Cationic Axial Ligand Effects on Sulfur-Substituted Subphthalocyanines

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Supplementary Materials

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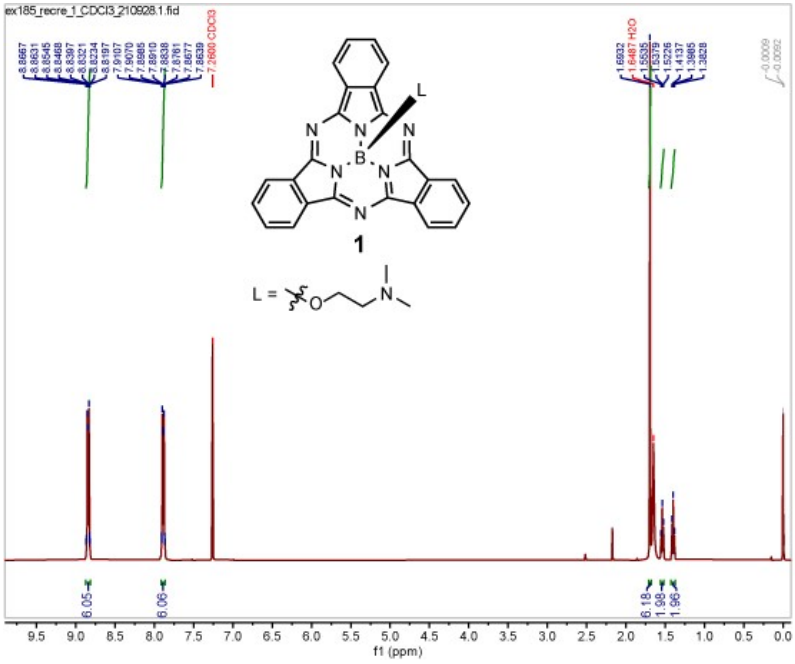
General Comments

Instrumentation

NMR spectra were obtained using JEOL ECA-500 or Bruker AVANCE 400 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H NMR spectra were referenced to the tetramethylsilane (TMS) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet, and brs = broad singlet. High-resolution mass spectra (HRMS) were recorded using a Bruker Daltonics solariX spectrometer (MALDI). Electronic absorption spectra were recorded on a JASCO V-770 spectrophotometer. Fluorescence spectra were obtained using a HITACHI F-4500 spectrofluorometer. Absolute fluorescence quantum yields (Φ_{PL}) were measured using a calibrated integrating sphere system (Quantaurus-QY Plus C13534-22, Hamamatsu photonics). Time-resolved photoluminescence lifetime (τ) measurements were carried out using a time-correlated single photon counting lifetime spectroscopy system (Quantaurus-Tau C11367-22, Hamamatsu photonics). The decay constants and fitting parameters for the transient decays were determined using the software embedded in the Quantaurus-Tau system. Cyclic voltammetry (CV) measurements were recorded using a Hokuto Denko HZ7000 potentiostat under a nitrogen atmosphere with 0.1 M of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Measurements were made using a glassy carbon electrode (area = 0.07 cm^2), an Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 0.5 mM, and the sweep rate was set to 100 mV/s. The ferrocenium/ferrocene (Fc^+/Fc) couple was used as an internal standard. Ionization potentials were determined from the onset of the photoelectron spectroscopy in air (AC-2, Riken Keiki).

Copies of the NMR Spectra of Studied Compounds



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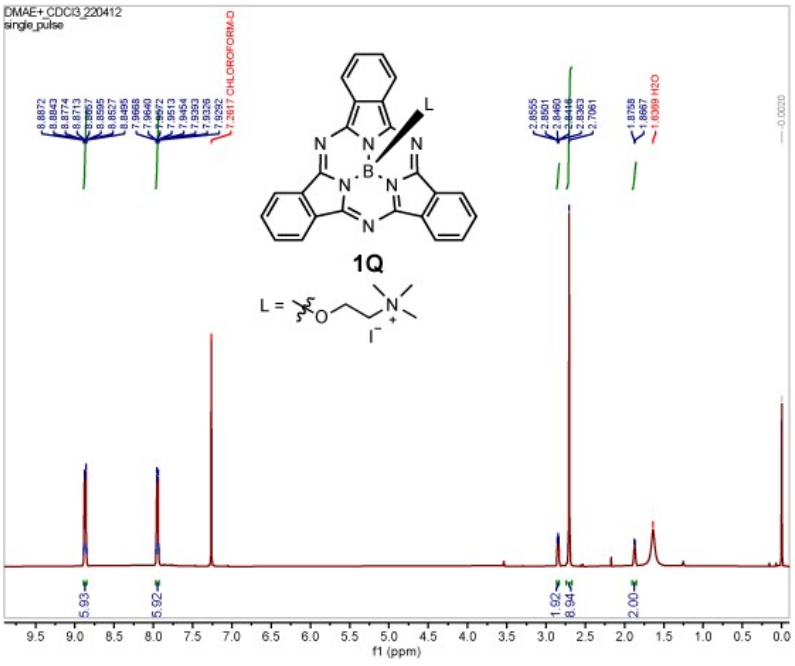

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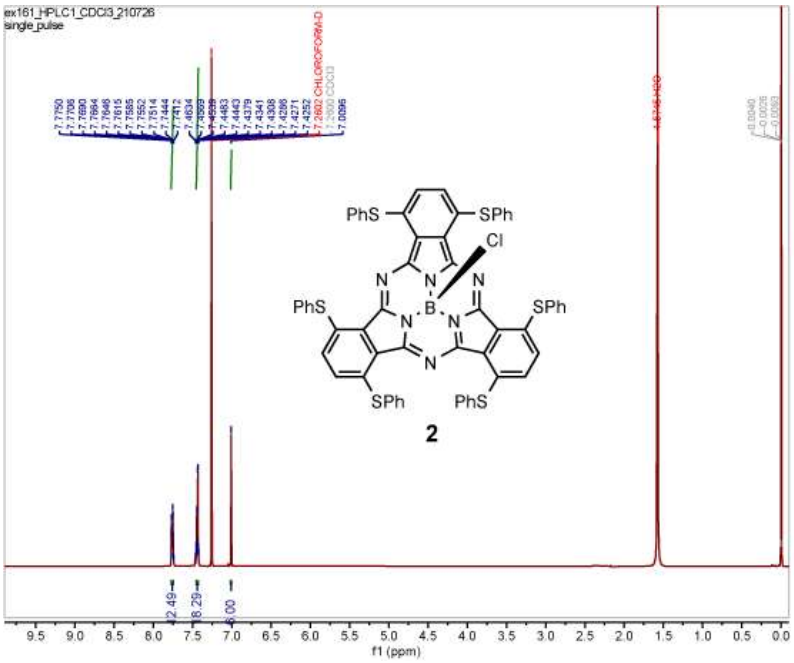

