Electronic supplementary information

Osmium sensitizer with enhanced spin-orbit coupling for panchromatic dye-sensitized solar cells

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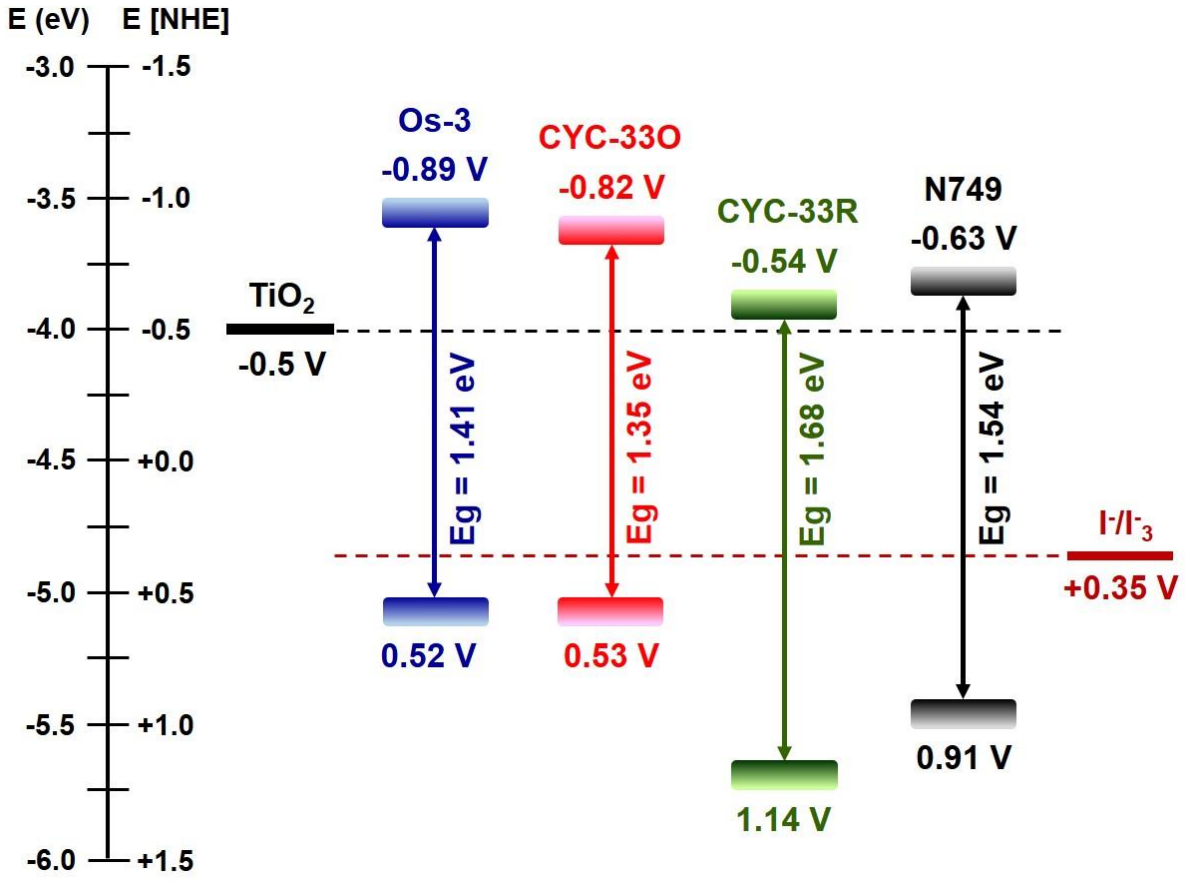

Fig. S1 Energy level diagram of **Os-3**, **CYC-33O**, **CYC-33R**, **N749**, TiO_2 and I^-/I_3^-.

