Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Stepwise photoconversion of an artificial light-harvesting array built from extended BODIPY units

Anthony Harriman, Patrycja Stachelek, Alexandra Sutter and Raymond Ziessel

Supporting Information

Experimental details for synthesis of new compounds

General features: ^{1}H and ^{13}C spectra were recorded at rt on 300 and 400 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^{1}H and ^{13}C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively. ^{11}B spectra were recorded at rt on a 400 MHz spectrometer using $BF_3.Et_2O$ as reference. FT-IR spectra were recorded using a spectrometer equipped with an ATR "diamond" apparatus. Chromatographic purification was conducted using 40-63 μm silica gel or aluminium oxide 90 standardized. Thin layer chromatography (TLC) was performed on silica gel or aluminium oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. All anhydrous reactions were carried out under dry argon by using Schlenk tube techniques.

Synthesis: Preparation and characterization of compound **1**. To a degassed solution of **A1** (63 mg, 0.038 mmol) and **D1** (22 mg, 0.046 mmol) in benzene (10 mL) and triethylamine (2 mL) was added $[Pd(PPh_3)_4]$ (10 mg). The resulting mixture was stirred at 70°C during 19 h and then was cooled to room temperature. After evaporation under vacuum, the organic product was extracted with CH_2Cl_2, washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel chromatography (from 50/50 to 40/60 Petroleum Ether/CH_2Cl_2) to obtain a brown compound (62 mg, 81%) and recrystallized by diffusion of pentane into a THF solution. The resulting crystalline compound was washed with pentane to afford analytically derivative **1** (54 mg, 71%). ^{1}H NMR (400 MHz, chloroform-d): δ (ppm) 7.71 (d, ^{3}J = 8.1 Hz, 4 H), 7.47 - 7.56 (m, 8 H), 7.33 - 7.41 (m, 6 H), 7.20 - 7.31 (m, 12 H), 7.02 - 7.16 (m, 18 H), 6.69 (d, ^{3}J = 9.0 Hz, 2 H), 6.62 (s, 1 H), 6.61 (s, 2 H), 5.99 (s, 1 H), 3.04 (s, 6 H), 2.61 (s, 3 H), 1.82 - 1.95 (m, 8 H), 1.50 (s, 9 H), 1.45 (s, 3 H), 1.11 - 1.25 (m, 24 H), 0.94 - 1.07 (m, 8 H), 0.83 (t, J=6.86 Hz, 12 H). ^{13}C NMR (101 MHz, chloroform -d): δ (ppm) 160.5, 158.7, 155.2, 153.1,

151.9, 151.1, 147.4, 147.1, 146.2, 143.0, 142.6, 140.7, 140.4, 140.0, 138.2, 137.7, 135.9, 135.8, 135.3, 134.7, 133.6, 132.9, 132.2, 132.2, 130.9, 129.7, 129.3, 129.3, 129.2, 129.1, 128.8, 126.1, 124.6, 124.4, 123.9, 123.5, 123.5, 123.1, 122.4, 120.6, 117.9, 116.8, 116.1, 114.2, 112.0, 90.0, 68.0, 54.0, 53.4, 40.2, 38.0, 34.1, 31.6, 29.7, 25.6, 24.5, 22.7, 22.3, 14.9, 14.8, 14.6, 14.5, 14.0. EI-MS, m/z (%) 2000.1 (100.0%), 1981.1 (35), 1963.2 (15). Anal. Calcd for $C_{129}H_{127}B_2F_4N_7S_4$: C, 77.42; H, 6.40; N, 4.90; found C, 77.20; H, 6.09; N, 4.68.

Calculation of the thermodynamic driving force for intramolecular electron transfer

To examine the free-energy gap (ΔG_{CS}) for light-induced electron transfer occurring within the target compound, we use the following expression:

$$\Delta G_{CS} = \Delta E\left(S_1\right) - \left(E_{OX} - E_{RED}\right) - \Delta G_S \tag{S1}$$

Here, $\Delta E(S_1)$ refers to the excitation energy of the relevant excited-singlet state as determined from the crossover point for normalized absorption and fluorescence spectra recorded in CH_2Cl_2. The terms, E_{OX} and E_{RED} refer respectively to the half-wave potentials for one-electron oxidation and reduction of the chromophore. Also required is the electrostatic correction term, ΔG_S, which is evaluated from the following expression:

$$\Delta G_S = \frac{z_D z_A e^2}{4\pi\varepsilon_0\varepsilon_S R_{DA}} \tag{S2}$$

Here, Z refers to the electronic charge, e_S is the static dielectric constant of the solvent and R_{DA} is the separation distance between the charges.

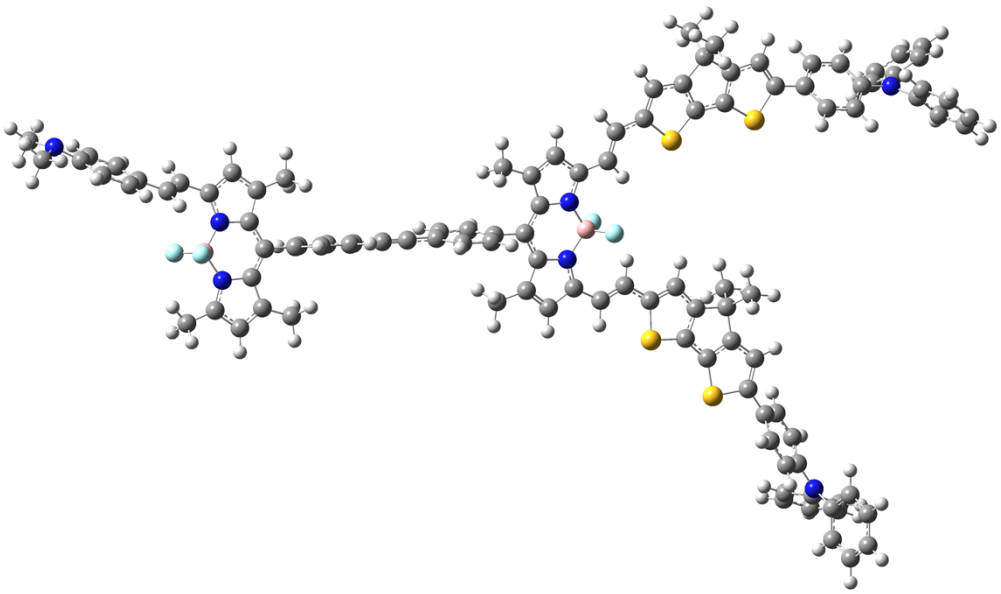

Figure S1. Energy-minimized geometry computed for the target compound **1**. The Cartesian coordinates are provided below:

