Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information (SI)

Effects of Terminal Donor Unit in Dyes with D–D–π–A Architecture on the Regeneration Mechanism in DSSCs: A Computational Study

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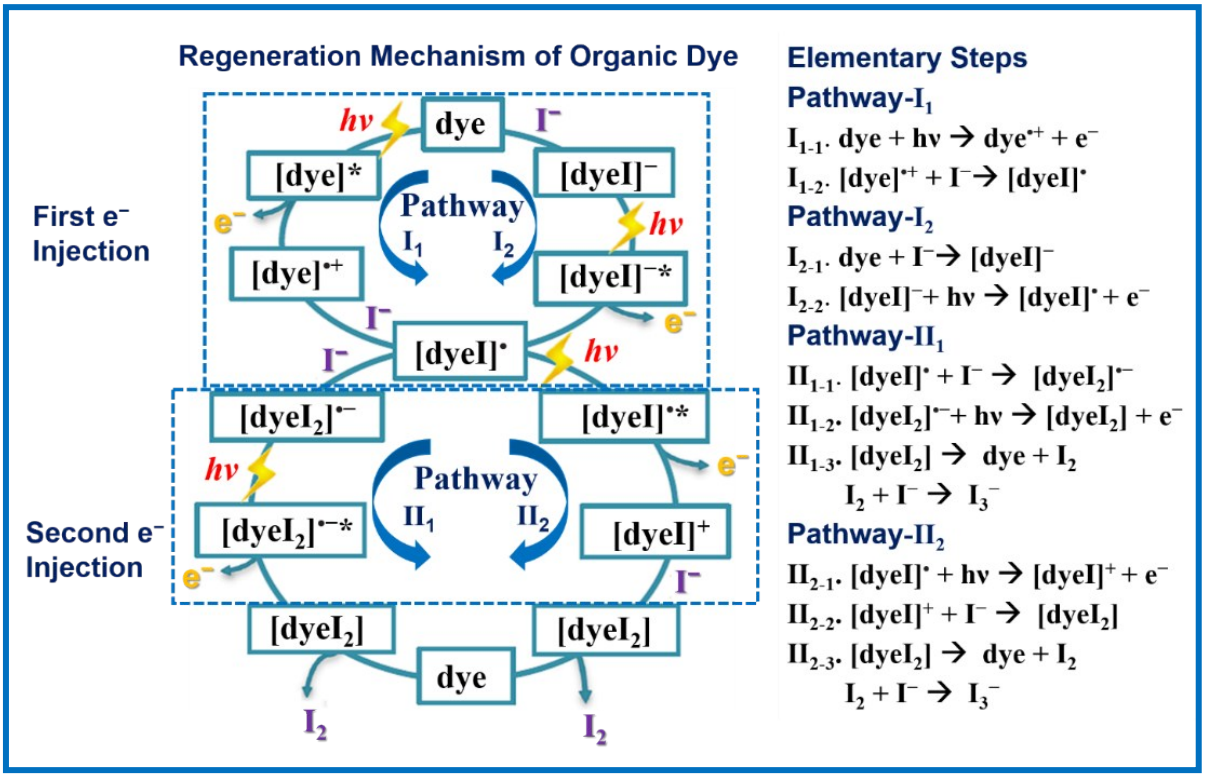


Scheme S 1. Proposed mechanisms for organic dye regeneration. Taken from ref.[1]

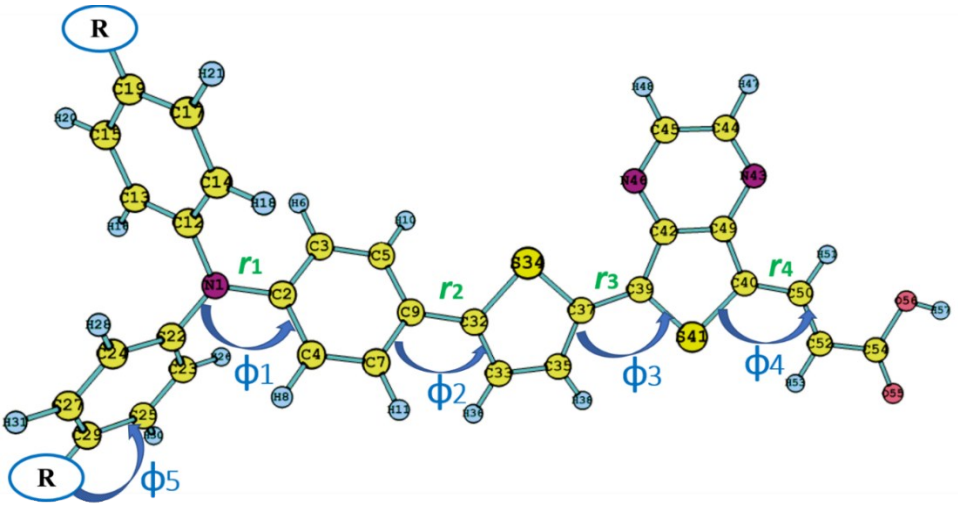


Figure S 1. The optimized structure of the selected bond lengths (r in Å) and dihedral angles (Φ in °) for triphenylamine-based D–π–A organic dyes. Labeling R denotes the different donor substituents.

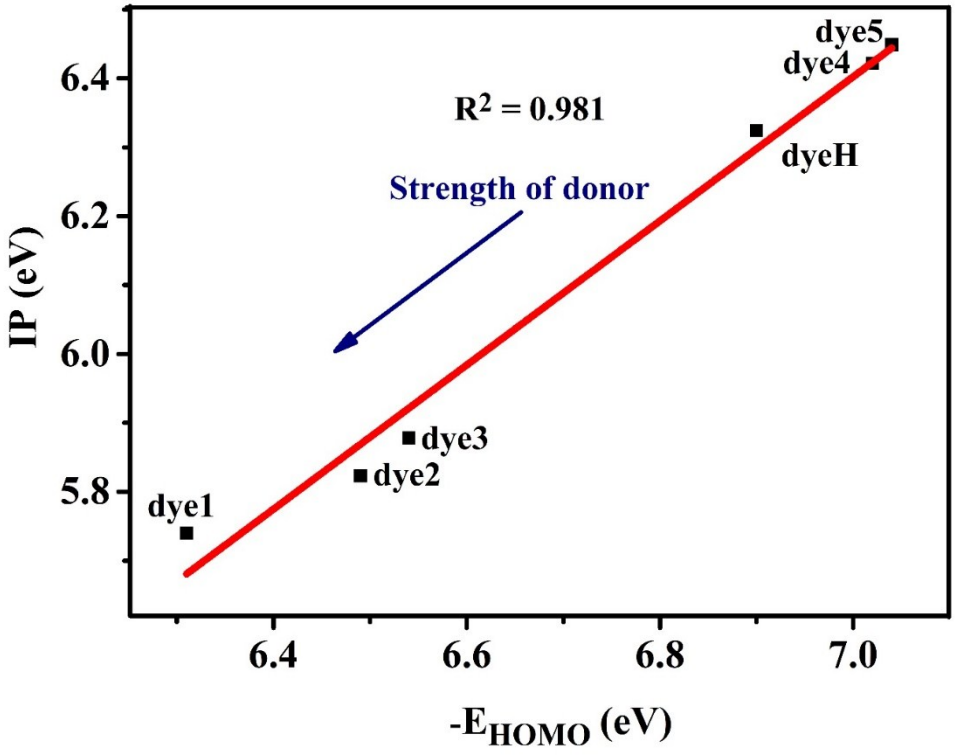


Figure S 2. Schematic representation plots of ionization potential (IP) versus HOMO energy levels of the designed dyes along the reference dye.

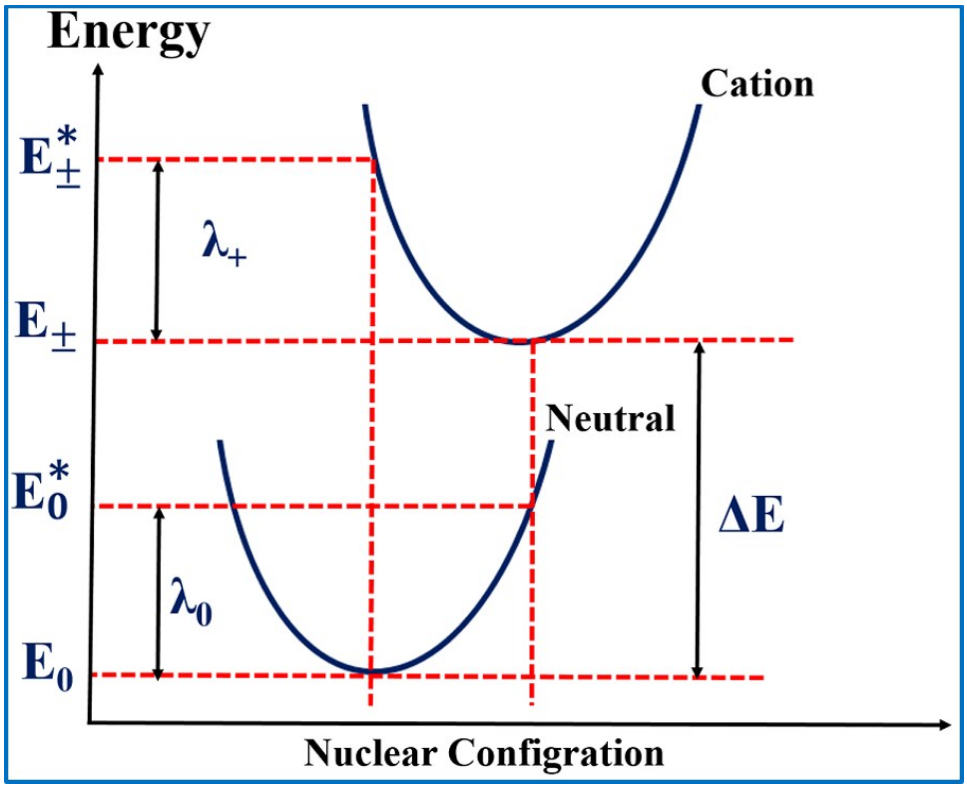


Figure S 3. Schematic of internal reorganization energy for hole/electron transfer.[2, 3]

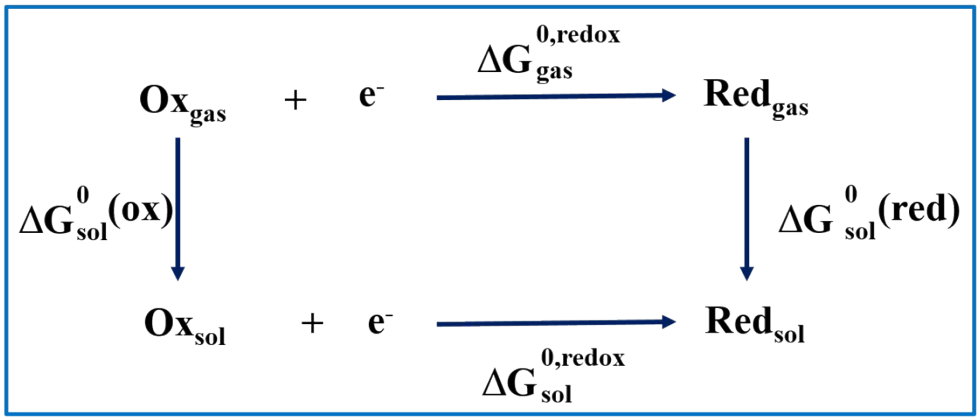


Figure S 4. Schematic representation of thermodynamic cycle used to calculate the reduction potentials of the designed dyes and iodide ion.[4]

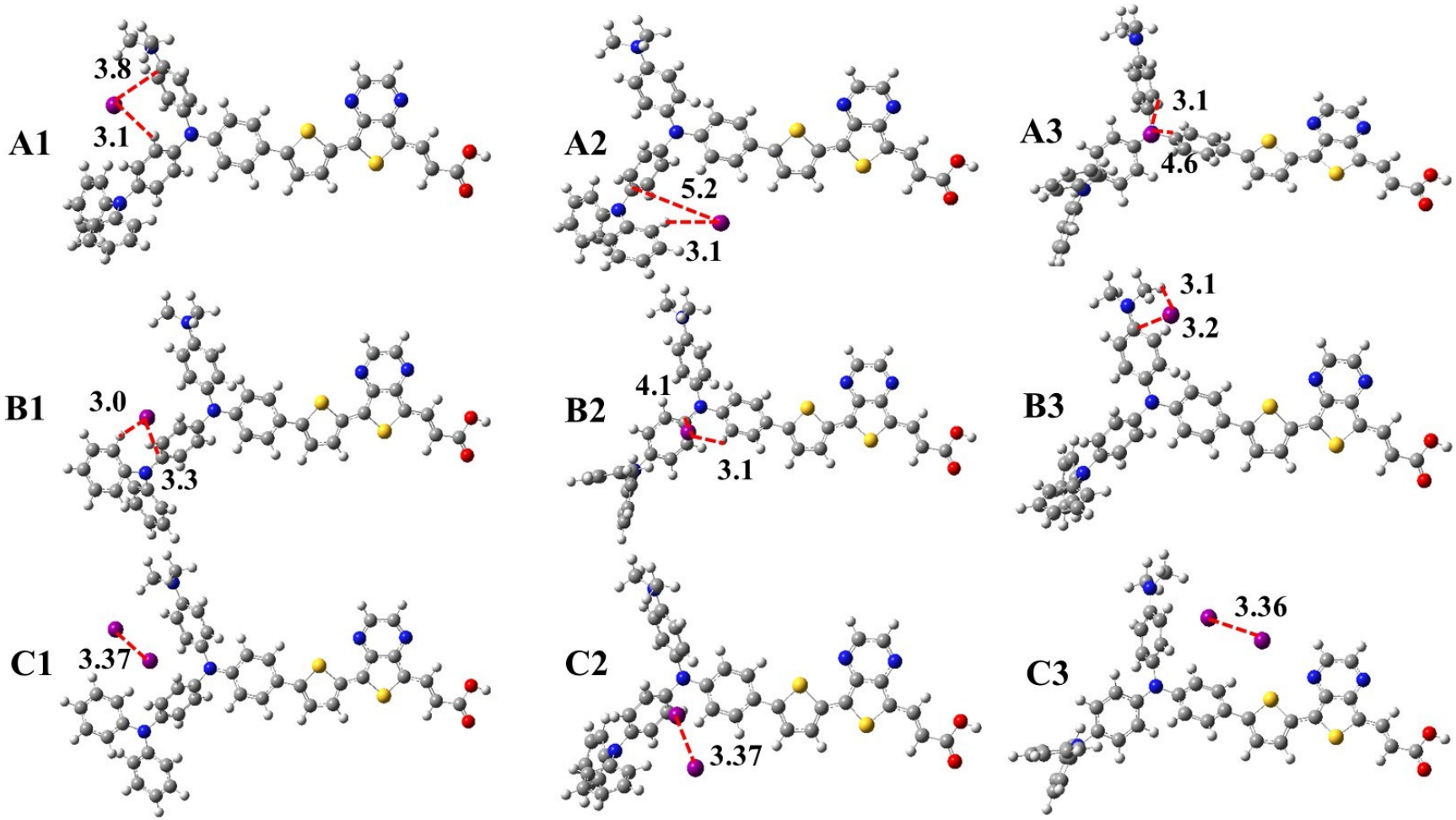


Figure S 5. The optimized geometries of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ dye-iodide complexes of the **dye2** sensitizer. The color scheme adopted is gray, white, blue, red, yellow and purple for C, H, N, O, S, and I atoms, respectively.

