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Supporting Information

Coherent internal conversion from high lying electronic states to S_1 in boron-dipyrromethene derivatives

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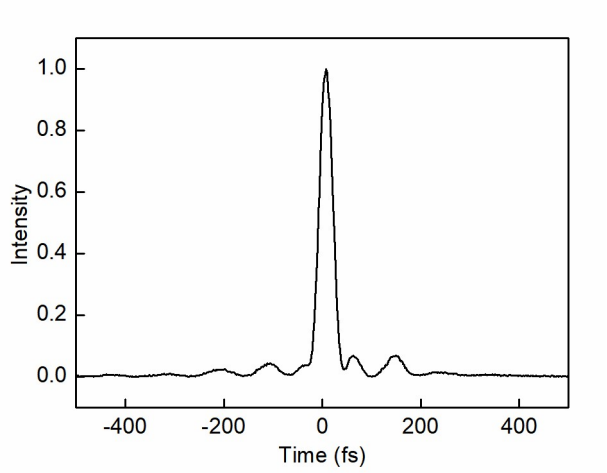

Figure S1. Instrumental response function of the TF apparatus with excitation at 550 nm.

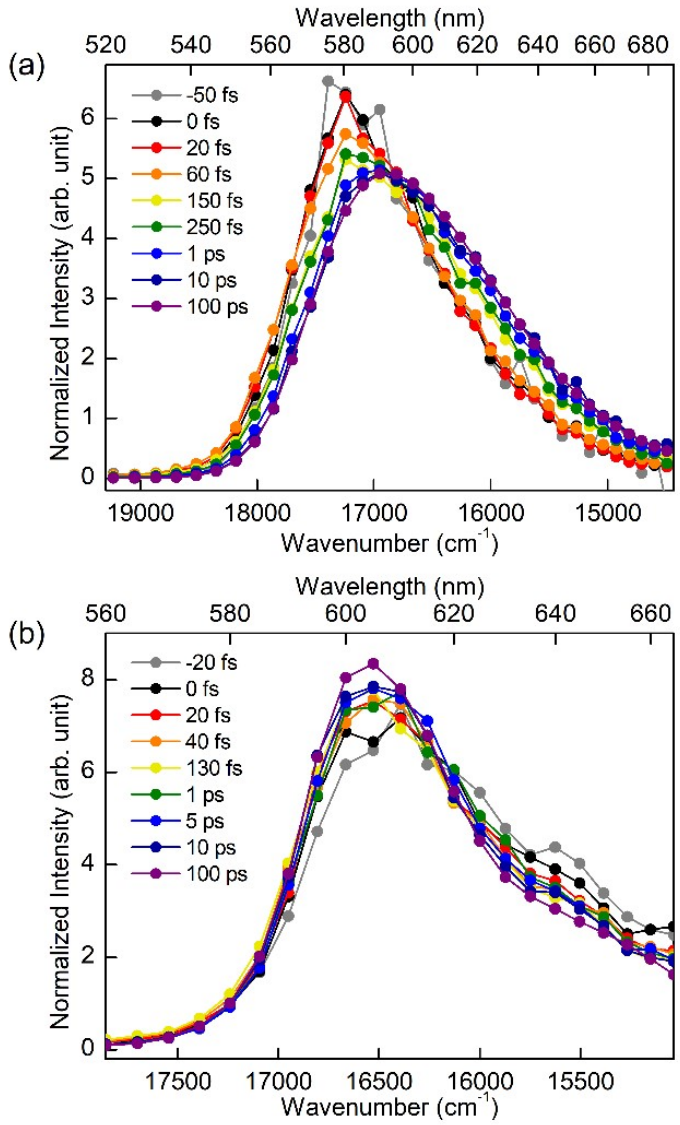

Figure S2. Area normalized time-resolved fluorescence spectra of (a) PM597 and (b) PM650.

