Electronic Supplementary Information

Facile and High-yield Formation of Dipyrrin-Boronic Acid Dyads and Triads: Light-Harvesting System in the Visible Region Based on Efficient Energy Transfer

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Table of contents

(1) ^{1}H and ^{13}C NMR spectra

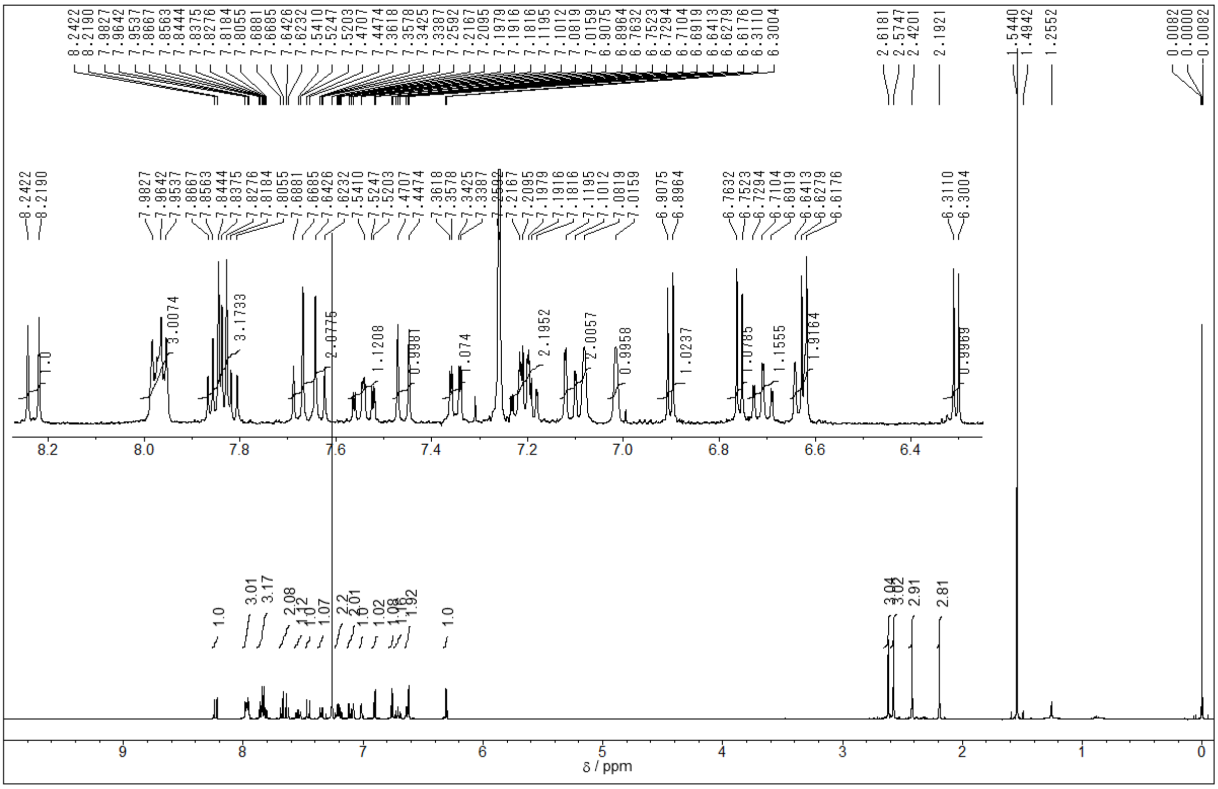


Figure S1. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

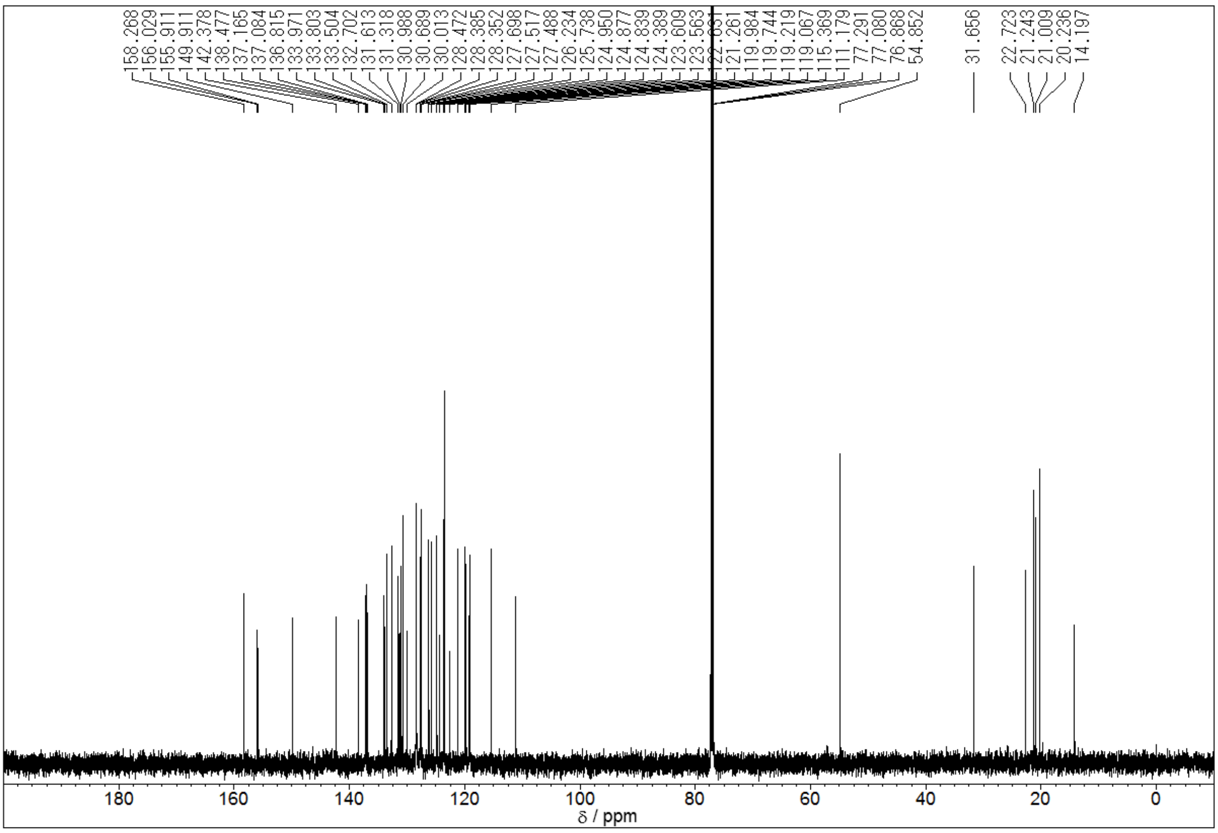


Figure S2. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$).

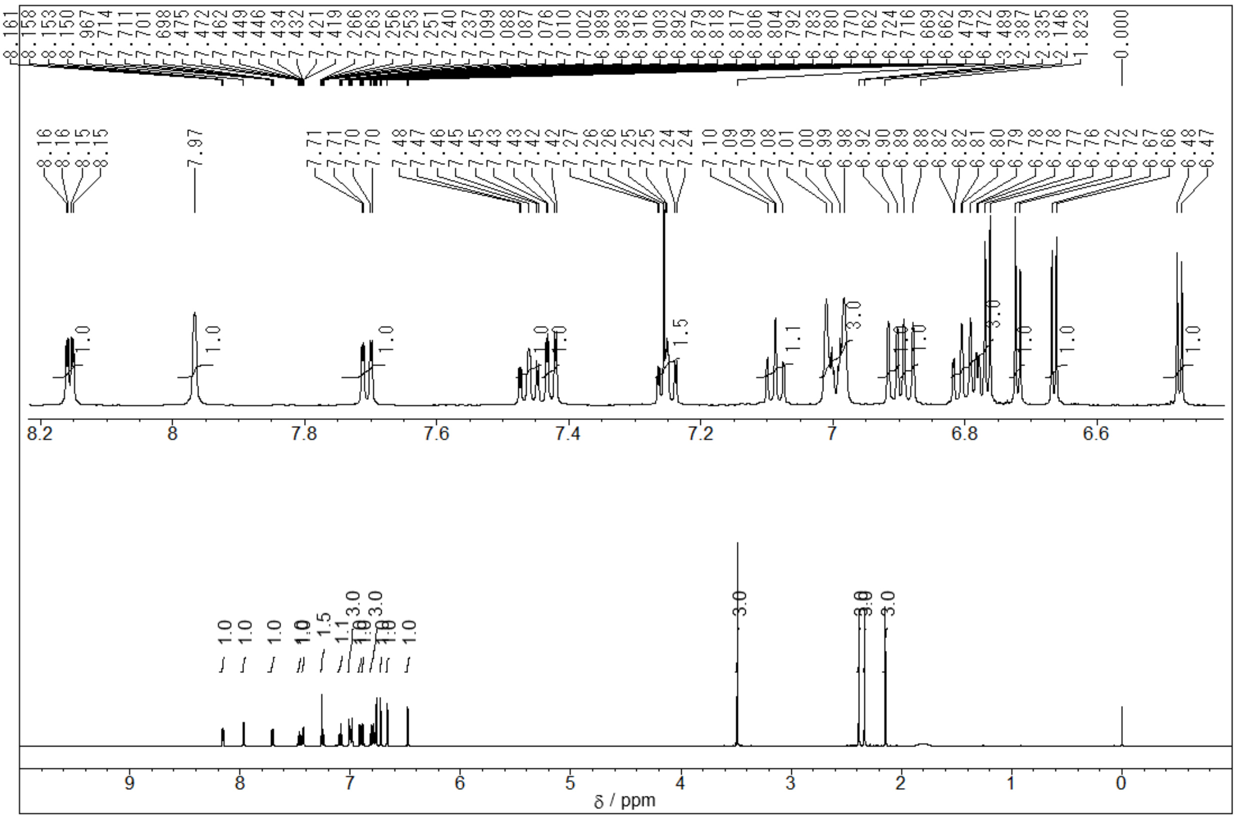


Figure S3. ^{1}H NMR spectrum of **3** (600 MHz, $CDCl_3$).

