Electronic Supplementary Material (ESI) for ChemComm.

Synthesis and spectroscopic properties of chial binaphtyl-linked subphthalocyanines

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Supporting information

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General Comments

Unless otherwise noted, solvents and reagents were purchased from Tokyo Kasei Co. and Wako Chemicals Co. and were used after appropriate purification (distillation or recrystallization).

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were obtained on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet capable of producing magnetic fields of up to 1.03 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ($[\theta]_M$ / deg $dm^3mol^{-1}cm^{-1}T^{-1}$). Fluorescence spectra in the UV-vis region were obtained on a HITACHI F-4500 spectrofluorometer. Absolute fluorescence quantum yields were measured on a Hamamatsu C9920-03G calibrated integrating sphere system. NMR spectra were obtained on a Bruker AVANCE III 500 spectrometer. Unless otherwise noted, samples were recorded in $CDCl_3$. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H-NMR spectra were referenced to the residual solvent as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Apex-III spectrometer. Cyclic voltammetry (CV) measurements were recorded with a Hokuto Denko HZ5000 potentiostat under a nitrogen atmosphere in solutions with 0.1 M of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Measurements were made with a glassy carbon (GC) 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 1.0 mM and the sweep rates were set to 100 mV/s.

Additional Experimental Results

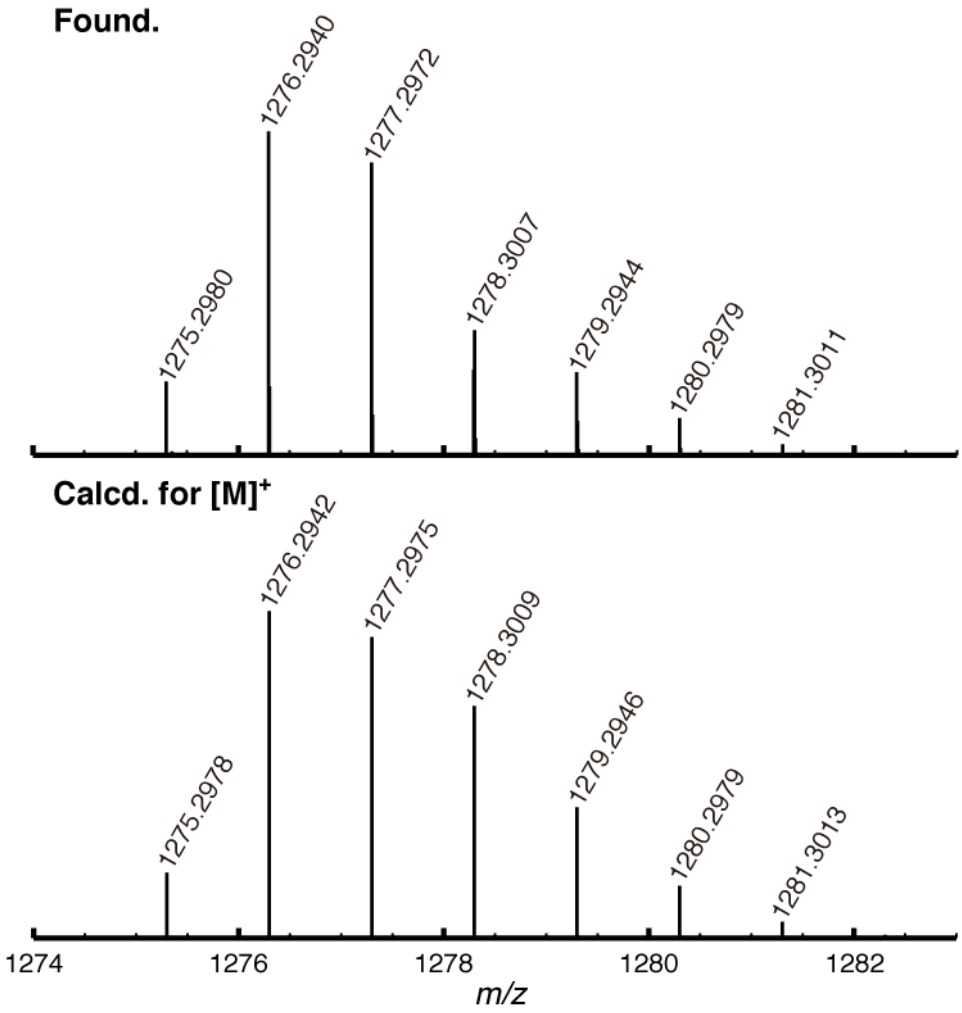


Figure S1. Observed high-resolution mass spectrum (top) of **1S** and the theoretical isotropic distribution pattern for $C_{84}H_{42}BClN_6O_6$ ($[M]^+$) (bottom).

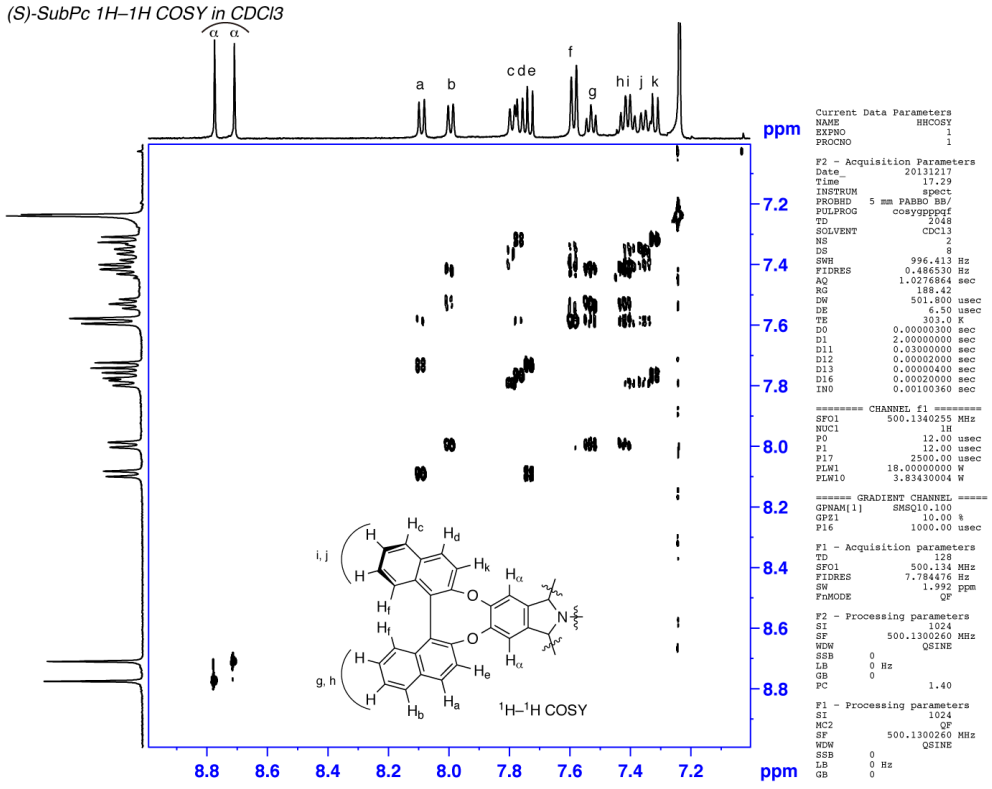


Figure S2. ^{1}H-^{1}H COSY spectrum of **1S** in $CDCl_3$.