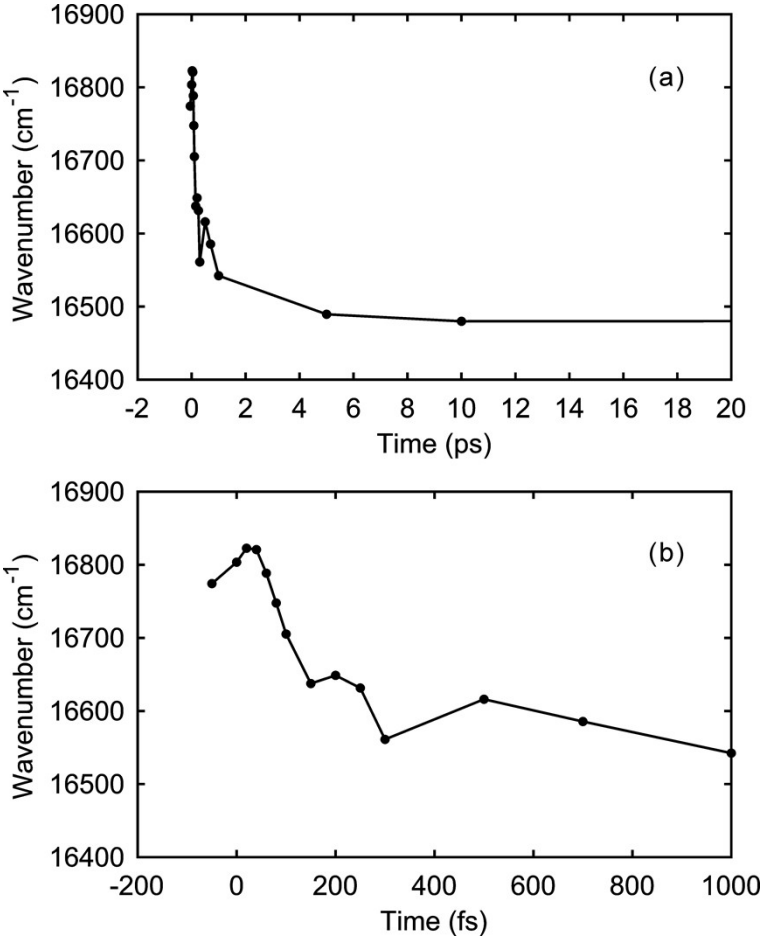

Figure S3. First moment of time-resolved fluorescence spectra of PM597 vs. time. (a) From -2 to 20 ps; (b) from -200 to 1000 fs. Note that the modulation of the first moment is not a noise but oscillations due to the nuclear wave packet motions (see I. Eom and T. Joo, *J. Chem. Phys.* **2009**, *113*, 244507)

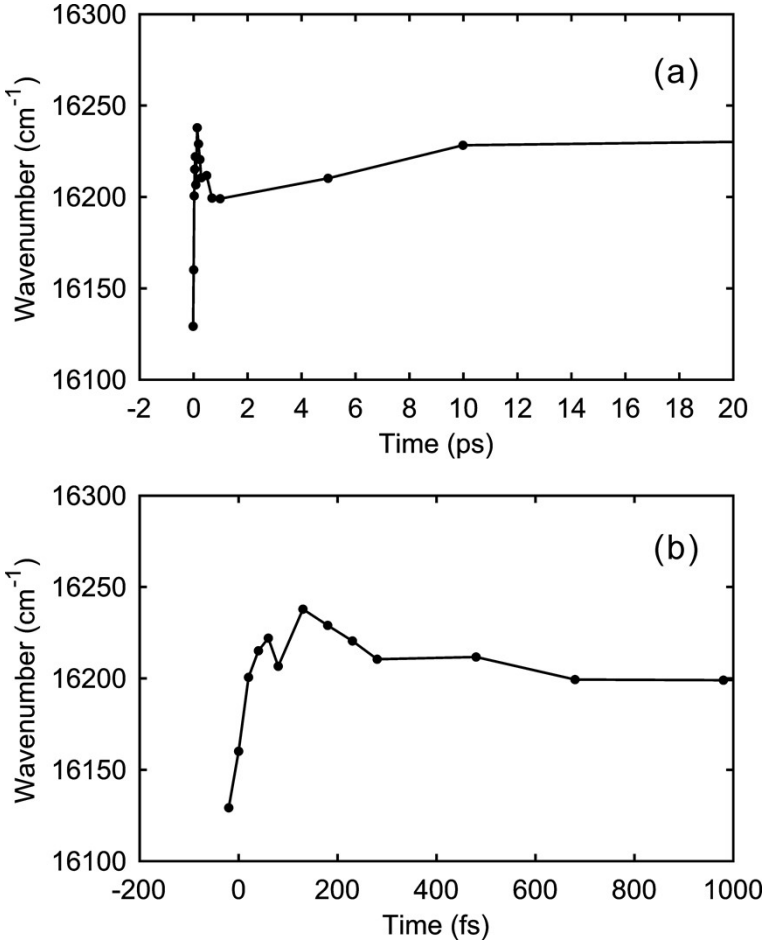

Figure S4. First moment of time-resolved fluorescence spectra of PM650 vs. time. (a) From -2 to 20 ps; (b) from -200 to 1000 fs.