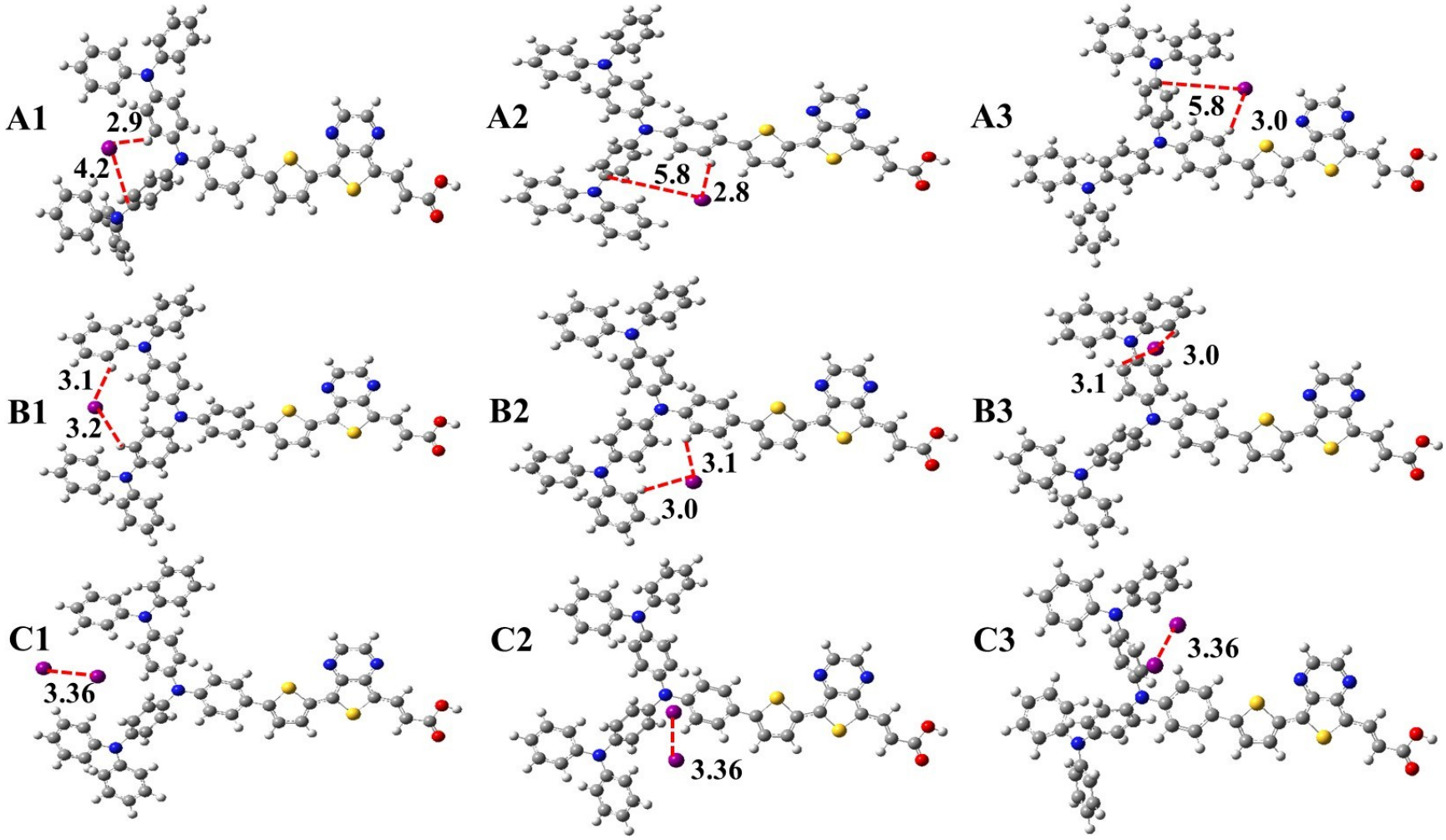


Figure S 6. The optimized geometries of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ dye-iodide complexes of the designed **dye3** sensitizer. The color scheme is gray, white, blue, red, yellow and purple for C, H, N, O, S, and I atoms, respectively.

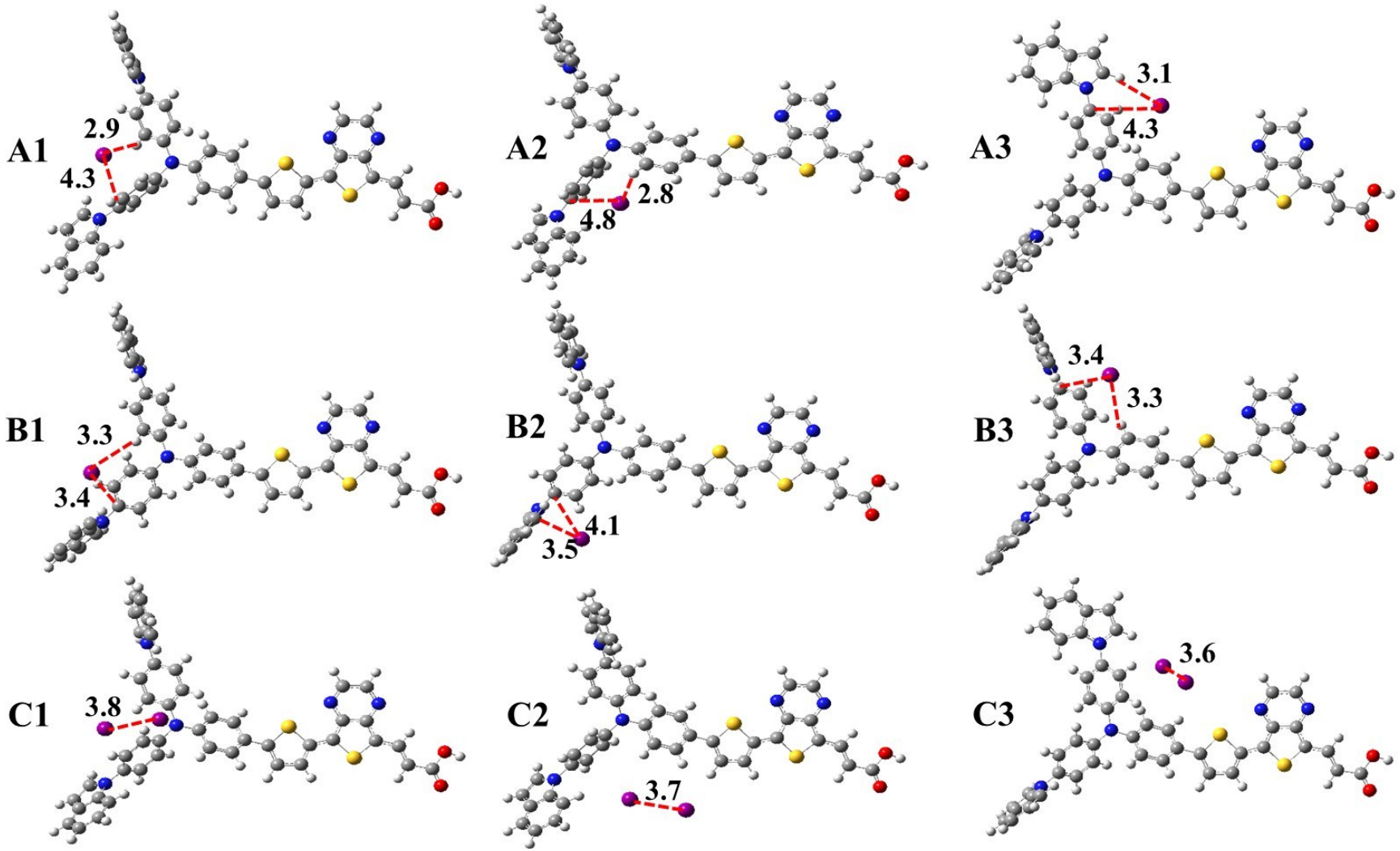


Figure S 7. The optimized geometries of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ dye-Iodide complexes of the designed **dye4** sensitizer. The color scheme is gray, white, blue, red, yellow and purple for C, H, N, O, S, and I atoms, respectively.

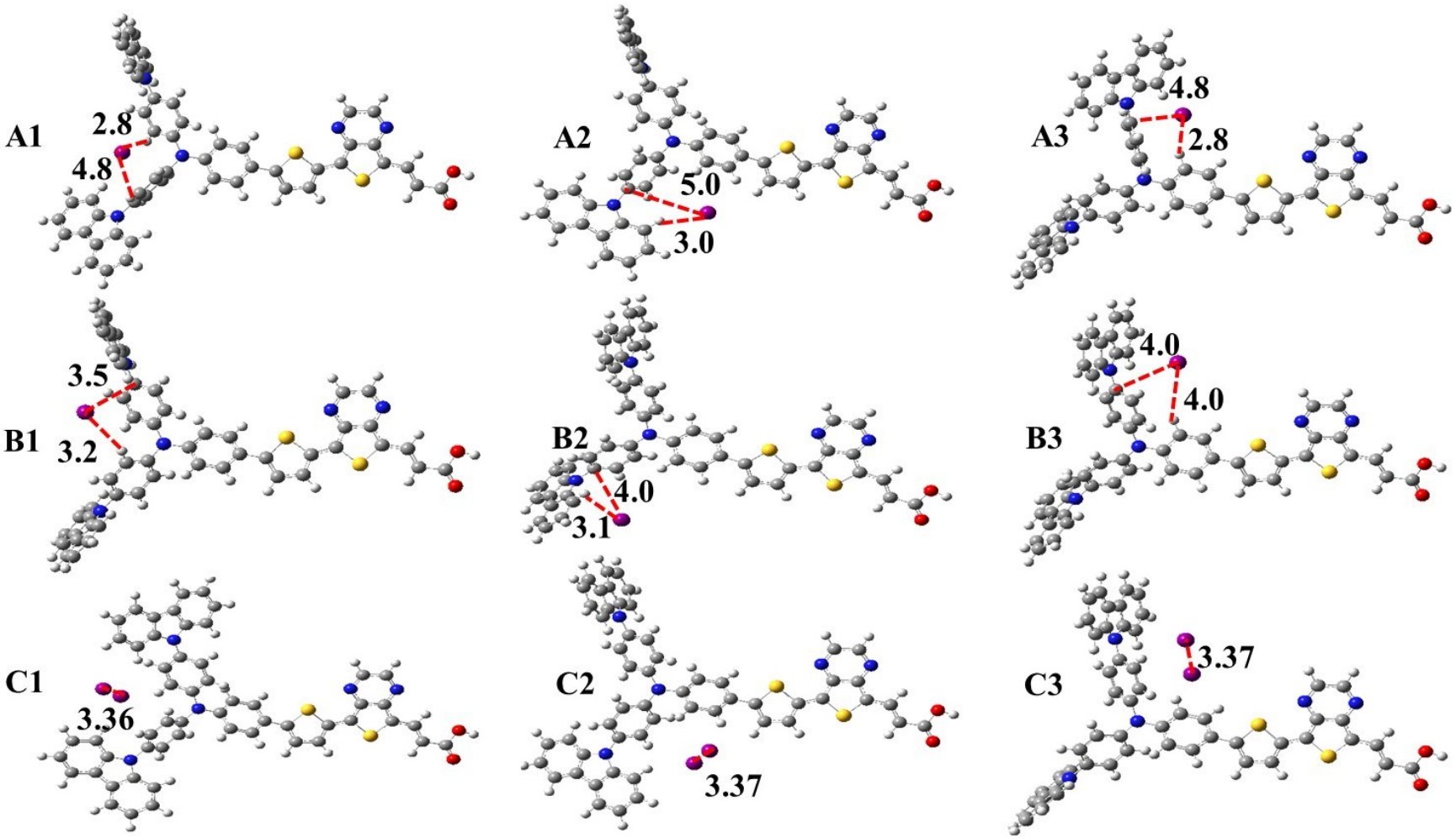


Figure S 8. The optimized geometries of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ dye-iodide complexes of the designed **dye5** sensitizer. The color scheme is gray, white, blue, red, yellow and purple for C, H, N, O, S, and I atoms, respectively.

