Phosphorus(V) Tetraazaporphyrins: Porphyrinoids Showing an Exceptionally Strong CT Band between the Soret and Q bands

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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 $dm^3mol^{-1}cm^{-1}T^{-1}$). 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 and ^{13}C-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. 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 0.5 mM and the sweep rates were set to 100 mV/s.

Crystallographic data collection

A needle shaped and purple single crystal of **1a** 0.48 × 0.08 × 0.07 mm, was selected for measurements. The diffraction data were collected using a RIGAKU AFC-8 diffractometer equipped with a Saturn70 CCD detector with Mo*K*α radiation by an oscillation method at 90 K. X-rays were monochromated and focused by a confocal mirror. Bragg spots were integrated, scaled and averaged up to 2θ = 25.354° by the program HKL2000.[i] Lorentz and polarization corrections were applied during the scaling processes. No absorption corrections were applied.

The number of measured and independent reflections, completeness, and R_{int} were 94546, 10853, 0.992 and 0.053, respectively, up to 2θ = 25.354°.

The initial structure of **1a** was solved by a direct method using the programs SIR2004,[ii] and

refined by a full matrix least-squares method using the program SHELXL2013.[iii] All non-hydrogen atoms were refined anisotropically. Positions of all hydrogen atoms were calculated geometrically, and refined by applying riding models. CCDC-984631 contains the supplementary crystallographic data for **1a**. 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 **1a**.

Empirical formula	$C_{110}H_{134}Cl_{13}N_8O_6P$	
Formula weight	2156.06	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c* (No. 15)	
Unit cell dimensions	a = 43.4252(18) Å	α = 90°
	b = 8.3330(4) Å	β = 113.9416(18)°
	c = 36.214(2) Å	γ = 90°
Volume	11976.9(11) Å^3	
Z	4	
Density (Calcd.)	1.196 Mg/m^3	
Absorption coefficient	0.365 mm^{-1}	
F(000)	4536	
Crystal size	0.477 x 0.085 x 0.070 mm^3	
Theta range for data collection	1.895 to 25.354°	
Index ranges	-52<=h<=52, -9<=k<=9, -43<=l<=43	
Reflections collected	94546	
Independent reflections	10853 [R(int) = 0.0530]	
Completeness to theta = 25.242°	99.7%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints /parameters	10853 / 1900 / 1133	
Goodness-of-fit on F^2	0.943	
Final R indices [I > 2sigma(I)]	R_1 = 0.0689, wR_2 = 0.1951	
R indices (all data)	R_1 = 0.1167, wR_2 = 0.2169	
Largest diff. peak and hole	0.578 and -0.352 e.Å^{-3}	
CCDC No.	984631	

Additional Experimental and Computational Results

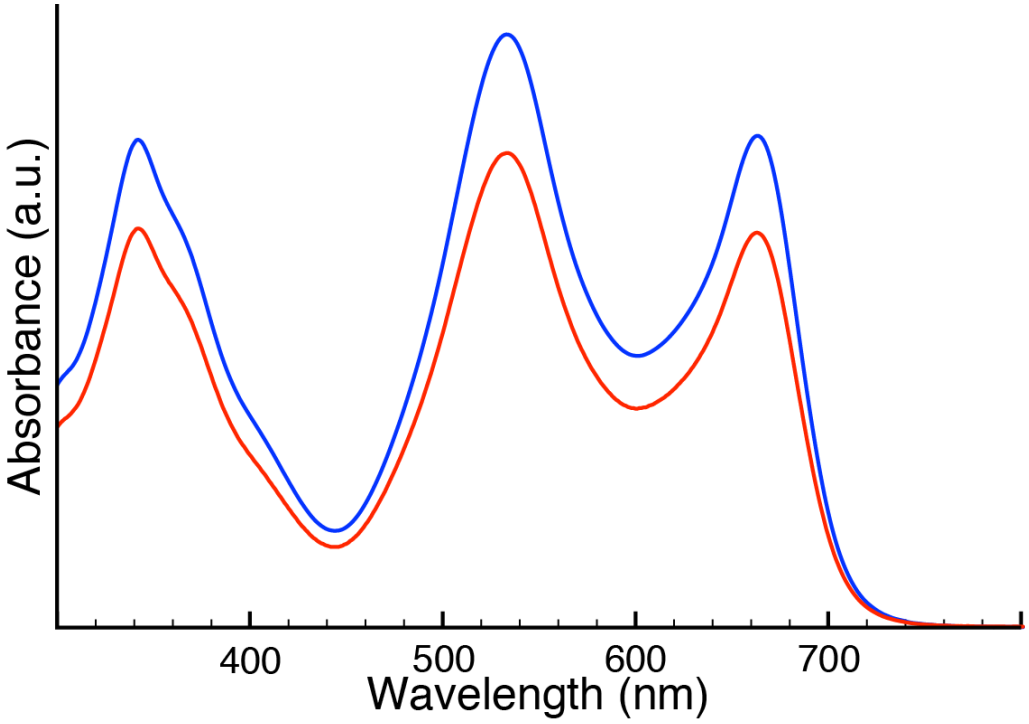


Figure S1. UV-vis absorption spectra of **1a** (blue line) and the counteranion mixture of $[(4\text{-}^{t}\text{BuPh})_8\text{TAPP(OMe)}_2]^+$ (mainly $[OH]^-$) (red line) in CH_2Cl_2. Concentration ~ 1 x 10^{-5} M and concentration of each sample is different for clarity.

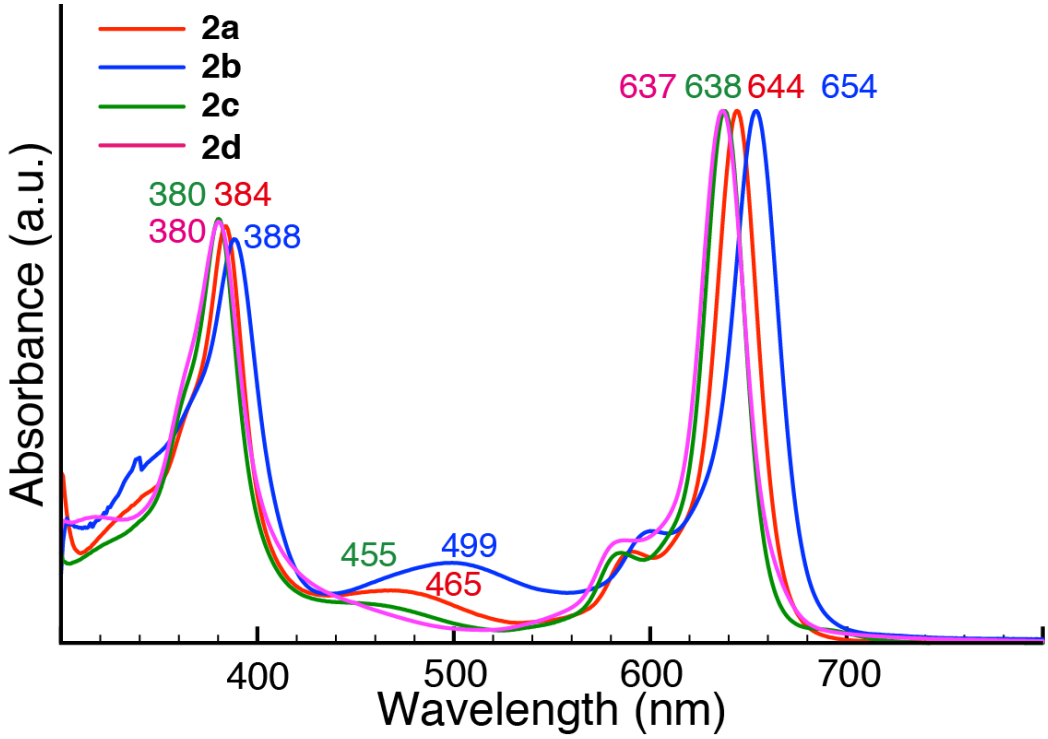


Figure S2. UV-vis absorption spectra of **2a** (red), **2b** (blue), **2c** (green) and **2d** (purple) in pyridine.

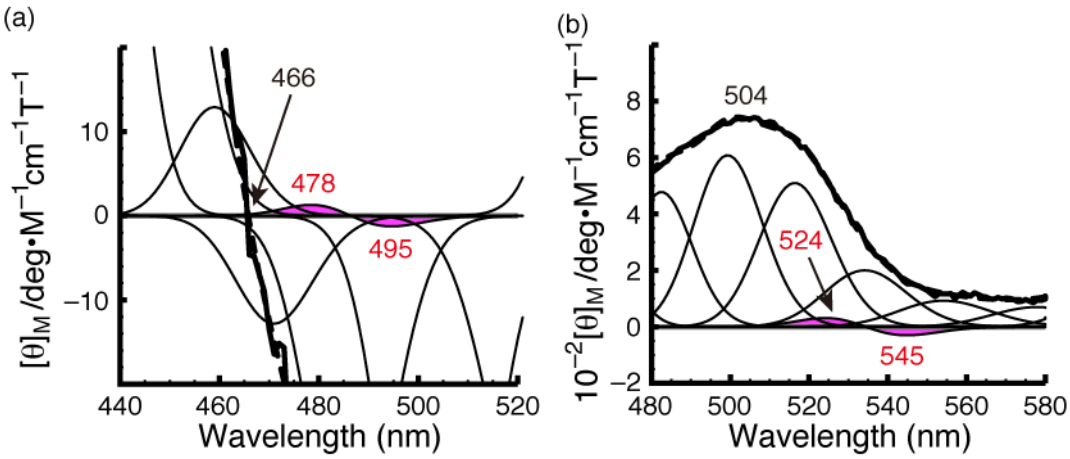


Figure S3. Magnified MCD spectra of **2a** (a) and **1a** (b) in CH_2Cl_2. Deconvoluted Gaussian curves and the simulated spectra are shown by the black solid lines and broken line with the CT bands denoted by the red colored Gaussian curves.

