Supplementary Materials: Photophysics of BODIPY Dyes as Readily Designable Photosensitisers in Light-Driven Proton Reduction

Laura Dura, Maria Wächtler, Stephan Kupfer, Joachim Kübel, Johannes Ahrens, Sebastian Höfler, Martin Bröring, Benjamin Dietzek, Torsten Beweries

S2	Volumetric curves (as measured) and Hg experiments
S3	Stationary emission spectra
S5	Stern Volmer experiments
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Volumetric Curves

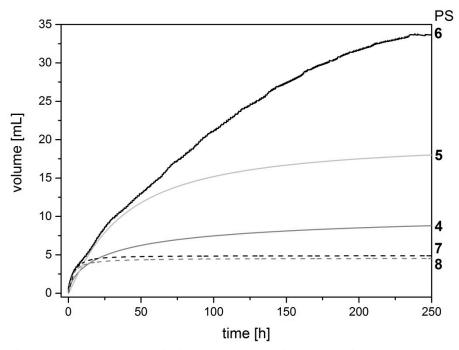


Figure S1. Volumetric curves (original data) as measured using multicomponent catalyst systems sensitized by **4–8** containing 10 mL of a 1 mM solution of the PS in THF, 1 mL of a 1 mM solution of [PdCl₂(PPh₃)]₂ in THF, 3 mL water, and 8 mL TEA.

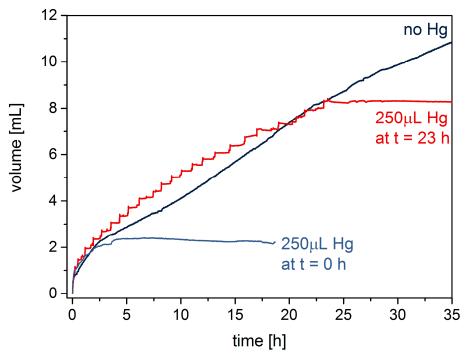


Figure S2. Comparison of volumetric curves (original data) as measured using multicomponent catalyst systems containing 10 mL of a 1 mM solution of in THF, 1 mL of a 1 mM solution of [PdCl₂(PPh₃)]₂ in THF, 3 mL water, 8 mL TEA, and 250 µL Hg.

Stationary Emission Spectra

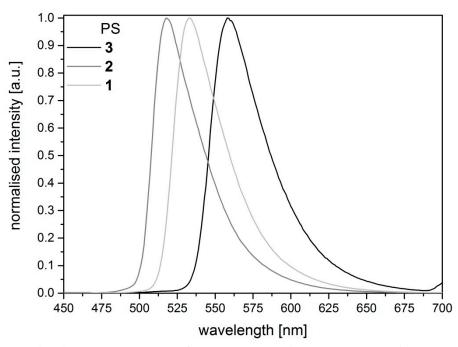


Figure S3. Normalised emission spectra of pure BODIPY dyes 1–3 measured in THF, $c = 5 \times 10^{-5}$ M, $\lambda_{exc} = 350$ nm.

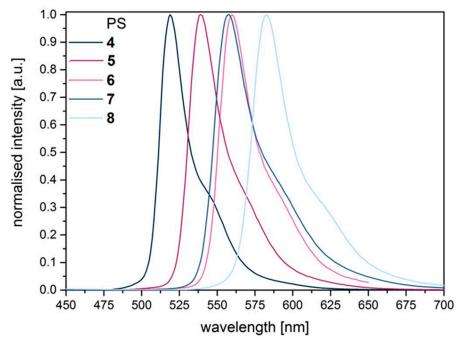


Figure S4. Normalised emission spectra of pure BODIPY dyes **4–8** measured in THF, $c = 5 \times 10^{-5}$ M, $\lambda_{exc} = 350$ nm.

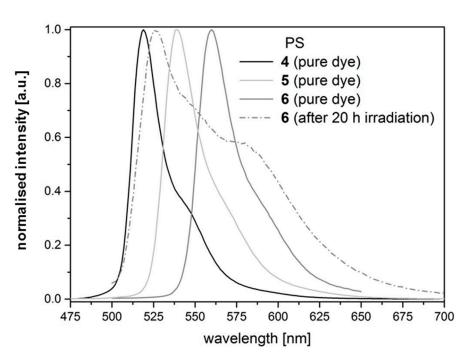


Figure S5. Emission spectra of pure BODIPY dyes **4–6** and a **6**-sensitised multicomponent catalyst system after 20 h of irradiation measured in THF, $c = 5 \times 10^{-5}$ M, $\lambda_{exc} = 350$ nm.

Stern-Volmer Experiments

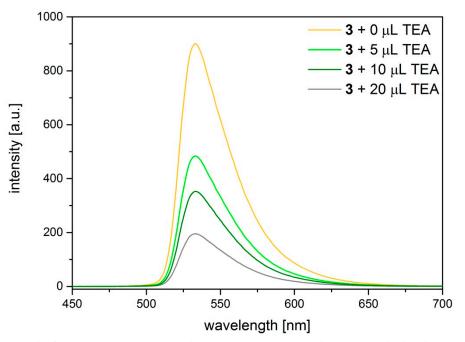


Figure S6. Example for stationary Stern-Volmer experiments with *meso*-methyl substituted BODIPY dyes. Fluorescence quenching with triethylamine (TEA) was observed on a 5×10⁻⁵ M solution of **3** in THF.

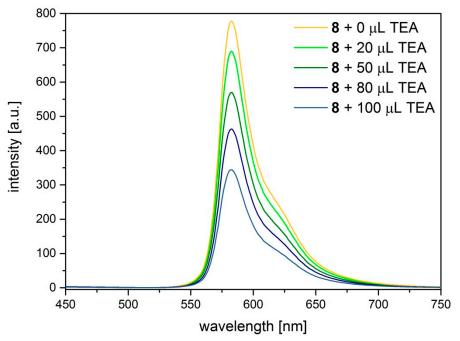


Figure S7. Example for stationary Stern-Volmer experiments with *meso*-mesityl substituted BODIPY dyes. Fluorescence quenching with triethylamine (TEA) was observed on a 5×10^{-5} M solution of **8** in THF.

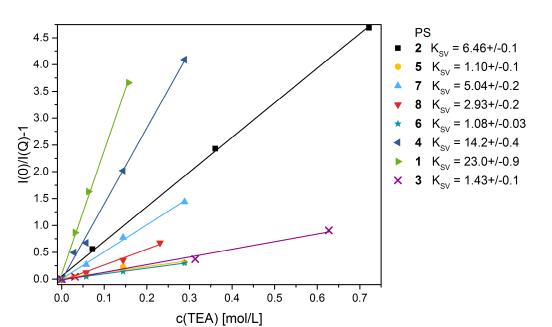


Figure S8. Stern-Volmer plots of fluorescence quenching experiments on BODIPY dyes with TEA.