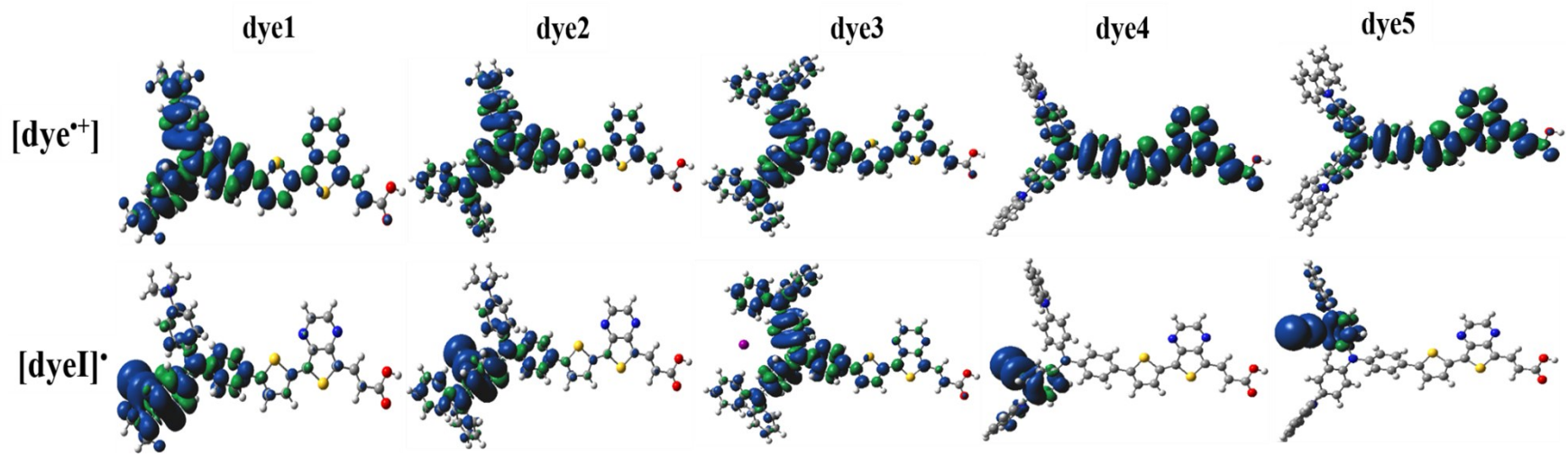


Figure S 9. Calculated isosurface plots of the spin density distribution of the radicaloid intermediate [dye$^{\bullet+}$] and [dyeI]$^{\bullet}$ for the investigated sensitizers.

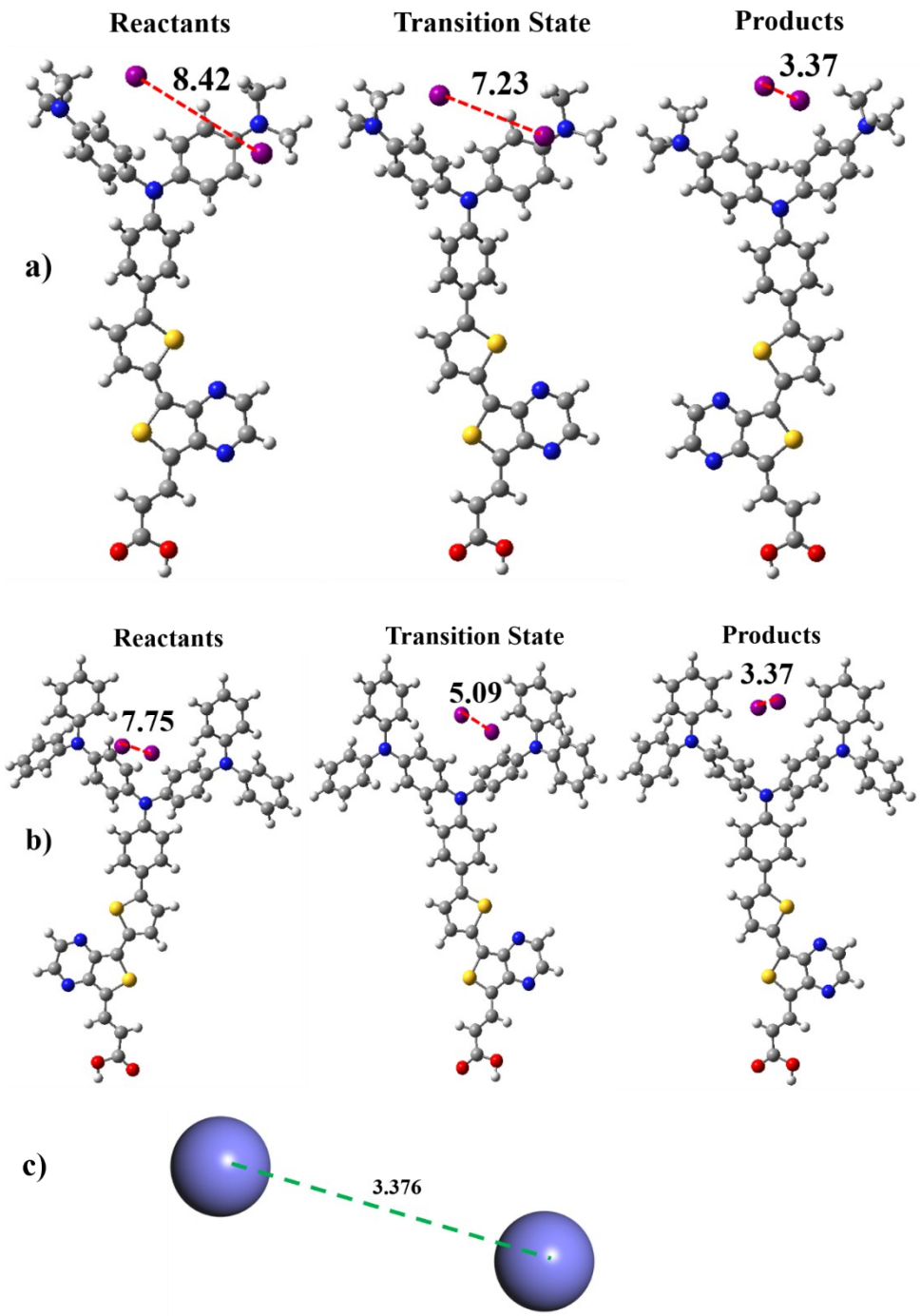
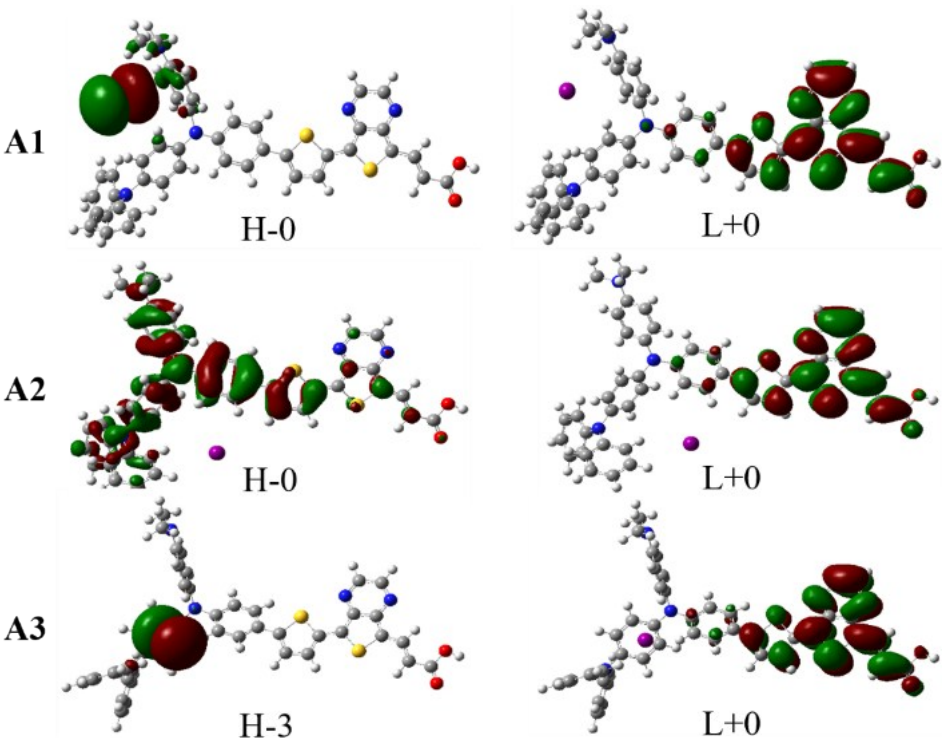
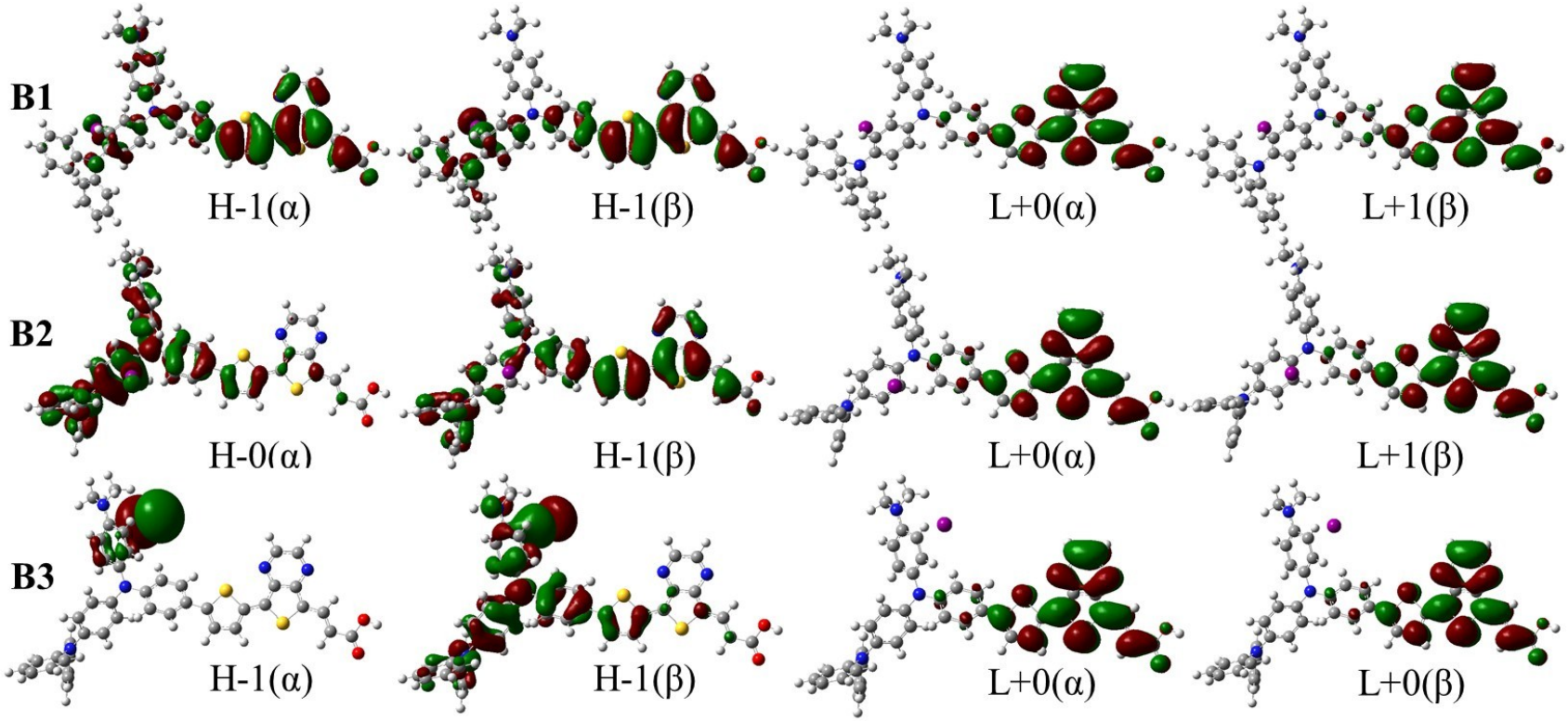


Figure S 10. The Schematic representaion of the geometries for the recombination reactions [dye$^{\bullet+}$…I^{-}…I^{-}] of the most stable intermediate of [dyeI$_2$]$^{\bullet-}$ complexes of a) dye1, b) dye3, and c) the diiodide radicaloid anion (I$_2^{\bullet-}$).


