Electronic Supplementary Information for *PCCP*

The relationship of boron dipyrromethene (BODIPY) structure to the effectiveness of homogeneous and heterogeneous solar hydrogen-generating systems as well as DSSCs

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Electronic Supplementary Information (ESI):

[Table S1-S4; Scheme S1-S3; Fig. S1-S11; Additional calculations]

(1) Table S1-Table S4

Table S1 Crystallographic data for **B1**, **B3** and **B9**

BODIPY	**B1**	**B3**	**B9**
formula	$C_{20}H_{19}BF_2N_2O_2$	$C_{20}H_{17}BF_2I_2N_2O_2$	$C_{21}H_{19}BF_2I_2N_2O_2$
formula weight	368.18	619.97	633.99
crystal system	triclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*-1
a (Å)	8.3643(17)	7.7470(19)	10.0744(9)
b (Å)	9.794(3)	10.414(3)	10.4080(10)
c (Å)	11.596(2)	14.007(3)	11.8050(11)
α (deg)	79.79(3)	91.746(4)	69.844(2)
β (deg)	71.08(3)	105.965(4)	85.884(2)
γ (deg)	87.20(3)	91.149(5)	68.191(2)
Z, D_{calcd}(g m^{-3})	2, 1.383	2, 1.897	2, 1.956
V ($Å^3$)	884.3(3)	1085.6(5)	1076.58(17)
μ (mm^{-1})	0.10	2.93	2.96
F (000)	384	592	608
T (K)	173(2)	173(2)	100(2)
no. of reflns collected	7041	5398	24030
no. of unique reflns.	3106 (R_{int} = 0.053)	3713 (R_{int} = 0.032)	9766 (R_{int} = 0.046)
no. of observed reflns	1832	3291	8491
parameters	245	262	276
R indices	R_1 = 0.0652,	R_1 = 0.0552,	R_1 = 0.0225,
[I > 2σ(I)][a,b]	wR_2 = 0.1890	wR_2 = 0.1495	wR_2 = 0.0513
R indices	R_1 = 0.1126,	R_1 = 0.0613,	R_1 = 0.0276,
all data	wR_2 = 0.2612	wR_2 = 0.1557	wR_2 = 0.0533
GOF	1.195	1.073	1.033
Max., min electron Density (e $Å^{-3}$)	0.49, -0.46	1.25, -0.84	1.003, -0.835

[a] $R_1 = \Sigma| |F_o|-|F_c| | / \Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$

Table S2 Crystallographic data for **B2**, **B3** and **B5**

Compound	**B2**	**B3**	**B5**
ΔG_1(eV)[a]	0.18	0.27	0.24
ΔG_2(eV)[b]	-0.60	-0.47	-0.48

a) In deoxygenated acetonitrile. b) $\Delta G_1 = E(\mathbf{PS}^{+\cdot}/\mathbf{PS}) - E(Co^{III}/Co^{II}) - E(^3\mathbf{PS}^*)$, $E(^{3*}\mathbf{PS}) = 1.51$ eV (obtained from TDDFT calculations in acetonitrile. c) $\Delta G_2 = E(\mathbf{PS}^{-\cdot}/\mathbf{PS}) - E(Co^{III}/Co^{II})$.

Table S3 Photovoltaic parameters of BODIPY-sensitized solar cells[a,b]

dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)	dye loading density (mol/cm^2)
B1	0.71	0.487	0.4	0.14	1.53×10^{-10}
B2	0.28	0.415	0.39	0.046	0.42×10^{-10}
B3	0.22	0.283	0.3	0.019	0.21×10^{-10}
B4	0.22	0.400	0.45	0.04	0.28×10^{-10}
B5	0.19	0.186	0.23	0.008	0.10×10^{-10}

[a] Open-circuit potential (V_{oc}), short-circuit current (J_{sc}), fill factor (*FF*), and overall efficiency (η).

[b] The dye loading was carried out in methanol for 1h for cell fabrication.

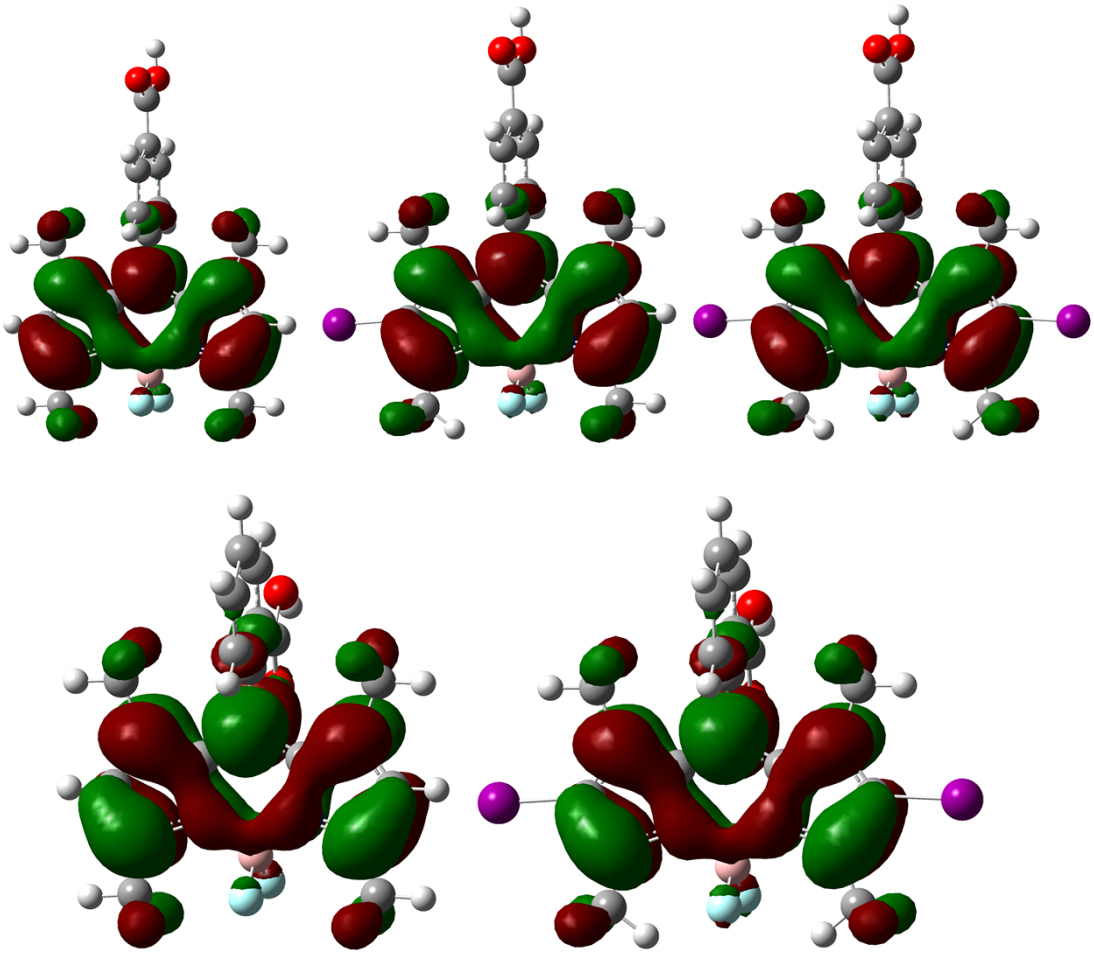
Table S4 The HOMO and LUMO energy levels for **B3**, **B3**$^{\cdot+}$ and **B3**$^{\cdot-}$

	B3 (eV)	**B3**$^{\cdot+}$ (eV)		**B3**$^{\cdot-}$ (eV)	
		α electron	β electron	α electron	β electron
HOMO	-3.03	-3.81	-5.44	-1.69	-2.17
LUMO	-2.07	-2.29	-3.57	-0.57	-1.45
Energy gap[a]	0.96	1.52	1.87	1.12	0.72

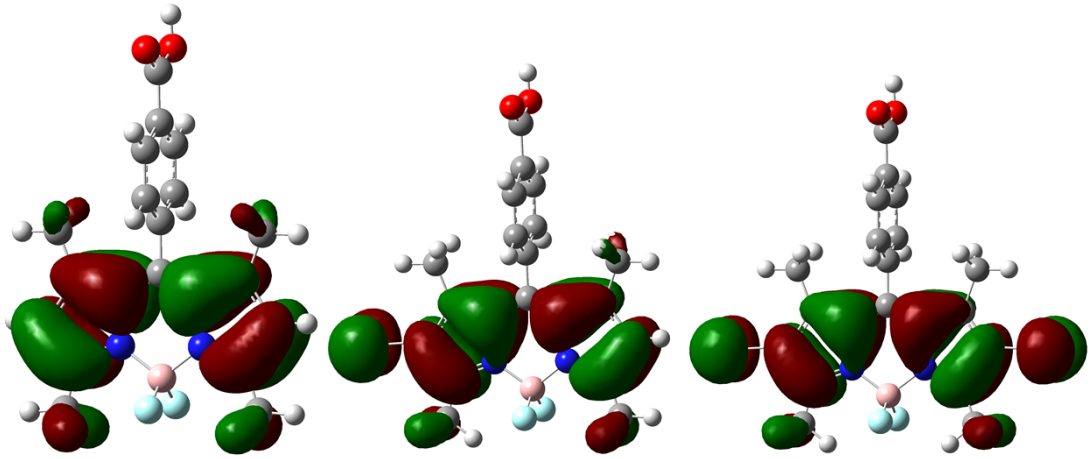
[a]Energy gap is the difference between LUMO and HOMO energy levels.

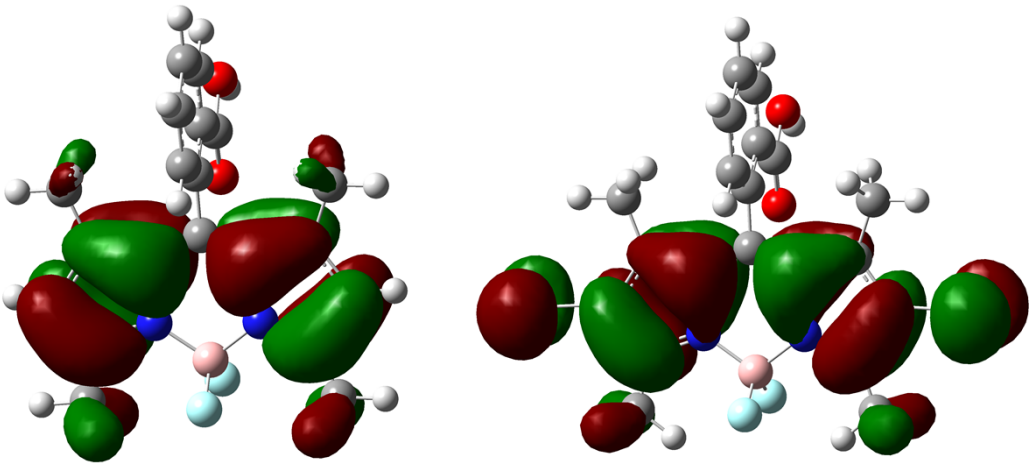
(2) Scheme S1-Scheme S3

(a) LUMOs of B1-B5

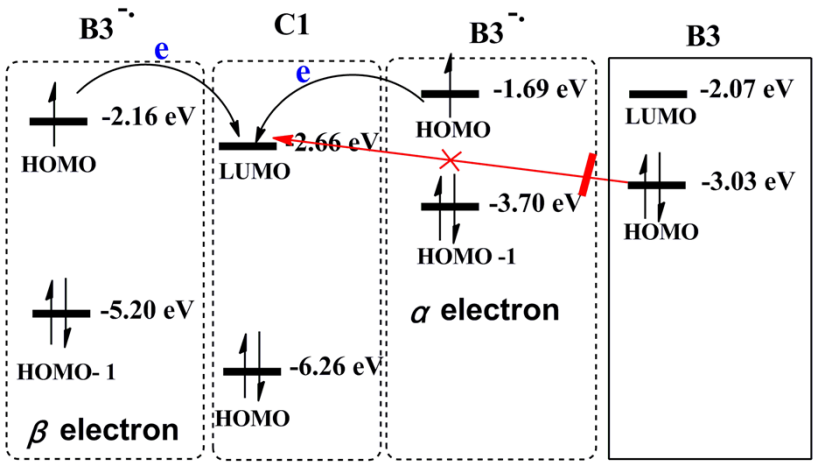


(b) HOMOs of B1-B5

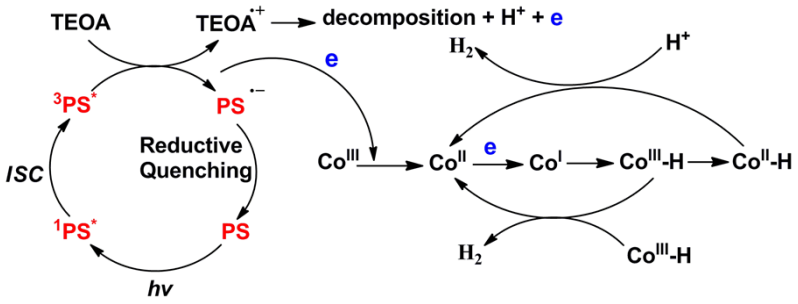




Scheme S1 LUMO (a) and HOMO (b) orbitals of **B1**-**B5** determined by DFT.