1	C	0.00000000	0.00000000	0.00000000
2	C	1.52760457	0.00000000	0.00000000
3	C	2.10011223	1.41614985	0.00000000
4	C	2.07952775	-0.81716878	-1.17631217
5	C	2.81677584	-1.91202629	-0.72121841
6	S	3.43356209	-2.82234380	-2.03655340
7	C	2.70868466	-1.72532680	-3.21399586
8	C	2.88395877	-2.01016562	-4.62481552
9	C	1.76619665	-2.03018784	-5.48039122
10	C	1.91400262	-2.30303954	-6.83623064
11	C	3.19576131	-2.57123920	-7.36280637
12	N	3.35391415	-2.85765881	-8.75309404
13	C	2.30423699	-3.51676159	-9.48788905
14	C	1.99195890	-3.08654745	-10.79149391
15	C	0.98000120	-3.73422840	-11.50085644
16	C	0.27491679	-4.79541139	-10.92403373
17	C	0.58848674	-5.21602417	-9.62769286
18	C	1.60259260	-4.58789337	-8.90364309
19	C	4.56483254	-2.49464089	-9.44347529
20	C	5.17813526	-1.25437920	-9.18412246
21	C	6.34859735	-0.91532038	-9.86368790
22	C	6.90551838	-1.79092538	-10.80127674
23	C	6.28721547	-3.01849728	-11.05939032
24	C	5.12096807	-3.38146346	-10.38478378
25	C	4.31977581	-2.55451696	-6.50986515
26	C	4.15953031	-2.27246171	-5.15659223
27	C	2.01917140	-0.71449199	-2.59561941
28	C	2.81818445	-1.91532363	0.70758741
29	C	2.08051954	-0.82058431	1.17158562
30	C	2.01635354	-0.73575792	2.58625958
31	C	2.70141475	-1.76208375	3.20201784
32	S	3.42946215	-2.83575152	2.01226618

33	C	2.84023044	-1.99486672	4.61902785
34	C	3.55328496	-3.00296149	5.15297496
35	C	3.76146456	-3.34273304	6.54981239
36	C	4.43252954	-4.57345248	6.91158929
37	C	4.51024752	-4.64757399	8.29104294
38	C	5.11577556	-5.73841787	9.07082223
39	C	3.88502485	-3.44648884	8.82253471
40	N	3.43820249	-2.67900549	7.69386860
41	B	2.71274259	-1.31286925	7.90076800
42	F	1.44191275	-1.35711189	7.35523419
43	F	3.37398657	-0.31286647	7.21225331
44	N	2.60419277	-0.93614320	9.40834985
45	C	2.05295773	0.17773734	9.97431299
46	C	1.44827765	1.27186211	9.23117999
47	C	0.92661119	2.35231061	9.84465028
48	C	0.31422407	3.46934168	9.17393929
49	C	-0.23487969	4.59771389	9.74523959
50	C	-0.74862391	5.49419513	8.77277451
51	C	-1.44778599	6.85916269	8.80349118
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53	C	-0.54025104	7.93008708	9.40605217
54	C	-1.64430864	7.08817051	7.29863520
55	C	-1.13398443	6.01828113	6.56120631
56	S	-1.35241558	6.27534924	4.88038713
57	C	-2.12692988	7.83671687	5.15803020
58	C	-2.59041983	8.59222785	4.01054615
59	C	-3.90656933	9.09081683	3.98358145
60	C	-4.36887604	9.81644522	2.89062031
61	C	-3.51479680	10.05109782	1.79162934
62	N	-3.98385229	10.78980531	0.66292653
63	C	-5.37351966	10.74442452	0.28477213
64	C	-6.02235104	11.92524495	-0.12319791
65	C	-7.36564415	11.87269692	-0.49673251
66	C	-8.06667770	10.66304694	-0.46017222
67	C	-7.41673096	9.49429712	-0.05107808
68	C	-6.07141659	9.52261844	0.31853939
69	C	-3.07717651	11.59294067	-0.11670582
70	C	-2.08971252	12.36417662	0.52489902
71	C	-1.22135337	13.13971106	-0.24419615
72	C	-1.33293956	13.16165996	-1.63801448
73	C	-2.32036110	12.39801024	-2.26879221
74	C	-3.19300859	11.60801014	-1.51969973
75	C	-2.19456766	9.55349566	1.81266853
76	C	-1.74144053	8.83676919	2.91597904
77	C	-2.20992510	8.12090362	6.49666763
78	C	-0.59002433	5.04684455	7.45669164
79	S	0.18507870	3.52328114	7.41901729
80	C	2.17625399	0.06841020	11.40315385
81	C	2.81118904	-1.13329072	11.69853899
82	C	3.13203329	-1.63893128	13.04288027
83	C	3.09308096	-1.79199571	10.43978801
84	C	3.71063248	-3.01295114	10.13639404
85	C	4.19506756	-3.86183769	11.25512569
86	C	3.34724710	-4.83205962	11.81020191
87	C	3.80040000	-5.63029083	12.86014297
88	C	5.10564830	-5.45969321	13.35993234
89	C	5.56722840	-6.27151425	14.42501337
90	C	5.96425392	-6.96562418	15.33315578
91	C	6.42469625	-7.77750029	16.39873958
92	C	7.62583423	-7.45802936	17.06008799
93	C	8.07818926	-8.25875855	18.10856635

94	C	7.33609130	-9.38317430	18.49922989
95	C	7.82220192	-10.23606643	19.61463353
96	C	8.63921018	-11.32800832	19.32619037
97	C	9.13670340	-11.87017086	18.07303732
98	C	8.87692510	-11.33012511	16.72913745
99	C	9.89140199	-12.99414592	18.37666010
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102	N	9.14403910	-12.18044369	20.36655795
103	B	8.88557346	-11.88156364	21.87531525
104	F	10.09311260	-11.57751821	22.48044347
105	F	8.43916765	-13.00766628	22.53891615
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107	N	7.87238756	-10.70996342	22.04201748
108	C	7.24861727	-10.26488842	23.16648767
109	C	7.36134573	-10.80386162	24.51335833
110	C	8.51096830	-11.04700022	25.16316310
111	C	8.59296015	-11.58684606	26.52184315
112	C	7.49072316	-12.17468951	27.16871706
113	C	7.59979712	-12.68594882	28.45633675
114	C	8.82662057	-12.60661869	29.15944475
115	N	8.89952283	-12.96211327	30.53206537
116	C	10.24949306	-13.26043838	31.08466987
117	C	7.87975489	-13.92552898	31.03360122
118	C	9.94240994	-12.03170763	28.50109359
119	C	9.82014485	-11.53035821	27.21204832
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121	C	6.51570524	-8.93557408	21.44916541
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123	C	6.13822615	-9.70605664	17.84398469
124	C	5.68283586	-8.90625313	16.79645280
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132	H	1.77666908	1.97708714	0.88566922
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138	H	0.04063456	-6.04577185	-9.17722656
139	H	1.84777618	-4.92721304	-7.89732357
140	H	4.74497067	-0.56312385	-8.46141118
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142	H	7.81790642	-1.51729296	-11.32928570
143	H	6.72077782	-3.70288249	-11.79092982
144	H	4.64730468	-4.34198274	-10.58705111
145	H	5.31486741	-2.76667199	-6.90335587
146	H	5.03794505	-2.25647437	-4.50649591
147	H	1.49016148	0.07985790	-3.10747795
148	H	1.48437183	0.05231174	3.10799239
149	H	2.29262131	-1.26745745	5.23071219
150	H	4.08037342	-3.71042165	4.48993634
151	H	4.79830205	-5.29258224	6.20210894
152	H	4.38706001	-6.21734278	9.74663693
153	H	5.52591353	-6.53554162	8.43019439
154	H	5.94538254	-5.38240941	9.70488093