A1
H-0
L+0
A2
H-0
L+0
A3
H-3
L+0


B1
H-1(α)
H-1(β)
L+0(α)
L+1(β)
B2
H-0(α)
H-1(β)
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L+1(β)
B3
H-1(α)
H-1(β)
L+0(α)
L+0(β)

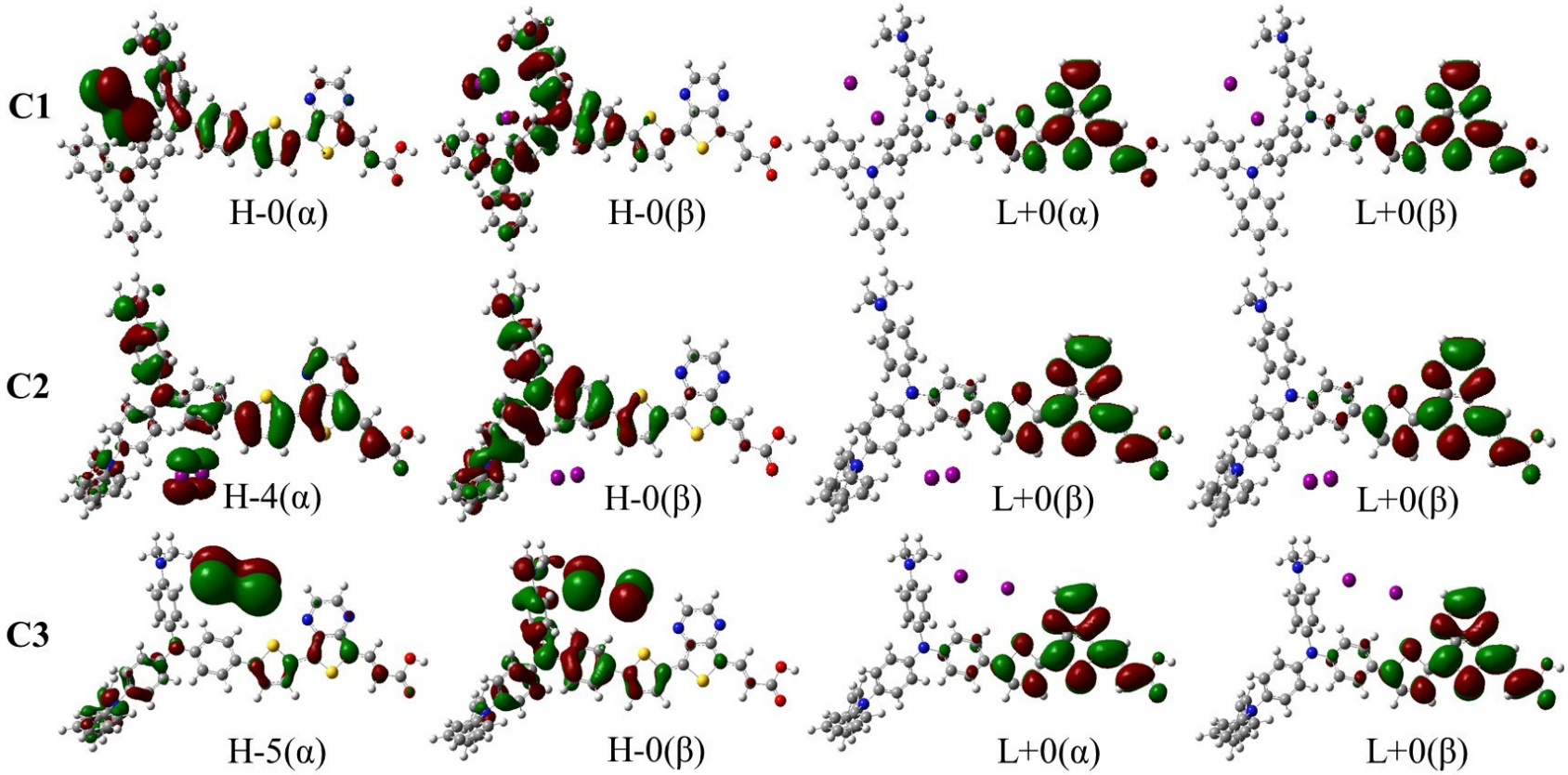
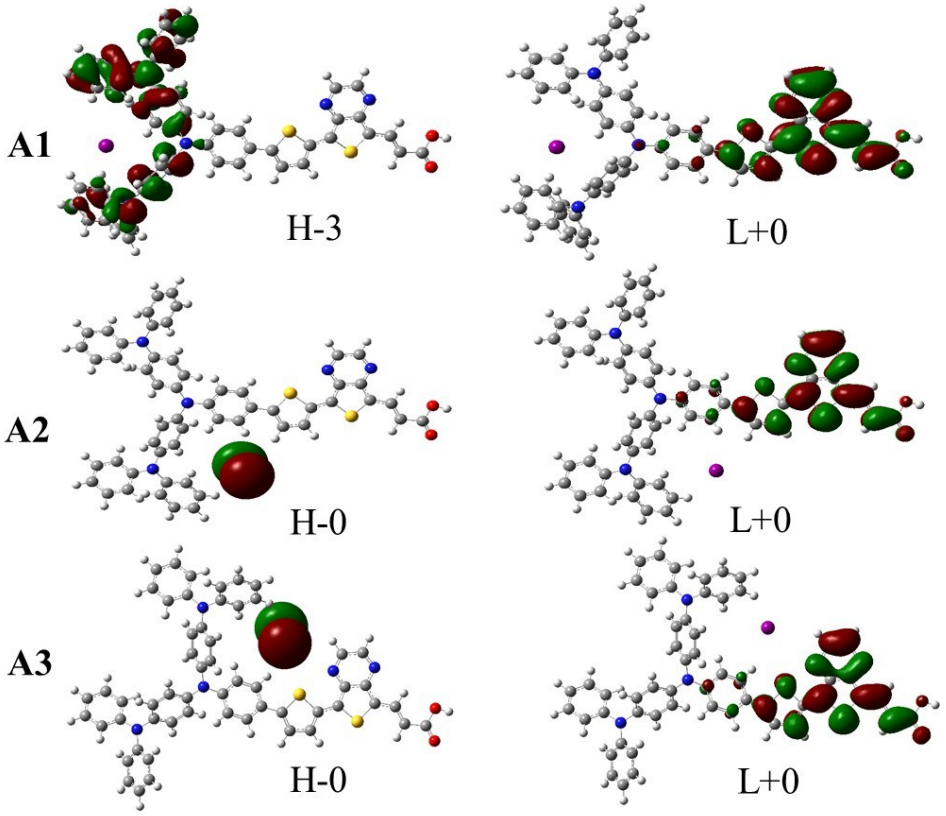
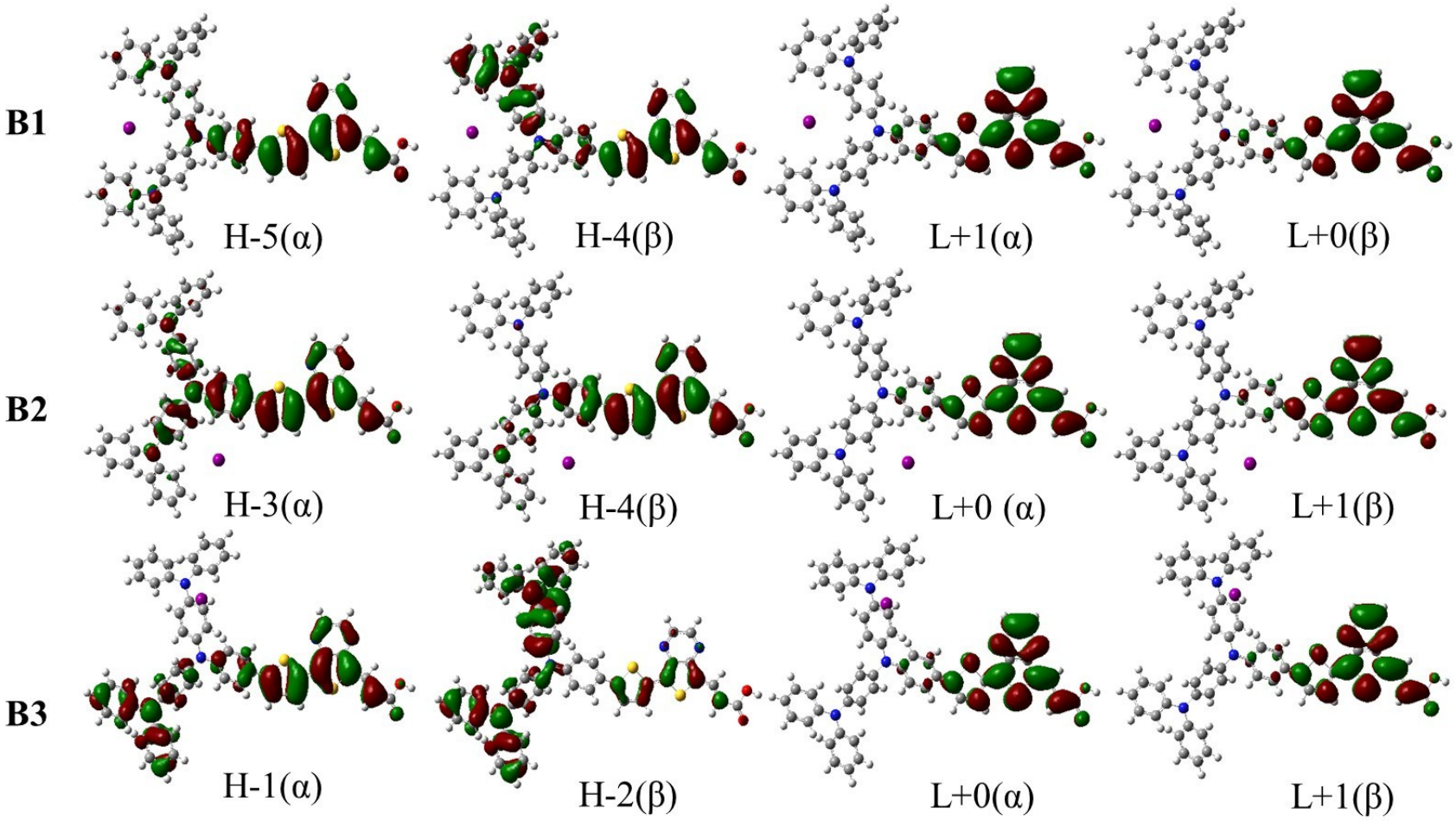


Figure S 11. Calculated isodensity plots of the selected frontier moleculer orbitals of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ complexes of the designed **dye2** sensitizer at different iodide interaction sites (Isovalue is 0.02 a.u.).


A1
H-3
L+0
A2
H-0
L+0
A3
H-0
L+0


B1
H-5(α)
H-4(β)
L+1(α)
L+0(β)
B2
H-3(α)
H-4(β)
L+0 (α)
L+1(β)
B3
H-1(α)
H-2(β)
L+0(α)
L+1(β)