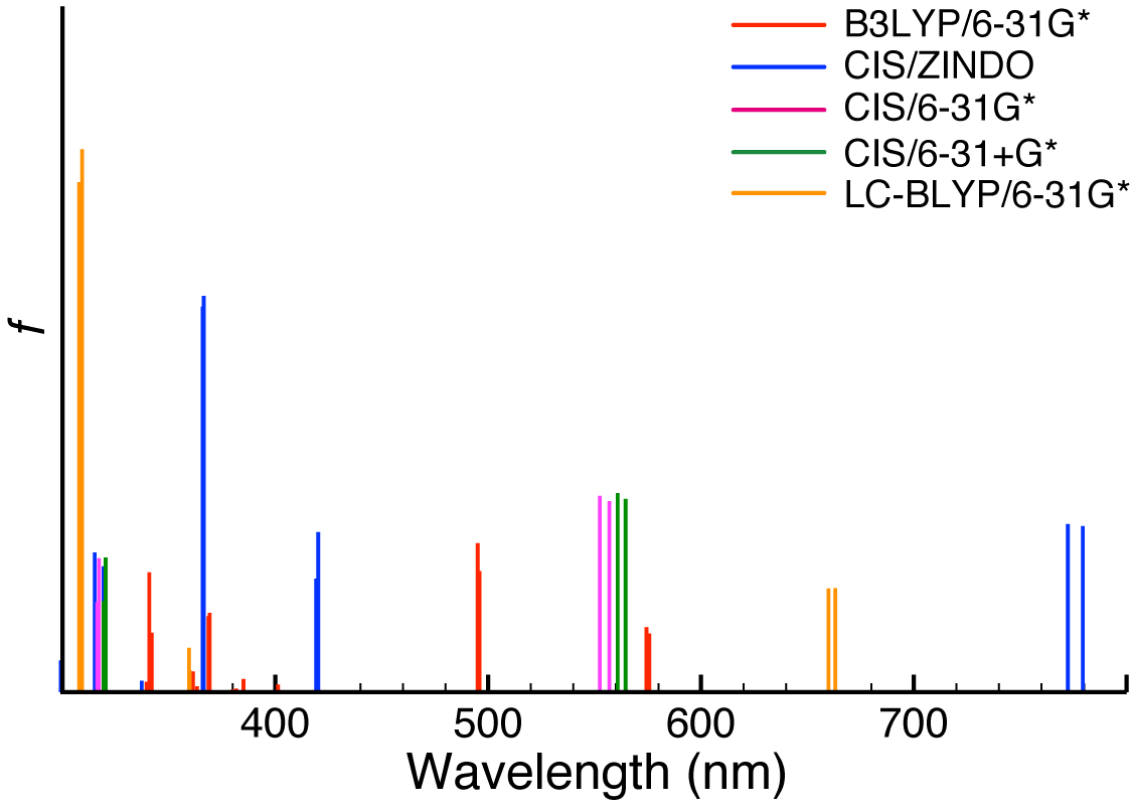


Figure S4. Calculated stick absorption spectra of **2e** by various levels. The structure was optimized by B3LYP/6-31G*.

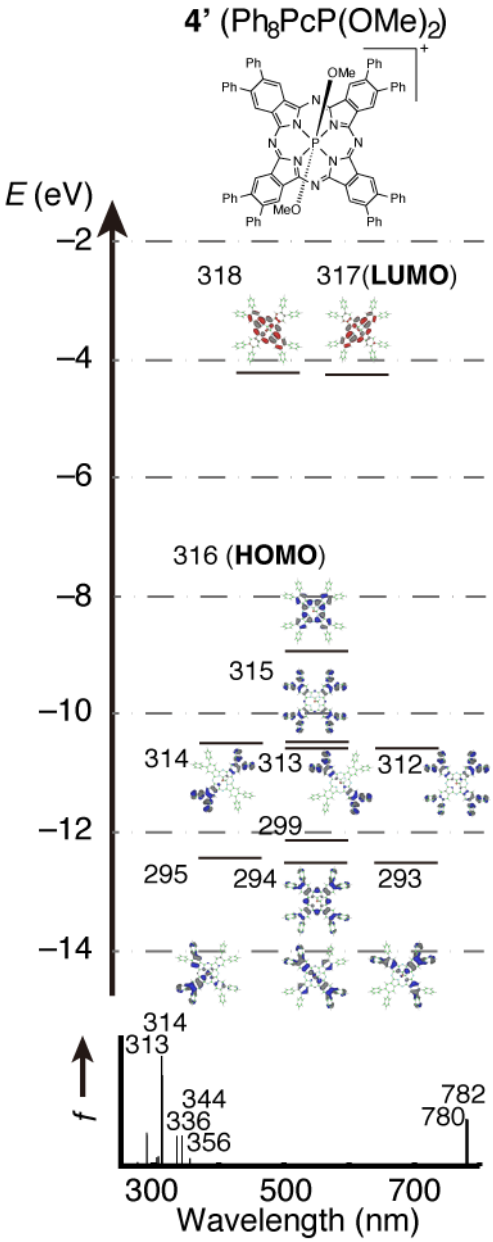


Figure S5. Partial molecular energy diagram and orbitals of $[Ph_8PcP(OMe)_2]^+$ (**4'**) (top) and their calculated absorption spectrum (bottom). Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were performed at the LC-BLYP/6-31G*//B3LYP/6-31G* level.

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

Compound	λ (nm)	*f*	Composition (%)	Assignment
1e	674	0.20	247–>265 (5%), 247–>266 (2%), 263–>265 (6%)	Q
			264–>265 (25%), 264–>266 (61%)	
	670	0.21	247–>265 (2%), 247–>266 (5%), 263–>266 (6%)	Q
			264–>265 (61%), 264–>266 (25%)	
	409	0.11	245–>266 (3%), 246–>265 (4%), 260–>265 (9%)	CT, n–>π*
			260–>267 (3%), 261–>265 (27%), 262–>266 (28%)	
			262–>267 (3%), 263–>265 (2%), 263–>266 (12%)	
	403	0.05	245–>266 (2%), 246–>265 (5%), 260–>265 (18%)	CT, n–>π*
			261–>265 (17%), 262–>265 (8%), 262–>266 (26%)	
			263–>266 (9%), 263–>267 (4%)	
	394	0.29	244–>266 (2%), 260–>265 (3%), 260–>266 (35%)	CT, n–>π*
			260–>267 (3%), 261–>265 (4%), 261–>266 (4%)	
			262–>266 (5%), 263–>265 (5%), 263–>266 (23%)	
			264–>265 (3%)	
	388	0.33	244–>265 (3%), 260–>265 (11%), 260–>266 (5%)	CT, n–>π*
			261–>265 (23%), 261–>267 (3%), 262–>265 (8%)	
			262–>266 (5%), 263–>265 (24%), 263–>266 (4%)	
			264–>266 (3%)	
	349	0.81	247–>265 (3%), 260–>265 (16%), 261–>265 (6%)	Soret
			262–>265 (8%), 263–>265 (51%), 264–>266 (5%)	
	345	0.71	244–>266 (2%), 247–>266 (3%), 260–>266 (18%)	Soret
			261–>266 (20%), 262–>265 (5%), 262–>266 (10%)	
			263–>266 (31%), 264–>265 (4%)	
2e	663	0.33	239–>248 (2%), 241–>248 (5%), 245–>248 (5%)	Q
			246–>247 (87%)	

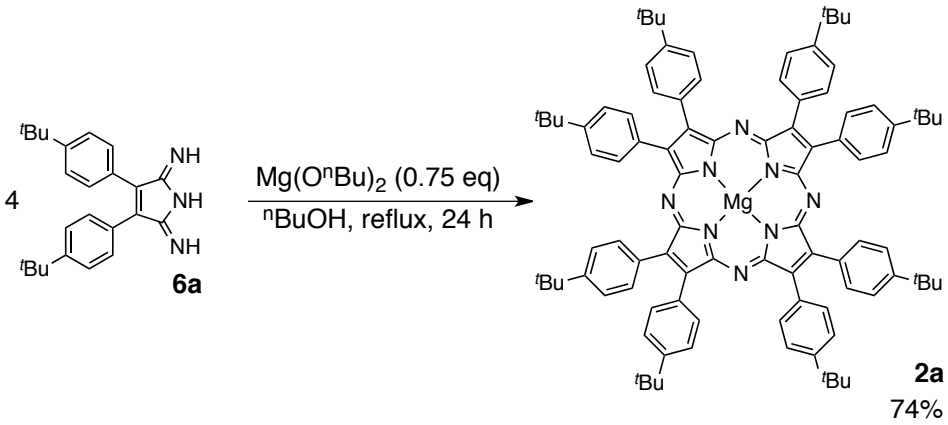
660	0.33	239–>247 (2%), 241–>247 (5%), 245–>247 (5%) 246–>248 (87%)	Q
360	0.07	222–>248 (3%), 227–>247 (5%), 239–>248 (4%) 241–>248 (5%), 242–>249 (8%), 244–>247 (55%) 245–>248 (15%)	CT, n–>π*
359	0.14	222–>247 (3%), 227–>248 (5%), 239–>247 (3%) 241–>247 (4%), 243–>249 (9%), 244–>248 (52%) 245–>247 (19%)	CT, n–>π*
309	1.74	239–>247 (7%), 241–>247 (16%), 244–>248 (7%) 245–>247 (54%), 246–>248 (11%)	Soret
308	1.64	239–>248 (9%), 241–>248 (13%), 244–>247 (4%) 245–>248 (59%), 246–>247 (12%)	Soret

Full Experimental Procedures

Materials

Pyrroline-2, 5-diimine derivatives **6a–d**,[iv] 4, 5-bis(4-*tert*-butylphenyl)phthalonitrile,[v] and free-base Pc **5**[vi] were synthesized according to published procedures.

(4-^{t}BuPh)$_8$TAPMg (2a)



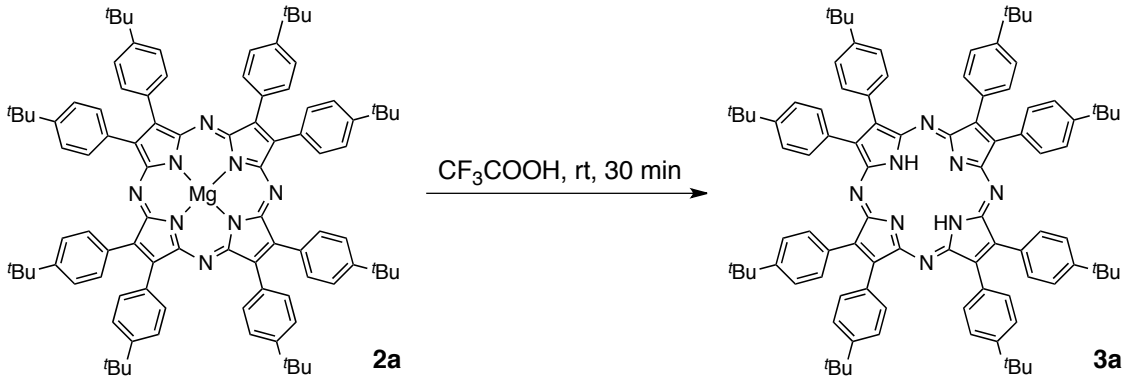
Mg (14.7 mg, 0.600 mmol) and a small crystal of I_2 in 1-butanol (7 ml) were heated to reflux. After Mg was consumed completely, **6a** (281 mg, 0.782 mmol) was added to the resulting Mg(O^{n}Bu)$_2$ suspension and the reaction mixture was heated to reflux for an additional 24 h. After solvent was removed, the compound was purified by alumina column chromatography (chloroform-methanol 95:5), followed by recrystallization from $CHCl_3$/MeOH. **2a** was obtained as a dark green solid. (202 mg, 74%)

500 MHz ^{1}H NMR (pyridine-d_5) δ (ppm): 8.72 (d, 16H, ^{t}BuPh-PhH), 7.77 (d, J = 8.5 Hz, 16H, ^{t}BuPh-PhH), 1.48 (s, 72H, ^{t}BuPh-^{t}BuH).

HRMS-MALDI (*m/z*) Calcd for $C_{96}H_{105}MgN_8$ $[M+H]^+$: 1393.8313. Found: 1393.8267.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 641 (10.7), 459 (0.12), 378 (9.1).