155	H	1.43751362	1.17260713	8.14022447
156	H	0.94486433	2.43816009	10.94304232
157	H	-0.27623884	4.79406432	10.81035558
158	H	-2.65771962	6.52951106	10.58743944
159	H	-3.33379358	7.72569629	9.47222857
160	H	-3.43729484	6.00198514	9.09096492
161	H	0.42375475	7.98422434	8.88439008
162	H	-1.00144691	8.92352311	9.34670104
163	H	-0.32942962	7.72572262	10.46276711
164	H	-4.57086845	8.90866280	4.83165887
165	H	-5.38821483	10.20470323	2.89081418
166	H	-5.48245041	12.87162729	-0.14888515
167	H	-7.87200695	12.78571310	-0.81534608
168	H	-9.11613651	10.63136660	-0.74975049
169	H	-7.96210229	8.54909926	-0.02439529
170	H	-5.56889009	8.60604691	0.62734892
171	H	-2.00230190	12.35876880	1.61121124
172	H	-0.45242545	13.73663767	0.24978002
173	H	-0.65286076	13.77189776	-2.23066605
174	H	-2.40855273	12.41435948	-3.35666648
175	H	-3.95690090	11.01130116	-2.01788412
176	H	-1.52698600	9.72276656	0.96661026
177	H	-0.71531425	8.46076345	2.92424181
178	H	-2.64453005	9.02050113	6.91444849
179	H	1.82889704	0.80226438	12.10509034
180	H	4.21651861	-1.78844969	13.17903057
181	H	2.80271560	-0.95378602	13.83986214
182	H	2.65415178	-2.61302560	13.24170763
183	H	2.33450359	-4.96310241	11.42153736
184	H	3.14427657	-6.38782782	13.29403927
185	H	8.20151615	-6.58222735	16.75361766
186	H	9.00937299	-8.01037026	18.62317287
187	H	7.80131540	-11.33600474	16.48422633
188	H	9.21343228	-10.28392192	16.63264072
189	H	9.38634091	-11.90386659	15.93885664
190	H	10.40081182	-13.64194287	17.68956564
191	H	10.07406118	-15.21900380	20.36627937
192	H	11.61668502	-14.37308233	20.16710011
193	H	10.64459564	-14.11009798	21.61835323
194	H	6.38636058	-10.97372747	24.98837744
195	H	9.47828027	-10.81671480	24.70139070
196	H	6.53202615	-12.24328797	26.64821116
197	H	6.72592932	-13.13981574	28.92276939
198	H	10.96218702	-12.45999770	30.81802512
199	H	10.19387225	-13.28901635	32.18689954
200	H	10.66528371	-14.22057640	30.73800235
201	H	7.96044154	-14.92795113	30.58207992
202	H	7.97886320	-14.03557411	32.12685315
203	H	6.86462630	-13.53731526	30.83862244
204	H	10.90694656	-11.97310516	29.00587208
205	H	10.69395360	-11.08749204	26.72733796
206	H	5.80264756	-8.60598254	23.51709733
207	H	5.21982335	-7.22701859	21.31529279
208	H	6.54230434	-7.23929361	20.13800880
209	H	5.15281407	-8.30930190	19.91741049
210	H	5.56274789	-10.58167194	18.15336687
211	H	4.75073177	-9.15345891	16.28422994
212	H	6.96312200	-4.34938227	13.18779438
213	H	6.15423550	-2.93249197	11.31113381

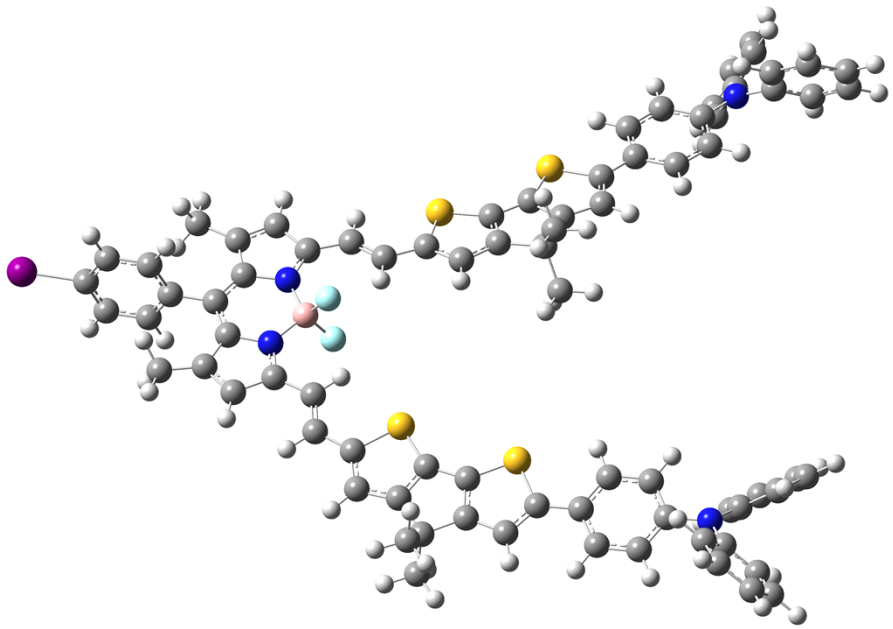

Figure S2. The energy-minimized geometry computed for **A1**. The Cartesian coordinates are given below:

1	I	0.00000000	0.00000000	0.00000000
2	C	2.11307398	0.00000000	0.00000000
3	C	2.79286589	1.21646379	0.00000000
4	C	4.19139561	1.21717229	-0.00005648
5	C	2.79182089	-1.21721215	0.00006965
6	C	4.19020677	-1.21807655	0.00478661
7	C	4.88729998	-0.00076852	0.00175975
8	C	6.37334615	0.00124096	0.01999475
9	C	7.07025362	0.15670101	-1.17748941
10	N	8.50539031	0.19024086	-1.23175166
11	B	9.35277831	0.06082276	0.07219608
12	F	10.12109624	1.19698074	0.25692427
13	F	10.25491234	-0.97965813	-0.04374136
14	N	8.45467127	-0.15017711	1.32725304
15	C	7.02990435	-0.15033362	1.24878369
16	C	6.53838955	-0.33816309	2.59860041
17	C	5.13043068	-0.39250911	3.02391431
18	C	7.64731007	-0.45396964	3.43024903
19	C	8.83345381	-0.33419422	2.62603654
20	C	10.21168821	-0.38578898	3.08788873
21	C	10.53079383	-0.72052935	4.35334024
22	C	11.87080808	-0.80232990	4.87379930
23	C	12.26478363	-1.20390823	6.13221617
24	C	13.67388588	-1.15722522	6.29240861
25	C	14.35545848	-0.71679364	5.15265814
26	C	15.75879048	-0.70668457	5.41968775
27	S	17.23908185	-0.33266824	4.64417636
28	C	18.17996270	-0.75862816	6.07685880
29	C	19.62407048	-0.64575620	6.04790783
30	C	20.37702074	-0.99372917	7.18842760