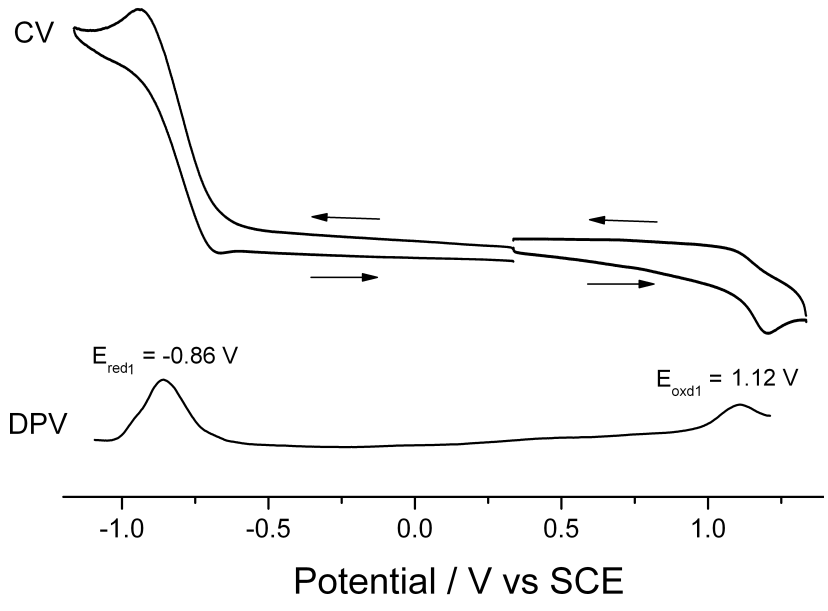


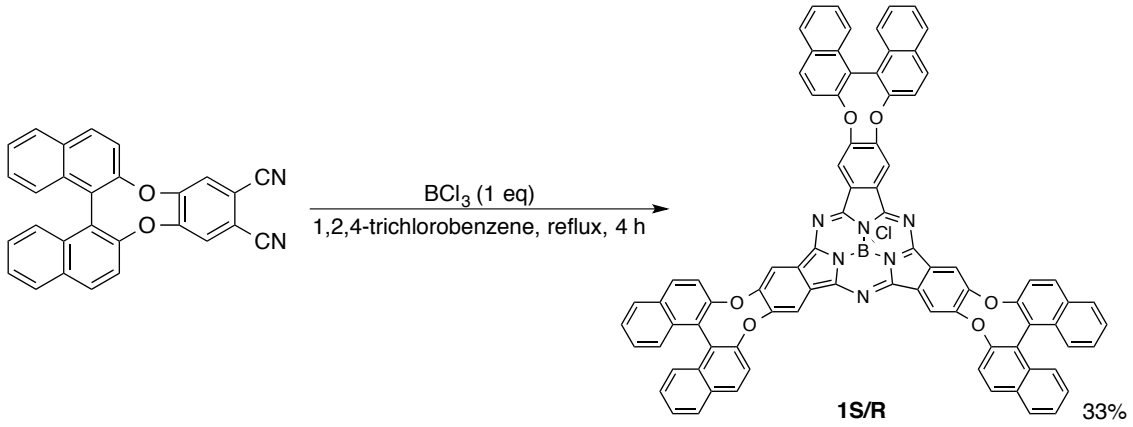
Figure S3. Cyclic voltammogram of **1** in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at scan rate of 40 mV s^{-1}.

Full Experimental Procedures

Materials

(S)/*(R)*- benzo[*b*]dinaphtho[2,1-*e*:1',2'-*g*][1,4]-dioxocine-5,6-dicarbonitrile were synthesized according to published procedures.[i]

Synthesis of SubPc (1S/R)



1.0 M CH_2Cl_2 solution of boron trichloride (1.0 mL, 1.0 eq) was added to a 1,2,4-trichlorobenzene solution (5.0 mL) of (*R*)/(*S*)-2 (410 mg, 1.0 mmol) at room temperature. The resultant mixture was gradually heated to reflux under nitrogen for 4 h. After removal of the solvent, the resultant solid was chromatographed on a silica gel column using $CHCl_3$ as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave **1** as a red powder (174 mg, 33%). 400 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.80 (s, 3H), 8.73 (d, 3H), 8.10 (d, 3H), 8.01 (d, 3H), 7.79-7.74 (m, 9H), 7.61-7.53 (m, 9H), 7.46-7.30 (m, 12H).

HRMS-MALDI Calcd for $C_{84}H_{42}BClN_6O_6$ $[M]^+$ 1276.2942. Found: 1276.2940.