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12	Experiment	1D
13	Probe	2756
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27	Acquired Size	16384
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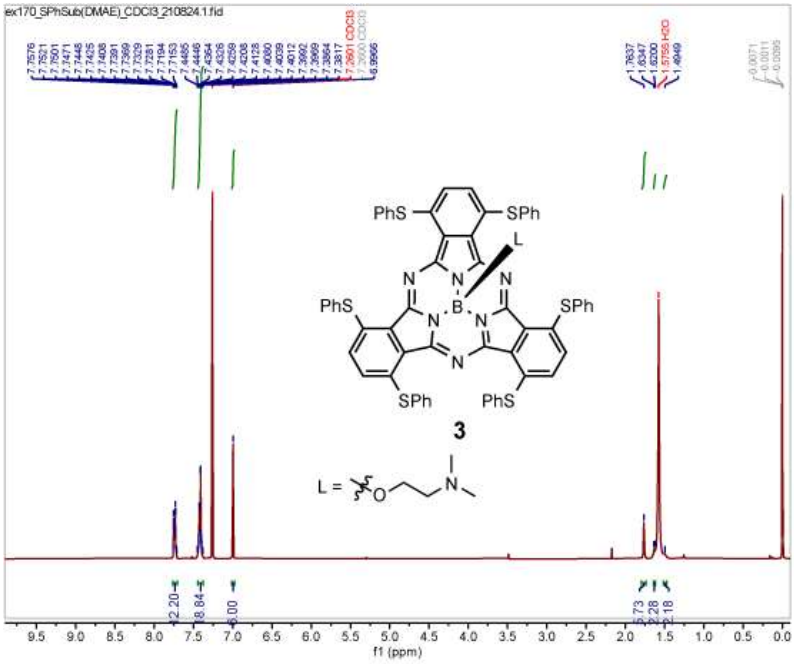

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8	Author	
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11	Pulse Sequence	ag30
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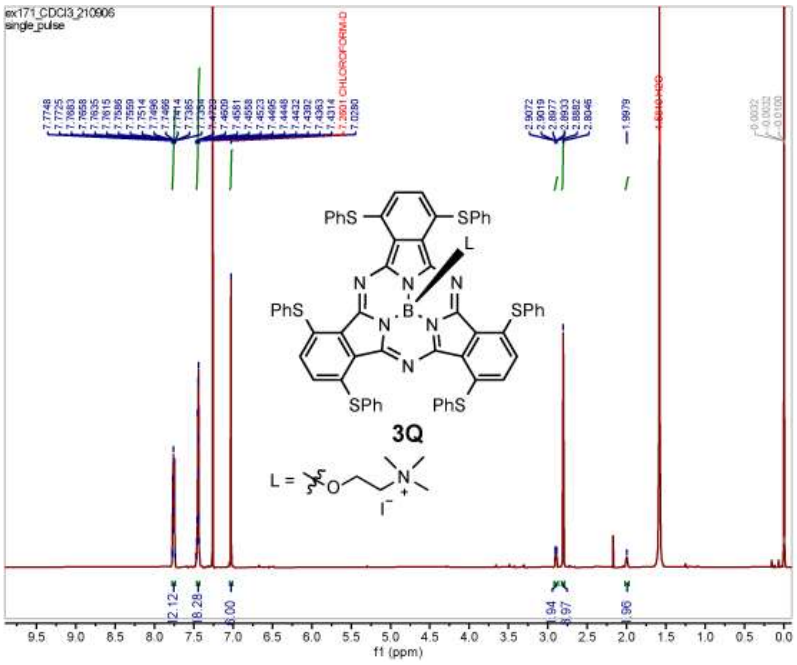

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8	Author	delta
9	Solvent	CHLOROFORM-D
10	Temperature	21.1
11	Pulse Sequence	protonjxp
12	Experiment	1D
13	Probe	2756
14	Number of Scans	8
15	Receiver Gain	54.0
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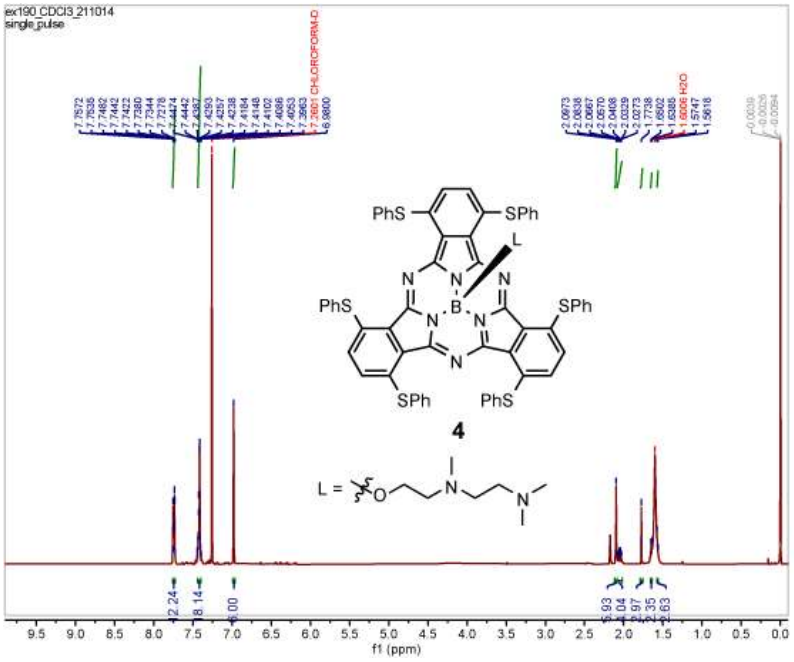

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13	Probe	2756
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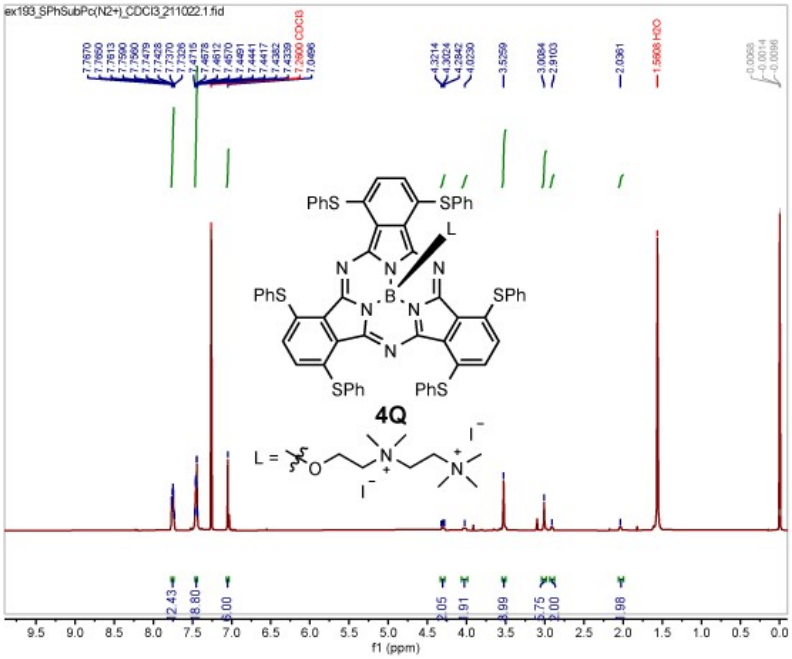