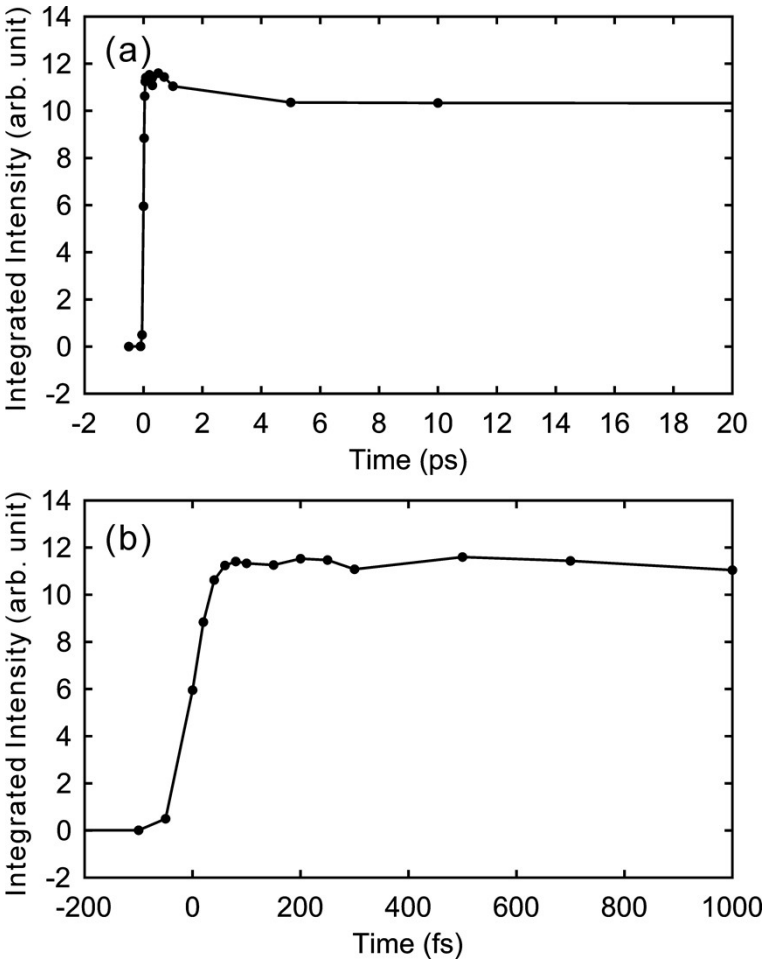

Figure S5. Area of time-resolved fluorescence spectra of PM597 in two different time ranges.

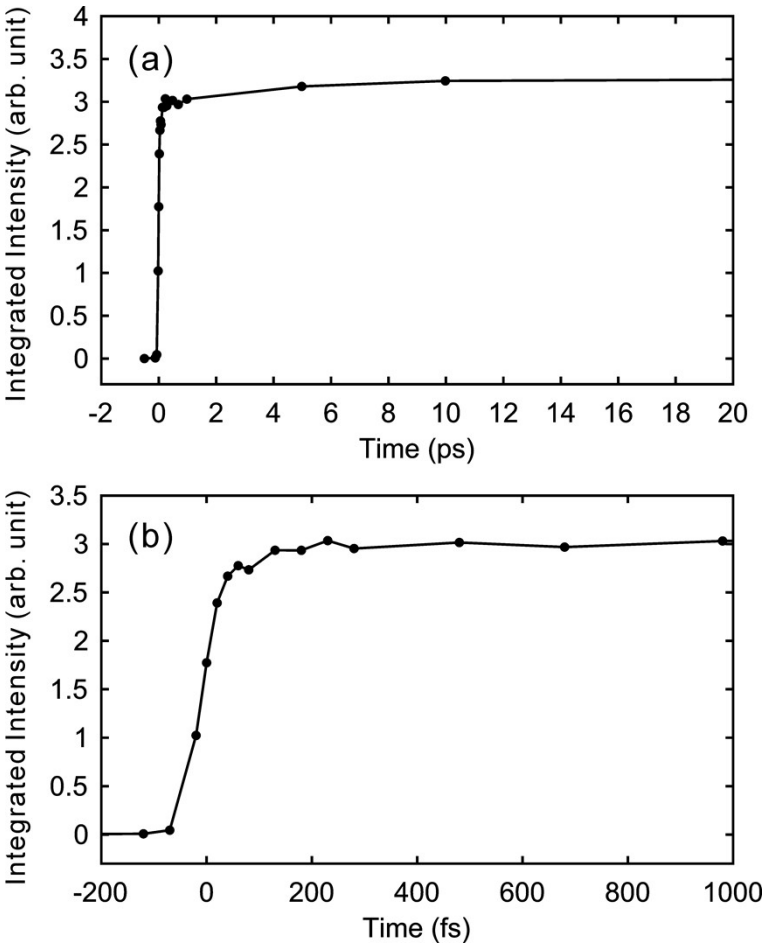

Figure S6. Area of time-resolved fluorescence spectra of PM650 in two different time ranges.

