Electronic Supplementary Material (ESI) for ChemComm.

Control of Absorption Properties of Tetrazaporphyrin Group 15 Complexes by Modification of their Axial Ligands

Taniyuki Furuyama, Mitsuo Asai and Nagao Kobayashi*

Department of Chemistry, Graduate School of Science, Tohoku University

nagaok@m.tohoku.ac.jp

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 $dm^3mol^{-1}cm^{-1}T^{-1}$). 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. ^{31}P-NMR spectra were referenced to external 85% H_3PO_4 solution (0.0 ppm). The following abbreviations are used: s = singlet, d = doublet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Apex-III spectrometer.

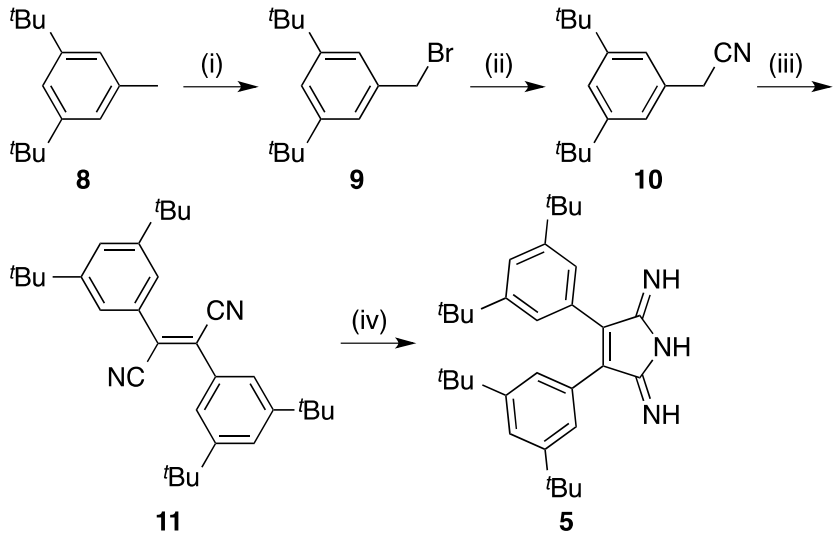
Crystallographic data collection

A needle shaped and green single crystal of **6•H_2O** 0.20 × 0.05 × 0.05 mm, was selected for measurements. The diffraction data were collected using a Bruker APEXII CCD diffractometer with Bruker Helios multilayered confocal mirror monochromatized Mo*K*α radiation (λ = 0.71073 Å) at –173°C. The structures were solved by a direct method (SIR2004)[i] and refined using a full-matrix least square technique (SHELXL-97).[ii] Yadokari-XG 2009 software was used as a GUI for SHELXL-97.[iii] All non-hydrogen atoms were refined anisotropically. Positions of all hydrogen atoms were calculated geometrically, and refined by applying riding models. The peripheral *tert*-butyl substituents were severely disordered despite the low measurement temperature. Therefore, the structure was refined under thermally and positionally restrained conditions, using DFIX, SIMU, ISOR, and DELU commands. Some large electron peaks due to solvent chloroform molecules (maybe 3 molecules) were found in the unit cell. As we failed to model them properly, the rest molecules were refined without the effect of the solvent molecules by the Platon squeeze technique.[iv] CCDC-1024678 contains the supplementary crystallographic data for **6•H_2O**. Its data can be obtained free of charge from Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **6•H_2O**.

Empirical formula	$C_{128}H_{168}MgN_8O_6$
Formula weight	1859.01
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pccn* (No. 56)
Unit cell dimensions	a = 22.085(9) Å α = 90°
	b = 35.163(14) Å β = 90°
	c = 18.194(7) Å γ = 90°
Volume	14129(10) $Å^3$
Z	4
Density (Calcd.)	0.874 Mg/m^3
Absorption coefficient	0.055 mm^{-1}
F(000)	4048
Crystal size	0.20 x 0.05 x 0.05 mm^3
Theta range for data collection	1.09 to 25.00°
Index ranges	-26<=h<=26, -41<=k<=24, -19<=l<=21
Reflections collected	65956
Independent reflections	12441 [R(int) = 0.2149]
Completeness to theta = 25.00°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints /parameters	12441 / 108 / 678
Goodness-of-fit on F^2	0.898
Final R indices [I > 2sigma(I)]	R_1 = 0.0967, wR_2 = 0.2113
R indices (all data)	R_1 = 0.2129, wR_2 = 0.2546
Largest diff. peak and hole	0.654 and -0.248 $e.Å^{-3}$
CCDC No.	1024678

Additional Experimental and Computational Results



Scheme S1. Synthesis of TAP precursor **5**. *Reagents and conditions*: (i) NBS (1 eq), benzoyl peroxide (3 mol%), CCl_4, reflux, 1 h, 97%; (ii) NaCN (1.2 eq), DMSO, rt, 24 h, 65%; (iii) I_2 (2 eq), MeONa (5 eq), Et_2O, 0°C, 1 h, 36%; (iv) MeONa (10 mol%), NH_3 (gas), ethylene glycol, 115°C, 6 h, 69%.

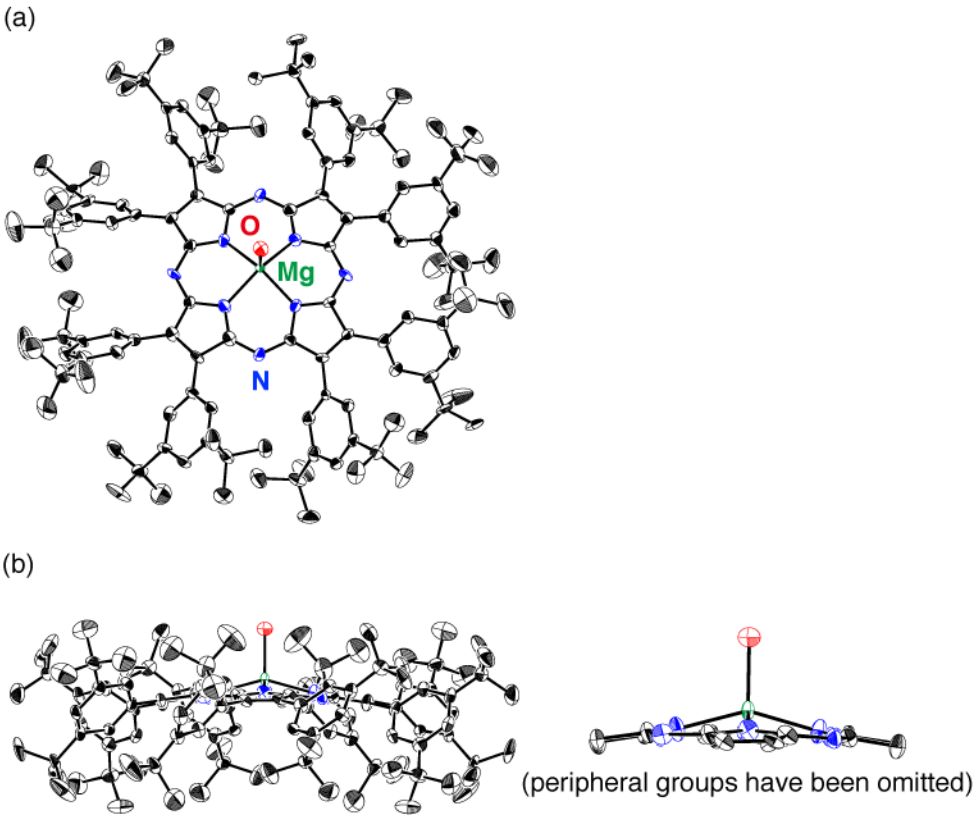


Figure S1. X-ray crystal structure of **6•H_2O**. The thermal ellipsoids were scaled to the 50% probability

level. H atoms have been omitted for clarity. (a) Top view; (b) side view.