31	C	21.76485736	-0.89881430	7.19114641
32	C	22.43754619	-0.43625565	6.04307891
33	N	23.86267595	-0.28257793	6.03196154
34	C	24.56005922	-0.02114480	7.26612676
35	C	25.73832666	-0.71944313	7.58782413
36	C	26.42739158	-0.39731842	8.75827461
37	C	25.94584929	0.59565423	9.61631547
38	C	24.76405846	1.27444591	9.30002729
39	C	24.06871837	0.97949153	8.12755299
40	C	24.61663676	-0.69431394	4.87457174
41	C	24.17134722	-1.75351305	4.06262428
42	C	24.89636847	-2.09239688	2.91879470
43	C	26.06506184	-1.40119405	2.58670634
44	C	26.51198061	-0.35862160	3.40573353
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46	C	21.69626265	-0.08722393	4.89493453
47	C	20.30908684	-0.19317773	4.90224178
48	C	17.35314899	-1.16840593	7.09665768
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52	C	14.59527485	-2.95314610	7.81025556
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56	C	11.41690191	0.52265707	-2.53221527
57	C	12.67257119	0.58873244	-3.23914784
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59	C	14.94205401	0.79166449	-3.68722759
60	C	16.46644894	0.95889181	-3.68797151
61	C	16.86992184	2.34136252	-3.17877702
62	C	17.14385359	-0.16117749	-2.90074235
63	C	16.74427987	0.82196446	-5.19138833
64	C	15.55982992	0.61295949	-5.90095689
65	S	15.87565543	0.46168126	-7.57705932
66	C	17.61329106	0.67887314	-7.34264177
67	C	18.50178592	0.65133994	-8.48637206
68	C	19.89471263	0.76588151	-8.29414404
69	C	20.77444972	0.74262222	-9.37062354
70	C	20.27479179	0.61502250	-10.68289884
71	N	21.15902432	0.63239926	-11.80737418
72	C	22.41426278	1.33708355	-11.72308439
73	C	23.59721723	0.74210242	-12.19906165
74	C	24.79140211	1.46326599	-12.15557161
75	C	24.82094796	2.75811666	-11.62897769
76	C	23.64459228	3.33835777	-11.14295018
77	C	22.43744182	2.64083143	-11.19151744
78	C	20.91281632	-0.22289216	-12.93966547
79	C	20.31231980	-1.48419455	-12.76886432
80	C	20.05071435	-2.27614044	-13.88796520
81	C	20.39364639	-1.83340868	-15.16890757
82	C	21.00217470	-0.58439292	-15.33216789
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84	C	18.88410632	0.49863455	-10.88844603
85	C	18.01545657	0.51410301	-9.80169971
86	C	17.90556879	0.85922516	-6.01083766
87	C	14.46195099	0.59467657	-4.98704259
88	S	12.76268442	0.40654971	-4.98722955
89	C	7.71302102	0.37370799	-3.35998250
90	C	6.59690461	0.27886810	-2.54823331
91	C	5.19545846	0.30775380	-2.99542011

92	H	2.25319583	2.16790081	0.00133830
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95	H	4.73431070	-2.16584542	0.00772832
96	H	4.65544853	-1.34560074	2.73398707
97	H	5.02028611	-0.30646738	4.11703372
98	H	4.52260192	0.41218215	2.57984783
99	H	7.64165933	-0.60193579	4.49338622
100	H	10.98257904	-0.14467058	2.34761260
101	H	9.74429376	-0.96195102	5.08628043
102	H	11.59101961	-1.52247295	6.91922495
103	H	19.86826447	-1.35133997	8.08716024
104	H	22.32420296	-1.18501371	8.08326550
105	H	26.11145007	-1.50844623	6.93514456
106	H	27.34714531	-0.93099404	9.00479113
107	H	26.48753097	0.83941962	10.52907611
108	H	24.38422758	2.04659190	9.97165057
109	H	23.15636801	1.52204475	7.87997825
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111	H	24.54737169	-2.90850931	2.28337247
112	H	26.62695252	-1.67413348	1.69467858
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117	H	17.68519813	-1.48183087	8.07896533
118	H	13.44371615	-0.74876651	9.08812446
119	H	15.18484547	-0.71902401	9.40273850
120	H	14.45531957	0.49693023	8.34620270
121	H	14.77355247	-3.60374298	6.94460925
122	H	15.34985645	-3.20029413	8.56693261
123	H	13.61421411	-3.21877640	8.22257155
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125	H	11.53081123	0.60808511	-1.44454114
126	H	14.12781525	0.92575750	-1.64152112
127	H	16.58357610	2.47834162	-2.12869956
128	H	17.95413818	2.49173226	-3.24773305
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130	H	16.84380244	-1.15183828	-3.26519593
131	H	18.23617737	-0.10002011	-2.97825397
132	H	16.88499552	-0.11268559	-1.83571648
133	H	20.29673531	0.86667321	-7.28280835
134	H	21.84812740	0.82042647	-9.19254076
135	H	23.58593515	-0.27300548	-12.59564304
136	H	25.70903035	1.00774451	-12.53236420
137	H	25.75745016	3.31314444	-11.59557216
138	H	23.66727724	4.34769604	-10.72785518
139	H	21.52130821	3.10377481	-10.82485599
140	H	20.05613350	-1.84750634	-11.77382442
141	H	19.57875952	-3.25180932	-13.75756814
142	H	20.18933193	-2.45903490	-16.03649401
143	H	21.27274115	-0.23806186	-16.33138404
144	H	21.72573269	1.20429284	-14.36293130
145	H	18.48354042	0.40325055	-11.89925839
146	H	16.94346948	0.42598765	-9.99726726
147	H	18.89879188	1.01456792	-5.60721535
148	H	7.73047273	0.47337271	-4.42975618
149	H	4.70093263	1.25573056	-2.72090056
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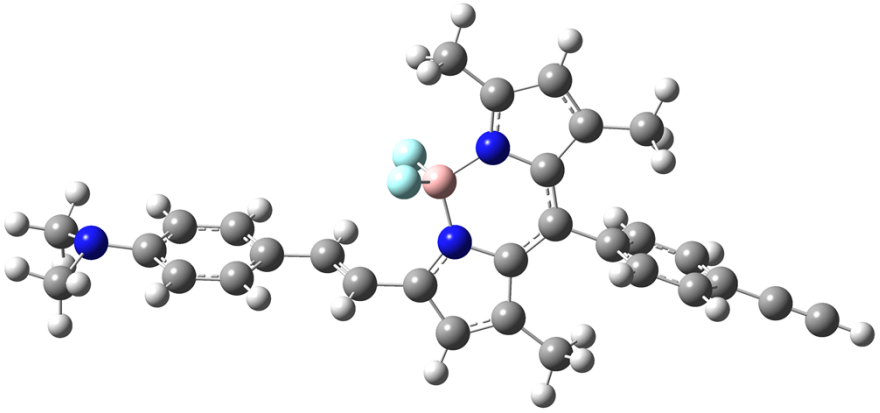