Scheme S2 Qualitative energy diagram for an electron transfer from HOMO of anion dye to the LUMO of caboloxime.



Scheme S3 Proposed reductive quenching mechanism of homogeneous photogeneration of H_2.

(3) Fig. S1-Fig. S11

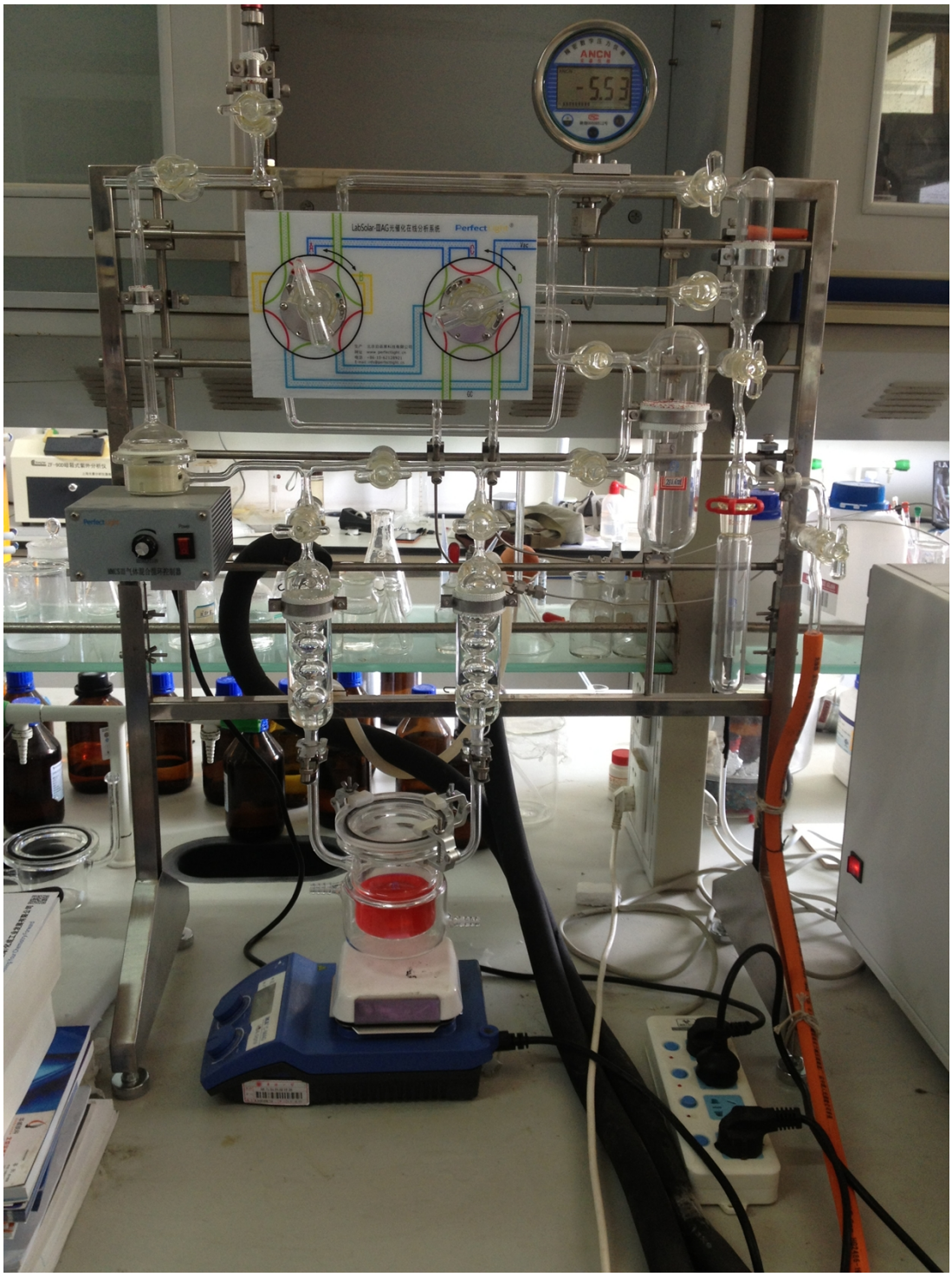


Fig. S1 Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system.

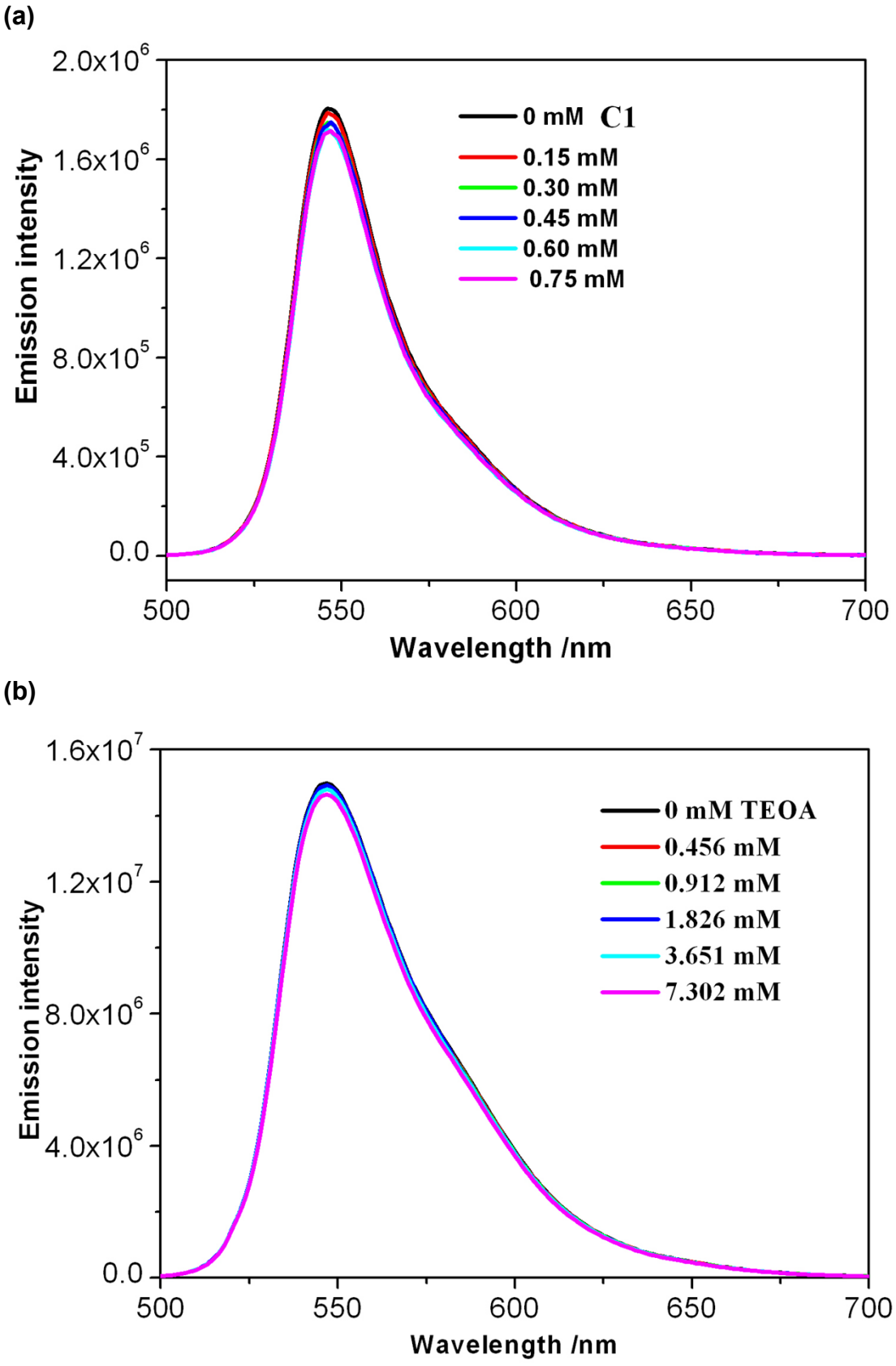
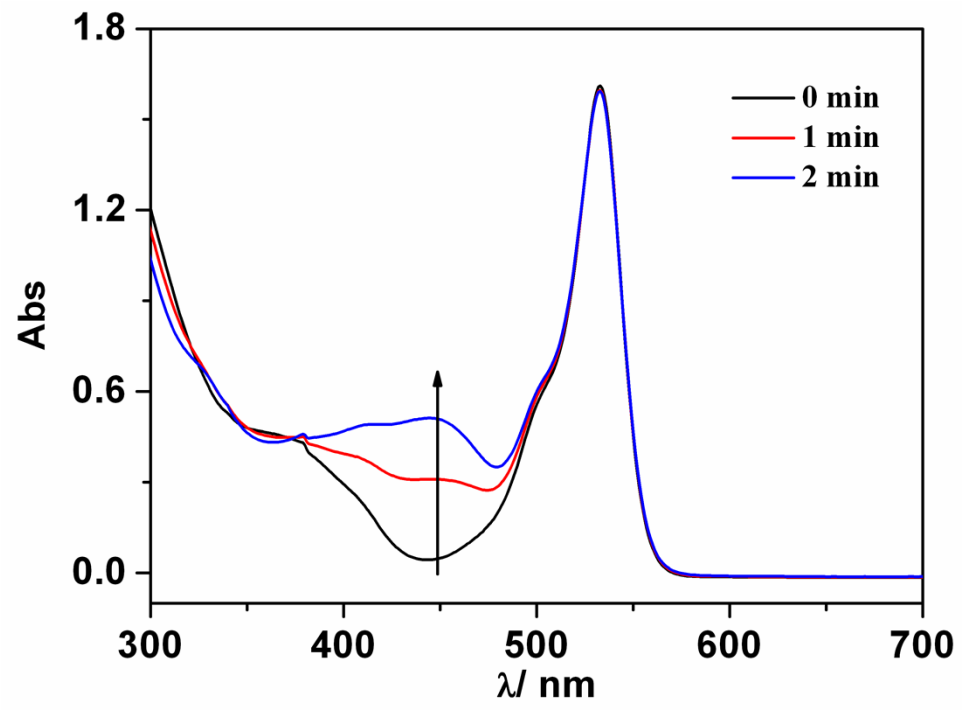


Fig. S2 Emission spectra of systems containing (a) **B3** + **C1**; and (b) **B3** + **C1** + TEOA.

