Supporting information

Ultrafast Excited-State Dynamics of a Cyano-Substituted "Proton Sponge"

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S_n	S_1^{FC} ($\lambda_{S0\rightarrow S1}$ 364.4 nm)		S_1^{eq} ($\lambda_{S1\rightarrow S0}$ 430 nm)	
n	[nm]	f	[nm]	f
3	1542.0	0.001	1195.0	0.002
4	1437.0	0.006	715.6	0.063
5	772.0	0.006	662.1	0.258
6	723.5	0.061	570.5	0.045
7	691.2	0.207	529.4	0.022
8	659.6	0.045	477.9	0.104
9	500.1	0.094	439.6	0.027
10	471.7	0.002	434.1	0.055
11	448.7	0.001	391.0	0.010
12	437.9	0.005	384.4	0.003
13	424.3	0.012	372.9	0.133
14	416.8	0.010	364.4	0.129
15	402.8	0.008	353.1	0.021

Table 1S *- Calculated $S_1 \rightarrow S_n$ vertical transition wavelengths and oscillator strengths at two geometries of the S_1 state: S_1^{FC} corresponds to the ground state equilibrium geometry after excitation at 364.4 nm; S_1^{eq} corresponds to the equilibrium geometry of the S_1 state. The calculation where performed at the TD DFT/6-31G (d, p) level.*

