Electronic Supplementary Material (ESI) for Chemical Communications

A Zinc Gable Phthalocyanine and a Planar Bis-phthalocyanine Sharing a Common Anthracene Unit

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Supporting information

General Comments

NMR spectra were obtained on a JEOL GSX-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 residual solvent as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and brs = broad singlet. Electronic absorption spectra were recorded using a Hitachi U-3410 spectrophotometer in a 1-cm quartz cell at room temperature. MCD spectra were recorded in the range of 260-900 nm with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet which produces parallel and antiparallel magnetic fields of 1.09 T (1T = 10000 gauss).

Additional Calculation Results

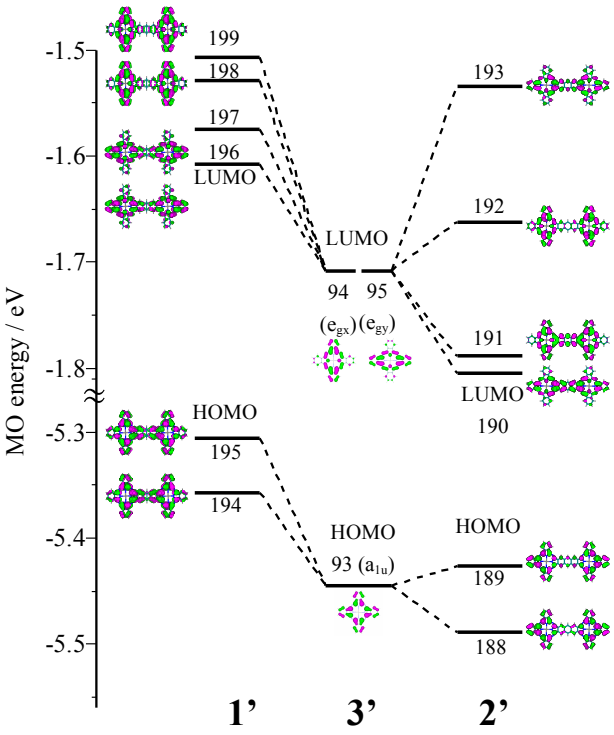

Figure S1. Partial molecular energy diagram and orbitals of **1′**, **2′** and **3′**. Calculated with ZINDO/S Hamiltonian.

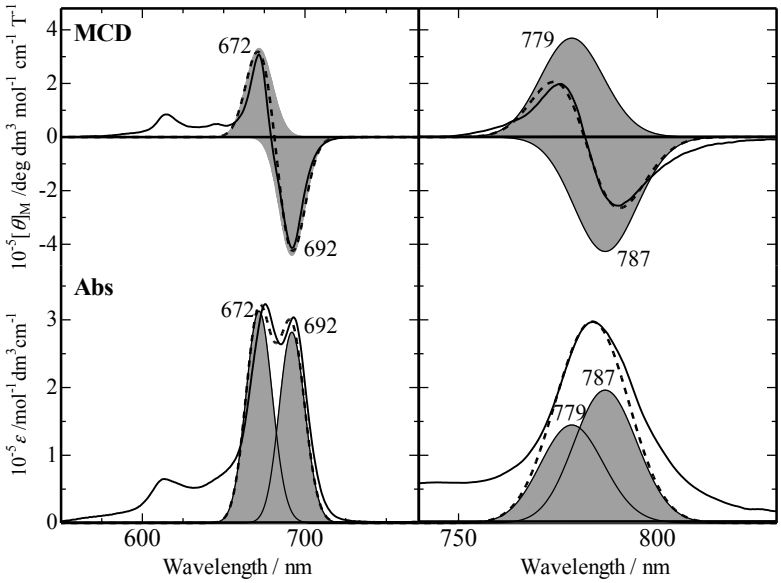

Figure S2. Simultaneous band deconvolution analyses of the absorption and MCD Q bands of **1** (left) and **2** (right). Deconvoluted bands are shown as shaded areas, the recorded data are shown as solid lines, and sum of the deconvoluted bands are shown as broken lines.

Experimental Procedures

Materials

Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation or recrystalization). 2,3,6,7-tetracyano-9,10,11,12,13,14-hexahydrofuranothracene was prepared according to the previous paper.[i]

Zn(II)GPc (1)

