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Supporting Information

Consecutive Photoinduced Electron Transfer (conPET): The Mechanism of the Photocatalyst Rhodamine 6G

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Author Contributions

C.A. Methodology: supporting
B.D. Conceptualization: lead; formal analysis: equal; funding acquisition: lead; software: lead; writing—original draft: lead; writing—review and editing: Equal.

Supplementary Information

Contents

Table X1: Absolute energies (Hartree) for the optimized ground state structures of the various DIPEA species (D1 – D7), the rhodamine-6G cation ($R6G^+$), and the rhodamine-6G radical ($R6G^\bullet$), obtained with B3LYP/cc-pVTZ and B3LYP/aug-cc-pVTZ both in vacuum and with DMSO as solvent (D-PCM model). The energy differences of products and reactants for the various electron and proton transfer reactions (see schemes 2 and 3) are given in kcal/mole units.

	DFT-CCT	DFT-CCT-DMSO	DFT-ACCT	DFT-ACCT-DMSO
D1	-371.174644	-371.176632	-371.177640	-371.179548
D2	-370.920076	-370.992858	-370.922477	-370.995096
D3a	-370.358991	-370.431713	-370.361424	-370.434097
D3b	-370.353349	-370.426873	-370.355768	-370.429218
D4a	-370.520662	-370.522418	-370.523809	-370.525571
D4b	-370.523621	-370.526147	-370.527238	-370.529726
D5	-371.568258	-371.642784	-371.570735	-371.645142
$R6G^+$	-1106.563577	-1106.634445	-1106.563577	-1106.634445
R6G°	-1106.736914	-1106.759222	-1106.736914	-1106.759222
Reaction	[kcal/mol]			
Reaction-1a	3.64	2.69	3.50	2.47
Reaction-1b	1.78	0.35	1.34	-0.14
Reaction-2a	-7.32	-21.38	-6.87	-20.90
Reaction-2b	-1.92	-16.00	-1.17	-15.23
Reaction-3	-5.40	-5.38	-5.70	-5.67

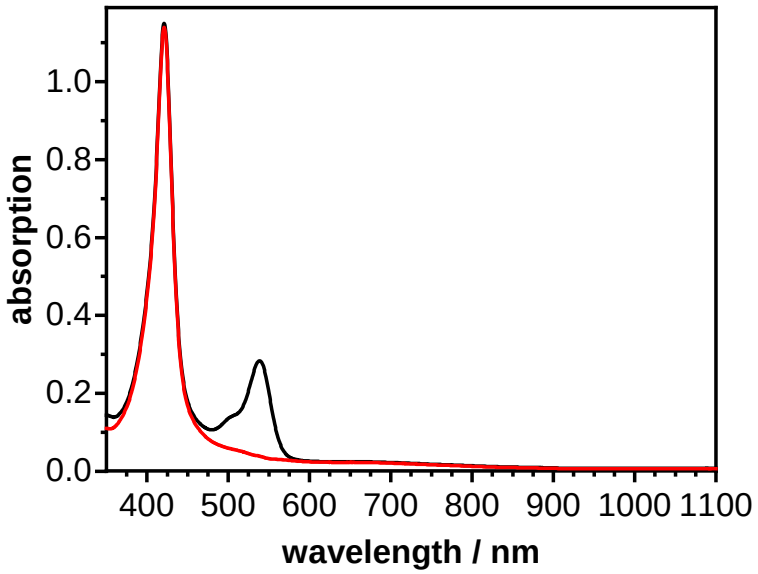

Figure S1: Absorption spectrum of R6G radical generated with Zn and some not converted $R6G^+$ (black spectrum). The spectrum of pure R6G radical (red spectrum) was obtained by subtraction of the $R6G^+$ spectrum.

