Electronic Supplementary Information (ESI)

One- and two-photon solvatochromism of the fluorescent dye Nile Red and its CF_3, F and Br-substituted analogues

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Table A1. Photophysical properties of Nile Red (**NR**) and the five analogs **1**–**5**.

Solute	Solvent	Solvent polarity	Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Stokes shift $\Delta\lambda_{max}$ [nm]	Quantum yield Φ	Molar extinction coefficient ε [10^3 $M^{-1}cm^{-1}$]	Fluorescence lifetime τ (ns)	~1050-nm 2PA band			~860-nm 2PA band		
									λ_{max} [nm]	Cross-section $\sigma^{2PA}{}_{max}$ [GM]	Brightness σ^{2PA} Φ [GM]	λ_{max} [nm]	Cross-section $\sigma^{2PA}{}_{max}$ [GM]	Brightness σ^{2PA} Φ [GM]
NR	MeOH	0.762	550	636	86	0.40	32.6	2.93	1057	104	42	872	20	8
	DMSO	0.444	548	627	79	0.76	32.0	4.11	1063	53	40	859	17	13
	Acetone	0.355	530	605	75	0.75	33.2	4.55	1045	89	67	871	40	30
	$CHCl_3$	0.259	537	594	57	0.81	32.6	4.27	1051	65	53	875	51	41
	THF	0.207	527	588	61	0.81	27.7	4.17	1038	45	36	868	45	36
	Toluene	0.099	521	566	45	0.81	28.9	3.85	1035	32	26	874	44	36
1	MeOH	0.762	565	638	73	0.35	36.4	2.36	1057	232	81	869	32	11
	DMSO	0.444	568	637	69	0.77	36.3	3.70	1063	144	111	850	27	21
	Acetone	0.355	549	618	69	0.69	36.1	4.37	1055	165	114	858	61	42
	$CHCl_3$	0.259	554	601	47	0.80	37.2	4.23	1057	185	148	863	39	31
	THF	0.207	546	603	57	0.76	33.3	4.07	1042	186	141	868	55	42
	Toluene	0.099	541	579	38	0.81	36.3	3.93	1040	75	61	871	60	49
2	MeOH	0.762	554	631	77	0.43	36.9	3.04	1055	183	79	873	36	15
	DMSO	0.444	558	632	74	0.74	35.5	3.89	1064	107	79	855	24	18
	Acetone	0.355	541	612	71	0.70	37.0	4.48	1050	170	119	862	62	43
	$CHCl_3$	0.259	543	595	52	0.78	36.1	4.23	1054	109	85	873	46	36
	THF	0.207	537	598	61	0.75	33.0	4.25	1038	120	90	868	56	42
	Toluene	0.099	530	571	41	0.76	35.0	3.91	1038	70	53	874	74	56
3	MeOH	0.762	569	632	63	0.45	20.8	2.44	1065	123	55	867	16	7
	DMSO	0.444	570	636	66	0.70	20.0	3.69	1063	88	62	850	18	13
	Acetone	0.355	549	615	66	0.73	20.1	4.37	1052	83	61	850	32	23
	$CHCl_3$	0.259	555	603	48	0.76	20.7	4.26	1058	106	81	863	24	18
	THF	0.207	546	603	57	0.80	19.2	4.13	1042	89	71	868	27	22
	Toluene	0.099	541	578	37	0.84	17.4	3.94	1037	38	32	872	27	23
4	MeOH	0.762	551	636	85	0.37	23.8	2.67	1055	95	35	872	18	7
	DMSO	0.444	553	633	80	0.70	23.7	4.03	1063	52	36	858	13	9
	Acetone	0.355	536	612	76	0.73	24.4	4.58	1049	67	49	869	29	21
	$CHCl_3$	0.259	543	596	53	0.76	24.0	4.29	1054	65	49	874	41	31
	THF	0.207	530	595	65	0.83	19.7	4.39	1039	50	42	869	33	27
	Toluene	0.099	527	567	40	0.87	21.2	3.94	1036	23	20	873	28	24
5	MeOH	0.762	561	637	76	0.36	27.6	2.71	1057	118	42	873	19	7
	DMSO	0.444	562	636	74	0.62	27.0	3.80	1063	66	41	857	12	7
	Acetone	0.355	543	615	72	0.70	26.8	4.33	1051	80	56	866	29	20
	$CHCl_3$	0.259	550	602	52	0.78	27.8	4.09	1056	82	64	872	26	20
	THF	0.207	541	600	59	0.76	24.9	4.05	1040	66	50	868	28	21
	Toluene	0.099	534	573	39	0.78	24.7	3.78	1036	30	23	873	31	24