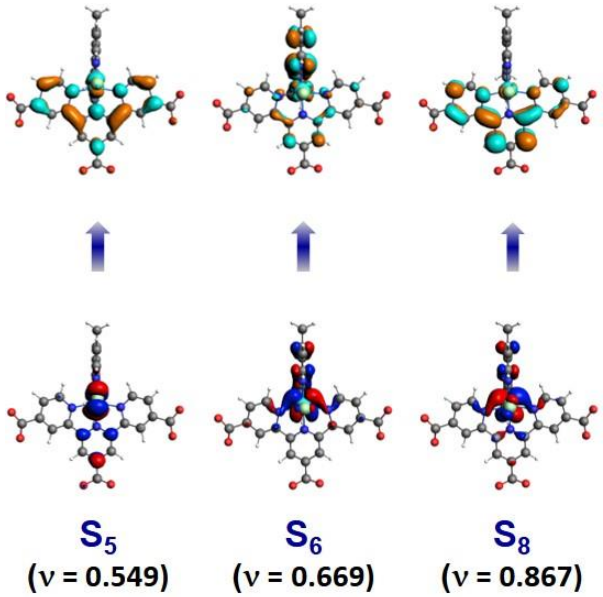

Fig. S2 Major NTOs for SR S_5, S_6 and S_8 states of **Os-3** calculated with SR-TDDFT. Hole and electron NTOs are displayed below and above the arrows, respectively. The ν is the associated eigenvalue.

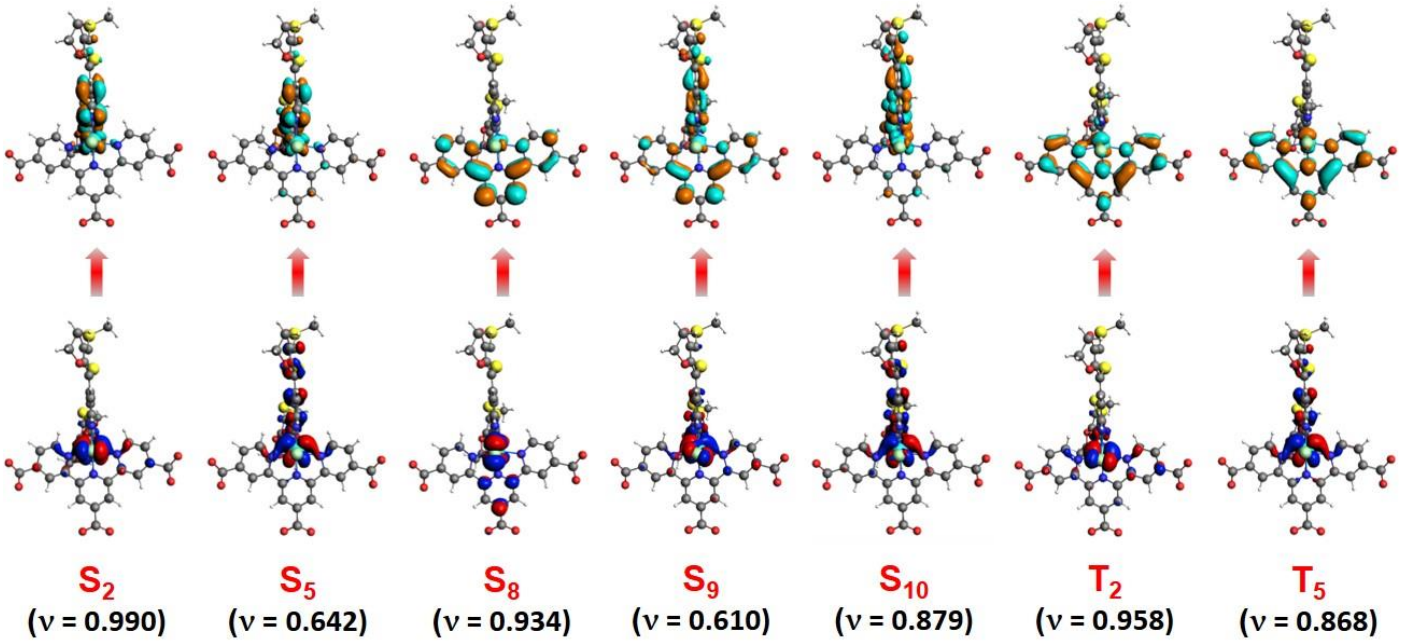

Fig. S3 Major NTOs for SR S_2, S_5, S_8, S_9, S_{10}, T_2 and T_5 states of **CYC-33O** calculated with SR-TDDFT. Hole and electron NTOs are displayed below and above the arrows, respectively. The ν is the associated eigenvalue.