(a)



(b)

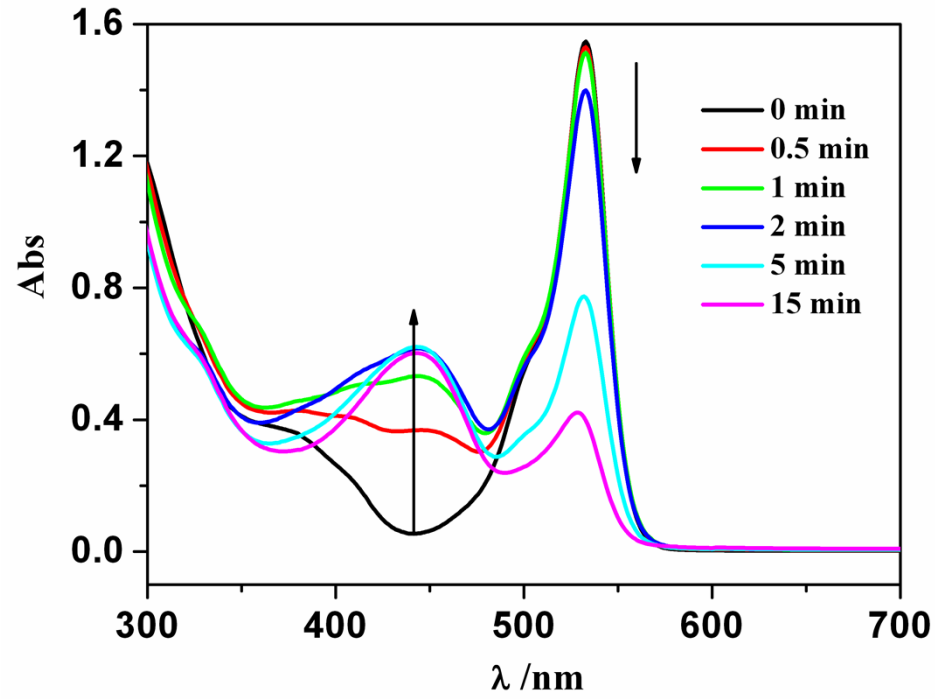


Fig. S3 UV-Vis spectra at pH 8.5 and pH 12 before and after visible light irradiation of degassed solutions (3:2 acetonitrile-water) containing **B3** (1.0 × 10-4 M), **C1** (2.5 × 10-4 M) and TEOA (5%, v/v).

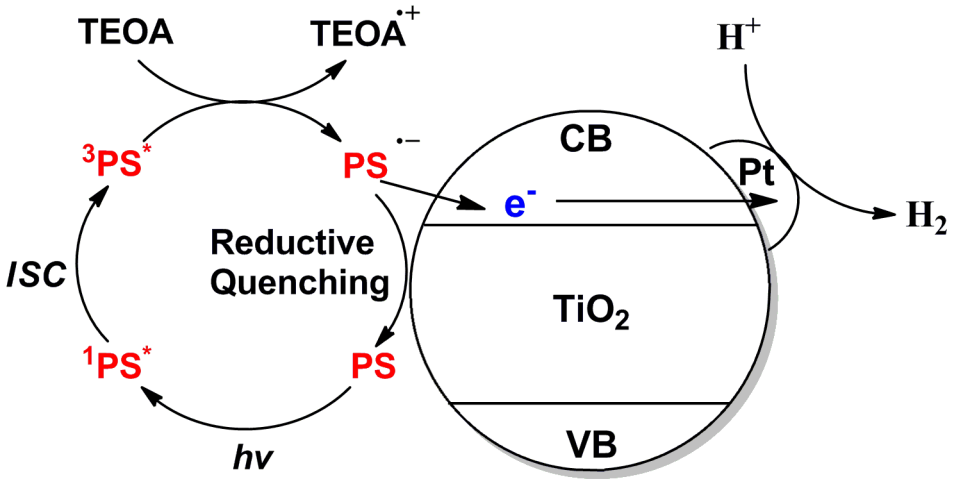


Fig. S4 Illustration of visible light induced H_2 production on a BODIPY-sensitized Pt/TiO_2 catalyst.

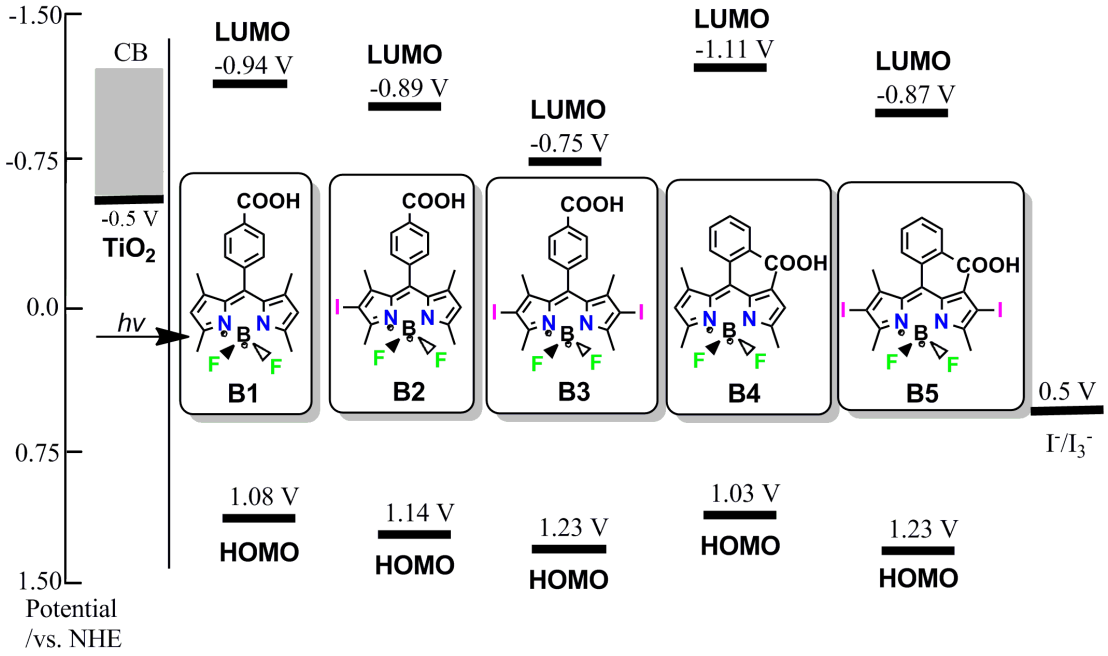


Fig. S5 Schematic energy diagrams for DSSCs based on BODIPY dyes, a nanocrystalline TiO_2 electrode, and I^-/I_3^- redox couple. The oxidation potential (E_{ox}) and E_{ox}-$E_{0\text{-}0}$ for BODIPYs are used as energy levels for the HOMO and LUMO, respectively.

Comments: In a conventional DSSC, the dye is excited by the absorbing photon and then forms oxidized dye after injection of the electron into the

conducting band (CB) of TiO_2. Then the oxidized dye accepts electron from iodine/iodide to be regenerated. Fig. S5 compares the HOMO-LUMO energy levels of the BODIPY dyes (**B1**-**B5**). The HOMO and LUMO levels of these organic dyes correspond to the oxidation potentials of the dyes and their E_{ox} – $E_{0\text{-}0}$ levels, respectively. $E_{0\text{-}0}$ energy levels were estimated from the absorption threshold of these dyes adsorbed onto TiO_2 films. All BODIPY dyes have higher LUMO energy levels than that of the base level of the CB of TiO_2 (-0.5 V vs NHE) and lower HOMO energy levels than that of the most commonly employed I^-/I_3^- redox couple (0.5 V vs NHE); these findings as well as dyes having the ability to bind to TiO_2 through their carboxylic groups, respectively reveal that both electron injection into TiO_2 from the dye's excited states and dye reduction by the I^-/I_3^-/ couple are exothermic, making DSSC operation feasible.

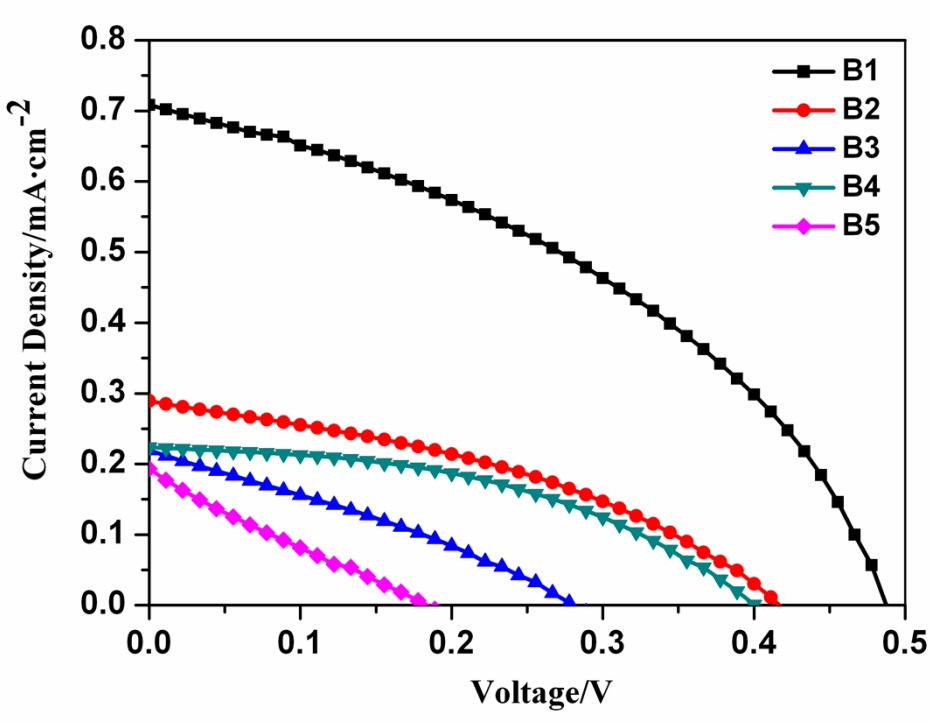


Fig. S6 The *J-V* curves of BODIPY-sensitized solar cells.

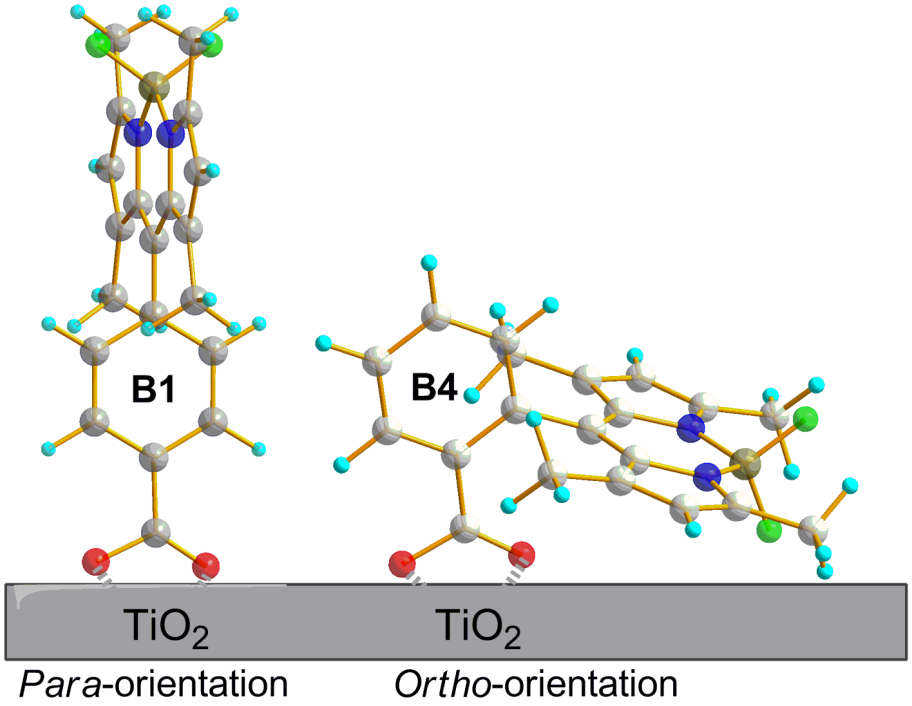


Fig. S7 Depiction of the possible orientations of BODIPYs with *para*-COOH and *ortho*-COOH anchoring groups to the TiO_2 semiconductor surface.