In the presence of lithium alcohoxide, 2,3,6,7-tetracyano-9,10,11,12,13,14-hexahydrofuranothracene (0.200 g, 0.575 mmol) and 4-*tert*-butylphthalonitrile (1.06 g, 5.75 mmol) were reacted at 185°C for 2 h hour to yield an crude metal-free GPc. To 1,2-dichloroethane-ethanol (3:2 v/v), the metal-free GPc and zinc(II)acetate dihydrate were added and the whole mixture was refluxed for 12 hours under dark. The unreacted zinc(II) acetate dihydrate was filtered off, and the filtrate was removed under reduced pressure to give a blue product. The product was first purified using silica gel TLC with $CHCl_3$-MeOH-triethylamine (100:10:1 v/v/v) as the eluent to give the desired dizinc complex (the first blue band). The product was further separated from minor unidentified debris by size-exclusion chromatography (Bio-beads SX-1, Bio-rad) using CH_2Cl_2. The first blue band was collected and recrystallized from pyridine-hexane, to give a blue powder of the desired gable bis-Zn(II)Pc (**1**) (11 mg, 1.2%). 400 MHz ^{1}H-NMR (pyridine-d_5) δ (ppm): 1.55-1.9 (m, 54H), 2.59 (s, 2H), 2.69 (s, 2H), 3.49 (s, 2H), 4.04 (s, 2H), 8.3-8.55 (m, 6H), 9.7-10.3 (m, 16H).

MALDI-TOF-MS Calcd for $C_{94}H_{82}N_{16}OZn_2$: 1584 ($[M]^+$); Found: 1584.

Anal. Calcd for $C_{94}H_{82}N_{16}OZn_2$: C, 71.34; H, 5.22; N, 14.16. Found: C, 70.96; H, 5.50; N, 13.75.

UV–vis (pyridine) λ_{max} nm (ε x 10^{-4}): 694 (29), 677 (31), 614 (6.3), 359 (14).

Conjugated planar bis-Zn(II)Pc (2)

1 (11.0 mg, 6.95 μmol) was heated at 300°C on a TLC plate under normal pressure or in a round bottomed flask under reduced pressure (10^{-4} Torr) for 24 hours. The product was purified using basic alumina TLC with CH_2Cl_2-methanol (100: 1 v/v) as eluent, and the second

green band was collected and crystallized from pyridine-hexane, to give a green powder of the desired conjugated planar bis-Zn(II)Pc (**2**) (1.48 mg, 14%). In its ^{1}H NMR spectrum, signals originated from the gable unit (at 2.4-4.1 ppm) disappeared. 400 MHz ^{1}H-NMR (dioxane-d_8) δ (ppm): 1.6-2.2 (m, 54H), 6.8-10.2 (br, 24H).

MALDI-TOF-MS Calcd for $C_{90}H_{78}N_{16}Zn_2$: 1514 ($[M]^+$); Found: 1514.

Anal. Calcd for $C_{90}H_{78}N_{16}Zn_2$: C, 71.37; H, 5.19; N, 14.80. Found: C, 71.02; H, 5.54; N, 14.41.

UV–vis (pyridine) λ_{max} nm (ε x 10^{-4}): 784 (29), 709 (6.9), 367 (10).

Full Computational Details

Computational Details

All calculations were performed at the DFT level, by means of the hybrid Becke3LYP[ii] (B3LYP) functional as implemented in Gaussian 2009.[iii] Zn atoms were described using an Ahlrichs' SVP[iv] all-electron basis set. The 6-31G* basis set was used for the C, H, N and O atoms (denoted as 631SVPs). Geometry optimization and vibrational analysis were performed at the same level. 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

Compound 1'

SCF Done: E(RB3LYP) = -7199.03505976 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	9.405853	1.123212	-1.799359
2	6	0	10.637285	0.705914	-2.468258
3	6	0	10.637277	-0.705622	-2.468350
4	6	0	9.405832	-1.122986	-1.799509
5	7	0	8.713076	0.000081	-1.423424
6	7	0	9.057312	-2.393603	-1.609429
7	6	0	7.940955	-2.791423	-1.001955
8	7	0	9.057326	2.393794	-1.609143
9	6	0	7.940963	2.791536	-1.001597
10	7	0	6.954857	-2.003525	-0.465407
11	6	0	7.575202	-4.192773	-0.802222
12	6	0	6.335083	-4.193127	-0.127608
13	6	0	5.968754	-2.791912	0.072583
14	7	0	4.854704	-2.394020	0.682936
15	6	0	4.507088	-1.122605	0.873995
16	7	0	6.955000	2.003573	-0.464934
17	6	0	5.968784	2.791893	0.072936
18	6	0	6.334954	4.193118	-0.127337
19	6	0	7.575073	4.192865	-0.801954
20	7	0	4.854720	2.393944	0.683231
21	7	0	5.197379	-0.000027	0.491912
22	6	0	3.282683	-0.705589	1.552993
23	6	0	3.282696	0.705425	1.553088
24	6	0	4.507093	1.122523	0.874155
25	6	0	11.688013	-1.425340	-3.038217
26	6	0	12.737433	-0.703726	-3.607073
27	6	0	12.737442	0.704138	-3.606980
28	6	0	11.688033	1.425692	-3.038028
29	6	0	8.207797	5.388042	-1.145615
30	6	0	7.574236	6.581932	-0.801126
31	6	0	6.337070	6.582265	-0.129021
32	6	0	5.702960	5.388785	0.215927
33	6	0	1.196976	-0.709857	2.710125
34	6	0	2.237695	-1.430474	2.134728
35	6	0	2.237719	1.430243	2.134930