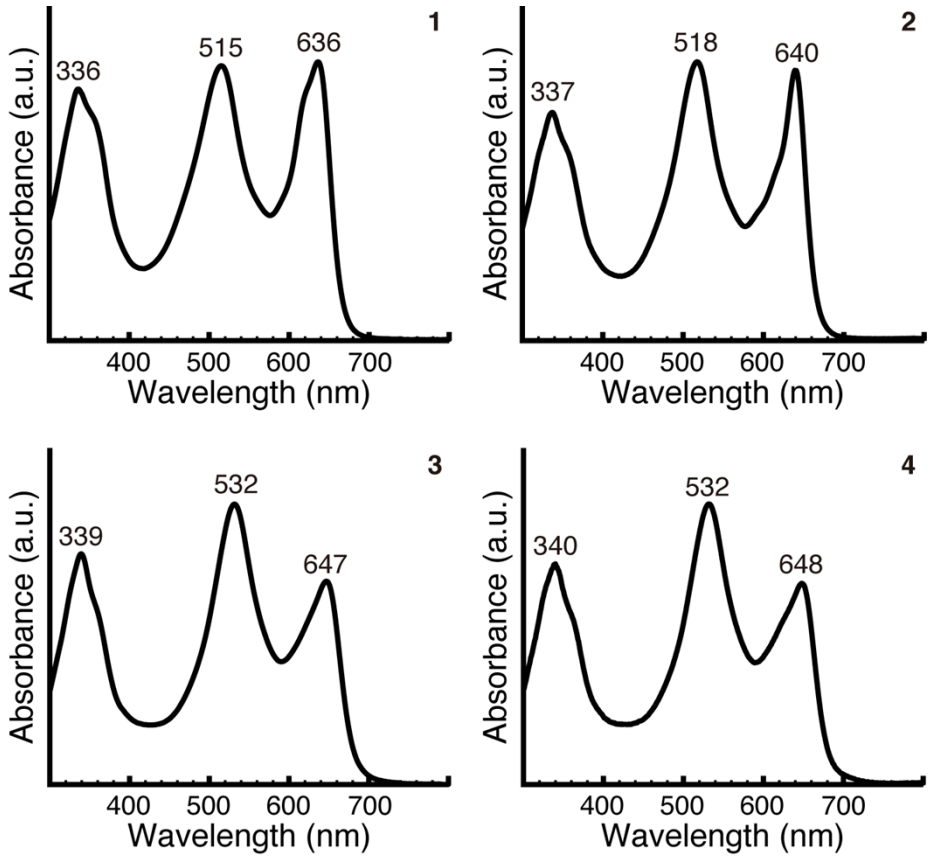


Figure S2. UV-vis absorption spectra of **1–4** in CH_2Cl_2.

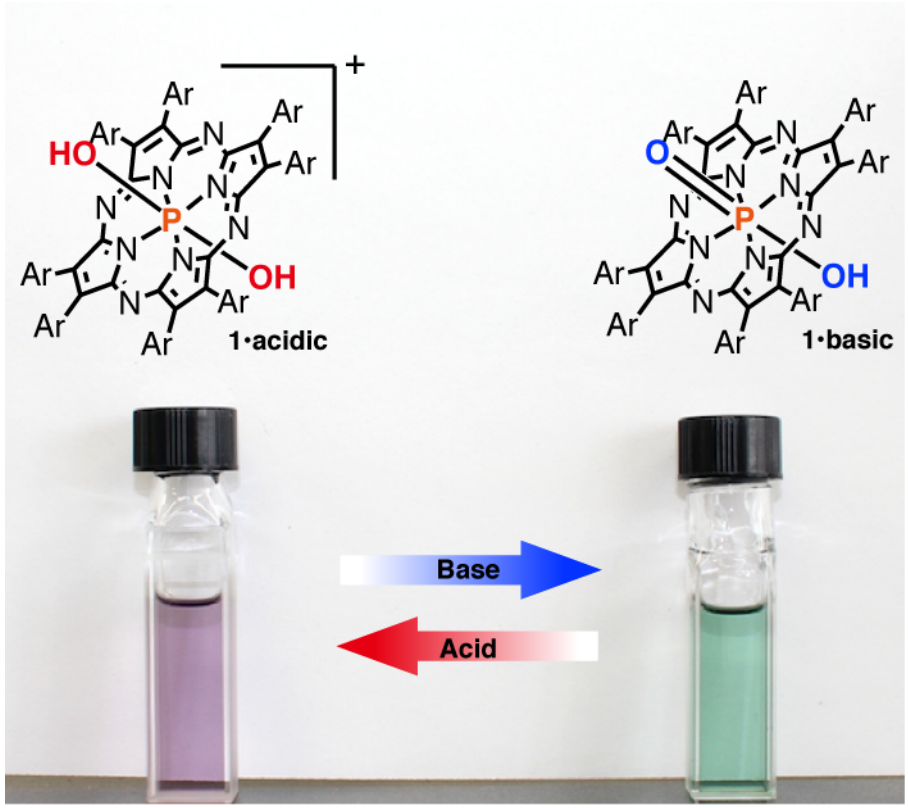


Figure S3. Photograph of PTAP **1** solutions under acidic and basic conditions.

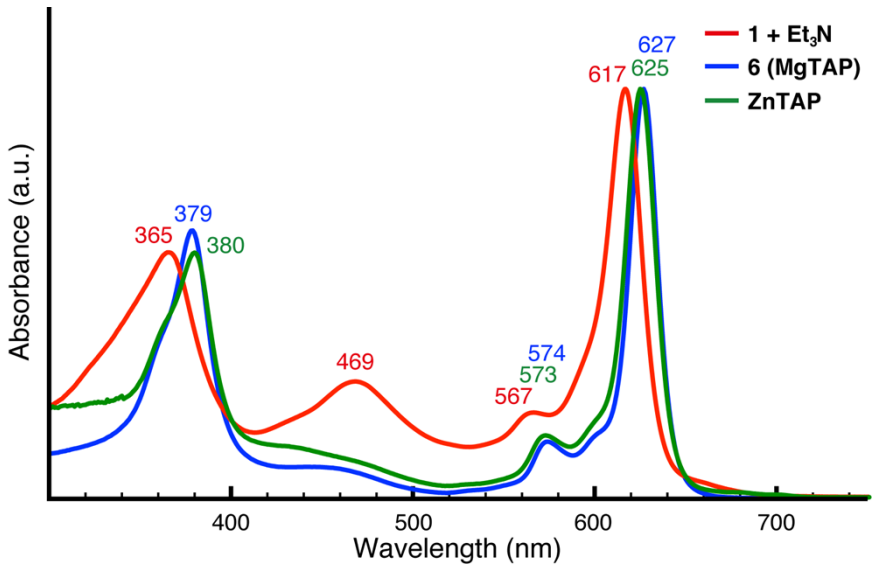


Figure S4. UV-vis absorption spectra of **1**+Et_3N (excess.) (red), **6** (blue), and ZnTAP (green) in toluene.

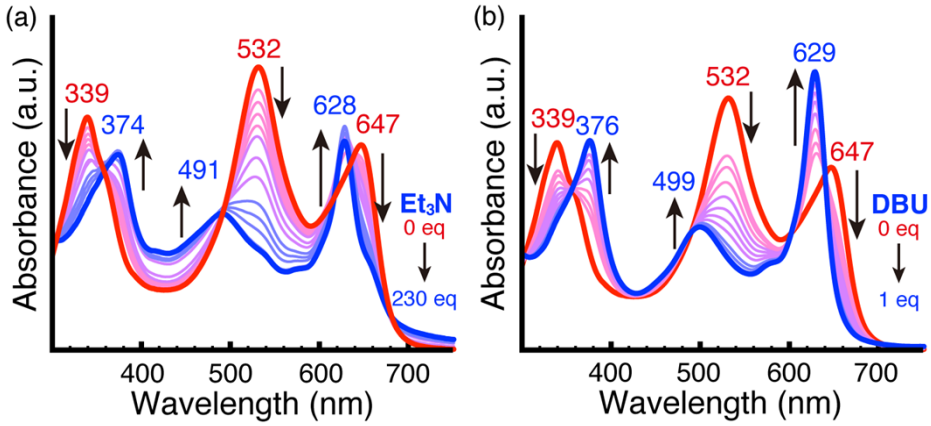


Figure S5. Spectral changes of **3** solution by (a) adding Et_3N (0~230 eq) and (b) adding DBU (~ 1 eq) in CH_2Cl_2.