(4-^{t}BuPh)$_8$TAPH$_2$ (3a)



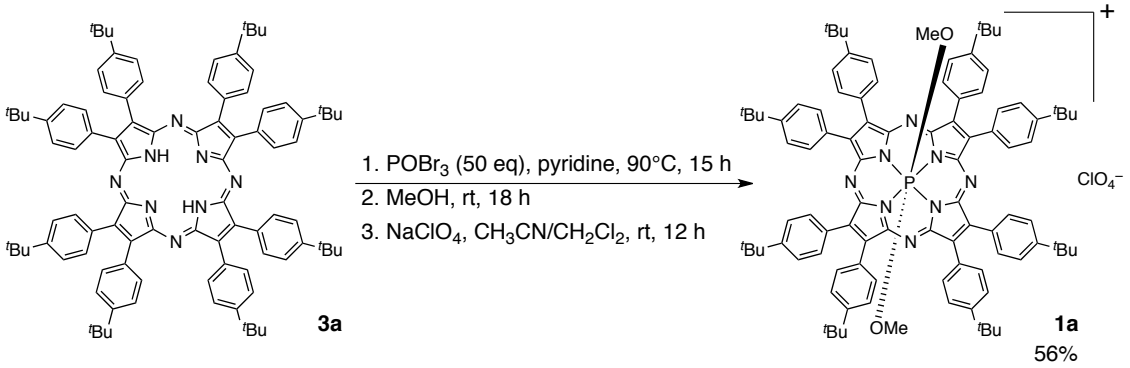
2a (59.0 mg, 42.3 μmol) was dissolved in 3 ml of trifluoroacetic acid and stirred for 30 min at room temperature. Then the solvent was neutralized by the addition of sat. $NaHCO_3$aq and the resulting precipitation was collected by filtration and washed by water. **3a** was obtained as a dark green solid. (50.0 mg, 86%)

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 8.33 (d, J = 8.2 Hz, 16H, ^{t}BuPh-PhH), 7.61 (d, J = 8.2 Hz, 16H, ^{t}BuPh-PhH), 1.52 (s, 72H, ^{t}BuPh-^{t}BuH).

HRMS-MALDI (*m/z*) Calcd for $C_{96}H_{107}N_8$ $[M+H]^+$: 1371.8619. Found: 1371.8571.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 671 (7.7), 606 (4.6), 467 (3.0), 370 (7.3).

[(4-^{t}BuPh)$_8$TAPP(OMe)$_2$]$^+$[ClO$_4$]$^-$ (1a)



$POBr_3$ (500 mg, 1.76 mmol) was added to a solution of free-base TAP **3a** (50.0 mg, 36.4 mmol) in 10 mL of pyridine. After the mixture was stirred for 15 h at 90°C, 5 mL of methanol was added and stirred for 18 h at room temperature. 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 (CH_2Cl_2-MeOH-trifluoroacetic acid 90:9.5:0.5) was performed and the purple band was collected and concentrated producing crude **1a**. Counteranion exchange was carried out by dissolving crude **1a** in CH_2Cl_2/CH_3CN (1/1 v/v) and sodium perchlorate (80.0 mg, 0.65 mmol) 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 CH_2Cl_2/^{n}hexane (1/2 v/v) and the excess amount of insoluble salts was removed by filtration. Then the filtrate was concentrated, and pure **1a** (32.0 mg, 56%) was obtained as purple powder by removing solvent followed by recrystallization from ethyl acetate/^{n}hexane.

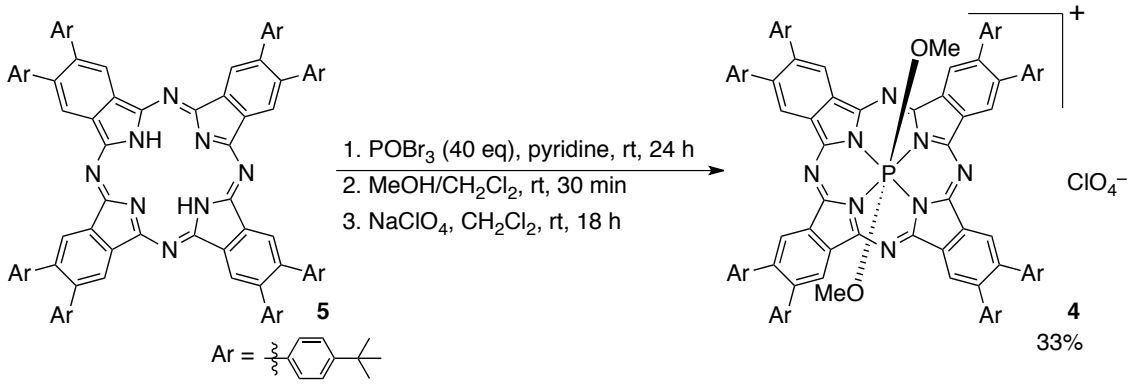
500 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.26 (d, 16H, J = 8.0 Hz, ^{t}BuPh-PhH), 7.65 (d, 16H, J = 8.0 Hz, ^{t}BuPh-PhH), 1.51 (s, 72H, ^{t}BuPh-^{t}BuH), –1.68 (d, 6H, $^3J_{PH}$ = 28.0 Hz, P–OMe). 125 MHz ^{13}C-NMR ($CDCl_3$) δ (ppm): 153.3, 149.6, 141.6 (d, $^2J_{PC}$ = 2.5 Hz), 132.8, 128.2, 125.9, 47.1 (d, $^2J_{PC}$ = 16.3 Hz), 35.1, 31.5. 200 MHz ^{31}P-NMR ($CDCl_3$) δ (ppm): –182.

HRMS-ESI (*m/z*) Calcd for $C_{98}H_{110}N_8O_2P$ $[M–ClO_4]^+$: 1462.8516. Found: 1462.8518.

Anal. Calcd for $C_{98}H_{110}ClN_8O_6P$: C, 75.34; H, 7.10; N, 7.17. Found: C, 75.37; H, 7.38; N, 6.87.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 342 (4.5), 534 (5.6), 664 (4.7).

[(4-^{t}BuPh)$_8$PcP(OMe)$_2$]$^+$[ClO$_4$]$^–$ (4)



$POBr_3$ (400 mg, 1.40 mmol) was added to a solution of free-base Pc **5** (51.2 mg, 32.6 mmol) in 10 mL of pyridine. After the mixture was stirred for 12 h at room temperature, a mixuture of dichloromethane/methanol (3 mL, 1/1 v/v) was added and stirred for 30 min at the same temperature. 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

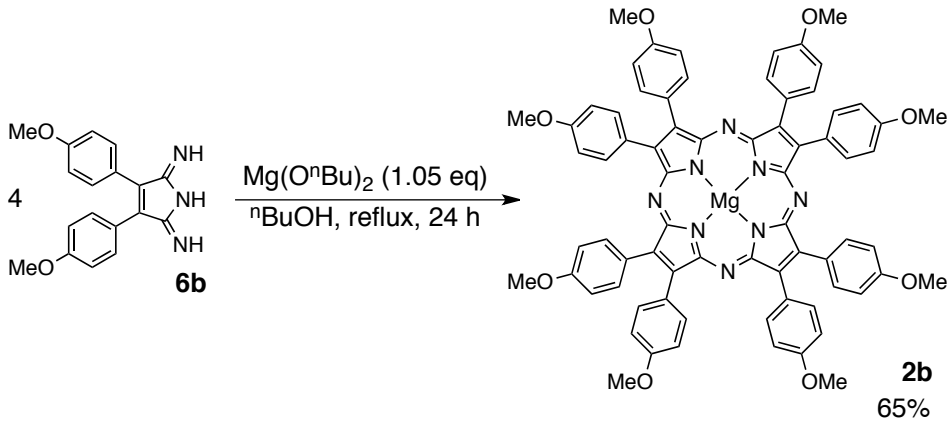
byproducts, SiO_2 open column chromatography (CH_2Cl_2-MeOH 95:5 to 80:20) was performed and the brownish band was collected and concentrated producing crude **4**. Counteranion exchange was carried out by dissolving crude 4 in CH_2Cl_2 and sodium perchlorate (15.0 mg, 123 mmol) was added to the solution. After the mixture was stirred for 18 h at room temperature, the solvent was removed. The residue was dissolved in small amount of CH_2Cl_2 and the excess amount of insoluble salts was removed by filtration. Then the filtrate was concentrated, and pure **4** (17.8 mg, 33%) was obtained as brown powder by removing solvent followed by recrystallization from CH_2Cl_2/^{n}hexane.

400 MHz ^{1}H-NMR ($CDCl_3$) δ (ppm): 9.65 (s, 8H, Pc-αH), 7.49 (d, 16H, J = 8.4 Hz, ^{t}BuPh-PhH), 7.45 (d, 16H, J = 8.4 Hz, ^{t}BuPh-PhH), 1.39 (s, 72H, ^{t}BuPh-^{t}BuH), –1.06 (d, 6H, $^3J_{PH}$ = 28.4 Hz, P–OMe). 200 MHz ^{31}P-NMR ($CDCl_3$) δ (ppm): –173.

HRMS-ESI (*m/z*) Calcd for $C_{114}H_{118}N_8O_2P$ $[M–ClO_4]^+$: 1662.9142. Found: 1662.9137.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 332 (7.9), 481 (3.3), 671 (3.1), 747 (19.2).

(4-MeOPh)$_8$TAPMg (2b)



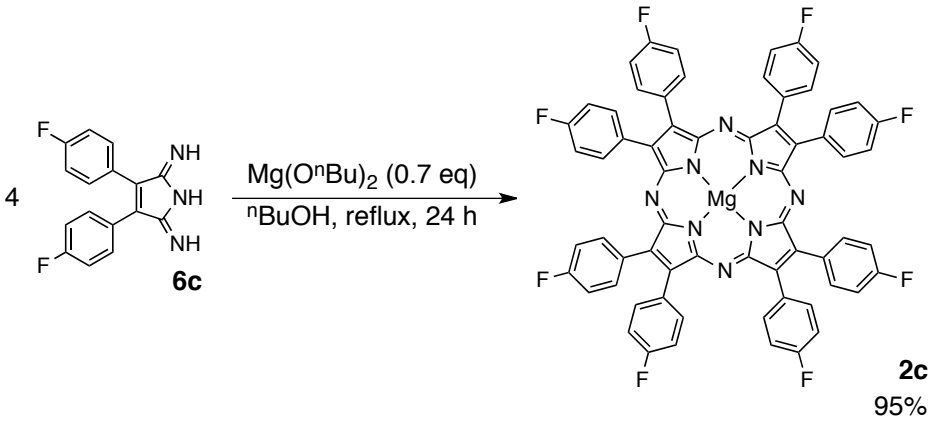
Mg (20.0 mg, 0.823 mmol) and a small crystal of I_2 in 1-butanol (12 ml) were heated to reflux. After Mg was consumed completely, **6b** (281 mg, 0.782 mmol) was added to the resulting Mg(O^{n}Bu)$_2$ suspension and the reaction mixture was heated to reflux for an additional 22 h. Methanol was poured to the reaction mixture and precipitation was filtrated and washed with methanol. **2b** was obtained as a dark green solid. (248 mg, 65%)

500 MHz ^{1}H NMR (pyridine-d_5) δ (ppm): 8.68 (d, J = 8.8 Hz, 16H, MeOPh-PhH), 7.39 (d, J = 8.8 Hz, 16H, MeOPh-PhH), 3.90 (s, 24H, MeOPh-OMeH).

HRMS-MALDI (*m/z*) Calcd for $C_{72}H_{56}MgN_8O_8$ $[M]^+$: 1184.4072. Found: 1184.4069.

UV-vis (pyridine) λ_{max} nm: 654, 499, 388.