Stern–Volmer Kinetics

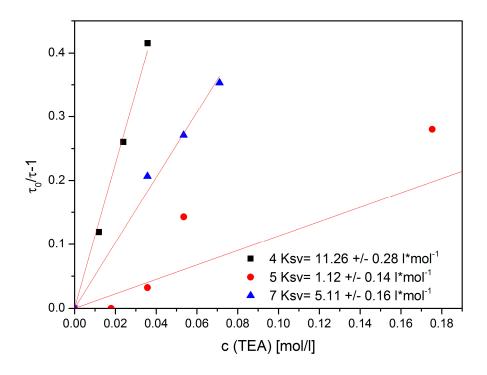
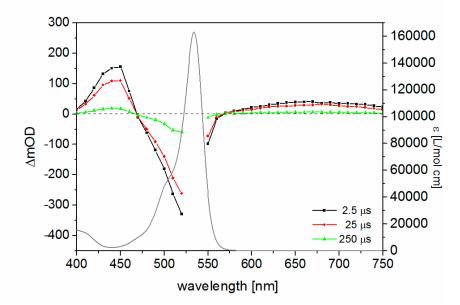


Figure S9. Stern–Volmer Plots from emission lifetime quenching with TEA.

4			5			7		
c(TEA)	τ_{em} / ns^*	$\tau_0/\tau_{em}-1$	c(TEA)	τ_{em} / ns^*	$\tau_0/\tau_{em}-1$	c(TEA)	τ_{em} / ns^*	$\tau_0/\tau_{em}-1$
0	4.62	0	0	0.32	0	0	5.02	0
0.01198	4.11	0.12	0.01793	0.32	0	0.03571	4.16	0.21
0.02393	3.65	0.26	0.03577	0.31	0.03	0.05344	3.95	0.27
0.03583	3.25	0.42	0.05352	0.28	0.14	0.07108	3.71	0.35
			0.17536	0.25	0.28			
			0.34239	0.24	0.33			

Table S1. Lifetimes and parameters for the Stern–Volmer Plots.

*+/- 1%



ns Time-Resolved Transient Absorption Spectra and Kinetics

Figure S10. Transient absorption spectra at chosen delay times (black, red, green) upon excitation with the pump pulse centred at 535 nm and stationary absorption spectrum (grey) of **6** in THF.

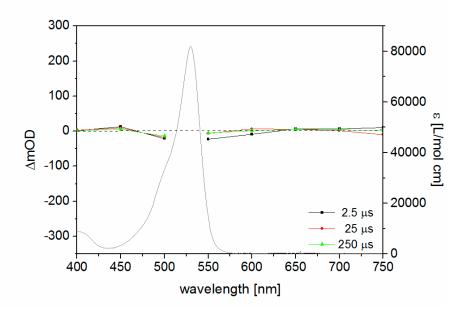


Figure S11. Transient absorption spectra at chosen delay times (black, red, green) upon excitation with the pump pulse centred at 530 nm and stationary absorption spectrum (grey) of **7** in THF.

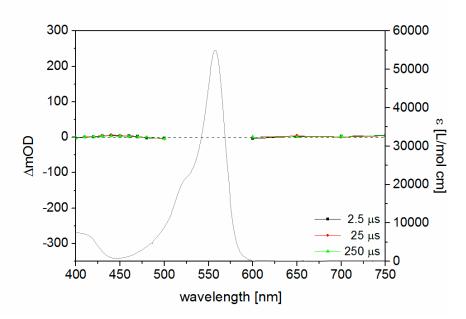


Figure S12. Transient absorption spectra at chosen delay times (black, red, green) upon excitation with the pump pulse centred at 560 nm and stationary absorption spectrum (grey) of **8** in THF.

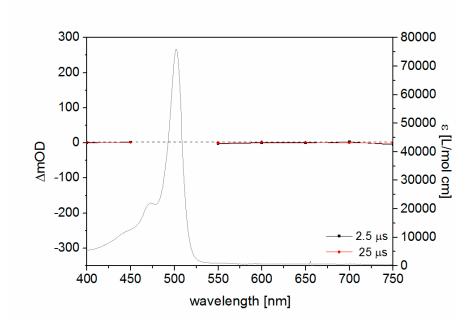


Figure S13. Transient absorption spectra at chosen delay times (black, red, green) upon excitation with the pump pulse centred at 500 nm and stationary absorption spectrum (grey) of **4** in THF.

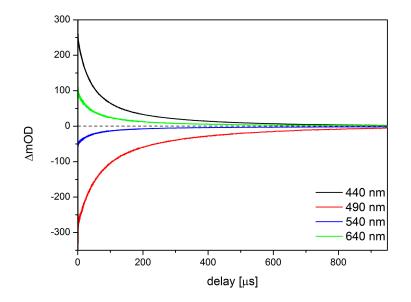


Figure S14. ns- transient absorption decay kinetics of the long-lived triplet state of **5** at chosen probe wavelengths.

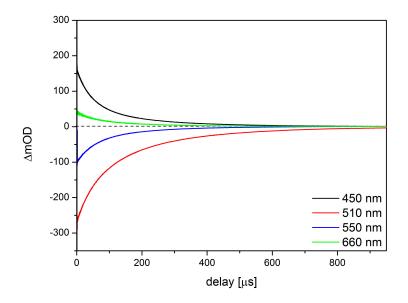


Figure S15. ns- transient absorption decay kinetics of the long-lived triplet state of 6 at chosen probe wavelengths.

Quantum Chemical Evaluation

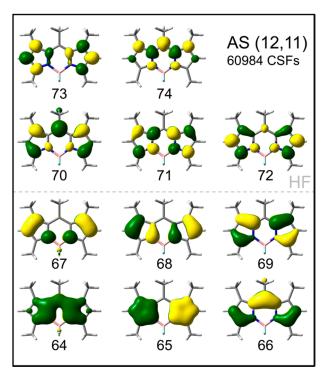


Figure S16. MOs of the AS (12,11), comprising the entire $\pi\pi^*$ system of **2**, used in the MS-CASPT2//CASSCF reference calculations. Grey line indicates to the occupation of the MOs within the Hartree-Fock wavefunction.