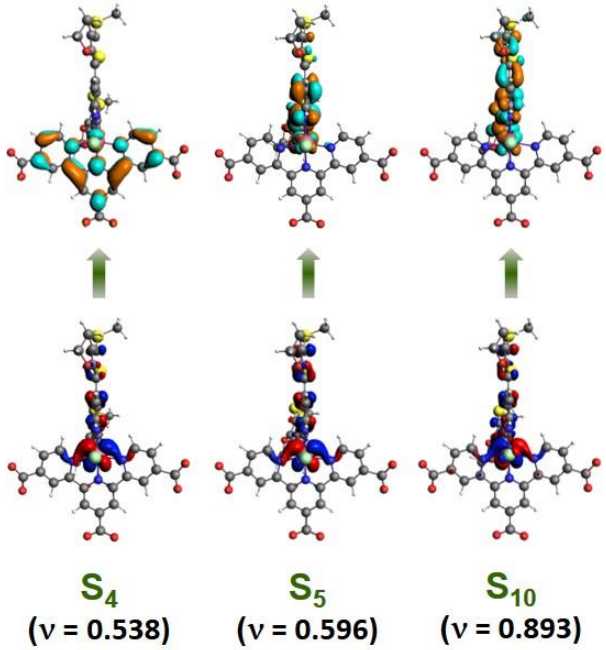

Fig. S4 Major NTOs for SR S_4, S_5 and S_{10} states of **CYC-33R** calculated with SR-TDDFT. Hole and electron NTOs are displayed below and above the arrows, respectively. The ν is the associated eigenvalue.

Table S1 Characteristics of the frontier molecular orbitals for **Os-3**, **CYC-33O** and **CYC-33R** calculated at the SR-B3LYP/ZOAR TZP level

			Os-3			
	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
% Os	54 d_{xz}	61 d_{yz}	53 d_{xy}	10 d_{yz}	3 d_{xz}	6 d_{xy}
	7 d_{xy}	2 d_{xy}	11 d_{xz}		1 d_{xy}	
	4 d_{z^2}		1 d_{yz}			
	1 $d_{x^2-y^2}$					
% Cl	0	10 p_z	8 p_x	1 p_y	0	0
% dmbpy	17	0	7	0	76	11
% H_3tctpy	3	14	11	85	14	79
			CYC-33O			
	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
% Os	60 d_{yz}	57 d_{xz}	55 d_{xy}	4 d_{xz}	9 d_{yz}	4 d_{xy}
	2 d_{xy}	2 d_{z^2}	2 d_{yz}	2 d_{xy}		
	2 d_{xz}	2 d_{z^2}	1 d_{xz}			
% Cl	11 p_z	0	7 p_x	0	0	0
% TH-EDOT-bpy	0	16	12	58	5	1
% H_3tctpy	12	3	11	20	75	87
			CYC-33R			
	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
% Ru	51 d_{yz}	49 d_{xz}	47 d_{xy}	3 d_{xz}	6 d_{yz}	3 d_{xy}
	13 d_{xz}	9 d_{yz}	6 d_{yz}	2 d_{xy}		
	4 d_{xy}	4 d_{xy}	6 $d_{x^2-y^2}$			
			3 d_{xz}			
% Cl	7 p_z	3 p_z	7 p_x	0	0	0
	2 p_x		1 p_y			
			1 p_z			
% TH-EDOT-bpy	0	9	9	64	10	0
% H_3tctpy	5	4	5	13	70	89

Table S2 Excitation wavelengths (nm), oscillator strengths (*f*) and contributions of SR states for **Os-3** calculated with SR-TDDFT and SOC-TDDFT

