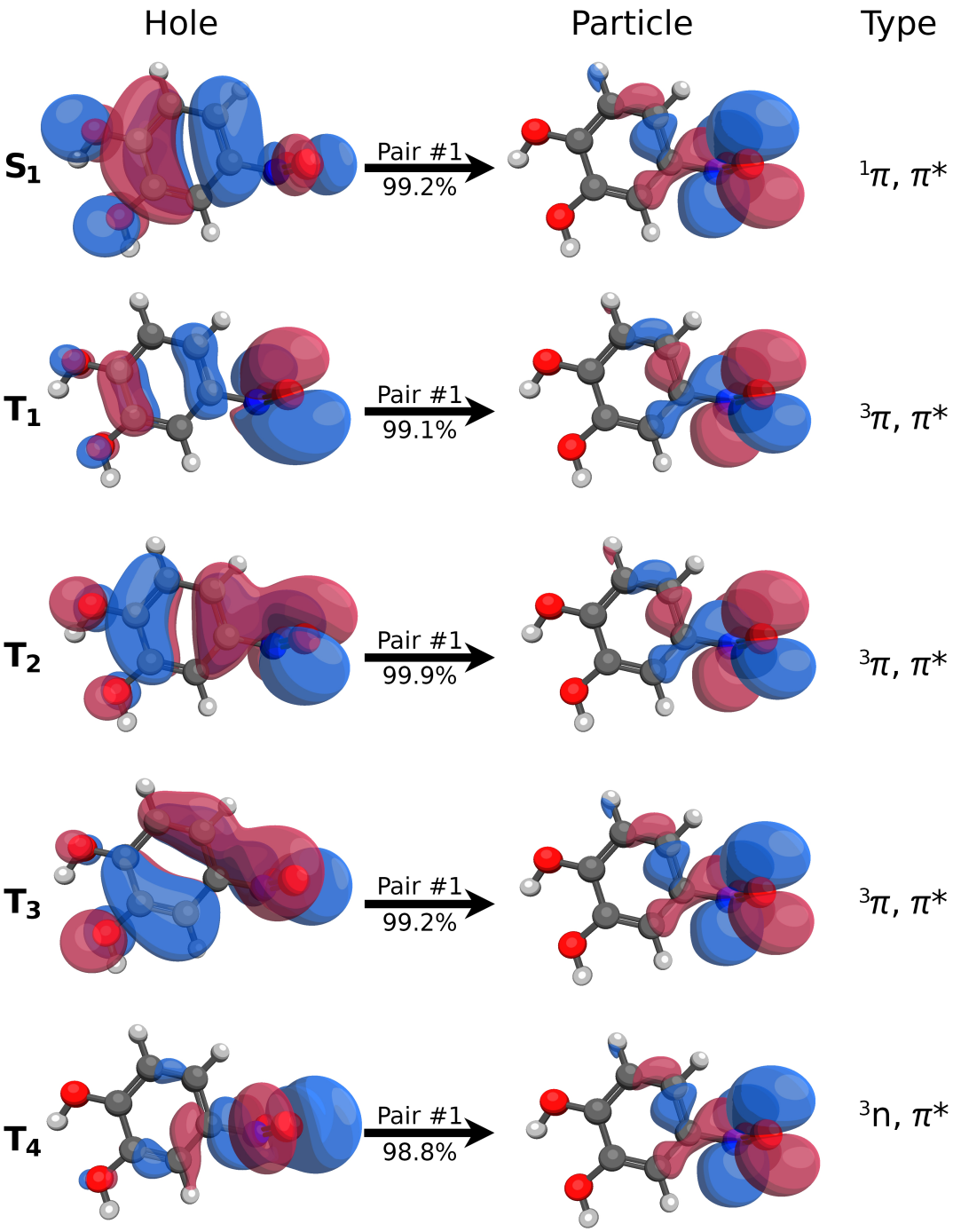

Figure S3. NTO pairs calculated at the TD-PBE0/6-311+G* level of theory at the **minimum geometry of the S_1** state, the twisted conformer of 4NC. T_4 is included because it appears that it is the T_3 $n\pi^*$ transition in the Franck-Condon (FC) conformer, and that the FC T_4 moves lower than the FC T_3 at S_1 geometry.