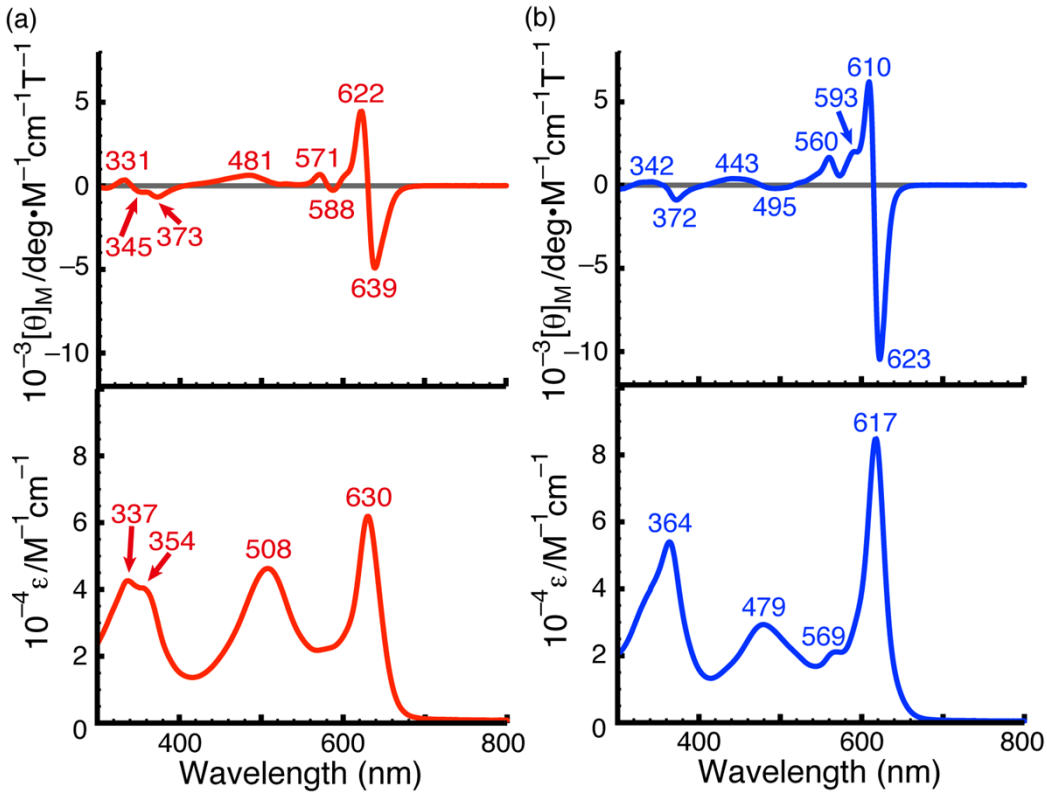


Figure S6. UV-vis absorption (bottom) and MCD (top) spectra of (a) **1•acidic** and (b) **1•basic** in CH_2Cl_2.

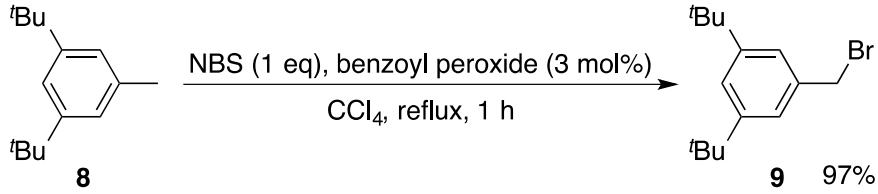
Table S2. Calculated excited wavelengths (λ) and oscillator strengths (*f*) for components of selected transition energies.

Compound	λ (nm)	*f*	Composition (%)	Assignment
1'•acidic	672	0.20	239–>258 (6%), 255–>258 (7%), 256–>257 (77%)	Q
			256–>258 (8%)	
	670	0.20	239–>257 (7%), 255–>257 (7%), 256–>257 (8%)	Q
			256–>258 (77%)	
	401	0.12	252–>257 (36%), 253–>257 (7%), 254–>258 (27%)	CT
			255–>258 (6%), 255–>259 (4%)	
	397	0.35	252–>258 (13%), 253–>257 (13%), 253–>258 (8%)	CT
			254–>258 (4%), 254–>259 (4%), 255–>258 (40%)	
			256–>257 (4%)	
	392	0.41	252–>257 (10%), 252–>258 (5%), 253–>257 (24%)	CT
			253–>258 (4%), 253–>259 (4%), 255–>257 (34%)	
			256–>258 (4%)	
	351	0.80	239–>257 (3%), 252–>257 (15%), 253–>257 (16%)	Soret
			253–>258 (3%), 255–>257 (47%), 256–>258 (5%)	
	348	0.70	239–>258 (2%), 252–>257 (4%), 252–>258 (7%)	Soret
			253–>257 (2%), 253–>258 (35%), 254–>257 (5%)	
			255–>258 (31%), 256–>257 (4%)	
1'•basic	633	0.32	244–>257 (2%), 256–>257 (44%), 256–>258 (45%)	Q
	626	0.32	244–>258 (2%), 256–>257 (45%), 256–>258 (43%)	Q
	352	0.10	244–>257 (3%), 244–>258 (2%), 252–>257 (27%)	CT
			252–>258 (16%), 253–>257 (12%), 253–>258 (5%)	
			254–>257 (3%), 255–>259 (9%)	
	345	0.19	244–>258 (3%), 252–>257 (18%), 252–>258 (27%)	CT
			253–>257 (8%), 253–>258 (9%), 253–>259 (2%)	
			254–>258 (5%), 254–>259 (7%)	

308	1.43	244–>257 (12%), 244–>258 (2%), 245–>257 (2%) 245–>258 (3%), 249–>257 (2%), 249–>258 (3%) 250–>257 (3%), 252–>258 (2%), 253–>257 (25%) 253–>258 (9%), 254–>257 (6%), 254–>258 (5%) 256–>257 (3%), 256–>258 (7%)	Soret
306	1.27	244–>257 (3%), 244–>258 (7%), 245–>257 (3%) 245–>258 (5%), 246–>257 (2%), 246–>258 (4%) 247–>258 (4%), 249–>257 (3%), 249–>258 (3%) 253–>257 (8%), 253–>258 (18%), 254–>257 (5%) 254–>258 (8%), 256–>257 (7%), 256–>258 (4%)	Soret

Full Experimental Procedures

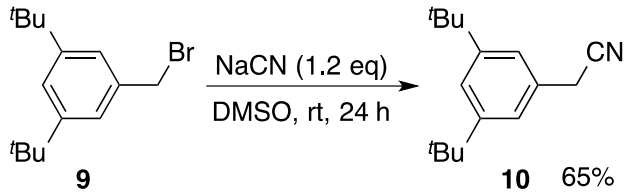
1-Bromomethyl-3,5-di-*tert*-butylbenzene (9)[v]



8 **9** 97%

A mixture of 3,5-di-*tert*-butyltoluene (**8**, 10.0 g, 49.0 mmol), NBS (9.0 g, 50.4 mmol) and benzoyl peroxide (0.4 g, 1.6 mmol) in 100 mL of CCl_4 was refluxed for 1 h. After cooling to rt, the mixture was filtered and the residue was washed with CCl_4, then the filtrate was concentrated *in vacuo*. The product was purified by silica gel column chromatography (^{n}hexane). Title compound was obtained as a white solid (13.5 g, 97%). 500 MHz ^{1}H NMR ($CDCl_3$): δ = 7.36 (t, J = 2.0 Hz, 1H), 7.23 (d, J = 2.0 Hz, 2H), 4.52 (s, 2H), 1.33 (s. 18H).