	MS-CASP7	Γ2				TD-PBE0				
	Transition	weight	E^e /	λ/	f	Transition	weight /	E^e /	λ/	f
			eV	nm			%	eV	nm	
S_0	HF	83	-	-	-	-	-	-	-	-
S_1	$69 \rightarrow 70$	57	2.72	456	0.672	$69 \rightarrow 70$	95 (99)	3.06	405	0.523
	$68 \rightarrow 70$	15						(2.96)	(419)	(0.641)
S ₂	$68 \rightarrow 70$	52	3.76	330	0.071	$68 \rightarrow 70$	96 (98)	3.65	340	0.062
	$69 \rightarrow 70$	13						(3.67)	(338)	(0.058)
	DE	12								
S ₃	$67 \rightarrow 70$	58	3.93	315	0.042	$67 \rightarrow 70$	99 (99)	3.88	320	0.030
	DE	15						(3.92)	(316)	(0.046)
S_4	DE	37	4.46	288	0.042	$66 \rightarrow 70$	91 (93)	4.94	251	0.138
	$66 \rightarrow 70$	26						(4.90)	(253)	(0.194)
	$69 \rightarrow 74$	8								
T_1	$69 \rightarrow 70$	82	1.99	623	-	$69 \rightarrow 70$	98 (98)	1.55	800	-
								(1.59)	(782)	
T_2	$68 \rightarrow 70$	72	3.23	384	0.004	$68 \rightarrow 70$	95 (95)	2.86	434	_
								(2.91)	(426)	
Тз	$67 \rightarrow 70$	67	3.40	365	0.005	$67 \rightarrow 70$	86 (83)	2.98	416	_
						$66 \rightarrow 70$	8 (11)	(3.04)	(408)	
T_4	$66 \rightarrow 70$	69	3.92	316	0.176	$66 \rightarrow 70$	88 (85)	3.44	361	_
	$67 \rightarrow 70$	5				$67 \rightarrow 70$	8 (12)	(3.45)	(359)	

Table S2. Leading transitions, excitation energies (in eV), wavelengths (in nm), and oscillator strengths obtained by MS-CASPT2 (gas phase) and by TDDFT using the PBE0 functional for the low-lying singlet and triplet states of **2**. TDDFT values are given in gas phase and in THF (in parentheses).

Table S3. MOs involved in leading transitions of low-lying bright excited singlet state (S1) and low-lying triplet states (T1-T3) within the fully optimized singlet ground state equilibrium structure of **2**. **2** (optimized S0 geometry)

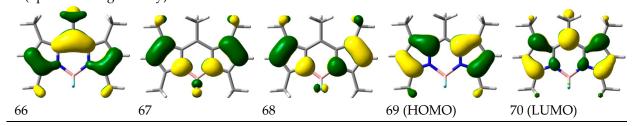
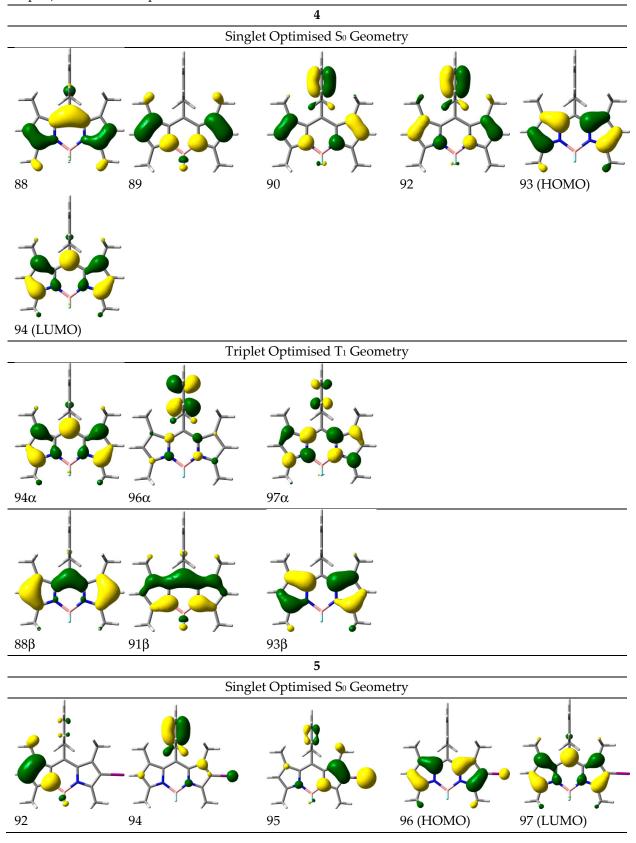
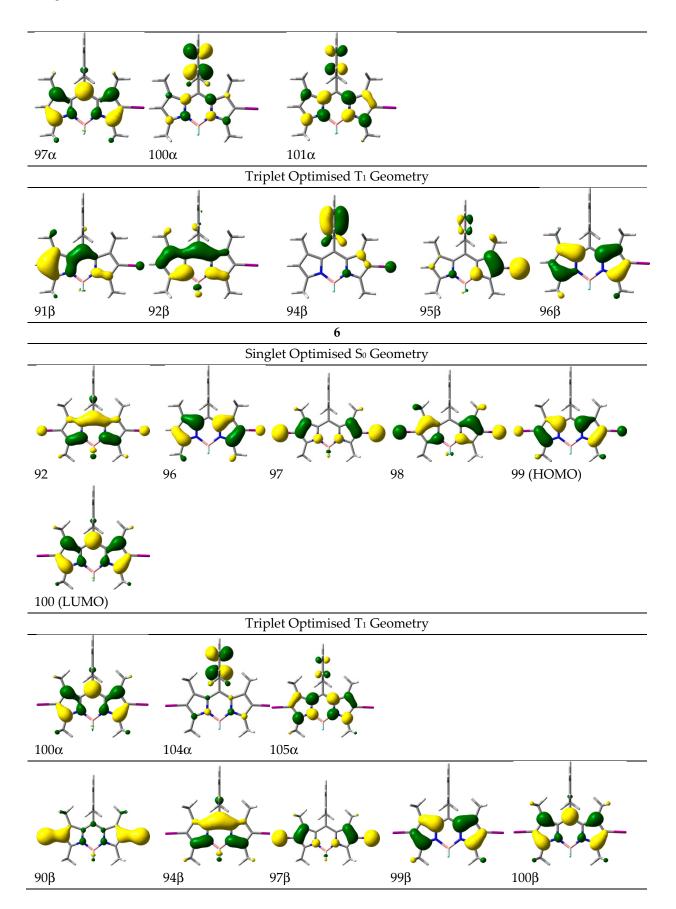


Table S4. Excited and ground state energies of S₀, S₁, T₁, T₂, and T₃ within optimized equilibrium geometries of S₀, S₁ and T₁ for dyes of **4–8**. All numbers are given relative to the ground state energy (S₀) in the optimized S₀ structure.