36	6	0	1.196990	0.709560	2.710227
37	6	0	6.337477	-6.582273	-0.129123
38	6	0	7.574642	-6.581842	-0.801226
39	6	0	8.208066	-5.387899	-1.145795
40	6	0	5.703231	-5.388838	0.215744
41	6	0	-4.582978	1.122341	0.916892
42	6	0	-3.349114	0.705259	1.578407
43	6	0	-3.349115	-0.705433	1.578336
44	6	0	-4.582992	-1.122434	0.916765
45	7	0	-5.278987	-0.000033	0.544083
46	7	0	-4.933477	-2.393855	0.730850
47	6	0	-6.055923	-2.791728	0.135856
48	7	0	-4.933457	2.393766	0.731083
49	6	0	-6.055912	2.791698	0.136137
50	7	0	-7.049366	-2.003571	-0.388521
51	6	0	-6.424794	-4.192998	-0.059335
52	6	0	-7.673949	-4.192843	-0.717111
53	6	0	-8.042623	-2.791549	-0.911782
54	7	0	-9.167156	-2.393709	-1.503792
55	6	0	-9.518253	-1.123000	-1.689045
56	7	0	-7.049439	2.003607	-0.388170
57	6	0	-8.042594	2.791649	-0.911490
58	6	0	-7.673815	4.192922	-0.716852
59	6	0	-6.424658	4.192978	-0.059077
60	7	0	-9.167140	2.393887	-1.503556
61	7	0	-8.820200	0.000073	-1.322850
62	6	0	-10.758963	-0.705649	-2.340377
63	6	0	-10.758961	0.705927	-2.340302
64	6	0	-9.518256	1.123213	-1.688925
65	6	0	-2.295779	-1.431078	2.145256
66	6	0	-2.295774	1.430839	2.145406
67	6	0	-5.787844	5.388572	0.275508
68	6	0	-6.426324	6.582175	-0.060802
69	6	0	-7.672474	6.582045	-0.716129
70	6	0	-8.310866	5.388261	-1.051931
71	6	0	-12.875044	-0.703754	-3.449311
72	6	0	-11.817733	-1.425342	-2.895317
73	6	0	-11.817731	1.425678	-2.895165
74	6	0	-12.875043	0.704151	-3.449235
75	6	0	-7.672822	-6.581967	-0.716329
76	6	0	-6.426675	-6.582195	-0.061002
77	6	0	-5.788090	-5.388635	0.275280
78	6	0	-8.311107	-5.388131	-1.052157
79	6	0	-0.024790	-1.301466	3.391671
80	6	0	-0.024787	1.301096	3.391811
81	6	0	-0.065742	-0.782741	4.868143
82	6	0	-0.065741	0.782228	4.868224
83	6	0	1.145240	-1.140338	5.757824
84	8	0	1.371332	-0.000342	6.580940
85	6	0	1.145248	1.139733	5.757931
86	6	0	-1.249840	-0.710248	2.707924
87	6	0	-1.249838	0.709946	2.708000
88	1	0	11.680707	-2.510842	-3.034294
89	1	0	13.570983	-1.234478	-4.058979
90	1	0	13.570999	1.234938	-4.058817
91	1	0	11.680743	2.511193	-3.033962
92	1	0	9.161463	5.379506	-1.664103
93	1	0	8.040828	7.529912	-1.054774
94	1	0	5.870844	7.530548	0.124219
95	1	0	4.749242	5.381029	0.734343
96	1	0	2.245492	-2.516826	2.129897
97	1	0	2.245525	2.516595	2.130240
98	1	0	5.871357	-7.530590	0.124182
99	1	0	8.041342	-7.529785	-1.054809
100	1	0	9.161735	-5.379283	-1.664276
101	1	0	4.749514	-5.381155	0.734164

102	1	0	-2.304183	-2.517398	2.140873
103	1	0	-2.304172	2.517159	2.141137
104	1	0	-4.827070	5.380610	0.780743
105	1	0	-5.956476	7.530380	0.185979
106	1	0	-8.142253	7.530102	-0.963556
107	1	0	-9.271465	5.379919	-1.557476
108	1	0	-13.714893	-1.234495	-3.889423
109	1	0	-11.810388	-2.510847	-2.891441
110	1	0	-11.810385	2.511184	-2.891175
111	1	0	-13.714891	1.234939	-3.889293
112	1	0	-8.142685	-7.529988	-0.963733
113	1	0	-5.956908	-7.530434	0.185802
114	1	0	-4.827317	-5.380747	0.780521
115	1	0	-9.271709	-5.379710	-1.557698
116	1	0	-0.024822	-2.395387	3.352120
117	1	0	-0.024818	2.395021	3.352376
118	1	0	-0.985141	-1.154425	5.330135
119	1	0	-0.985139	1.153875	5.330249
120	1	0	2.034386	-1.359323	5.146311
121	1	0	0.959655	-1.992085	6.418445
122	1	0	2.034392	1.358774	5.146434
123	1	0	0.959669	1.991418	6.418634
124	30	0	-7.047704	0.000007	-0.390999
125	30	0	6.954027	0.000011	-0.466643