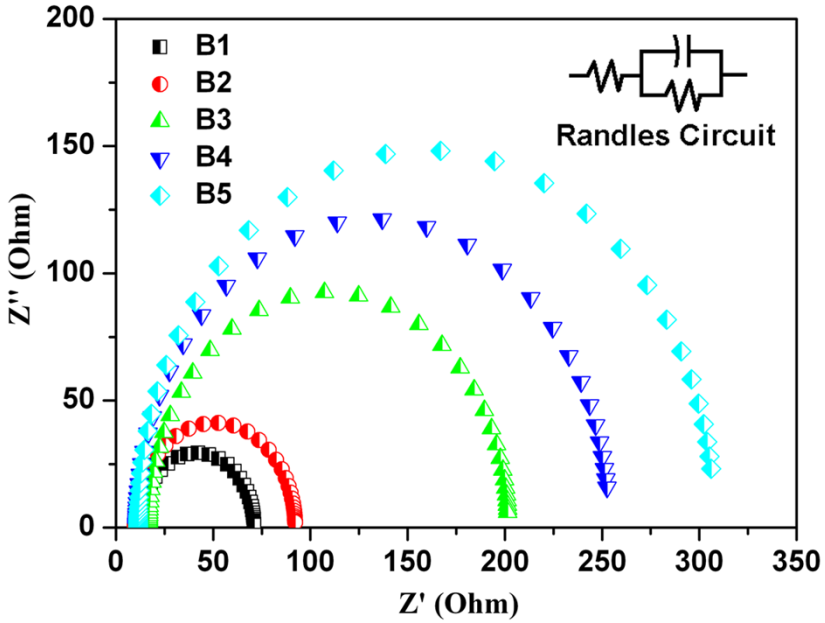


Fig. S8 Nyquist plots of the EIS of DSSCs that were sensitized by BODIPY dyes under bias of -0.5 V. Inset is the equivalent Randle's circuit impedance model used for data fitting.

Comments: Fig. S8 shows the typical Nyquist plots at an applied voltage of -0.5 V. The simplified Randle's model was used to fit the data. The observed trend in $R_{ct}(TiO_2)$ for a given series was **B1** < **B2** < **B3**, and **B4** < **B5**, respectively, indicating that the substitution of iodine atoms indeed raised the recombination resistance. The radii of the semicircles lie in the order **B4** > **B1**, indicating the sequence of the charge transfer resistance at the interface when the orientation of carboxyl group varies from *ortho*- to *para*-position. These results support the overall lower efficiency of the *ortho*-COOH and iodinated dyes compared with either *para*-COOH or noniodinated BODIPYs.

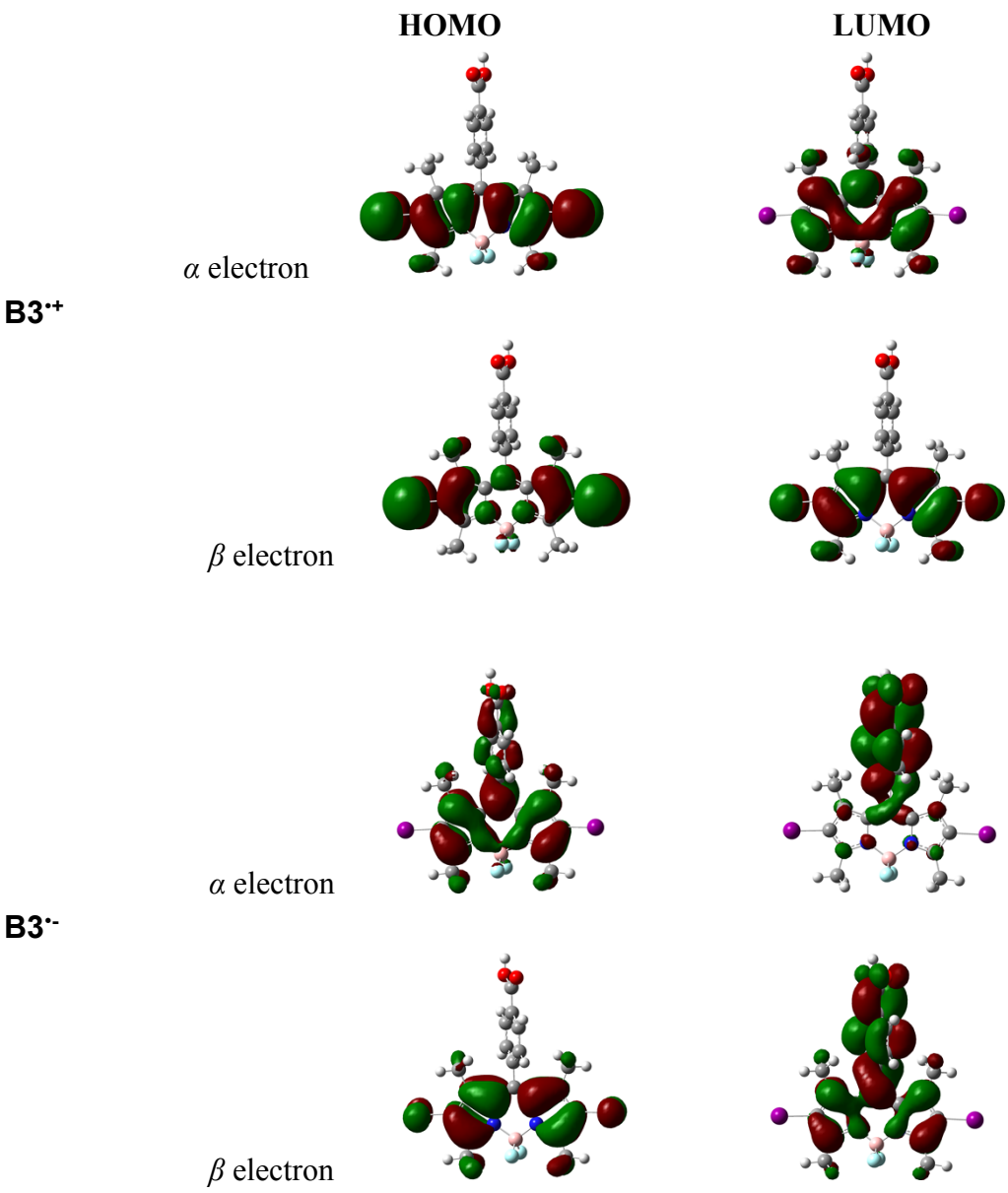
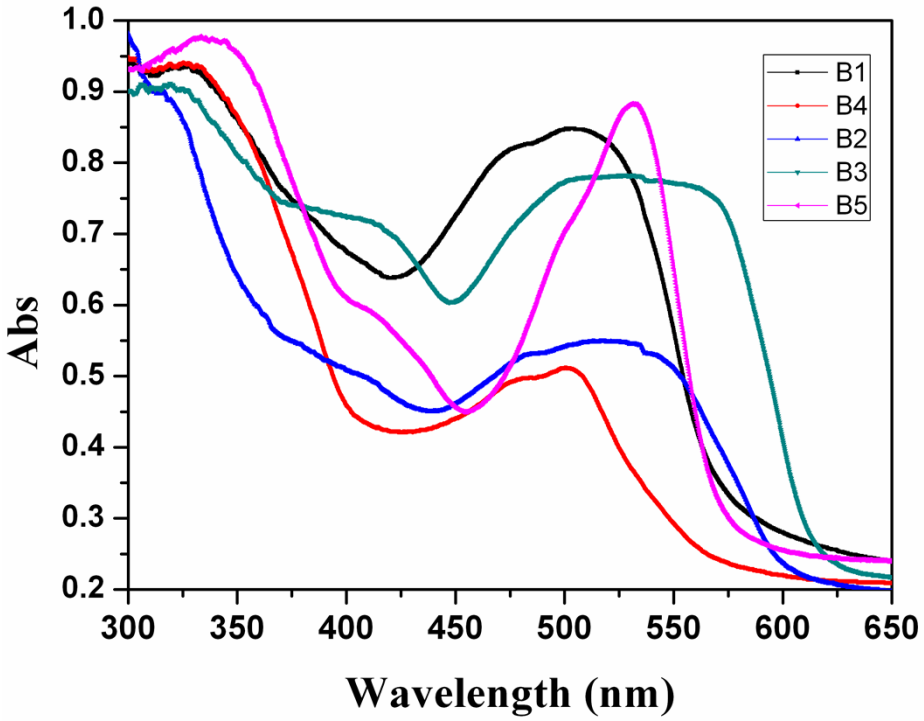


Fig. S9 Frontier molecular molecular orbitals of **B3**$^{\bullet+}$ and **B3**$^{\bullet-}$ obtained through DFT calculations. Since the cation and anion dye have unpaired electrons, the alpha/beta molecular orbitals were all defined due to the positive and negative charge the open-shell system adopted.

(a)



(b)

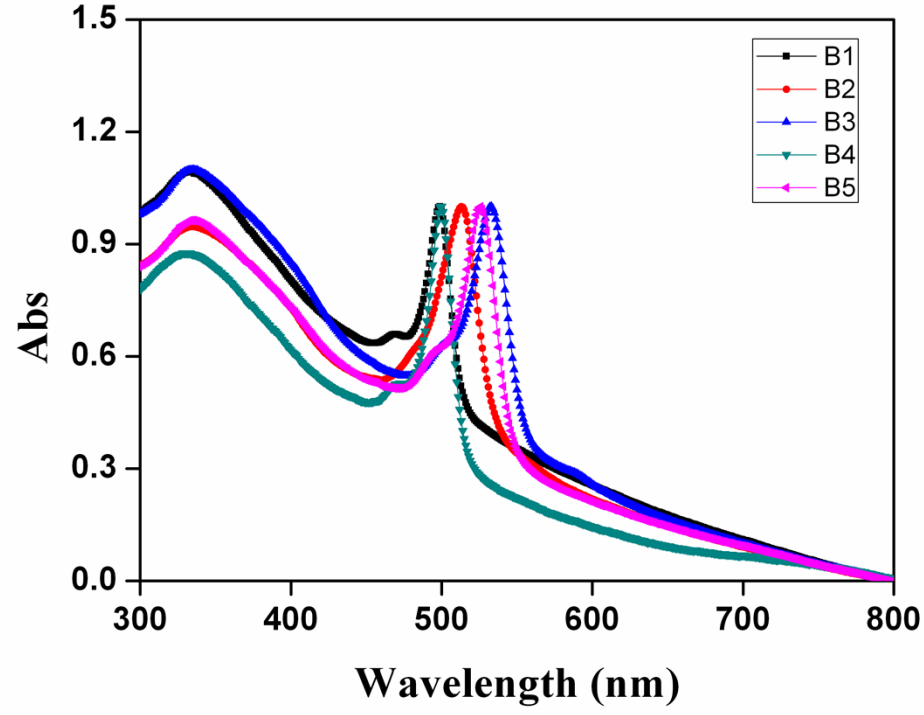
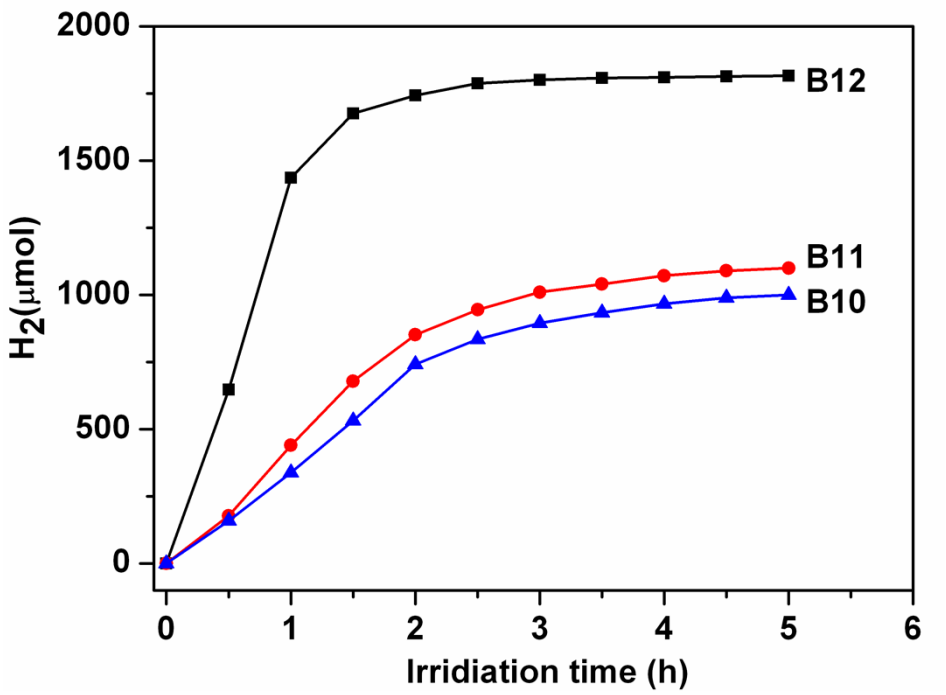
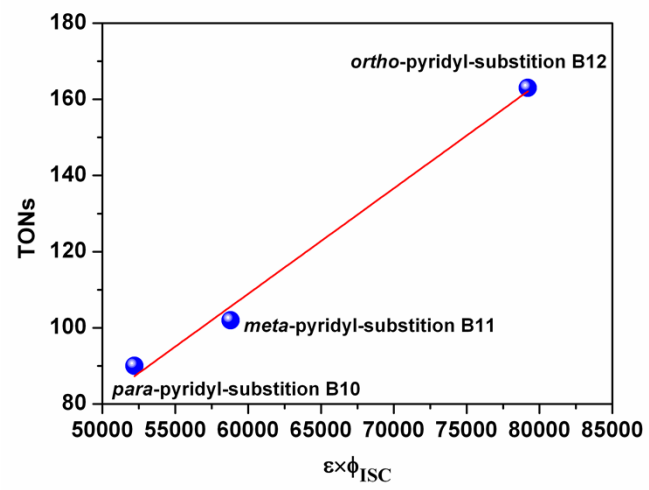