		Equilibrium Geometry														
			4			5			6		-	7			8	
		S_0	S_1	T_1	S_0	S_1	T_1	S ₀	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
>	S_0	0.00	0.04	0.13	0.00	0.04	0.12	0.00	0.05	0.09	0.00	0.04	0.11	0.00	0.04	0.10
/eV	S_1	2.91	2.71	2.91	2.81	2.63	2.84	2.75	2.59	2.80	2.80	2.62	2.81	2.69	2.52	2.72
$E^{\ell}(state)$	T_1	1.49	1.41	1.53	1.48	1.45	1.53	1.54	1.56	1.59	1.46	1.41	1.51	1.43	1.40	1.48
(ste	T_2	2.83	2.88	3.13	2.68	2.66	2.94	2.61	2.57	2.83	2.68	2.69	2.97	2.63	2.63	2.91
E^{e}	Т3	3.00	2.99	3.15	2.92	2.94	3.10	2.79	2.73	3.38	2.99	3.00	3.15	2.87	2.88	3.09

Table S5. MOs involved in leading transitions of bright excited singlet states (and low-lying triplet states (T₁-T₃)) of **4–8** within the S₀ equilibrium structure and bright triplet excited states (triplet-to-triplet) within the T₁ equilibrium structure.





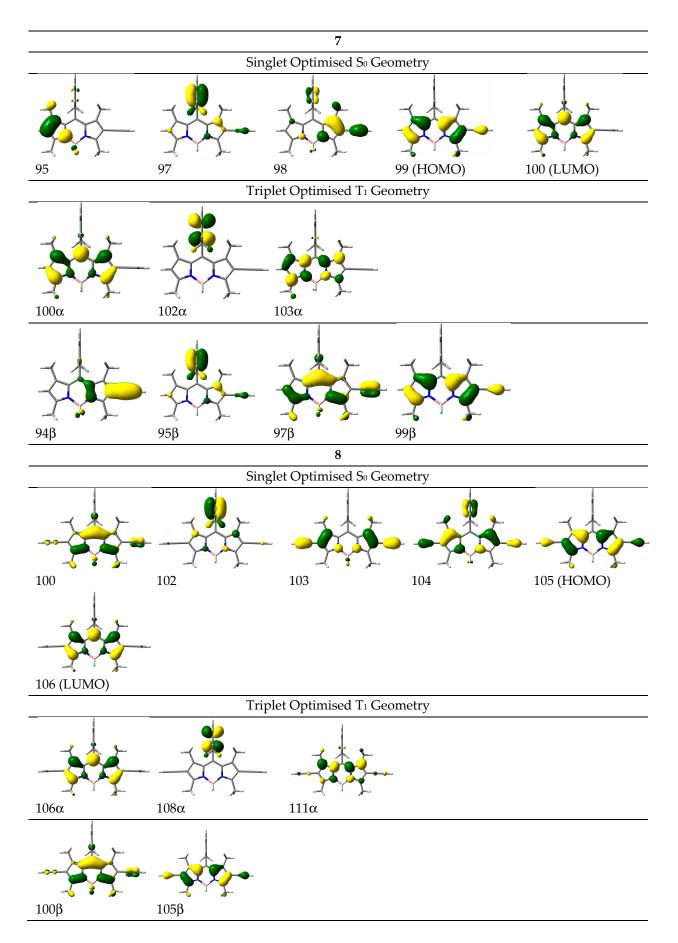


Table S6: Leading transitions, excitation energies (in eV), wavelengths (in nm), oscillator strengths and $\langle s^2 \rangle$ expectation value (spin-contamination) of bright UV-VIS excitations (singlet and triplet)

obtained at the TDDFT level of theory in THF for dyes 4–8 . Singlet-to-singlet and triplet-to-triplet
excitations were obtained within the respective equilibrium structure.