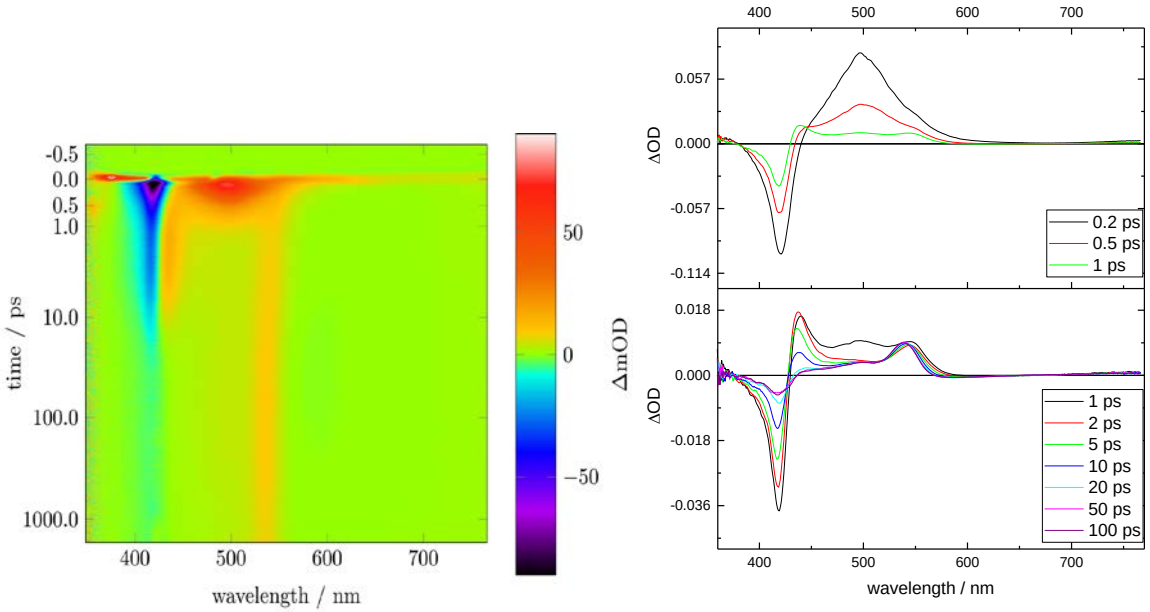

Figure S2: Transient absorption spectrum of R6G• in DMSO, generated with DIPEA. Blue shades mark a loss of absorption, like the ground state bleach at 420nm. Red shades mark excited state absorption. On the right time profiles are shown. Fitting this spectrum leads to DADS seen in Figure 5.