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6	Site	
7	Instrument	Avance
8	Author	
9	Solvent	CDCl3
10	Temperature	298.2
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	Z116098_0842 (PA BBO 400S1 BBF-H-D-05 Z SP)
14	Number of Scans	16
15	Receiver Gain	101.0
16	Relaxation Delay	1.0000
17	Pulse Width	10.0000
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22	Class	
23	Spectrometer Frequency	400.13
24	Spectral Width	8196.7
25	Lowest Frequency	- 1627.6
26	Nucleus	1H
27	Acquired Size	32768
28	Spectral Size	65536

Full Computational Details

Computational Details

Geometry optimization for all molecules was performed at the DFT level, by means of the hybrid Becke3LYP [36–39] (B3LYP) functional as implemented in Gaussian 16 [40]. The 6-31G(d) basis set was used for the all atoms. After the geometry optimization, the time-dependent (TD) DFT calculations [41,42] were performed to evaluate the stick absorption spectrum employing the same level or ωB97XD [43] and basis set. All calculations used a relatively simple self-consistent reaction field (SCRF) method based on the polarizable continuum model (PCM) [44] that mimicked the solvation effect of dichloromethane (ε = 8.93). All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG was 0).

Table S1. Calculated excited wavelengths (λ) and oscillator strengths (*f*) for components of selected transition energies. Calculations were performed at the ωB97XD/6-31G*//B3LYP/6-31G* level of theory using a polarizable continuum model (PCM), which mimicked the solvation effect of dichloromethane.

	λ / nm	*f*	Composition
1	504	0.46	HOMO-4→LUMO+1 (2.5%), HOMO→LUMO (94.9%)
	503	0.46	HOMO-4→LUMO (2.4%), HOMO→LUMO+1 (94.8%)
1Q	507	0.45	HOMO→LUMO (95.2%)
	504	0.45	HOMO→LUMO+1 (95.1%)
3'	553	0.57	HOMO→LUMO (93.1%)
	552	0.57	HOMO→LUMO+1 (93.0%)
3Q'	561	0.57	HOMO→LUMO (93.3%)
	558	0.57	HOMO→LUMO+1 (93.3%)

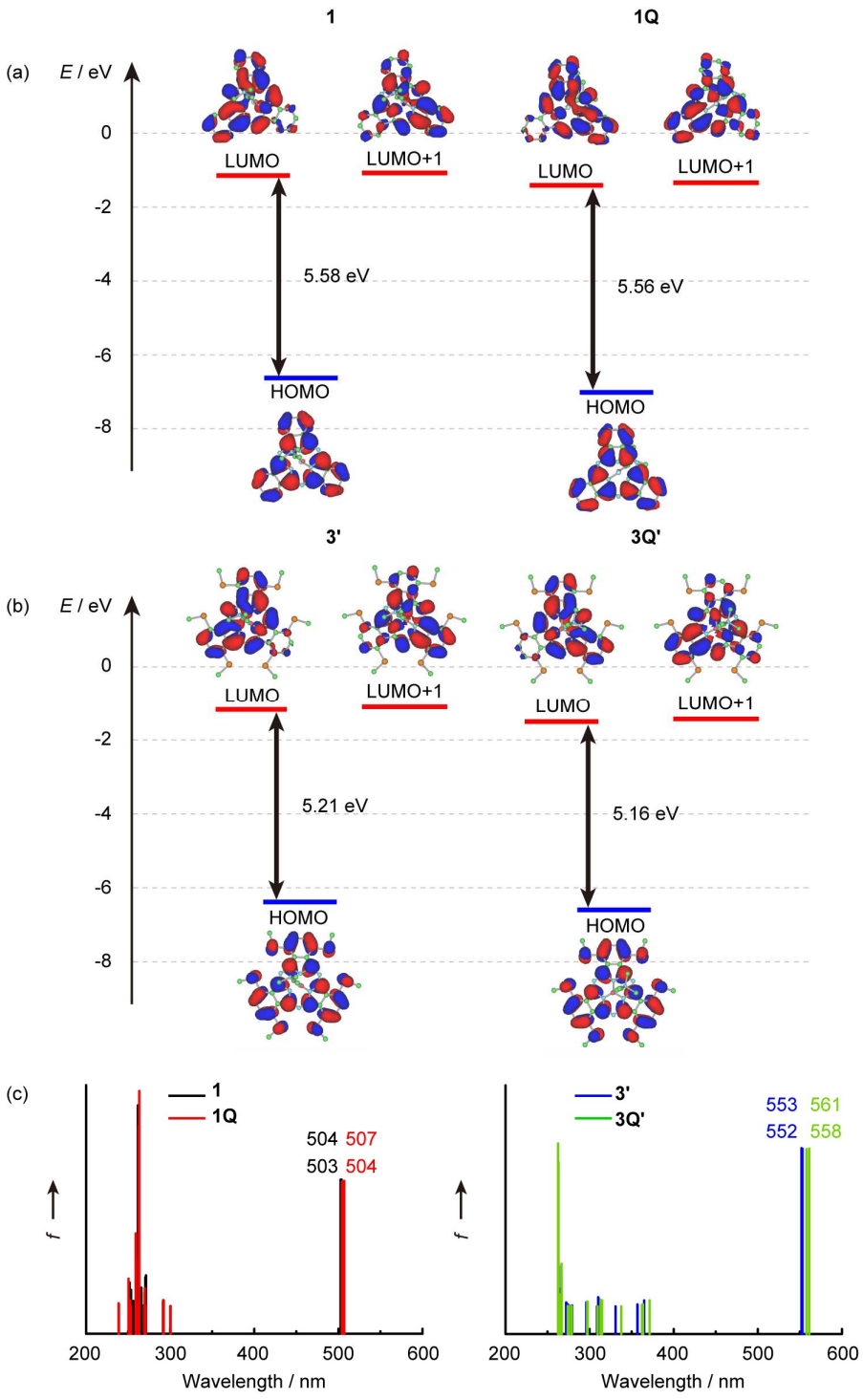

Figure S1. Partial molecular energy diagram and orbitals of (a) peripherally unsubstituted SubPcs (**1** and **1Q**), (b) peripherally substituted $(MeS)_6$SubPcs (**3'** and **3Q'**), and (c) their calculated absorption spectra. Calculations were performed at the ωB97XD/6-31G*//B3LYP/6-31G* level of theory, using a polarizable

continuum model (PCM), which mimicked the solvation effect of dichloromethane.