(4-FPh)$_8$TAPMg (2c)

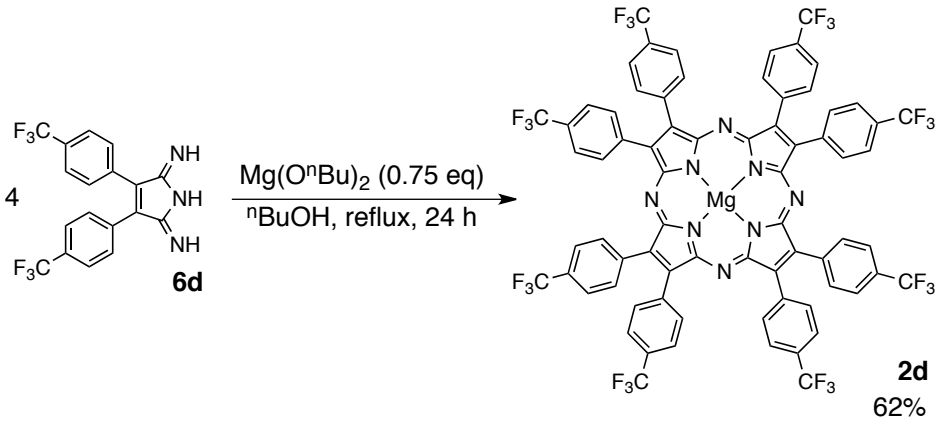


Mg (27.0 mg, 1.11 mmol) and a small crystal of I_2 in 1-butanol (15 ml) were heated to reflux. After Mg was consumed completely, **6c** (467 mg, 1.65 mmol) was added to the resulting Mg(O^{n}Bu)$_2$ suspension and the reaction mixture was heated to reflux for an additional 24 h. Methanol-water (1:1 v/v) was poured to the reaction mixture and precipitation was collected by filtration and washed with methanol, and a small amount of $CHCl_3$. **2c** was obtained as a dark green solid. (426 mg, 95%)

HRMS-MALDI (*m/z*) Calcd for $C_{64}H_{32}F_8MgN_8$ $[M]^+$: 1088.2473. Found: 1088.2469.

UV-vis (pyridine) λ_{max} nm: 638, 380.

(4-F$_3$CPh)$_8$TAPMg (2d)



Mg (15.0 mg, 0.593 mmol) and a small crystal of I_2 in 1-butanol (7 ml) were heated to reflux.

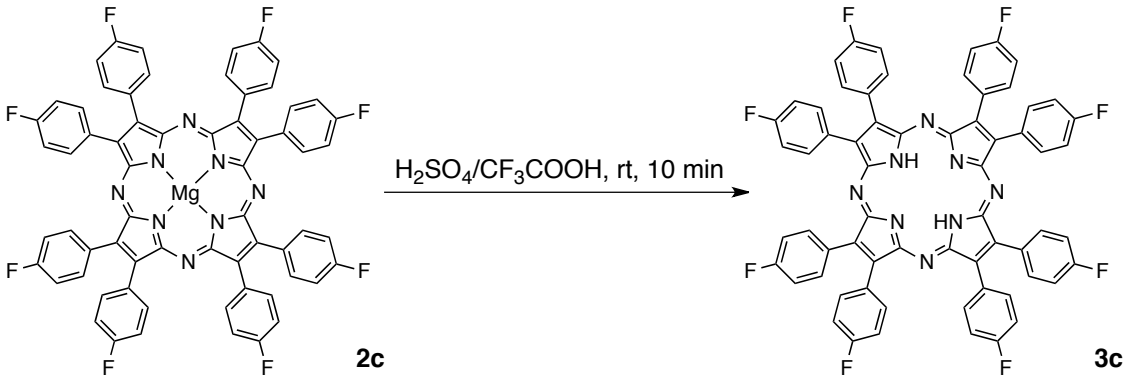
After Mg was consumed completely, **6d** (290 mg, 0.757 mmol) was added to the resulting $Mg(OBu)_2$ suspension and the reaction mixture was heated to reflux for an additional 24 h. Methanol-water (1:1 v/v) was poured to the reaction mixture and precipitation was collected by filtration and washed with methanol. **2d** was obtained as a dark green solid. (195 mg, 62%)

500 MHz ^{1}H NMR (pyridine-d_5) δ (ppm): 8.63 (d, J = 8.3 Hz, 16H, CF_3Ph-PhH), 8.09 (d, J = 8.3 Hz, 16H, CF_3Ph-PhH).

HRMS-MALDI (*m/z*) Calcd for $C_{72}H_{32}F_{24}MgN_8$ $[M]^+$: 1488.2217. Found: 1488.2214.

UV-vis (pyridine) λ_{max} nm: 637, 380.

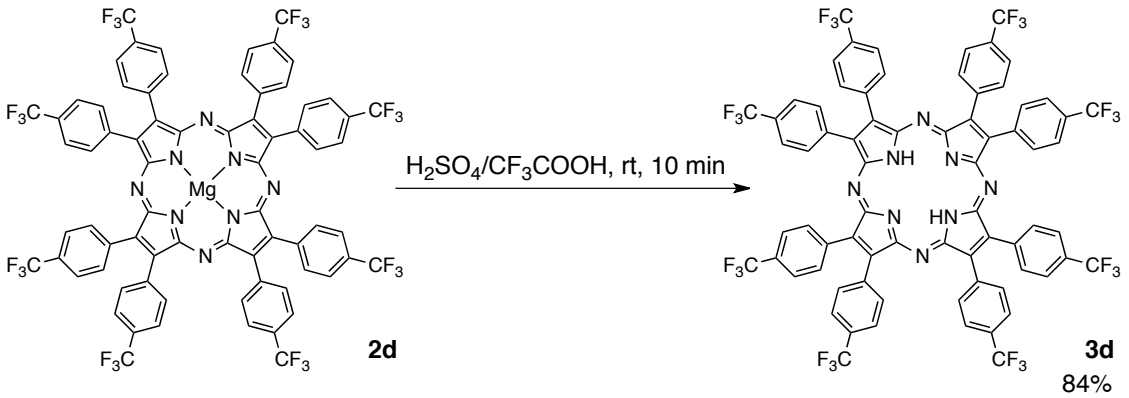
(4-FPh)$_8$TAPH$_2$ (3c)



2c (50.0 mg, 45.9 μmol) was dissolved in 4 ml of trifluoroacetic acid and a few drop of conc. H_2SO_4 was added. After stirring for 10 min at room temperature, the solvent was neutralized by the addition of sat. $NaHCO_3$aq and the resulting precipitation was filtrated and washed by water and methanol. **3c** was obtained as a dark green solid. (38.0 mg, 78%) Since the solubility of this compound was very low in general organic solvents, it was used for a next reaction without further purification.

HRMS-MALDI (*m/z*) Calcd for $C_{64}H_{34}F_8N_8$ $[M]^+$: 1066.2779. Found: 1066.2773.

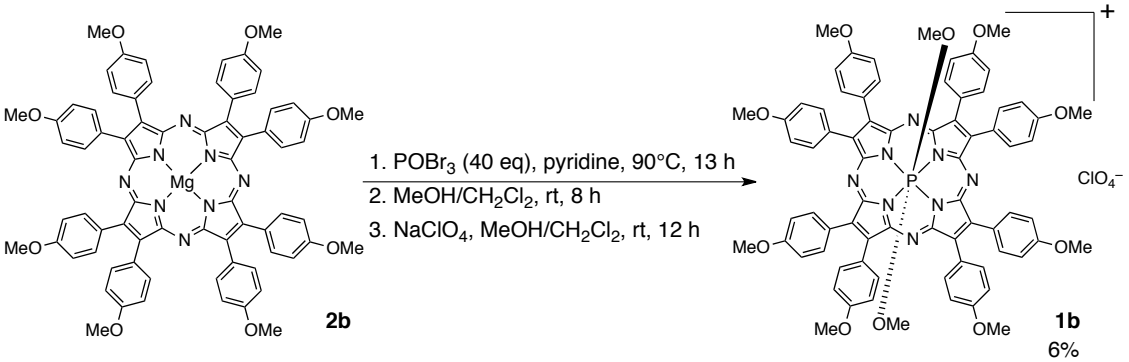
(4-F_3CPh)$_8$TAPH_2 (3d)



2d (70.0 mg, 47.0 μmol) was dissolved in 5 ml of trifluoroacetic acid and a few drop of conc. H_2SO_4 was added. After stirring for 10 min at room temperature, the solvent was neutralized by the addition of sat. $NaHCO_3$aq and the resulting precipitation was collected by filtration and washed by water/MeOH (1/1 v/v). **3d** was obtained as a dark green solid. (56.6 mg, 84%) Since the solubility of this compound was very low in general organic solvents, it was used for a next reaction without further purification.

HRMS-MALDI (*m/z*) Calcd for $C_{72}H_{35}F_{24}N_8$ $[M+H]^+$: 1467.2601. Found: 1467.2595.

[(4-MeOPh)$_8$TAPP(OMe)$_2$]$^+$[ClO_4]$^-$ (1b)



$POBr_3$ (400 mg, 1.40 mmol) was added to a solution of magnesium TAP **2b** (41.0 mg, 34.6 mmol) in 10 mL of pyridine. After the mixture was stirred for 13 h at 90°C, 5 mL of methanol and dichloromethane was added and stirred for 8 h at room temperature. Then the solvent was removed and the residue was dissolved in dichloromethane, 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

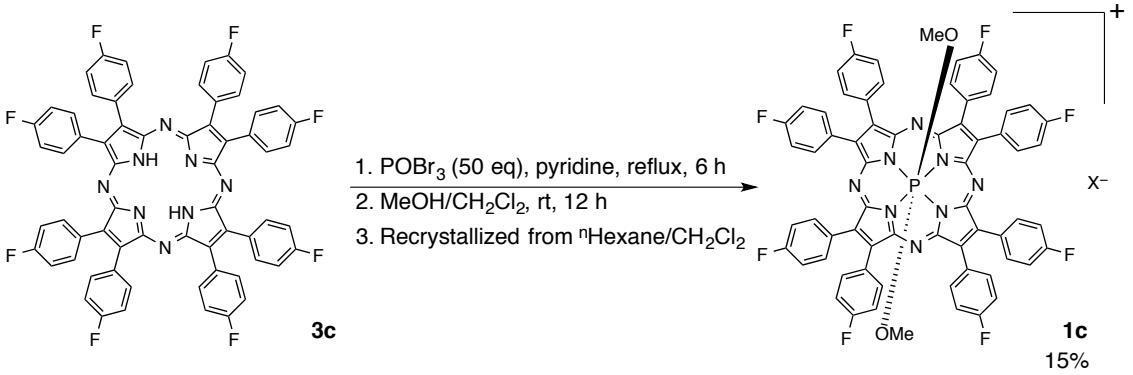
column chromatography (CH_2Cl_2-MeOH 95:5→80:20) was performed and the blue purple band was collected and concentrated producing crude **1b**. Counteranion exchange was carried out by dissolving crude **1b** in dichloromethane/methanol (1/1 v/v) and sodium perchlorate (20.0 mg, 0.201 mmol) was added to the solution. After the mixture was stirred for 12 h at room temperature, the solvent was removed and the residue was treated with dichloromethane to be filtered. Pure **1b** (5.7 mg, 5.8%) was obtained as a dark purple powder by recrystallization from CH_2Cl_2/^{n}hexane.