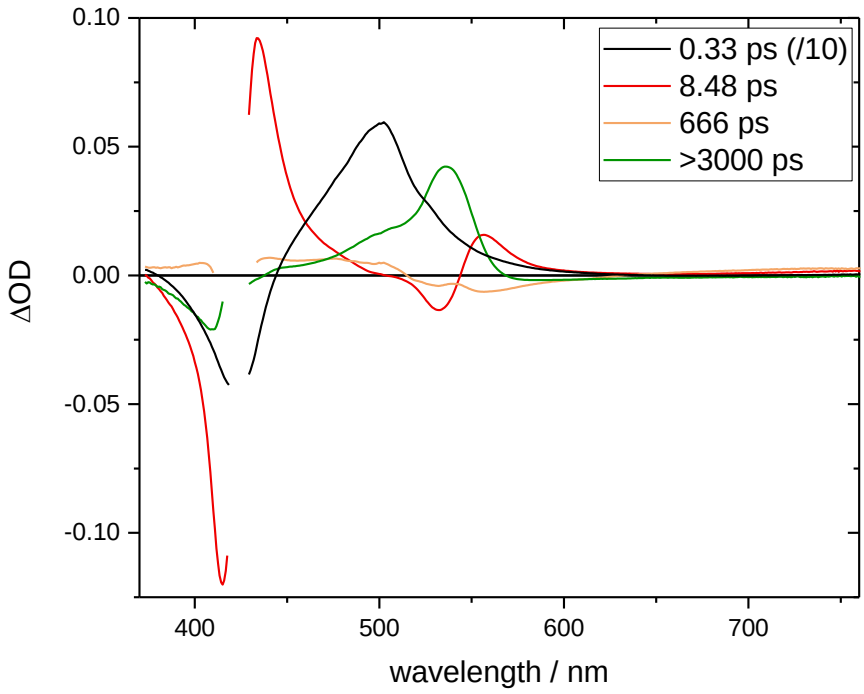

Figure S3: DADS of excited rhodamine radical generated with DIPEA in DMSO and with 2-Bromobenzonitrile(c = 8.6×10^{-2} M). The substrate shows now influence, the results are similar to the measurements without substrate.

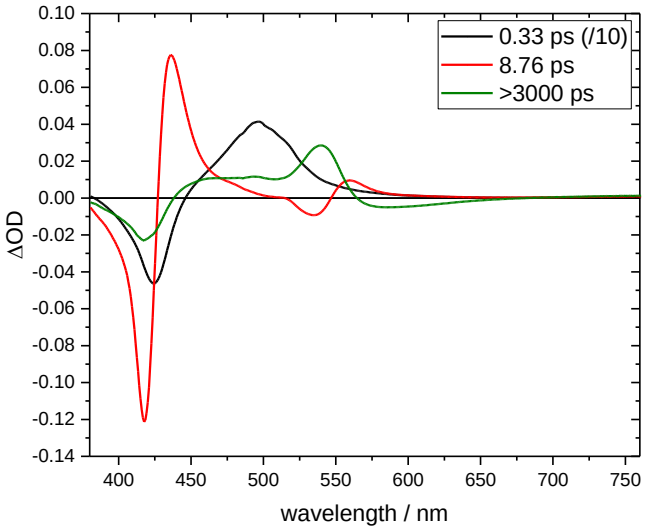

Figure S4: DADS of excited rhodamine radical generated with Zn in DMSO. A fast component (black) mainly describing the decay of the excited radical state to electronic groundstate of the radical. The intensity was divided by ten to plot it together with other components. The red component describes the spectral shift of both, radical and rhodamine 6g due to vibrational cooling. The long component consists of the stimulated emission, belonging to the not converted rhodamine 6g, and the remaining rhodamine after oxidation of the radical and cooling together with the radical groundstate bleach.

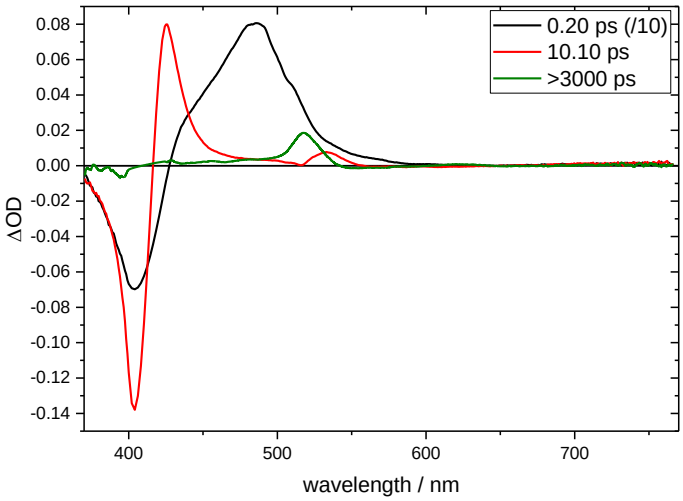

Figure S5: DADS of excited rhodamine radical generated with a green LED and DIPEA in MeCN. A fast component (black) mainly describing the decay of the excited radical state to electronic groundstate of the radical. The intensity was divided by ten to plot it together with other components. The red component describes the spectral shift of both, radical and rhodamine 6g due to vibrational cooling. The long component consists of the remaining rhodamine after oxidation of the radical and cooling together with the radical groundstate bleach.