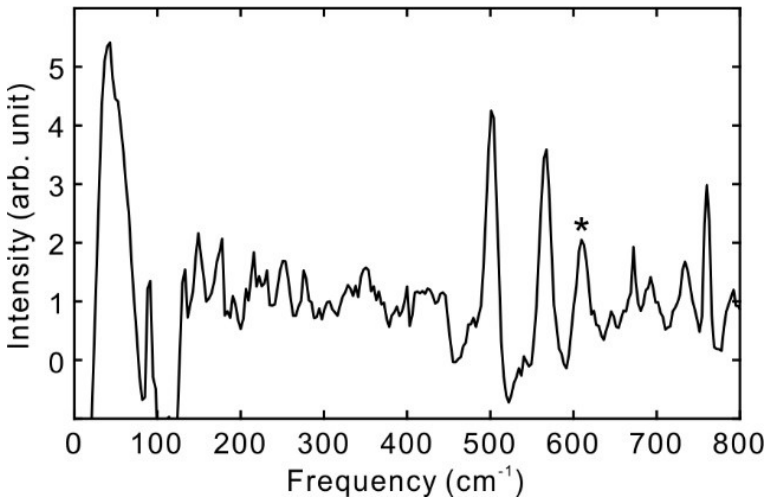

Figure S7. Raman spectrum of PM597 in benzene measured by 632.8 nm excitation. Because of the strong fluorescence of PM597, only the two peaks at 503 and 567 cm^{-1} are observed. * represents the Raman peak of benzene at 609 cm^{-1}. Raman spectrum of PM650 could not be obtained because of the much stronger fluorescence.

Table S1. Vertical transition wavelengths of PM597 and PM650 calculated by TDDFT method using CAM-B3LYP/6-31+G(d,p).

	PM597		PM650	
	Wavelength (nm)[a)]	Osc. Strength[a)]	Wavelength (nm)	Osc. strength
S_1	473 (486)	0.596 (0.453)	496	0.466
S_2	341 (393)	0.077 (0.191)	386	0.125
S_3	319 (378)	0.046 (0.036)	362	0.040

[a)] Numbers in parentheses were calculated by B3LYP/6-31+G(d,p).

Table S2. Vibrational reorganization energies (λ_i) and Huang-Rhys factors (HRF) for transition from the ground to S_1 states of PM597 and PM650 calculated by TDDFT method using CAM-B3LYP/6-31+G(d,p). Total vibrational reorganization energies ($\Sigma\lambda_i$) are 616 and 512 cm^{-1} for PM597 and PM650, respectively.

PM597			PM650		
Freq (cm^{-1})	λ_i (cm^{-1})	HRF	Freq (cm^{-1})	λ_i (cm^{-1})	HRF
24	32.3	1.34583	23	0.0	0.00000
30	0	0.00000	49	0.0	0.00000
38	3.6	0.09474	54	0.0	0.00000
54	0	0.00000	73	0.0	0.00000
66	10	0.15152	74	0.0	0.00000
69	0	0.00000	75	0.0	0.00000
83	8.6	0.10361	95	0.0	0.00000
126	13	0.10317	108	0.0	0.00000
135	1.4	0.01037	118	0.0	0.00000
143	0	0.00000	144	0.0	0.00000
158	58.9	0.37278	150	0.0	0.00000
170	0	0.00000	152	0.0	0.00000
182	0	0.00000	153	21.3	0.13901
188	7.3	0.03883	153	0.2	0.00137
197	0	0.00000	171	0.0	0.00000
204	0.7	0.00343	226	0.0	0.00000
220	0	0.00000	244	0.0	0.00000
222	6.6	0.02973	247	31.7	0.12848
232	1.8	0.00776	257	0.0	0.00000
237	0	0.00000	270	0.0	0.00000
241	0	0.00000	284	0.0	0.00000
250	6.3	0.02520	292	20.0	0.06869
261	0	0.00000	306	2.9	0.00932
274	2.4	0.00876	313	0.0	0.00000
279	0	0.00000	322	0.0	0.00000
286	1.8	0.00629	348	0.0	0.00000
299	6.8	0.02274	371	11.6	0.03131
299	0	0.00000	389	0.0	0.00000
317	0	0.00000	406	0.0	0.00000
320	33	0.10313	425	39.1	0.09180
321	0	0.00000	472	0.0	0.00000
330	0.2	0.00061	485	0.0	0.00000
337	0	0.00000	539	0.0	0.00000
346	0	0.00000	546	0.0	0.00001
356	0	0.00000	546	5.6	0.01027