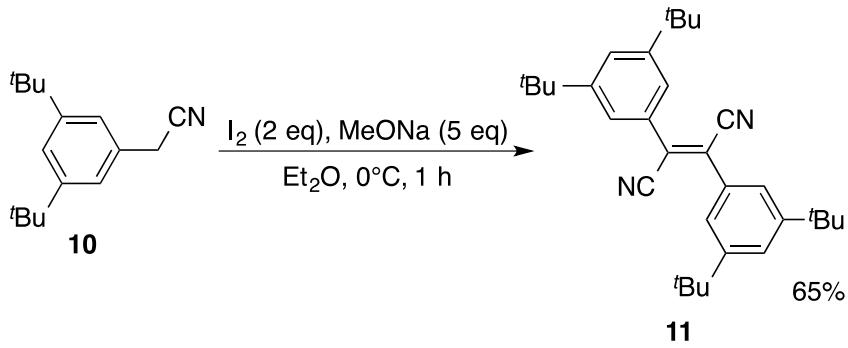
1,3-Di-*tert*-butyl-5-(cyanomethyl)benzene (10)[v]



9 **10** 65%

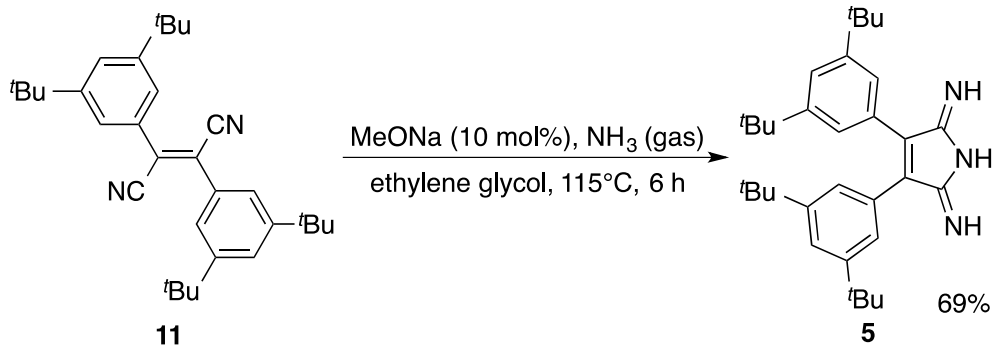
Compound **9** (5.0 g, 17.7 mmol) was added dropwise to a solution of sodium cyanide (1.43 g, 22.0 mmol) in 20 mL of DMSO. After additional 10 mL of DMSO was added to dissolve all precipitates, the mixture was stirred at rt for 24 h. Then, the reaction mixture was poured into 100 mL of water and extracted with ethyl acetate (50 mL X 3). The organic layer was washed with brine and dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (^{n}hexane-ethyl acetate 98 : 2). Title compound was obtained as a white solid (2.74 g, 65%). 500 MHz ^{1}H NMR ($CDCl_3$): δ = 7.38 (t, J = 1.5 Hz, 1H), 7.15 (d, J = 1.5 Hz, 2H), 3.74 (s, 2H), 1.33 (s, 18H).

Bis(3,5-di-*tert*-butylphenyl)fumaronitrile (11)



Sodium methoxide (Na 0.26 g, 11.5 mmol) – methanol solution was slowly (over a period of 1 h) added to a solution of **10** (1.00 g, 4.19 mmol) and I_2 (1.06 g, 4.19 mmol) in 20 mL of dry diethyl ether at 0°C. The reaction mixture was stirred for 1 h at the same temperature. The title compound (0.34 g, 36%) as white solid was collected by filteration. 500 MHz ^{1}H NMR ($CDCl_3$): δ = 7.66 (d, *J* = 1.5 Hz, 4H), 7.58 (t, *J* = 1.5 Hz, 2H), 1.39 (s, 36H).

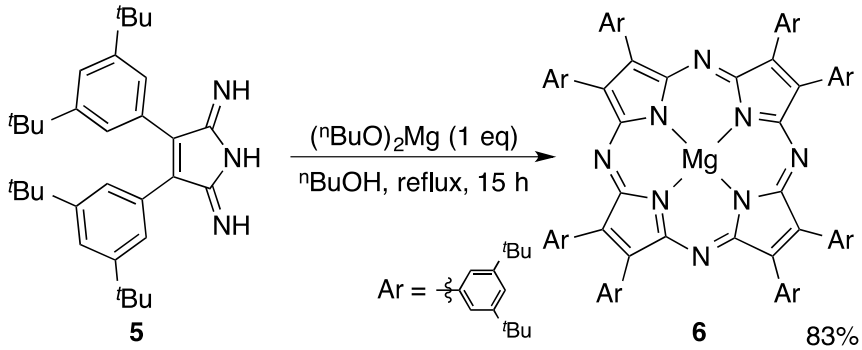
3,4-Bis-(3,5-di-*tert*-butylphenyl)pyrroline-2,5-diimine (5)



Compound **11** (0.52 g, 1.14 mmol) was suspended in 30 mL of ethylene glycol and heated to 115°C. Sodium (ca. 3 mg) was added to the solution and gaseous NH_3 was bubbled through the suspension for 6 h. Then, the hot solution was poured over iced water and a yellowish-green precipitate was collected by filtration. The title compound (0.37 g, 69%) was obtained as yellow powder after the precipitate was washed with water and dried under vacuum. 500 MHz ^{1}H NMR ($CDCl_3$): δ = 7.39 (t, *J* = 1.5 Hz, 2H), 6.97 (d, *J* = 1.5 Hz, 4H), 3.75 (br, 3H), 1.20 (s, 36H).

ESI-MS Calcd for $C_{32}H_{45}N_3Na$ $[M+Na]^+$: 494.4. Found: 494.4.

MgTAP (6)



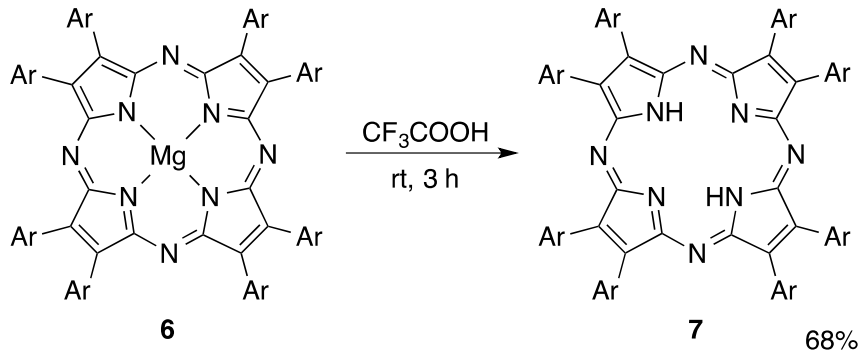
Mg (18.0 mg, 0.74 mmol) and a small crystal of I_2 in 1-butanol (7 ml) were heated to reflux. After Mg was consumed completely, **5** (370 mg, 0.78 mmol) was added to the resulting $Mg(O^nBu)_2$ suspension and the reaction mixture was heated to reflux for an additional 15 h. After solvent was removed, the compound was purified by alumina column chromatography (chloroform), followed by recrystallization from $CHCl_3$/MeOH. **6** was obtained as a dark green solid. (300 mg, 83%)

500 MHz ^{1}H NMR (pyridine-d_5) δ (ppm): 8.00 (d, 16H, J = 1.5 Hz), 7.69 (t, 8H, J = 1.5 Hz), 1.37 (s, 144H).

LR-MALDI (*m/z*) Calcd for $[M+H]^+$: 1842.3. Found: 1842.8.

UV-vis (toluene) λ_{max} nm (ε x 10^{-4}): 627 (18.6), 575 (2.60), 379 (12.2).

H_2TAP (7)



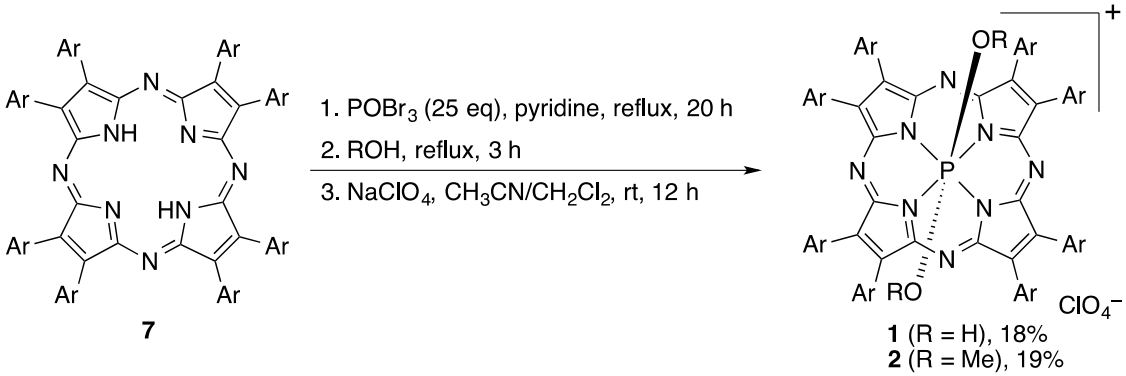
6 (100 mg, 55.0 μmol) was dissolved in 5 ml of trifluoroacetic acid and stirred for 3 h at room temperature. Then the solvent was neutralized by the addition of sat. $NaHCO_3$aq and the resulting precipitation was collected by filtration and washed by water. **7** was obtained as a dark green solid. (67.0 mg, 68%)

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.66 (d, 16H, *J* = 1.5 Hz), 7.41 (t, 8H, *J* = 1.5 Hz), 1.15 (s, 144H).