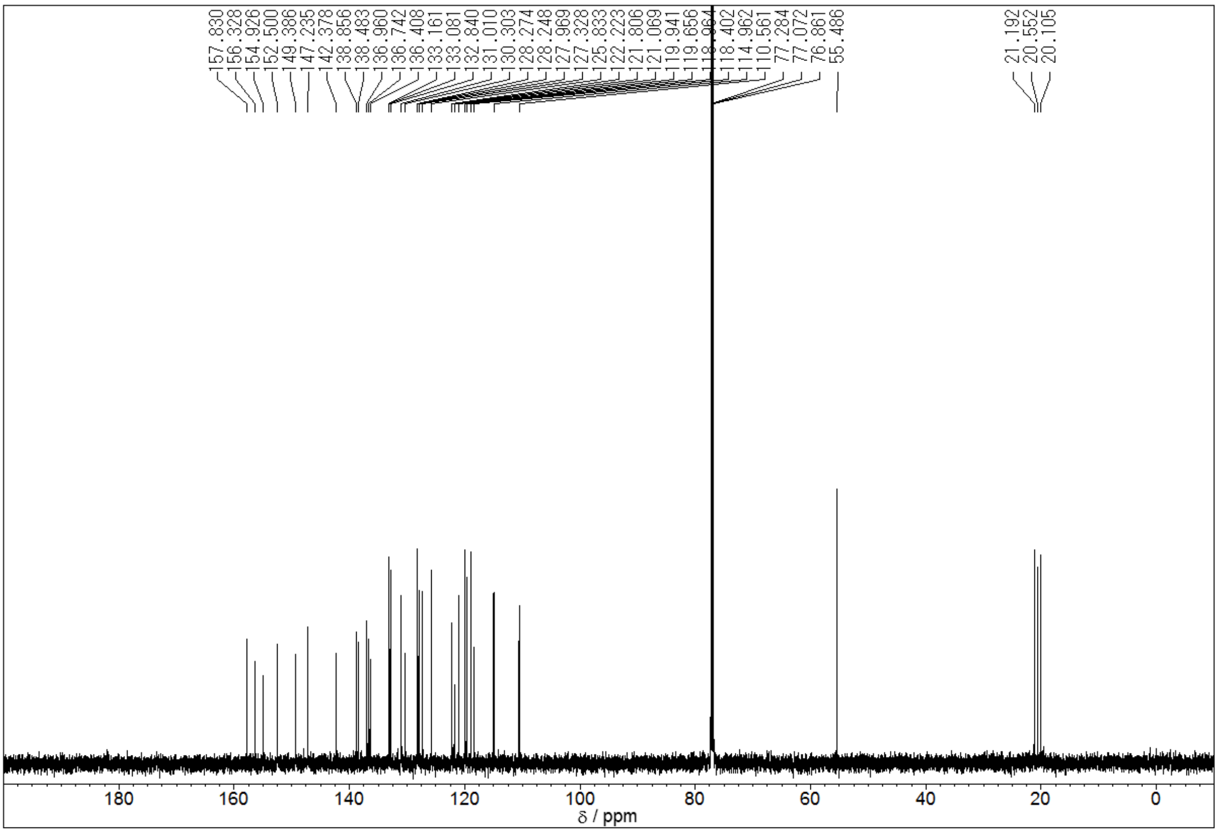


Figure S4. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

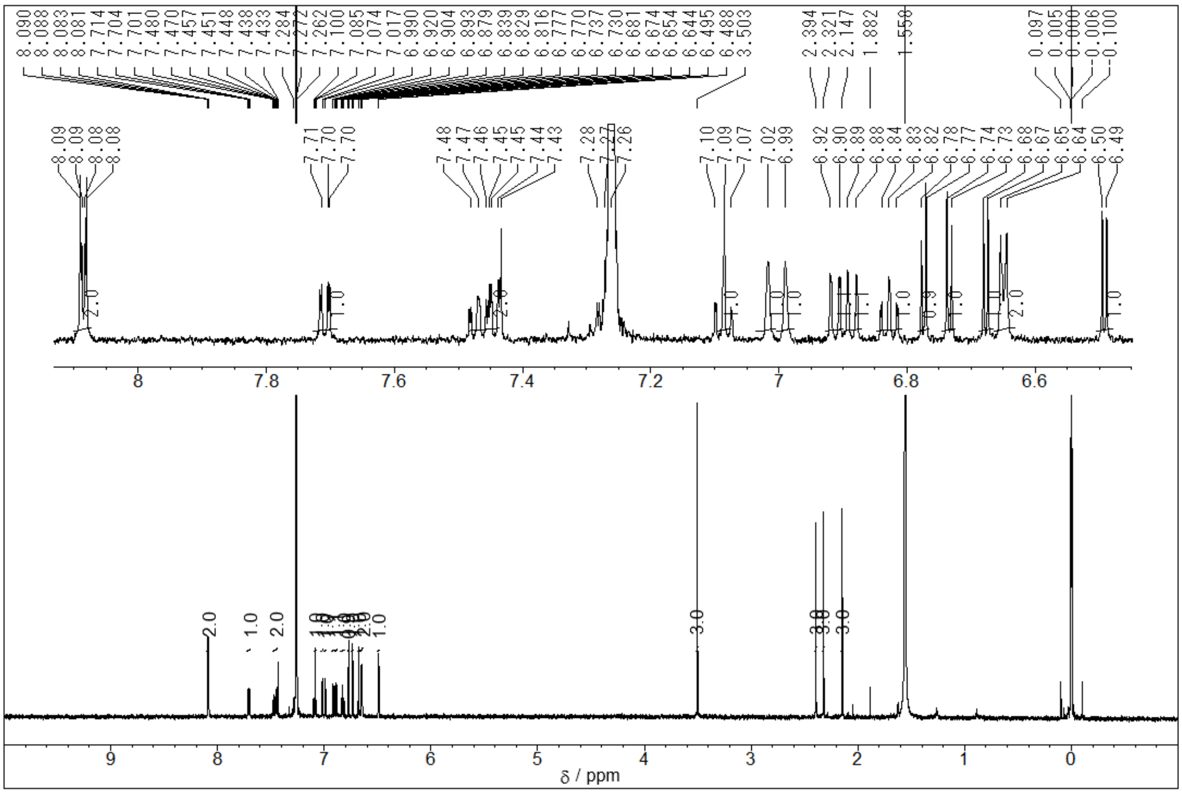


Figure S5. ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$).

