Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Photophysics of Galvinoxyl Free Radical Revisited

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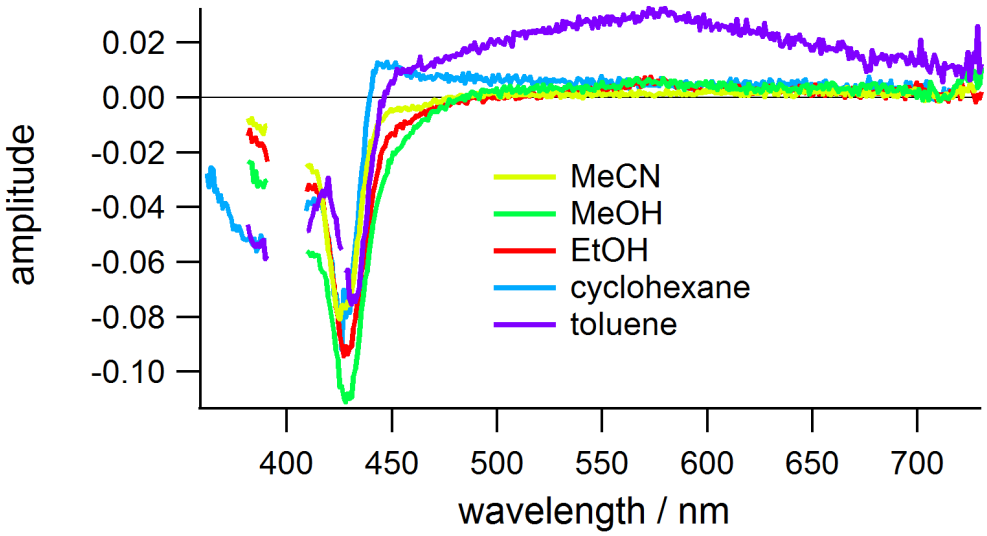


Figure S1: Residuals of the target analysis of TA spectra of galvinoxyl at intermediate pump intensity (3 mJ/cm^2). The absorption at 580 nm in alcohol solutions that is ascribed to galvinoxylate anion is not present in cyclohexane and MeCN, solvents with higher IP. The amplitude has been scaled to the initial intensity of the bleach signal.

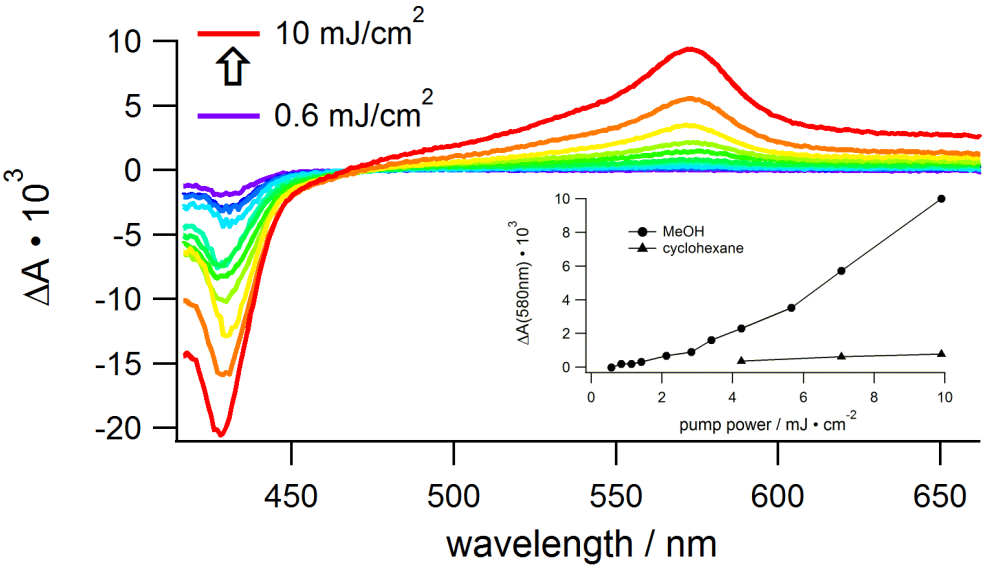


Figure S2: Pump intensity dependence of the absorbance at 580 nm of a methanol solution of galvinoxyl 25 ps after light excitation. The inset shows the pump power dependence of the 580nm ESA in methanol and cyclohexane solution.