365	3.5	0.00959	554	33.3	0.06010
369	0	0.00000	555	0.0	0.00000
388	3.1	0.00799	649	1.1	0.00175
392	0	0.00000	674	0.0	0.00000
400	3.7	0.00925	676	0.0	0.00000
404	0	0.00000	694	0.0	0.00000
425	3	0.00706	699	0.0	0.00000
440	0	0.00000	721	0.0	0.00000
447	0.6	0.00134	789	0.6	0.00072
456	9	0.01974	794	0.0	0.00000
491	0	0.00000	831	1.3	0.00158
504	60	0.11905	868	0.0	0.00000
534	2	0.00375	953	0.0	0.00000
559	0.3	0.00054	955	4.2	0.00435
562	0	0.00000	992	0.0	0.00000
565	58.2	0.10301	1045	0.0	0.00000
593	0	0.00000	1048	0.0	0.00000
625	0	0.00000	1049	0.5	0.00047
680	0.1	0.00015	1054	3.5	0.00328
698	0	0.00000	1063	0.0	0.00000
702	4.7	0.00670	1066	0.0	0.00000
727	0.4	0.00055	1079	0.0	0.00000
730	0	0.00000	1080	0.0	0.00000
737	0.1	0.00014	1091	0.0	0.00000
763	0	0.00000	1098	0.0	0.00000
834	0	0.00000	1123	4.1	0.00363
853	0	0.00000	1128	0.0	0.00000
865	4.8	0.00555	1129	14.2	0.01262
896	0	0.00000	1155	0.0	0.00000
929	0	0.00000	1186	0.2	0.00020
950	0	0.00000	1262	0.0	0.00000
950	0	0.00000	1273	115.5	0.09077
959	0	0.00000	1330	0.0	0.00000
960	0	0.00000	1356	0.0	0.00000
977	0	0.00000	1380	9.6	0.00698
977	0	0.00000	1434	0.0	0.00000
1006	7.7	0.00765	1441	7.7	0.00532
1018	0	0.00000	1448	0.0	0.00000
1044	0	0.00000	1451	0.0	0.00000
1045	0.3	0.00029	1453	2.5	0.00170
1053	1.9	0.00180	1454	1.6	0.00108
1054	0	0.00000	1466	0.0	0.00000
1059	0	0.00000	1477	4.0	0.00269
1061	2.3	0.00217	1494	0.0	0.00000
1066	0.7	0.00066	1495	0.0	0.00000

1068	0	0.00000	1496	0.0	0.00000
1073	0	0.00000	1498	105.5	0.07041
1074	0	0.00000	1504	11.8	0.00782
1084	0	0.00000	1508	0.0	0.00000
1089	4.1	0.00376	1508	0.0	0.00000
1095	6	0.00548	1508	0.0	0.00000
1111	0	0.00000	1519	0.1	0.00008
1123	20.8	0.01852	1521	0.0	0.00000
1145	1.1	0.00096	1524	0.0	0.00000
1158	0	0.00000	1524	0.0	0.00000
1236	0	0.00000	1531	12.5	0.00815
1238	81.7	0.06599	1554	0.0	0.00000
1249	1.4	0.00112	1558	8.4	0.00541
1250	0	0.00000	1576	0.0	0.00000
1257	0	0.00000	1592	0.6	0.00037
1257	0	0.00000	2336	33.6	0.01436
1277	0	0.00000	3064	0.0	0.00000
1287	1.1	0.00085	3064	0.1	0.00002
1329	0	0.00000	3072	2.8	0.00092
1387	0	0.00000	3072	0.0	0.00000
1396	2.3	0.00165	3081	0.0	0.00000
1429	0	0.00000	3081	0.2	0.00006
1432	0.9	0.00063	3111	0.0	0.00000
1433	0	0.00000	3111	0.0	0.00000
1433	0.2	0.00014	3121	0.0	0.00000
1436	0	0.00000	3123	0.0	0.00000
1442	0.8	0.00055	3137	0.0	0.00000
1443	0	0.00000	3137	0.0	0.00000
1445	5.5	0.00381	3160	0.0	0.00000
1452	0.1	0.00007	3161	0.0	0.00000
1454	0	0.00000	3166	0.0	0.00000
1458	8.8	0.00604	3166	0.0	0.00000
1467	0	0.00000	3183	0.0	0.00000
1467	1.1	0.00075	3183	0.2	0.00008
1478	0	0.00000			
1484	40.2	0.02709			
1489	40.5	0.02720			
1504	0	0.00000			
1505	0.2	0.00013			
1509	6.4	0.00424			
1510	0	0.00000			
1513	0	0.00000			
1518	0.2	0.00013			
1519	0	0.00000			
1520	0.1	0.00007			