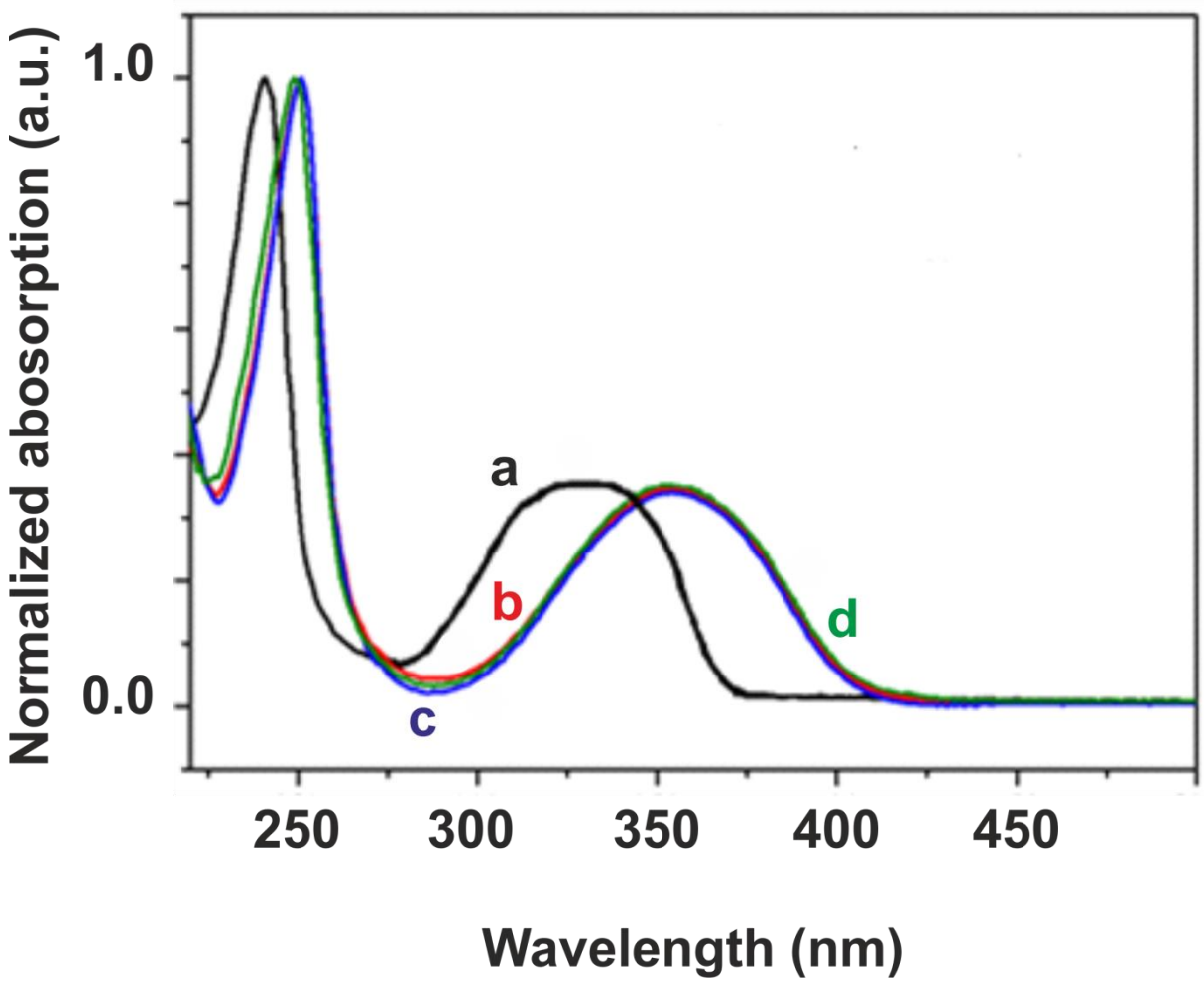

Figure 1S *- Normalized absorption spectra of DMAN in n-hexane (a, black curve) and DMAN-CN in several solvents: n-hexane (b, red curve), dodecane (c, blue curve), diethyl ether (d, green curve).*