		4					
Singlet Excited States (Optimised S ₀ Geometry)							
state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$	
S ₁	$93 \rightarrow 94 \text{ LE}$	99	2.91	427	0.591	-	
S ₄	$90 \rightarrow 94 \text{ CT}$	95	3.76	330	0.046	-	
S ₅	$89 \rightarrow 94 \text{ LE}$	99	3.85	322	0.043	-	
	Triplet Excite	d States (Opti	imised T	Geomet	ry)		
state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$	
T ₂	$91\beta \rightarrow 93\beta$ LE	93	1.60	774	0.036	2.05	
T5	$88\beta \rightarrow 93\beta$ LE	90	2.22	560	0.067	2.04	
T ₈	$94\alpha \rightarrow 96\alpha \text{ CT}$	84	3.27	380	0.195	2.05	
	$94\alpha \rightarrow 97\alpha$ LE	10					
T 10	$94\alpha \rightarrow 97\alpha$ LE	83	3.54	351	0.168	2.06	
	$94\alpha \rightarrow 96\alpha \text{ CT}$	13					
		5					
Singlet Excited States (Optimised S ₀ Geometry)							
	Singlet Excite	d States (Opt	imised So	Geomet	ry)		
state	Singlet Excite transition	ed States (Opt weight / %			ry) F	$\langle s^2 \rangle$	
state S1	0					(s ²)	
	transition	weight / %	E^e / eV	λ / nm	F		
S 1	transition $96 \rightarrow 97 \text{ LE}$	weight / %	<i>E^e</i> / eV 2.81	λ/nm 441	<i>F</i> 0.616		
S1 S2	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$	weight / % 97 93	<i>E^e</i> / eV 2.81 3.33	λ/nm 441 373	<i>F</i> 0.616 0.055		
S1 S2 S4	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$	weight / % 97 93 95 98	<i>E^e</i> / eV 2.81 3.33 3.60 3.73	λ/nm 441 373 344 332	<i>F</i> 0.616 0.055 0.067 0.049	- -	
S1 S2 S4 S5	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$	weight / % 97 93 95 98	<i>E^e</i> / eV 2.81 3.33 3.60 3.73 imised Tr	λ/nm 441 373 344 332	<i>F</i> 0.616 0.055 0.067 0.049	-	
S1 S2 S4	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excite	weight / % 97 93 95 98 d States (Opti	<i>E^e</i> / eV 2.81 3.33 3.60 3.73 imised Tr	λ/nm 441 373 344 332 Geomet	<i>F</i> 0.616 0.055 0.067 0.049 rry)	- - -	
S1 S2 S4 S5 state	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excited transition	weight / % 97 93 95 98 d States (Opti weight / %	E^{e} / eV 2.81 3.33 3.60 3.73 imised Tr E^{e} / eV	λ / nm 441 373 344 332 Geomet λ / nm	F 0.616 0.055 0.067 0.049 rry) f	- - - - (s ²)	
S1 S2 S4 S5 state T3	transition $96 \rightarrow 97$ LE $95 \rightarrow 97$ LE $94 \rightarrow 97$ CT $92 \rightarrow 97$ LE Triplet Excite transition $92\beta \rightarrow 96\beta$ LE	weight / % 97 93 95 98 d States (Opti weight / % 85	<i>E^e</i> / eV 2.81 3.33 3.60 3.73 imised Tr <i>E^e</i> / eV 1.58	λ / nm 441 373 344 332 Geomet λ / nm 786	<i>F</i> 0.616 0.055 0.067 0.049 rry) <i>f</i> 0.026	- - - - (s ²) 2.05	
S1 S2 S4 S5 state T3	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excite transition $92\beta \rightarrow 96\beta \text{ LE}$ $94\beta \rightarrow 96\beta \text{ CT}$	weight / % 97 93 95 98 d States (Opti weight / % 85 55	<i>E^e</i> / eV 2.81 3.33 3.60 3.73 imised Tr <i>E^e</i> / eV 1.58	λ / nm 441 373 344 332 Geomet λ / nm 786	<i>F</i> 0.616 0.055 0.067 0.049 rry) <i>f</i> 0.026	- - - - (s ²) 2.05	
S1 S2 S4 S5 state T3	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excite transition $92\beta \rightarrow 96\beta \text{ LE}$ $94\beta \rightarrow 96\beta \text{ LE}$ $91\beta \rightarrow 96\beta \text{ LE}$	weight / % 97 93 95 98 d States (Opti weight / % 85 55 31	<i>E^e</i> / eV 2.81 3.33 3.60 3.73 imised Tr <i>E^e</i> / eV 1.58	λ / nm 441 373 344 332 Geomet λ / nm 786	<i>F</i> 0.616 0.055 0.067 0.049 rry) <i>f</i> 0.026	- - - - (s ²) 2.05	
S1 S2 S4 S5 state T3 T5	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excite transition $92\beta \rightarrow 96\beta \text{ LE}$ $94\beta \rightarrow 96\beta \text{ LE}$ $91\beta \rightarrow 96\beta \text{ LE}$ $92\beta \rightarrow 96\beta \text{ LE}$	weight / % 97 93 95 98 d States (Opti weight / % 85 55 31 10	E^{e} / eV 2.81 3.33 3.60 3.73 imised Tr E^{e} / eV 1.58 1.99	λ / nm 441 373 344 332 Geomet λ / nm 786 622	<i>F</i> 0.616 0.055 0.067 0.049 ry) <i>f</i> 0.026 0.068	- - - - 2.05 2.04	
S1 S2 S4 S5 state T3 T5	transition $96 \rightarrow 97 \text{ LE}$ $95 \rightarrow 97 \text{ LE}$ $94 \rightarrow 97 \text{ CT}$ $92 \rightarrow 97 \text{ LE}$ Triplet Excite transition $92\beta \rightarrow 96\beta \text{ LE}$ $94\beta \rightarrow 96\beta \text{ LE}$ $92\beta \rightarrow 96\beta \text{ LE}$ $92\beta \rightarrow 96\beta \text{ LE}$ $91\beta \rightarrow 96\beta \text{ LE}$	weight / % 97 93 95 98 d States (Opti weight / % 85 55 31 10 55	E^{e} / eV 2.81 3.33 3.60 3.73 imised Tr E^{e} / eV 1.58 1.99	λ / nm 441 373 344 332 Geomet λ / nm 786 622	<i>F</i> 0.616 0.055 0.067 0.049 ry) <i>f</i> 0.026 0.068	- - - - 2.05 2.04	
S1 S2 S4 S5 state T3 T5	transition $96 \rightarrow 97$ LE $95 \rightarrow 97$ LE $94 \rightarrow 97$ CT $92 \rightarrow 97$ LE Triplet Excite transition $92\beta \rightarrow 96\beta$ LE $94\beta \rightarrow 96\beta$ LE $92\beta \rightarrow 96\beta$ LE $91\beta \rightarrow 96\beta$ LE $91\beta \rightarrow 96\beta$ LE $91\beta \rightarrow 96\beta$ LE $94\beta \rightarrow 96\beta$ CT	weight / % 97 93 95 98 d States (Opti weight / % 85 55 31 10 55 34	E^{e} / eV 2.81 3.33 3.60 3.73 imised Tr E^{e} / eV 1.58 1.99	λ / nm 441 373 344 332 Geomet λ / nm 786 622	<i>F</i> 0.616 0.055 0.067 0.049 ry) <i>f</i> 0.026 0.068	- - - - 2.05 2.04	