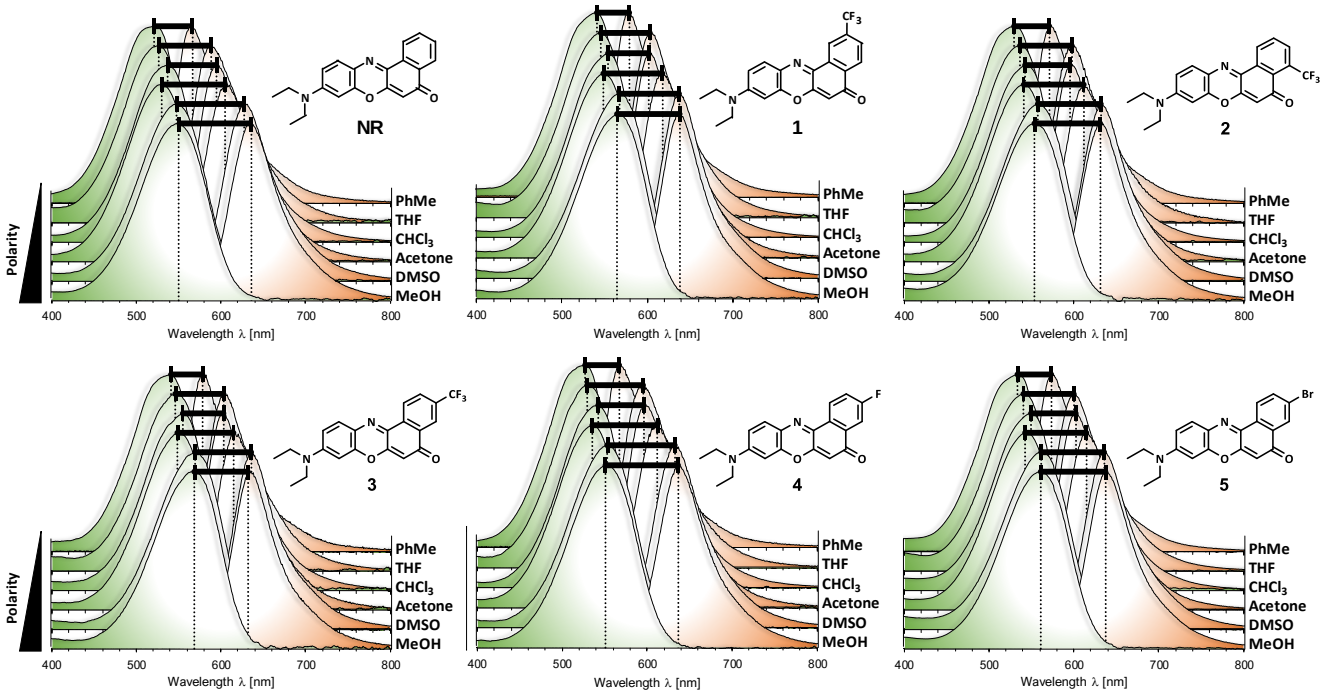


Figure A1. Normalized absorption (green) and fluorescence (orange) spectra for Nile Red (**NR**) and the five analogs **1**–**5** at concentrations of 3.0 μM in the following six solvents with relative polarities given in parentheses (listed in order of decreasing polarity): MeOH (0.762), DMSO (0.444), acetone (0.355), chloroform (0.259), THF (0.207) and toluene (0.099).