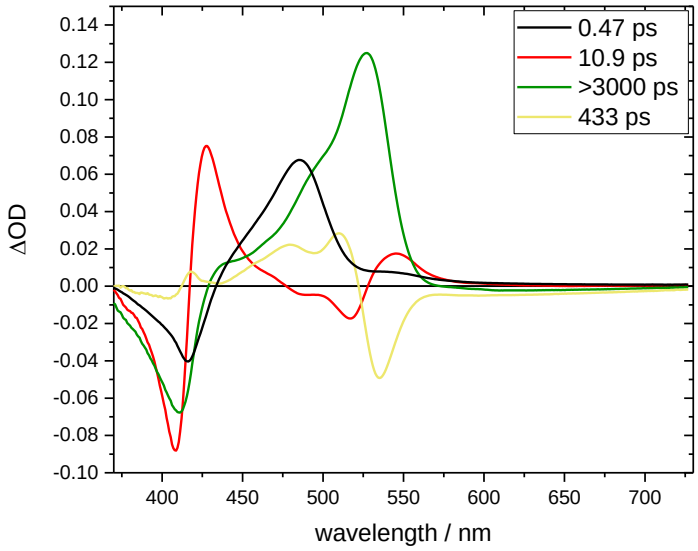

Figure S6: DADS of excited rhodamine radical generated with a green LED and DIPEA in DCM . The fast component (black) mainly describing the decay of the excited radical state to electronic groundstate of the radical. The intensity was divided by ten to plot it together with other components. The red component describes the spectral shift of both, radical and rhodamine 6g due to vibrational cooling. The Yellow component contains the stimulated emission. The long component consists of the remaining rhodamine after oxidation of the radical and cooling together with the radical groundstate bleach.

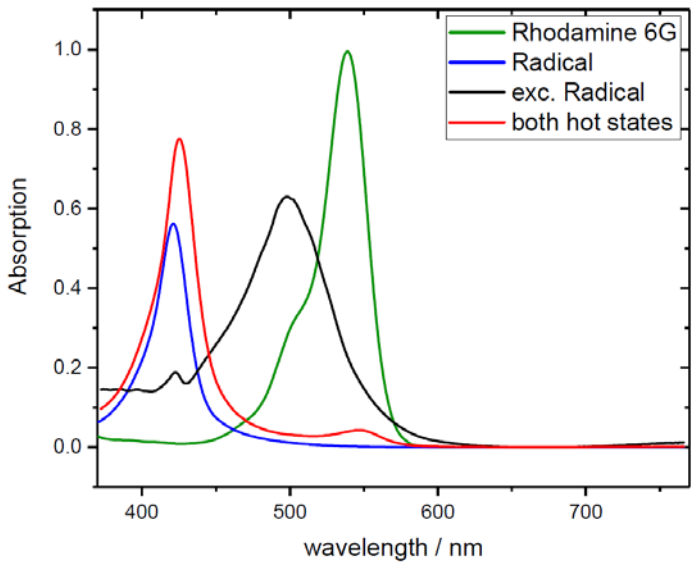

Figure S7: Absorption spectra of all rhodamine 6g species in DMSO. Green is the rhodamine 6g and blue the radical in their ground states respectively. Black is the decomposed excited radical and red is the combined vibrational hot state of rhodamine 6g and radical.