Singlet Excite States (OFF eV 8 λ/nm f $\langle s^2 \rangle$ stateiransition ψ eight / $\%$ k^2 , eV λ/nm f $\langle s^2 \rangle$ S199 \rightarrow 100 LE933.393660.102-S298 \rightarrow 100 LE983.443600.062-S396 \rightarrow 100 LE973.533510.036-S396 \rightarrow 100 LE973.533510.036-S497 \rightarrow 100 LE973.533510.036-S497 \rightarrow 99 β LE1053.743.0152.03994 β \rightarrow 99 β LE1072.03897 β \rightarrow 99 β LE101022.03897 β \rightarrow 99 β LE1072.03897 β \rightarrow 99 β LE1012.03897 β \rightarrow 99 β LE1072.0382.051100 α \rightarrow 104 α CT513.353700.2892.035100 α \rightarrow 104 α CT513.353700.2892.0512.06498 β \rightarrow 99 β LE1271.490 β \rightarrow 99 β LE1271.4100 α \rightarrow 104 α CT9121.43610.0212.041100 α \rightarrow 104 α CT9121.543500.1162.041100 α \rightarrow 104 α CT92.804.330.60-3.543500.1162.041100 α \rightarrow 104 α CT92.804.330.613.613.613.61 <th></th> <th></th> <th>6</th> <th></th> <th></th> <th></th> <th></th>			6				
Sin 99 → 100 LE 96 2.75 450 0.692 - Si 97 → 100 LE 93 3.39 366 0.192 - Si 97 → 100 LE 98 3.44 360 0.062 - Si 97 → 100 LE 97 3.53 351 0.036 - Si 96 → 100 LE 97 3.53 351 0.036 - Ti 96 → 999 LE Si 1.42 873 0.015 2.039 94β → 999 LE 10 - - - - - - - 713 97β → 99β LE 10 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -		Singlet Excite	d States (Opt	imised S	Geomet	ry)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S_1	$99 \rightarrow 100 \text{ LE}$	96	2.75	450	0.692	-
S2 96 → 100 LE 97 3.53 351 0.036 - Triplet Excite< States (Optimised Ti Geometri	S ₂	$98 \rightarrow 100 \text{ LE}$	93	3.39	366	0.192	-
Triplet Excited States (Optimised Ti Geometry) state transition weight / % E^r / eV $\lambda/$ nm f $\langle s^2 \rangle$ T ₃ 97 $\beta \rightarrow$ 99 β LE 85 1.42 873 0.015 2.039 94 $\beta \rightarrow$ 99 β LE 10 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -	S_4	$97 \rightarrow 100 \text{ LE}$	98	3.44	360	0.062	-
state transition weight / % E' / eV λ / nm f $\langle s^2 \rangle$ T3 97β \rightarrow 99β LE 85 1.42 873 0.015 2.039 94β \rightarrow 99β LE 10	S_5	$96 \rightarrow 100 \text{ LE}$	97	3.53	351	0.036	-
T3 97β → 99β LE 85 1.42 873 0.015 2.039 94β → 99β LE 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 100 10 100 10 10 10 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 100 <td></td> <td>Triplet Excited</td> <td>d States (Opti</td> <td>imised T</td> <td>Geomet</td> <td>ry)</td> <td></td>		Triplet Excited	d States (Opti	imised T	Geomet	ry)	
94β → 99β LE 10 T5 94β → 99β LE 84 1.80 691 0.217 2.038 97β → 99β LE 10	state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
T5 94β → 99β LE 84 1.80 691 0.217 2.038 97β → 99β LE 10	T ₃	$97\beta \rightarrow 99\beta$ LE	85	1.42	873	0.015	2.039
97β → 99β LE10T13 $100\alpha \rightarrow 104\alpha$ CT51 3.35 370 0.289 2.035 $100\alpha \rightarrow 105\alpha$ LE 30 $-100\alpha \rightarrow 105\alpha$ LE 30 $-100\alpha \rightarrow 105\alpha$ LE 30 $90\beta \rightarrow 99\beta$ LE 12 $-100\alpha \rightarrow 109\alpha$ CT 9 $-100\alpha \rightarrow 104\alpha$ CT 9 T14 $90\beta \rightarrow 99\beta$ LE 67 3.44 361 0.025 2.064 $98\beta \rightarrow 100\beta$ LE 12 $-100\alpha \rightarrow 104\alpha$ CT 9 $-100\alpha \rightarrow 104\alpha$ CT 9 T16 $100\alpha \rightarrow 104\alpha$ CT 38 $-100\alpha \rightarrow 104\alpha$ CT 38 $-100\alpha \rightarrow 104\alpha$ CTSinglet ExciteStates (Optimized So Geometry)State $100\alpha \rightarrow 1004\alpha$ CT 38 S1 $99 \rightarrow 100$ LE 97 2.80 443 0.640 S2 $98 \rightarrow 100$ LE 97 2.80 443 0.640 S2 $98 \rightarrow 100$ LE 92 3.33 372 0.058 S4 $97 \rightarrow 100$ CT 94 3.61 344 0.075 S3 $95 \rightarrow 100$ LE 98 3.74 332 0.049 S4 $97 \rightarrow 99\beta$ LE 75 1.64 755 0.034 S4 $97\beta \rightarrow 99\beta$ LE 79 1.64 755 0.034 S4 $97\beta \rightarrow 99\beta$ LE 79 2.13 583 0.086 $75 \rightarrow 99\beta$ CT 15 -164 755 0.34 2.05 $75 \rightarrow 99\beta$ CT 12 -133 583 0.192 2.05 $75 \rightarrow 99\beta$ CT 12 $-1100\alpha \rightarrow 102\alpha$ CT 86 3.23 384 0.192 2.05		$94\beta \rightarrow 99\beta$ LE	10				
T13100α → 104α CT513.353700.2892.035100α → 105α LE3090β → 99β LE12	T ₅	$94\beta \rightarrow 99\beta$ LE	84	1.80	691	0.217	2.038
100α \rightarrow 105α LE3090β \rightarrow 99β LE12T1490β \rightarrow 99β LE673.443610.0252.06498β \rightarrow 100β LE12100α \rightarrow 104α CT9T16100α \rightarrow 104α CT38500.1162.044100α \rightarrow 104α CT38FSinglet Excites (Optimised So Geometrystateframsitionweight/% E^e/eV λ/nm f $\langle s^2 \rangle$ S199 \rightarrow 100 LE972.804430.640-S298 \rightarrow 100 LE923.333720.058-S497 \rightarrow 100 CT943.613440.075-S595 \rightarrow 100 LE983.743320.049-S497 \rightarrow 99β LE751.647550.0342.05T397β \rightarrow 99β LE792.135830.0862.04T594β \rightarrow 99β LE792.135830.0862.04T8100α \rightarrow 103α LE82.05T1100α \rightarrow 103α LE833.503540.1902.06		$97\beta \rightarrow 99\beta$ LE	10				
90β \rightarrow 99β LE12T1490β \rightarrow 99β LE673.443610.0252.06498β \rightarrow 100β LE12100α \rightarrow 104α CT911T16100α \rightarrow 105α LE583.543500.1162.044100α \rightarrow 104α CT385555Singlet Excited States (Optimation of the second colspan="4">Singlet States (Optimatio	T13	$100\alpha \rightarrow 104\alpha \ CT$	51	3.35	370	0.289	2.035
T1490β → 99β LE673.443610.0252.06498β → 100β LE12100α → 104α CT91100α → 105α LE583.543500.1162.044100α → 104α CT387100α → 104α CT3811111Singlet ExciteStates (Optimised So Geometry)statetransitionweight /% E^e / eV λ / nm f $\langle s^2 \rangle$ S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet ExciteStates (Optimised Ti Geometry)statetransitionweight /% E^e/ eV $\lambda/$ nm f $\langle s^2 \rangle$ S595 → 100 LE983.743320.049-Triplet ExciteStates (Optimised Ti Geometry)statetransitionweight /% E^e/ eV $\lambda/$ nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT15777100α → 102α CT863.233840.1922.05T4100α → 103α LE87100α → 0.19α LE8710.1902.06		$100\alpha \rightarrow 105\alpha$ LE	30				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$90\beta \rightarrow 99\beta$ LE	12				