Table A2. Natural transition orbitals (NTOs) for the five lowest transitions of **1**.

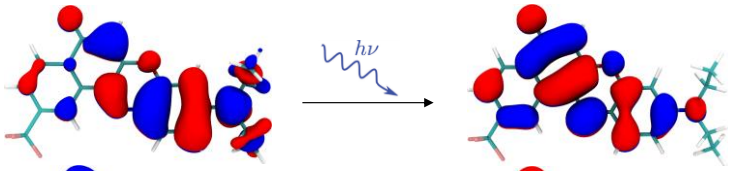
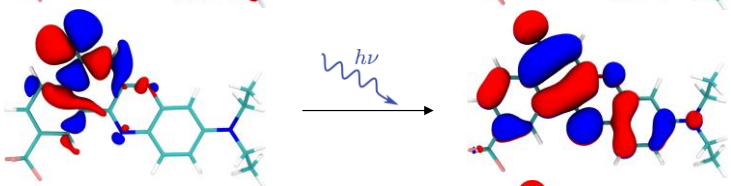
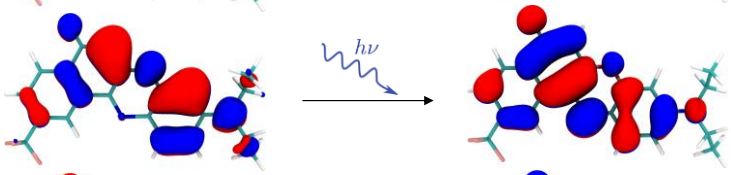
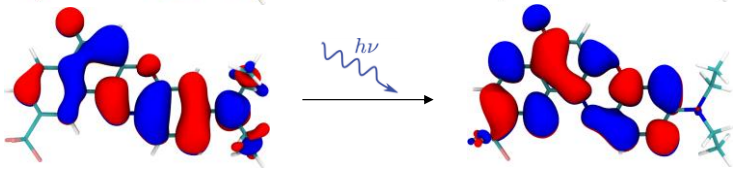
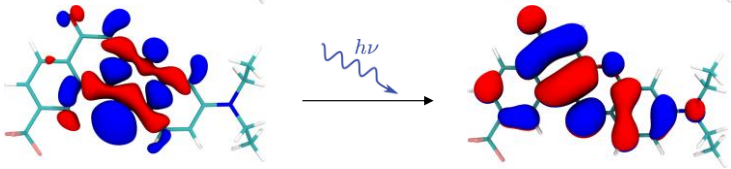
State	Occupied NTO	Virtual NTO	Transition
S_1			$\pi \rightarrow \pi^*$
S_2			$n \rightarrow \pi^*$
S_3			$\pi \rightarrow \pi^*$
S_4			$\pi \rightarrow \pi^*$
S_5			$n \rightarrow \pi^*$

Table A3. Natural transition orbitals (NTOs) for the five lowest transitions of **2**.