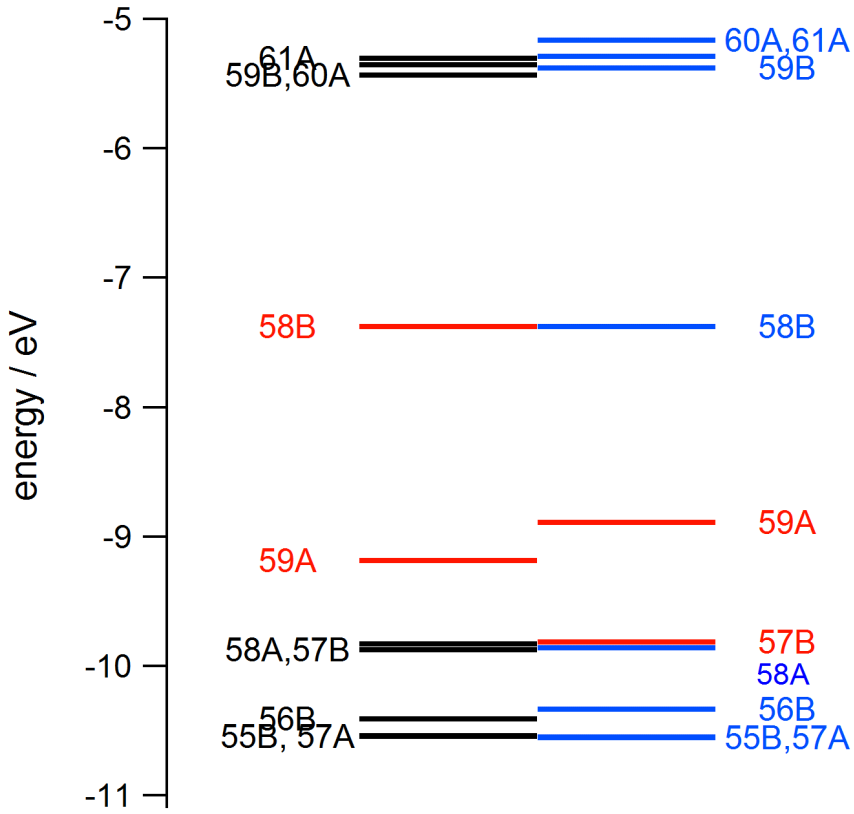
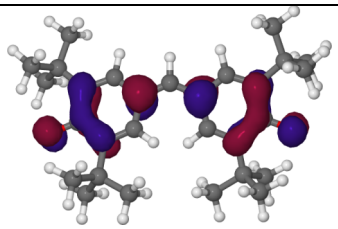
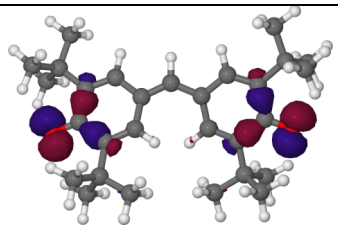
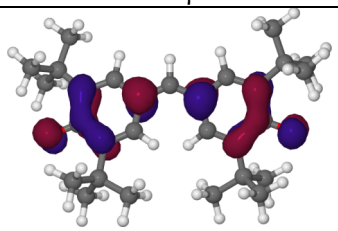
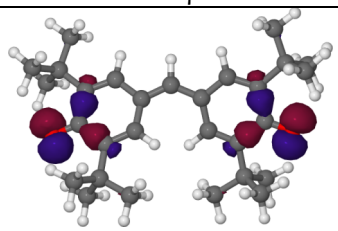
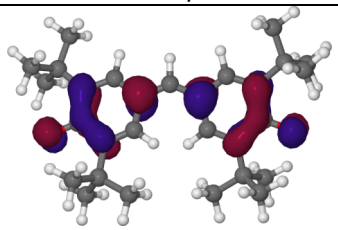
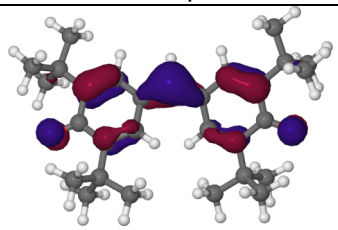