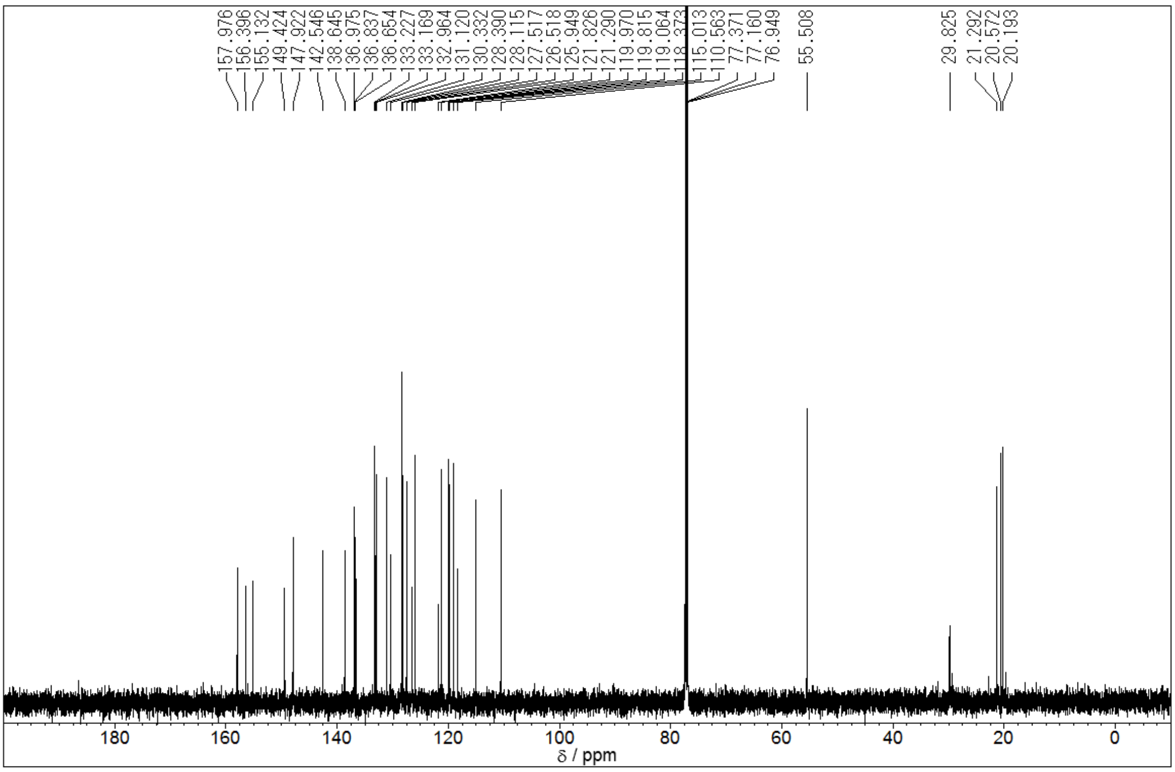


Figure S6. ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

(2) ESI-TOF mass spectra

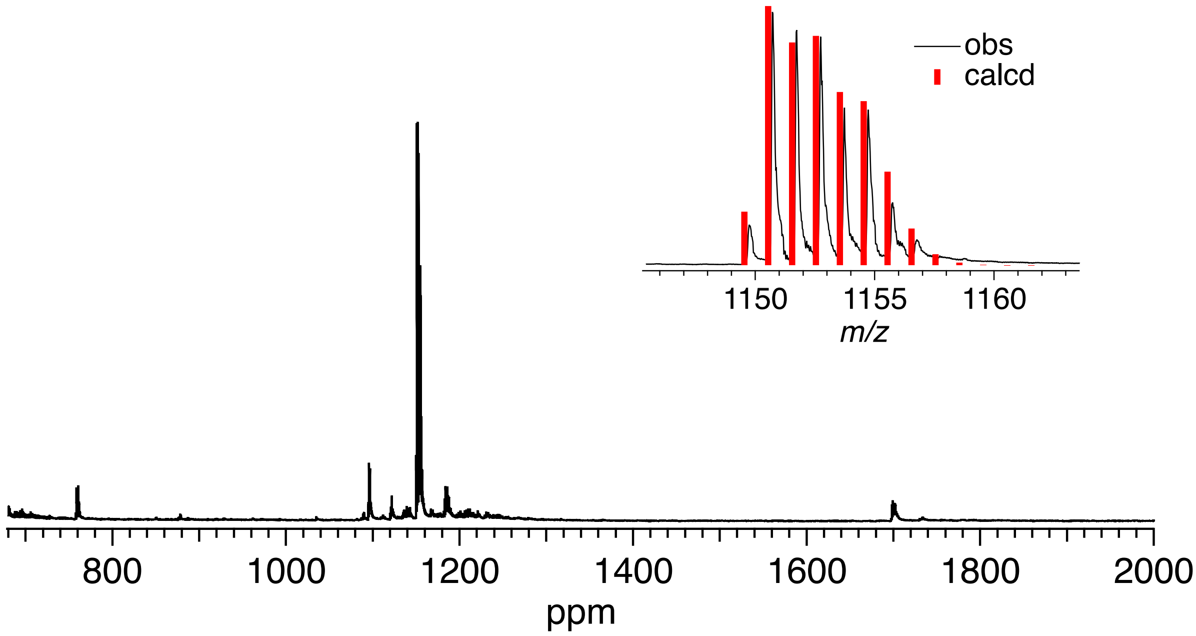


Figure S7. ESI-TOF MS of **3**·**5**. The observed ion peaks: [**3**·**5**+H]$^+$.

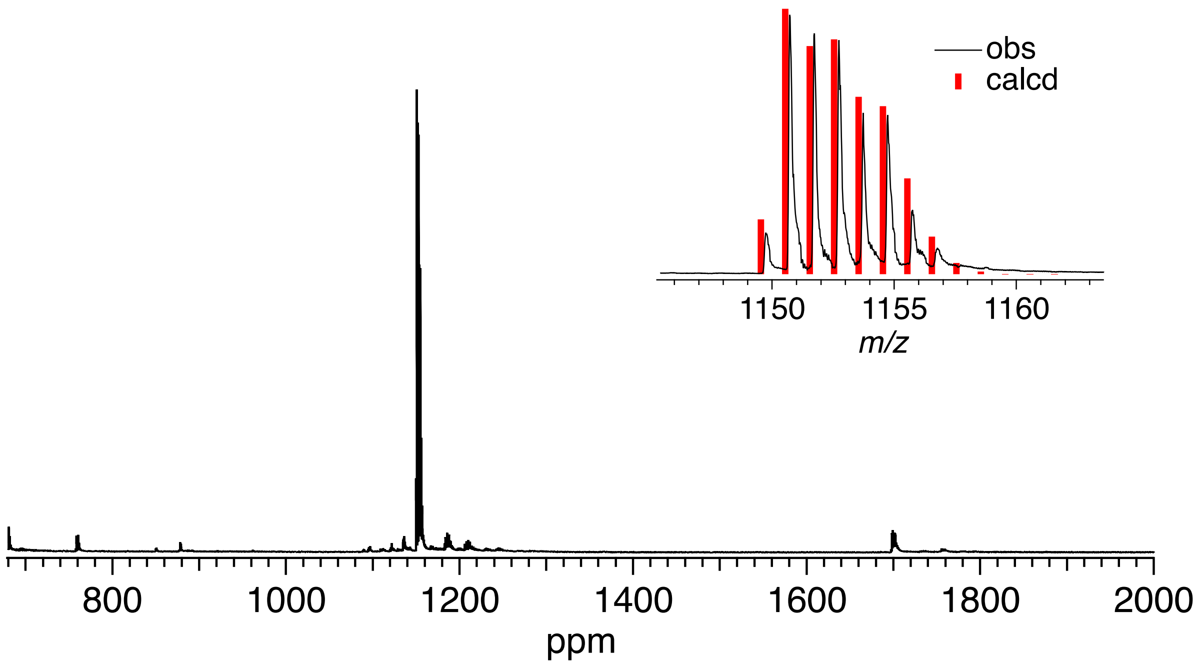
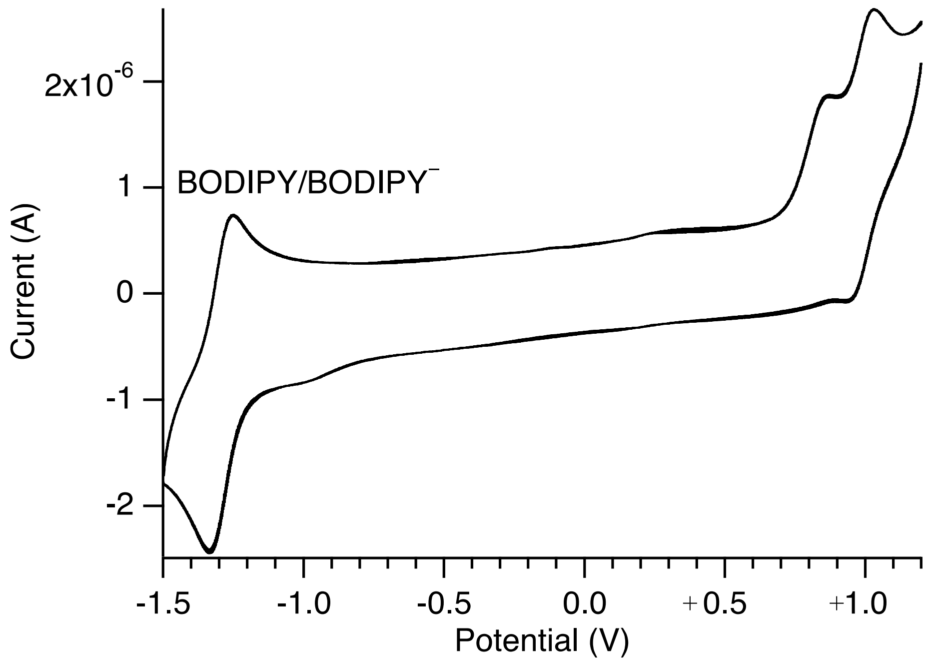


Figure S8. ESI-TOF MS of **4**·**5**. The observed ion peaks: [**4**·**5**+H]$^+$.