Figure S3. Energy-minimized geometry computed for **D1**. The Cartesian coordinates are given below:

1	F	0.00000000	0.00000000	0.00000000
2	B	1.38333734	0.00000000	0.00000000
3	F	1.72280642	1.33966440	0.00000000
4	N	1.91364532	-0.70693921	-1.28481931
5	C	2.68758648	-1.91600429	-1.22998610
6	C	3.06959670	-2.48229127	-0.01482818
7	C	3.87142267	-3.73266380	-0.01755965
8	C	5.27249356	-3.66450108	-0.03375902
9	C	6.02501810	-4.83868551	-0.03797686
10	C	5.37778516	-6.08825602	-0.02424566
11	C	6.14211797	-7.28432108	-0.02927757
12	C	6.79181318	-8.30046608	-0.03362421
13	C	3.97191746	-6.15163706	-0.00562735
14	C	3.22169119	-4.97589716	-0.00260075
15	C	2.72178066	-1.90067035	1.21135661
16	N	1.93473013	-0.70589896	1.27304782
17	C	1.78742551	-0.33758080	2.57261491
18	C	1.07683237	0.84529222	3.04530211
19	C	-0.25638012	0.98429040	2.98298778
20	C	-0.99805803	2.14801935	3.47207185
21	C	-0.35882854	3.31320990	3.93315992
22	C	-1.09029300	4.40182660	4.39283442
23	C	-2.50553431	4.36631050	4.40160507
24	N	-3.25778815	5.53044585	4.72244993
25	C	-4.67732132	5.31470536	5.12169594
26	C	-2.59158711	6.53092229	5.60337919
27	C	-3.15066200	3.19213083	3.94120591
28	C	-2.40641804	2.11256978	3.48258383
29	C	2.47211560	-1.28851340	3.40453873
30	C	3.04022547	-2.25425329	2.57988137
31	C	3.83036948	-3.41630696	3.01843159
32	C	2.93927280	-2.30153620	-2.60859922
33	C	3.69454355	-3.48316239	-3.05359075

34	C	2.34071656	-1.35147202	-3.42458830
35	C	1.70635111	-0.36933505	-2.58377130
36	C	0.96767513	0.81964610	-3.04248202
37	H	5.77387520	-2.69401143	-0.04330595
38	H	7.11568689	-4.78917018	-0.05250114
39	H	7.35081170	-9.17368663	-0.03758977
40	H	3.46974006	-7.12105821	0.00646400
41	H	2.13049823	-5.02414906	0.01176488
42	H	1.73038164	1.60908987	3.48052350
43	H	-0.87696319	0.18764910	2.55189511
44	H	0.73281904	3.36765221	3.93130533
45	H	-0.56069466	5.28915630	4.74000242
46	H	-4.79401867	4.71188463	6.03676810
47	H	-5.16897770	6.28777001	5.29074166
48	H	-5.22541256	4.81533889	4.30322133
49	H	-1.61810700	6.82795871	5.17448350
50	H	-3.21087196	7.44261339	5.65824428
51	H	-2.42141792	6.17137339	6.63107948
52	H	-4.23814539	3.12697623	3.93501305
53	H	-2.92699669	1.21969178	3.12747113
54	H	2.51358593	-1.23909157	4.47510676
55	H	3.86837331	-3.50943935	4.11501088
56	H	3.42373282	-4.36488184	2.62996243
57	H	4.87422171	-3.35654866	2.66646126
58	H	4.73813277	-3.46338872	-2.69578163
59	H	3.25329676	-4.42073517	-2.67463127
60	H	3.73539885	-3.56951217	-4.15075757
61	H	2.33417650	-1.32694496	-4.49723486
62	H	1.51573047	1.75344440	-2.82146671
63	H	0.79242449	0.80327966	-4.13021911
64	H	-0.02049270	0.92414674	-2.56202619

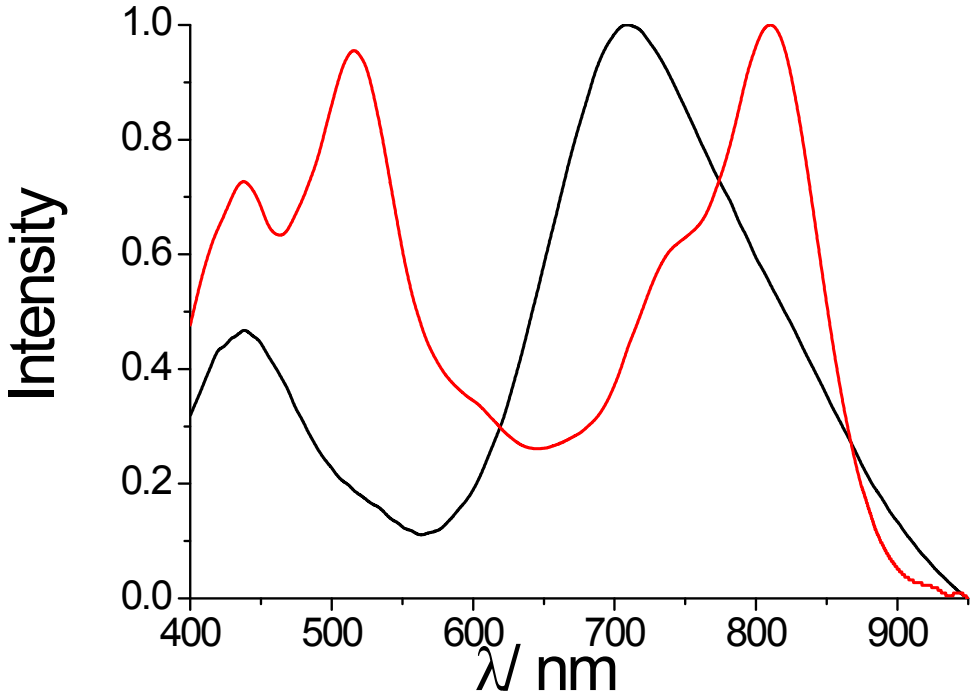

Figure S4. Absorption spectra recorded before (red curve) and after (black curve) illumination with white light of **A1** in deoxygenated CH_2Cl_2.