Os-3			
SR States (TDDFT Singlet-Singlet Excitations)			
State	λ (nm)	*f*	Compositions
S_1	657	0.052	(H → L) (94%), (H-2 → L) (5%)
S_2	608	0.013	(H → L+1) (90%)
S_3	599	0.025	(H-2 → L) (86%), (H-1 → L+1) (7%), (H → L) (5%)
S_4	561	0.005	(H-1 → L+1) (87%), (H-2 → L) (8%)
S_5	553	0.159	(H-1 → L) (69%), (H → L+2) (18%), (H-2 → L+1) (9%)
S_6	528	0.270	(H-2 → L+1) (59%), (H → L+2) (30%), (H → L+1) (8%)
S_7	503	0.012	(H-2 → L+2) (45%), (H → L+2) (22%), (H-2 → L+1) (19%), (H-1 → L) (11%)
S_8	493	0.110	(H-1 → L+2) (94%)
S_9	457	0.028	(H-2 → L+2) (46%), (H → L+2) (23%), (H-1 → L) (10%), (H → L+3) (7%)
S_{10}	410	0.036	(H → L+3) (85%)
S_{11}	406	0.244	(H → L+4) (95%)
SR States (TDDFT Singlet-Triplet Excitations)			
State	λ (nm)	*f*	Compositions
T_1	725	0.000	(H-1 → L) (88%)
T_2	722	0.000	(H → L) (94%)
T_3	665	0.000	(H → L+1) (85%), (H → L+2) (10%)
T_4	650	0.000	(H-2 → L+1) (78%), (H-2 → L+2) (12%)
T_5	636	0.000	(H-2 → L) (95%)
T_6	582	0.000	(H-1 → L+1) (90%), (H-1 → L+2) (5%)
T_7	568	0.000	(H → L+2) (81%), (H → L+1) (10%)
T_8	525	0.000	(H-1 → L+2) (91%)
T_9	504	0.000	(H-2 → L+2) (81%), (H-2 → L+1) (14%)
T_{10}	438	0.000	(H → L+3) (90%)
T_{11}	424	0.000	(H → L+4) (87%), (H-1 → L+3) (9%)
T_{12}	417	0.000	(H-2 → L+3) (61%), (H-2 → L+5) (13%), (H → L+6) (13%)
T_{13}	409	0.000	(H-1 → L+4) (71%), (H-3 → L+2) (6%)
T_{14}	405	0.000	(H-1 → L+3) (81%), (H → L+4) (10%)
T_{15}	403	0.000	(H → L+5) (35%), (H-2 → L+6) (23%), (H → L+6) (14%), (H-1 → L+4) (5%)
States calculated by SOC-TDDFT			
State	λ (nm)	*f*	Contributions of SR states
ST_3	787	0.011	T_1 (27%), S_1 (21%), T_1 (8%), T_5 (6%)
ST_8	694	0.012	T_3 (29%), T_4 (7%), T_6 (7%), T_6 (4%), S_6 (4%), $S_{2,3}$ (2%)
ST_{23}	569	0.047	S_5 (22%), T_6 (15%), T_8 (9%), T_6 (8%), T_9 (5%), S_6 (4%), S_7 (2%), T_3 (2%)
ST_{27}	533	0.136	S_5 (62%), S_6 (14%), T_6 (4%), T_5 (3%), $T_{8,9}$ (2%), S_7 (2%)
ST_{30}	509	0.156	S_6 (56%), T_8 (15%), S_7 (5%), S_5 (3%), T_6 (2%)
ST_{35}	477	0.074	S_8 (67%), T_9 (30%)
ST_{44}	422	0.093	S_{11} (38%), T_{13} (24%), T_{12} (4%), T_{13} (3%)
ST_{52}	400	0.004	T_{15} (32%), T_{13} (11%), T_{11} (9%), T_{15} (7%), $T_{11,13}$ (4%), T_{14} (3%), T_{14} (2%)