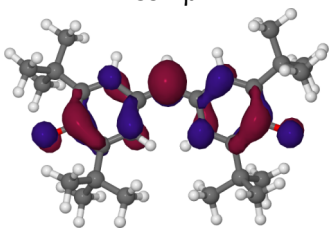
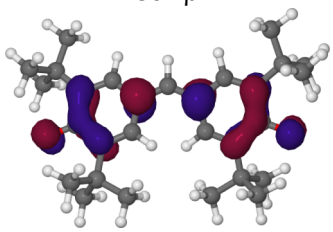
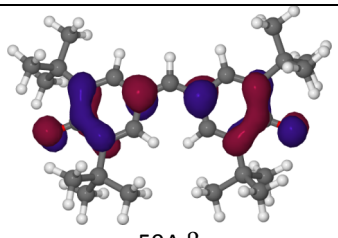
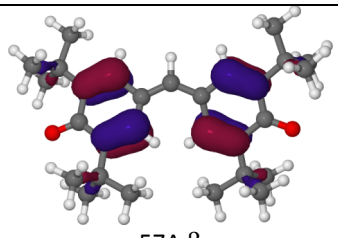
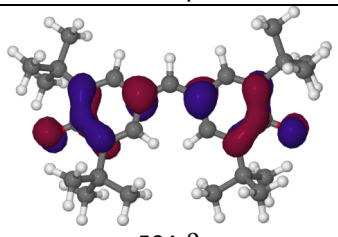
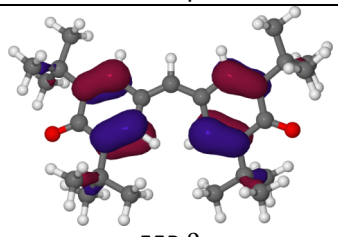