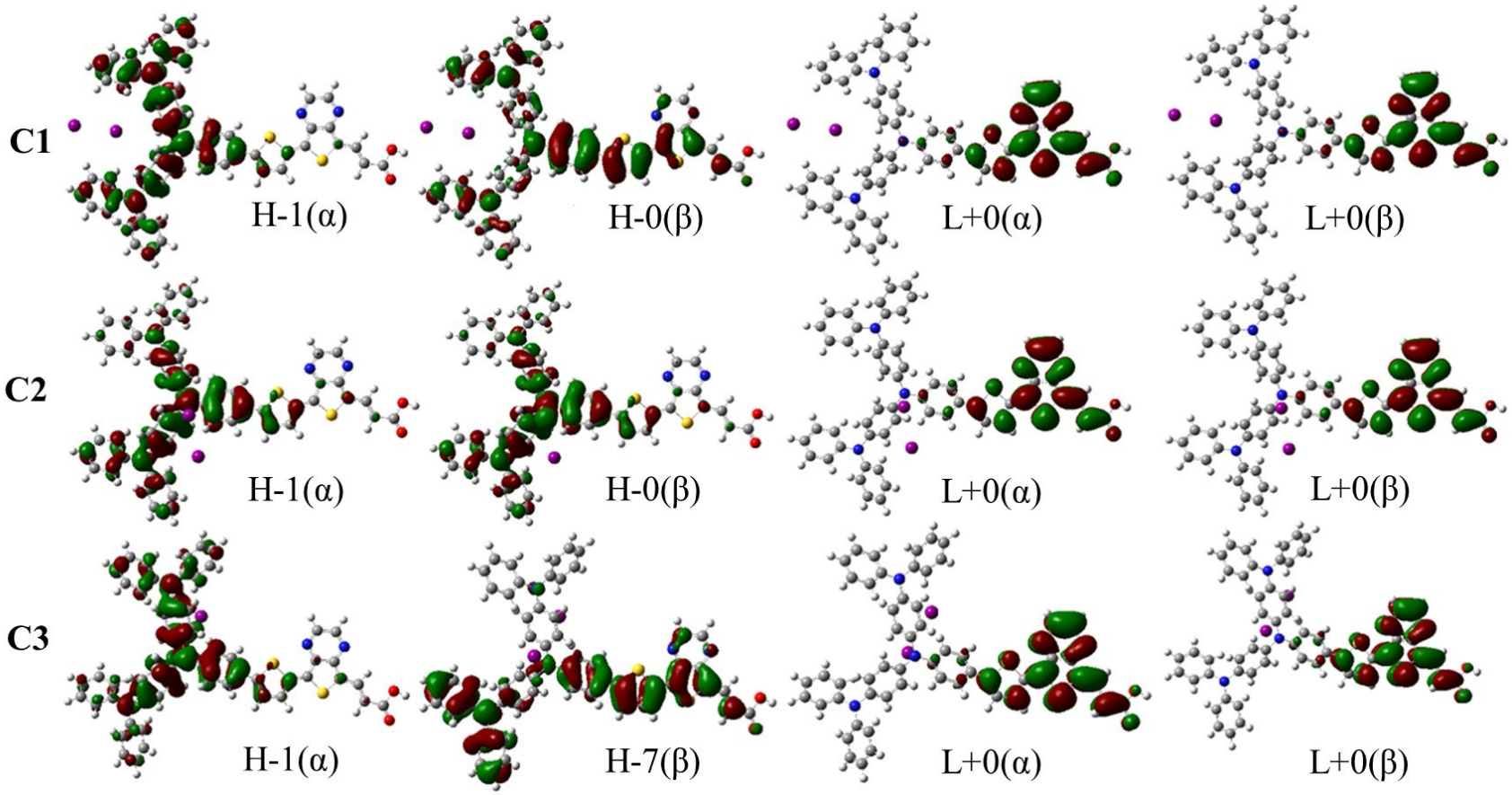
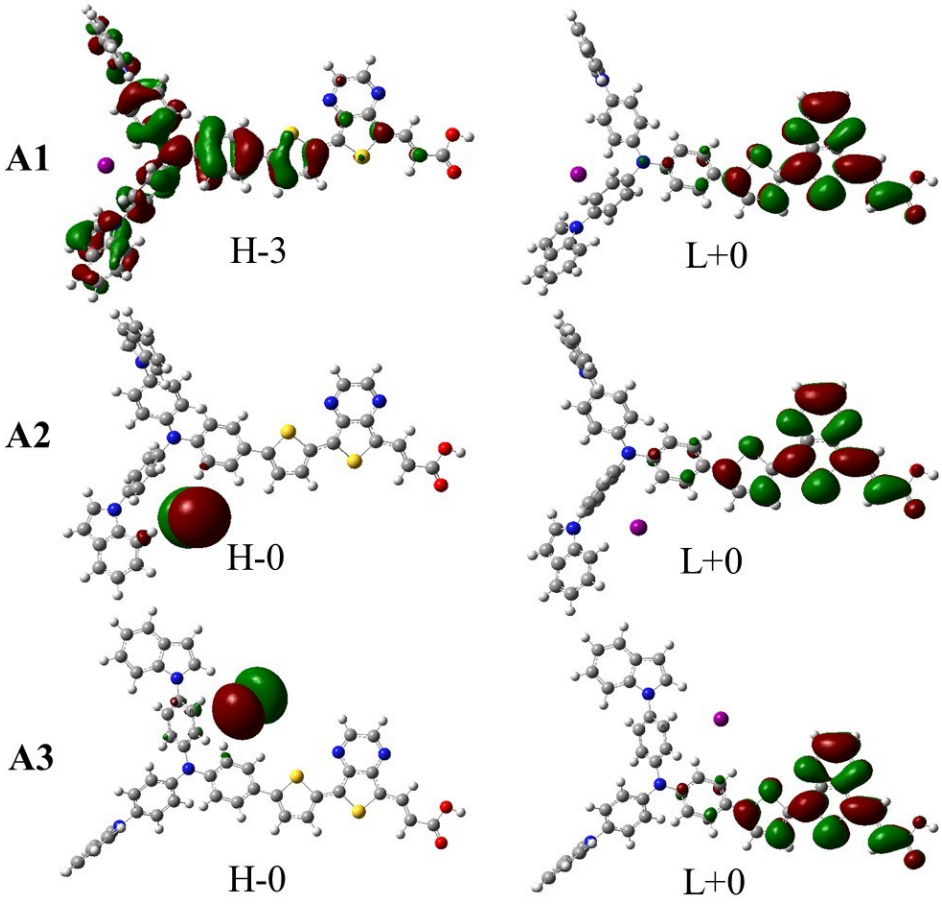
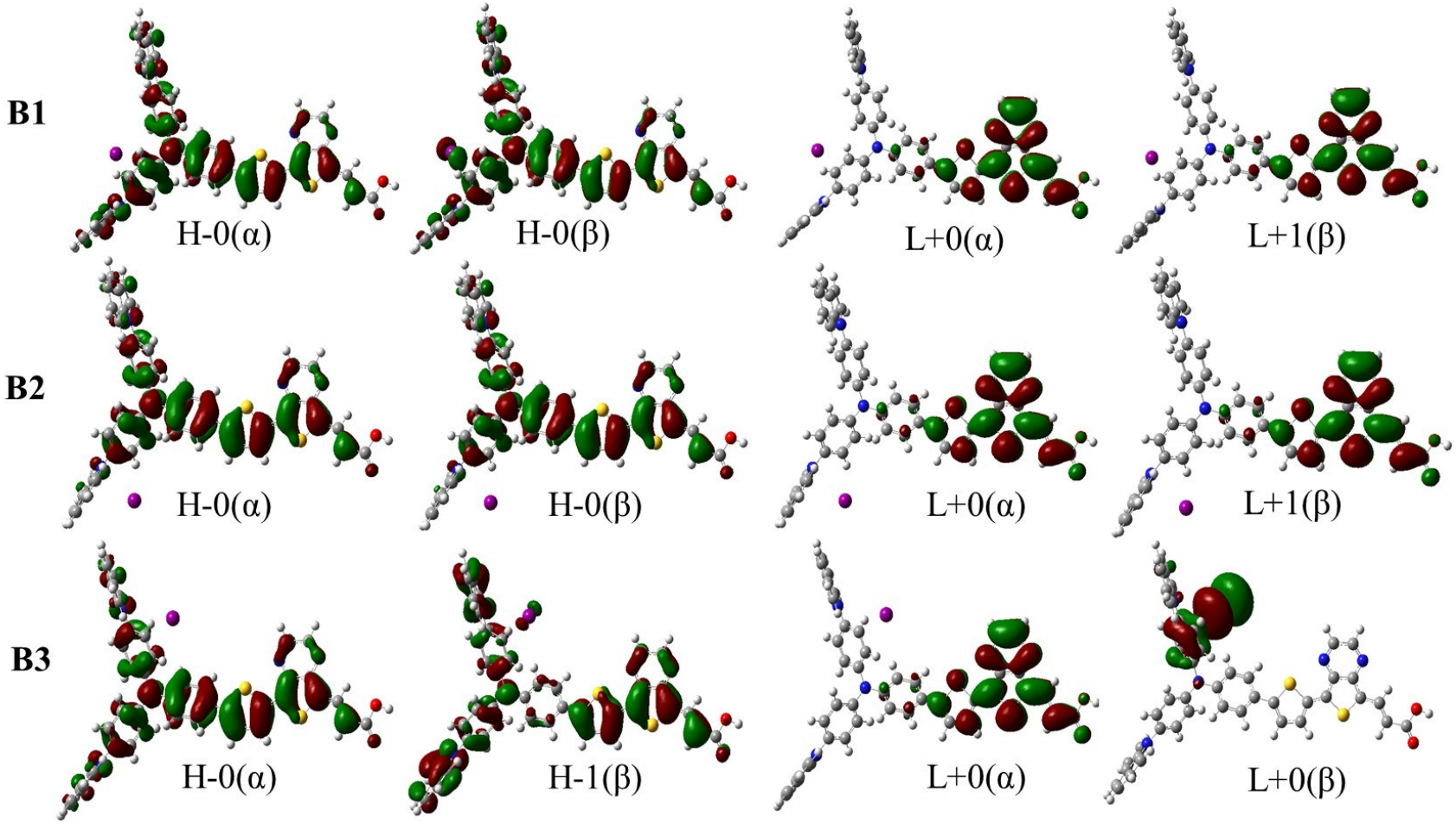


Figure S 12. Calculated isodensity plots of the selected frontier moleculer orbitals of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ complexes of the designed **dye3** sensitizer at different iodide interaction sites (Isovalue is 0.02 a.u.).


A1
H-3
L+0
A2
H-0
L+0
A3
H-0
L+0


B1
H-0(α)
H-0(β)
L+0(α)
L+1(β)
B2
H-0(α)
H-0(β)
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B3
H-0(α)
H-1(β)
L+0(α)
L+0(β)

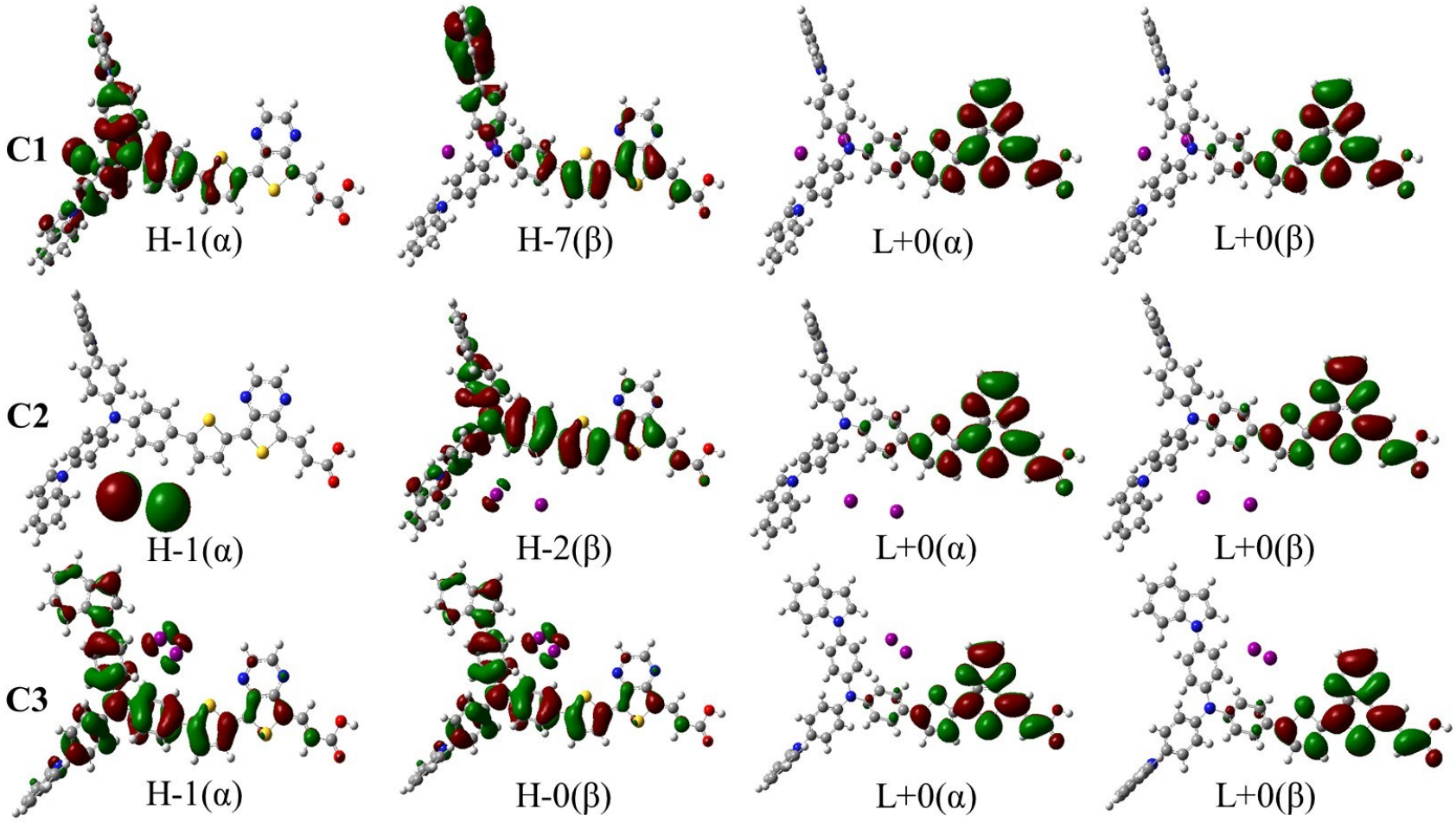
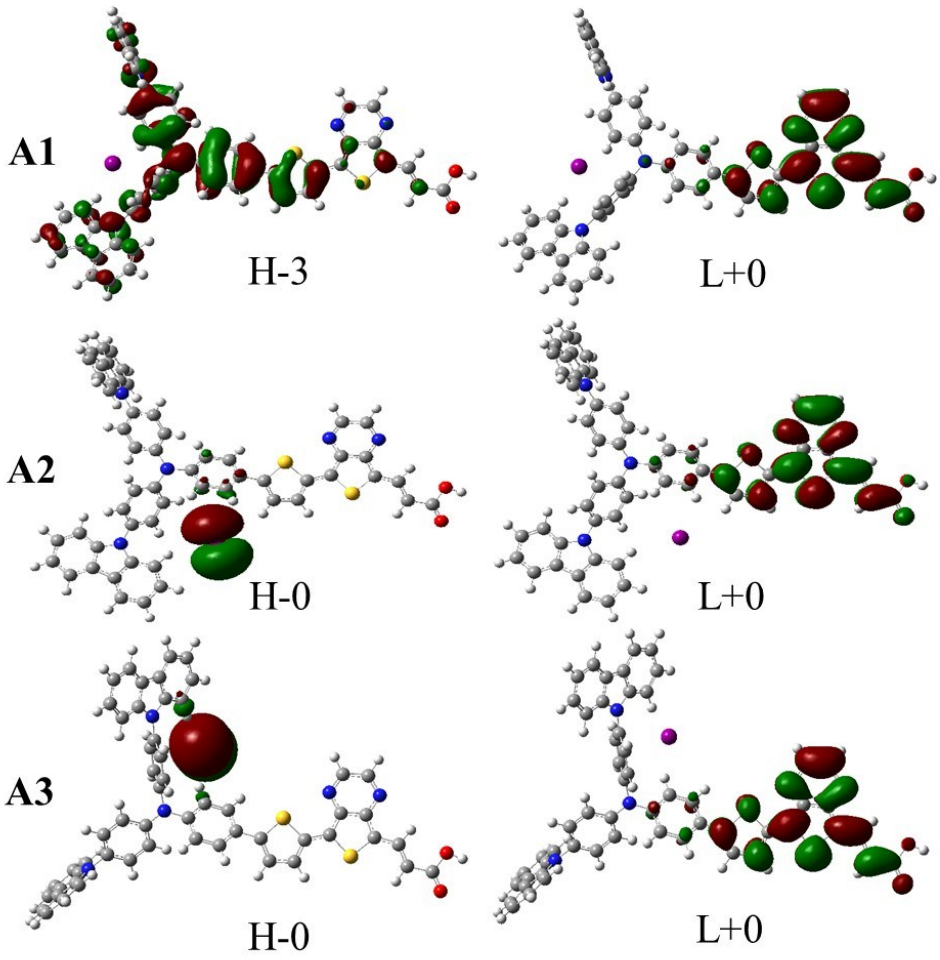
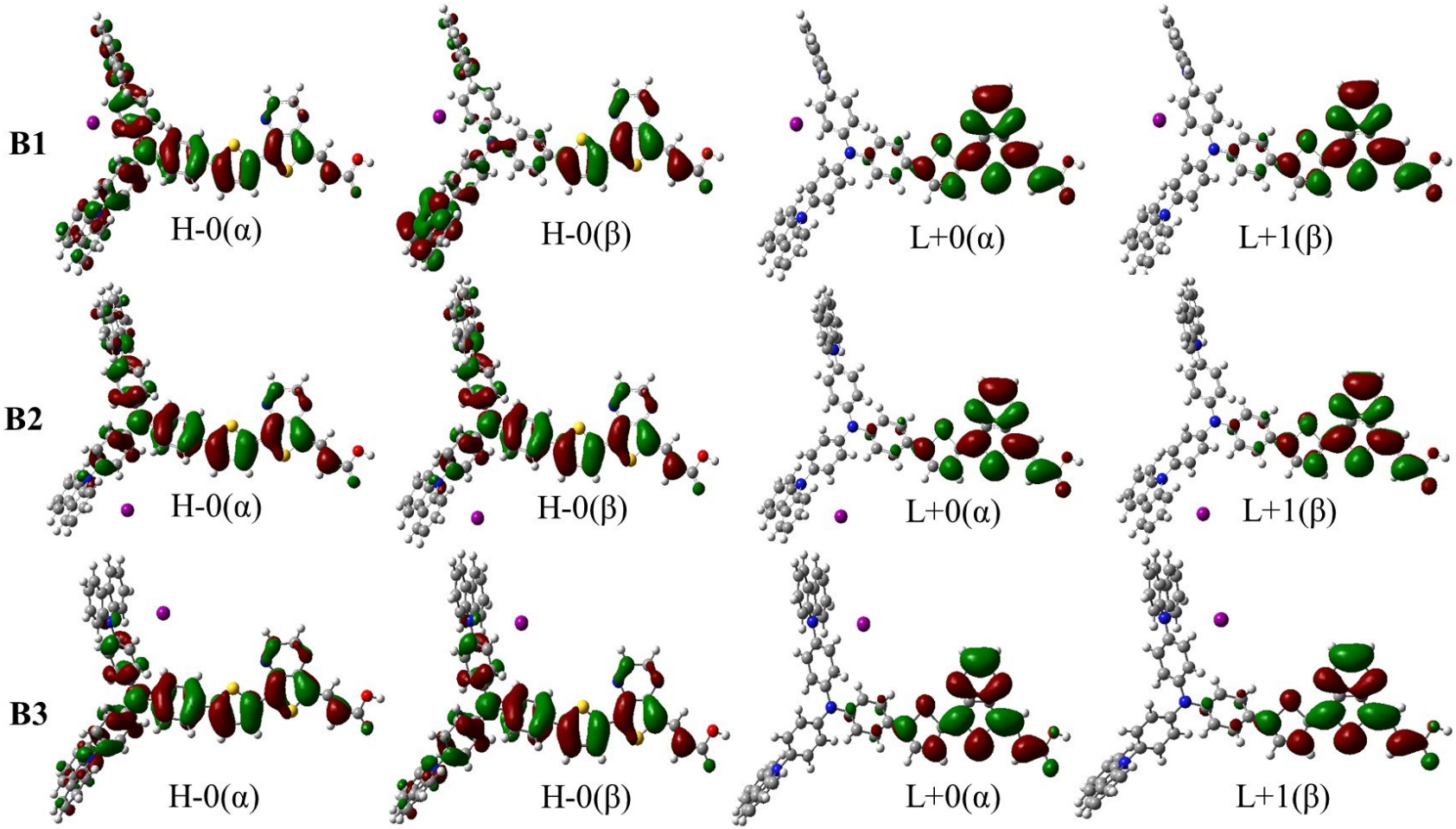