Fig. S10 Absorption spectra of the BODIPYs **Bn** (n = 1-5), bound to a TiO_2 film in methanol (a) and bound to colloidal TiO_2 particles in methanol (b).

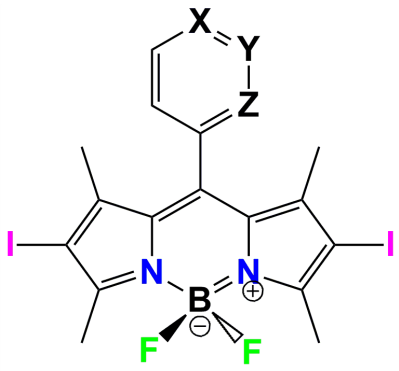
(a)



(b)



(c)

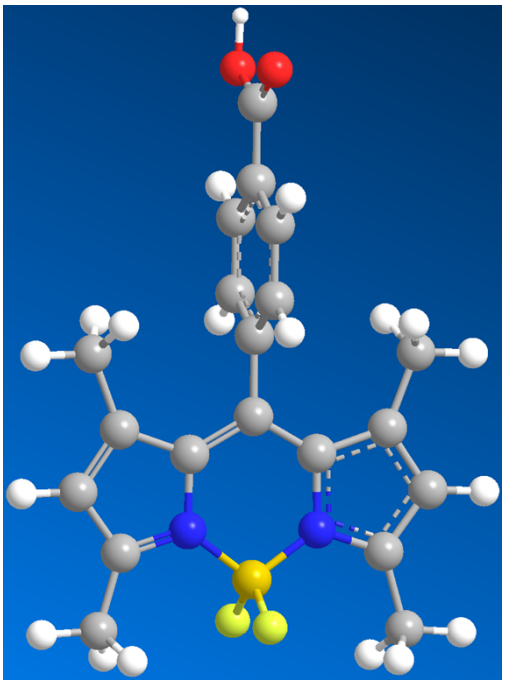


B10: X = N, Y = Z = CH
B11: X = Z = CH, Y = N
B12: X = Y = CH, Z = N

Fig. S11 (a) Hydrogen production *vs*. pyridyl-substition BODIPYs **B10-B12** obtained in the photocatalytic reaction with continuous irradiation (λ > 420 nm), containing a BODIPY sensitizer (1.0×10^{-4} M), **C1** (2.5×10^{-4} M) and TEOA (5%, v/v). (b) Linear relationship (r = 0.99) of $\varepsilon \times \Phi_{ISC}$ *versus* TONs of H_2 production for iodinated BODIPYs (**B10**, **B11** and **B12**). (c) The structures of **B10-B12**.

(4) Additional calculations

B1:



DFT B3LYP/6-31+G(d) optimized structure of B1

Optimized Geometry：

Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.596416	0.000051	0.083331
2	6	0	4.110664	0.000057	0.029701
3	6	0	3.397674	0.000212	1.237961
4	1	0	3.940855	0.000325	2.177347
5	6	0	2.005055	0.000223	1.230747
6	1	0	1.459470	0.000341	2.170131
7	6	0	1.303074	0.000085	0.015853
8	6	0	2.017177	-0.000104	-1.191042
9	1	0	1.481003	-0.000242	-2.135833
10	6	0	3.411224	-0.000108	-1.187073
11	1	0	3.953004	-0.000242	-2.126341
12	6	0	-0.192781	0.000056	0.008046
13	6	0	-0.882281	-1.224291	0.004462
14	6	0	-0.421028	-2.583121	0.007524
15	6	0	0.979884	-3.121965	0.015803
16	1	0	0.951050	-4.215947	0.015714
17	1	0	1.540667	-2.798610	0.899251

18	1	0	1.551225	-2.798696	-0.860883
19	6	0	-1.565889	-3.376532	0.001349
20	1	0	-1.595214	-4.459127	0.001624
21	6	0	-2.697123	-2.537563	-0.005294
22	6	0	-4.132595	-2.953480	-0.013034
23	1	0	-4.662309	-2.570402	0.866390
24	1	0	-4.202564	-4.044244	-0.014230
25	1	0	-4.653314	-2.568968	-0.897181
26	6	0	-2.697386	2.537426	-0.005373
27	6	0	-4.132904	2.953181	-0.013094
28	1	0	-4.653721	2.568224	-0.896987
29	1	0	-4.202996	4.043936	-0.014744
30	1	0	-4.662436	2.570428	0.866585
31	6	0	-1.566247	3.376520	0.001182
32	1	0	-1.595695	4.459112	0.001350
33	6	0	-0.421297	2.583240	0.007476
34	6	0	0.979541	3.122275	0.015758
35	1	0	0.950555	4.216254	0.015292
36	1	0	1.551052	2.798784	-0.860731
37	1	0	1.540242	2.799308	0.899401
38	6	0	-0.882395	1.224348	0.004429
39	7	0	-2.287295	1.247306	-0.003405
40	7	0	-2.287174	-1.247397	-0.003395
41	9	0	-4.020122	-0.000141	-1.163175
42	9	0	-4.036325	-0.000122	1.131801
43	5	0	-3.199079	-0.000091	-0.009756
44	8	0	6.175138	-0.000088	-1.138344
45	1	0	7.143326	-0.000104	-1.012579
46	8	0	6.254588	0.000121	1.112456

Excitation Energies and Oscillator Strengths：

HOMO = 96

LUMO = 97

Excited State 1: Triplet-A 1.5200 eV 815.70 nm f=0.0000 <S**2>=2.000

96 -> 97 0.71015

96 <- 97 0.11701

Excited State 2: Triplet-A 2.7292 eV 454.29 nm f=0.0000 <S**2>=2.000

95 -> 97 0.69147

Excited State 3: Singlet-A 2.8695 eV 432.07 nm f=0.5806 <S**2>=0.000

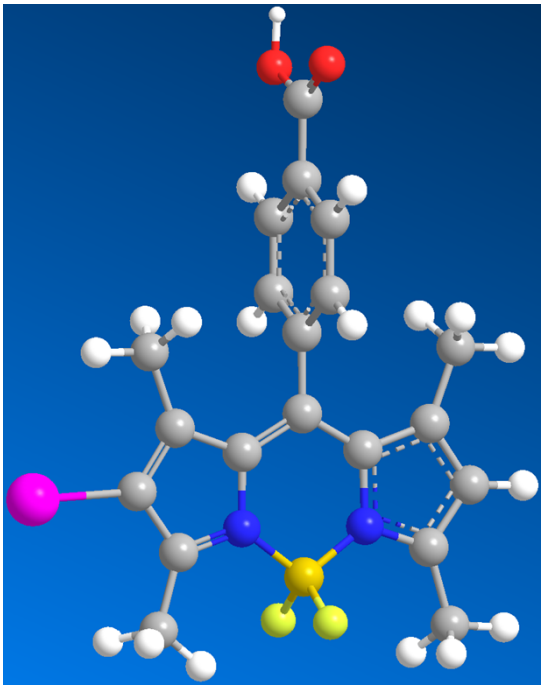
95 -> 97 0.12773

96 -> 97 0.69844

```
        96 <- 97       -0.10459
 Excited State   4:      Triplet-A      2.9265 eV  423.66 nm  f=0.0000
<S**2>=2.000
        91 -> 97       -0.11049
        94 -> 97        0.68364
 Excited State   5:      Triplet-A      3.2469 eV  381.85 nm  f=0.0000
<S**2>=2.000
        96 -> 98        0.70482
 Excited State   6:      Singlet-A      3.2652 eV  379.71 nm  f=0.0000
<S**2>=0.000
        96 -> 98        0.70550
 Excited State   7:      Triplet-A      3.3975 eV  364.93 nm  f=0.0000
<S**2>=2.000
        92 -> 98       -0.26300
        92 -> 99       -0.25916
        93 -> 98        0.56643
        93 -> 99       -0.13075
 Excited State   8:      Singlet-A      3.4032 eV  364.32 nm  f=0.0711
<S**2>=0.000
        95 -> 97        0.69338
        96 -> 97       -0.13059
 Excited State   9:      Triplet-A      3.4687 eV  357.44 nm  f=0.0000
<S**2>=2.000
        90 -> 97       -0.11939
        91 -> 97        0.66869
        94 -> 97        0.11848
 Excited State  10:      Singlet-A      3.6661 eV  338.19 nm  f=0.0483
<S**2>=0.000
        94 -> 97        0.70387
 Excited State  11:      Triplet-A      3.9078 eV  317.27 nm  f=0.0000
<S**2>=2.000
        92 -> 97       -0.24535
        93 -> 97        0.65964
 Excited State  12:      Singlet-A      3.9323 eV  315.30 nm  f=0.0000
<S**2>=0.000
        92 -> 97       -0.24833
        93 -> 97        0.65953
 Excited State  13:      Triplet-A      3.9795 eV  311.56 nm  f=0.0000
<S**2>=2.000
        92 -> 98        0.58121
        93 -> 98        0.27614
        95 -> 98       -0.26170
 Excited State  14:      Triplet-A      4.0082 eV  309.33 nm  f=0.0000
<S**2>=2.000
```

92 -> 97 0.65947
93 -> 97 0.24495
Excited State 15: Singlet-A 4.0369 eV 307.13 nm f=0.0023
<S**2>=0.000
92 -> 97 0.66095
93 -> 97 0.24912
Excited State 16: Triplet-A 4.2404 eV 292.39 nm f=0.0000
<S**2>=2.000
96 -> 99 0.64871
96 ->104 0.23089
Excited State 17: Singlet-A 4.3275 eV 286.50 nm f=0.0093
<S**2>=0.000
96 -> 99 0.70142
Excited State 18: Singlet-A 4.3735 eV 283.49 nm f=0.0014
<S**2>=0.000
95 -> 98 0.70292
Excited State 19: Singlet-A 4.6113 eV 268.87 nm f=0.0000
<S**2>=0.000
94 -> 98 0.70509
Excited State 20: Singlet-A 4.6816 eV 264.83 nm f=0.0247
<S**2>=0.000
92 -> 98 0.57484
92 -> 99 -0.12187
93 -> 98 0.29980
93 -> 99 0.24217