Table S3 Excitation wavelengths (nm), oscillator strengths (*f*) and contributions of SR states for **CYC-33O** calculated with SR-TDDFT and SOC-TDDFT

CYC-33O			
SR States (TDDFT Singlet-Singlet Excitations)			
State	λ (nm)	*f*	Compositions
S_1	655	0.052	(H → L) (69%), (H → L+1) (16%), (H-1 → L) (11%)
S_2	635	0.076	(H → L+1) (69%), (H → L) (14%), (H-1 → L+1) (10%)
S_3	609	0.052	(H-1 → L+1) (37%), (H-1 → L) (25%), (H-2 → L) (22%), (H-2 → L+1) (5%), (H → L+1) (5%)
S_4	587	0.002	(H-2 → L) (69%), (H-1 → L+1) (19%)
S_5	568	0.594	(H-1 → L) (42%), (H-2 → L+1) (31%), (H-1 → L+1) (13%), (H → L) (8%)
S_6	539	0.012	(H → L+2) (38%), (H-2 → L+1) (36%), (H-1 → L+1) (9%), (H-1 → L) (5%)
S_7	502	0.068	(H-1 → L+2) (57%), (H → L+2) (19%), (H-2 → L+1) (8%)
S_8	487	0.108	(H-2 → L+2) (90%), (H-1 → L+2) (5%)
S_9	478	0.121	(H → L+3) (39%), (H-1 → L+2) (25%), (H → L+2) (21%)
S_{10}	461	0.464	(H → L+3) (44%), (H-1 → L+3) (19%), (H → L+2) (11%), (H → L+4) (6%)
S_{11}	448	0.095	(H-1 → L+3) (57), (H → L+4) (32%)
S_{12}	439	0.003	(H-2 → L+3) (97%)
S_{13}	435	0.013	(H → L+4) (58%), (H-1 → L+4) (15%), (H-1 → L+3) (14%)
S_{14}	419	0.411	(H-1 → L+4) (69%), (H → L+6) (12%)
S_{15}	413	0.019	(H-2 → L+4) (96%)
SR States (TDDFT Singlet-Triplet Excitations)			
State	λ (nm)	*f*	Compositions
T_1	747	0.000	(H → L) (61%), (H-1 → L) (11%), (H-2 → L+1) (6%)
T_2	713	0.000	(H-1 → L) (41%), (H → L) (29%), (H-2 → L+1) (8%), (H-2 → L) (5%), (H → L+1) (5%)
T_3	704	0.000	(H → L+1) (80%), (H-1 → L+1) (10%)
T_4	690	0.000	(H-2 → L+1) (57%), (H-1 → L) (26%), (H-2 → L) (9%)
T_5	638	0.000	(H-1 → L+1) (68%), (H-2 → L) (18%), (H-1 → L) (5%)
T_6	614	0.000	(H-2 → L) (58%), (H-2 → L+1) (22%), (H-1 → L+1) (9%), (H-1 → L) (5%)
T_7	563	0.000	(H → L+2) (82%)
T_8	526	0.000	(H → L+3) (63%), (H-1 → L+3) (9%), (H-3 → L) (5%)
T_9	517	0.000	(H-2 → L+2) (85%), (H-1 → L+2) (7%)
T_{10}	505	0.000	(H-1 → L+2) (80%), (H-2 → L+2) (8%)
T_{11}	494	0.000	(H-1 → L+3) (40%), (H-1 → L+4) (30%), (H → L+3) (7%)
T_{12}	457	0.000	(H → L+4) (48%), (H-1 → L+4) (18%), (H-1 → L+3) (14%), (H-2 → L+3) (10%)
T_{13}	452	0.000	(H → L+4) (40%), (H-1 → L+4) (26%), (H-1 → L+3) (13%)
T_{14}	442	0.000	(H-2 → L+3) (94%)
T_{15}	439	0.000	(H-3 → L) (26%), (H-3 → L+3) (11%), (H-1 → L+3) (10%), (H → L+3) (9%), (H-6 → L) (8%), (H-1 → L+4) (7%)
States calculated by SOC-TDDFT			
State	λ (nm)	*f*	Contributions of SR states
ST_6	760	0.025	S_1 (12%), T_4 (10%), T_3 (9%), $T_{2,5}$ (6%), T_5 (4%), S_5 (3%), T_4 (3%), T_1 (2%)
ST_7	756	0.021	T_4 (13%), S_2 (12%), T_2 (9%), T_5 (7%), T_2 (6%), T_5 (4%), T_4 (3%), T_3 (2%), $S_{1,5}$ (2%)
ST_{13}	642	0.026	S_1 (22%), T_5 (14%), S_2 (14%), T_4 (11%), T_1 (5%), T_6 (5%), $T_{3,6}$ (2%)
ST_{20}	595	0.030	S_3 (51%), T_6 (10%), T_7 (9%), $T_{2,3,6}$ (2%)
ST_{27}	553	0.484	S_5 (81%), T_5 (6%), T_6 (3%)
ST_{35}	507	0.044	T_{11} (20%), S_6 (11%), T_9 (9%), S_{10} (8%), T_9 (5%), S_9 (3%), T_{14} (3%), T_7 (2%)
ST_{41}	479	0.102	S_{10} (16%), S_9 (16%), T_{11} (10%), T_{12} (9%), S_7 (6%), T_{13} (3%), T_9 (3%), S_{11} (3%), T_{14} (3%), S_{13} (2%)
ST_{47}	456	0.105	S_{11} (27%), S_9 (17%), T_{14} (11%), S_{10} (10%), T_{17} (7%), S_{14} (3%), T_{12} (3%), T_{13} (2%)
ST_{50}	445	0.205	S_{10} (41%), S_{11} (11%), T_{12} (11%), S_{13} (8%), T_{13} (6%), T_{11} (2%)
ST_{59}	414	0.358	S_{14} (87%), T_{12} (3%), T_{13} (2%)