Figure S 13. Calculated isodensity plots of the selected frontier moleculer orbitals of A) $[dyeI]^-$ B) $[dyeI]^\bullet$, and C) $[dyeI_2]^{\bullet-}$ complexes of the designed **dye4** sensitizer at different iodide interaction sites (Isovalue is 0.02 a.u.).


A1
H-3
L+0
A2
H-0
L+0
A3
H-0
L+0


B1
H-0(α)
H-0(β)
L+0(α)
L+1(β)
B2
H-0(α)
H-0(β)
L+0(α)
L+1(β)
B3
H-0(α)
H-0(β)
L+0(α)
L+1(β)

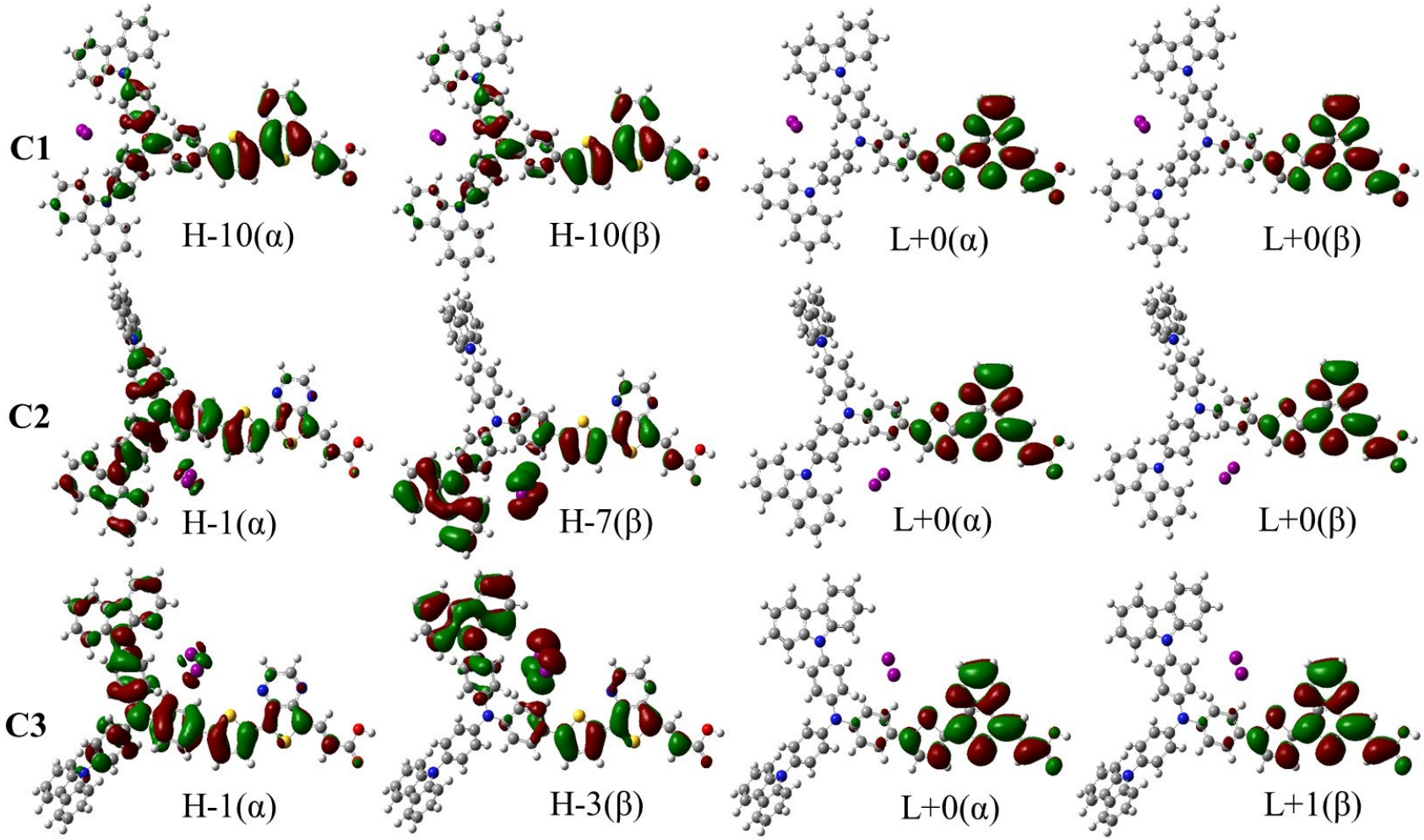


Figure S 14. Calculated isodensity plots of the selected frontier moleculer orbitals of A) $[dyeI]^-$ B) $[dyeI]^{\bullet}$, and C) $[dyeI_2]^{\bullet-}$ complexes of the designed **dye5** sensitizer at different iodide interaction sites (Isovalue is 0.02 a.u.).

Table S 1. Simulated UV-Vis absorption wavelength (λ in nm) for L1, L2[5] and TT2A[6] organic dyes with different DFT functional.

DFT Methods	**L1** λ (nm) in CH_3CN	[a]**Exp.**
TDB3LYP//B3LYP	555	**404** nm in CH_3CN
TDCAM-B3LYP//B3LYP	449	
TDCAMB3LYP//CAMB3LYP	422	
TDM06-2X//M06-2X	429	
TDWB97XD//WB97XD	**403**	
	L2 λ (nm) in CH_3CN	**427 nm** in CH_3CN
TDB3LYP//B3LYP	597	
TDCAM-B3LYP//B3LYP	458	
TDCAMB3LYP//CAMB3LYP	430	
TDM06-2X//M06-2X	435	
TDWB97XD//WB97XD	**413**	
	TT2A λ (nm) in DCM	**405** nm (in DCM)
TDB3LYP//B3LYP	630	
TDCAM-B3LYP//B3LYP	481	
TDCAMB3LYP//CAMB3LYP	441	
TDM06-2X//M06-2X	445	
TDWB97XD//WB97XD	**416**	

[a] taken from Ref[1]

Table S 2. The selected bond lengths (in Å) and dihedral angles (in °) for the D–D–π–A organic dyes.

Parameters	**dye1**	**dye2**	**dye3**	**dye4**	**dye5**	**dyeH**
r_1 (N_1-C_2)	1.395	1.398	1.402	1.411	1.411	1.408
r_2 (C_9-C_{32})	1.465	1.465	1.466	1.467	1.467	1.467
r_3 (C_{37}-C_{39})	1.442	1.442	1.443	1.443	1.443	1.443
r_4 (C_{40}-C_{50})	1.436	1.437	1.437	1.438	1.437	1.437
ϕ_1 (C_{22}-N_1-C_2-C_4)	–28.03	–26.82	–32.61	–38.97	–39.41	–36.49
ϕ_2 (C_7-C_9-C_{32}-S_{33})	31.31	33.54	32.11	32.69	33.12	32.82
ϕ_3 (C_{35}-C_{37}-C_{39}-C_{41})	–0.91	0.67	–2.67	–1.78	–2.06	–0.47
ϕ_4 (S_{41}-C_{40}-C_{50}-C_{52})	0.19	–0.29	0.26	0.29	0.33	0.04
ϕ_5 (S_{25}-C_{29}-R)	11.0	–46 (–10)	–40.0	–50.0	–61.0	–

dye1			dye3			dye3			dye4			dye5		
Atoms	NBO Charge	f^+	Atoms	NBO Charge	f^+	Atoms	NBO Charge	f^+	Atoms	NBO Charge	f^+	Atoms	NBO Charge	f^+
1N	-0.49	-0.49	1N	-0.49	-0.48	1N	-0.49	-0.48	1N	-0.49	-0.36	1N	-0.49	-0.36
2C	0.20	0.17	2C	0.19	0.16	2C	0.19	0.15	2C	0.17	0.01	2C	0.18	0.01
3C	-0.25	-0.18	3C	-0.24	-0.17	3C	-0.24	-0.17	3C	-0.22	-0.12	3C	-0.23	-0.12
4C	-0.24	-0.18	4C	-0.24	-0.17	4C	-0.24	-0.17	4C	-0.22	-0.12	4C	-0.22	-0.11
5C	-0.17	-0.05	5C	-0.17	-0.06	5C	-0.17	-0.06	5C	-0.17	-0.11	5C	-0.17	-0.11
6H	0.22	0.10	6H	0.22	0.11	6H	0.22	0.11	6H	0.22	0.11	6H	0.22	0.10
7C	-0.16	-0.05	7C	-0.16	-0.06	7C	-0.16	-0.06	7C	-0.17	-0.12	7C	-0.16	-0.12
8H	0.22	0.11	8H	0.22	0.11	8H	0.22	0.11	8H	0.22	0.11	8H	0.22	0.10
9C	-0.13	-0.15	9C	-0.12	-0.13	9C	-0.12	-0.13	9C	-0.10	-0.09	9C	-0.09	-0.08
10H	0.21	0.09	10H	0.21	0.09	10H	0.21	0.10	10H	0.23	0.12	10H	0.22	0.10
11H	0.21	0.09	11H	0.22	0.09	11H	0.21	0.10	11H	0.22	0.11	11H	0.21	0.10
12C	0.12	0.07	12C	0.11	0.06	12C	0.15	0.10	12C	0.16	0.11	12C	0.17	0.12
13C	-0.19	-0.14	13C	-0.19	-0.13	13C	-0.21	-0.15	13C	-0.21	-0.13	13C	-0.22	-0.13
14C	-0.19	-0.14	14C	-0.19	-0.13	14C	-0.21	-0.15	14C	-0.22	-0.12	14C	-0.22	-0.13
15C	-0.26	-0.13	15C	-0.26	-0.13	15C	-0.22	-0.09	15C	-0.19	-0.09	15C	-0.19	-0.09
16H	0.22	0.11	16H	0.22	0.10	16H	0.22	0.11	16H	0.22	0.11	16H	0.22	0.11
17C	-0.26	-0.13	17C	-0.26	-0.13	17C	-0.22	-0.09	17C	-0.19	-0.09	17C	-0.19	-0.09
18H	0.22	0.10	18H	0.22	0.10	18H	0.22	0.11	18H	0.22	0.11	18H	0.23	0.11
19C	0.19	0.04	19C	0.19	0.05	19C	0.16	0.01	19C	0.14	0.04	19C	0.14	0.04
20H	0.21	0.09	20H	0.21	0.09	20H	0.22	0.10	20H	0.22	0.11	20H	0.22	0.11
21H	0.21	0.09	21H	0.21	0.09	21H	0.22	0.10	21H	0.23	0.11	21H	0.22	0.11
22C	0.12	0.06	22C	0.16	0.08	22C	0.15	0.08	22C	0.16	0.11	22C	0.17	0.11
23C	-0.19	-0.14	23C	-0.22	-0.16	23C	-0.21	-0.15	23C	-0.23	-0.12	23C	-0.21	-0.12
24C	-0.19	-0.13	24C	-0.21	-0.15	24C	-0.20	-0.15	24C	-0.23	-0.13	24C	-0.21	-0.13
25C	-0.26	-0.13	25C	-0.21	-0.09	25C	-0.22	-0.09	25C	-0.19	-0.09	25C	-0.19	-0.09
26H	0.22	0.10	26H	0.22	0.11	26H	0.22	0.11	26H	0.23	0.11	26H	0.22	0.11

Table S 3. Calculated atomic charges from NBO Method[a] and the condensed Fukui functions (f^+)[b] values (for nucleophilic attack).