500 MHz ^{1}H-NMR (CD_2Cl_2) δ (ppm): 8.25 (d, 16H, J = 8.6 Hz, MeOPh-PhH), 7.21 (d, 16H, J = 8.0 Hz, MeOPh-PhH), 4.02 (s, 24H, MeOPh-MeH), –1.65 (d, 6H, $^3J_{PH}$ = 24.0 Hz, P-OMe). 200 MHz ^{31}P NMR (CD_2Cl_2) δ (ppm): –181.

HRMS-ESI (*m/z*) Calcd for $C_{74}H_{62}N_8O_{10}P$ $[M–ClO_4]^+$: 1253.4321. Found: 1253.4322.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 343 (5.0), 572 (6.2), 675 (3.8).

$[(4\text{-FPh})_8TAPP(OMe)_2]^+[X]^-$ (1c)



$POBr_3$ (200 mg, 0.70 mmol) was added to a solution of free-base TAP **3c** (15.0 mg, 14.1 mmol) in 4 mL of pyridine. After the mixture was stirred for 6 h under reflux, 2 mL of methanol and dichloromethane was added and stirred for 12 h at room temperature. Then the solvent was removed and the residue was dissolved in dichloromethane, and washed with water twice. The organic layer was collected, dried over $MgSO_4$, filtered and concentrated *in vacuo*. To remove byproducts, SiO_2 open column chromatography (CH_2Cl_2-MeOH-trifluoroacetic acid 90:9.5:0.5) was performed and the purple band was collected and concentrated producing crude **1c**. Pure **1c** (2.5 mg, 15%) was obtained as a dark purple powder by recrystallization from CH_2Cl_2/^{n}hexane. Since the solubility was severely decreased after a counteranion exchange, measurements were carried out with the counteranion mixture of

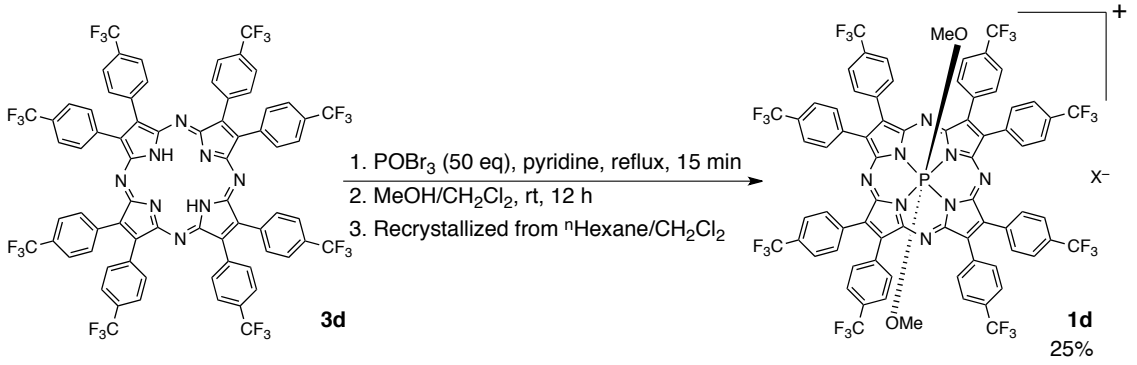
$[(4\text{-FPh})_8\text{TAPP(OMe)}_2]^+$. The purity of chromophore was confirmed with NMR.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 8.27 (br, 16H, FPh-PhH), 7.37 (br, 16H, FPh-PhH), –1.71 (brs, 6H, J = 28.0 Hz, P-OMe). 200 MHz ^{31}P NMR ($CDCl_3$) δ (ppm): –180.

HRMS-ESI (*m/z*) Calcd for $C_{66}H_{38}F_8N_8O_2P$ $[M–ClO_4]^+$: 1157.2722. Found: 1157.2724.

UV-vis (CH_2Cl_2) λ_{max} nm: 342, 360, 512, 650.

$[(4\text{-}F_3CPh)_8TAPP(OMe)_2]^+[X]^-$ (1d)



$POBr_3$ (200 mg, 0.70 mmol) was added to a solution of free-base TAP **3d** (20.0 mg, 13.1 mmol) in 4 mL of pyridine. After the mixture was stirred for 15 min under 90ºC, 2 mL of methanol and dichloromethane was added and stirred for 12 h at room temperature. Then the solvent was removed and the residue was dissolved in dichloromethane, and washed with water twice. The organic layer was collected, dried over $MgSO_4$, filtered and concentrated *in vacuo*. To remove byproducts, SiO_2 open column chromatography (CH_2Cl_2-MeOH-trifluoroacetic acid 95:4.5:0.5) was performed and the green band was collected and concentrated producing crude **1d**. Pure **1d** (5.2 mg, 25%) was obtained as a dark green powder by recrystallization from CH_2Cl_2/^{n}hexane. Since the solubility was severely decreased after a counteranion exchange, measurements were carried out with the counteranion mixture of $[(4\text{-}F_3CPh)_8TAPP(OMe)_2]^+$. The purity of chromophore was confirmed with NMR.

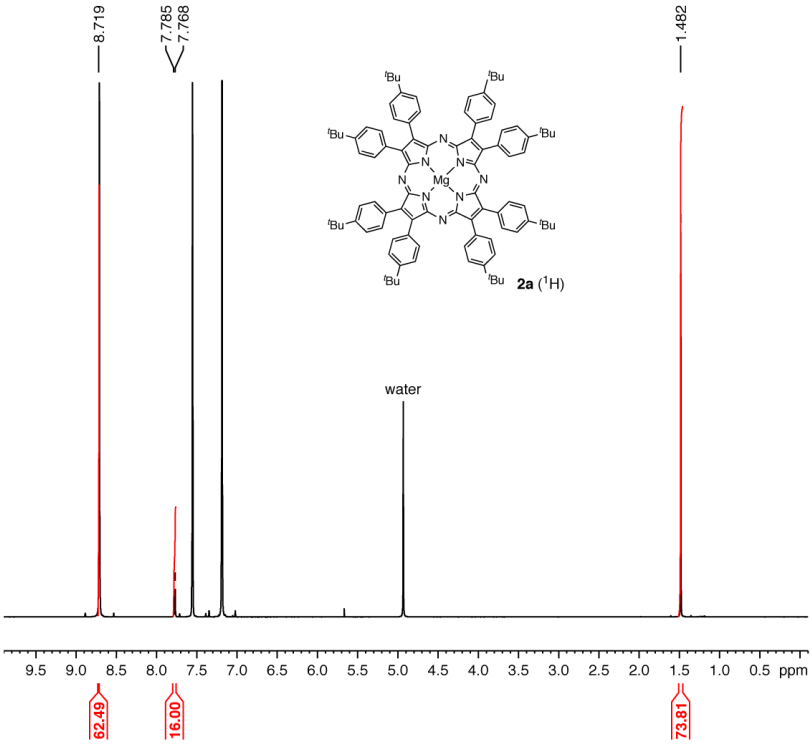
500 MHz ^{1}H NMR ($CDCl_3$-TFA-*d* 95:5) δ (ppm): 8.35 (br, 16H, CF_3Ph-PhH), 7.94 (br, 16H, CF_3Ph-PhH), –1.79 (br, 6H, P-OMe). 200 MHz ^{31}P NMR ($CDCl_3$-TFA-*d* 95:5) δ (ppm): –178.

HRMS-ESI (*m/z*) Calcd for $C_{74}H_{38}F_{24}N_8O_2P$ $[M–ClO_4]^+$: 1557.2467. Found: 1557.2468.

UV-vis (CH_2Cl_2-TFA 99:1) λ_{max} nm: 361, 480, 632.

Copies of the NMR Spectra of Studied Compounds

2a beta–(tBuPh)8TAPMg 1H in pyridine–d5

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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_               20121128
Time                   13.09
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                 Pyr
NS                       32
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                 3.2767999 sec
RG                     76.66
DW                    50.000 usec
DE                    10.00 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                      1H
P1                     12.00 usec
PLW1           18.39999962 W

F2 - Processing parameters
SI                    65536
SF              500.1299986 MHz
WDW                      EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
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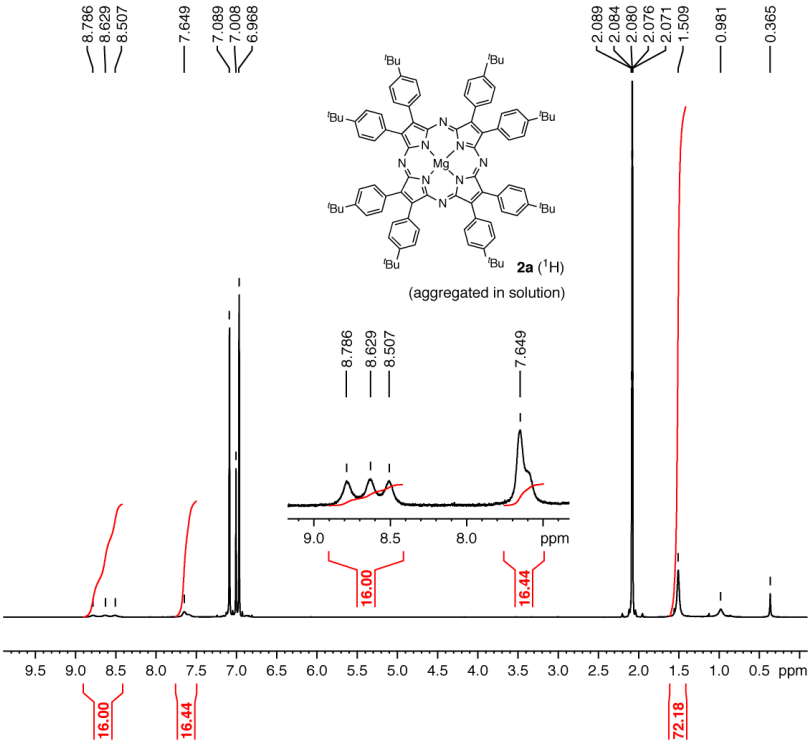
2a beta-(tBuPh)8TAPMg 1H in toluene–d8

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Current Data Parameters
NAME      1H NMR (t-buph)8TAPMg toluene-d8
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_               20120413
Time                   13.47
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT                 Tol
NS                       32
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                 3.2767999 sec
RG                     29.48
DW                    50.000 usec
DE                     6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                      1H
P1                     10.40 usec
PLW1           17.50000000 W

F2 - Processing parameters
SI                    65536
SF              500.1300249 MHz
WDW                      EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
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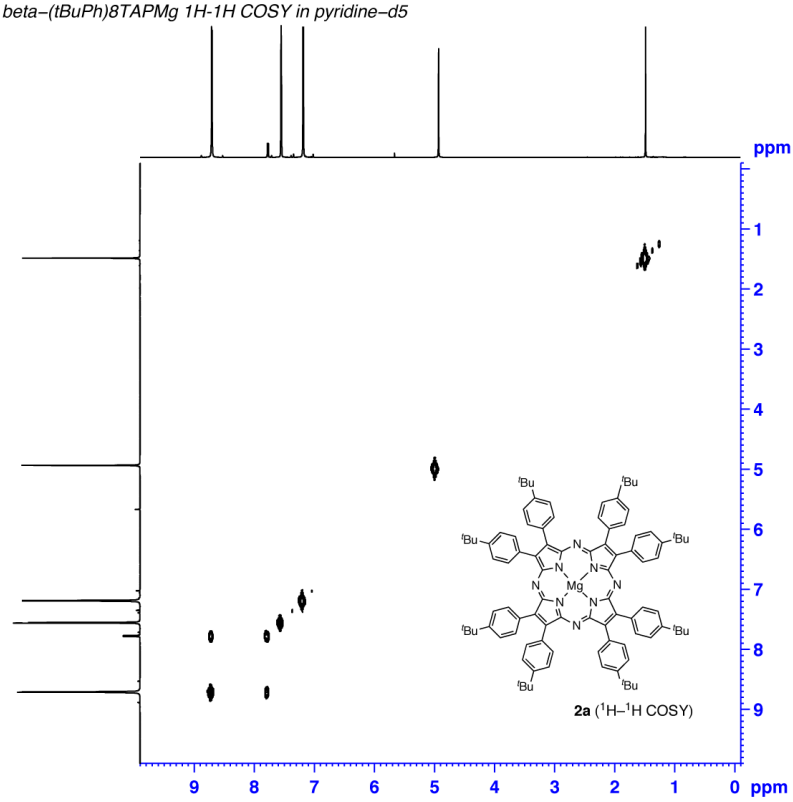
2a beta–(tBuPh)8TAPMg 1H-1H COSY in pyridine–d5