Results from CAM-B3LYP

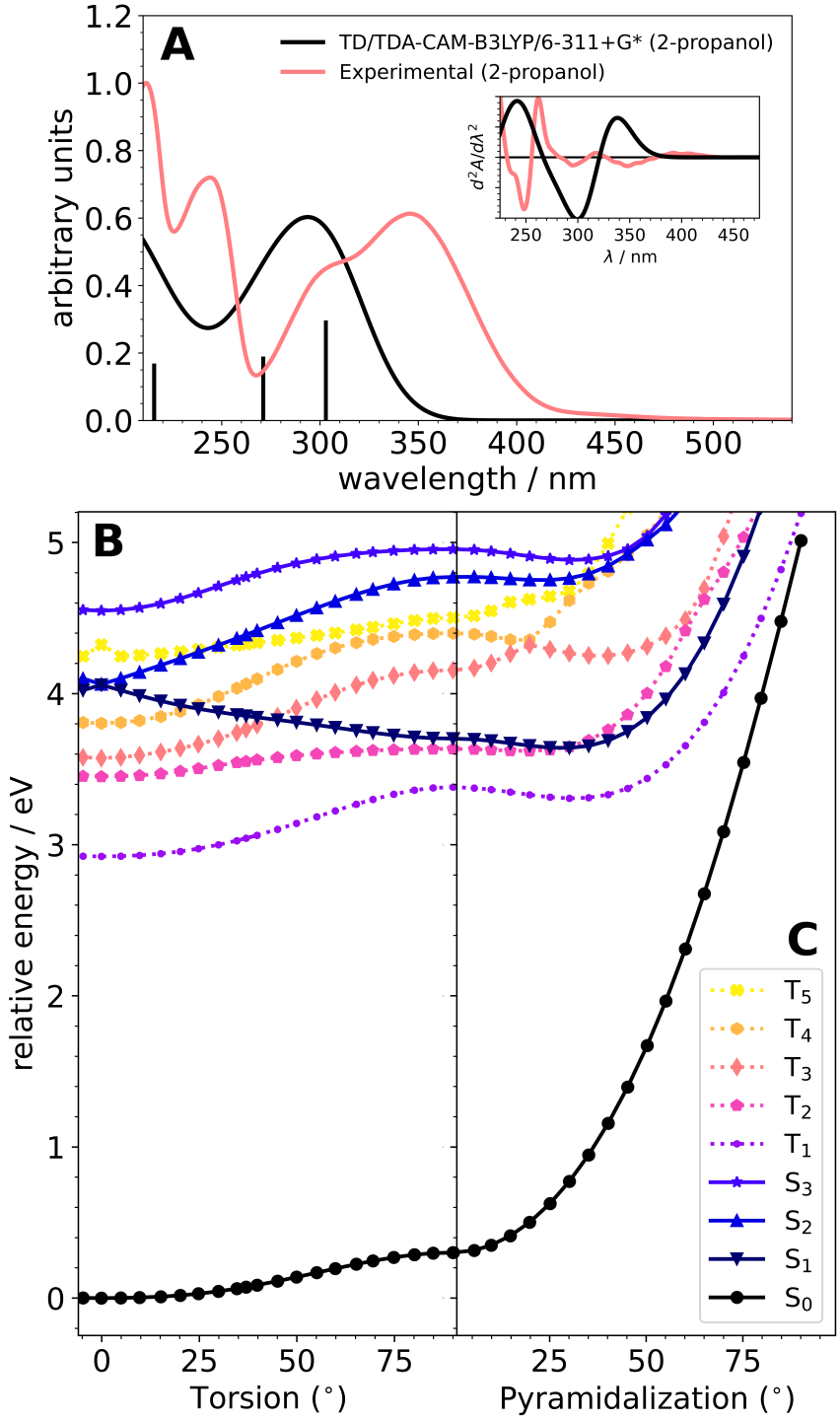

Figure S4. Effect of torsion angle and pyramidalization angle of the -NO_2 on the potential energies of excited singlets and triplets in 4NC with a C-PCM for water at TD/TDA-CAM-B3LYP/6-311+G(d) level of theory.