1520	0	0.00000
1521	0	0.00000
1531	2.3	0.00150
1531	0	0.00000
1532	0	0.00000
1536	1.5	0.00098
1540	0	0.00000
1542	2.2	0.00143
1543	0	0.00000
1545	1.7	0.00110
1553	0	0.00000
1554	0.1	0.00006
1556	0	0.00000
1565	0.5	0.00032
1568	0	0.00000
1574	6.1	0.00388
3055	3.3	0.00108
3067	0.4	0.00013
3067	0	0.00000
3069	0	0.00000
3069	0.1	0.00003
3073	0	0.00000
3073	1.1	0.00036
3076	0	0.00000
3076	6.6	0.00215
3085	0	0.00000
3085	2.8	0.00091
3119	1	0.00032
3131	0	0.00000
3131	0	0.00000
3132	0	0.00000
3133	0	0.00000
3143	0	0.00000
3143	0	0.00000
3146	0	0.00000
3147	1	0.00032
3149	0	0.00000
3150	0	0.00000
3154	0	0.00000
3163	0	0.00000
3163	0	0.00000
3176	0.6	0.00019
3176	0	0.00000
3186	0	0.00000
3186	0	0.00000

3193	0	0.00000	
3193	0	0.00000	
3212	0	0.00000	
3213	0.1	0.00003	
	$\sum\lambda i = 616$		$\sum\lambda i = 512$

Table S3. Phases of the oscillations obtained by LPSVD analyses of the time-resolved fluorescence signals acquired by excitation of either S_2 or direct S_1 states. Fluorescence was detected at 650 nm for both dyes in the direct excitation of S_1 state. For the S_2 excitation, fluorescence was detected at 630 and 652 nm for PM597 and PM650, respectively.

PM597			PM650		
Freq (cm^{-1})	Phase (deg.)		Freq (cm^{-1})	Phase (deg.)	
	S_1	S_2		S_1	S_2
93	160	120	152	240	200
139	230	210	292	140	130
			412	170	220
			548	230	200

Table S4. Geometry of the S_0 state of PM597 calculated by DFT method using CAM-B3LYP/6-31+G(d,p).

Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.221496	0.827483	0.048589
2	6	1.221525	0.827448	0.048553
3	6	0.000021	1.518881	-0.026428
4	6	-2.577430	1.277758	0.072221
5	6	-3.397144	0.142400	0.013235
6	6	-2.516440	-0.977866	0.029874
7	7	1.244308	-0.559813	0.059544
8	7	-1.244328	-0.559772	0.059584
9	5	-0.000025	-1.475031	0.091279
10	6	2.577483	1.277661	0.072133
11	6	3.397140	0.142279	0.013160
12	6	2.516402	-0.977962	0.029769
13	6	4.925736	0.026906	-0.079547
14	6	-4.925741	0.026954	-0.079575
15	6	5.638304	1.361426	-0.368442
16	1	5.662643	2.027392	0.496327
17	1	6.680479	1.152453	-0.632112
18	1	5.186795	1.895472	-1.209943
19	6	5.507738	-0.524932	1.236427
20	1	5.117417	-1.514369	1.486245
21	1	6.599022	-0.605153	1.165615
22	1	5.271101	0.142931	2.071552
23	6	5.305975	-0.896322	-1.257827
24	1	4.911920	-1.907326	-1.162925
25	1	4.937829	-0.481763	-2.202612
26	1	6.396707	-0.975778	-1.327640
27	6	-5.638511	1.361402	-0.368295
28	1	-6.680488	1.152239	-0.632600
29	1	-5.663518	2.027003	0.496728
30	1	-5.186709	1.895915	-1.209343
31	6	-5.507753	-0.525229	1.236248
32	1	-6.599019	-0.605605	1.165346
33	1	-5.117290	-1.514659	1.485887
34	1	-5.271272	0.142500	2.071524
35	6	-5.305818	-0.896102	-1.258037
36	1	-4.937595	-0.481376	-2.202718
37	1	-4.911726	-1.907103	-1.163254
38	1	-6.396540	-0.975595	-1.327972
39	9	-0.000019	-2.229891	1.275132
40	9	-0.000056	-2.332162	-1.012720
41	6	-2.807858	-2.447176	0.022488
42	1	-2.786766	-2.842206	-0.999149
43	1	-2.049854	-2.984320	0.592743
44	1	-3.781911	-2.670085	0.454717
45	6	2.807746	-2.447287	0.022314
46	1	2.049745	-2.984414	0.592589
47	1	2.786575	-2.842278	-0.999337
48	1	3.781811	-2.670268	0.454475
49	6	2.991858	2.708770	0.283966
50	1	3.175690	3.247247	-0.653991