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Current Data Parameters
NAME      1H-1H COSY (t-BuPh)8TAPMg pyridine-d5
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140217
Time              11.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG     cosygpppqf
TD                2048
SOLVENT            Pyr
NS                   3
DS                   8
SWH           6684.492 Hz
FIDRES        3.263912 Hz
AQ            0.1531904 sec
RG               188.42
DW               74.800 usec
DE                6.50 usec
TE               294.6 K
D0            0.00000300 sec
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00014960 sec

======== CHANNEL f1 ========
SFO1        500.1330069 MHz
NUC1               1H
P0               12.00 usec
P1               12.00 usec
P17            2500.00 usec
PLW1        18.00000000 W
PLW10        3.83430004 W

====== GRADIENT CHANNEL =====
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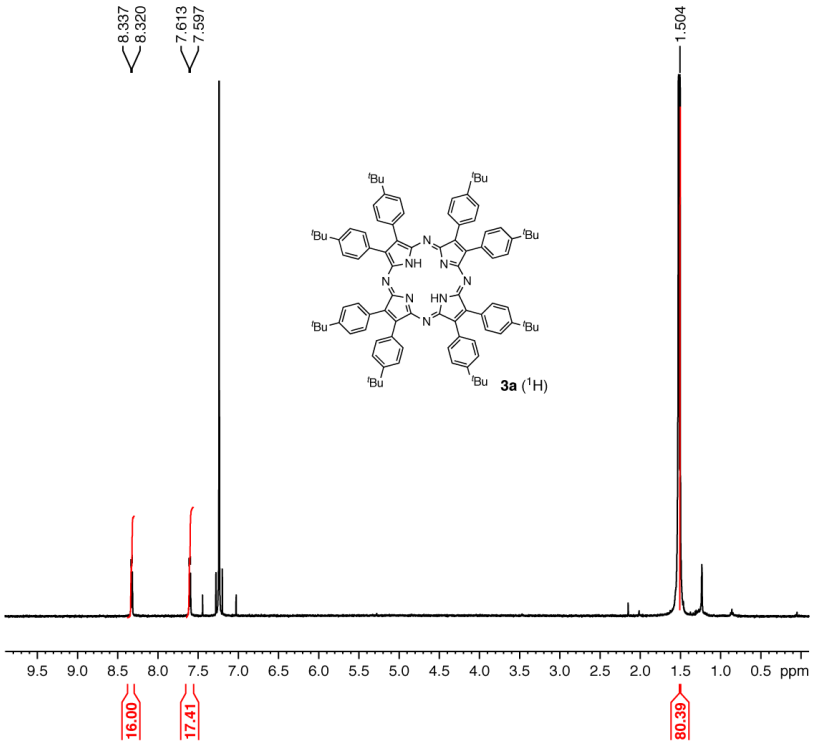
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                 128
SFO1        500.133 MHz
FIDRES      52.222595 Hz
SW             13.365 ppm
FnMODE              QF

F2 - Processing parameters
SI                1024
SF          500.1300000 MHz
WDW               QSINE
SSB       0
LB        0 Hz
GB        0
PC                1.40

F1 - Processing parameters
SI                1024
MC2                QF
SF          500.1300000 MHz
WDW               QSINE
SSB       0
LB        0 Hz
GB        0
```

3a beta–(tBuPh)TAPH2 1H in CDCl3

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Current Data Parameters
NAME      1H NMR (t-buph)8TAPH2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120507
Time              20.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          10000.000 Hz
FIDRES           0.152588 Hz
AQ            3.2767999 sec
RG               167.37
DW               50.000 usec
DE                6.50 usec
TE               299.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1               1H
P1               10.40 usec
PLW1        17.50000000 W

F2 - Processing parameters
SI               65536
SF          500.1300243 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC                1.00
```
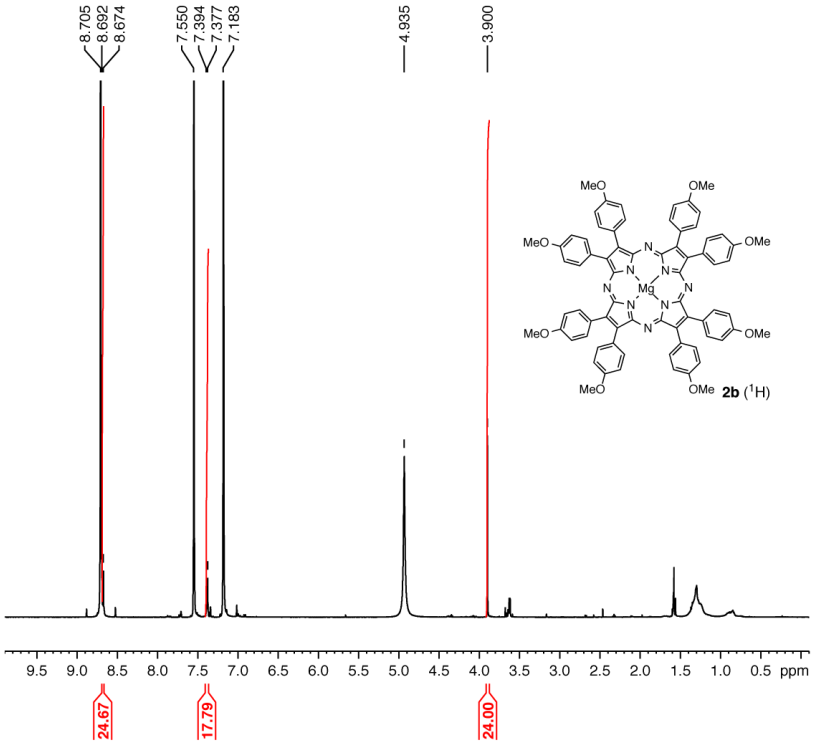
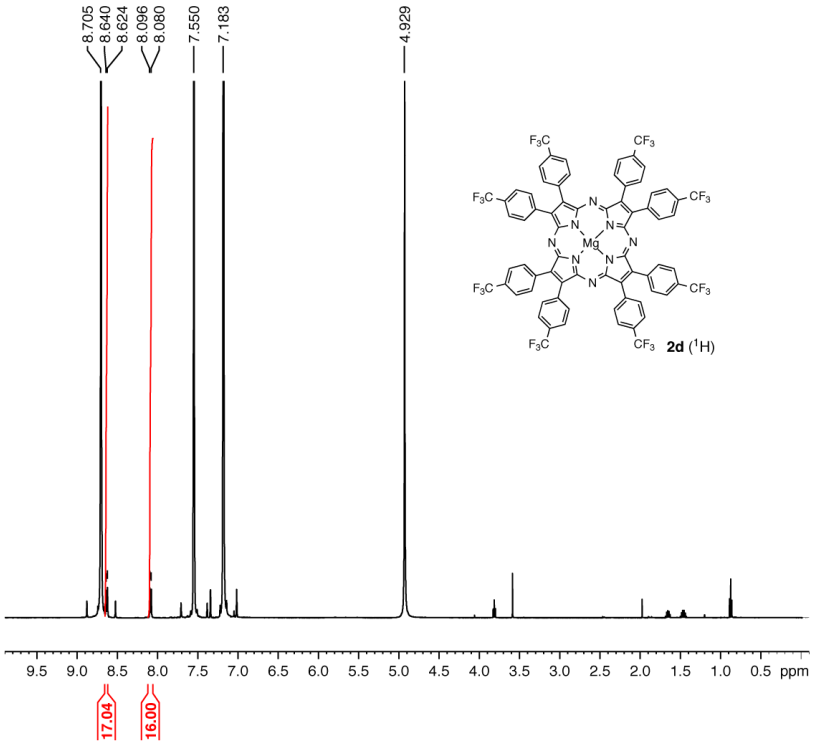

2b beta–(MeO)8TAPMg 1H in pyridine–d5




```
Current Data Parameters
NAME      1H NMR (MeOPh)8TAPMg pyridine-d5
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20130112
Time                 16.08
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT               Pyr
NS                     32
DS                      2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2767999 sec
RG                   29.48
DW                 50.000 usec
DE                 10.00 usec
TE                 298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           18.39999962 W

F2 - Processing parameters
SI                   65536
SF              500.1300004 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

2d beta–(F3CPh)TAPMg 1H in pyridine–d5

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Current Data Parameters
NAME      1H NMR (CF3Ph)8TAPMg pyridine-d5
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20130201
Time                 16.51
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT               Pyr
NS                     64
DS                      2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2767999 sec
RG                   29.48
DW                 50.000 usec
DE                 10.00 usec
TE                 298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           18.39999962 W

F2 - Processing parameters
SI                   65536
SF              500.1300006 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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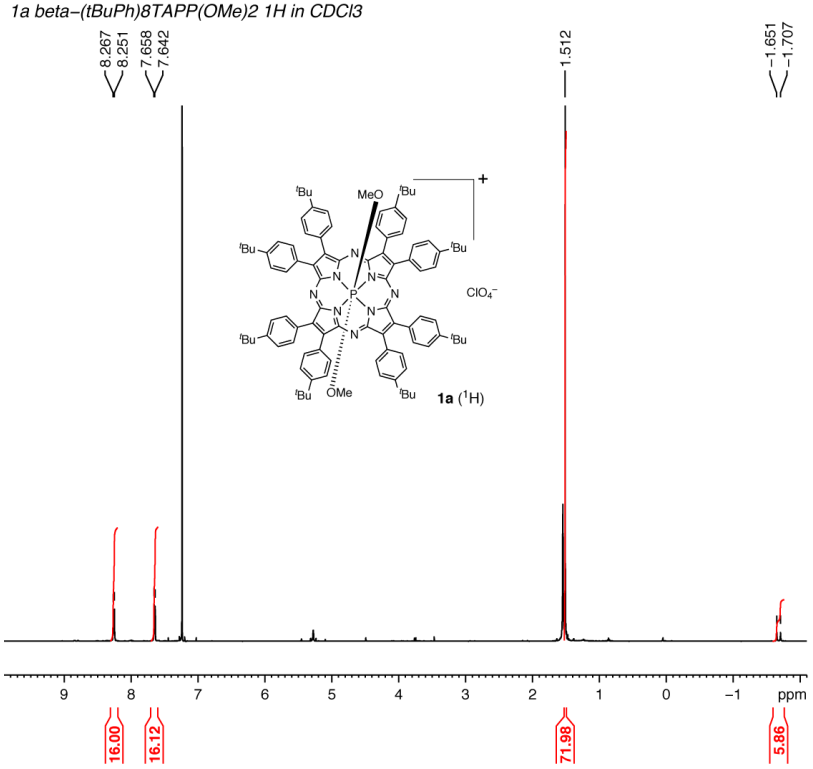
1a beta–(tBuPh)8TAPP(OMe)2 1H in CDCl3



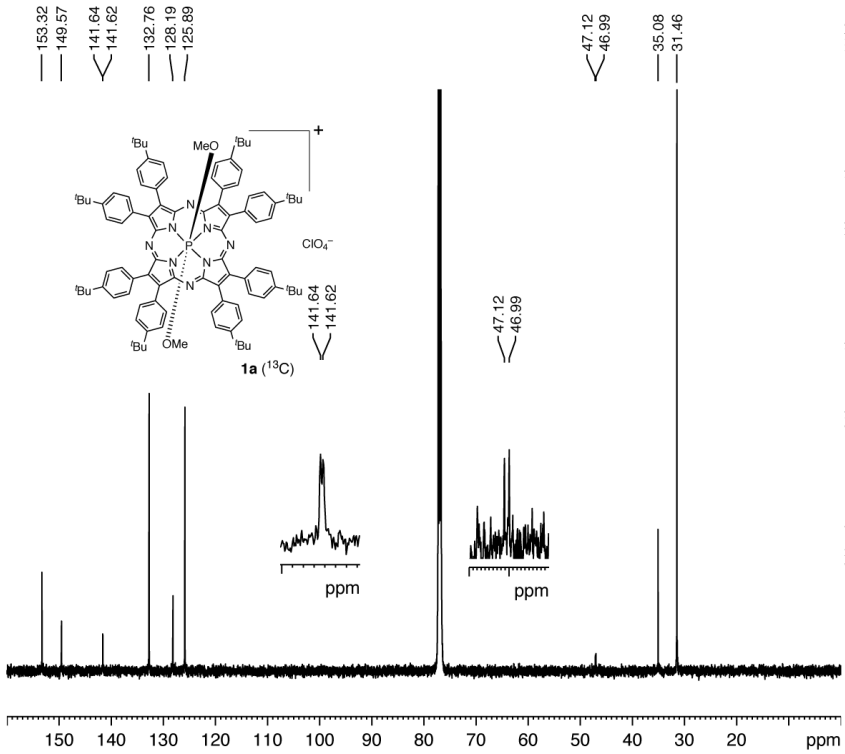