(3) Electrochemical Studies



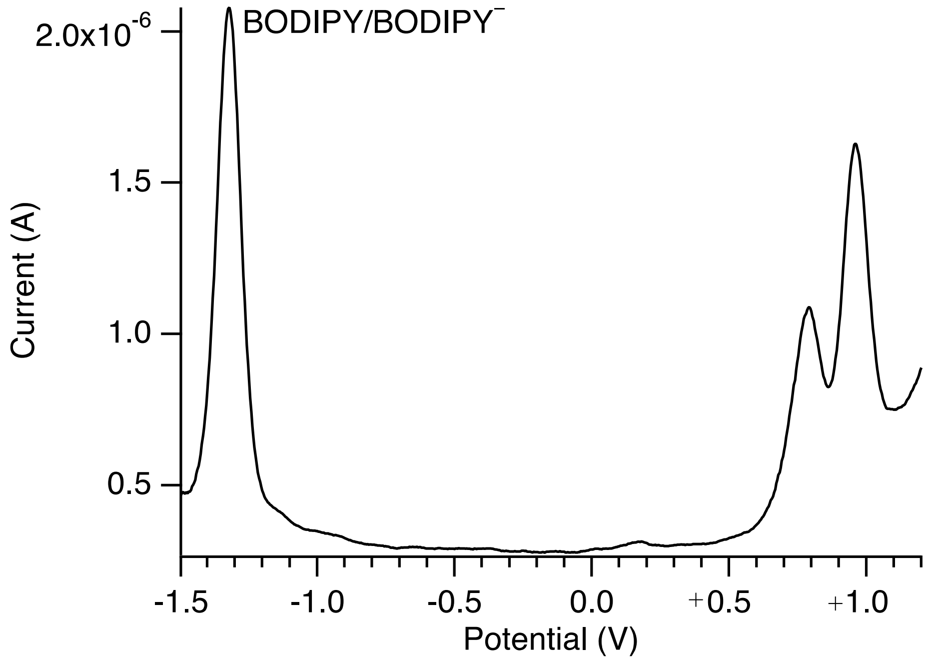


Figure S9. Cyclic (upper) and differential pulse (lower) voltammograms of **3** in CH_2Cl_2 (0.1 M $TBAClO_4$). Working: glassy carbon, counter: Pt, reference: Ag/Ag^+, Scan rate: 0.1 V/s. Potential vs Fc/Fc^+ = +0.20 V.

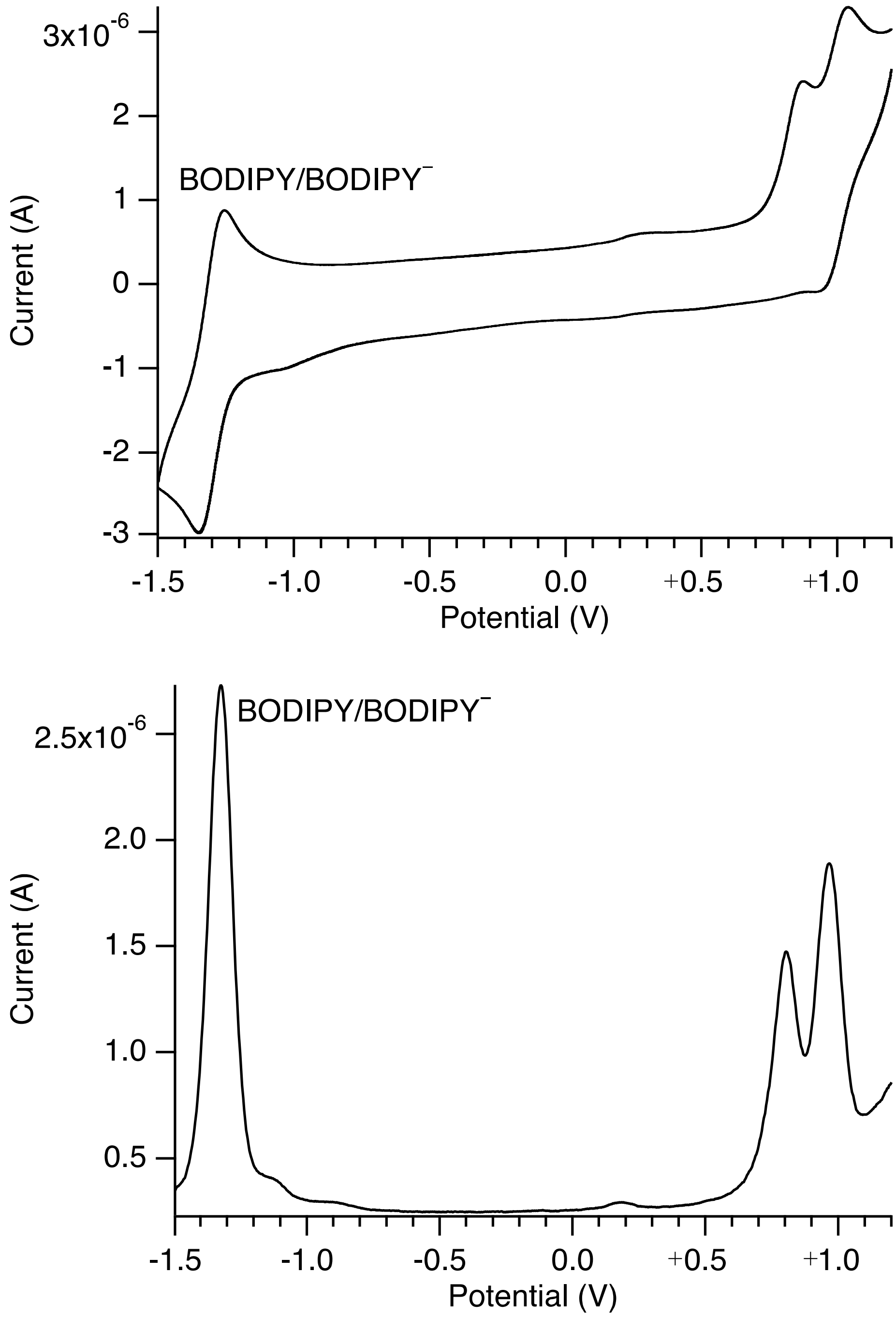


Figure S10. Cyclic (upper) and differential pulse (lower) voltammograms of **4** in CH_2Cl_2 (0.1 M $TBAClO_4$). Working: glassy carbon, counter: Pt, reference: Ag/Ag^+, Scan rate: 0.1 V/s. Potential vs Fc/Fc^+ = +0.20 V.

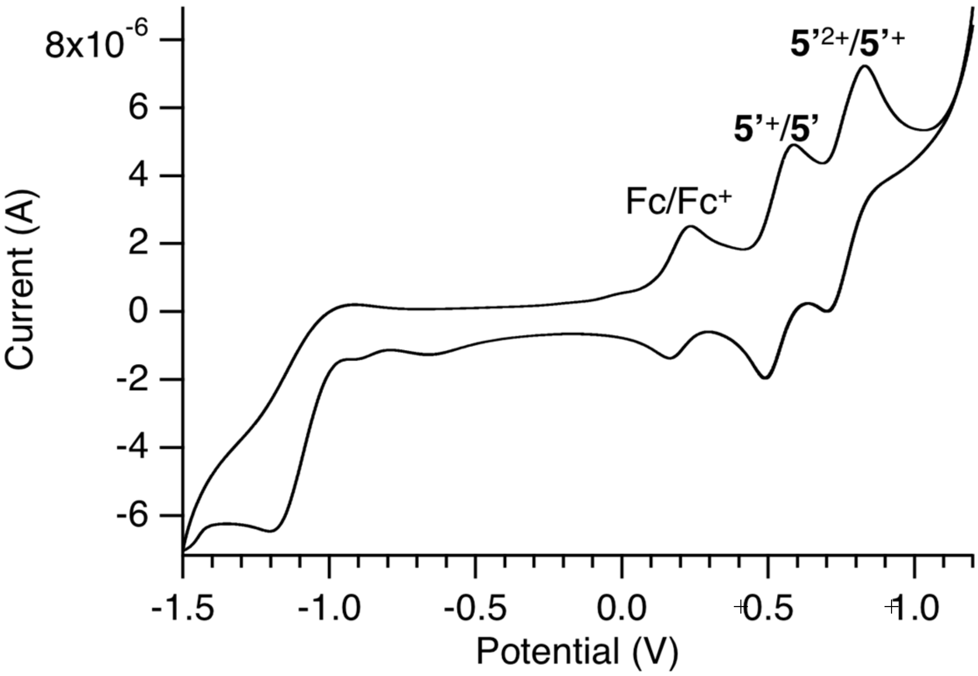


Figure S11. Cyclic voltammogram of **5'** (= **5**·pyridine) in CH_2Cl_2 (0.1 M $TBAClO_4$). Working: glassy carbon, counter: Pt, reference: Ag/Ag^{+}, Scan rate: 0.1 V/s. Potential vs Fc/Fc^{+} = +0.20 V.