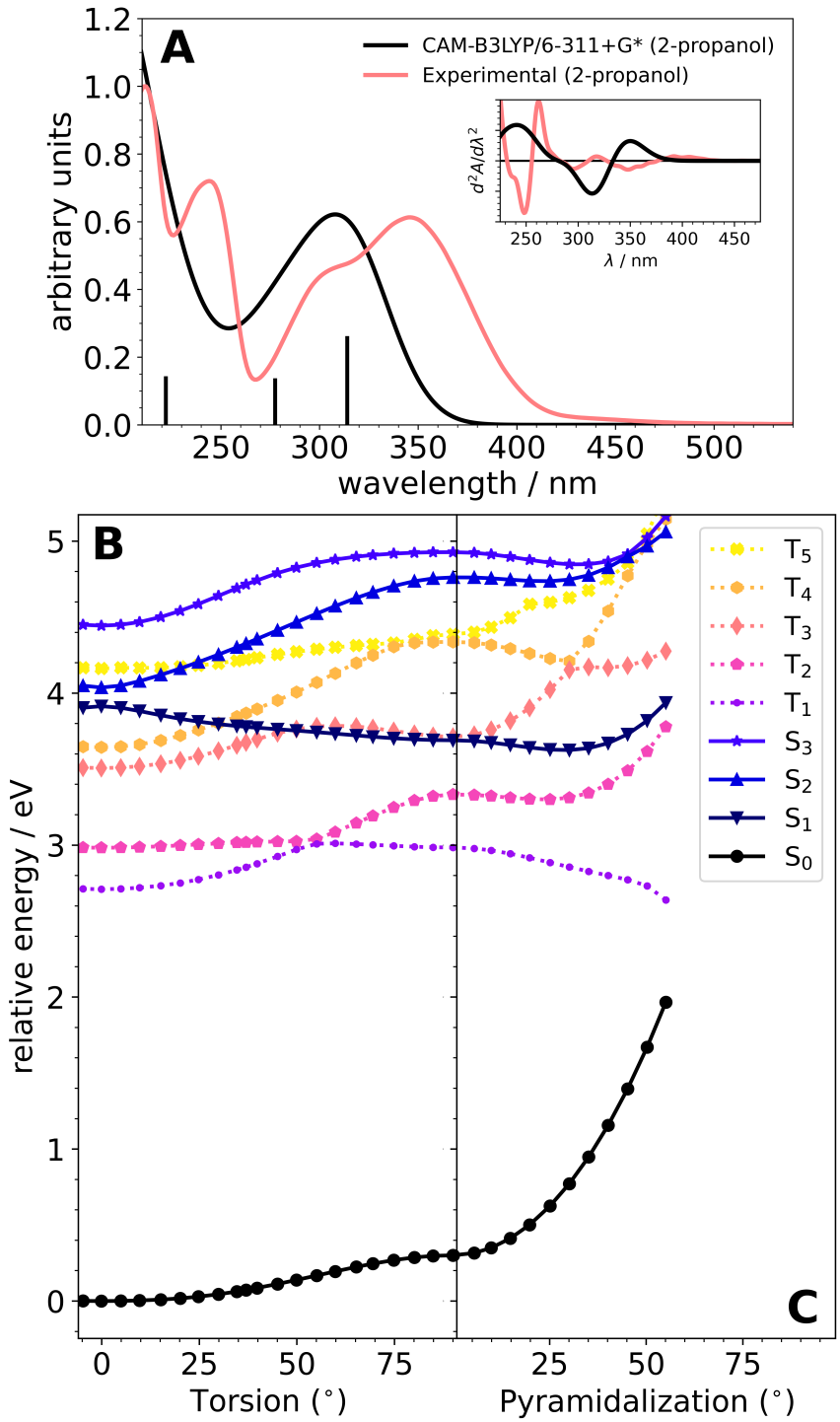

Figure S5. Vertical excitation spectra (A) of torsion angle (B) and pyramidalization angle (C) of the -NO_2 on the potential energies of excited singlets and triplets in 4NC with a C-PCM for water at TD-CAM-B3LYP/6-311+G(d) level of theory.