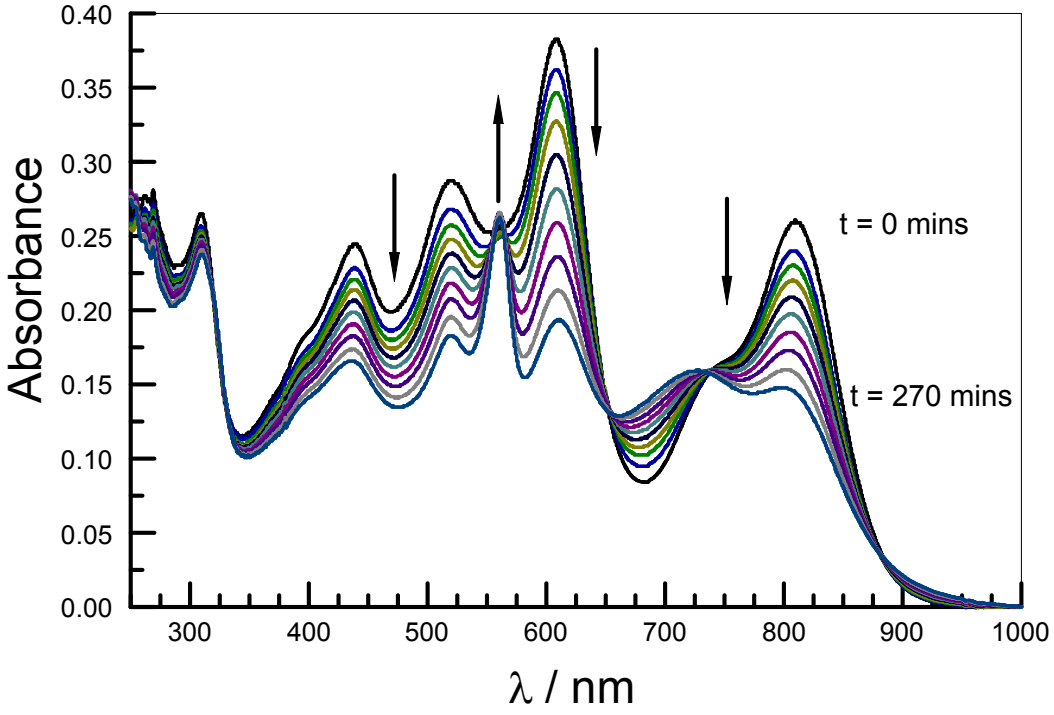

Figure S5. Absorption spectra recorded during the early stages of photolysis of **1** in deoxygenated CH_2Cl_2, spectra being recorded at 30 minute intervals. Note the series of isosbestic points.

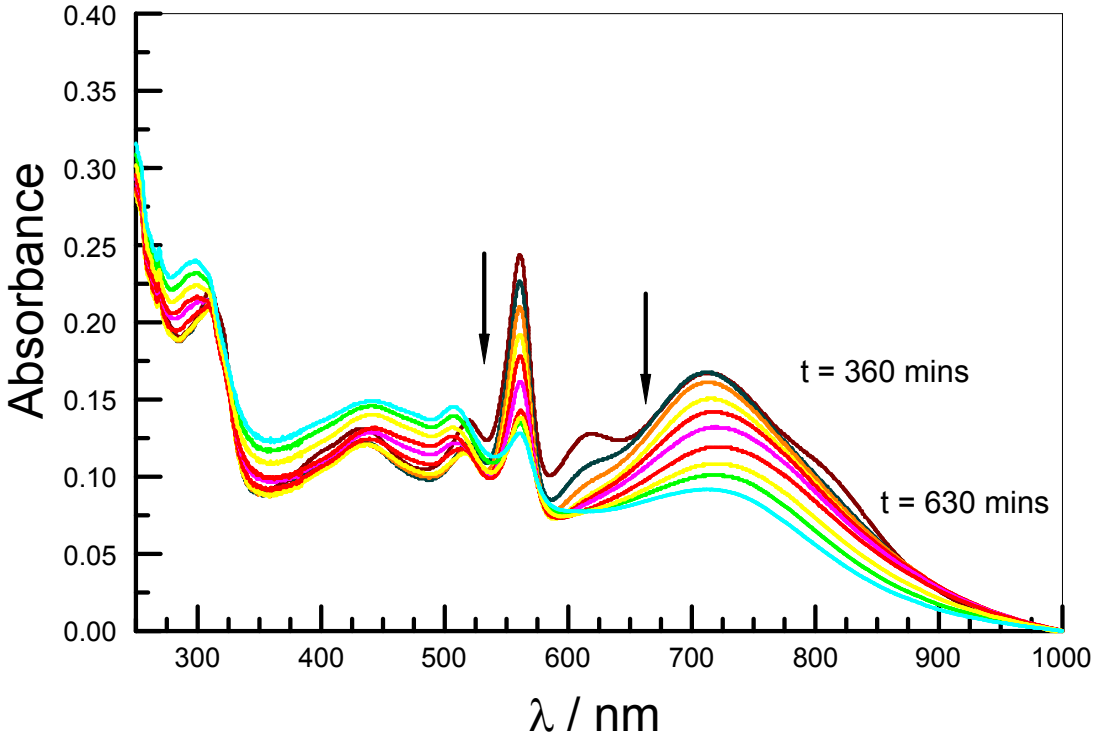

Figure S6. Absorption spectra recorded during the later stages of photolysis of **1** in deoxygenated CH_2Cl_2, spectra being recorded at 30 minute intervals. Note the series of isosbestic points.

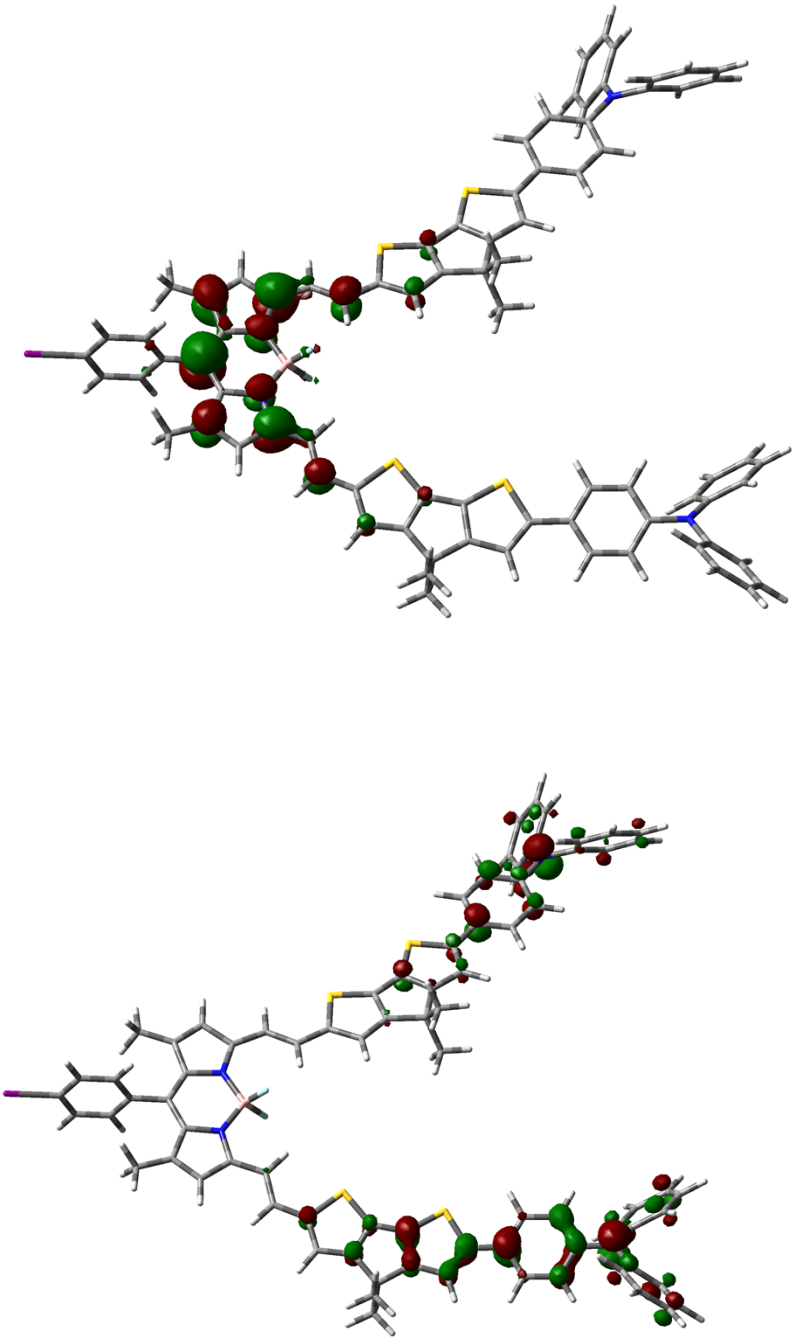

Figure S7. Kohn-Sham molecular orbital representations for **A1** at an isodensity of 0.015 shown for the LUMO (top) and the HOMO (lower).