Cartesian Coordinates and Total Electron Energies

1

SCF Done: E(RB3LYP) = -1563.69370529 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-0.169416	0.024748	0.627028
2	7	0	-0.190207	1.252469	-0.257152
3	6	0	-0.953279	1.352177	-1.389242
4	6	0	-0.686028	2.680105	-1.929668
5	6	0	-1.195068	3.364136	-3.036803
6	6	0	-0.665332	4.617232	-3.338535
7	1	0	-1.056741	5.174075	-4.184858
8	6	0	0.374463	5.174258	-2.568643
9	1	0	0.767331	6.151346	-2.834231
10	6	0	0.910328	4.491998	-1.478096
11	6	0	0.370650	3.246141	-1.147088
12	6	0	0.733712	2.256322	-0.139392
13	7	0	1.870045	2.112916	0.562270
14	7	0	1.288165	-0.160692	0.939115
15	6	0	2.167460	0.884053	1.016554
16	6	0	3.456491	0.287114	1.347123
17	6	0	4.714878	0.843453	1.591715
18	6	0	5.787399	-0.019913	1.806515
19	1	0	6.771173	0.390373	2.014876
20	6	0	5.621011	-1.417650	1.752895
21	1	0	6.479292	-2.061653	1.920752
22	6	0	4.377907	-1.986637	1.483112
23	6	0	3.287332	-1.133851	1.292707
24	6	0	1.897343	-1.385300	0.929773
25	7	0	1.324196	-2.472340	0.387026
26	7	0	-0.469811	-1.093814	-0.346628
27	6	0	0.192144	-2.292244	-0.313149
28	6	0	-0.383783	-3.090539	-1.389116
29	6	0	-0.148550	-4.399846	-1.817555
30	6	0	-0.820081	-4.853722	-2.951041
31	1	0	-0.665136	-5.872957	-3.292672
32	6	0	-1.693679	-4.012296	-3.667395
33	1	0	-2.197503	-4.396843	-4.549361
34	6	0	-1.917255	-2.696166	-3.267895
35	6	0	-1.271418	-2.235343	-2.117407
36	6	0	-1.224779	-0.926333	-1.476258
37	7	0	-1.543735	0.287207	-1.956722
38	8	0	-0.944835	0.071481	1.820528
39	6	0	-2.352880	0.241109	1.750316
40	1	0	-2.802604	-0.558060	1.143521
41	1	0	-2.614117	1.201158	1.281143
42	6	0	-2.896438	0.219305	3.180119
43	1	0	-2.619981	-0.742096	3.656349
44	1	0	-2.378362	1.008641	3.736473
45	7	0	-4.334436	0.478148	3.250294
46	6	0	-4.734678	0.867948	4.598909
47	1	0	-5.803378	1.109330	4.609562
48	1	0	-4.558904	0.074751	5.351941
49	1	0	-4.179570	1.759525	4.909390
50	6	0	-5.129520	-0.658604	2.792748
51	1	0	-4.972853	-1.566699	3.408000
52	1	0	-6.193214	-0.400605	2.834760
53	1	0	-4.888025	-0.907310	1.755420
54	1	0	-1.985426	2.929673	-3.640997

55	1	0	1.722400	4.916221	-0.895816
56	1	0	4.848811	1.920413	1.618046
57	1	0	4.255162	-3.063768	1.426610
58	1	0	0.536269	-5.045172	-1.276199
59	1	0	-2.578484	-2.044622	-3.830710

TD–DFT output
HOMO**: 126**, LUMO**: 127**

Excited State 1: Singlet-A 2.4498 eV 506.10 nm f=0.4147 <S**2>=0.000
122 ->128 0.11055
126 ->127 0.69569
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1563.60367664
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.4553 eV 504.97 nm f=0.4143 <S**2>=0.000
122 ->127 -0.11127
126 ->128 0.69524

Excited State 3: Singlet-A 2.8262 eV 438.70 nm f=0.0005 <S**2>=0.000
125 ->127 0.70591

Excited State 4: Singlet-A 2.8477 eV 435.39 nm f=0.0006 <S**2>=0.000
125 ->128 0.70583

Excited State 5: Singlet-A 3.6344 eV 341.14 nm f=0.0000 <S**2>=0.000
123 ->128 0.36552
124 ->127 0.57376
126 ->131 0.12842

Excited State 6: Singlet-A 3.6960 eV 335.45 nm f=0.0009 <S**2>=0.000
122 ->127 0.12013
123 ->127 0.44567
124 ->128 0.47302
126 ->129 0.15753
126 ->130 -0.13851

Excited State 7: Singlet-A 3.7012 eV 334.99 nm f=0.0015 <S**2>=0.000
123 ->128 0.55165
124 ->127 -0.34802
126 ->129 0.13861
126 ->130 0.15163

Excited State 8: Singlet-A 3.8671 eV 320.62 nm f=0.0187 <S**2>=0.000
120 ->127 -0.16141
121 ->128 0.20167
123 ->127 0.45171
124 ->128 -0.44795

Excited State 9: Singlet-A 3.8753 eV 319.93 nm f=0.0212 <S**2>=0.000
123 ->127 -0.14692
126 ->129 0.64948

Excited State 10: Singlet-A 3.8776 eV 319.75 nm f=0.0211 <S**2>=0.000
123 ->128 -0.10046
124 ->127 0.11043
126 ->130 0.65340

Excited State 11: Singlet-A 3.9138 eV 316.79 nm f=0.0000 <S**2>=0.000
121 ->127 0.17249
123 ->128 -0.11860
126 ->131 0.65717

Excited State 12: Singlet-A 3.9838 eV 311.22 nm f=0.0274 <S**2>=0.000
119 ->127 0.56088

121 ->127	-0.34474				
122 ->128	-0.12141				
126 ->131	0.17365				
Excited State 13:	Singlet-A	4.0405 eV	306.85 nm	f=0.3596	<S**2>=0.000
118 ->127	-0.16506				
119 ->128	-0.24441				
120 ->127	0.12838				
122 ->127	0.59328				
123 ->127	-0.13580				
Excited State 14:	Singlet-A	4.0464 eV	306.41 nm	f=0.0113	<S**2>=0.000
115 ->128	0.10290				
118 ->127	-0.11435				
119 ->128	0.49831				
120 ->127	-0.25162				
121 ->128	-0.24123				
122 ->127	0.26964				
Excited State 15:	Singlet-A	4.0514 eV	306.03 nm	f=0.2756	<S**2>=0.000
118 ->128	-0.19470				
121 ->127	-0.11052				
122 ->128	0.64061				
Excited State 16:	Singlet-A	4.0799 eV	303.89 nm	f=0.0005	<S**2>=0.000
116 ->128	0.12118				
119 ->127	0.27175				
120 ->128	0.50576				
121 ->127	0.36468				
Excited State 17:	Singlet-A	4.0963 eV	302.68 nm	f=0.0148	<S**2>=0.000
115 ->128	0.17354				
116 ->127	0.18890				
120 ->127	0.41591				
121 ->128	-0.41060				
123 ->127	0.17205				
124 ->128	-0.15786				
Excited State 18:	Singlet-A	4.1242 eV	300.62 nm	f=0.1869	<S**2>=0.000
116 ->128	0.12331				
119 ->127	-0.29239				
120 ->128	0.41903				
121 ->127	-0.39062				
126 ->130	0.10068				
Excited State 19:	Singlet-A	4.1307 eV	300.15 nm	f=0.1471	<S**2>=0.000
116 ->127	0.11874				
118 ->127	0.12941				
119 ->128	0.41163				
120 ->127	0.34773				
121 ->128	0.36580				
Excited State 20:	Singlet-A	4.3135 eV	287.43 nm	f=0.0591	<S**2>=0.000
115 ->127	0.39280				
115 ->128	-0.10795				
116 ->128	0.40651				
118 ->128	0.36870				