(4) Photophysical studies

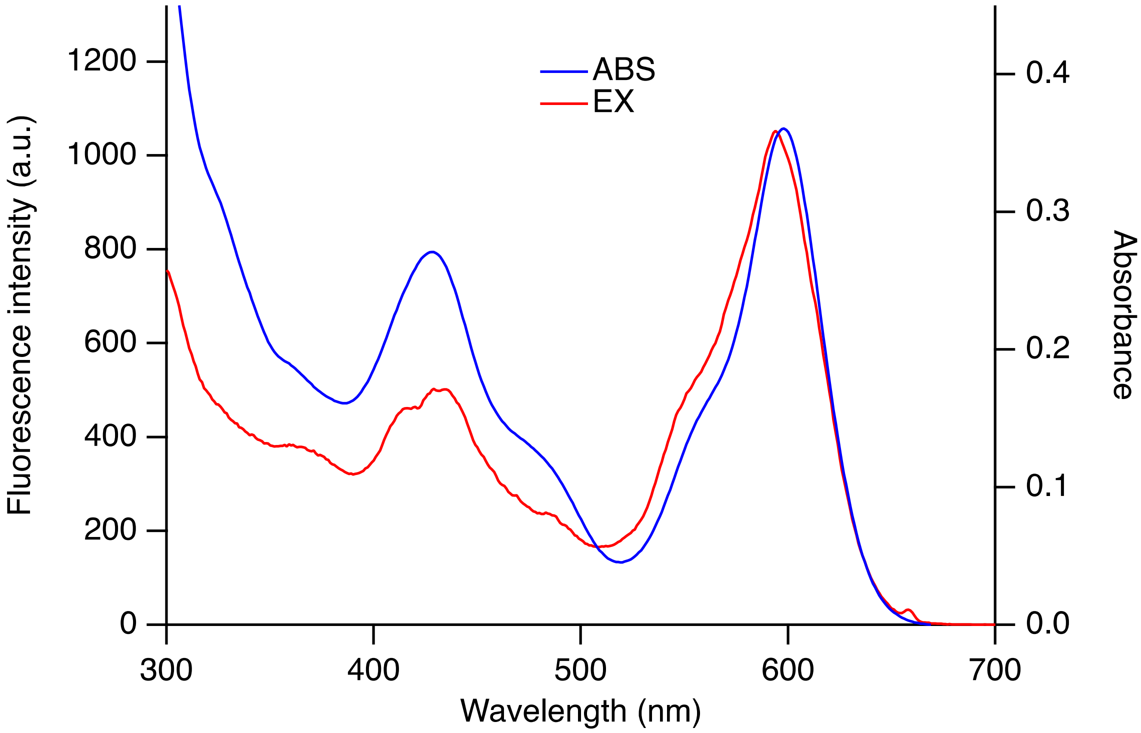


Figure S12. Absorption and excitation (650 nm) spectra of **3·5** (*n*-hexane, 1.0×10^{-5} M, rt).

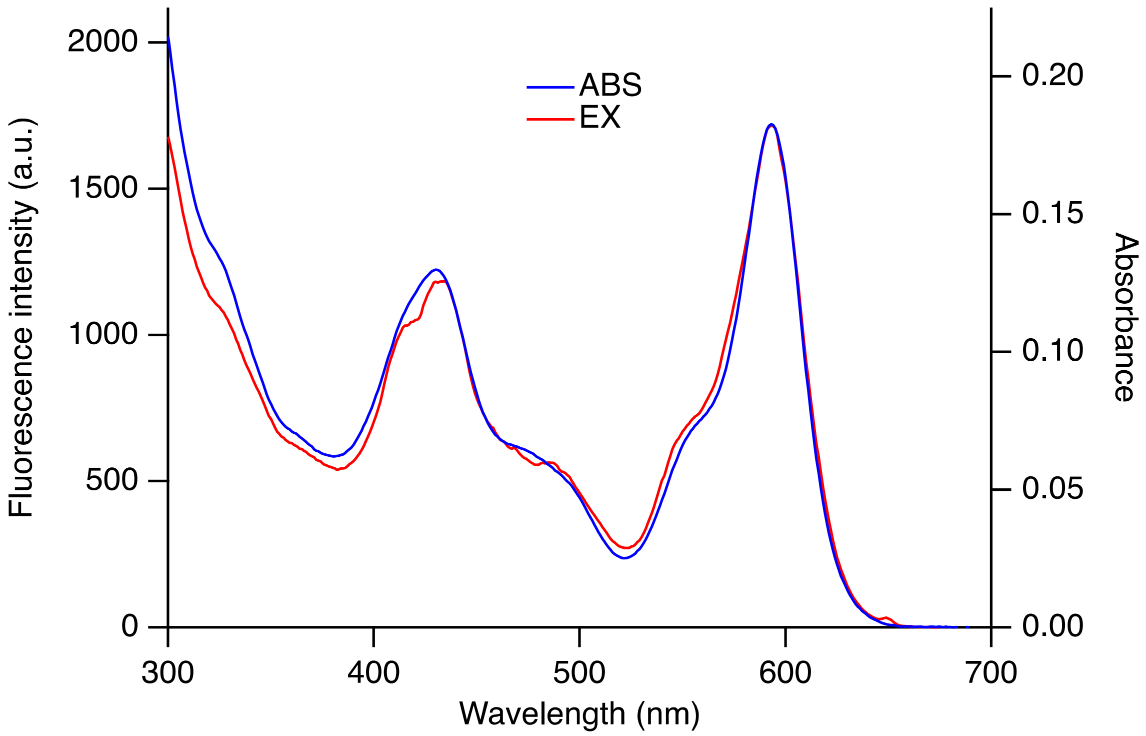


Figure S13. Absorption and excitation (650 nm) spectra of **4·5** (*n*-hexane, 5.0×10^{-6} M, rt).

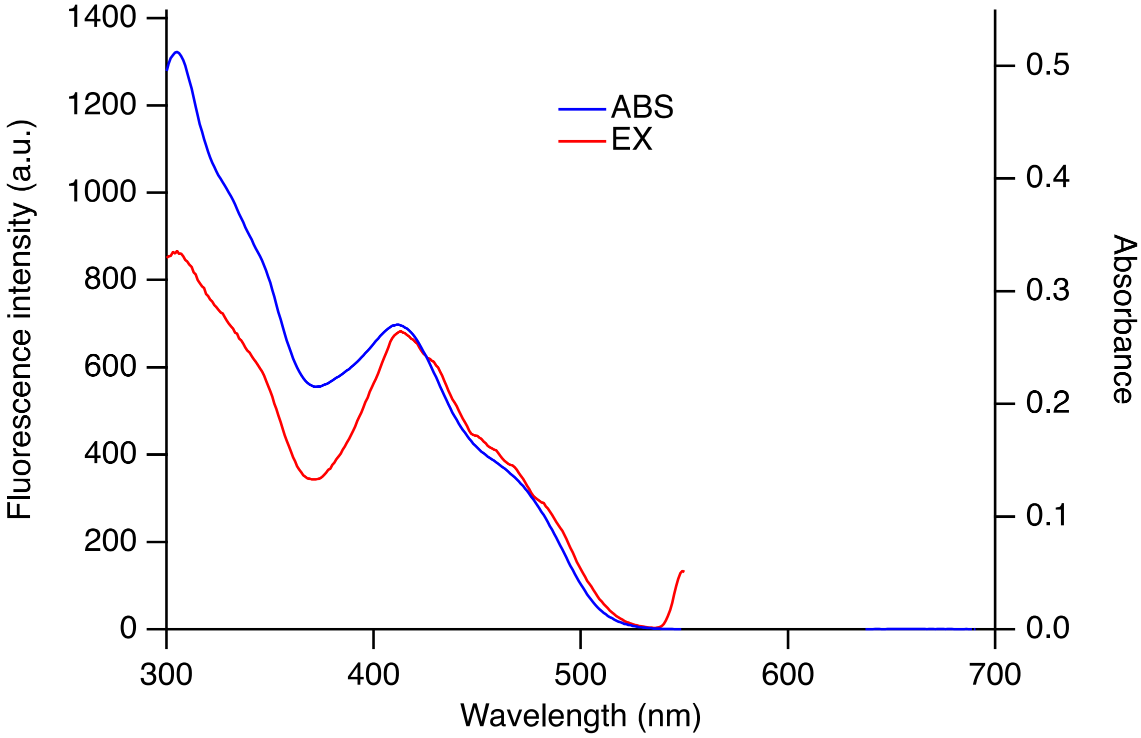


Figure S14. Absorption and excitation (550 nm) spectra of **5** (*n*-hexane, 1.0×10^{-5} M, rt).