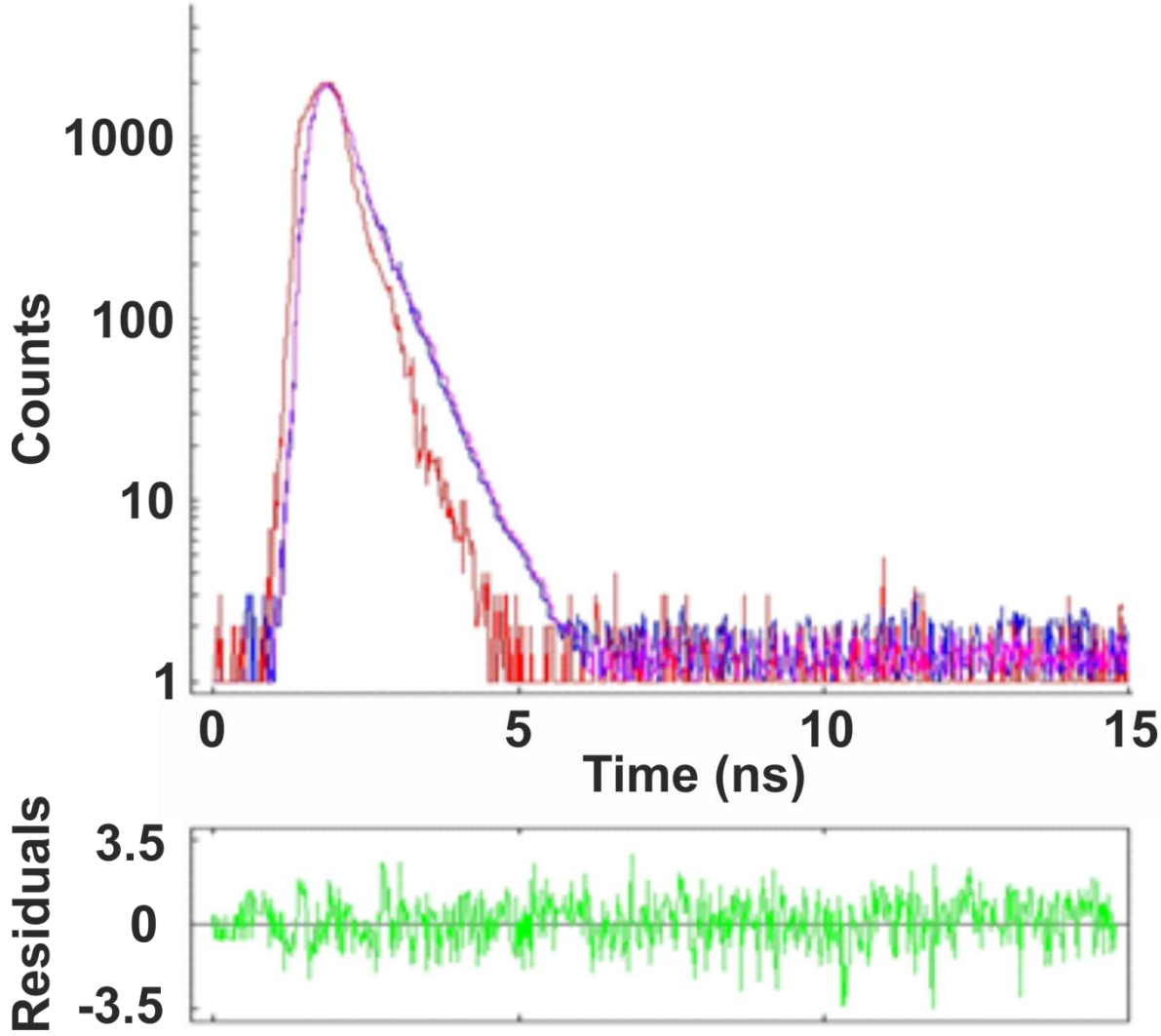

Figure 2S *- Decay of the Time-Correlated Single Photon Counting detected emission of DMAN-CN in n-hexane at 620 nm after excitation at 375 nm (blue curve). The Instrumental Response Function (IRF) is indicated by the red trace. The black trace passing through the blue curve is a fit assuming an exponential decay with a time constant of 238±8 ps convoluted by the IRF.*

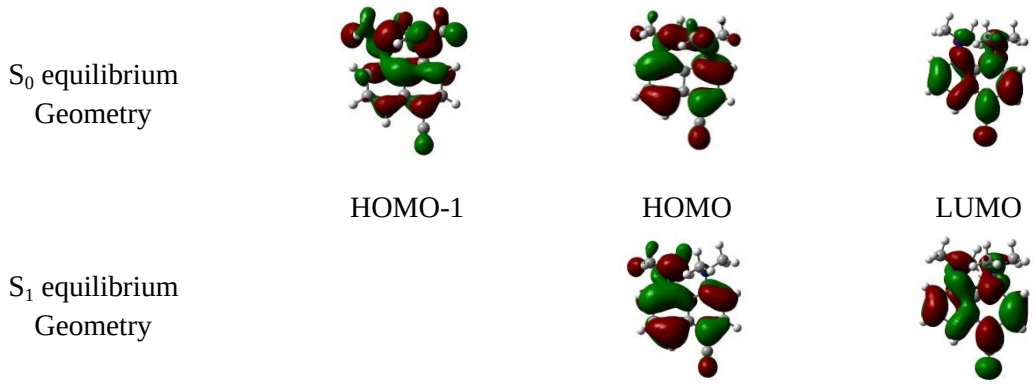

Figure 3S *- HOMO-1, HOMO and LUMO orbitals at two equilibrium geometries of the DMAN-CN molecule, that of the ground state S_0 (top) and that of the excited state S_1 (bottom).*

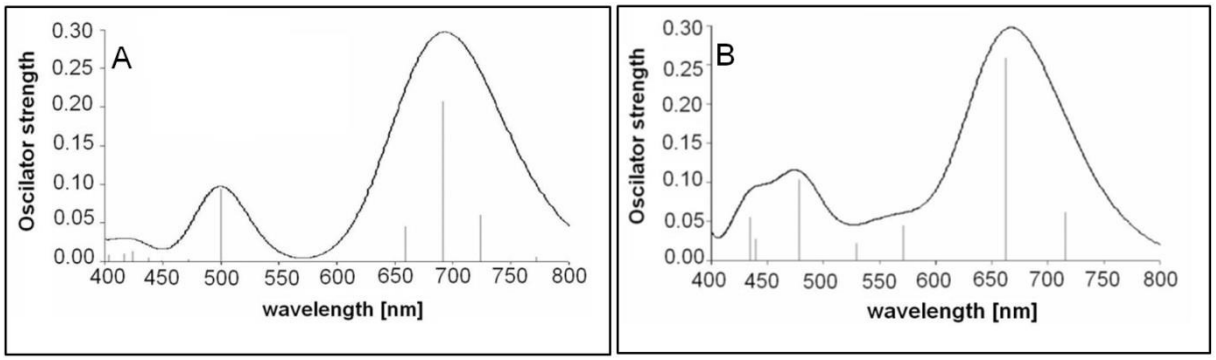

Figure 4S *- Simulated absorption spectra of DMAN-CN excited in the S_1 state at two geometries of the molecule. Panel A displays the spectrum calculated for $S_1^{FC} \rightarrow S_n^{FC}$ transitions that is transitions starting from the Franck-Condon excited S1 state, panel B- the spectrum calculated for the CIS geometry-optimized S1 state. The full spectra have been constructed from the stick spectra by convolution with Gaussian envelopes with a half-width of 900 cm^{-1}.*