IntIntIntIntIntIntIntIntIntIntIntIntIntIntIntIntT16100α → 104α CT383500.1162.044Int100α → 104α CT383500.1162.044Int100α → 104α CT383500.1162.044IntInt77777Statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet ExcitedStates (Optimized Ti Geometry)state(s²)Statetransitionweight / % E^e / eV λ / nm f $\langle s² \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT151515151515T8100α → 102α CT863.233840.1922.05100α → 103α LE8100α → 0.193α LE810001.1932.06	T14	$90\beta \rightarrow 99\beta$ LE	67	3.44	361	0.025	2.064
T16100α → 105α LE583.543500.1162.044100α → 104α CT38755555556Singlet Excited States (Optimised So Geometrystatetransitionweight/% E^e/eV λ/nm f $\langle s^2 \rangle$ S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet Excited States (Optimised Ti Geometrystatetransitionweight/% E^e/eV λ/nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT15751.647550.0862.0495β → 99β CT1278100α → 102α CT863.233840.1922.05T1100α → 103α LE83.503540.1902.06		$98\beta \rightarrow 100\beta$ LE	12				
100α → 104α CT 387Singlet Excites (Optimised So Geometrystatetransitionweight /% E^e/eV λ/nm f $\langle s^2 \rangle$ S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet Excited States (Optimised T1 Geometrystatetransitionweight /% E^e/eV λ/nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT15751.647552.04Ts94β → 99β LE792.135830.0862.0495β → 99β CT1277100α → 102α CT863.233840.1922.05100α → 103α LE8773.503540.1902.06		$100\alpha \rightarrow 104\alpha \ CT$	9				
7Singlet Excited States (Optimised So Geometry)statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ S199 \rightarrow 100 LE972.804430.640-S298 \rightarrow 100 LE923.333720.058-S497 \rightarrow 100 CT943.613440.075-S595 \rightarrow 100 LE983.743320.049-Triplet Excited States (Optimised T1 Geometry)statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T397 β \rightarrow 99 β LE751.647550.0342.0595 β \rightarrow 99 β CT15T594 β \rightarrow 99 β LE792.135830.0862.0495 β \rightarrow 99 β CT12T8100 α \rightarrow 102 α CT863.233840.1922.05100 α \rightarrow 103 α LE8T1100 α \rightarrow 103 α LE833.503540.1902.06	T ₁₆	$100\alpha \rightarrow 105\alpha$ LE	58	3.54	350	0.116	2.044
Singlet Excites (Optimised So Geometrystatetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ S199 \rightarrow 100 LE972.804430.640-S298 \rightarrow 100 LE923.333720.058-S497 \rightarrow 100 CT943.613440.075-S595 \rightarrow 100 LE983.743320.049-Triplet Excites (Optimised T1 Geometrystatetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T397 β \rightarrow 99 β LE751.647550.0342.0595 β \rightarrow 99 β CT15151100 α \rightarrow 102 α CT863.233840.1922.05T8100 α \rightarrow 103 α LE81100 α \rightarrow 103 α LE8111.09 α 2.06		$100\alpha \rightarrow 104\alpha \ CT$	38				
statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet Excited States (Optimised T1 Geometry)statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT1515T594β → 99β LE792.135830.0862.0495β → 99β CT12T8100α → 102α CT863.233840.1922.05100α → 103α LE8T1100α → 103α LE833.503540.1902.06			7				
S199 → 100 LE972.804430.640-S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet Excited States (Optimised T1 Geometry)statetransitionweight /% E^e / eV λ / nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT15751.647550.0862.04T8100α → 102α CT863.233840.1922.05100α → 103α LE83.503540.1902.06		Singlet Excite	d States (Opt	imised S	Geomet	ry)	
S298 → 100 LE923.333720.058-S497 → 100 CT943.613440.075-S595 → 100 LE983.743320.049-Triplet Excited Voltation (Optimized T1 Geometrystatetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.05T594β → 99β CT15 I I I I T594β → 99β CT12 I I I I I T8100α → 102α CT86 3.23 384 0.192 2.05 T1 $100\alpha \rightarrow 103\alpha$ LE83 3.50 354 0.190 2.06	state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S ₁	$99 \rightarrow 100 \text{ LE}$	97	2.80	443	0.640	-
S₅95 → 100 LE983.743320.049-Triplet ExciteStates (Optimised T1 Geometry)statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T₃97β → 99β LE751.647550.0342.0595β → 99β CT15755830.0862.04T₅94β → 99β LE792.135830.0862.0495β → 99β CT1275100α → 102α CT863.233840.1922.05100α → 103α LE871100α → 103α LE833.503540.1902.06	S_2	$98 \rightarrow 100 \text{ LE}$	92	3.33	372	0.058	-
Triplet Excited States (Optimised T1 Geometry)statetransitionweight / % E^e / eV λ / nmf $\langle s^2 \rangle$ T397β \rightarrow 99β LE751.647550.0342.0595β \rightarrow 99β CT155830.0862.04T594β \rightarrow 99β LE792.135830.0862.0495β \rightarrow 99β CT125830.1922.05T8100α \rightarrow 102α CT863.233840.1922.05T1100α \rightarrow 103α LE833.503540.1902.06	S_4	$97 \rightarrow 100 \text{ CT}$	94	3.61	344	0.075	-
statetransitionweight / % E^e / eV λ / nm f $\langle s^2 \rangle$ T397β → 99β LE751.647550.0342.0595β → 99β CT15T594β → 99β LE792.135830.0862.0495β → 99β CT12T8100α → 102α CT863.233840.1922.05100α → 103α LE8T1100α → 103α LE833.503540.1902.06	S 5	$95 \rightarrow 100 \text{ LE}$	98	3.74	332	0.049	-
T397β → 99β LE751.647550.0342.0595β → 99β CT1515751.647550.0862.047594β → 99β LE792.135830.0862.0495β → 99β CT1278100α → 102α CT863.233840.1922.05100α → 103α LE871100α → 103α LE833.503540.1902.06		Triplet Excited	d States (Opti	imised T	Geomet	ry)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
T5 $94\beta \rightarrow 99\beta$ LE792.135830.0862.04 $95\beta \rightarrow 99\beta$ CT1212100a $\rightarrow 102a$ CT863.233840.1922.05 $100a \rightarrow 103a$ LE8100a $\rightarrow 103a$ LE833.503540.1902.06	T ₃	$97\beta \rightarrow 99\beta$ LE	75	1.64	755	0.034	2.05
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$95\beta \rightarrow 99\beta \text{ CT}$	15				
T8 $100\alpha \rightarrow 102\alpha \text{ CT}$ 86 3.23 384 0.192 2.05 $100\alpha \rightarrow 103\alpha \text{ LE}$ 8T1 $100\alpha \rightarrow 103\alpha \text{ LE}$ 83 3.50 354 0.190 2.06	T ₅	$94\beta \to 99\beta \ \text{LE}$	79	2.13	583	0.086	2.04
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$95\beta \rightarrow 99\beta \text{ CT}$	12				
$T_1 100\alpha \to 103\alpha \text{ LE} 83 \qquad \qquad 3.50 354 0.190 2.06$	T 8	$100\alpha \rightarrow 102\alpha \ CT$	86	3.23	384	0.192	2.05
		$100\alpha \rightarrow 103\alpha$ LE	8				
$100\alpha \rightarrow 102\alpha \text{ CT}$ 11	T_1	$100\alpha \rightarrow 103\alpha$ LE	83	3.50	354	0.190	2.06
		$100\alpha \rightarrow 102\alpha \text{ CT}$	11				