```
Current Data Parameters
NAME      1H NMR (t-buph)8TAPP(OMe)2 ClO4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_               20120607
Time                   19.50
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                    3.2767999 sec
RG                      188.42
DW                     50.000 usec
DE                      6.50 usec
TE                     299.7 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1              500.1330885 MHz
NUC1                      1H
P1                     10.40 usec
PLW1              17.50000000 W

F2 - Processing parameters
SI                    65536
SF                500.1300243 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

1a beta–(tBuPh)8TAPP(OMe)2 13C in CDCl3

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Current Data Parameters
NAME      13C NMR (t-buph)8TAPP(OMe)2 ClO4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_               20121112
Time                   17.38
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      961
DS                        4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010048 sec
RG                      188.42
DW                     16.800 usec
DE                     18.00 usec
TE                     298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1              125.7703637 MHz
NUC1                      13C
P1                     10.00 usec
PLW1              75.00000000 W

======== CHANNEL f2 ========
SFO2              500.1320005 MHz
NUC2                      1H
CPDPRG[2               waltz16
PCPD2                  80.00 usec
PLW2              18.39999962 W
PLW12              0.41400000 W
PLW13              0.26495999 W

F2 - Processing parameters
SI                    32768
SF                125.7577918 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
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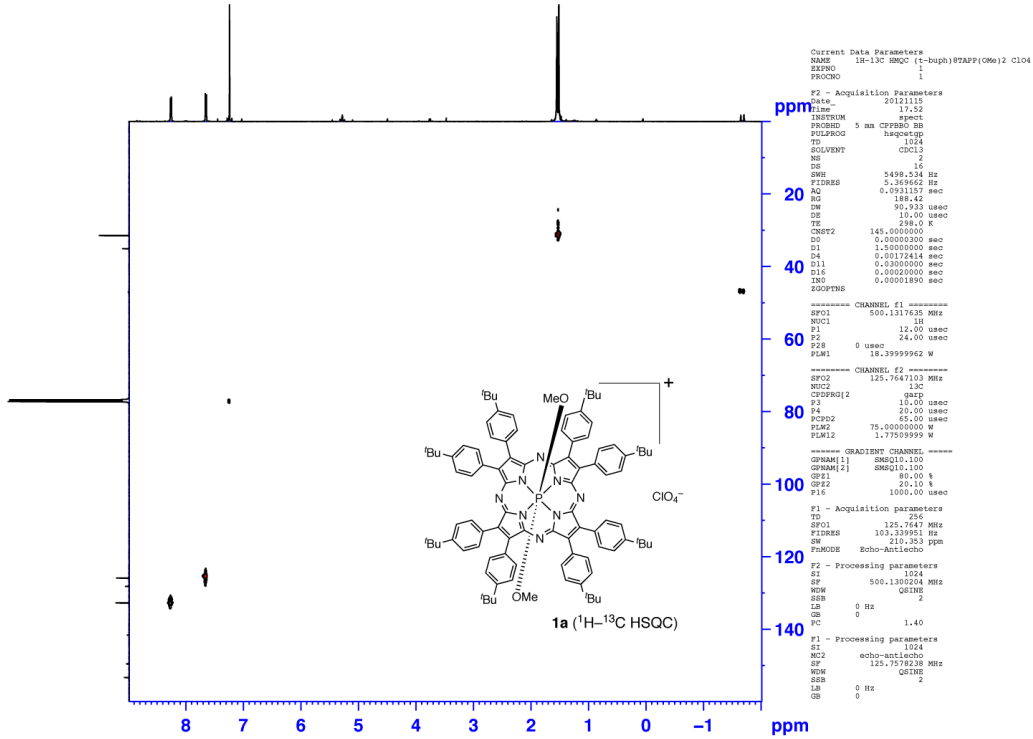
1a beta–(tBuPh)8TAPP(OMe)2 1H–13C HSQC in CDCl3

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Current Data Parameters
NAME      1H-13C HMQC (t-buph)8TAPP(OMe)2 ClO4
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20121115
Time               17.52
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG         hsqcetgp
TD                 1024
SOLVENT            CDCl3
NS                    2
DS                   16
SWH             5498.534 Hz
FIDRES          5.369662 Hz
AQ              0.0931157 sec
RG                 188.42
DW                90.933 usec
DE                10.00 usec
TE                298.0 K
CNST2          145.0000000
D0              0.00000300 sec
D1              1.50000000 sec
D4              0.00172414 sec
D11             0.03000000 sec
D16             0.00020000 sec
IN0             0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1          500.1317635 MHz
NUC1                     1H
P1                   12.00 usec
P2                   24.00 usec
P28       0 usec
PLW1         18.39999962 W

======== CHANNEL f2 ========
SFO2          125.7647103 MHz
NUC2                     13C
CPDPRG[2                garp
P3                   10.00 usec
P4                   20.00 usec
PCPD2                65.00 usec
PLW2          75.00000000 W
PLW12          1.77509999 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPZ1                 80.00 %
GPZ2                 20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    256
SFO1          125.7647 MHz
FIDRES        103.339951 Hz
SW              210.353 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF            500.1300204 MHz
WDW                  QSINE
SSB                     2
LB          0 Hz
GB          0
PC                    1.40

F1 - Processing parameters
SI                   1024
MC2        echo-antiecho
SF            125.7578238 MHz
WDW                  QSINE
SSB                     2
LB          0 Hz
GB          0
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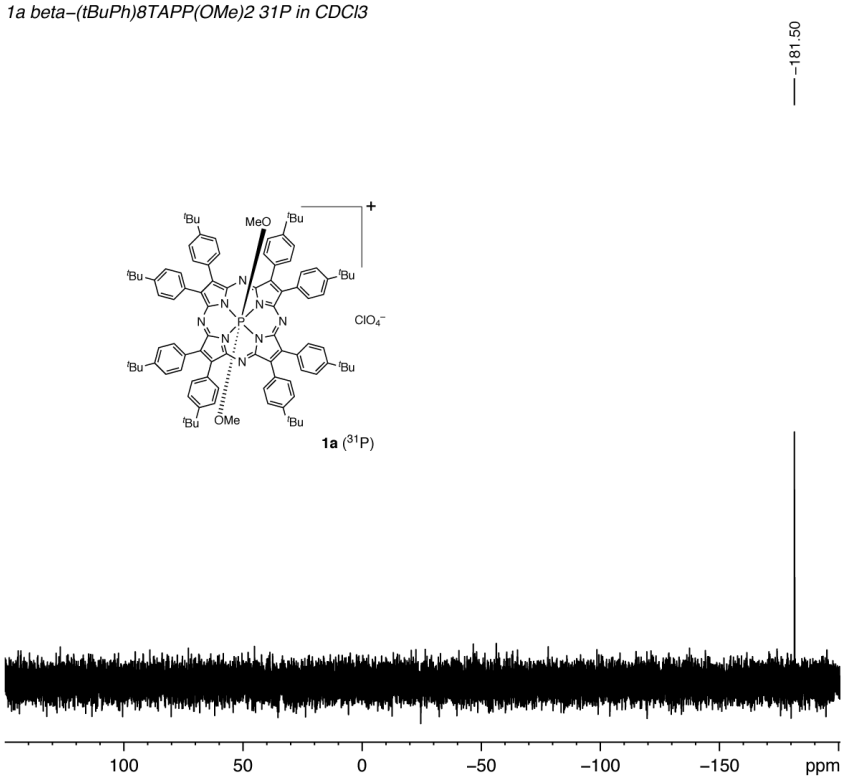
1a beta–(tBuPh)8TAPP(OMe)2 31P in CDCl3

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Current Data Parameters
NAME      31P NMR (t-buph)8TAPP(OMe)2 ClO4
EXPNO                 1
PROCNO                1

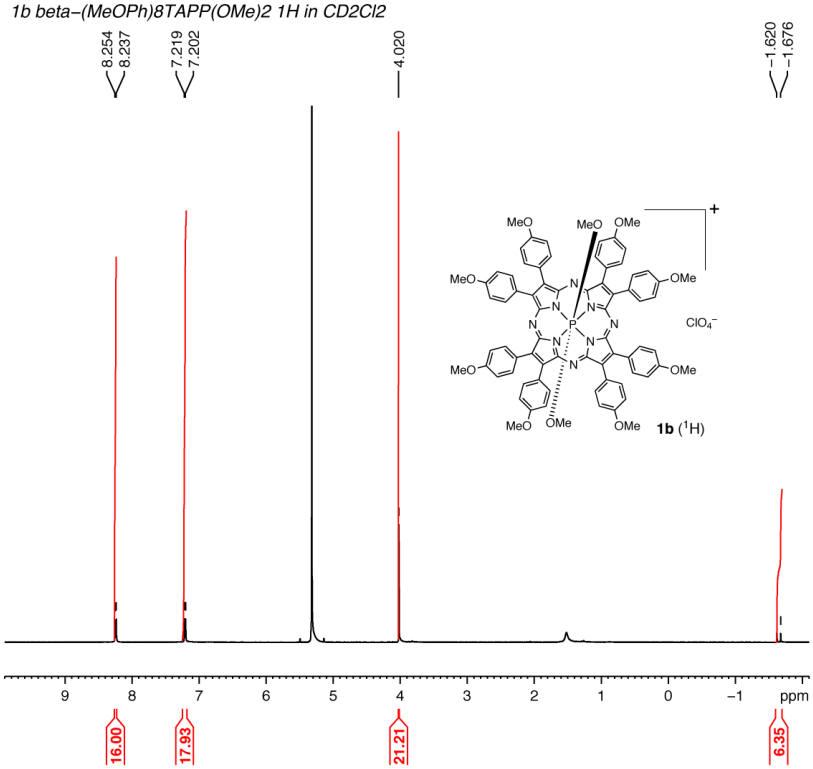
F2 - Acquisition Parameters
Date_          20120427
Time               16.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                  251
DS                    4
SWH            81521.742 Hz
FIDRES          1.243923 Hz
AQ              0.4019541 sec
RG                 188.42
DW                 6.133 usec
DE                  6.50 usec
TE                299.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1          202.4563350 MHz
NUC1                    31P
P1                   14.00 usec
PLW1         46.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                    1H
CPDPRG[2          waltz65
PCPD2                90.00 usec
PLW2          17.50000000 W
PLW12          0.23367999 W
PLW13          0.18928000 W