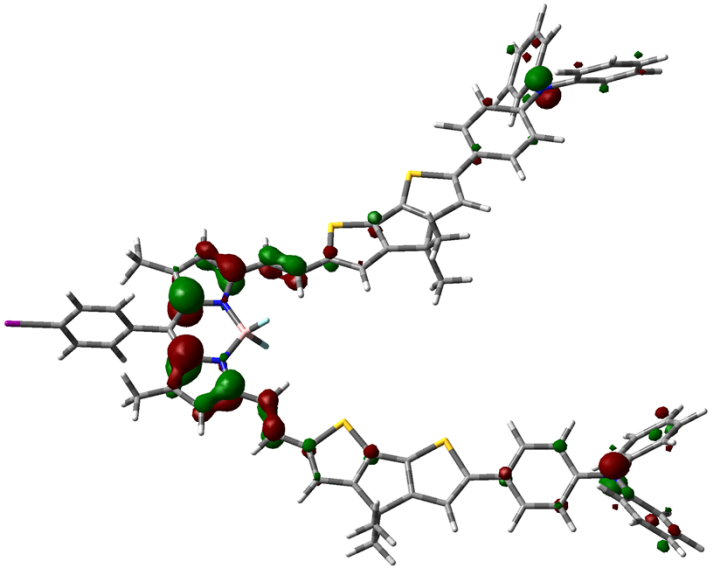

Figure S8. Kohn-Sham molecular orbital representation for **A1** at an isodensity of 0.015 shown for the HOMO(-2).

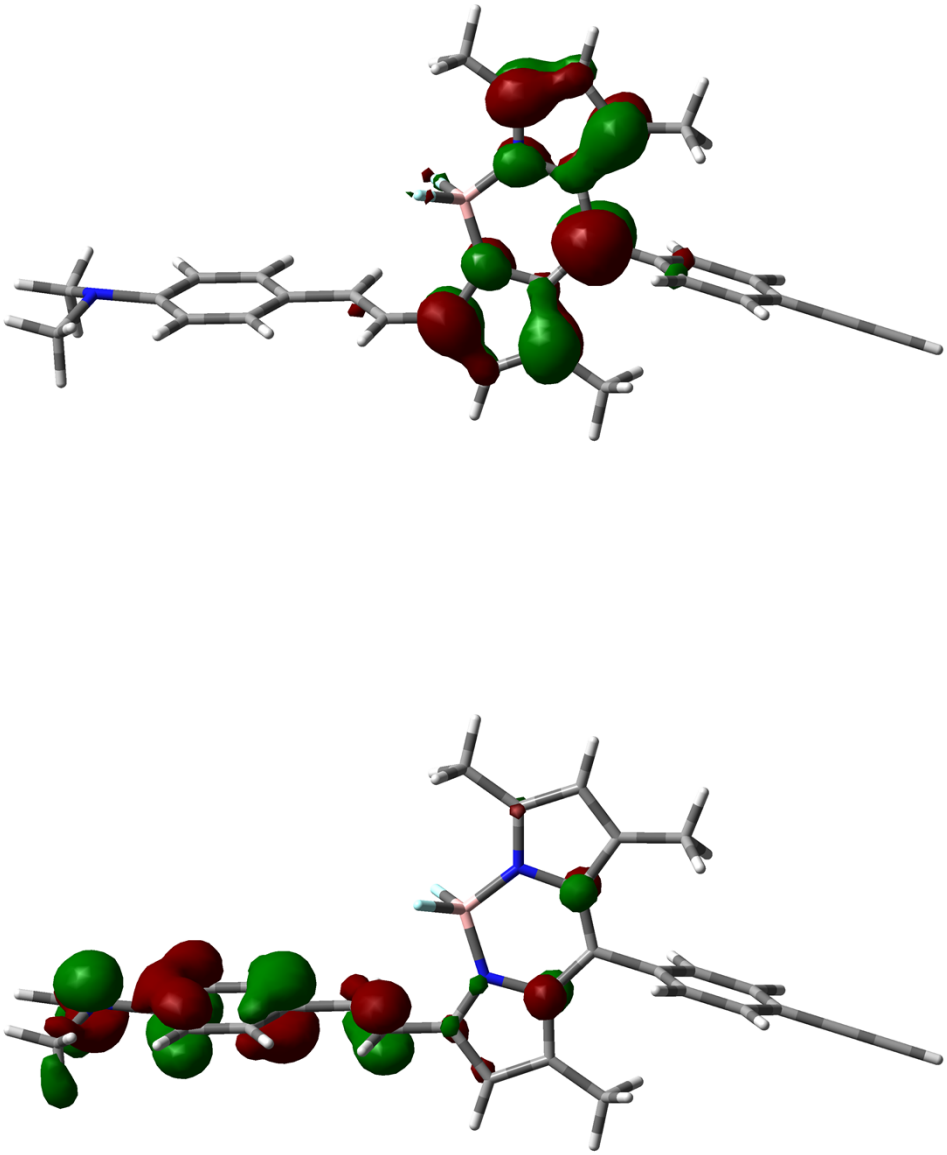

Figure S9. Kohn-Sham molecular orbital representation for **D1** at an isodensity of 0.015 shown for the LUMO (upper) and the HOMO (lower).