1Q

SCF Done: E(RB3LYP) = -1603.45188257 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.090501	-0.000953	-0.494225
2	7	0	0.076985	1.209193	0.403356
3	6	0	0.641002	1.225921	1.652602

4	6	0	0.396514	2.563771	2.176652
5	6	0	0.763360	3.185321	3.373673
6	6	0	0.294410	4.474424	3.617454
7	1	0	0.578883	4.982861	4.533931
8	6	0	-0.549703	5.129969	2.699514
9	1	0	-0.901330	6.132611	2.923948
10	6	0	-0.946032	4.512702	1.515036
11	6	0	-0.461425	3.230065	1.243653
12	6	0	-0.729570	2.291072	0.161647
13	7	0	-1.738161	2.255374	-0.724316
14	7	0	-1.292027	-0.054540	-1.063399
15	6	0	-2.056532	1.064386	-1.256738
16	6	0	-3.314967	0.585521	-1.816083
17	6	0	-4.463313	1.252847	-2.250528
18	6	0	-5.552104	0.488726	-2.665634
19	1	0	-6.449475	0.985568	-3.022292
20	6	0	-5.513913	-0.918791	-2.625264
21	1	0	-6.382474	-1.483122	-2.951538
22	6	0	-4.385996	-1.597795	-2.168728
23	6	0	-3.276139	-0.845489	-1.774984
24	6	0	-1.994523	-1.222564	-1.190914
25	7	0	-1.613057	-2.361922	-0.591253
26	7	0	0.140571	-1.155680	0.472119
27	6	0	-0.605701	-2.291885	0.294196
28	6	0	-0.289229	-3.150762	1.428421
29	6	0	-0.703880	-4.440043	1.774315
30	6	0	-0.276681	-4.965398	2.991887
31	1	0	-0.573674	-5.971081	3.274272
32	6	0	0.529042	-4.213066	3.869240
33	1	0	0.839160	-4.651596	4.813101
34	6	0	0.927701	-2.916695	3.550645
35	6	0	0.529637	-2.386097	2.320264
36	6	0	0.702622	-1.069654	1.719397
37	7	0	1.035730	0.105214	2.279212
38	8	0	1.069029	-0.006071	-1.551505
39	6	0	2.440517	0.033789	-1.234098
40	1	0	2.720912	-0.805959	-0.583677
41	1	0	2.698829	0.966861	-0.714660
42	6	0	3.150511	-0.062626	-2.588603
43	1	0	2.885252	-1.007057	-3.068042
44	1	0	2.819120	0.757558	-3.229010
45	6	0	5.171875	-0.153461	-3.971852
46	1	0	6.261363	-0.116094	-3.962199
47	1	0	4.833284	-1.112518	-4.364240
48	1	0	4.773107	0.662373	-4.574626
49	6	0	5.239209	-1.123886	-1.721716
50	1	0	4.851773	-2.070343	-2.099722
51	1	0	6.325840	-1.100736	-1.806918
52	1	0	4.948154	-0.985943	-0.681801
53	6	0	5.148179	1.322051	-2.013665
54	1	0	4.696906	2.122140	-2.600778
55	1	0	4.858715	1.413045	-0.968210
56	1	0	6.234153	1.359540	-2.099031
57	7	0	4.671373	-0.002605	-2.555223
58	1	0	-1.338772	-5.015350	1.107840
59	1	0	1.533976	-2.332783	4.236079
60	1	0	1.399097	2.675657	4.090915
61	1	0	-1.610405	5.012903	0.817411
62	1	0	-4.501192	2.337542	-2.266868
63	1	0	-4.365067	-2.682101	-2.122932

TD–DFT output
HOMO**: 130**, LUMO**: 131**

Excited State 1: Singlet-A 2.4355 eV 509.06 nm f=0.4096 <S**2>=0.000
127 ->132 0.11111

```
      130 ->131         0.69588
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =    -1603.36237802
 Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:      Singlet-A      2.4450 eV  507.10 nm  f=0.4060  <S**2>=0.000
      127 ->131        -0.11152
      130 ->132         0.69541

Excited State   3:      Singlet-A      3.6280 eV  341.74 nm  f=0.0000  <S**2>=0.000
      128 ->131         0.51732
      129 ->132         0.45414
      130 ->135        -0.11835

Excited State   4:      Singlet-A      3.6873 eV  336.25 nm  f=0.0018  <S**2>=0.000
      128 ->131        -0.41848
      128 ->132         0.11013
      129 ->131         0.11373
      129 ->132         0.49185
      130 ->134        -0.17704

Excited State   5:      Singlet-A      3.6909 eV  335.92 nm  f=0.0008  <S**2>=0.000
      127 ->131        -0.15206
      128 ->131         0.11074
      128 ->132         0.42659
      129 ->131         0.46671
      129 ->132        -0.11146
      130 ->133         0.19124

Excited State   6:      Singlet-A      3.8561 eV  321.52 nm  f=0.0138  <S**2>=0.000
      125 ->131        -0.18734
      126 ->132        -0.21901
      128 ->132         0.45175
      129 ->131        -0.44314

 Excited State   7:      Singlet-A      3.8904 eV  318.69 nm  f=0.0121  <S**2>=0.000
      125 ->131         0.18217
      126 ->132        -0.12471
      128 ->132        -0.16564
      130 ->133         0.64030

 Excited State   8:      Singlet-A      3.8938 eV  318.42 nm  f=0.0135  <S**2>=0.000
      125 ->132        -0.15995
      126 ->131        -0.13759
      128 ->131        -0.13006
      130 ->134         0.64896

 Excited State   9:      Singlet-A      3.9370 eV  314.92 nm  f=0.0001  <S**2>=0.000
      126 ->131        -0.25023
      130 ->135         0.63936

 Excited State  10:      Singlet-A      4.0005 eV  309.92 nm  f=0.3890  <S**2>=0.000
      124 ->131         0.14918
      127 ->131         0.65802
      128 ->132         0.11823
      129 ->131         0.12035

 Excited State  11:      Singlet-A      4.0171 eV  308.64 nm  f=0.3514  <S**2>=0.000
      124 ->132         0.14069
      127 ->132         0.65731

Excited State  12:      Singlet-A      4.0261 eV  307.95 nm  f=0.0004  <S**2>=0.000
      123 ->131        -0.11048
      125 ->132        -0.31210
      126 ->131         0.53200
      127 ->132         0.13249
      130 ->135         0.25431
```