B2:



DFT B3LYP/6-31+G(d) optimized structure of B2

Optimized Geometry：

Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.520950	-2.537988	0.081895
2	6	0	-4.311731	-1.673661	0.029664
3	6	0	-3.739895	-1.248416	1.238512
4	6	0	-2.607586	-0.437255	1.231505
5	6	0	-2.029746	-0.039449	0.016345
6	6	0	-2.602039	-0.464980	-1.191142
7	6	0	-3.735688	-1.276562	-1.187343
8	6	0	-0.818690	0.838251	0.008393
9	6	0	-0.985407	2.231168	0.004921
10	6	0	-2.162216	3.056202	0.006630
11	6	0	-3.611199	2.665413	0.013251
12	6	0	-1.707582	4.371721	0.000698
13	6	0	-0.298188	4.363858	-0.004952
14	6	0	0.614860	5.546784	-0.012453
15	6	0	2.705156	0.280800	-0.008014
16	6	0	4.108301	0.790659	-0.017380
17	6	0	2.279691	-1.063761	0.000921
18	53	0	3.617544	-2.701155	0.002608
19	6	0	0.886953	-1.112778	0.008738
20	6	0	0.045900	-2.353017	0.019774
21	6	0	0.464652	0.256727	0.004063
22	7	0	1.608528	1.069016	-0.005733
23	7	0	0.133202	3.081402	-0.002577
24	9	0	2.261675	3.101417	-1.166954
25	9	0	2.278865	3.110147	1.129980
26	5	0	1.603981	2.618950	-0.011546
27	8	0	-5.981490	-2.885936	-1.140029
28	8	0	-6.064446	-2.911243	1.110607
29	1	0	-4.187743	-1.556407	2.177651
30	1	0	-2.169878	-0.110549	2.170512
31	1	0	-2.160202	-0.159558	-2.135369
32	1	0	-4.171040	-1.599569	-2.126392
33	1	0	-4.232624	3.566166	0.001490
34	1	0	-3.876355	2.083195	0.902233
35	1	0	-3.878301	2.058208	-0.858150
36	1	0	-2.323794	5.262104	0.000164
37	1	0	1.269124	5.548349	0.866620
38	1	0	0.028701	6.469266	-0.013126

39	1	0	1.262219	5.542691	-0.896621
40	1	0	4.149035	1.878868	-0.031932
41	1	0	4.645012	0.408821	-0.894478
42	1	0	4.648299	0.432702	0.867902
43	1	0	0.684763	-3.239647	0.036364
44	1	0	-0.595269	-2.418007	-0.865303
45	1	0	-0.608621	-2.393878	0.896201
46	1	0	-6.770143	-3.448171	-1.016099

Excitation Energies and Oscillator Strengths：

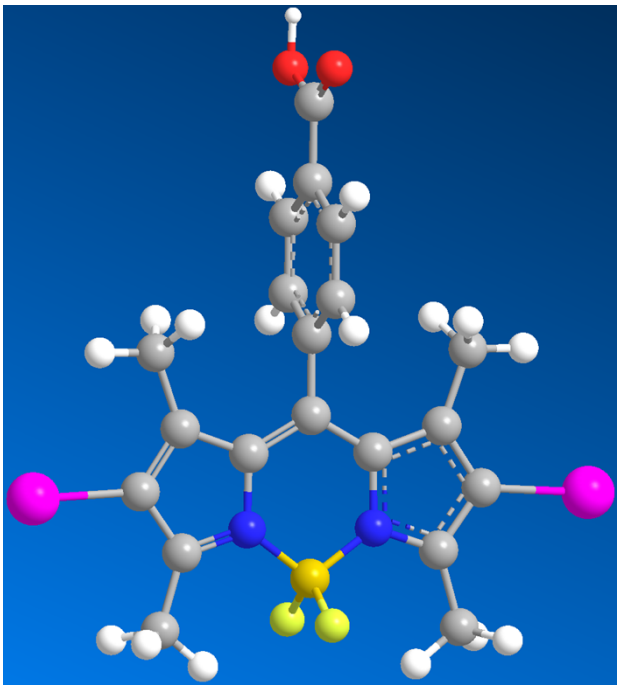
HOMO = 122
LUMO = 123
Excited State 1: Triplet-A 1.5230 eV 814.10 nm f=0.0000
<S**2>=2.000
121 ->123 -0.13632
122 ->123 0.70019
122 <-123 0.11016

Excited State 2: Triplet-A 2.5733 eV 481.80 nm f=0.0000
<S**2>=2.000
120 ->123 -0.16898
121 ->123 0.65528
122 ->123 0.13428
Excited State 3: Singlet-A 2.7581 eV 449.53 nm f=0.5371
<S**2>=0.000
121 ->123 0.20265
122 ->123 0.67764
Excited State 4: Triplet-A 2.8535 eV 434.51 nm f=0.0000
<S**2>=2.000
116 ->123 0.11107
120 ->123 0.66311
121 ->123 0.15733
Excited State 5: Singlet-A 3.2500 eV 381.48 nm f=0.2225
<S**2>=0.000
121 ->123 0.66944
122 ->123 -0.20964
Excited State 6: Triplet-A 3.2827 eV 377.69 nm f=0.0000
<S**2>=2.000
122 ->124 0.70349
Excited State 7: Singlet-A 3.3009 eV 375.60 nm f=0.0013
<S**2>=0.000
122 ->124 0.70354
Excited State 8: Triplet-A 3.3733 eV 367.54 nm f=0.0000
<S**2>=2.000

```
      114 ->123         0.23883
      116 ->123         0.58174
      117 ->124         0.15554
      118 ->124         0.15996
Excited State   9:      Triplet-A      3.3957 eV  365.12 nm  f=0.0000
<S**2>=2.000
      116 ->123        -0.23065
      117 ->124         0.39326
      117 ->125        -0.18809
      118 ->124         0.40546
      118 ->125         0.19254
      119 ->124        -0.14468
Excited State  10:      Singlet-A      3.5352 eV  350.71 nm  f=0.0477
<S**2>=0.000
      120 ->123         0.69963
Excited State  11:      Triplet-A      3.8263 eV  324.03 nm  f=0.0000
<S**2>=2.000
      117 ->123        -0.29949
      118 ->123        -0.34984
      119 ->123         0.53276
Excited State  12:      Singlet-A      3.8453 eV  322.43 nm  f=0.0001
<S**2>=0.000
      117 ->123        -0.27800
      118 ->123        -0.32815
      119 ->123         0.55931
Excited State  13:      Triplet-A      3.8915 eV  318.60 nm  f=0.0000
<S**2>=2.000
      117 ->123         0.30910
      118 ->123         0.42422
      119 ->123         0.45367
Excited State  14:      Singlet-A      3.9137 eV  316.80 nm  f=0.0001
<S**2>=0.000
      117 ->123         0.32667
      118 ->123         0.45346
      119 ->123         0.43033
Excited State  15:      Triplet-A      3.9255 eV  315.84 nm  f=0.0000
<S**2>=2.000
      121 ->126         0.35842
      122 ->126         0.58397
Excited State  16:      Triplet-A      3.9405 eV  314.64 nm  f=0.0000
<S**2>=2.000
      117 ->123         0.53846
      117 ->124        -0.11633
      118 ->123        -0.40376
```

118 ->124 0.10597
Excited State 17: Singlet-A 3.9690 eV 312.38 nm f=0.0030
<S**2>=0.000
117 ->123 0.55978
118 ->123 -0.42863
Excited State 18: Singlet-A 4.1613 eV 297.95 nm f=0.0003
<S**2>=0.000
121 ->124 0.70227
Excited State 19: Singlet-A 4.3015 eV 288.24 nm f=0.0001
<S**2>=0.000
121 ->126 0.12648
122 ->126 0.69165
Excited State 20: Singlet-A 4.3564 eV 284.60 nm f=0.0052
<S**2>=0.000
116 ->123 -0.16011
122 ->125 0.68577

B3:



DFT B3LYP/6-31+G(d) optimized structure of B3

Optimized Geometry：

Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000292	4.933829	-1.147224
2	6	0	-0.000561	3.974551	-2.162895
3	6	0	-0.000718	2.616290	-1.838693

4	6	0	-0.000041	2.190572	-0.504169
5	6	0	0.000815	3.161442	0.523525
6	6	0	0.000999	4.526104	0.185532
7	6	0	-0.000113	0.713508	-0.257349
8	6	0	-1.226085	0.027377	-0.190742
9	6	0	-2.579973	0.491813	-0.261636
10	6	0	-3.086078	1.890386	-0.444781
11	6	0	-3.364393	-0.651110	-0.120462
12	53	0	-5.475384	-0.763894	-0.126466
13	6	0	-2.532277	-1.779181	0.034079
14	6	0	-2.950397	-3.200984	0.212926
15	6	0	2.531759	-1.779426	0.034445
16	6	0	2.949703	-3.201216	0.213799
17	6	0	3.364012	-0.651527	-0.120651
18	53	0	5.474987	-0.764617	-0.126896
19	6	0	2.579736	0.491452	-0.262130
20	6	0	3.086025	1.889864	-0.446004
21	6	0	1.225786	0.027244	-0.190779
22	7	0	1.248153	-1.362824	-0.009676
23	7	0	-1.248612	-1.362745	-0.010103
24	9	0	-0.000544	-2.915496	1.375420
25	9	0	-0.000109	-3.243158	-0.899762
26	5	0	-0.000287	-2.266494	0.120792
27	6	0	0.001439	2.754557	1.956798
28	8	0	0.000046	1.603114	2.362093
29	8	0	0.003778	3.807250	2.805789
30	1	0	0.000407	5.992370	-1.389452
31	1	0	-0.001103	4.278338	-3.205817
32	1	0	-0.001346	1.871926	-2.629920
33	1	0	0.001651	5.266344	0.977052
34	1	0	-4.178391	1.892288	-0.478268
35	1	0	-2.720994	2.339009	-1.373898
36	1	0	-2.778522	2.547886	0.375118
37	1	0	-2.098493	-3.863837	0.357336
38	1	0	-3.514287	-3.544595	-0.663370
39	1	0	-3.617491	-3.293890	1.078255
40	1	0	2.097757	-3.863804	0.359177
41	1	0	3.617371	-3.293756	1.078720
42	1	0	3.512920	-3.545456	-0.662687
43	1	0	4.178287	1.891400	-0.481146
44	1	0	2.779972	2.547437	0.374410
45	1	0	2.719671	2.338661	-1.374528
46	1	0	0.003965	3.453910	3.716173

Excitation Energies and Oscillator Strengths：

HOMO = 148
LUMO = 149

Excited State 1: Triplet-A 1.5227 eV 814.21 nm f=0.0000
<S**2>=2.000
147 ->149 -0.16754
148 ->149 0.69357
148 <-149 0.10403

Excited State 2: Triplet-A 2.5044 eV 495.06 nm f=0.0000
<S**2>=2.000
139 ->149 -0.12590
147 ->149 0.66952
148 ->149 0.15928

Excited State 3: Triplet-A 2.6581 eV 466.44 nm f=0.0000
<S**2>=2.000
141 ->149 0.11342
146 ->149 0.68218

Excited State 4: Singlet-A 2.6652 eV 465.20 nm f=0.5523
<S**2>=0.000
147 ->149 0.21103
148 ->149 0.67626

Excited State 5: Singlet-A 3.2045 eV 386.90 nm f=0.0578
<S**2>=0.000
146 ->149 0.70257