Anal. Calcd (%) for (*R*)-$C_{84}H_{42}BClN_6O_6 \cdot CH_3OH$: C, 77.96; H, 3.54; N, 6.42; Found: C, 77.82; H, 3.59; N, 6.38 and for (*S*)-$C_{84}H_{42}BClN_6O_6 \cdot 2CH_3OH$: C, 76.99; H, 3.76; N, 6.26; Found: C, 76.81; H, 3.74; N, 6.00.

UV–vis ($CHCl_3$) λ_{max} ($10^{-4}\varepsilon$): 573 nm (9.8).

$\lambda_{FL,\,max}$ ($CHCl_3$): 585 nm.

Φ_{FL} = 0.25, $\lambda_{FL,\,max}$ ($CHCl_3$): 585 nm.

Full Computational Details

Computational Details

Geometry optimization for all molecules was performed at the DFT level, by means of the hybrid Becke3LYP[ii] (B3LYP) functional as implemented in Gaussian 2009.[iii] The 6-31G* basis set was used for the all atoms. After the geometry optimization, the time-dependent (TD) DFT calculations[iv] were performed to evaluate the stick absorption spectrum employing with the same theory and basis set. All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of the theory (the number of imaginary frequency, Nimag, 0).

Cartesian Coordinates and Total Electron Energies

1S

SCF Done: E(RB3LYP) = -4491.24239114 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.000000	3.261207
2	17	0	0.000000	0.000000	5.141258
3	6	0	1.255408	4.411288	1.206873
4	6	0	-1.586295	4.287232	1.171631
5	6	0	-0.839982	3.244757	1.722867
6	6	0	0.589479	3.298853	1.722391
7	6	0	1.070102	2.028308	2.245638
8	7	0	-0.052257	1.362598	2.665355
9	6	0	-1.222347	1.941196	2.245955
10	7	0	2.259639	1.422556	2.110992
11	1	0	2.337975	4.477946	1.198468
12	1	0	-2.669494	4.254466	1.126697
13	6	0	-0.916556	5.394563	0.661581
14	6	0	0.503481	5.470177	0.708548
15	8	0	-1.681884	6.429862	0.169523
16	8	0	1.187943	6.554649	0.204296
17	6	0	0.854364	7.826498	0.677254
18	6	0	0.000000	8.624633	-0.061578
19	6	0	1.481435	8.272998	1.860245
20	6	0	-0.291981	9.943357	0.422548
21	6	0	1.237036	9.545962	2.315795
22	1	0	2.156429	7.600868	2.380384
23	6	0	-1.222370	10.806400	-0.220835
24	6	0	0.347652	10.408025	1.620886
25	1	0	1.718832	9.905703	3.221375
26	6	0	-1.482487	12.065341	0.273918
27	1	0	-1.735167	10.458478	-1.110718
28	6	0	0.062194	11.715926	2.097856
29	6	0	-0.829649	12.531410	1.440013
30	1	0	-2.199237	12.705473	-0.233280
31	1	0	0.559163	12.057794	3.002665
32	1	0	-1.041897	13.527882	1.817395
33	6	0	-1.411458	6.906061	-1.116049
34	6	0	-0.628925	8.035543	-1.274617
35	6	0	-2.031032	6.250706	-2.201845
36	6	0	-0.401939	8.527972	-2.603267
37	6	0	-1.851187	6.733723	-3.475372