pH dependence of 4NC UV/vis absorption

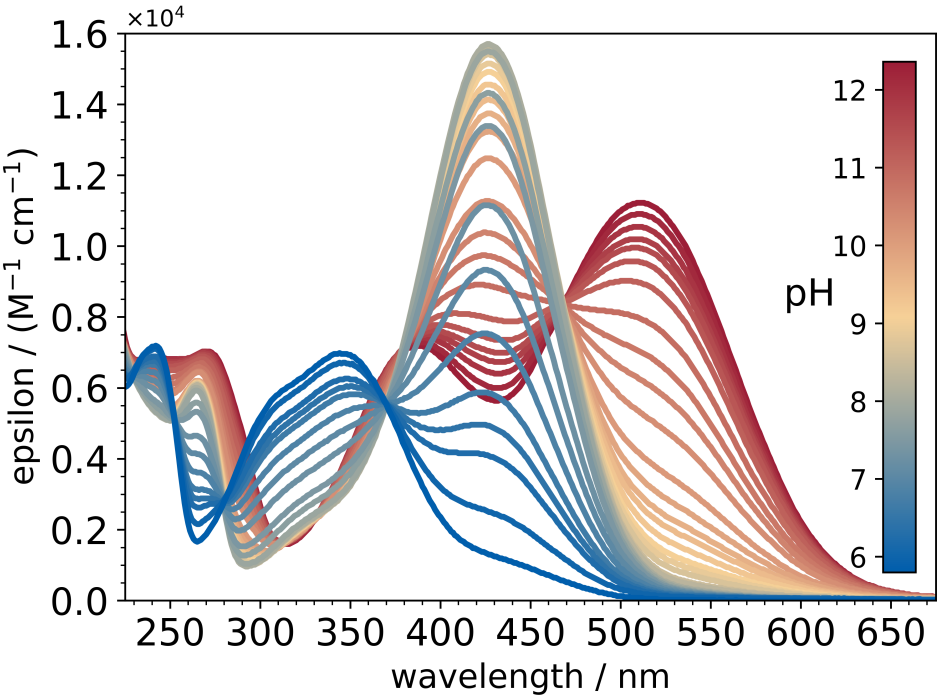

Figure S6. UV/vis absorption spectra of 4NC at a range of pH values, from the 'native' pH of 4NC in water to 12.4 adjusted by KOH. Two deprotonations are observed, first from the #1 C atom to form $4NC^-$ and subsequently from the #2 C atom.

Time Profiles of Transient Absorption at 420 nm

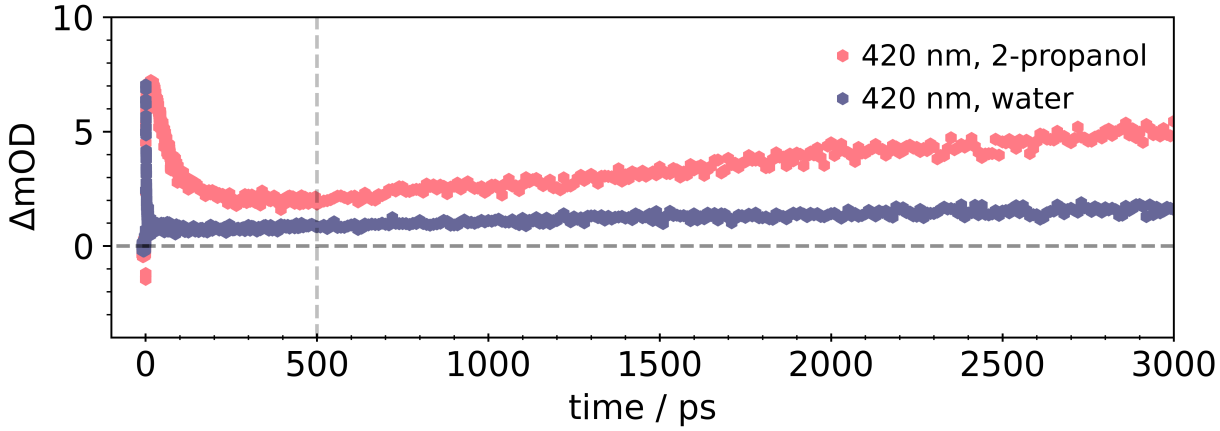

Figure S7. Transient absorption at 420 nm by 4NC in 2-propanol and in water over the full 3 ns experiment. A linear increase in transient absorption is observed in both solvents, apparently after completion of the transient dynamics (around 500 ps in 2-propanol, earlier in water). This is believed to be the result of a build-up of $4NC^-$ throughout the experiment.