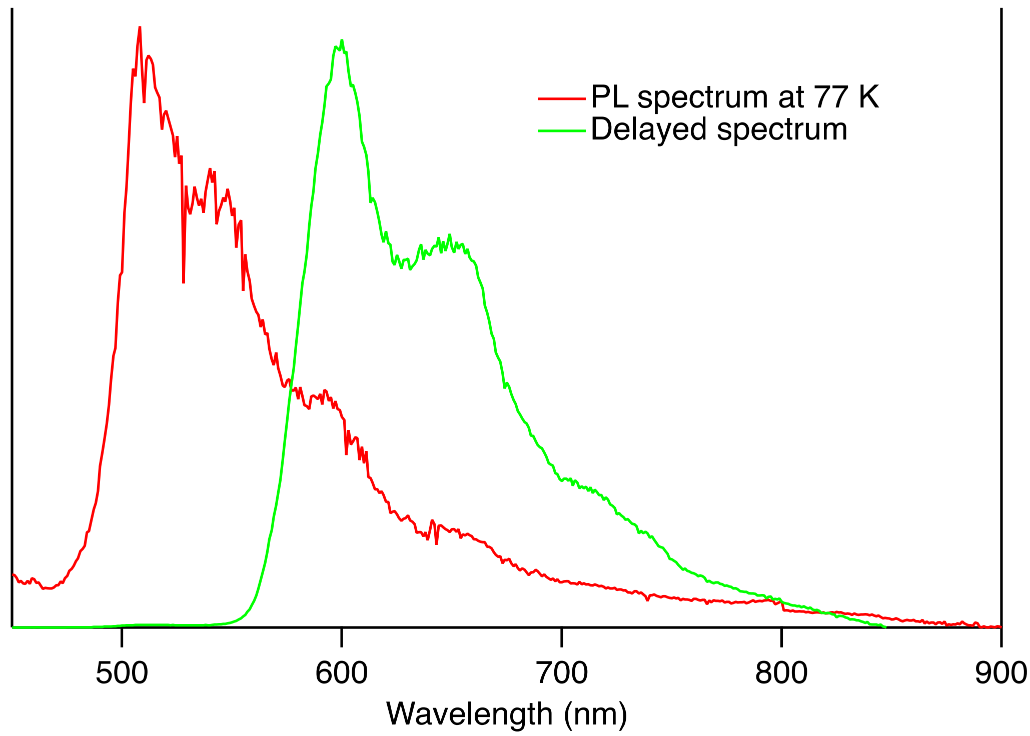


Figure S15. Photoluminescence spectrum of **5** (degassed methylcyclohexane-glass-matrix, 77 K, λ_{ex} = 420 nm) and delayed spectrum (delay time: 20 msec).

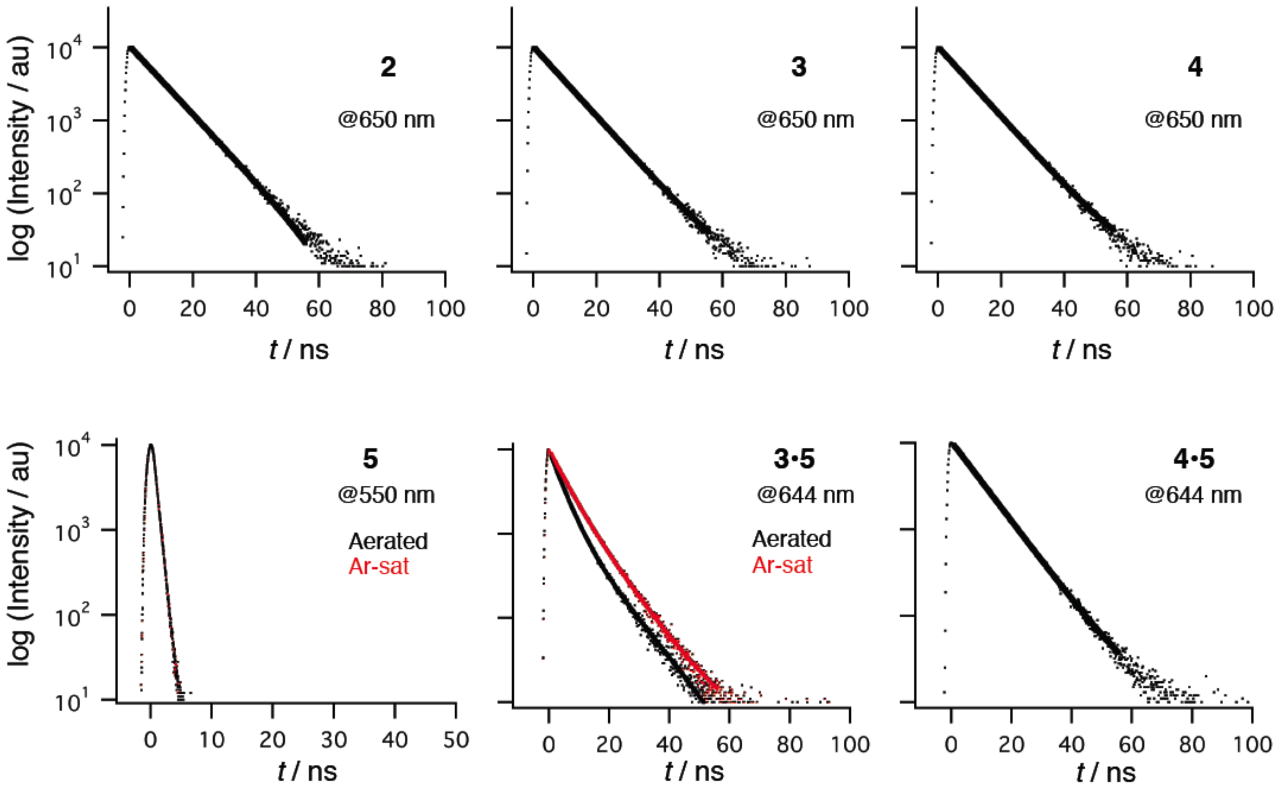


Figure S16. Fluorescence decay of **2**, **3**, **4**, **5**, **3**·**5**, and **4**·**5** at the λ_{max} (n-hexane, 1.0×10^{-5} M, λ_{ex} = 371 nm, rt).

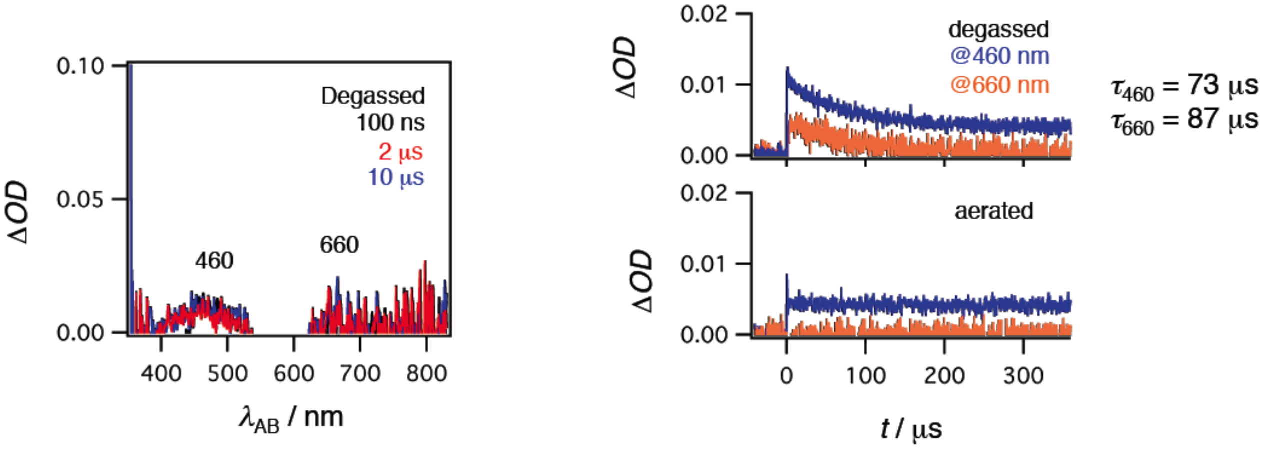


Figure S17. Transient absorption spectra of **3**·**5** (n-hexane, 1.0×10^{-5} M, λ_{ex} = 355 nm, rt).