Excited State 13:	Singlet-A	4.0705 eV	304.59 nm	f=0.0737	<S**2>=0.000
120 ->132	0.14248				
123 ->132	-0.16680				
126 ->132	0.60172				
129 ->131	-0.19161				
130 ->133	0.12490				
Excited State 14:	Singlet-A	4.0767 eV	304.13 nm	f=0.0839	<S**2>=0.000
121 ->131	-0.20063				
125 ->131	0.60615				
128 ->132	0.19222				
130 ->133	-0.14467				
Excited State 15:	Singlet-A	4.0824 eV	303.70 nm	f=0.1625	<S**2>=0.000
121 ->132	-0.14333				
125 ->132	0.56785				
126 ->131	0.28482				
130 ->134	0.18012				
Excited State 16:	Singlet-A	4.2784 eV	289.79 nm	f=0.0236	<S**2>=0.000
120 ->132	-0.28179				
121 ->131	0.23801				
122 ->132	0.20491				
123 ->132	0.49988				
126 ->132	0.19337				
Excited State 17:	Singlet-A	4.2866 eV	289.23 nm	f=0.0136	<S**2>=0.000
120 ->131	-0.23469				
121 ->132	0.20345				
122 ->131	0.14377				
123 ->131	0.56862				
124 ->132	0.14327				
126 ->131	0.15983				
Excited State 18:	Singlet-A	4.3130 eV	287.46 nm	f=0.0096	<S**2>=0.000
120 ->132	0.10523				
121 ->131	0.62275				
122 ->132	-0.11514				
123 ->132	-0.19744				
124 ->131	-0.10078				
125 ->131	0.16273				
Excited State 19:	Singlet-A	4.3611 eV	284.30 nm	f=0.0044	<S**2>=0.000
121 ->132	0.61895				
122 ->131	-0.11188				
123 ->131	-0.22965				
124 ->132	0.15422				
125 ->132	0.12629				
Excited State 20:	Singlet-A	4.4628 eV	277.82 nm	f=0.0927	<S**2>=0.000
120 ->131	0.24059				
121 ->132	-0.12094				
122 ->131	-0.39458				
123 ->131	0.15749				
124 ->132	0.45233				

3'

SCF Done: E(RB3LYP) = -4188.68073062 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.012470	0.002721	1.197531
2	7	0	-0.335877	1.292471	0.492417
3	6	0	-1.549695	1.528416	-0.087866
4	6	0	-1.481018	2.884623	-0.616242

5	6	0	-2.442177	3.694265	-1.251646
6	6	0	-2.010675	4.953561	-1.685065
7	1	0	-2.704159	5.631911	-2.167360
8	6	0	-0.688847	5.388179	-1.520191
9	1	0	-0.438384	6.377294	-1.884414
10	6	0	0.289383	4.592264	-0.912120
11	6	0	-0.125556	3.328727	-0.448654
12	6	0	0.604521	2.232731	0.177139
13	7	0	1.922783	1.967503	0.212919
14	7	0	1.405641	-0.290477	0.725717
15	6	0	2.298787	0.689464	0.401335
16	6	0	3.529645	-0.003588	0.040212
17	6	0	4.808123	0.470908	-0.311583
18	6	0	5.760907	-0.494905	-0.657277
19	1	0	6.768204	-0.197008	-0.922509
20	6	0	5.464740	-1.864312	-0.677488
21	1	0	6.260100	-2.544326	-0.958067
22	6	0	4.196202	-2.358879	-0.351911
23	6	0	3.227168	-1.407906	0.021779
24	6	0	1.819658	-1.542505	0.374266
25	7	0	0.954396	-2.549811	0.159864
26	7	0	-0.831216	-1.016042	0.467363
27	6	0	-0.356283	-2.251275	0.125982
28	6	0	-1.466360	-2.938382	-0.521579
29	6	0	-1.598670	-4.249880	-1.017476
30	6	0	-2.812946	-4.563532	-1.639672
31	1	0	-2.984888	-5.559557	-2.029692
32	6	0	-3.842501	-3.624306	-1.786842
33	1	0	-4.749775	-3.949806	-2.281499
34	6	0	-3.725727	-2.308936	-1.321923
35	6	0	-2.521284	-1.975793	-0.672609
36	6	0	-2.032269	-0.721845	-0.113351
37	7	0	-2.438441	0.544644	-0.314743
38	16	0	3.764456	-4.083108	-0.374611
39	16	0	5.130582	2.218620	-0.280934
40	16	0	1.980176	5.092356	-0.689312
41	16	0	-4.102150	3.089153	-1.448770
42	16	0	-4.994040	-1.075601	-1.495250
43	16	0	-0.257156	-5.398952	-0.816673
44	6	0	-0.963213	-6.967239	-1.427714
45	1	0	-1.199192	-6.918790	-2.493623
46	1	0	-0.177659	-7.711332	-1.274624
47	1	0	-1.846802	-7.260934	-0.855412
48	6	0	-6.382599	-2.010980	-2.221679
49	1	0	-7.199961	-1.290085	-2.301564
50	1	0	-6.142633	-2.383494	-3.220584
51	1	0	-6.696655	-2.833528	-1.574232
52	6	0	-4.986021	4.529030	-2.139323
53	1	0	-4.611807	4.798564	-3.130064
54	1	0	-6.026129	4.206685	-2.231319
55	1	0	-4.939242	5.390101	-1.467894
56	6	0	1.979084	6.822826	-1.269018
57	1	0	2.999046	7.178438	-1.103735
58	1	0	1.749732	6.894092	-2.335101
59	1	0	1.289177	7.441097	-0.689222
60	6	0	6.921406	2.314364	-0.619305
61	1	0	7.166090	1.951283	-1.620563
62	1	0	7.165004	3.378058	-0.561184
63	1	0	7.502287	1.775390	0.133355
64	6	0	5.356233	-4.901353	-0.732205
65	1	0	5.733489	-4.640484	-1.724099
66	1	0	6.105290	-4.675694	0.030991
67	1	0	5.137131	-5.971686	-0.709120
68	8	0	-0.054925	0.001592	2.619673
69	6	0	-1.284618	0.267657	3.278159
70	1	0	-2.057582	-0.438023	2.941215
71	1	0	-1.642276	1.283628	3.054906

72	6	0	-1.041464	0.141394	4.783221
73	1	0	-0.675069	-0.880638	5.004109
74	1	0	-0.229311	0.831109	5.039452
75	7	0	-2.211911	0.495010	5.586070
76	6	0	-1.838389	0.761839	6.971629
77	1	0	-2.722545	1.078549	7.536014
78	1	0	-1.407112	-0.120433	7.484359
79	1	0	-1.100571	1.570349	7.009621
80	6	0	-3.257735	-0.523048	5.528321
81	1	0	-2.924134	-1.503375	5.922669
82	1	0	-4.119006	-0.195338	6.120475
83	1	0	-3.597981	-0.670441	4.499395