51	1	2.231765	3.259000	0.837831
52	1	3.903359	2.767426	0.873803
53	6	0.000015	2.999523	-0.314684
54	1	0.000059	3.603361	0.600245
55	1	0.876077	3.278167	-0.896697
56	1	-0.876107	3.278170	-0.896606
57	6	-2.991637	2.708914	0.284074
58	1	-2.231353	3.259096	0.837731
59	1	-3.175625	3.247364	-0.653868
60	1	-3.902980	2.767704	0.874126

Table S5. Geometry of the S_1 state of PM597 calculated by TDDFT method using CAM-B3LYP/6-31+G(d,p).

Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.216148	0.816135	-0.003970
2	6	1.216150	0.816130	-0.003971
3	6	0.000003	1.529403	-0.174324
4	6	-2.564383	1.276086	0.104435
5	6	-3.390507	0.142002	0.050567
6	6	-2.516033	-0.994087	0.022353
7	7	1.235815	-0.581623	0.002575
8	7	-1.235817	-0.581619	0.002577
9	5	-0.000003	-1.498801	-0.012325
10	6	2.564387	1.276078	0.104425
11	6	3.390507	0.141990	0.050567
12	6	2.516030	-0.994097	0.022351
13	6	4.916287	0.047836	0.000521
14	6	-4.916287	0.047841	0.000517
15	6	5.602834	1.407385	-0.214726
16	1	5.519982	2.064946	0.652212
17	1	6.671138	1.240036	-0.388638
18	1	5.203889	1.930536	-1.088834
19	6	5.461141	-0.540327	1.318349
20	1	5.076198	-1.541737	1.524064
21	1	6.555087	-0.604364	1.277578
22	1	5.190875	0.098165	2.165948
23	6	5.348934	-0.829662	-1.194905
24	1	4.966482	-1.848987	-1.147063
25	1	5.005675	-0.388482	-2.136784
26	1	6.442790	-0.889866	-1.230578
27	6	-5.602850	1.407380	-0.214743
28	1	-6.671147	1.240013	-0.388683
29	1	-5.520032	2.064939	0.652198
30	1	-5.203891	1.930540	-1.088840
31	6	-5.461141	-0.540320	1.318346
32	1	-6.555086	-0.604368	1.277571
33	1	-5.076187	-1.541725	1.524068
34	1	-5.190885	0.098180	2.165943
35	6	-5.348923	-0.829670	-1.194902
36	1	-5.005662	-0.388496	-2.136783
37	1	-4.966463	-1.848992	-1.147050
38	1	-6.442778	-0.889883	-1.230580

39	9	-0.000003	-2.315827	1.135143
40	9	-0.000005	-2.314915	-1.150785
41	6	-2.813689	-2.456329	0.011644
42	1	-2.722211	-2.864475	-1.003574
43	1	-2.087910	-2.989250	0.630189
44	1	-3.813189	-2.677192	0.380606
45	6	2.813679	-2.456340	0.011645
46	1	2.087897	-2.989256	0.630191
47	1	2.722199	-2.864488	-1.003572
48	1	3.813177	-2.677208	0.380609
49	6	2.924306	2.708669	0.386269
50	1	3.307632	3.249422	-0.487079
51	1	2.054743	3.254003	0.753770
52	1	3.683613	2.776142	1.167386
53	6	0.000007	2.941192	-0.691745
54	1	0.000007	3.714168	0.087101
55	1	0.882254	3.112813	-1.314602
56	1	-0.882234	3.112817	-1.314607
57	6	-2.924292	2.708677	0.386297
58	1	-2.054723	3.254003	0.753794
59	1	-3.307624	3.249440	-0.487042
60	1	-3.683589	2.776148	1.167424

Table S6. Geometry of the S_0 state of PM650 calculated by DFT method using CAM-B3LYP/6-31+G(d,p).

Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.225047	0.681922	0.000001
2	6	1.225047	0.681919	0.000002
3	6	0.000002	1.352524	-0.000012
4	6	-2.570977	1.151322	-0.000004
5	6	-3.381300	0.022709	-0.000035
6	6	-2.527072	-1.108212	-0.000007
7	7	1.246352	-0.706481	0.000063
8	7	-1.246355	-0.706478	0.000029
9	5	-0.000004	-1.629559	0.000077
10	6	2.570978	1.151316	-0.000007
11	6	3.381299	0.022702	-0.000001
12	6	2.527067	-1.108219	0.000027
13	9	-0.000028	-2.432797	1.143290
14	9	0.000019	-2.432877	-1.143073
15	6	-2.892087	-2.552769	-0.000019
16	1	-2.475852	-3.054079	-0.879141
17	1	-2.475750	-3.054120	0.879027
18	1	-3.974683	-2.684645	0.000040
19	6	2.892080	-2.552776	-0.000014
20	1	2.475458	-3.054223	0.878840
21	1	2.476129	-3.053988	-0.879327
22	1	3.974675	-2.684653	0.000370
23	6	3.049061	2.569038	-0.000050
24	1	2.699006	3.120266	-0.878447
25	1	2.699129	3.120280	0.878388
26	1	4.141010	2.598822	-0.000131
27	6	-3.049060	2.569045	0.000003
28	1	-2.698997	3.120301	0.878378
29	1	-2.699138	3.120258	-0.878457
30	1	-4.141009	2.598826	0.000094
31	6	-4.880916	0.007567	-0.000065
32	1	-5.289878	0.511216	0.882937
33	1	-5.289838	0.511856	-0.882715
34	1	-5.272772	-1.011733	-0.000449
35	6	4.880914	0.007556	-0.000048
36	1	5.289832	0.511118	-0.883120
37	1	5.289884	0.511929	0.882532
38	1	5.272767	-1.011746	0.000412
39	6	0.000006	2.788139	-0.000046
40	7	0.000025	3.944456	-0.000080

Table S7. Geometry of the S_1 state of PM650 calculated by TDDFT method using CAM-B3LYP/6-31+G(d,p).

Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.228646	0.696586	0.000002
2	6	1.228645	0.696581	0.000002
3	6	0.000002	1.408303	-0.000009
4	6	-2.570743	1.153775	0.000003
5	6	-3.373920	0.011600	-0.000024
6	6	-2.510915	-1.123688	-0.000017
7	7	1.234408	-0.705943	0.000055
8	7	-1.234412	-0.705938	0.000003
9	5	-0.000004	-1.627529	0.000038
10	6	2.570743	1.153766	-0.000016
11	6	3.373918	0.011590	0.000022
12	6	2.510909	-1.123696	0.000054
13	9	-0.000037	-2.439344	1.141257
14	9	0.000025	-2.439374	-1.141152
15	6	-2.863599	-2.566476	-0.000031
16	1	-2.439509	-3.068448	-0.877658
17	1	-2.439413	-3.068487	0.877525
18	1	-3.945015	-2.708989	0.000024
19	6	2.863592	-2.566484	0.000036
20	1	2.439157	-3.068562	0.877431
21	1	2.439748	-3.068388	-0.877752
22	1	3.945007	-2.708999	0.000373
23	6	3.052305	2.570476	-0.000067
24	1	2.704131	3.124208	-0.877960
25	1	2.704238	3.124239	0.877850
26	1	4.144762	2.597829	-0.000138
27	6	-3.052305	2.570484	0.000034
28	1	-2.704097	3.124241	0.877897
29	1	-2.704273	3.124223	-0.877913
30	1	-4.144762	2.597836	0.000146
31	6	-4.867346	-0.014981	-0.000026
32	1	-5.275795	0.493995	0.881465
33	1	-5.275798	0.494597	-0.881163
34	1	-5.256719	-1.034888	-0.000373
35	6	4.867344	-0.014995	-0.000002
36	1	5.275776	0.493892	-0.881553
37	1	5.275815	0.494670	0.881075
38	1	5.256714	-1.034902	0.000437
39	6	0.000007	2.823812	-0.000054
40	7	0.000033	3.985897	-0.000097