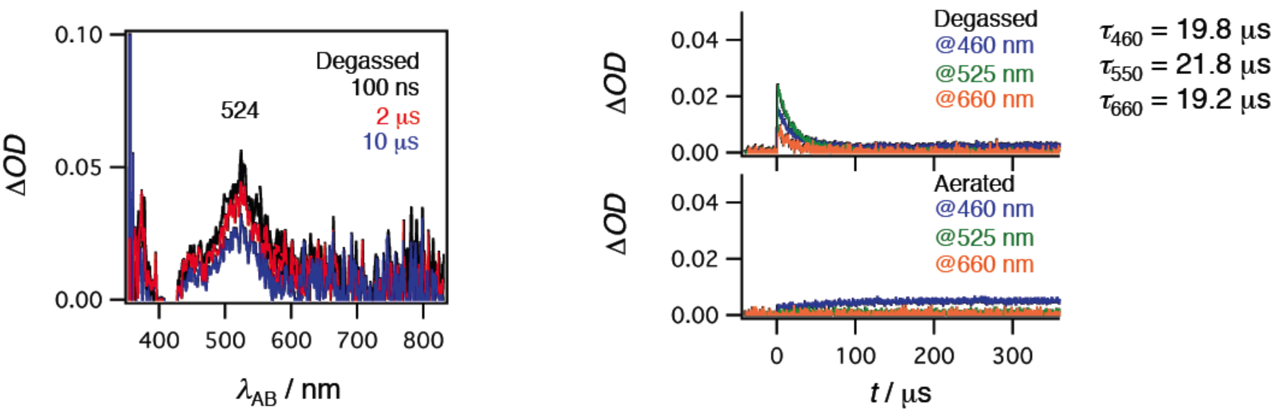


Figure S18. Transient absorption spectra of **5** (n-hexane, 1.0×10^{-5} M, λ_{ex} = 355 nm, rt).

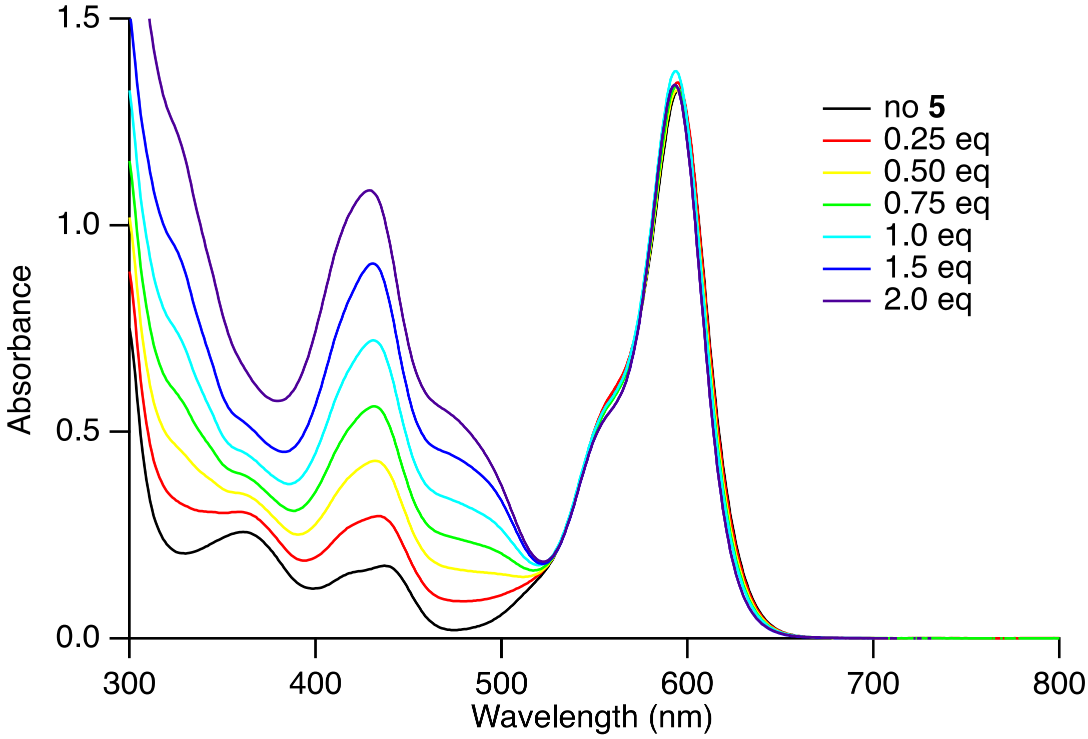


Figure S19. UV−vis spectroscopic titration of **4** with the addition of **5** (*n*-hexane, [**4**] = 2.0×10^{-5} M).

(5) Computational details

The geometry optimization and time-dependent calculation of **3** and **5**·pyridine were performed at the RM06-2X[S1]/6-31G(d,p) level using Gaussian09 program.[S2] Coordinates for the optimized structures were shown in Table S1–S2.

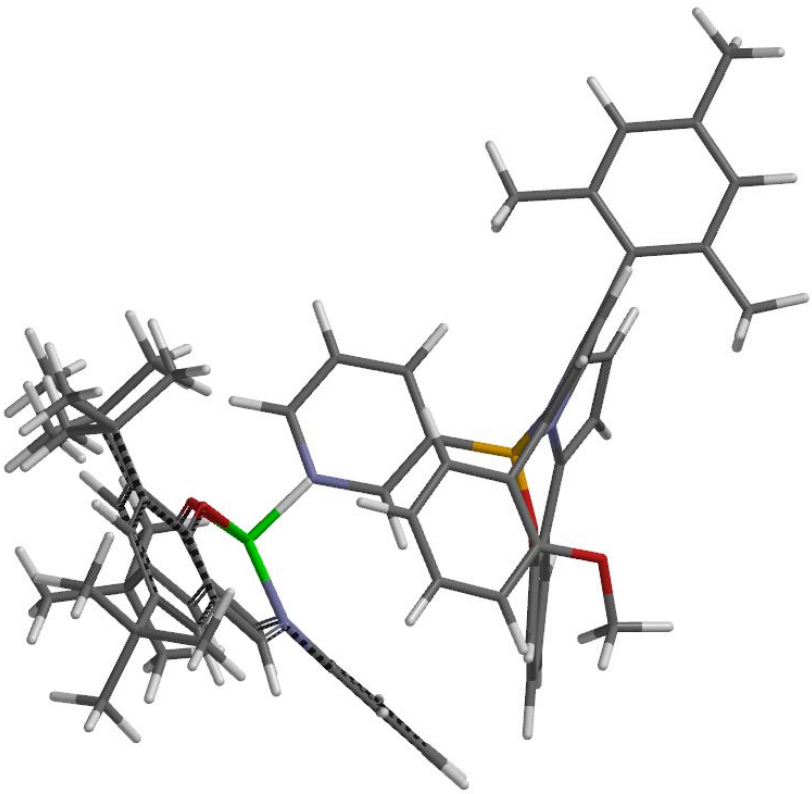


Figure S20. Model structure of **3**·**5**.

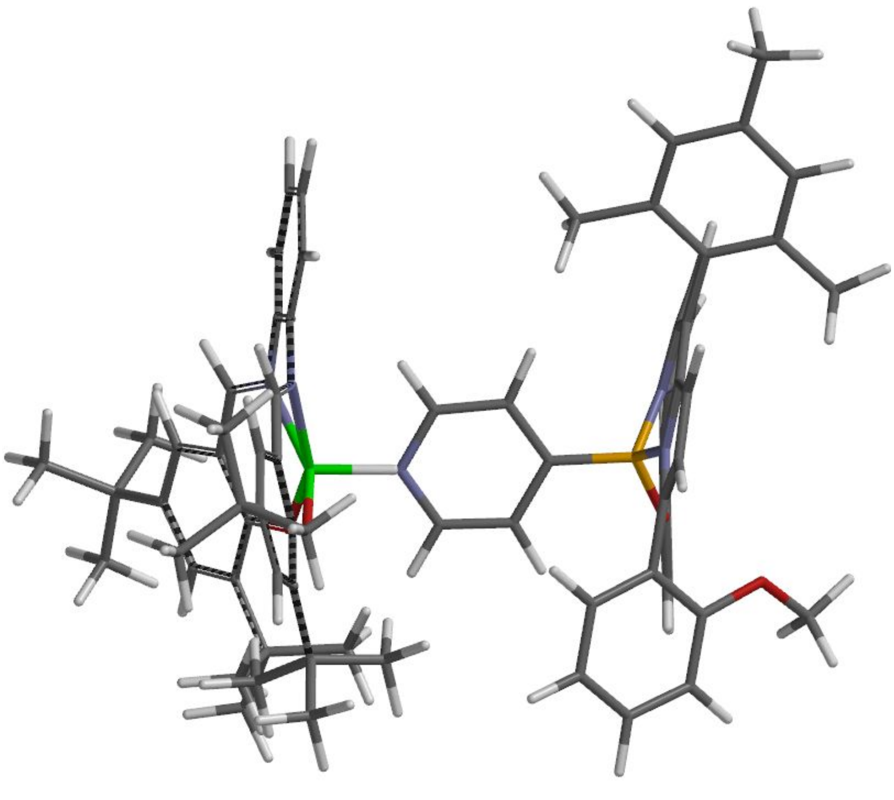


Figure S21. Model structure of **4**·**5**.

Table S1. Coordinates of the optimized **3**.