HRMS-MALDI (*m/z*) Calcd for $C_{128}H_{170}N_8$ $[M]^+$: 1820.3576. Found: 1820.3587.

UV-vis ($CHCl_3$) λ_{max} nm (ε x 10^{-4}): 656 (10.4), 592 (5.51), 453 (3.49), 366 (7.99).

PTAP (1, 2)



$POBr_3$ (200 mg, 0.70 mmol) was added to a solution of free-base TAP **7** (20.0 mg, 11.0 μmol) in 7 mL of pyridine. After the mixture was stirred for 20 h under reflux, 5 mL of water (for **1**) or methanol (for **2**) was added and stirred for 3 h under reflux. Then the solvent was removed and the residue was dissolved in CH_2Cl_2, and washed with 2 M HClaq and water. The organic layer was collected, dried over $MgSO_4$, filtered and concentrated *in vacuo*. To remove byproducts, SiO_2 open column chromatography ($CHCl_3$-MeOH 9:1) was performed and the purple band was collected and concentrated producing crude PTAP. Counteranion exchange was carried out by dissolving crude PTAP in $CHCl_3/CH_3CN$ (1/1 v/v) and sodium perchlorate was added to the solution. After the mixture was stirred for 12 h at room temperature, the solvent was removed. The residue was dissolved in $CHCl_3/^n$hexane (1/2 v/v) and the excess amount of insoluble salts was removed by filtration. Then the filtrate was concentrated, and pure PTAP was obtained as purple powder by removing solvent followed by recrystallization from $CHCl_3/^n$hexane.

1: 500 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): (acidic form) 7.69 (brs, 16H), 7.51 (brs, 8H), 1.16 (s, 144H); (basic form) 7.66 (d, 16H, *J* = 1.5 Hz), 7.45 (t, 8H, *J* = 1.5 Hz), 1.15 (s, 144H). 200 MHz ^{31}P-NMR ($CDCl_3$) δ (ppm): (acidic form) –193; (basic form) –177.

LR-MALDI (*m/z*) Calcd for $[M]^+$: 1882.3. Found: 1882.6.

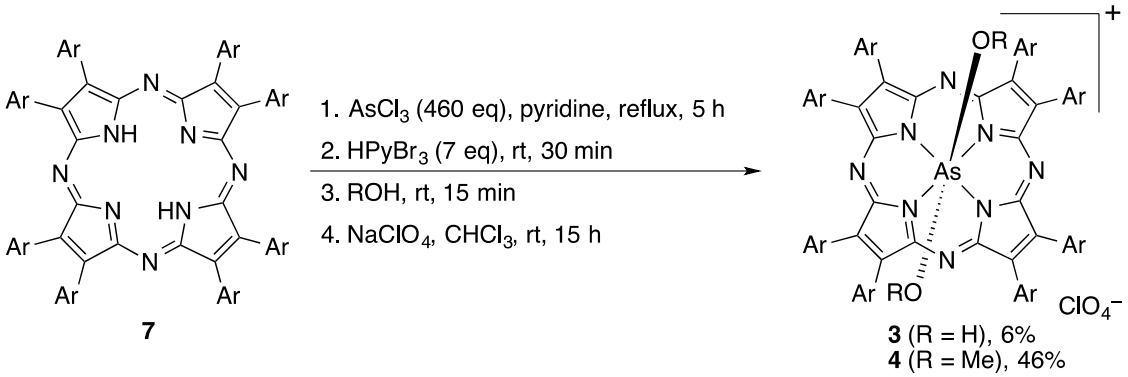
UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): (acidic form) 630 (6.20), 508 (4.63), 337 (4.26); (basic form) 617 (8.50), 569 (2.12), 479 (2.93), 364 (5.40).

2: 500 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.68 (d, 16H, J = 1.5 Hz), 7.57 (t, 8H, J = 1.5 Hz), 1.17 (s, 144H), –1.76 (d, 6H, $^{3}J_{PH}$ = 31.0 Hz). 200 MHz ^{31}P-NMR ($CDCl_3$) δ (ppm): –178.

HRMS-MALDI (*m/z*) Calcd for $C_{130}H_{174}N_8O_2P$ $[M–ClO_4]^+$: 1910.3492. Found: 1910.3492.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 640 (5.95), 518 (6.12), 337 (5.01).

AsTAP (3, 4)



$AsCl_3$ (0.3 mL, 460 eq) was added a solution of **7** (9.5 mg, 5.2 μmol) in a mixture of 5 mL of pyridine and stirred for 5 h under reflux. Then, $HPyBr_3$ (10 mg, 31.2 μmol) was added to the mixture and stirred for 30 min at room temperature. After the solvent was removed *in vacuo*, 5 mL of water (for **3**) or methanol (for **4**) was added and stirred for 15 min at the same temperature. To remove byproducts, SiO_2 open column chromatography ($CHCl_3$-MeOH 9:1) was performed and the purple band was collected and concentrated producing crude AsTAP. Counteranion exchange was carried out by dissolving crude PTAP in $CHCl_3$ and sodium perchlorate was added to the solution. After the mixture was stirred for 15 h at room temperature, the solvent was removed. The residue was dissolved in $CHCl_3$/^{n}hexane (1/2 v/v) and the excess amount of insoluble salts was removed by filtration. Then the filtrate was concentrated, and pure PTAP was obtained as purple powder by removing solvent followed by recrystallization from $CHCl_3$/^{n}hexane.

3: 500 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): (acidic form) 7.71 (d, 16H, J = 1.5 Hz), 7.53 (t, 8H, J = 1.5 Hz), 1.16 (s, 144H); (basic form) 7.69 (d, 16H, J = 1.5 Hz), 7.46 (t, 8H, J = 1.5 Hz), 1.15 (s, 144H).

LR-MALDI (*m/z*) Calcd for $[M]^+$: 1926.3. Found: 1926.5.

UV-vis (CH_2Cl_2) λ_{max} nm: (acidic form) 647, 532, 339; (basic form) 629, 499, 376.

4: 500 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.71 (d, 16H, J = 1.5 Hz), 7.60 (t, 8H, J = 1.5 Hz), 1.18 (s,

144H), –1.54 (s, 6H).

HRMS-MALDI (*m/z*) Calcd for $C_{130}H_{174}AsN_8O_2$ $[M–ClO_4]^+$: 1955.3003. Found: 1955.3001.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 648 (3.96), 532 (5.51), 340 (4.34).