TD–DFT output
HOMO**: 318,** LUMO**: 319**
Excited State 1: Singlet-A 1.9442 eV 637.71 nm f=0.1875 <S**2>=0.000
317 -> 319 -0.12813
317 -> 322 -0.17937
318 -> 319 0.64989
318 -> 322 0.16164
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -7198.96361110
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.9674 eV 630.18 nm f=0.0641 <S**2>=0.000
317 -> 319 0.51334
317 -> 322 -0.20196
318 -> 319 0.14655
318 -> 322 -0.41556

Excited State 3: Singlet-A 1.9769 eV 627.16 nm f=0.0001 <S**2>=0.000
317 -> 320 -0.28324
317 -> 321 -0.19287
318 -> 320 0.56326
318 -> 321 0.25450

Excited State 4: Singlet-A 1.9933 eV 622.02 nm f=0.0002 <S**2>=0.000
317 -> 320 -0.35014
317 -> 321 0.41785
318 -> 320 -0.21167
318 -> 321 0.39681

Excited State 5: Singlet-A 2.0412 eV 607.41 nm f=0.7551 <S**2>=0.000
317 -> 322 0.64372
318 -> 319 0.21404
318 -> 322 -0.11528

Excited State 6: Singlet-A 2.0888 eV 593.56 nm f=0.0003 <S**2>=0.000
317 -> 320 0.18420
317 -> 321 0.52554
318 -> 320 0.35480
318 -> 321 -0.19395

Excited State 7:	Singlet-A	2.1026 eV	589.66 nm	f=0.7804	<S**2>=0.000
317 -> 320	0.49629				
318 -> 321	0.47244				
Excited State 8:	Singlet-A	2.1095 eV	587.73 nm	f=0.1848	<S**2>=0.000
317 -> 319	0.44211				
318 -> 322	0.52050				
Excited State 9:	Singlet-A	3.0446 eV	407.22 nm	f=0.0000	<S**2>=0.000
315 -> 322	0.18270				
316 -> 319	0.64924				
316 -> 322	-0.11238				
Excited State 10:	Singlet-A	3.0958 eV	400.49 nm	f=0.0049	<S**2>=0.000
315 -> 319	0.22360				
316 -> 319	0.10618				
316 -> 322	0.63179				
Excited State 11:	Singlet-A	3.1606 eV	392.28 nm	f=0.2000	<S**2>=0.000
307 -> 320	-0.10310				
307 -> 321	-0.10592				
315 -> 321	0.12998				
316 -> 320	0.62754				
316 -> 321	-0.16998				
Excited State 12:	Singlet-A	3.1864 eV	389.11 nm	f=0.0142	<S**2>=0.000
307 -> 320	-0.25708				
308 -> 321	0.22421				
316 -> 320	0.13355				
316 -> 321	0.56446				
Excited State 13:	Singlet-A	3.1992 eV	387.55 nm	f=0.0001	<S**2>=0.000
307 -> 319	-0.20991				
308 -> 319	-0.38476				
308 -> 322	0.50793				
315 -> 319	-0.16022				
315 -> 322	0.12786				
Excited State 14:	Singlet-A	3.2031 eV	387.08 nm	f=0.0000	<S**2>=0.000
307 -> 319	0.49698				
307 -> 322	0.41276				
308 -> 319	-0.23691				
315 -> 322	0.10223				
Excited State 15:	Singlet-A	3.2148 eV	385.66 nm	f=0.0213	<S**2>=0.000
307 -> 321	0.23055				
308 -> 320	-0.36375				
308 -> 321	0.47875				
315 -> 321	0.18416				
316 -> 321	-0.15776				
Excited State 16:	Singlet-A	3.2242 eV	384.54 nm	f=0.0150	<S**2>=0.000
307 -> 320	0.50576				
307 -> 321	0.26504				
308 -> 321	-0.18580				
315 -> 320	0.17577				
316 -> 320	0.16346				
316 -> 321	0.24243				
Excited State 17:	Singlet-A	3.3489 eV	370.22 nm	f=0.0003	<S**2>=0.000
311 -> 320	0.57316				
311 -> 321	0.34067				
313 -> 319	-0.15385				
313 -> 322	-0.10499				
Excited State 18:	Singlet-A	3.3516 eV	369.92 nm	f=0.0008	<S**2>=0.000