TD–DFT output
HOMO**: 198**, LUMO**: 199**

Excited State 1: Singlet-A 2.0201 eV 613.76 nm f=0.4299 <S**2>=0.000
198 ->199 0.70092
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -4188.60649362
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.0268 eV 611.72 nm f=0.4324 <S**2>=0.000
198 ->200 0.70085

Excited State 3: Singlet-A 2.5625 eV 483.84 nm f=0.0176 <S**2>=0.000
196 ->199 0.10768
197 ->199 0.69411

Excited State 4: Singlet-A 2.5689 eV 482.63 nm f=0.0304 <S**2>=0.000
196 ->199 0.51049
197 ->200 -0.48362

Excited State 5: Singlet-A 2.5760 eV 481.31 nm f=0.0132 <S**2>=0.000
196 ->200 0.68904
197 ->200 -0.12412

Excited State 6: Singlet-A 2.6297 eV 471.47 nm f=0.0142 <S**2>=0.000
196 ->199 0.46420
196 ->200 0.14247
197 ->199 -0.11621
197 ->200 0.49291

Excited State 7: Singlet-A 2.7580 eV 449.55 nm f=0.0003 <S**2>=0.000
195 ->199 0.70636

Excited State 8: Singlet-A 2.7797 eV 446.03 nm f=0.0003 <S**2>=0.000
195 ->200 0.70629

Excited State 9: Singlet-A 3.1742 eV 390.60 nm f=0.0492 <S**2>=0.000
188 ->200 0.11837
194 ->199 0.68585

Excited State 10: Singlet-A 3.1799 eV 389.90 nm f=0.0467 <S**2>=0.000
188 ->199 -0.11908
194 ->200 0.68561

Excited State 11: Singlet-A 3.4652 eV 357.80 nm f=0.0004 <S**2>=0.000
189 ->200 0.11829
190 ->199 -0.14044

192 ->199	0.13261				
192 ->200	0.39346				
193 ->199	0.51197				
193 ->200	-0.12620				
Excited State 12:	Singlet-A	3.5217 eV	352.06 nm	f=0.0242	<S**2>=0.000
189 ->199	0.10563				
190 ->200	-0.10293				
191 ->199	-0.17628				
192 ->199	0.41737				
192 ->200	0.16114				
193 ->199	-0.13072				
193 ->200	0.40400				
198 ->201	-0.14912				
198 ->202	0.17587				
Excited State 13:	Singlet-A	3.5254 eV	351.69 nm	f=0.0204	<S**2>=0.000
189 ->200	0.12180				
191 ->200	0.16142				
192 ->199	-0.12640				
192 ->200	0.46521				
193 ->199	-0.34970				
193 ->200	-0.16123				
198 ->201	0.18371				
198 ->202	0.14906				
Excited State 14:	Singlet-A	3.6378 eV	340.82 nm	f=0.0077	<S**2>=0.000
192 ->199	0.19043				
193 ->200	0.12117				
198 ->201	0.63683				
198 ->202	-0.12449				
Excited State 15:	Singlet-A	3.6397 eV	340.64 nm	f=0.0067	<S**2>=0.000
192 ->200	-0.15129				
193 ->199	0.16423				
198 ->201	0.12375				
198 ->202	0.63822				
Excited State 16:	Singlet-A	3.6625 eV	338.53 nm	f=0.0077	<S**2>=0.000
192 ->199	-0.45983				
192 ->200	0.14071				
193 ->199	0.13208				
193 ->200	0.49094				
Excited State 17:	Singlet-A	3.7195 eV	333.34 nm	f=0.0000	<S**2>=0.000
189 ->200	-0.11221				
190 ->199	0.10412				
198 ->203	0.67202				
Excited State 18:	Singlet-A	3.7595 eV	329.79 nm	f=0.0008	<S**2>=0.000
191 ->199	0.65609				
192 ->199	0.14144				
193 ->200	0.13230				
Excited State 19:	Singlet-A	3.7663 eV	329.19 nm	f=0.0004	<S**2>=0.000
188 ->200	0.10483				
190 ->199	-0.10888				
191 ->200	0.65661				

192 ->200 -0.12869
193 ->199 0.11449

Excited State 20: Singlet-A 3.8340 eV 323.38 nm f=0.0000 <S**2>=0.000
187 ->199 0.15808
189 ->200 -0.24767
190 ->199 0.59120
193 ->199 0.14080
198 ->203 -0.15387

3Q'

SCF Done: E(RB3LYP) = -4228.44003253 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-0.020118	0.000442	1.042665
2	7	0	0.556614	-1.180260	0.311725
3	6	0	1.766097	-1.152701	-0.326547
4	6	0	1.950569	-2.487372	-0.880359
5	6	0	3.025152	-3.075784	-1.575539
6	6	0	2.838995	-4.391298	-2.016967
7	1	0	3.631515	-4.906212	-2.546434
8	6	0	1.644411	-5.090659	-1.801602
9	1	0	1.584312	-6.105426	-2.176064
10	6	0	0.554740	-4.521067	-1.132002
11	6	0	0.723730	-3.203694	-0.662623
12	6	0	-0.186006	-2.290507	0.015988
13	7	0	-1.527417	-2.301663	0.114663
14	7	0	-1.461599	0.007690	0.652524
15	6	0	-2.149344	-1.131578	0.345290
16	6	0	-3.511807	-0.701535	0.058353
17	6	0	-4.679603	-1.426038	-0.249344
18	6	0	-5.827615	-0.673013	-0.525319
19	1	0	-6.762905	-1.169037	-0.755034
20	6	0	-5.822937	0.727472	-0.519358
21	1	0	-6.755017	1.231606	-0.744398
22	6	0	-4.669887	1.470651	-0.237604
23	6	0	-3.506618	0.736050	0.063242
24	6	0	-2.140637	1.154078	0.352173
25	7	0	-1.509477	2.320462	0.127830
26	7	0	0.565562	1.181752	0.319883
27	6	0	-0.168065	2.299455	0.030372
28	6	0	0.750832	3.211408	-0.637756
29	6	0	0.592483	4.532617	-1.099941
30	6	0	1.690758	5.101366	-1.756218
31	1	0	1.638464	6.118582	-2.125145
32	6	0	2.884959	4.398811	-1.962929
33	1	0	3.685773	4.914301	-2.479214
34	6	0	3.060827	3.079604	-1.528363
35	6	0	1.975077	2.489795	-0.852369
36	6	0	1.777243	1.150758	-0.313727
37	7	0	2.423739	-0.002837	-0.562284
38	16	0	-4.611245	3.246406	-0.226930
39	16	0	-4.631697	-3.202052	-0.255178
40	16	0	-0.981402	-5.363735	-0.838097
41	16	0	4.516056	-2.143664	-1.831600
42	16	0	4.554518	2.146533	-1.764467
43	16	0	-0.942343	5.380219	-0.814927
44	6	0	-0.601005	7.068476	-1.418533
45	1	0	-0.408570	7.083855	-2.494079
46	1	0	-1.515058	7.632124	-1.216254
47	1	0	0.228163	7.530077	-0.876484
48	6	0	5.692142	3.366393	-2.505339
49	1	0	6.640777	2.836440	-2.620792