38	1	0	-2.650169	5.381594	-2.003740
39	6	0	0.458804	9.627846	-2.875326
40	6	0	-1.033949	7.870874	-3.712371
41	1	0	-2.328866	6.243732	-4.320020
42	6	0	0.659438	10.070681	-4.164106
43	1	0	0.966359	10.115538	-2.050513
44	6	0	-0.811999	8.360772	-5.027810
45	6	0	0.012929	9.438712	-5.253084
46	1	0	1.323963	10.910687	-4.347247
47	1	0	-1.303172	7.858343	-5.857836
48	1	0	0.177126	9.800924	-6.264162
49	6	0	3.192583	-3.292859	1.206873
50	6	0	4.505999	-0.769844	1.171631
51	6	0	3.230033	-0.894933	1.722867
52	6	0	2.562151	-2.159930	1.722391
53	6	0	1.221515	-1.940889	2.245638
54	7	0	1.206173	-0.636043	2.665355
55	6	0	2.292299	0.087986	2.245955
56	7	0	0.102150	-2.668183	2.110992
57	1	0	2.709027	-4.263719	1.198468
58	1	0	5.019223	0.184617	1.126697
59	6	0	5.130107	-1.903521	0.661581
60	6	0	4.485572	-3.171116	0.708548
61	8	0	6.409366	-1.758377	0.169523
62	8	0	5.082521	-4.306113	0.204296
63	6	0	6.350764	-4.653150	0.677254
64	6	0	7.469151	-4.312316	-0.061578
65	6	0	6.423909	-5.419459	1.860245
66	6	0	8.757190	-4.718816	0.422548
67	6	0	7.648528	-5.844286	2.315795
68	1	0	5.504330	-5.667956	2.380384
69	6	0	9.969802	-4.344597	-0.220835
70	6	0	8.839788	-5.505088	1.620886
71	1	0	7.719174	-6.441404	3.221375
72	6	0	11.190135	-4.748799	0.273918
73	1	0	9.924891	-3.726540	-1.110718
74	6	0	10.115193	-5.911825	2.097856
75	6	0	11.267344	-5.547208	1.440013
76	1	0	12.102881	-4.448141	-0.233280
77	1	0	10.162774	-6.513146	3.002665
78	1	0	12.236438	-5.861632	1.817395
79	6	0	6.686553	-2.230672	-1.116049
80	6	0	7.273447	-3.473106	-1.274617
81	6	0	6.428786	-1.366428	-2.201845
82	6	0	7.586410	-3.915897	-2.603267
83	6	0	6.757169	-1.763687	-3.475372
84	1	0	5.985682	-0.395683	-2.003740
85	6	0	8.108557	-5.211259	-2.875326
86	6	0	7.333351	-3.040011	-3.712371
87	1	0	6.571664	-1.105009	-4.320020
88	6	0	8.391747	-5.606431	-4.164106
89	1	0	8.277133	-5.894660	-2.050513
90	6	0	7.646640	-3.477174	-5.027810
91	6	0	8.167700	-4.730553	-5.253084
92	1	0	8.786951	-6.601929	-4.347247
93	1	0	7.457111	-2.800591	-5.857836
94	1	0	8.399286	-5.053858	-6.264162
95	6	0	-4.447991	-1.118429	1.206873
96	6	0	-2.919704	-3.517388	1.171631
97	6	0	-2.390051	-2.349824	1.722867
98	6	0	-3.151630	-1.138923	1.722391
99	6	0	-2.291617	-0.087418	2.245638
100	7	0	-1.153916	-0.726555	2.665355
101	6	0	-1.069952	-2.029182	2.245955
102	7	0	-2.361789	1.245627	2.110992
103	1	0	-5.047002	-0.214227	1.198468
104	1	0	-2.349729	-4.439083	1.126697

105	6	0	-4.213551	-3.491042	0.661581
106	6	0	-4.989053	-2.299061	0.708548
107	8	0	-4.727482	-4.671485	0.169523
108	8	0	-6.270464	-2.248536	0.204296
109	6	0	-7.205128	-3.173348	0.677254
110	6	0	-7.469151	-4.312317	-0.061578
111	6	0	-7.905344	-2.853539	1.860245
112	6	0	-8.465209	-5.224541	0.422548
113	6	0	-8.885564	-3.701676	2.315795
114	1	0	-7.660759	-1.932912	2.380384
115	6	0	-8.747432	-6.461803	-0.220835
116	6	0	-9.187440	-4.902937	1.620886
117	1	0	-9.438006	-3.464299	3.221375
118	6	0	-9.707648	-7.316542	0.273918
119	1	0	-8.189724	-6.731938	-1.110718
120	6	0	-10.177387	-5.804101	2.097856
121	6	0	-10.437695	-6.984202	1.440013
122	1	0	-9.903644	-8.257332	-0.233280
123	1	0	-10.721937	-5.544648	3.002665
124	1	0	-11.194541	-7.666250	1.817395
125	6	0	-5.275095	-4.675389	-1.116049
126	6	0	-6.644522	-4.562437	-1.274617
127	6	0	-4.397754	-4.884278	-2.201845
128	6	0	-7.184471	-4.612075	-2.603267
129	6	0	-4.905982	-4.970036	-3.475372
130	1	0	-3.335513	-4.985911	-2.003740
131	6	0	-8.567361	-4.416587	-2.875326
132	6	0	-6.299402	-4.830863	-3.712371
133	1	0	-4.242798	-5.138723	-4.320020
134	6	0	-9.051185	-4.464250	-4.164106
135	1	0	-9.243492	-4.220878	-2.050513
136	6	0	-6.834641	-4.883598	-5.027810
137	6	0	-8.180629	-4.708159	-5.253084
138	1	0	-10.110914	-4.308758	-4.347247
139	1	0	-6.153939	-5.057752	-5.857836
140	1	0	-8.576412	-4.747066	-6.264162