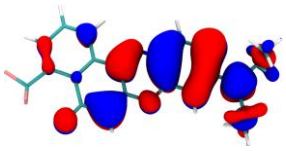
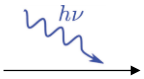
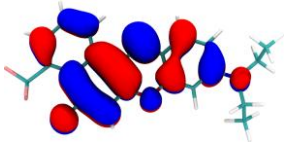
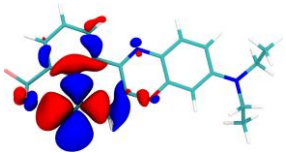
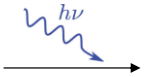
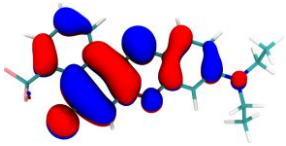
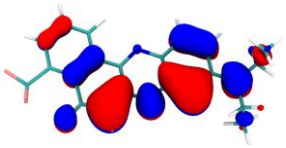
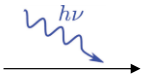
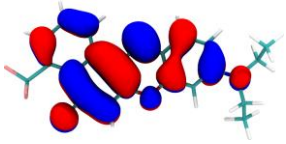
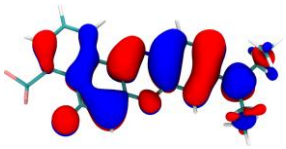
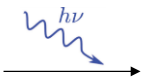
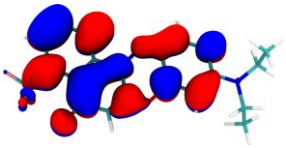
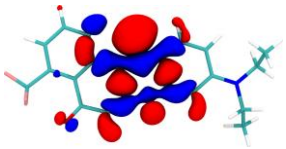
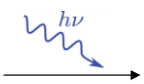
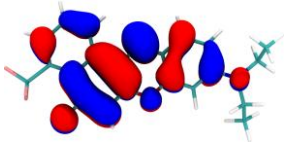
State	Occupied NTO		Virtual NTO	Transition
S_1				$\pi \rightarrow \pi^*$
S_2				$n \rightarrow \pi^*$
S_3				$\pi \rightarrow \pi^*$
S_4				$\pi \rightarrow \pi^*$
S_5				$n \rightarrow \pi^*$

Table A4. Natural transition orbitals (NTOs) for the five lowest transitions of **3**.

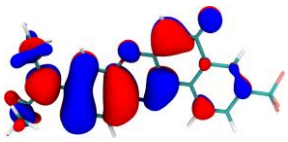
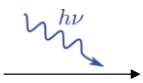
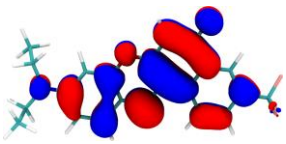
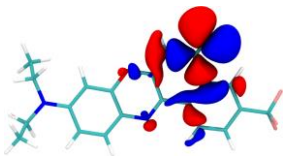
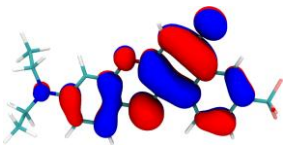
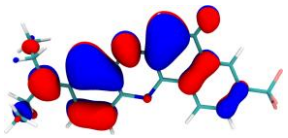
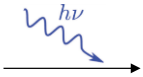
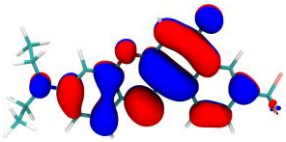
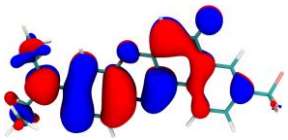
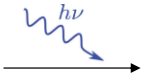
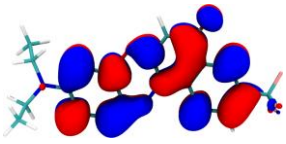
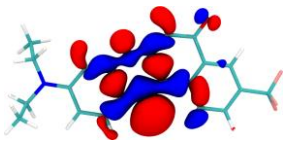
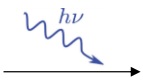
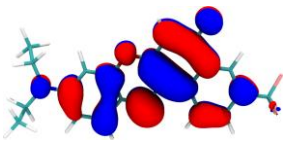
State	Occupied NTO		Virtual NTO	Transition
S_1				$\pi \rightarrow \pi^*$
S_2				$n \rightarrow \pi^*$
S_3				$\pi \rightarrow \pi^*$
S_4				$\pi \rightarrow \pi^*$
S_5				$n \rightarrow \pi^*$

Table A5. Natural transition orbitals (NTOs) for the five lowest transitions of **4**.