50	1	0	5.349710	3.693870	-3.489953
51	1	0	5.843191	4.227057	-1.848977
52	6	0	5.635736	-3.357968	-2.608098
53	1	0	5.270814	-3.676584	-3.587543
54	1	0	6.581924	-2.827570	-2.740320
55	1	0	5.801074	-4.224399	-1.962852
56	6	0	-0.650486	-7.051631	-1.448568
57	1	0	-1.562743	-7.614237	-1.235617
58	1	0	-0.471621	-7.065866	-2.526468
59	1	0	0.184773	-7.515124	-0.917582
60	6	0	-6.376757	-3.662835	-0.525976
61	1	0	-6.735525	-3.336851	-1.505296
62	1	0	-6.389991	-4.754964	-0.491795
63	1	0	-7.023125	-3.274979	0.265280
64	6	0	-6.353323	3.720476	-0.493739
65	1	0	-6.714021	3.405331	-1.475901
66	1	0	-7.002133	3.329745	0.294106
67	1	0	-6.359694	4.812320	-0.449996
68	8	0	0.111596	-0.003859	2.476857
69	6	0	1.391536	-0.039123	3.063449
70	1	0	2.001247	0.814533	2.736403
71	1	0	1.924910	-0.960629	2.792722
72	6	0	1.120864	0.024022	4.570430
73	1	0	0.621826	0.965425	4.809355
74	1	0	0.459825	-0.798820	4.850173
75	6	0	1.855034	0.036705	6.906649
76	1	0	2.716730	-0.017763	7.572069
77	1	0	1.339985	0.988749	7.034814
78	1	0	1.173139	-0.789942	7.105761
79	6	0	3.304588	1.058914	5.211794
80	1	0	2.776743	2.007472	5.313390
81	1	0	4.113590	0.999989	5.940248
82	1	0	3.707967	0.956746	4.205854
83	6	0	3.046238	-1.388835	5.308610
84	1	0	2.329404	-2.193811	5.472772
85	1	0	3.461689	-1.451123	4.304272
86	1	0	3.849956	-1.446545	6.042983
87	7	0	2.338431	-0.067639	5.480203

TD–DFT output
HOMO**: 202**, LUMO**: 203**

Excited State 1: Singlet-A 1.9743 eV 627.99 nm f=0.4190 <S**2>=0.000
202 ->203 0.70144
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -4228.36747882
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.9866 eV 624.12 nm f=0.4223 <S**2>=0.000
202 ->204 0.70135

Excited State 3: Singlet-A 2.4900 eV 497.93 nm f=0.0202 <S**2>=0.000
201 ->203 0.70534

Excited State 4: Singlet-A 2.5070 eV 494.55 nm f=0.0317 <S**2>=0.000
200 ->203 0.49692
201 ->204 0.50022

Excited State 5: Singlet-A 2.5213 eV 491.75 nm f=0.0160 <S**2>=0.000
200 ->204 0.70501

Excited State 6: Singlet-A 2.5742 eV 481.64 nm f=0.0139 <S**2>=0.000
200 ->203 0.49783

```
      201 ->204         -0.49429

Excited State   7:      Singlet-A      3.1541 eV  393.09 nm  f=0.0539  <S**2>=0.000
      193 ->204         -0.11966
      199 ->203          0.68624

Excited State   8:      Singlet-A      3.1651 eV  391.73 nm  f=0.0528  <S**2>=0.000
      193 ->203          0.12147
      199 ->204          0.68595

Excited State   9:      Singlet-A      3.4357 eV  360.87 nm  f=0.0000  <S**2>=0.000
      194 ->203          0.13540
      195 ->204          0.13306
      197 ->203          0.47842
      198 ->204          0.47064

Excited State  10:      Singlet-A      3.4884 eV  355.42 nm  f=0.0243  <S**2>=0.000
      194 ->203         -0.10562
      195 ->204          0.10825
      196 ->204          0.16081
      197 ->203         -0.44174
      198 ->204          0.46333
      202 ->206          0.17031

Excited State  11:      Singlet-A      3.4944 eV  354.81 nm  f=0.0257  <S**2>=0.000
      194 ->204          0.10035
      195 ->203          0.10388
      196 ->203         -0.22116
      197 ->204          0.39837
      198 ->203          0.47155
      202 ->205         -0.18778

Excited State  12:      Singlet-A      3.6154 eV  342.94 nm  f=0.0048  <S**2>=0.000
      197 ->204         -0.40090
      198 ->203          0.48557
      202 ->205          0.30593

Excited State  13:      Singlet-A      3.6259 eV  341.94 nm  f=0.0055  <S**2>=0.000
      196 ->203         -0.12710
      197 ->204          0.34255
      202 ->205          0.58681

Excited State  14:      Singlet-A      3.6289 eV  341.66 nm  f=0.0038  <S**2>=0.000
      197 ->203          0.13605
      198 ->204         -0.11534
      202 ->206          0.66339

Excited State  15:      Singlet-A      3.6960 eV  335.46 nm  f=0.0008  <S**2>=0.000
      196 ->203          0.64816
      197 ->204          0.21218
      198 ->203          0.13143

Excited State  16:      Singlet-A      3.7121 eV  334.00 nm  f=0.0002  <S**2>=0.000
      195 ->204          0.17715
      196 ->204         -0.45104
      197 ->203         -0.16196
      202 ->207          0.47035
```

Excited State 17:	Singlet-A	3.7192 eV	333.36 nm	f=0.0007	<S**2>=0.000
194 ->203	0.14057				
196 ->204	0.49534				
198 ->204	-0.15013				
202 ->207	0.43845				
Excited State 18:	Singlet-A	3.8169 eV	324.83 nm	f=0.0001	<S**2>=0.000
194 ->203	0.47695				
195 ->203	0.11262				
195 ->204	0.38444				
197 ->203	-0.11900				
202 ->207	-0.26756				
Excited State 19:	Singlet-A	3.8636 eV	320.90 nm	f=0.0014	<S**2>=0.000
194 ->203	0.25606				
194 ->204	0.32863				
195 ->203	0.36800				
195 ->204	-0.34421				
202 ->206	0.10225				
Excited State 20:	Singlet-A	3.8641 eV	320.86 nm	f=0.0011	<S**2>=0.000
193 ->203	-0.11422				
194 ->203	-0.33937				
194 ->204	0.26468				
195 ->203	0.33083				
195 ->204	0.36335				