Figure S3: Energies of the relevant Kohn-Sham orbitals. α-MOs are in black, β-MOs in blue, the HOMO and LUMO of each set are in red.

Table S1: Excitation energies, oscillator strength and assignments calculated for the first 10 transitions of galvinoxyl radical in the ^{2}A ground state (SAOP/TZP results).

excited state		E / eV ($f \cdot 10^4$)	major MO-MO transitions			contr.	main character
1	^{2}B	0.929 (1)	 59A β	←	 57B β	100%	nπ*
2	^{2}A	0.971 (0)	 59A β	←	 58A β	100%	nπ*
3	^{2}B	1.509 (261)	 59A β	←	 56B β	66 %	ππ*
			 58B α	←	 59A α	34%	
4	^{2}A	1.705 (133)	 59A β	←	 57A β	99%	ππ*
5	^{2}B	1.705 (34)	 59A β	←	 55B β	99%	ππ*

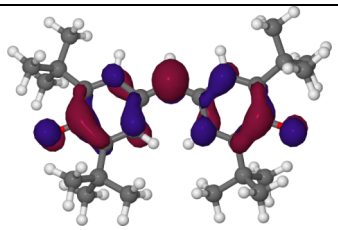
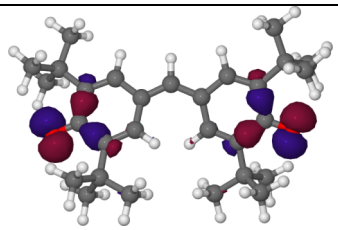
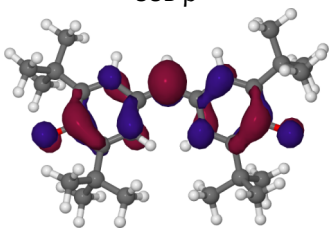
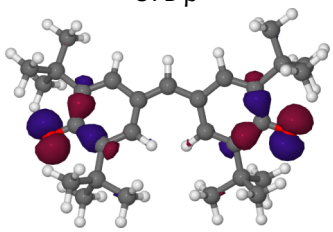
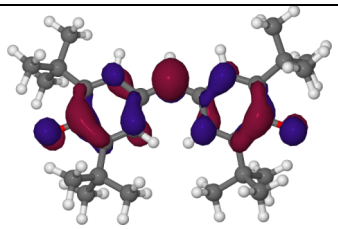
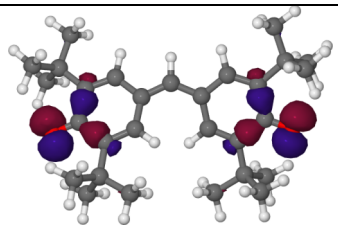
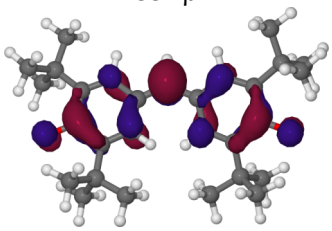
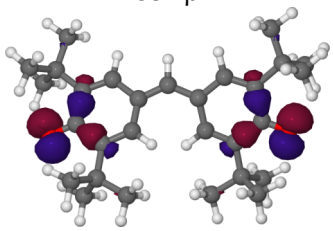
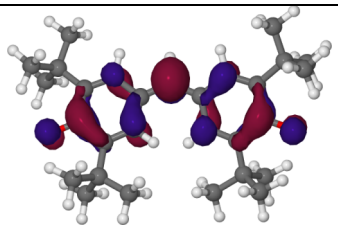
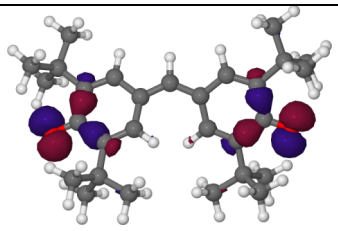
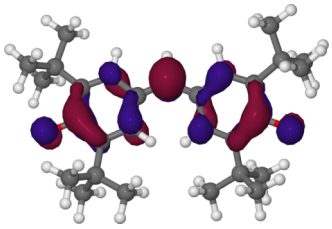
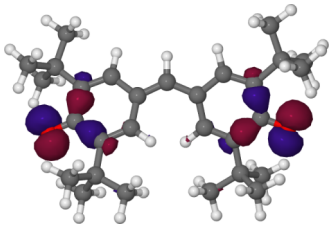
6	^{2}A	2.383 (0)	 58B β	←	 57B β	57%	nπ*
			 58B α	←	 57B α	43%	
7	^{2}B	2.427 (4)	 58B β	←	 58A β	57%	nπ*
			 58B α	←	 58A α	43%	
8	^{2}A	2.519 (0)	 58B α	←	 57B α	56%	nπ*
			 58B β	←	 57B β	43%	

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Table S1 (continued)