Full Computational Details

Computational Details

Geometry optimization for all molecules was performed at the DFT level, by means of the hybrid Becke3LYP[vi] (B3LYP) functional as implemented in Gaussian 2009.[vii] The 6-31G* basis set was used for the all atoms. After the geometry optimization, the time-dependent (TD) DFT calculations[viii] were performed to evaluate the stick absorption spectrum employing the BLYP functionals with the long-range correction (LC)[ix] (LC-BLYP) with the same 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

$[Ph_8TAPP(OH)_2]^+$ (1'•acidic)

SCF Done: E(RB3LYP) = -3393.73882216 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.754828	0.960841	-0.252340
2	6	0	3.533713	2.183871	-0.241996
3	6	0	2.644631	3.212732	0.019831
4	6	0	1.328721	2.614070	0.114023
5	7	0	1.403630	1.237819	-0.084377
6	7	0	3.310135	-0.232220	-0.270921
7	6	0	2.607183	-1.326070	-0.075162
8	6	0	3.216073	-2.638155	0.012234
9	7	0	1.227203	-1.414135	0.083201
10	6	0	2.186636	-3.541811	0.202614
11	6	0	0.953937	-2.775406	0.191449
12	7	0	-0.237603	-3.331908	0.229910
13	7	0	0.229648	3.321786	0.266852
14	6	0	-1.333849	-2.615724	0.092338
15	6	0	-2.653798	-3.211591	0.034415
16	7	0	-1.419602	-1.235017	-0.018317
17	6	0	-3.554841	-2.177890	-0.111583
18	6	0	-2.770329	-0.953126	-0.145166
19	6	0	-0.958883	2.763551	0.187811
20	6	0	-2.184419	3.538464	0.159148
21	7	0	-1.231816	1.416138	-0.019819
22	6	0	-3.208440	2.652610	-0.118802
23	6	0	-2.604134	1.334636	-0.185760
24	7	0	-3.319983	0.233915	-0.266988
25	15	0	-0.024694	-0.000249	-0.009881
26	8	0	-0.073580	0.113188	1.660627
27	8	0	-0.050033	-0.115272	-1.680664
28	6	0	-4.654338	2.896858	-0.233145
29	6	0	-5.297680	3.771833	0.662818
30	6	0	-5.419465	2.259960	-1.227381
31	6	0	-6.667456	4.000558	0.565730
32	1	0	-4.722451	4.259811	1.442730
33	6	0	-6.788689	2.500850	-1.326783
34	1	0	-4.939023	1.582932	-1.924786
35	6	0	-7.416535	3.369482	-0.431672

36	1	0	-7.151508	4.671000	1.269963
37	1	0	-7.364472	2.008832	-2.105200
38	6	0	-2.231051	5.001606	0.315172
39	6	0	-1.580701	5.630470	1.390541
40	6	0	-2.935480	5.791476	-0.610959
41	6	0	-1.642359	7.014751	1.540233
42	1	0	-1.042857	5.029295	2.116310
43	6	0	-2.982309	7.175730	-0.465515
44	1	0	-3.435266	5.317159	-1.449648
45	6	0	-2.339576	7.791014	0.612138
46	1	0	-1.147992	7.487625	2.384059
47	1	0	-3.521125	7.774944	-1.193718
48	6	0	-5.015918	-2.234345	-0.269989
49	6	0	-5.595131	-3.235378	-1.073672
50	6	0	-5.859079	-1.304416	0.366401
51	6	0	-6.975782	-3.299648	-1.238467
52	1	0	-4.958278	-3.952187	-1.581068
53	6	0	-7.241303	-1.380104	0.205688
54	1	0	-5.431604	-0.529230	0.990814
55	6	0	-7.804005	-2.374676	-0.596686
56	1	0	-7.405830	-4.071546	-1.870096
57	1	0	-7.878244	-0.658870	0.709363
58	6	0	-2.914848	-4.657859	0.167120
59	6	0	-2.328519	-5.580838	-0.713654
60	6	0	-3.779061	-5.126618	1.170601
61	6	0	-2.604074	-6.942649	-0.594748
62	1	0	-1.677968	-5.225108	-1.506647
63	6	0	-4.040036	-6.489766	1.295862
64	1	0	-4.237963	-4.419977	1.855439
65	6	0	-3.455552	-7.400914	0.412793
66	1	0	-2.158584	-7.645399	-1.293415
67	1	0	-4.702243	-6.840319	2.082181
68	6	0	2.271243	-4.990470	0.456116
69	6	0	1.414370	-5.905072	-0.178799
70	6	0	3.230049	-5.477392	1.364897
71	6	0	1.519474	-7.269799	0.084147
72	1	0	0.671227	-5.545223	-0.879358
73	6	0	3.324273	-6.840310	1.631858
74	1	0	3.892300	-4.781624	1.870018
75	6	0	2.471352	-7.741954	0.989592
76	1	0	0.853138	-7.965089	-0.417998
77	1	0	4.062683	-7.198821	2.343131
78	6	0	4.657169	-2.888636	-0.158612
79	6	0	5.090131	-3.949325	-0.976765
80	6	0	5.621379	-2.082006	0.472293
81	6	0	6.448551	-4.192921	-1.159130
82	1	0	4.357399	-4.572808	-1.478760
83	6	0	6.980393	-2.337040	0.294867
84	1	0	5.306317	-1.260827	1.105517
85	6	0	7.398271	-3.390069	-0.520845
86	1	0	6.766526	-5.009419	-1.800966
87	1	0	7.712383	-1.709564	0.794899
88	6	0	4.998224	2.222068	-0.375448
89	6	0	5.659842	1.431178	-1.332601
90	6	0	5.764776	3.049776	0.467260
91	6	0	7.047928	1.477065	-1.449662
92	1	0	5.085414	0.785764	-1.987560
93	6	0	7.151638	3.084336	0.353041
94	1	0	5.270150	3.655917	1.218942
95	6	0	7.797605	2.302050	-0.608693
96	1	0	7.542992	0.867022	-2.199500
97	1	0	7.729491	3.721725	1.016030
98	6	0	2.895545	4.661721	0.098427
99	6	0	3.695094	5.289338	-0.874510
100	6	0	2.344679	5.440161	1.130483
101	6	0	3.933008	6.659990	-0.816267
102	1	0	4.119018	4.700495	-1.681812

103	6	0	2.596066	6.809666	1.191912
104	1	0	1.728976	4.967558	1.887885
105	6	0	3.387800	7.423696	0.219307
106	1	0	4.543638	7.132714	-1.580034
107	1	0	2.172638	7.398150	2.000692
108	1	0	2.548026	-8.805724	1.195560
109	1	0	-3.666241	-8.462309	0.507190
110	1	0	-8.881707	-2.430139	-0.721680
111	1	0	-8.484080	3.554850	-0.509954
112	1	0	-2.383379	8.870191	0.727842
113	1	0	3.579043	8.491902	0.266919
114	1	0	8.879457	2.335984	-0.701033
115	1	0	8.457861	-3.585446	-0.659386
116	1	0	0.408224	0.634061	-2.095380
117	1	0	0.610306	-0.439110	2.074166

TD–DFT output

HOMO**: 256**, LUMO**: 257**

Excited State 1: Singlet-A 1.8441 eV 672.35 nm f=0.2006 <S**2>=0.000

239 -> 258	0.17977
255 -> 258	-0.19024
256 -> 257	0.62132
256 -> 258	-0.19594
239 <- 258	0.11220

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3384.42433853

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.8497 eV 670.29 nm f=0.2027 <S**2>=0.000

239 -> 257	-0.18142
255 -> 257	0.19045
256 -> 257	0.19613
256 -> 258	0.62003
239 <- 257	-0.11230

Excited State 3: Singlet-A 3.0427 eV 407.48 nm f=0.0105 <S**2>=0.000

237 -> 258	-0.14660
238 -> 257	0.13199
252 -> 257	0.21898
252 -> 258	0.11699
252 -> 259	-0.15326
253 -> 257	0.29081
253 -> 258	0.12531
254 -> 257	-0.18177
254 -> 258	0.44969

Excited State 4: Singlet-A 3.0913 eV 401.08 nm f=0.1204 <S**2>=0.000

237 -> 258	0.11249
238 -> 257	0.13961
252 -> 257	0.42202
253 -> 257	0.18448
254 -> 258	-0.36580
255 -> 258	-0.17166
255 -> 259	0.13300

Excited State 5: Singlet-A 3.1239 eV 396.90 nm f=0.3521 <S**2>=0.000

234 -> 258	-0.10132
236 -> 258	0.10899
252 -> 258	0.25321
253 -> 257	0.25182
253 -> 258	-0.20018
254 -> 258	-0.14954
254 -> 259	-0.14786
255 -> 258	0.44818
256 -> 257	0.14111