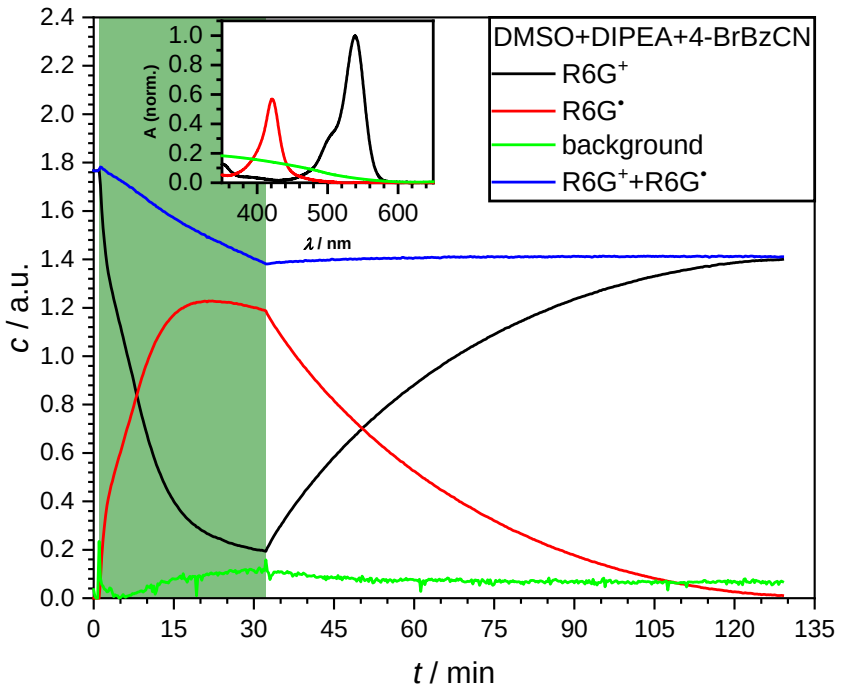

Figure S8: Concentration profiles of $R6G^+$ and $R6G^\bullet$ in a solution of $R6G^+$ in DMSO with DIPEA and 4-Bromobenzonitrile (4-BrBzCN) irradiated with green LEDs in the green highlighted time range. A third component denoted by background was used to describe instrumental drifts and other generated species. The corresponding spectra are displayed in the inset.

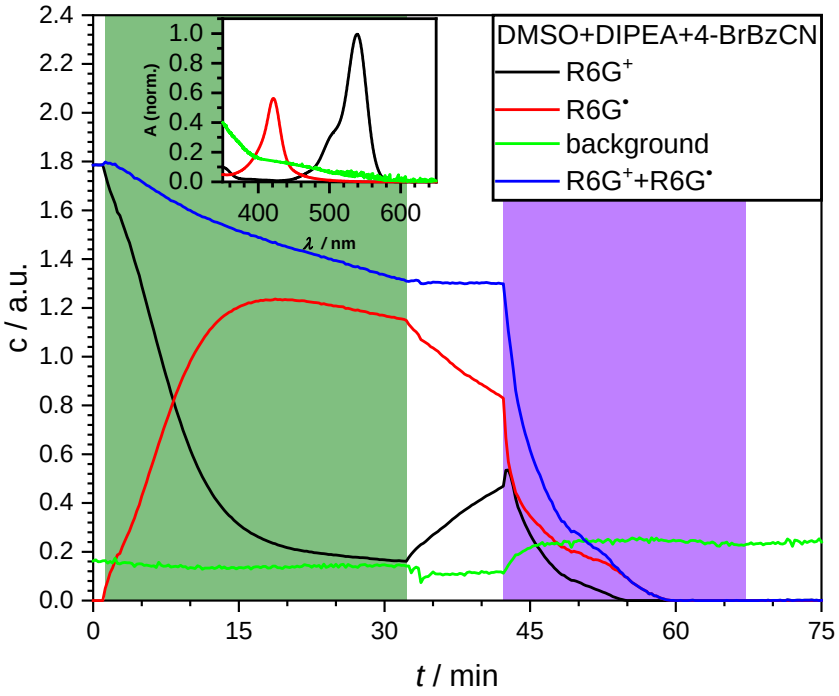

Figure S9: Concentration profiles of $R6G^+$ and $R6G^\bullet$ in a solution of $R6G^+$ in DMSO with DIPEA and 4-Bromobenzonitrile (4-BrBzCN) irradiated with green or blue (420 nm) LEDs in the highlighted time ranges. A third component denoted by background was used to describe instrumental drifts and other generated species. The corresponding spectra are displayed in the inset.