309 -> 319	-0.10859				
311 -> 320	-0.15839				
312 -> 320	-0.24659				
312 -> 321	0.42141				
313 -> 319	-0.34677				
313 -> 322	-0.24551				
Excited State 19:	Singlet-A	3.3519 eV	369.90 nm	f=0.0016	<S**2>=0.000
309 -> 319	0.11029				
311 -> 321	0.11182				
312 -> 320	-0.27620				
312 -> 321	0.40587				
313 -> 319	0.35153				
313 -> 322	0.25592				
Excited State 20:	Singlet-A	3.3567 eV	369.37 nm	f=0.0026	<S**2>=0.000
310 -> 319	-0.11706				
310 -> 322	0.13582				
314 -> 319	-0.42939				
314 -> 322	0.48562				

Compound 2′

SCF Done: E(RB3LYP) = -6967.79440345 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-10.631462	-1.122906	0.001165
2	6	0	-12.031848	-0.706818	0.001459
3	6	0	-12.032353	0.705488	0.001922
4	6	0	-10.632583	1.123411	0.001901
5	7	0	-9.843456	-0.000324	0.001539
6	7	0	-10.231657	2.394192	0.001731
7	6	0	-8.963204	2.791094	0.001559
8	7	0	-10.231002	-2.395076	0.000499
9	6	0	-8.962834	-2.790692	0.000109
10	7	0	-7.835575	2.001259	0.001338
11	6	0	-8.545434	4.191803	0.001934
12	6	0	-7.133891	4.192145	0.002230
13	6	0	-6.716058	2.791501	0.002087
14	7	0	-5.442953	2.396333	0.002804
15	6	0	-5.041415	1.129914	0.003395
16	7	0	-7.835126	-2.001171	-0.000150
17	6	0	-6.714733	-2.790506	0.001546
18	6	0	-7.132819	-4.192116	0.001752
19	6	0	-8.543843	-4.192120	0.000798
20	7	0	-5.441762	-2.395765	0.003099
21	7	0	-5.822861	0.000537	0.004187
22	6	0	-3.636308	0.719233	0.002897
23	6	0	-3.636120	-0.717414	0.003085
24	6	0	-5.041528	-1.127326	0.003552
25	6	0	-13.228898	1.424237	0.002164
26	6	0	-14.421749	0.702482	0.001951
27	6	0	-14.421177	-0.705823	0.001483
28	6	0	-13.227628	-1.426536	0.001217
29	6	0	-9.262745	-5.387548	0.000603
30	6	0	-8.540743	-6.581220	0.001430
31	6	0	-7.133205	-6.581112	0.002446
32	6	0	-6.412462	-5.386814	0.002628
33	6	0	-1.226501	0.729225	0.001002
34	6	0	-2.467997	1.434719	0.001915
35	6	0	-2.467911	-1.432833	0.002336
36	6	0	-1.226394	-0.727226	0.001249
37	6	0	-7.134843	6.581244	0.002346
38	6	0	-8.543038	6.580985	0.002034
39	6	0	-9.264540	5.387701	0.001817