Excited State 6:	Singlet-A	3.1634 eV	391.94 nm	f=0.4079	<S**2>=0.000
236 -> 257	-0.12051				
252 -> 257	-0.22553				
252 -> 258	-0.15386				
253 -> 257	0.34500				
253 -> 258	0.14144				
253 -> 259	0.14171				
255 -> 257	0.41426				
256 -> 258	-0.14851				
Excited State 7:	Singlet-A	3.5308 eV	351.15 nm	f=0.8036	<S**2>=0.000
239 -> 257	-0.11883				
252 -> 257	0.27263				
253 -> 257	-0.28349				
253 -> 258	-0.11227				
255 -> 257	0.48341				
256 -> 258	-0.16427				
Excited State 8:	Singlet-A	3.5606 eV	348.21 nm	f=0.7007	<S**2>=0.000
239 -> 258	-0.10100				
252 -> 257	0.14180				
252 -> 258	-0.19239				
253 -> 257	-0.10418				
253 -> 258	0.41763				
254 -> 257	0.15081				
255 -> 258	0.39264				
256 -> 257	0.13920				
Excited State 9:	Singlet-A	3.6209 eV	342.41 nm	f=0.0985	<S**2>=0.000
237 -> 257	-0.10336				
252 -> 258	0.35400				
254 -> 257	0.52915				
255 -> 258	-0.10420				
Excited State 10:	Singlet-A	3.7141 eV	333.82 nm	f=0.0511	<S**2>=0.000
238 -> 258	0.11736				
252 -> 257	-0.14860				
252 -> 258	0.35700				
253 -> 257	-0.11813				
253 -> 258	0.39128				
254 -> 257	-0.30115				
254 -> 258	-0.18631				
Excited State 11:	Singlet-A	4.2019 eV	295.07 nm	f=0.0134	<S**2>=0.000
243 -> 257	0.20393				
245 -> 257	0.11824				
246 -> 257	0.14944				
248 -> 257	-0.30521				
249 -> 257	0.11169				
250 -> 257	0.18326				
251 -> 257	0.32461				
251 -> 258	0.14698				
251 -> 259	-0.10192				
256 -> 259	-0.13611				
Excited State 12:	Singlet-A	4.2296 eV	293.13 nm	f=0.0622	<S**2>=0.000
235 -> 257	-0.20980				
239 -> 257	-0.24138				
241 -> 258	-0.12088				
243 -> 257	-0.18611				
245 -> 258	-0.14626				
247 -> 257	0.31689				
248 -> 258	-0.14078				
250 -> 258	0.16230				
251 -> 257	0.20323				
256 -> 259	0.13704				

Excited State 13:	Singlet-A	4.2437 eV	292.16 nm	f=0.0305	<S**2>=0.000
235 -> 258	-0.20633				
239 -> 258	-0.14658				
247 -> 258	0.30739				
248 -> 257	0.15418				
248 -> 258	-0.15592				
250 -> 258	0.30953				
250 -> 259	0.14142				
251 -> 258	-0.28878				
Excited State 14:	Singlet-A	4.2844 eV	289.39 nm	f=0.0268	<S**2>=0.000
235 -> 257	0.17952				
239 -> 257	0.20316				
242 -> 258	0.12450				
243 -> 258	0.11459				
244 -> 258	0.24383				
245 -> 257	0.15938				
247 -> 258	-0.22243				
248 -> 257	0.13049				
248 -> 258	-0.21348				
249 -> 257	0.12270				
251 -> 257	0.16018				
256 -> 259	0.14664				
Excited State 15:	Singlet-A	4.2884 eV	289.12 nm	f=0.0191	<S**2>=0.000
248 -> 258	0.27612				
249 -> 257	0.24008				
249 -> 258	-0.21733				
250 -> 257	0.12173				
250 -> 258	0.36038				
251 -> 257	-0.11366				
251 -> 258	0.21109				
251 -> 259	-0.12082				

Ph_8TAPP(O)(OH) (1'•basic)

SCF Done: E(RB3LYP) = -3393.30899613 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.127218	-2.082294	0.016038
2	6	0	-4.073989	-1.052342	0.012372
3	6	0	-4.191444	0.317757	0.054009
4	6	0	-5.406731	1.151518	-0.004940
5	6	0	-2.831791	0.853871	0.099456
6	7	0	-1.920782	-0.174032	0.096389
7	6	0	-2.638838	-1.339227	0.041715
8	7	0	-2.153225	-2.566828	0.048804
9	6	0	-0.858029	-2.819839	0.062151
10	6	0	-0.322284	-4.179009	0.029334
11	6	0	1.047627	-4.055947	-0.011250
12	6	0	2.075010	-5.114513	-0.005535
13	6	0	-1.150763	-5.395932	-0.029274
14	6	0	1.343354	-2.627513	0.011596
15	7	0	0.170618	-1.908635	0.061170
16	7	0	2.577023	-2.155383	0.017803
17	6	0	2.837094	-0.860412	0.046613
18	6	0	4.195845	-0.318712	0.059160
19	6	0	4.069641	1.051109	0.092964
20	6	0	5.115156	2.088085	0.041011
21	6	0	5.418480	-1.141154	0.109907
22	6	0	2.632830	1.332252	0.104038
23	7	0	1.921104	0.160183	0.090779
24	7	0	2.148925	2.561114	0.091509
25	6	0	0.854030	2.821116	0.086694
26	6	0	0.320923	4.176815	-0.001562
27	6	0	-1.052349	4.057925	0.022615

28	6	0	-2.076469	5.109558	-0.115813
29	6	0	1.152116	5.393508	-0.029537
30	6	0	-1.345473	2.631969	0.123444
31	7	0	-0.172513	1.910302	0.194149
32	7	0	-2.575886	2.150572	0.110543
33	15	0	0.001106	-0.030983	-0.049370
34	8	0	-0.008403	0.055211	-1.565526
35	6	0	7.121457	4.059368	-0.094268
36	1	0	7.895962	4.820097	-0.145889
37	6	0	6.033243	4.221766	0.764866
38	1	0	5.954645	5.110395	1.385194
39	6	0	7.207227	2.914087	-0.890304
40	1	0	8.045590	2.782095	-1.569073
41	6	0	6.215929	1.938115	-0.823259
42	1	0	6.283016	1.056079	-1.451705
43	6	0	5.036802	3.248351	0.831980
44	1	0	4.191365	3.386357	1.495495
45	6	0	6.420742	-0.856659	1.054583
46	1	0	6.279774	-0.032858	1.747243
47	6	0	7.580367	-1.626341	1.114431
48	1	0	8.340950	-1.395701	1.855570
49	6	0	7.763022	-2.691394	0.228928
50	1	0	8.668209	-3.291008	0.275051
51	6	0	6.774767	-2.982994	-0.712902
52	1	0	6.908771	-3.810291	-1.404637
53	6	0	5.610091	-2.218459	-0.770674
54	1	0	4.844570	-2.448505	-1.502801
55	6	0	3.110355	-5.125867	-0.954148
56	1	0	3.152595	-4.342208	-1.703051
57	6	0	4.067012	-6.140520	-0.946987
58	1	0	4.856501	-6.140389	-1.693876
59	6	0	4.011805	-7.152981	0.012839
60	1	0	4.760585	-7.940546	0.019699
61	6	0	2.989617	-7.147822	0.964902
62	1	0	2.941871	-7.929066	1.718746
63	6	0	2.027130	-6.140176	0.954136
64	1	0	1.234962	-6.137039	1.696551
65	6	0	-0.810007	-6.443331	-0.905282
66	1	0	0.062128	-6.342323	-1.542905
67	6	0	-1.587665	-7.597040	-0.971634
68	1	0	-1.311415	-8.391736	-1.659489
69	6	0	-2.719073	-7.729978	-0.162610
70	1	0	-3.324148	-8.631385	-0.213620
71	6	0	-3.069244	-6.696878	0.708679
72	1	0	-3.949106	-6.788727	1.339565
73	6	0	-2.295889	-5.538358	0.774718
74	1	0	-2.578294	-4.738142	1.448538
75	6	0	-5.015300	-3.244012	-0.769395
76	1	0	-4.138395	-3.387133	-1.389183
77	6	0	-6.020130	-4.210730	-0.752877
78	1	0	-5.914957	-5.100108	-1.368095
79	6	0	-7.150657	-4.040469	0.048278
80	1	0	-7.931893	-4.795979	0.059984
81	6	0	-7.270494	-2.893666	0.837593
82	1	0	-8.142499	-2.755234	1.471259
83	6	0	-6.270707	-1.924141	0.821610
84	1	0	-6.365933	-1.040988	1.444755
85	6	0	-6.366980	0.934260	-1.008133
86	1	0	-6.198525	0.155044	-1.745021
87	6	0	-7.519625	1.715003	-1.068519
88	1	0	-8.247809	1.538032	-1.855472
89	6	0	-7.737163	2.721772	-0.124780
90	1	0	-8.637473	3.328603	-0.171275
91	6	0	-6.790914	2.945153	0.877129
92	1	0	-6.954369	3.724247	1.617115
93	6	0	-5.632666	2.170754	0.934414
94	1	0	-4.900441	2.345016	1.715721