Table S4 Excitation wavelengths (nm), oscillator strengths (*f*) and contributions of SR states for **CYC-33R** calculated with SR-TDDFT and SOC-TDDFT

CYC-33R			
SR States (TDDFT Singlet-Singlet Excitations)			
State	λ (nm)	*f*	Compositions
S_1	589	0.107	(H → L) (75%), (H → L+1) (15%), (H-1 → L) (5%)
S_2	572	0.016	(H → L+1) (69%), (H → L) (10%), (H-1 → L) (9%)
S_3	553	0.007	(H-1 → L+1) (56%), (H-2 → L) (25%), (H-1 → L) (6%)
S_4	534	0.103	(H-1 → L) (45%), (H-2 → L) (26%), (H-2 → L+1) (18%), (H → L) (7%)
S_5	526	0.434	(H-2 → L) (45%), (H-1 → L+1) (35%), (H-1 → L) (9%), (H-2 → L+1) (5%)
S_6	500	0.029	(H-2 → L+1) (44%), (H → L+2) (35%), (H-1 → L) (9%), (H → L+1) (5%)
S_7	472	0.043	(H-1 → L+2) (66%), (H → L+2) (17%), (H-2 → L+1) (6%), (H-1 → L) (5%)
S_8	453	0.069	(H-2 → L+2) (71%), (H → L+2) (8%), (H → L+3) (7%), (H-1 → L+2) (5%)
S_9	450	0.052	(H → L+2) (25%), (H-2 → L+2) (24%), (H-1 → L+2) (22%), (H → L+3) (13%)
S_{10}	431	0.409	(H → L+3) (56%), (H-1 → L+3) (28%)
S_{11}	417	0.125	(H-1 → L+3) (54%), (H → L+4) (18%), (H → L+3) (9%)
S_{12}	409	0.037	(H-2 → L+3) (71%), (H → L+4) (24%)
S_{13}	407	0.084	(H → L+4) (55%), (H-2 → L+3) (21%), (H-1 → L+3) (7%)
SR States (TDDFT Singlet-Triplet Excitations)			
State	λ (nm)	*f*	Compositions
T_1	650	0.000	(H → L) (51%), (H-1 → L) (25%), (H → L+1) (9%)
T_2	640	0.000	(H → L) (37%), (H → L+1) (27%), (H-1 → L) (15%), (H-1 → L+1) (9%)
T_3	618	0.000	(H-1 → L) (41%), (H → L+1) (31%), (H-1 → L+1) (8%), (H-2 → L) (5%)
T_4	600	0.000	(H-1 → L+1) (30%), (H → L+1) (24%), (H-2 → L) (22%), (H-2 → L+1) (19%)
T_5	569	0.000	(H-2 → L+1) (51%), (H-1 → L+1) (36%), (H-1 → L) (5%)
T_6	556	0.000	(H-2 → L) (65%), (H-2 → L+1) (12%), (H-1 → L+1) (10%)
T_7	515	0.000	(H → L+2) (85%)