Excited State 6: Singlet-A 3.2370 eV 383.02 nm f=0.3118
<S**2>=0.000
147 ->149 0.67213
148 ->149 -0.21446

Excited State 7: Triplet-A 3.3093 eV 374.65 nm f=0.0000
<S**2>=2.000
148 ->150 0.70287

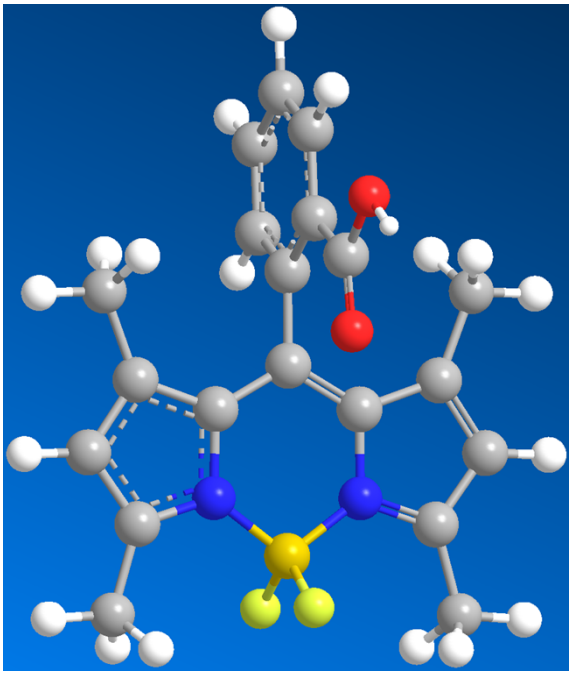
Excited State 8: Triplet-A 3.3236 eV 373.04 nm f=0.0000
<S**2>=2.000
138 ->149 -0.23127
141 ->149 0.63891

Excited State 9: Singlet-A 3.3269 eV 372.67 nm f=0.0000
<S**2>=0.000
148 ->150 0.70398

Excited State 10: Triplet-A 3.3909 eV 365.64 nm f=0.0000
<S**2>=2.000
142 ->150 0.52544
142 ->151 -0.12492
143 ->150 -0.26633

143 ->151 -0.26384
145 ->150 -0.20437
Excited State 11: Triplet-A 3.7476 eV 330.84 nm f=0.0000
<S**2>=2.000
142 ->149 -0.29135
143 ->149 0.17147
145 ->149 0.61907
Excited State 12: Singlet-A 3.7657 eV 329.24 nm f=0.0000
<S**2>=0.000
142 ->149 -0.27508
143 ->149 0.16020
145 ->149 0.62992
Excited State 13: Triplet-A 3.8223 eV 324.37 nm f=0.0000
<S**2>=2.000
144 ->149 0.70558
Excited State 14: Singlet-A 3.8386 eV 322.99 nm f=0.0000
<S**2>=0.000
144 ->149 0.70629
Excited State 15: Triplet-A 3.8429 eV 322.63 nm f=0.0000
<S**2>=2.000
142 ->149 0.47229
143 ->149 -0.39747
145 ->149 0.33325
Excited State 16: Singlet-A 3.8669 eV 320.63 nm f=0.0003
<S**2>=0.000
142 ->149 0.48210
143 ->149 -0.40659
145 ->149 0.31539
Excited State 17: Triplet-A 3.8812 eV 319.45 nm f=0.0000
<S**2>=2.000
142 ->149 0.43013
143 ->149 0.55727
Excited State 18: Singlet-A 3.9057 eV 317.45 nm f=0.0045
<S**2>=0.000
142 ->149 0.43457
143 ->149 0.55375
Excited State 19: Singlet-A 4.1715 eV 297.22 nm f=0.0003
<S**2>=0.000
147 ->150 0.70273
Excited State 20: Singlet-A 4.2332 eV 292.88 nm f=0.0000
<S**2>=0.000
146 ->150 0.69505
148 ->152 0.11816

B4:



DFT B3LYP/6-31+G(d) optimized structure of B4

Optimized Geometry：

Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.535305	0.000063	-1.164791
2	6	0	3.584936	0.000086	-2.188366
3	6	0	2.224428	0.000067	-1.875371
4	6	0	1.785141	0.000028	-0.545142
5	6	0	2.747890	-0.000008	0.490410
6	6	0	4.115531	0.000016	0.163642
7	6	0	0.304601	0.000021	-0.315442
8	6	0	-0.383063	1.224431	-0.259794
9	6	0	0.072696	2.581361	-0.326049
10	6	0	1.463696	3.122796	-0.487840
11	6	0	-1.066497	3.375663	-0.206144
12	6	0	-2.188618	2.537083	-0.068916
13	6	0	-3.616616	2.951625	0.084428
14	6	0	-2.188565	-2.537097	-0.069000
15	6	0	-3.616552	-2.951677	0.084334
16	6	0	-1.066420	-3.375648	-0.206229
17	6	0	0.072752	-2.581314	-0.326123

18	6	0	1.463772	-3.122698	-0.487902
19	6	0	-0.383042	-1.224398	-0.259839
20	7	0	-1.778176	-1.246836	-0.101154
21	7	0	-1.778198	1.246832	-0.101096
22	9	0	-3.354523	-0.000050	1.265469
23	9	0	-3.654929	0.000003	-1.009294
24	5	0	-2.681457	-0.000013	0.019132
25	6	0	2.333154	-0.000082	1.921247
26	8	0	1.181214	-0.000247	2.323678
27	8	0	3.382909	0.000023	2.775861
28	1	0	5.596054	0.000075	-1.397536
29	1	0	3.897530	0.000121	-3.228791
30	1	0	1.486937	0.000089	-2.672995
31	1	0	4.849059	-0.000011	0.961359
32	1	0	1.429266	4.216361	-0.514024
33	1	0	1.937085	2.777687	-1.413106
34	1	0	2.121877	2.829563	0.337479
35	1	0	-1.096431	4.458268	-0.216072
36	1	0	-4.228442	2.585144	-0.747704
37	1	0	-3.685231	4.042250	0.111870
38	1	0	-4.051657	2.550903	1.006704
39	1	0	-4.228395	-2.585163	-0.747771
40	1	0	-4.051593	-2.551018	1.006637
41	1	0	-3.685144	-4.042306	0.111717
42	1	0	-1.096327	-4.458253	-0.216170
43	1	0	1.429390	-4.216265	-0.514050
44	1	0	2.121941	-2.829405	0.337406
45	1	0	1.937144	-2.777597	-1.413179
46	1	0	3.023761	-0.000052	3.683751

Excitation Energies and Oscillator Strengths：

HOMO = 96

LUMO = 97

Excited State 1: Triplet-A 1.5460 eV 801.96 nm f=0.0000
<S**2>=2.000

96 -> 97 0.70937

96 <- 97 0.11274

Excited State 2: Triplet-A 2.7587 eV 449.42 nm f=0.0000
<S**2>=2.000

95 -> 97 0.69264

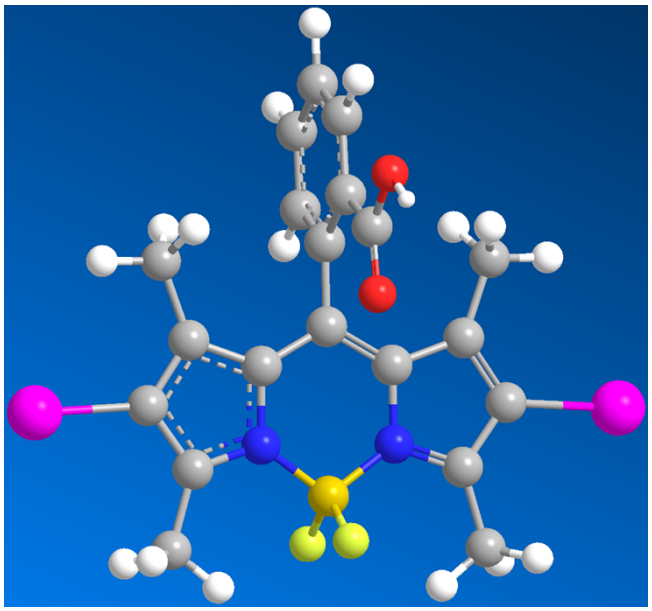
Excited State 3: Singlet-A 2.8656 eV 432.67 nm f=0.5672
<S**2>=0.000

95 -> 97 0.11883

96 -> 97 0.69975
96 <- 97 -0.10256
Excited State 4: Triplet-A 2.9284 eV 423.38 nm f=0.0000
<S**2>=2.000
92 -> 97 -0.15568
94 -> 97 0.67031
Excited State 5: Triplet-A 3.1014 eV 399.77 nm f=0.0000
<S**2>=2.000
96 -> 98 0.70164
Excited State 6: Singlet-A 3.1202 eV 397.36 nm f=0.0007
<S**2>=0.000
96 -> 98 0.70571
Excited State 7: Triplet-A 3.3292 eV 372.41 nm f=0.0000
<S**2>=2.000
90 -> 97 -0.20159
92 -> 97 0.64271
94 -> 97 0.17322
Excited State 8: Singlet-A 3.4270 eV 361.78 nm f=0.0620
<S**2>=0.000
95 -> 97 0.69487
96 -> 97 -0.12150
Excited State 9: Triplet-A 3.4377 eV 360.66 nm f=0.0000
<S**2>=2.000
91 -> 98 0.55506
93 -> 98 0.20570
93 -> 99 0.33084
95 -> 98 0.11577
Excited State 10: Singlet-A 3.6856 eV 336.40 nm f=0.0371
<S**2>=0.000
94 -> 97 0.70412
Excited State 11: Triplet-A 3.9097 eV 317.12 nm f=0.0000
<S**2>=2.000
93 -> 97 0.70243
Excited State 12: Singlet-A 3.9356 eV 315.03 nm f=0.0006
<S**2>=0.000
93 -> 97 0.70314
Excited State 13: Triplet-A 3.9401 eV 314.67 nm f=0.0000
<S**2>=2.000
91 -> 98 -0.20187
93 -> 98 0.64378
95 -> 98 -0.16368
Excited State 14: Triplet-A 4.1183 eV 301.06 nm f=0.0000
<S**2>=2.000
96 -> 99 0.68780

96 ->104 -0.10076
Excited State 15: Singlet-A 4.1561 eV 298.32 nm f=0.0003
<S**2>=0.000
96 -> 99 0.70036
Excited State 16: Triplet-A 4.1656 eV 297.64 nm f=0.0000
<S**2>=2.000
91 -> 97 0.69757
Excited State 17: Singlet-A 4.1933 eV 295.67 nm f=0.0040
<S**2>=0.000
91 -> 97 0.70403
Excited State 18: Singlet-A 4.2590 eV 291.11 nm f=0.0045
<S**2>=0.000
95 -> 98 0.70516
Excited State 19: Singlet-A 4.3741 eV 283.45 nm f=0.2115
<S**2>=0.000
90 -> 97 0.17369
92 -> 97 0.66919
Excited State 20: Singlet-A 4.4318 eV 279.76 nm f=0.0002
<S**2>=0.000
90 -> 98 -0.11266
92 -> 98 -0.31653
94 -> 98 0.61908

B5



DFT B3LYP/6-31+G(d) optimized structure of B5

Optimized Geometry：

Center Atomic Atomic Coordinates (Angstroms)