95	6	0	-3.192685	5.157257	0.735540
96	1	0	-3.305515	4.404268	1.507405
97	6	0	-4.148703	6.162639	0.596775
98	1	0	-5.004063	6.186568	1.266585
99	6	0	-4.012321	7.131181	-0.399265
100	1	0	-4.760852	7.911354	-0.508994
101	6	0	-2.910801	7.088954	-1.257467
102	1	0	-2.800521	7.833321	-2.041436
103	6	0	-1.950292	6.089887	-1.116281
104	1	0	-1.099537	6.056900	-1.789434
105	6	0	0.808224	6.503482	0.764616
106	1	0	-0.072452	6.453922	1.396973
107	6	0	1.590607	7.655732	0.754975
108	1	0	1.311203	8.499957	1.379714
109	6	0	2.730669	7.724227	-0.050158
110	1	0	3.339760	8.624325	-0.059060
111	6	0	3.083495	6.629238	-0.840943
112	1	0	3.969659	6.671134	-1.468235
113	6	0	2.305045	5.472104	-0.830944
114	1	0	2.588438	4.624292	-1.443133
115	8	0	0.014500	-0.140548	1.658434
116	1	0	-0.042696	0.753168	2.032289

TD–DFT output

HOMO**: 256**, LUMO**: 257**

Excited State 1: Singlet-A 1.9593 eV 632.79 nm f=0.3199 <S**2>=0.000
244 -> 257 0.10664
256 -> 257 -0.46653
256 -> 258 0.47206
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3383.99244811
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.9817 eV 625.66 nm f=0.3246 <S**2>=0.000
244 -> 258 -0.10006
256 -> 257 0.47342
256 -> 258 0.46618

Excited State 3: Singlet-A 3.0218 eV 410.29 nm f=0.0003 <S**2>=0.000
249 -> 257 0.15405
251 -> 257 0.12219
251 -> 258 0.12666
252 -> 259 -0.11926
254 -> 257 0.24994
255 -> 257 0.38632
255 -> 258 0.37927

Excited State 4: Singlet-A 3.0893 eV 401.33 nm f=0.0001 <S**2>=0.000
247 -> 257 -0.12291
247 -> 258 0.13196
249 -> 258 0.11545
253 -> 257 -0.16026
253 -> 258 0.20914
254 -> 257 -0.23378
254 -> 258 0.41224
255 -> 257 0.28319

Excited State 5: Singlet-A 3.4058 eV 364.04 nm f=0.0002 <S**2>=0.000
246 -> 258 -0.10498
247 -> 257 -0.12335
247 -> 258 -0.15574
249 -> 257 -0.21924
249 -> 258 0.11883
251 -> 258 0.20494
253 -> 257 -0.13338
253 -> 258 -0.10819

254 -> 257	-0.30137					
255 -> 257	-0.15506					
255 -> 258	0.34494					
256 -> 259	0.10430					
Excited State 6:	Singlet-A	3.5234 eV	351.89 nm	f=0.0986	<S**2>=0.000	
234 -> 257	-0.12922					
234 -> 258	-0.10139					
244 -> 257	-0.12690					
244 -> 258	-0.10052					
252 -> 257	0.36972					
252 -> 258	0.28722					
253 -> 257	-0.24235					
253 -> 258	-0.16147					
254 -> 257	0.11791					
255 -> 259	-0.20959					
Excited State 7:	Singlet-A	3.5966 eV	344.73 nm	f=0.1891	<S**2>=0.000	
232 -> 258	0.10964					
234 -> 258	-0.11938					
244 -> 258	0.11823					
252 -> 257	-0.29985					
252 -> 258	0.36536					
253 -> 257	-0.19440					
253 -> 258	0.20926					
253 -> 259	0.10292					
254 -> 258	-0.15024					
254 -> 259	0.18131					
Excited State 8:	Singlet-A	3.7628 eV	329.50 nm	f=0.0046	<S**2>=0.000	
247 -> 257	0.17440					
249 -> 258	0.20542					
251 -> 257	-0.13883					
251 -> 258	0.10904					
253 -> 257	0.15076					
253 -> 258	0.13642					
254 -> 257	0.22661					
254 -> 258	0.31676					
255 -> 257	-0.31173					
255 -> 258	0.20661					
Excited State 9:	Singlet-A	3.8883 eV	318.87 nm	f=0.0257	<S**2>=0.000	
236 -> 257	0.17584					
236 -> 258	0.13318					
246 -> 257	-0.13196					
247 -> 258	-0.11969					
249 -> 257	0.32043					
249 -> 258	0.20734					
250 -> 257	0.13235					
251 -> 257	0.27636					
251 -> 258	0.21804					
252 -> 259	0.12505					
255 -> 257	-0.13541					
255 -> 258	-0.11801					
Excited State 10:	Singlet-A	4.0195 eV	308.46 nm	f=1.4343	<S**2>=0.000	
244 -> 257	-0.24925					
244 -> 258	-0.10221					
245 -> 257	0.10349					
245 -> 258	0.11479					
249 -> 257	0.10128					
249 -> 258	0.12685					
250 -> 257	-0.11415					
252 -> 258	0.10961					
253 -> 257	0.35572					
253 -> 258	0.21608					
254 -> 257	-0.17199					

254 -> 258	-0.16018				
256 -> 257	-0.12934				
256 -> 258	0.19360				
Excited State 11:	Singlet-A	4.0558 eV	305.69 nm	f=1.2663	<S**2>=0.000
244 -> 257	0.12338				
244 -> 258	-0.18923				
245 -> 257	-0.13197				
245 -> 258	0.16344				
246 -> 257	-0.10007				
246 -> 258	0.14115				
247 -> 258	0.14008				
249 -> 257	-0.12827				
249 -> 258	0.12272				
253 -> 257	-0.20397				
253 -> 258	0.29617				
254 -> 257	0.15411				
254 -> 258	-0.19564				
256 -> 257	-0.18127				
256 -> 258	-0.13471				
Excited State 12:	Singlet-A	4.1149 eV	301.31 nm	f=0.1918	<S**2>=0.000
233 -> 257	-0.11521				
233 -> 258	0.14866				
244 -> 257	0.11358				
244 -> 258	-0.24044				
246 -> 257	0.10325				
247 -> 257	0.23106				
247 -> 258	-0.25278				
249 -> 258	-0.13932				
250 -> 258	-0.15845				
253 -> 258	0.25472				
254 -> 257	-0.11233				
Excited State 13:	Singlet-A	4.3048 eV	288.01 nm	f=0.0024	<S**2>=0.000
235 -> 257	0.13108				
236 -> 258	0.10494				
247 -> 258	-0.17998				
249 -> 257	-0.15631				
249 -> 258	0.14886				
251 -> 258	0.18895				
254 -> 257	0.16273				
255 -> 257	0.15084				
255 -> 258	-0.28578				
256 -> 259	0.35962				
Excited State 14:	Singlet-A	4.3402 eV	285.66 nm	f=0.0009	<S**2>=0.000
244 -> 257	0.23068				
244 -> 258	-0.24008				
252 -> 257	-0.21967				
252 -> 258	0.34675				
253 -> 257	0.17118				
253 -> 258	-0.19664				
254 -> 257	-0.10292				
Excited State 15:	Singlet-A	4.3892 eV	282.47 nm	f=0.0048	<S**2>=0.000
235 -> 258	0.22890				
236 -> 257	0.12881				
246 -> 257	-0.10057				
246 -> 258	0.11028				
247 -> 257	-0.11343				
249 -> 258	-0.18026				
251 -> 257	0.13718				
251 -> 258	-0.12518				
255 -> 257	-0.11950				
255 -> 258	0.11322				
256 -> 259	0.42041				

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