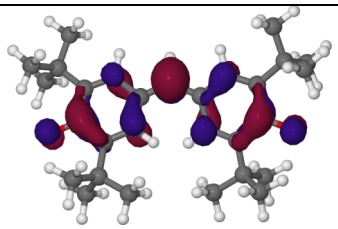
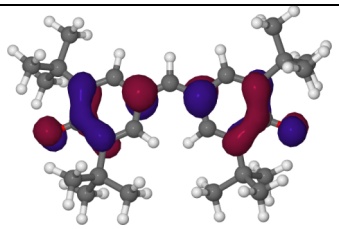
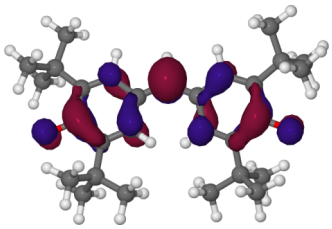
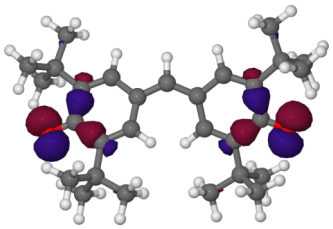
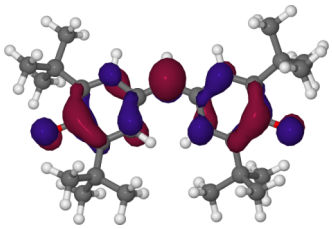
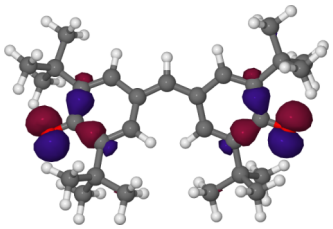
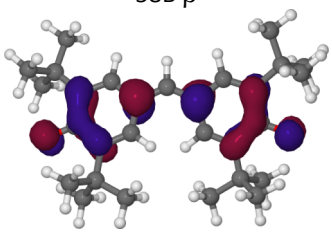
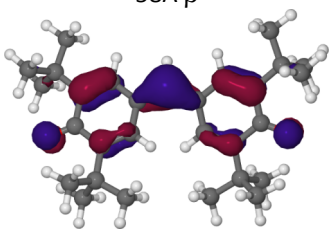
9	^{2}B	2.53 (4045)	 58B α	←	 59A α	32%	ππ* nπ*
			 58B α	←	 58A α	29%	
			 58B β	←	 58A β	19%	
			 59A β	←	 56B β	16%	

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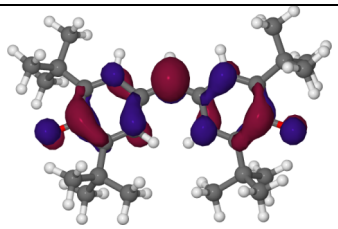
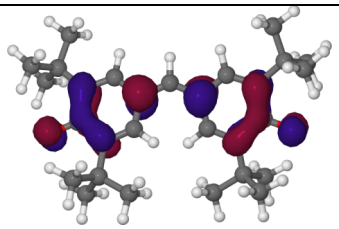
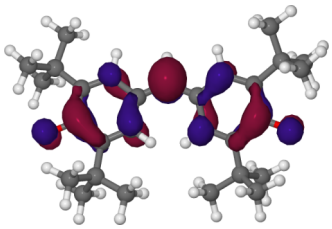
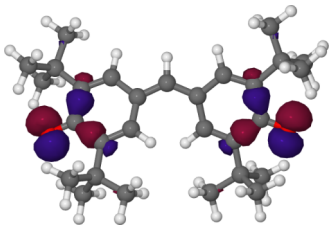
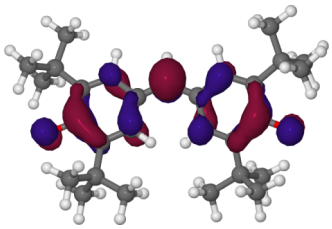
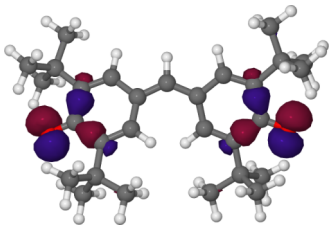
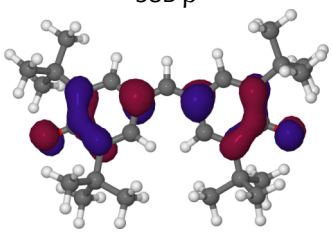
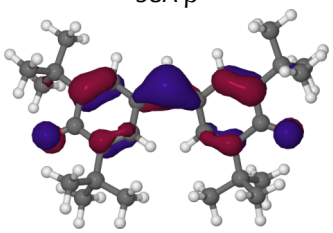
Table S1 (continued)

10	^{2}B	2.594 (4405)	 58B α	←	 59A α	29%	ππ* nπ*
			 58B α	←	 58A α	28%	
			 58B β	←	 58A β	23%	
			 59A β	←	 56B β	15%	