		8				
Singlet Excited States (Optimised So Geometry)						
state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
S ₁	$105 \rightarrow 106 \text{ LE}$	96	2.69	461	0.713	-
S ₂	$104 \rightarrow 106 \; \text{LE}$	94	3.24	383	0.071	-
S_4	$103 \rightarrow 106 \text{ LE}$	97	3.40	365	0.071	-
S 5	$102 \rightarrow 106 \text{ CT}$	95	3.53	351	0.109	-
	Triplet Excited	d States (Opti	mised T	Geomet	ry)	
state	transition	weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
T ₄	$100\beta \rightarrow 105\beta$ LE	91	2.00	619	0.138	2.04
T 8	$106\alpha \rightarrow 108\alpha \ CT$	88	3.19	389	0.187	2.05
T9	$106\alpha \rightarrow 111\alpha$ LE	85				
	$106\alpha \rightarrow 108\alpha \text{ CT}$	10	3.47	358	0.221	2.05

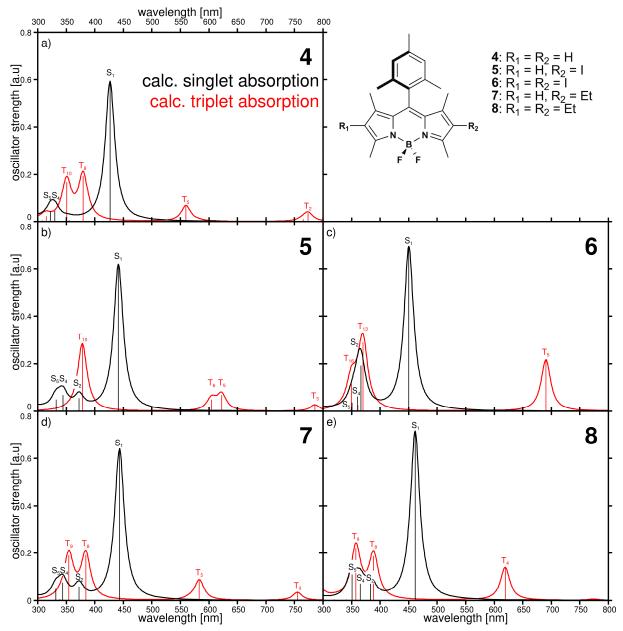
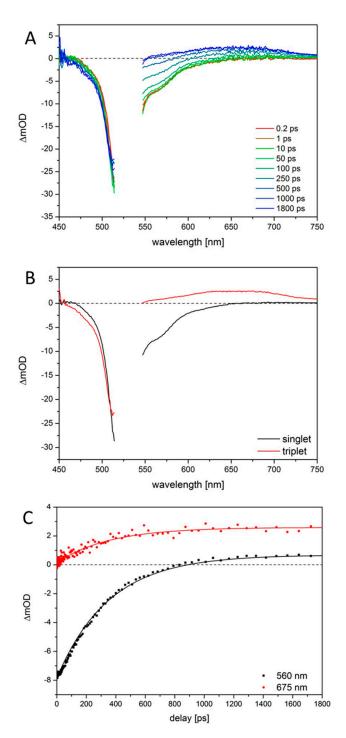


Figure S17. Calculated singlet (in black) and triplet (in red) absorption spectra (THF) of dyes **4–8** within optimised singlet and triplet ground state structures. Triplet absorption spectra are correlated to excited states absorption signals in the transient absorption spectra.



Analysis of fs Transient Absorption Data

Figure S18. Formation of triplet state in **5**: (**A**) transient spectra at selected delay times, (**B**) species spectra resulting from the global fit of the data, the spectrum of the initially populated species is assigned to the singlet state and contains mainly contributions of ground-state bleach and stimulated emission, the spectrum of the subsequently with a time constant of 354 ps populated species agrees well with the spectrum of the long-lived species in ns time-resolved measurements, which is assigned to the triplet state (**C**) kinetic traces at chosen probe wavelengths (line fits). The spectral region around the excitation wavelength (530 nm) was neglected in data evaluation due to a scattered pump.

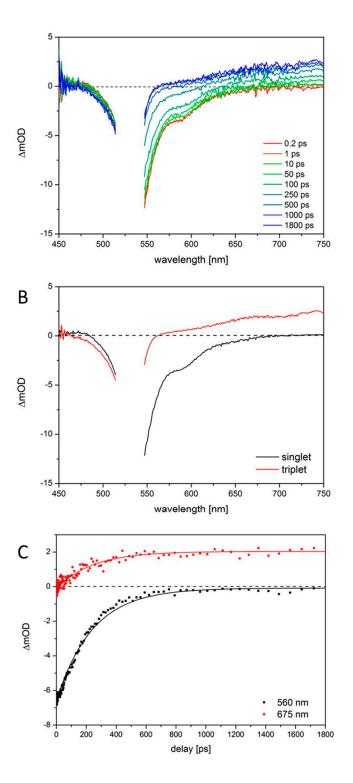


Figure S19. Formation of triplet state in **6**: (**A**) transient spectra at selected delay times, (**B**) species spectra resulting from the global fit of the data, the spectrum of the initially populated species is assigned to the singlet state and contains mainly contributions of ground-state bleach and stimulated emission, the spectrum of the subsequently with a time constant of 240 ps populated species agrees well with the spectrum of the long-lived species in ns time-resolved measurements, which is assigned to the triplet state (**C**) kinetic traces at chosen probe wavelengths (line fits). The spectral region around the excitation wavelength (530 nm) was neglected in data evaluation due to a scattered pump.

ESI-MS Data

Table S1. ESI MS data of BODIPY dyes before and after photolysis ($\lambda > 420$ nm) of multicomponent catalyst systems with BODIPY dyes as PS, [Pd(PPh₃)Cl₂]₂ as WRC and TEA as SA in THF/H₂O (11:3) at *T* = 25° C.

BODIPY	ESI MS of the pure dye	ESI MS after reaction	Comment
dye			
1	m/z = no fragments could be assigned yet	$m/z = 266.21 (M-Cl+5H)^+$	Hydrogenated fragment
2	$m/z = 285.13 (M+Na)^{+}$ 263.15 (M+H)^{+}	<i>m</i> / <i>z</i> = 215.16 (M-BF ₂ +2H) ⁺ 235.14 (M-2F+11H) ⁺	Hydrogenated fragments
3	$243.15 (M-F)^+$ $m/z = 512.93 (M-H)^-$	m/z = no fragments could be assigned yet	
4	$m/z = 319.22 (M-BF_2+H)^+$	$m/z = 319.22 (M-BF_2+H)^+$	
5	<i>m/z</i> = 515.09 (M+Na) ⁺ 493.11 (M+H) ⁺ 473.10 (M-BF ₂) ⁺	<i>m</i> / <i>z</i> = 319.22 (M-I-BF ₂ +H) ⁺	Iodine free fragment
6	$m/z = 616.99 (M-H)^{-1}$	$m/z = 319.22 (M-2I-BF_2+H)^+$	Iodine free fragment