40	6	0	-6.413981	5.387714	0.002448
41	6	0	5.042587	-1.127549	-0.010986
42	6	0	3.638457	-0.716826	-0.007616
43	6	0	3.638375	0.719742	-0.007671
44	6	0	5.042265	1.130993	-0.011077
45	7	0	5.824195	0.001426	-0.013986
46	7	0	5.441893	2.399125	-0.012596
47	6	0	6.713405	2.798346	-0.008978
48	7	0	5.441020	-2.396856	-0.013076
49	6	0	6.712788	-2.796205	-0.009392
50	7	0	7.832615	2.007808	0.001724
51	6	0	7.133844	4.198144	-0.013587
52	6	0	8.545971	4.195209	-0.005955
53	6	0	8.961047	2.793544	0.002822
54	7	0	10.232002	2.395091	0.009249
55	6	0	10.633619	1.124182	0.012675
56	7	0	7.832547	-2.007432	0.000644
57	6	0	8.961028	-2.793133	0.002491
58	6	0	8.544149	-4.195137	-0.005710
59	6	0	7.132402	-4.197218	-0.013383
60	7	0	10.231948	-2.396927	0.009212
61	7	0	9.846468	-0.001832	0.009864
62	6	0	12.033365	0.704743	0.018649
63	6	0	12.032901	-0.707782	0.018301
64	6	0	10.632833	-1.125214	0.012387
65	6	0	2.469465	1.435330	-0.004736
66	6	0	2.469778	-1.432665	-0.004357
67	6	0	6.414151	-5.393216	-0.022520
68	6	0	7.136576	-6.586531	-0.023835
69	6	0	8.543949	-6.584636	-0.016332
70	6	0	9.264221	-5.389839	-0.007257
71	6	0	14.422213	0.701818	0.028133
72	6	0	13.229732	1.423884	0.023540
73	6	0	13.228546	-1.427830	0.023118
74	6	0	14.421668	-0.706694	0.027979
75	6	0	8.547420	6.584692	-0.017762
76	6	0	7.139337	6.587522	-0.025173
77	6	0	6.416401	5.395272	-0.023276
78	6	0	9.266693	5.390007	-0.008176
79	6	0	0.000773	1.404897	-0.000499
80	6	0	0.000991	-1.402694	0.000013
81	6	0	1.228867	0.729457	-0.002263
82	6	0	1.228984	-0.727051	-0.002017
83	1	0	-13.221419	2.509991	0.002482
84	1	0	-15.370351	1.232859	0.002156
85	1	0	-15.369349	-1.236946	0.001331
86	1	0	-13.218856	-2.512253	0.000824
87	1	0	-10.348423	-5.379606	-0.000161
88	1	0	-9.071687	-7.529480	0.001266
89	1	0	-6.601787	-7.529082	0.003060
90	1	0	-5.326750	-5.378069	0.003396
91	1	0	-2.477778	2.521220	0.001593
92	1	0	-2.477943	-2.519298	0.002351
93	1	0	-6.604463	7.529813	0.002474
94	1	0	-9.073438	7.529566	0.001945
95	1	0	-10.350241	5.378985	0.001549
96	1	0	-5.328239	5.378775	0.002678
97	1	0	2.479454	2.521763	-0.004571
98	1	0	2.480187	-2.519078	-0.003789
99	1	0	5.328406	-5.386424	-0.028297
100	1	0	6.606544	-7.535253	-0.030820
101	1	0	9.076195	-7.532149	-0.017770
102	1	0	10.349858	-5.380675	-0.001591
103	1	0	15.371047	1.231762	0.031998
104	1	0	13.221927	2.509609	0.023620
105	1	0	13.219405	-2.513480	0.023100

106	1	0	15.370125	-1.237287	0.031841
107	1	0	9.079436	7.532346	-0.019696
108	1	0	6.610753	7.537066	-0.032530
109	1	0	5.330601	5.388667	-0.028930
110	1	0	10.352347	5.379363	-0.002657
111	1	0	0.000736	2.492947	-0.000664
112	1	0	0.001146	-2.490753	0.000224
113	30	0	-7.841138	-0.001482	0.002915
114	30	0	7.832577	-0.000728	0.001183

TD–DFT output
HOMO: **299**, LUMO: **300**
Excited State 1: Singlet-A 1.5861 eV 781.71 nm f=0.1639 <S**2>=0.000
299 -> 300 0.69706
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -6967.73611665
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.6855 eV 735.58 nm f=1.7265 <S**2>=0.000
299 -> 301 0.70336

Excited State 3: Singlet-A 1.7191 eV 721.21 nm f=0.0004 <S**2>=0.000
298 -> 300 -0.23251
299 -> 302 0.66309

Excited State 4: Singlet-A 1.8963 eV 653.81 nm f=0.0001 <S**2>=0.000
298 -> 300 0.65171
298 -> 304 -0.12379
299 -> 302 0.22541

Excited State 5: Singlet-A 1.8985 eV 653.07 nm f=0.0001 <S**2>=0.000
298 -> 301 -0.47390
299 -> 303 0.52275

Excited State 6: Singlet-A 2.0634 eV 600.87 nm f=0.3766 <S**2>=0.000
298 -> 302 0.67497
299 -> 304 -0.17592

Excited State 7: Singlet-A 2.0997 eV 590.48 nm f=0.0001 <S**2>=0.000
298 -> 301 0.50730
299 -> 303 0.46181

Excited State 8: Singlet-A 2.2037 eV 562.62 nm f=0.1508 <S**2>=0.000
297 -> 300 0.11095
298 -> 302 0.15921
299 -> 304 0.67038

Excited State 9: Singlet-A 2.2074 eV 561.68 nm f=0.2534 <S**2>=0.000
298 -> 303 0.69401

Excited State 10: Singlet-A 2.4462 eV 506.85 nm f=0.0000 <S**2>=0.000
298 -> 300 0.11571
298 -> 304 0.68959

Excited State 11: Singlet-A 2.6819 eV 462.29 nm f=0.0989 <S**2>=0.000
297 -> 300 0.68962

Excited State 12: Singlet-A 2.7465 eV 451.43 nm f=0.0438 <S**2>=0.000
297 -> 301 0.68096

Excited State 13: Singlet-A 2.8008 eV 442.67 nm f=0.0001 <S**2>=0.000
297 -> 302 0.69376

Excited State 14: Singlet-A 3.0378 eV 408.14 nm f=0.0000 <S**2>=0.000
297 -> 303 0.68710