T_8	492	0.000	(H → L+3) (29%), (H-3 → L) (19%), (H-1 → L+3) (15%), (H-3 → L+3) (5%)
T_9	484	0.000	(H-1 → L+2) (74%), (H-2 → L+2) (16%)
T_{10}	473	0.000	(H-1 → L+3) (19%), (H → L+3) (13%), (H-1 → L+4) (9%), (H-6 → L) (6%)
T_{11}	465	0.000	(H-2 → L+2) (71%), (H-1 → L+2) (16%)
T_{12}	455	0.000	(H → L+10) (54%), (H-2 → L+10) (5%)
T_{13}	432	0.000	(H → L+3) (42%), (H-3 → L) (14%), (H-1 → L+10) (11%), (H-3 → L+3) (7%)
T_{14}	430	0.000	(H-1 → L+10) (32%), (H-2 → L+10) (19%), (H-1 → L+3) (15%), (H-2 → L+3) (8%)
T_{15}	425	0.000	(H-2 → L+10) (34%), (H → L+4) (14%), (H → L+10) (9%), (H-2 → L+3) (5%)
T_{16}	423	0.000	(H-5 →L) (27%), (H-5 → L+3) (16%), (H-6 → L) (13%), (H-3 → L) (7%)
T_{17}	419	0.000	(H → L+4) (44%), (H-1 → L+10) (14%), (H → L+10) (8%), (H-3 → L) (6%)
T_{18}	417	0.000	(H-1 → L+3) (26%), (H → L+4) (24%), (H-1 → L+10) (12%), (H-3 → L) (6%)
T_{19}	410	0.000	(H-4 → L) (19%), (H-4 → L+3) (12%), (H-1 → L+4) (10%), (H-5 → L) (8%), (H-2 → L+3) (7%), (H-4 → L+1) (6%), (H-5 → L+3) (5%), (H-4 → L+4) (5%)
T_{20}	409	0.000	(H-1 → L+4) (50%), (H-6 → L) (14%), (H-5 → L) (5%)
States calculated by SOC-TDDFT			
State	λ (nm)	*f*	Contributions of SR states
ST_3	662	0.002	T_1 (26%), T_1 (22%), T_2 (17%), T_2 (4%), T_3 (2%), S_1 (2%)
ST_{13}	585	0.079	S_1 (74%), T_4 (6%), S_2 (2%)
ST_{22}	532	0.098	S_4 (94%)
ST_{23}	524	0.405	S_5 (93%), T_6 (2%), T_5 (2%)
ST_{37}	473	0.024	S_7 (54%), T_{11} (18%), T_{10} (7%), T_{10} (3%), T_9 (3%), T_7 (2%)
ST_{46}	437	0.093	T_{14} (22%), S_{10} (22%), T_{15} (8%), $T_{13,15}$ (3%), S_8 (2%), S_{11} (2%)
ST_{47}	435	0.106	T_{13} (28%), S_{10} (25%), T_{14} (6%), T_{13} (4%)
ST_{52}	427	0.120	S_{10} (29%), T_{14} (15%), T_{14} (12%), T_{13} (5%), $T_{15,17}$ (2%)