27C	-0.26	-0.13	27C	-0.21	-0.08	27C	-0.22	-0.09	27C	-0.19	-0.09	27C	-0.19	-0.09
28H	0.22	0.10	28H	0.22	0.11	28H	0.22	0.11	28H	0.22	0.11	28H	0.22	0.11
29C	0.19	0.04	29C	0.16	-0.01	29C	0.17	0.01	29C	0.14	0.04	29C	0.15	0.04
30H	0.21	0.09	30H	0.22	0.10	30H	0.22	0.10	30H	0.22	0.11	30H	0.22	0.12
31H	0.21	0.09	31H	0.22	0.10	31H	0.22	0.10	31H	0.22	0.11	31H	0.22	0.11
32C	-0.35	-0.17	32C	-0.35	-0.17	32C	-0.16	-0.04	32C	-0.12	-0.09	32C	-0.17	-0.14
33H	0.19	0.09	33H	0.19	0.09	33C	-0.25	-0.16	33C	-0.26	-0.22	33C	-0.25	-0.21
34H	0.17	0.08	34H	0.18	0.08	34S	0.47	0.23	34S	0.37	0.16	34S	0.47	0.26
35H	0.19	0.09	35H	0.19	0.09	35C	-0.21	-0.08	35C	-0.21	-0.09	35C	-0.21	-0.10
36C	-0.35	-0.17	36C	-0.16	-0.04	36H	0.22	0.11	36H	0.23	0.11	36H	0.22	0.11
37H	0.19	0.08	37C	-0.26	-0.16	37C	-0.24	-0.15	37C	-0.19	-0.21	37C	-0.23	-0.25
38H	0.19	0.09	38S	0.47	0.23	38H	0.22	0.11	38H	0.22	0.11	38H	0.22	0.10
39H	0.18	0.08	39C	-0.21	-0.09	39C	-0.17	-0.06	39C	-0.12	0.04	39C	-0.17	-0.02
40C	-0.15	-0.04	40H	0.22	0.11	40C	-0.25	-0.14	40C	-0.15	-0.22	40C	-0.22	-0.29
41C	-0.26	-0.17	41C	-0.24	-0.15	41S	0.50	0.24	41S	0.38	0.14	41S	0.50	0.26
42S	0.47	0.23	42H	0.22	0.11	42C	0.09	0.03	42C	0.06	-0.07	42C	0.09	-0.04
43C	-0.21	-0.08	43C	-0.17	-0.06	43N	-0.41	-0.22	43N	-0.40	-0.24	43N	-0.41	-0.25
44H	0.22	0.11	44C	-0.23	-0.16	44C	0.06	0.03	44C	0.05	0.05	44C	0.06	0.06
45C	-0.24	-0.16	45S	0.49	0.24	45C	0.04	0.01	45C	0.04	-0.04	45C	0.05	-0.03
46H	0.22	0.11	46C	0.09	0.03	46N	-0.41	-0.19	46N	-0.39	-0.16	46N	-0.41	-0.17
47C	-0.16	-0.05	47N	-0.42	-0.21	47H	0.19	0.09	47H	0.19	0.09	47H	0.19	0.09
48C	-0.23	-0.14	48C	0.06	0.03	48H	0.19	0.09	48H	0.19	0.09	48H	0.19	0.09
49S	0.49	0.24	49C	0.04	0.01	49C	0.13	0.07	49C	0.09	0.07	49C	0.13	0.11
50C	0.09	0.03	50N	-0.41	-0.19	50C	-0.15	-0.06	50C	-0.15	0.01	50C	-0.15	0.01
51N	-0.42	-0.23	51H	0.19	0.09	51H	0.27	0.12	51H	0.26	0.13	51H	0.25	0.12
52C	0.06	0.04	52H	0.19	0.09	52C	-0.32	-0.18	52C	-0.29	-0.29	52C	-0.32	-0.31
53C	0.04	0.01	53C	0.13	0.07	53H	0.21	0.11	53H	0.22	0.11	53H	0.21	0.11
54N	-0.41	-0.19	54C	-0.15	-0.06	54C	0.80	0.40	54C	0.75	0.36	54C	0.80	0.41
55H	0.19	0.09	55H	0.25	0.12	55O	-0.61	-0.31	55O	-0.57	-0.31	55O	-0.60	-0.34
56H	0.19	0.09	56C	-0.32	-0.18	56O	-0.70	-0.35	56O	-0.71	-0.36	56O	-0.70	-0.36
57C	0.13	0.07	57H	0.21	0.12	57H	0.48	0.24	57H	0.48	0.24	57H	0.48	0.24
58C	-0.15	-0.06	58C	0.80	0.40	58N	-0.49	-0.32	58N	-0.41	-0.21	58N	-0.43	-0.23
59H	0.25	0.12	59O	-0.61	-0.31	59N	-0.49	-0.32	59C	0.16	0.08	59C	0.20	0.10
60C	-0.32	-0.19	60O	-0.70	-0.36	60C	0.17	0.11	60C	0.00	0.00	60C	0.20	0.11
61H	0.21	0.11	61H	0.48	0.24	61C	-0.23	-0.13	61C	-0.09	-0.05	61C	-0.25	-0.12

62C	0.80	0.40	62N	-0.49	-0.34	62C	-0.23	-0.13	62C	-0.24	-0.12	62C	-0.08	-0.05
63O	-0.61	-0.31	63N	-0.46	-0.29	63C	-0.18	-0.09	63C	-0.28	-0.15	63C	-0.25	-0.13
64O	-0.70	-0.35	64C	-0.35	-0.17	64H	0.22	0.11	64H	0.21	0.11	64C	-0.08	-0.05
65H	0.48	0.24	65H	0.19	0.09	65C	-0.18	-0.09	65C	-0.18	-0.10	65C	-0.18	-0.09
66N	-0.46	-0.31	66H	0.19	0.09	66H	0.22	0.11	66C	-0.20	-0.11	66H	0.22	0.11
67N	-0.46	-0.31	67H	0.18	0.08	67C	-0.22	-0.13	67H	0.21	0.11	67C	-0.17	-0.09
68C	-0.35	-0.17	68C	0.18	0.11	68H	0.21	0.09	68H	0.22	0.11	68C	-0.18	-0.09
69H	0.19	0.09	69C	-0.24	-0.14	69H	0.21	0.09	69C	-0.22	-0.12	69H	0.22	0.11
70H	0.19	0.09	70C	-0.24	-0.13	70H	0.21	0.09	70H	0.21	0.10	70C	-0.17	-0.09
71H	0.17	0.08	71C	-0.18	-0.09	71C	0.17	0.11	71H	0.20	0.09	71C	-0.23	-0.12
72C	-0.35	-0.17	72H	0.22	0.12	72C	-0.23	-0.13	72H	0.20	0.09	72H	0.20	0.10
73H	0.19	0.09	73C	-0.19	-0.09	73C	-0.23	-0.13	73N	-0.41	-0.21	73H	0.21	0.10
74H	0.19	0.09	74H	0.22	0.11	74C	-0.19	-0.09	74C	0.16	0.08	74C	-0.23	-0.12
75H	0.18	0.08	75C	-0.23	-0.14	75H	0.22	0.11	75C	0.00	0.0	75H	0.20	0.09
			76H	0.21	0.09	76C	-0.18	-0.09	76C	-0.09	-0.05	76H	0.21	0.10
			77H	0.21	0.09	77H	0.22	0.11	77C	-0.24	-0.12	77H	0.20	0.09
			78H	0.21	0.09	78C	-0.22	-0.13	78C	-0.28	-0.18	78H	0.20	0.09
			79C	0.18	0.11	79H	0.21	0.09	79H	0.21	0.11	79N	-0.43	-0.21
			80C	-0.24	-0.14	80H	0.21	0.09	80C	-0.19	-0.09	80C	0.20	0.10
			81C	-0.24	-0.13	81H	0.21	0.09	81C	-0.20	-0.11	81C	0.20	0.10
			82C	-0.19	-0.09	82C	0.17	0.11	82H	0.22	0.11	82C	-0.25	-0.12
			83H	0.22	0.11	83C	-0.23	-0.13	83H	0.22	0.11	83C	-0.08	-0.04
			84C	-0.18	-0.09	84C	-0.23	-0.13	84C	-0.22	-0.12	84C	-0.25	-0.12
			85H	0.22	0.11	85C	-0.18	-0.09	85H	0.21	0.10	85C	-0.09	-0.04
			86C	-0.23	-0.14	86H	0.22	0.11	86H	0.20	0.09	86C	-0.19	-0.09
			87H	0.20	0.09	87C	-0.19	-0.09	87H	0.20	0.09	87H	0.22	0.11
			88H	0.20	0.09	88H	0.22	0.11	88N	-0.49	-0.36	88C	-0.17	-0.09
			89H	0.20	0.09	89C	-0.22	-0.13				89C	-0.18	-0.09
						90H	0.21	0.10				90H	0.22	0.11
						91H	0.21	0.10				91C	-0.17	-0.09
						92H	0.21	0.10				92C	-0.23	-0.12
						93C	0.17	0.11				93H	0.20	0.09
						94C	-0.23	-0.13				94H	0.21	0.10
						95C	-0.24	-0.13				95C	-0.23	-0.12
						96C	-0.19	-0.09				96H	0.20	0.09

						97H	0.22	0.11				97H	0.21	0.10
						98C	-0.19	-0.09				98H	0.20	0.09
						99H	0.22	0.11				99H	0.20	0.09
						100C	-0.22	-0.13						
						101H	0.21	0.10						
						102H	0.21	0.10						
						103H	0.21	0.10						

[a] The calculated atomic charge represents for the isolated neutral dyes, which is employed for the complexes [dyeI]$^-$ and [dyeI]$^\bullet$ formation. [b] f^+ values also denotes the Fukui function calculated by $f_k^+ = q_k(N+1) - q_k(N)$ for the nucleophilic attacks; where $q_k(N+1)$ and $q_k(N)$ are represents the electron density at atom k.

Table S 4. Calculated relative Gibbs free energies (ΔG_{rel} in kcal/mol) and the corresponding NBO charges for the $[dyeI]^-$, $[dyeI]^{\bullet}$ and $[dyeI_2]^{\bullet-}$ intermediates complexes of the different donor groups of the designed sensitizers.

	ΔG_{rel}			NBO Charge (I^-)		
Complexes	$[dyeI]^-_{A1}$	$[dyeI]^-_{A2}$	$[dyeI]^-_{A3}$	$[dyeI]^-_{A1}$	$[dyeI]^-_{A2}$	$[dyeI]^-_{A3}$
$[dye_1I]^-$	0.0	0.23	2.77	-0.961	-0.962	-0.959
$[dye_2I]^-$	4.51	0.0	3.79	-0.958	-0.953	-0.958
$[dye_3I]^-$	2.51	0.07	0.00	-0.939	-0.948	-0.956
$[dye_4I]^-$	0.47	1.14	0.00	-0.945	-0.941	-0.951
$[dye_5I]^-$	0.89	0.00	1.77	-0.938	-0.944	-0.939
Complexes	$[dyeI]^{\bullet}_{B1}$	$[dyeI]^{\bullet}_{B2}$	$[dyeI]^{\bullet}_{B3}$	$[dyeI]^{\bullet}_{B1}$	$[dyeI]^{\bullet}_{B2}$	$[dyeI]^{\bullet}_{B3}$
$[dye_1I]^{\bullet}$	0.00	1.38	0.69	-0.562	-0.577	-0.573
$[dye_2I]^{\bullet}$	2.25	2.28	0.00	-0.508	-0.416	-0.501
$[dye_3I]^{\bullet}$	2.32	4.17	0.00	-0.352	-0.231	-0.358
$[dye_4I]^{\bullet}$	1.39	0.00	0.23	-0.113	-0.194	-0.109

$[dye_5I]^{\bullet}$	0.11	0.01	0.00	-0.107		-0.191		-0.155	
Complexes	$[dyeI_2]^{\bullet-}{}_{C1}$	$[dyeI_2]^{\bullet-}{}_{C2}$	$[dyeI_2]^{\bullet-}{}_{C3}$	$[dyeI_2]^{\bullet-}{}_{C1}$		$[dyeI_2]^{\bullet-}{}_{C2}$		$[dyeI_2]^{\bullet-}{}_{C3}$	
				I(1)	I(2)	I(1)	I(2)	I(1)	I(2)
$[dye_1I_2]^{\bullet-}$	0.00	1.15	0.92	-0.489	-0.489	-0.486	-0.486	-0.493	-0.483
$[dye_2I_2]^{\bullet-}$	0.00	3.87	1.54	-0.473	-0.498	-0.499	-0.472	-0.495	-0.448
$[dye_3I_2]^{\bullet-}$	0.00	2.14	2.07	-0.484	-0.484	-0.462	-0.501	-0.497	-0.466
$[dye_4I_2]^{\bullet-}$	0.32	1.72	0.00	-0.493	-0.473	-0.492	-0.474	-0.499	-0.471
$[dye_5I_2]^{\bullet-}$	0.00	0.04	0.09	-0.483	-0.483	-0.493	-0.472	-0.501	-0.468

The parenthesis values indicate I(1) for first and I(2) for the second iodide interactions. Dye1-dye5 represents the different donor substituents of the sensitizers.