Excited State 15:	Singlet-A	3.1843 eV	389.37 nm	f=0.0427	<S**2>=0.000
299 -> 305	0.66616				
Excited State 16:	Singlet-A	3.1917 eV	388.45 nm	f=0.0000	<S**2>=0.000
288 -> 302	0.34096				
289 -> 300	0.52805				
289 -> 302	0.30937				
Excited State 17:	Singlet-A	3.1942 eV	388.16 nm	f=0.0000	<S**2>=0.000
288 -> 300	0.53885				
288 -> 302	-0.27271				
289 -> 302	0.35043				
Excited State 18:	Singlet-A	3.2850 eV	377.42 nm	f=0.0320	<S**2>=0.000
292 -> 300	0.37439				
292 -> 302	-0.24514				
293 -> 300	0.35252				
293 -> 302	-0.29221				
295 -> 302	-0.10526				
296 -> 300	0.18695				
297 -> 304	-0.11829				
Excited State 19:	Singlet-A	3.2897 eV	376.88 nm	f=0.2659	<S**2>=0.000
280 -> 300	0.10516				
283 -> 302	0.11195				
292 -> 300	-0.24296				
293 -> 302	0.19827				
295 -> 302	-0.28838				
296 -> 300	0.49186				
Excited State 20:	Singlet-A	3.2941 eV	376.38 nm	f=0.0439	<S**2>=0.000
292 -> 300	-0.24737				
292 -> 302	-0.33674				
293 -> 300	0.41737				
293 -> 302	0.20738				
296 -> 300	-0.18612				
297 -> 304	0.10739				

Compound 3′ (Phthalocyanine zinc)

SCF Done: E(RB3LYP) = -3446.38225203 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.000000	0.000000	0.000000
2	6	0	1.425623	5.387548	0.000000
3	6	0	0.703882	6.581248	0.000000
4	6	0	-0.703882	6.581248	0.000000
5	6	0	-1.425623	5.387548	0.000000
6	6	0	-0.705928	4.192273	0.000000
7	6	0	0.705928	4.192273	0.000000
8	6	0	1.123027	2.791180	0.000000
9	6	0	-1.123027	2.791180	0.000000
10	7	0	0.000000	2.002956	0.000000
11	6	0	5.387548	-1.425623	0.000000
12	6	0	6.581248	-0.703882	0.000000
13	6	0	6.581248	0.703882	0.000000
14	6	0	5.387548	1.425623	0.000000
15	6	0	4.192273	0.705928	0.000000
16	6	0	4.192273	-0.705928	0.000000
17	6	0	2.791180	-1.123027	0.000000
18	6	0	2.791180	1.123027	0.000000
19	7	0	2.002956	0.000000	0.000000
20	6	0	-5.387548	1.425623	0.000000
21	6	0	-6.581248	0.703882	0.000000

22	6	0	-6.581248	-0.703882	0.000000
23	6	0	-5.387548	-1.425623	0.000000
24	6	0	-4.192273	-0.705928	0.000000
25	6	0	-4.192273	0.705928	0.000000
26	6	0	-2.791180	1.123027	0.000000
27	6	0	-2.791180	-1.123027	0.000000
28	7	0	-2.002956	0.000000	0.000000
29	6	0	-1.425623	-5.387548	0.000000
30	6	0	-0.703882	-6.581248	0.000000
31	6	0	0.703882	-6.581248	0.000000
32	6	0	1.425623	-5.387548	0.000000
33	6	0	0.705928	-4.192273	0.000000
34	6	0	-0.705928	-4.192273	0.000000
35	6	0	-1.123027	-2.791180	0.000000
36	6	0	1.123027	-2.791180	0.000000
37	7	0	0.000000	-2.002956	0.000000
38	7	0	2.393665	2.393665	0.000000
39	7	0	2.393665	-2.393665	0.000000
40	7	0	-2.393665	2.393665	0.000000
41	7	0	-2.393665	-2.393665	0.000000
42	1	0	2.511111	5.379672	0.000000
43	1	0	1.234848	7.529299	0.000000
44	1	0	-1.234848	7.529299	0.000000
45	1	0	-2.511111	5.379672	0.000000
46	1	0	5.379672	-2.511111	0.000000
47	1	0	7.529299	-1.234848	0.000000
48	1	0	7.529299	1.234848	0.000000
49	1	0	5.379672	2.511111	0.000000
50	1	0	-5.379672	2.511111	0.000000
51	1	0	-7.529299	1.234848	0.000000
52	1	0	-7.529299	-1.234848	0.000000
53	1	0	-5.379672	-2.511111	0.000000
54	1	0	-2.511111	-5.379672	0.000000
55	1	0	-1.234848	-7.529299	0.000000
56	1	0	1.234848	-7.529299	0.000000
57	1	0	2.511111	-5.379672	0.000000