#	#	Type	X	Y	Z
1	6	0	0.000292	4.933829	-1.147224
2	6	0	-0.000561	3.974551	-2.162895
3	6	0	-0.000718	2.616290	-1.838693
4	6	0	-0.000041	2.190572	-0.504169
5	6	0	0.000815	3.161442	0.523525
6	6	0	0.000999	4.526104	0.185532
7	6	0	-0.000113	0.713508	-0.257349
8	6	0	-1.226085	0.027377	-0.190742
9	6	0	-2.579973	0.491813	-0.261636
10	6	0	-3.086078	1.890386	-0.444781
11	6	0	-3.364393	-0.651110	-0.120462
12	53	0	-5.475384	-0.763894	-0.126466
13	6	0	-2.532277	-1.779181	0.034079
14	6	0	-2.950397	-3.200984	0.212926
15	6	0	2.531759	-1.779426	0.034445
16	6	0	2.949703	-3.201216	0.213799
17	6	0	3.364012	-0.651527	-0.120651
18	53	0	5.474987	-0.764617	-0.126896
19	6	0	2.579736	0.491452	-0.262130
20	6	0	3.086025	1.889864	-0.446004
21	6	0	1.225786	0.027244	-0.190779
22	7	0	1.248153	-1.362824	-0.009676
23	7	0	-1.248612	-1.362745	-0.010103
24	9	0	-0.000544	-2.915496	1.375420
25	9	0	-0.000109	-3.243158	-0.899762
26	5	0	-0.000287	-2.266494	0.120792
27	6	0	0.001439	2.754557	1.956798
28	8	0	0.000046	1.603114	2.362093
29	8	0	0.003778	3.807250	2.805789
30	1	0	0.000407	5.992370	-1.389452
31	1	0	-0.001103	4.278338	-3.205817
32	1	0	-0.001346	1.871926	-2.629920
33	1	0	0.001651	5.266344	0.977052
34	1	0	-4.178391	1.892288	-0.478268
35	1	0	-2.720994	2.339009	-1.373898
36	1	0	-2.778522	2.547886	0.375118
37	1	0	-2.098493	-3.863837	0.357336
38	1	0	-3.514287	-3.544595	-0.663370
39	1	0	-3.617491	-3.293890	1.078255
40	1	0	2.097757	-3.863804	0.359177
41	1	0	3.617371	-3.293756	1.078720
42	1	0	3.512920	-3.545456	-0.662687

43	1	0	4.178287	1.891400	-0.481146
44	1	0	2.779972	2.547437	0.374410
45	1	0	2.719671	2.338661	-1.374528
46	1	0	0.003965	3.453910	3.716173

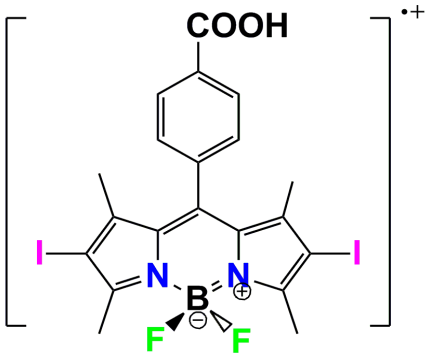
Excitation Energies and Oscillator Strengths：

HOMO = 148
LUMO = 149
Excited State 1: Triplet-A 1.5519 eV 798.89 nm f=0.0000
<S**2>=2.000
147 ->149 0.16277
148 ->149 0.69388
148 <-149 0.10018
Excited State 2: Triplet-A 2.5393 eV 488.27 nm f=0.0000
<S**2>=2.000
140 ->149 -0.12433
147 ->149 0.67066
148 ->149 -0.15552
Excited State 3: Singlet-A 2.6782 eV 462.94 nm f=0.5630
<S**2>=0.000
147 ->149 -0.19507
148 ->149 0.68087
Excited State 4: Triplet-A 2.6982 eV 459.51 nm f=0.0000
<S**2>=2.000
139 ->149 -0.10587
146 ->149 0.68185
Excited State 5: Triplet-A 3.1567 eV 392.76 nm f=0.0000
<S**2>=2.000
138 ->149 -0.15602
142 ->149 0.51071
148 ->150 -0.43830
Excited State 6: Triplet-A 3.1799 eV 389.90 nm f=0.0000
<S**2>=2.000
138 ->149 -0.12496
142 ->149 0.41288
148 ->150 0.54553
Excited State 7: Singlet-A 3.1881 eV 388.90 nm f=0.0001
<S**2>=0.000
148 ->150 0.70214
Excited State 8: Singlet-A 3.2444 eV 382.14 nm f=0.0556
<S**2>=0.000
146 ->149 0.70021
Excited State 9: Singlet-A 3.2543 eV 380.99 nm f=0.2714

<S**2>=0.000
147 ->149 0.67706
148 ->149 0.19828
Excited State 10: Triplet-A 3.4275 eV 361.73 nm f=0.0000
<S**2>=2.000
141 ->150 0.56226
143 ->150 -0.15379
143 ->151 -0.31361
145 ->150 0.10055
145 ->151 0.11325
147 ->150 -0.11400
Excited State 11: Triplet-A 3.7715 eV 328.74 nm f=0.0000
<S**2>=2.000
143 ->149 -0.45710
145 ->149 0.53356
Excited State 12: Singlet-A 3.7922 eV 326.94 nm f=0.0006
<S**2>=0.000
143 ->149 -0.43355
145 ->149 0.55364
Excited State 13: Triplet-A 3.8745 eV 320.00 nm f=0.0000
<S**2>=2.000
143 ->149 0.46354
145 ->149 0.40133
146 ->153 -0.14199
147 ->152 -0.10440
148 ->152 0.29563
Excited State 14: Triplet-A 3.8770 eV 319.79 nm f=0.0000
<S**2>=2.000
144 ->149 0.70472
Excited State 15: Triplet-A 3.8887 eV 318.83 nm f=0.0000
<S**2>=2.000
143 ->149 -0.25855
145 ->149 -0.22823
146 ->153 -0.24862
147 ->152 -0.18266
148 ->152 0.52956
Excited State 16: Singlet-A 3.8931 eV 318.47 nm f=0.0000
<S**2>=0.000
144 ->149 0.70629
Excited State 17: Singlet-A 3.8996 eV 317.94 nm f=0.0001
<S**2>=0.000
143 ->149 0.55148
145 ->149 0.43795
Excited State 18: Singlet-A 4.0606 eV 305.33 nm f=0.0021

<S**2>=0.000
147 ->150 0.70179
Excited State 19: Singlet-A 4.0682 eV 304.76 nm f=0.0077
<S**2>=0.000
141 ->149 0.70150
Excited State 20: Singlet-A 4.1333 eV 299.97 nm f=0.0002
<S**2>=0.000
146 ->150 0.70466

B3$^{\cdot+}$.



Optimized Geometry:

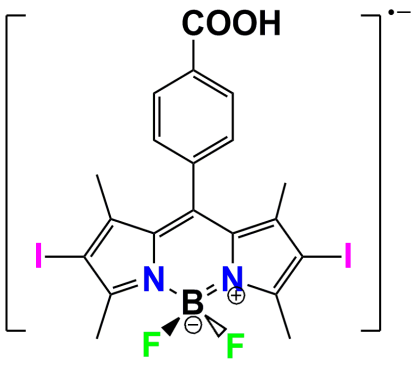
Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-5.462045	-1.077210	-0.002370
2	53	0	5.461981	-1.077387	-0.002295
3	6	0	0.000154	6.175738	0.090289
4	6	0	0.000123	4.686636	0.032745
5	6	0	-0.000537	3.973619	1.240372
6	1	0	-0.001008	4.515444	2.180192
7	6	0	-0.000569	2.580611	1.232555
8	1	0	-0.001077	2.033530	2.170817
9	6	0	0.000030	1.886431	0.013382
10	6	0	0.000681	2.597380	-1.194991
11	1	0	0.001161	2.063706	-2.140958
12	6	0	0.000740	3.991925	-1.186087
13	1	0	0.001255	4.535911	-2.123766
14	6	0	-0.000006	0.390159	0.004433
15	6	0	1.220778	-0.309564	0.001641
16	6	0	2.590932	0.174826	0.001870
17	6	0	3.073289	1.589300	0.003260
18	1	0	4.164960	1.611193	0.003139
19	1	0	2.721897	2.132561	0.885446

20	1	0	2.721657	2.134034	-0.877950
21	6	0	3.372300	-0.957274	-0.000827
22	6	0	2.517541	-2.124033	-0.002824
23	6	0	2.952023	-3.540175	-0.005059
24	1	0	2.115301	-4.235658	-0.008126
25	1	0	3.577863	-3.732277	0.875646
26	1	0	3.581540	-3.728684	-0.883850
27	6	0	-2.517638	-2.123950	-0.003207
28	6	0	-2.952162	-3.540079	-0.005365
29	1	0	-2.115465	-4.235581	-0.010640
30	1	0	-3.583685	-3.728085	-0.882796
31	1	0	-3.575995	-3.732657	0.876686
32	6	0	-3.372361	-0.957165	-0.001116
33	6	0	-2.590958	0.174910	0.001708
34	6	0	-3.073278	1.589397	0.003369
35	1	0	-4.164948	1.611317	0.002977
36	1	0	-2.721402	2.134392	-0.877570
37	1	0	-2.722105	2.132377	0.885825
38	6	0	-1.220817	-0.309521	0.001431
39	7	0	-1.246279	-1.718183	-0.002112
40	7	0	1.246194	-1.718227	-0.001845
41	5	0	-0.000058	-2.653457	-0.003659
42	9	0	0.000091	-3.445151	-1.154129
43	9	0	-0.000234	-3.449601	1.143678
44	8	0	0.000798	6.753785	-1.129074
45	1	0	0.000760	7.722716	-1.006594
46	8	0	-0.000385	6.826128	1.123243

α state:
HOMO = 148
LUMO = 149

β state:
HOMO = 724
LUMO = 725

$B3^{\cdot-}$:



Optimized Geometry：

Center #	Atomic #	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-5.484897	-1.106803	0.019305
2	53	0	5.491426	-1.085998	-0.052682
3	6	0	0.016739	6.222799	0.085865
4	6	0	-0.000564	4.746441	0.036141
5	6	0	0.503237	4.025492	1.134480
6	1	0	0.883549	4.567449	1.994830
7	6	0	0.508911	2.635739	1.120407
8	1	0	0.897510	2.091417	1.976685
9	6	0	-0.000440	1.914132	0.019771
10	6	0	-0.509041	2.648464	-1.071761
11	1	0	-0.896709	2.114222	-1.934753
12	6	0	-0.504555	4.039590	-1.071979
13	1	0	-0.886648	4.581184	-1.930805
14	6	0	0.000597	0.433017	0.011596
15	6	0	1.239649	-0.281836	0.013118
16	6	0	2.587314	0.159569	-0.087359
17	6	0	3.119616	1.547235	-0.299977
18	1	0	4.111388	1.501683	-0.762282
19	1	0	3.226844	2.112733	0.636074
20	1	0	2.473906	2.137806	-0.955417
21	6	0	3.367775	-1.017102	-0.009578
22	6	0	2.545351	-2.131801	0.098071
23	6	0	2.898699	-3.582314	0.187346
24	1	0	2.435321	-4.055385	1.060808
25	1	0	3.982009	-3.702043	0.267569
26	1	0	2.559690	-4.137536	-0.695924
27	6	0	-2.533489	-2.141135	-0.101495
28	6	0	-2.880861	-3.591857	-0.209104
29	1	0	-2.526417	-4.022911	-1.153710
30	1	0	-3.964595	-3.724080	-0.161623

31	1	0	-2.428916	-4.176886	0.600175
32	6	0	-3.361095	-1.030072	0.002818
33	6	0	-2.586029	0.149557	0.091446
34	6	0	-3.125899	1.534113	0.305267
35	1	0	-4.123908	1.482217	0.753187
36	1	0	-3.221729	2.105672	-0.628280
37	1	0	-2.491550	2.122349	0.973886
38	6	0	-1.235799	-0.286071	0.000548
39	7	0	-1.234962	-1.682955	-0.091987
40	7	0	1.245274	-1.678697	0.100139
41	5	0	0.004993	-2.574033	0.027687
42	9	0	0.090823	-3.460768	-1.091130
43	9	0	-0.081645	-3.398300	1.196571
44	8	0	-0.492635	6.809232	-1.026904
45	1	0	-0.436729	7.775680	-0.902688
46	8	0	0.440194	6.892571	1.021036

α state:
HOMO = 149
LUMO = 150

β state:
HOMO = 724
LUMO = 725