Center Number	Atom	Coordinates (Angstroms) X	Y	Z
1	C	-0.518236	-2.269984	-0.412814
2	C	0.566183	-3.176175	-0.438239
3	H	0.469887	-4.247312	-0.538924
4	C	1.723850	-2.425949	-0.345798
5	H	2.749110	-2.771057	-0.347181
6	C	1.333410	-1.068672	-0.262677
7	C	2.140139	0.073221	-0.146995
8	C	1.544701	1.331899	-0.077653
9	C	2.051278	2.655949	-0.190090
10	H	3.100136	2.914830	-0.241201
11	C	0.963201	3.503339	-0.276839
12	H	0.977306	4.574848	-0.411793
13	C	-0.205137	2.688720	-0.207475
14	C	-1.960948	-2.568305	-0.433199
15	C	-2.759108	-2.093041	-1.489019
16	C	-4.143119	-2.257922	-1.438233
17	H	-4.772278	-1.877070	-2.234026
18	C	-4.717248	-2.933750	-0.361724
19	H	-5.795519	-3.055185	-0.330803
20	C	-3.931288	-3.453843	0.659597
21	H	-4.386442	-3.971496	1.495913
22	C	-2.552230	-3.266226	0.616788
23	H	-1.922274	-3.614694	1.429914
24	C	-1.625041	2.955724	-0.359519
25	C	-2.466183	1.851155	-0.645907
26	C	-3.824751	2.076018	-0.887268
27	H	-4.457032	1.214253	-1.078518
28	C	-4.340433	3.363392	-0.845539
29	H	-5.400243	3.518691	-1.021698
30	C	-3.515604	4.455872	-0.563388
31	H	-3.927373	5.458045	-0.525001
32	C	-2.166906	4.245466	-0.325479
33	H	-1.512145	5.082855	-0.100831
34	F	-1.996111	0.592913	-0.730746
35	N	-0.059768	-1.011367	-0.318422
36	N	0.169957	1.416705	-0.066015
37	B	-0.851373	0.268947	0.125315
38	C	3.623975	-0.058828	-0.157059
39	C	4.326313	-0.058196	1.057060
40	C	5.713947	-0.190937	1.025858
41	H	6.262888	-0.200938	1.964874
42	C	6.411498	-0.313886	-0.174546
43	C	5.687362	-0.310438	-1.366256
44	H	6.216171	-0.408992	-2.311796
45	C	4.299069	-0.186363	-1.381497
46	C	3.594684	0.071343	2.369043
47	H	4.277962	-0.058994	3.210357
48	H	2.798956	-0.676517	2.450762
49	H	3.124111	1.056244	2.459640
50	C	7.914598	-0.421705	-0.188041
51	H	8.258541	-1.048298	-1.014589
52	H	8.289766	-0.847908	0.745215
53	H	8.373601	0.564953	-0.309569
54	C	3.540847	-0.190393	-2.684948
55	H	2.880323	0.679195	-2.757243
56	H	2.909187	-1.080145	-2.770404
57	H	4.227922	-0.173796	-3.532949
58	C	-1.297228	0.108438	1.669888
59	C	-2.607789	-0.253934	2.006778
60	H	-3.343847	-0.386741	1.212940
61	N	-3.052074	-0.464445	3.249404
62	C	-2.172618	-0.307724	4.240621
63	H	-2.549679	-0.480422	5.247217
64	C	-0.844331	0.058769	4.041333
65	H	-0.176298	0.179370	4.888042
66	C	-0.410161	0.266797	2.736726
67	H	0.621524	0.562106	2.545928
68	F	-2.093159	-1.522282	-2.517285
69	C	-2.830900	-0.716447	-3.409556
70	H	-3.386558	0.054557	-2.865220
71	H	-3.519095	-1.315964	-4.017741
72	H	-2.099169	-0.240764	-4.062018

Table S2. Coordinates of the optimized **5**·pyridine.

Center Number	Atom	Coordinates (Angstroms) X	Y	Z
1	C	4.901261	-1.461082	-0.512029
2	C	3.346308	0.820029	-0.397637
3	C	3.651270	-1.569437	0.071216
4	C	5.435892	-0.264938	-1.046014
5	C	4.631574	0.850228	-0.981351
6	C	2.830059	-0.394111	0.162487
7	H	4.977301	1.798968	-1.390469
8	C	2.602646	2.044581	-0.424808
9	H	3.125977	2.894364	-0.881726
10	N	1.388401	2.222227	-0.004548
11	C	0.773815	3.485578	-0.051280
12	C	-0.634167	5.901179	-0.045997
13	C	-0.639304	3.484149	-0.122689
14	C	1.455964	4.700794	0.032274
15	C	0.757053	5.902623	0.020015
16	C	-1.328280	4.697781	-0.103149
17	H	2.535537	4.702998	0.142755
18	H	-2.413416	4.701809	-0.108271
19	N	-1.238082	2.212149	-0.168589
20	C	-2.417411	2.026922	-0.668987
21	H	-2.970544	2.890888	-1.059227
22	C	-3.101065	0.769639	-0.779369
23	C	-4.588870	-1.537447	-1.054997
24	C	-2.444486	-0.493180	-0.607640
25	C	-4.474410	0.833000	-1.124139
26	C	-5.243824	-0.295290	-1.258680
27	C	-3.251831	-1.681681	-0.751075
28	H	-4.907459	1.819933	-1.266880
29	F	-1.183702	-0.600713	-0.355780
30	F	1.677439	-0.447481	0.745051
31	H	-1.182196	6.837190	-0.028041
32	H	1.298379	6.840068	0.091173
33	H	-5.190933	-2.435636	-1.151294
34	H	5.512176	-2.353420	-0.567760
35	Zn	0.065729	0.653085	0.483182
36	N	-0.544065	0.398871	2.478312
37	C	-1.402531	-0.263059	5.023719
38	C	0.343367	0.082104	3.427497
39	C	-1.850515	0.381869	2.766916

40	C	-2.323491	0.056552	4.030974
41	C	-0.045630	-0.251090	4.718820
42	H	1.382521	0.081633	3.111337
43	H	-2.525059	0.626320	1.949098
44	H	-3.389491	0.048605	4.224617
45	H	0.703033	-0.502239	5.460918
46	H	-1.739179	-0.524781	6.021752
47	C	3.112670	-2.907162	0.595407
48	C	-2.605062	-3.057997	-0.555951
49	C	6.824940	-0.186249	-1.688349
50	C	-6.732494	-0.279349	-1.605040
51	C	-7.531012	-0.946246	-0.472292
52	H	-7.384557	-0.409293	0.470021
53	H	-7.221344	-1.984374	-0.319338
54	H	-8.600925	-0.946272	-0.707663
55	C	-6.966297	-1.052871	-2.913622
56	H	-6.414677	-0.590725	-3.737838
57	H	-8.031626	-1.056171	-3.169069
58	H	-6.638000	-2.093014	-2.830862
59	C	-7.259009	1.146740	-1.789943
60	H	-6.737879	1.663327	-2.602235
61	H	-7.145671	1.736891	-0.874720
62	H	-8.323874	1.117894	-2.040197
63	C	-3.627123	-4.192724	-0.695470
64	H	-3.120690	-5.151214	-0.547691
65	H	-4.084577	-4.209620	-1.690318
66	H	-4.424022	-4.116583	0.052404
67	C	-1.516114	-3.274557	-1.623174
68	H	-1.025562	-4.241987	-1.463764
69	H	-0.761743	-2.488858	-1.578236
70	H	-1.962797	-3.279884	-2.623184
71	C	-1.991543	-3.162778	0.853979
72	H	-1.563119	-4.161374	0.996341
73	H	-2.763680	-3.013071	1.617373
74	H	-1.202144	-2.424952	1.000542
75	C	2.816879	-2.814728	2.104005
76	H	3.715228	-2.515783	2.655001
77	H	2.498099	-3.793889	2.479053
78	H	2.023048	-2.092897	2.297828
79	C	4.118677	-4.046176	0.391005
80	H	4.355008	-4.194819	-0.667730
81	H	3.686680	-4.977944	0.768322
82	H	5.053393	-3.867759	0.933577
83	C	1.821812	-3.277412	-0.159361
84	H	2.023912	-3.400082	-1.228907
85	H	1.057776	-2.508452	-0.034815
86	H	1.426305	-4.226795	0.221620
87	C	7.567892	-1.525035	-1.625767
88	H	8.556212	-1.416212	-2.083059
89	H	7.033224	-2.310019	-2.169784
90	H	7.710737	-1.858011	-0.592633
91	C	7.673846	0.865805	-0.955809
92	H	8.670285	0.933874	-1.406160
93	H	7.788919	0.603317	0.100206
94	H	7.214665	1.857285	-1.008316
95	C	6.684920	0.217474	-3.165473
96	H	7.670447	0.281396	-3.640157
97	H	6.197744	1.191667	-3.267459
98	H	6.084793	-0.516700	-3.711320

(6) References

(S1) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(S2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *GAUSSIAN 09, Revision A.02*, Gaussian, Inc., Wallingford CT, **2009**.