TD–DFT output
HOMO: **147**, LUMO: **148, 149**
Excited State 1: Singlet-EU 2.0917 eV 592.73 nm f=0.4213 <S**2>=0.000
143 ->149 0.15253
147 ->148 0.62219
147 ->149 -0.29249
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3446.30538224
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-EU 2.0917 eV 592.73 nm f=0.4213 <S**2>=0.000
143 ->148 -0.15253
147 ->148 0.29249
147 ->149 0.62219

Excited State 3: Singlet-EG 3.2156 eV 385.57 nm f=0.0000 <S**2>=0.000
142 ->148 0.21691
142 ->149 0.67150

Excited State 4: Singlet-EG 3.2156 eV 385.57 nm f=0.0000 <S**2>=0.000
142 ->148 0.67150
142 ->149 -0.21691

Excited state symmetry could not be determined.
Excited State 5: Singlet-?Sym 3.3473 eV 370.40 nm f=0.0000 <S**2>=0.000
144 ->149 -0.49403
145 ->148 0.49403

Excited state symmetry could not be determined.
Excited State 6: Singlet-?Sym 3.3475 eV 370.37 nm f=0.0000 <S**2>=0.000
144 ->148 0.34817
144 ->149 0.35078
145 ->148 0.35078
145 ->149 -0.34817

Excited State 7: Singlet-EU 3.3733 eV 367.54 nm f=0.0081 <S**2>=0.000
137 ->148 -0.16166
146 ->148 0.64144
146 ->149 -0.20951

Excited State 8: Singlet-EU 3.3733 eV 367.54 nm f=0.0081 <S**2>=0.000
137 ->149 0.16166
146 ->148 0.20951
146 ->149 0.64144

Excited State 9: Singlet-EG 3.4236 eV 362.14 nm f=0.0000 <S**2>=0.000
138 ->148 0.29668
138 ->149 0.63699

Excited State 10: Singlet-EG 3.4236 eV 362.14 nm f=0.0000 <S**2>=0.000
138 ->148 0.63699
138 ->149 -0.29668

Excited State 11: Singlet-B1G 3.4594 eV 358.40 nm f=0.0000 <S**2>=0.000
144 ->148 -0.35463
145 ->149 -0.35463
147 ->150 0.47759

Excited State 12: Singlet-B1G 3.5043 eV 353.81 nm f=0.0000 <S**2>=0.000
140 ->149 0.18508
141 ->148 -0.18508
144 ->148 0.33840
145 ->149 0.33840
147 ->150 0.44495

Excited state symmetry could not be determined.
Excited State 13: Singlet-?Sym 3.5559 eV 348.67 nm f=0.0000 <S**2>=0.000
140 ->148 0.11931
140 ->149 0.17469
141 ->148 0.17469
141 ->149 -0.11931
144 ->148 0.32022
144 ->149 -0.31783
145 ->148 -0.31783
145 ->149 -0.32022

Excited State 14: Singlet-B2G 3.6311 eV 341.45 nm f=0.0000 <S**2>=0.000
140 ->148 0.20705
141 ->149 0.20705
147 ->151 0.63829

Excited state symmetry could not be determined.
Excited State 15: Singlet-?Sym 3.6427 eV 340.36 nm f=0.0000 <S**2>=0.000
140 ->148 0.41090
140 ->149 -0.28063
141 ->148 -0.28063
141 ->149 -0.41090

Excited State 16: Singlet-EU 3.6548 eV 339.24 nm f=0.1474 <S**2>=0.000
137 ->148 0.41899
137 ->149 -0.20798
139 ->149 0.17316
143 ->148 0.42118
143 ->149 -0.20906

146 ->148 0.14145

Excited State 17: Singlet-EU 3.6548 eV 339.24 nm f=0.1473 <S**2>=0.000
137 ->148 0.20798
137 ->149 0.41900
139 ->148 0.17316
143 ->148 0.20906
143 ->149 0.42117
146 ->149 -0.14145

Excited State 18: Singlet-EU 3.7430 eV 331.24 nm f=0.3328 <S**2>=0.000
139 ->148 0.14936
139 ->149 0.62961
143 ->148 -0.18900
147 ->153 -0.10398
147 ->154 0.10400

Excited State 19: Singlet-EU 3.7430 eV 331.24 nm f=0.3326 <S**2>=0.000
139 ->148 0.62960
139 ->149 -0.14935
143 ->149 -0.18900
147 ->153 0.10400
147 ->154 0.10398

Excited state symmetry could not be determined.
Excited State 20: Singlet-?Sym 3.7610 eV 329.65 nm f=0.0000 <S**2>=0.000
140 ->148 0.24996
140 ->149 0.36600
141 ->148 0.36600
141 ->149 -0.24996
144 ->148 -0.14578
144 ->149 0.14469
145 ->148 0.14469
145 ->149 0.14578

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