Table S 5. Calculated absorption wavelength (λ in nm), oscillator strengths (f in a.u.), light harvesting efficiency (LHE), and the corresponding transitions assignments of the dye-iodide complexes.

Complexes	**Transition States**	**λ**	**f**	**LHE**	***Transition assignment**
dye1	$S_0 \rightarrow S_1$	518.5	0.85	0.86	H-1 → L (54.2 %) H→ L (38.8 %)
$[dye_1I]^{\bullet}_{B1}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	591.2 527.8	0.17 0.37	0.32 0.57	H-2→L β (42.7 %)H-5→ Lβ(17.4 %) H→L β(14.7 %) H→L α (17.9 %) H-1→L α(20.7 %) H-1→ L+1 β (15.6 %)
$[dye_1I]^{\bullet}_{B2}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	621.1 496.8	0.28 0.74	0.48 0.82	H-4→L β (47.1 %)H-5→ Lβ(17.5 %) H-2→L β (13.5 %) H-1→L α (26.1 %) H→L α (15.8 %) H-2→ L+1β(23.3 %) H-3→ L+1β(11.8 %)
$[dye_1I]^{\bullet}_{B3}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	608.9 494.0	0.25 0.76	0.44 0.83	H-4→L β(47.4 %) H-5→ Lβ(17.6 %) H-2→L β (15.1 %) H-1→Lα(27.6 %) H→L α (16.2 %) H-2→L+1β(28.9%)
dye2	$S_0 \rightarrow S_1$	507.6	0.84	0.85	H-1→ L (41.3 %) H → L (33 %) H-2→ L (17.7 %)
$[dye_2I]^{\bullet}_{B1}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	680.8 498.2	0.31 0.83	0.51 0.85	H-4→L β (42.0 %)H-1→Lβ(30.7 %) H-5→L β (13.2 %) H-1→Lα (30.6 %) H→Lα (12.0 %) H-1→L+1 β (84.9 %)
$[dye_2I]^{\bullet}_{B2}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_7$	581.4 497.7	0.25 0.59	0.44 0.74	H-1→Lβ (70.4 %) H →Lα (19.1%) H-1→Lα (16.4%) H-1→L+1β(17.2%)H → L+1 β (10.3 %)
$[dye_2I]^{\bullet}_{B3}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	582.0 500.3	0.26 0.59	0.45 0.74	H-1→Lβ (52.1 %) H-2→ Lβ (30.3 %) H-2→Lβ (24.1%) H-5→Lβ (21.9%) H-1→ L+1β(13.6 %) H-1→Lα(15.8%)
dye3	$S_0 \rightarrow S_1$	516.4	0.92	0.88	H-2→ L (64.7 %) H → L (26.9 %)
$[dye_3I]^{\bullet}_{B1}$	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_7$	599.0 483.6	0.48 0.63	0.67 0.76	H-5→Lβ (42.0 %) H-4→ Lβ (35.4 %) H-5→L α(25.1 %) H-4→ Lα(11.2 %) H-4→L+1β(33.1%)
$[dye_3I]^{\bullet}_{B2}$	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_7$	546.4 491.9	0.42 0.47	0.62 0.66	H-5→Lβ (35.1%) H-4→ Lβ (28.4 %) H-3→L α (93.1 %) H-4→L+1β (14.6%)

$[dye_3I]^{\bullet}_{B3}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_7$	582.1 497.9	0.23 0.70	0.41 0.80	H-2→Lβ (73.9 %) H-1→Lα (25.0 %) H→Lα (17.3 %) H-2→L+1β (25.7%)
dye4	$S_0 \rightarrow S_1$	494.0	0.81	0.84	H → L (49.8 %) H-1→ L (40.4 %)
$[dye_4I]^{\bullet}_{B1}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_7$	758.6 491.8	0.04 0.82	0.10 0.85	H-3→Lβ (48.0 %) H-2→ Lβ(34.9 %) H→Lα (24.7%) H→L+1α (23.5 %) H-1→L+1β (19.8 %)H-1→L+1 β (18.8%)
$[dye_4I]^{\bullet}_{B2}$	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_7$	529.7 493.6	0.07 0.77	0.15 0.83	H→Lβ (51.7 %) H-5→Lβ (16.1 %) H-3→ Lβ (15.8 %) H→L α (29.2 %) H-1→L α (16.0 %) H→L+1β (29.2%) H-1→L+1β (15.6 %)
$[dye_4I]^{\bullet}_{B3}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_7$	753.1 492.9	0.04 0.42	0.09 0.62	H-3→L β (45.2 %) H-2→ L β (33.1 %) H-1→L β (24.8%) H-0→L+1 β (13.6%)H-0→L+0 α (13.0 %)
dye5	$S_0 \rightarrow S_1$	484.4	0.82	0.85	H → L (52.6 %) H-1→ L (35.2 %)
$[dye_5I]^{\bullet}_{B1}$	$S_0 \rightarrow S_7$ $S_0 \rightarrow S_8$	510.7 491.2	0.03 0.81	0.07 0.84	H-1→Lβ (42.9 %) H-2→ Lβ (26.2 %) H-5→L β (10.7%) H →L α (22.1%) H-1→L α (20.1%) H-1→L+1 β (21.2 %)H →L+1 β (21.1%)
$[dye_5I]^{\bullet}_{B2}$	$S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	544.1 491.2	0.23 0.68	0.41 0.79	H-1→L β (61.6 %) H-7→ L β (12.5 %) H →L α (32.0 %) H →L+1 β (26.3 %) H-1→L+1 β (10.7 %)
$[dye_5I]^{\bullet}_{B3}$	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_7$	553.4 492.9	0.05 0.78	0.11 0.83	H-4→ Lα (29.5 %) H→L β (58.5 %) H→L α (28.8 %) H-1→L α (14.5 %) H→L+1β (28.9%) H-1→L+1 β (14.1 %)

Labeling B1, B2 and B3 denotes the three stable interaction sites of the $[dyeI_2]^{\bullet-}$ complexes. [a] H = HOMO and L = LUMO. **dye_1-dye_5** denotes the different donor groups of the designed sensitizers.

Table S 6. Calculated absorption wavelength (λ in nm), oscillator strengths (f in a.u.), light harvesting efficiency (LHE), and the corresponding electronic transition of the dye-iodide $[dyeI_2]^{\bullet-}$ complexes for all the designed sensitizers.

Complexes	States	λ	f	LHE	[a]Electronic Transition
dye1	$S_0 \rightarrow S_1$	518.5	0.85	0.86	H-1 → L(54.2 %) H → L(38.8 %)
$[dye_1I_2]^{\bullet-}$**C1**	$S_0 \rightarrow S_6$	614.8	0.98	0.90	H-5→ Lα(26.5 %) H→L α(11.4 %) H → L β (26.8 %)
	$S_0 \rightarrow S_8$	456.7	0.25	0.44	H-7→L β (35.4 %) H-6→ Lβ(30.8 %) H-1→L β(20.7 %)
$[dye_1I_2]^{\bullet-}$**C2**	$S_0 \rightarrow S_6$	586.6	0.87	0.86	H-4→ Lα(15.6 %) H-1→Lα (13.2 %) H→L β(22.2 %)
	$S_0 \rightarrow S_8$	463.0	0.42	0.62	H-7→L β (40.9 %) H-4→ L β(21.3 %) H-5→L β (11.0 %)
$[dye_1I_2]^{\bullet-}$**C3**	$S_0 \rightarrow S_6$	540.4	0.77	0.83	H-4→ Lα(18.3 %) H-1→Lα (16.8 %) H→L β(20.7 %)
	$S_0 \rightarrow S_9$	461.6	0.70	0.80	H-7→L β (37.7 %) H-4→ Lβ(21.8 %) H-8→L β (12.6 %)
dye2	$S_0 \rightarrow S_1$	507.6	0.84	0.85	H-1→ L (41.3 %) H → L(33 %) H-2→ L (17.7 %)
$[dye_2I_2]^{\bullet-}$**C1**	$S_0 \rightarrow S_6$	576.1	0.99	0.90	H-5→Lα (15.1 %) H→Lα(13.1 %) H→L β (19.7 %) H-7→ Lβ(15.3 %)
	$S_0 \rightarrow S_8$	450.8	0.33	0.53	H-6→L+1 β (84.9 %)
$[dye_2I_2]^{\bullet-}$**C2**	$S_0 \rightarrow S_6$	550.2	0.87	0.86	H-4→ Lα(18.0 %) H-1→Lα (11.4%) H-1→Lα(10.6%) H-7→Lβ (22.0 %)
	$S_0 \rightarrow S_8$	457.5	0.44	0.64	H-6→L+1β(78.2%) H-4→ L+1β(10.3 %)
$[dye_2I_2]^{\bullet-}$**C3**	$S_0 \rightarrow S_6$	561.4	0.86	0.86	H-5→Lα (20.1 %) H→ Lβ(16.9 %) H-6→Lβ (10.2%) H-7→Lβ(10.1%)
	$S_0 \rightarrow S_8$	453.9	0.34	0.54	H-7→L+1 β (37.2%) H-6→L+1β(34.6 %) H-5→ L+1β(23.2 %)
dye3	$S_0 \rightarrow S_1$	516.4	0.92	0.88	H-2→ L (64.7 %) H → L(26.9 %)
$[dye_3I_2]^{\bullet-}$**C1**	$S_0 \rightarrow S_6$	564.6	1.03	0.91	H-1→ Lα(15.8 %) H-7→Lβ (20.8 %) H→Lβ (15.6%)
	$S_0 \rightarrow S_8$	461.6	0.42	0.62	H-7→L+1 β (79.4 %)
$[dye_3I_2]^{\bullet-}$**C2**	$S_0 \rightarrow S_6$	557.5	0.94	0.88	H-1→ Lα(18.4 %) H→Lβ (18.4 %) H-8→Lβ(14.6%)
	$S_0 \rightarrow S_8$	457.4	0.35	0.55	H-7→L+1β(93.1%)

$[dye_3I_2]^{\bullet-}$**C3**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	557.4 454.0	1.03 0.42	0.91 0.62	H-1→ Lα(15.8 %) H-7→Lβ(20.9 %) H→Lβ(15.5%) H-6→L+1β(82.4 %)
dye4	$S_0 \rightarrow S_1$	494.0	0.81	0.84	H → L(49.8 %) H-1→ L(40.4 %)
$[dye_4I_2]^{\bullet-}$**C1**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	541.1 465.5	0.96 0.33	0.89 0.53	H-1→Lα(17.2 %) H-7→ Lβ(11.9 %) H-6→Lβ(10.8%) H-5→L+1β(69.3 %) H-4→L+1β(19.2%)
$[dye_4I_2]^{\bullet-}$**C2**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	546.0 460.7	0.84 0.48	0.85 0.67	H-1→ Lα(16.7 %) H-4→Lα(12.1%) H-2→Lβ(25.9 %) H-5→L+1β(71.3 %) H-7→L+1β(16.0%)
$[dye_4I_2]^{\bullet-}$**C3**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	517.6 449.6	0.88 0.35	0.87 0.55	H-1→Lα (19.4 %) H-4→ Lα (16.6 %) H→L β (11.4%) H-3→L β (10.7%) H-6→L+1 β (90.7 %)
dye5	$S_0 \rightarrow S_1$	484.4	0.82	0.85	H → L (52.6 %) H-1→ L (35.2 %)
$[dye_5I_2]^{\bullet-}$**C1**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	536.6 446.9	0.93 0.33	0.88 0.53	H-10→ Lα (19.1 %) H-1→L α (14.4%) H-5→L α (13.5%) H-10→L β (19.1 %) H-7→L+1 β (90.2 %)
$[dye_5I_2]^{\bullet-}$**C2**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	536.0 458.3	0.87 0.39	0.86 0.59	H-1→Lα (15.3 %) H-5→ Lα (13.4 %) H-7→L β (13.0 %) H-9→L β (11.8 %) H-6→L+1 β (78.2 %)
$[dye_5I_2]^{\bullet-}$**C3**	$S_0 \rightarrow S_6$ $S_0 \rightarrow S_8$	538.9 447.7	0.82 0.34	0.85 0.54	H-1→Lα (18.6 %) H-4→ Lα (17.6 %) H-3→L β (16.5%) H-3→L β (10.7%) H-6→L+1 β (74.5 %) H-5→L+1 β (17.5 %)

Labeling C1, C2 and C3 represents the three most stable interaction sites of the $[dyeI_2]^{\bullet-}$ complexes. [a] H = HOMO and L = LUMO. **dye_1-dye_5** denotes the different donor groups of the designed sensitizers.

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