TD–DFT output

HOMO**: 329**, LUMO**: 330**

Excited State 1: Singlet-E 2.4523 eV 505.59 nm f=0.4840 <S**2>=0.000
311 -> 330 -0.10378
320 -> 330 0.11971
329 -> 331 0.68586
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4491.15227172
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-E 2.4523 eV 505.59 nm f=0.4840 <S**2>=0.000
311 -> 331 0.10378
320 -> 331 -0.11972
329 -> 330 0.68586

Excited State 3: Singlet-A 2.9500 eV 420.28 nm f=0.0000 <S**2>=0.000
327 -> 330 -0.22019
327 -> 331 0.44788
328 -> 330 -0.44786
328 -> 331 -0.22007

Excited State 4: Singlet-E 2.9501 eV 420.28 nm f=0.0000 <S**2>=0.000
326 -> 330 -0.33740
326 -> 331 0.36695
327 -> 330 -0.33493
327 -> 331 0.11221
328 -> 330 0.11235
328 -> 331 0.33500

Excited State 5:	Singlet-E	2.9501 eV	420.28 nm	f=0.0000	<S**2>=0.000
326 -> 330	0.36695				
326 -> 331	0.33740				
327 -> 330	-0.11227				
327 -> 331	-0.33498				
328 -> 330	-0.33495				
328 -> 331	0.11229				
Excited State 6:	Singlet-A	3.0062 eV	412.43 nm	f=0.0006	<S**2>=0.000
327 -> 330	0.44792				
327 -> 331	0.22023				
328 -> 330	-0.22021				
328 -> 331	0.44798				
Excited State 7:	Singlet-E	3.0062 eV	412.43 nm	f=0.0001	<S**2>=0.000
326 -> 331	0.49968				
327 -> 330	0.31953				
327 -> 331	0.14901				
328 -> 330	0.14898				
328 -> 331	-0.31948				
Excited State 8:	Singlet-E	3.0062 eV	412.43 nm	f=0.0001	<S**2>=0.000
326 -> 330	0.49968				
327 -> 330	-0.14902				
327 -> 331	0.31949				
328 -> 330	0.31952				
328 -> 331	0.14896				
Excited State 9:	Singlet-A	3.1662 eV	391.58 nm	f=0.0002	<S**2>=0.000
321 -> 330	-0.19119				
322 -> 331	-0.19119				
324 -> 330	-0.40239				
324 -> 331	-0.21011				
325 -> 330	-0.21011				
325 -> 331	0.40239				
Excited State 10:	Singlet-E	3.1856 eV	389.20 nm	f=0.0013	<S**2>=0.000
321 -> 331	-0.12672				
322 -> 330	-0.12672				
323 -> 330	0.37328				
324 -> 330	-0.35196				
324 -> 331	-0.18185				
325 -> 330	0.18185				
325 -> 331	-0.35196				
Excited State 11:	Singlet-E	3.1856 eV	389.20 nm	f=0.0013	<S**2>=0.000
321 -> 330	-0.12672				
322 -> 331	0.12672				
323 -> 331	0.37328				
324 -> 330	-0.18185				
324 -> 331	0.35196				
325 -> 330	-0.35196				
325 -> 331	-0.18185				
Excited State 12:	Singlet-E	3.2451 eV	382.06 nm	f=0.0463	<S**2>=0.000
323 -> 330	0.54201				
323 -> 331	0.24154				
324 -> 330	0.25455				
325 -> 331	0.25468				
Excited State 13:	Singlet-E	3.2451 eV	382.06 nm	f=0.0463	<S**2>=0.000
323 -> 330	-0.24154				
323 -> 331	0.54201				
324 -> 331	-0.25406				
325 -> 330	0.25516				
Excited State 14:	Singlet-A	3.2452 eV	382.05 nm	f=0.0024	<S**2>=0.000