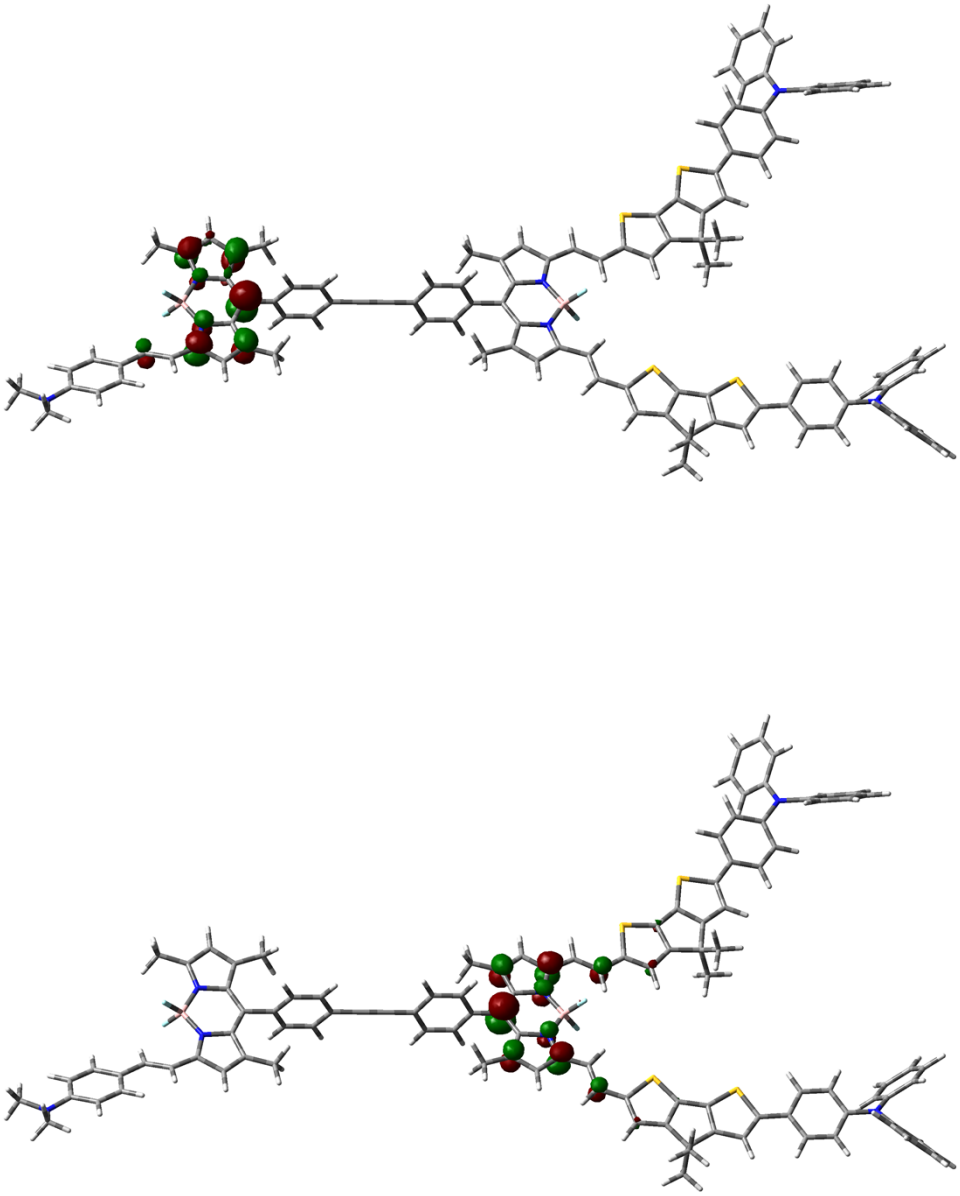

Figure S10. Kohn-Sham molecular orbital representation for **1** at an isodensity of 0.015 shown for the LUMO (lower) and the LUMO(1) (upper).

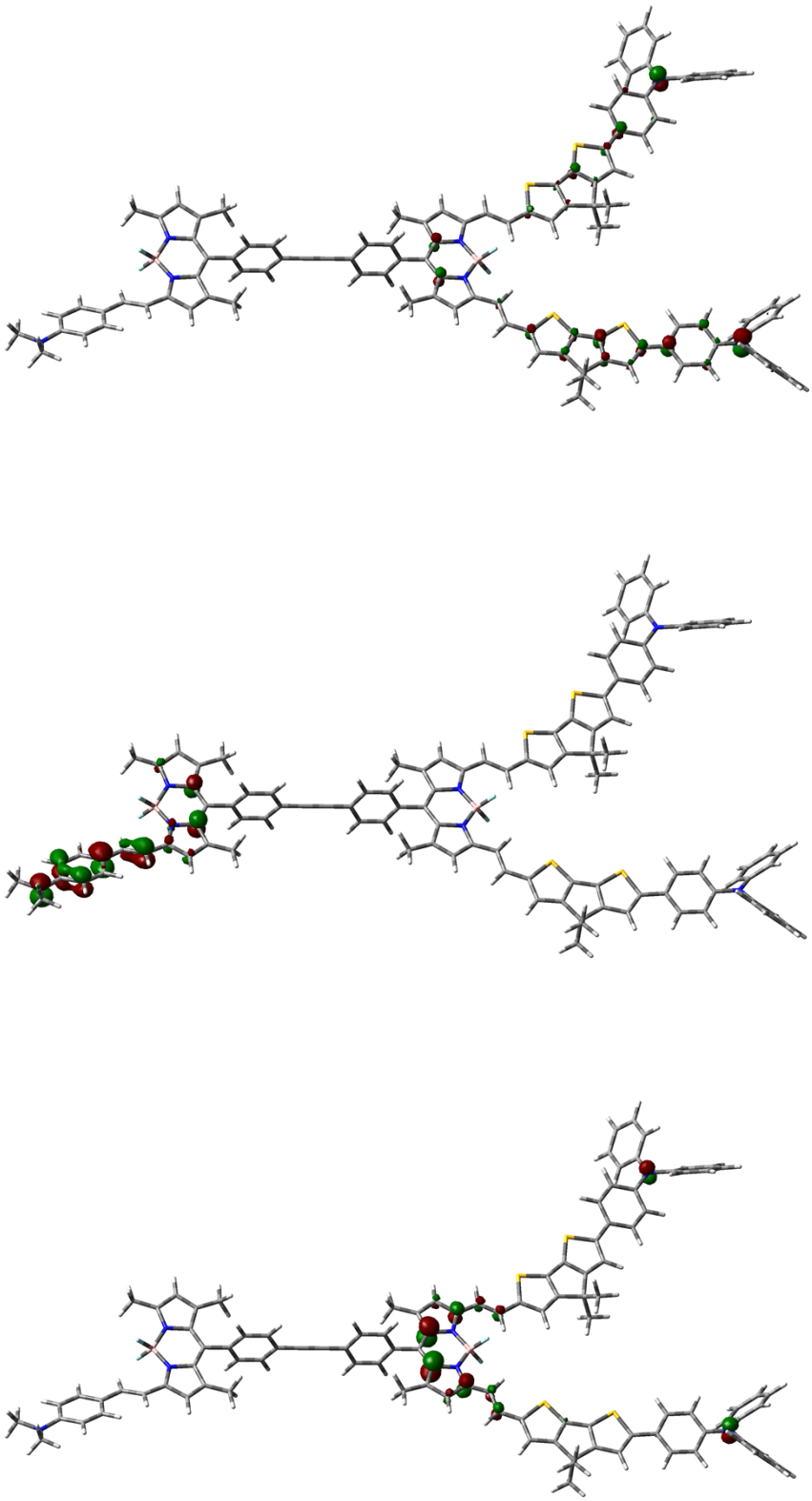

Figure S11. Kohn-Sham molecular orbital representation for **1** at an isodensity of 0.015 shown for the HOMO (upper), the HOMO(-1) (centre) and the HOMO(-2) (lower).