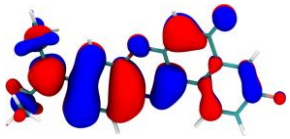
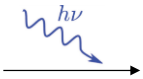
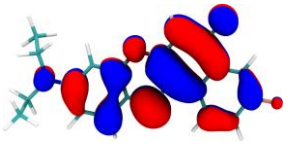
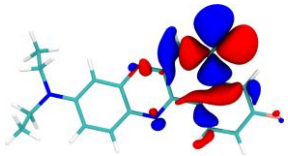
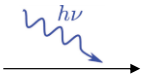
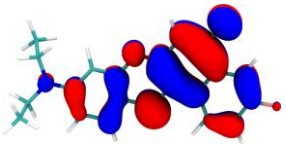
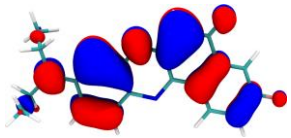
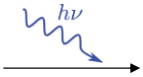
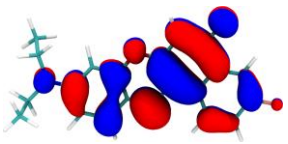
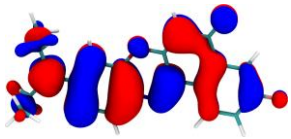
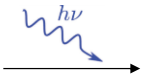
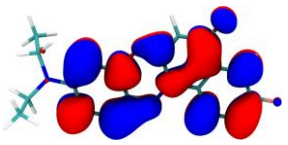
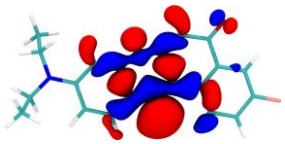
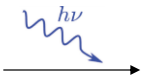
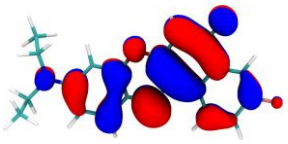
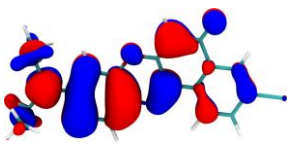
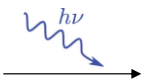
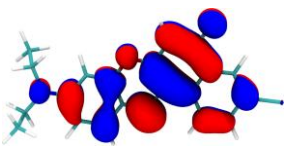
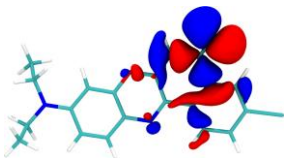
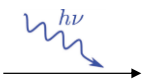
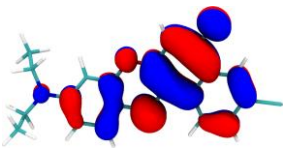
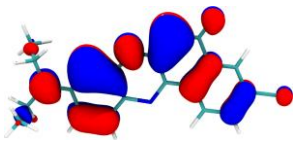
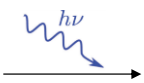
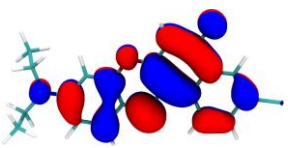
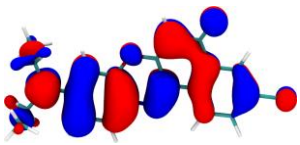
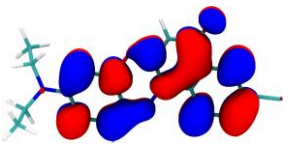
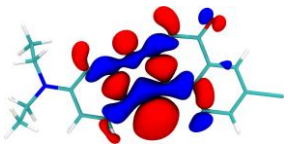
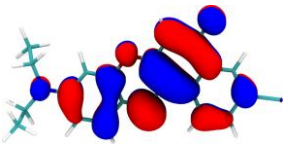
State	Occupied NTO		Virtual NTO	Transition
S_1				$\pi \rightarrow \pi^*$
S_2				$n \rightarrow \pi^*$
S_3				$\pi \rightarrow \pi^*$
S_4				$\pi \rightarrow \pi^*$
S_5				$n \rightarrow \pi^*$

Table A6. Natural transition orbitals (NTOs) for the five lowest transitions of **5**.

State	Occupied NTO		Virtual NTO	Transition
S_1				$\pi \rightarrow \pi^*$
S_2				$n \rightarrow \pi^*$
S_3				$\pi \rightarrow \pi^*$
S_4				$\pi \rightarrow \pi^*$
S_5				$n \rightarrow \pi^*$