324 -> 330	-0.22690				
324 -> 331	0.43871				
325 -> 330	0.43807				
325 -> 331	0.22676				
Excited State 15:	Singlet-A	3.3440 eV	370.76 nm	f=0.0001	<S**2>=0.000
321 -> 330	0.40990				
321 -> 331	-0.13728				
322 -> 330	0.13728				
322 -> 331	0.40990				
324 -> 330	-0.18467				
325 -> 331	0.18468				
329 -> 332	0.17243				
Excited State 16:	Singlet-A	3.3822 eV	366.58 nm	f=0.0004	<S**2>=0.000
320 -> 330	-0.14803				
321 -> 331	0.40656				
322 -> 330	0.40656				
324 -> 330	-0.12494				
324 -> 331	-0.10051				
325 -> 330	0.10051				
325 -> 331	-0.12494				
329 -> 333	-0.22453				
329 -> 334	-0.14048				
Excited State 17:	Singlet-A	3.3822 eV	366.58 nm	f=0.0004	<S**2>=0.000
320 -> 331	0.14803				
321 -> 330	-0.40656				
322 -> 331	0.40656				
324 -> 330	0.10051				
324 -> 331	-0.12494				
325 -> 330	0.12494				
325 -> 331	0.10051				
329 -> 333	-0.14048				
329 -> 334	0.22452				
Excited State 18:	Singlet-A	3.4247 eV	362.03 nm	f=0.0000	<S**2>=0.000
321 -> 330	-0.11825				
322 -> 331	-0.11825				
329 -> 332	0.67921				
Excited State 19:	Singlet-E	3.4382 eV	360.60 nm	f=0.0102	<S**2>=0.000
321 -> 331	0.16025				
322 -> 330	0.16025				
329 -> 333	0.41378				
329 -> 334	0.50008				
Excited State 20:	Singlet-E	3.4382 eV	360.60 nm	f=0.0102	<S**2>=0.000
321 -> 330	-0.16025				
322 -> 331	0.16025				
329 -> 333	0.50008				
329 -> 334	-0.41378				
Excited State 21:	Singlet-A	3.5085 eV	353.38 nm	f=0.0159	<S**2>=0.000
321 -> 330	-0.15450				
321 -> 331	-0.45814				
322 -> 330	0.45815				
322 -> 331	-0.15451				
Excited State 22:	Singlet-E	3.5763 eV	346.69 nm	f=0.4262	<S**2>=0.000
320 -> 330	0.60434				
320 -> 331	0.25651				
Excited State 23:	Singlet-E	3.5763 eV	346.69 nm	f=0.4262	<S**2>=0.000
320 -> 330	-0.25651				
320 -> 331	0.60434				

Excited State 24:	Singlet-E	3.7819 eV	327.84 nm	f=0.0056	<S**2>=0.000
329 -> 335	0.51581				
329 -> 336	-0.46174				
Excited State 25:	Singlet-E	3.7819 eV	327.84 nm	f=0.0056	<S**2>=0.000
329 -> 335	0.46174				
329 -> 336	0.51581				

References for Supporting Information

[i] Wang, K.; Qi, D.; Wang, H.; Cao, W.; Li, W.; Jiang, J. *Chem. Eur. J.* **2012**, *18*, 15948-15952.

[ii] (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098-3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785-788.

[iii] *Gaussian 09*, Revision C.01, 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.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[iv] (a) Bauernschmitt, R. d.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454-464. (b) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009-4037.