F2 - Processing parameters
SI                   32768
SF            202.4562044 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

1b beta–(MeOPh)8TAPP(OMe)2 1H in CD2Cl2

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Current Data Parameters
NAME      1H NMR (MeOPh)8TAPP(OMe)2 ClO4 CD2Cl2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20121201
Time              14.38
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                  16
DS                   2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG                29.48
DW               50.000 usec
DE               10.00 usec
TE               298.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1               1H
P1                12.00 usec
PLW1         18.39999962 W

F2 - Processing parameters
SI                65536
SF           500.1300206 MHz
WDW                EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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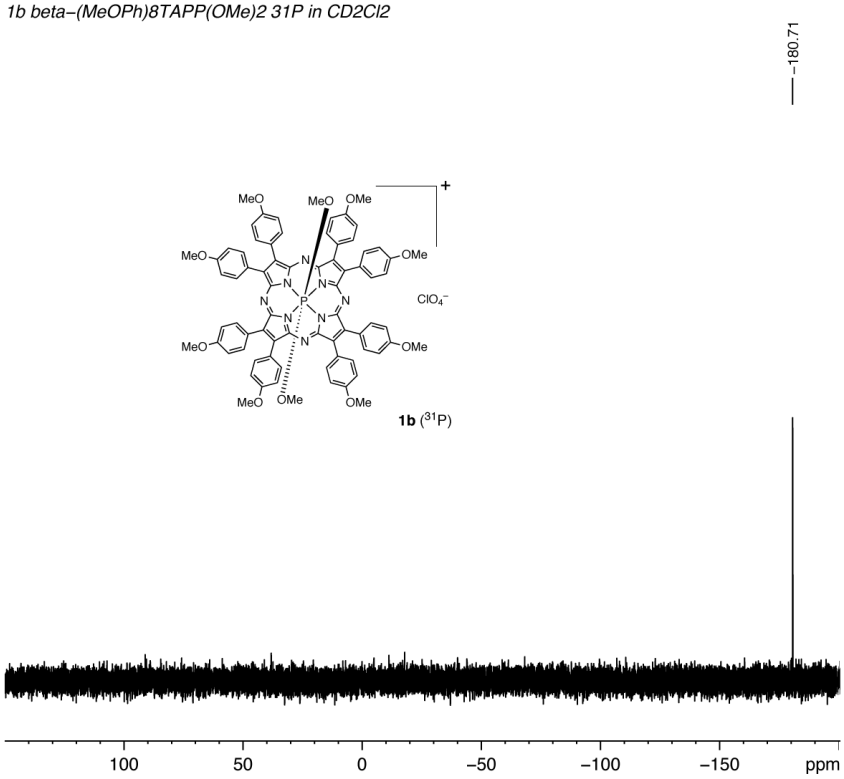
1b beta–(MeOPh)8TAPP(OMe)2 31P in CD2Cl2

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Current Data Parameters
NAME      31P NMR (MeOPh)8TAPP(OMe)2 ClO4 CD2Cl2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20121201
Time              14.43
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD               65536
SOLVENT          CD2Cl2
NS                 256
DS                   4
SWH           81521.742 Hz
FIDRES        1.243923 Hz
AQ            0.4019541 sec
RG                188.42
DW                6.133 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         202.4462121 MHz
NUC1               31P
P1                12.00 usec
PLW1         41.20000076 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2               1H
CPDPRG[2         waltz65
PCPD2             80.00 usec
PLW2         18.39999962 W
PLW12         0.41400000 W
PLW13         0.26495999 W

F2 - Processing parameters
SI                32768
SF           202.4562046 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```
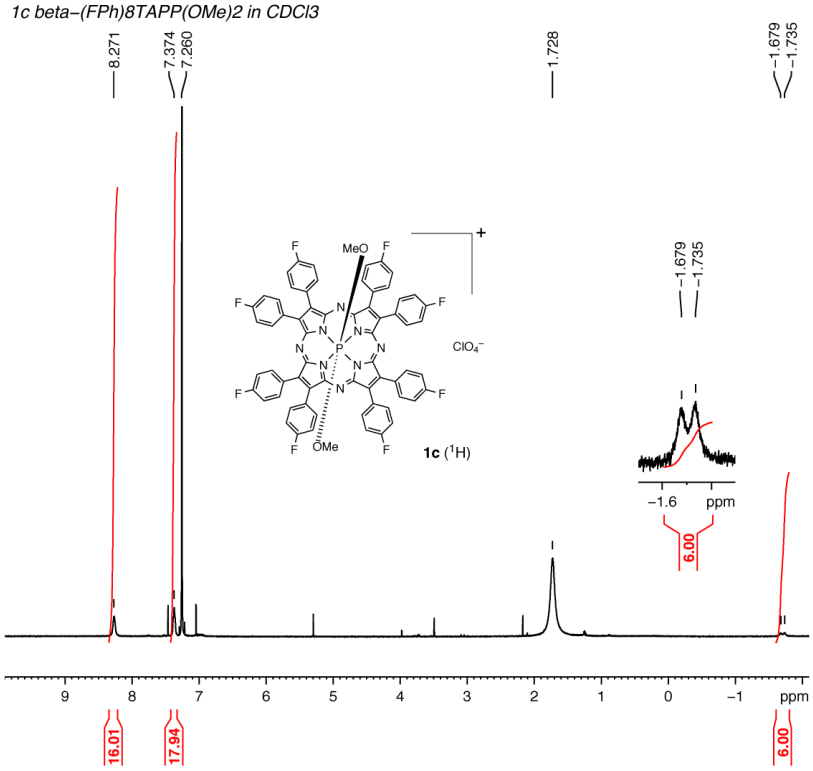
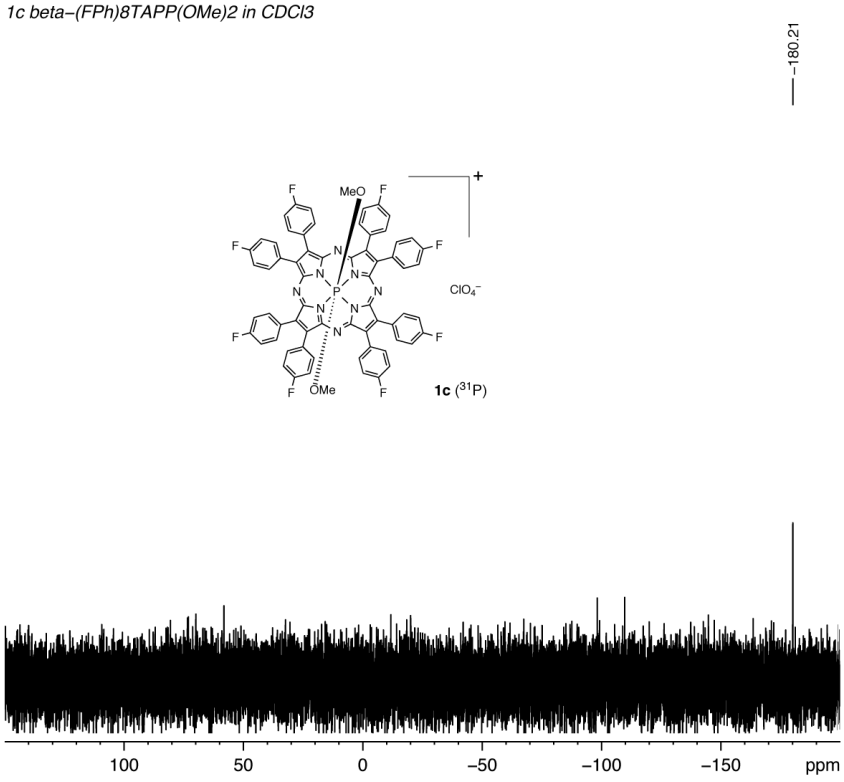

1c beta–(FPh)8TAPP(OMe)2 in CDCl3



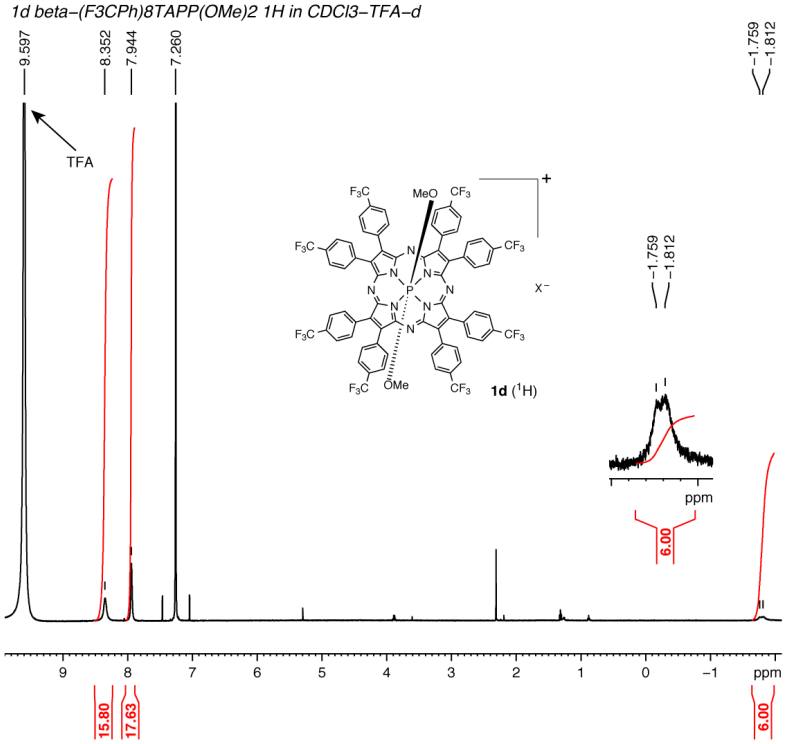

```
Current Data Parameters
NAME      1H NMR (FPh)8TAPP(OMe)2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130226
Time              20.31
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  64
DS                   2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG               29.48
DW              50.000 usec
DE              10.00 usec
TE              300.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1               1H
P1              12.00 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                65536
SF          500.1300136 MHz
WDW                EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

1c beta–(FPh)8TAPP(OMe)2 in CDCl3



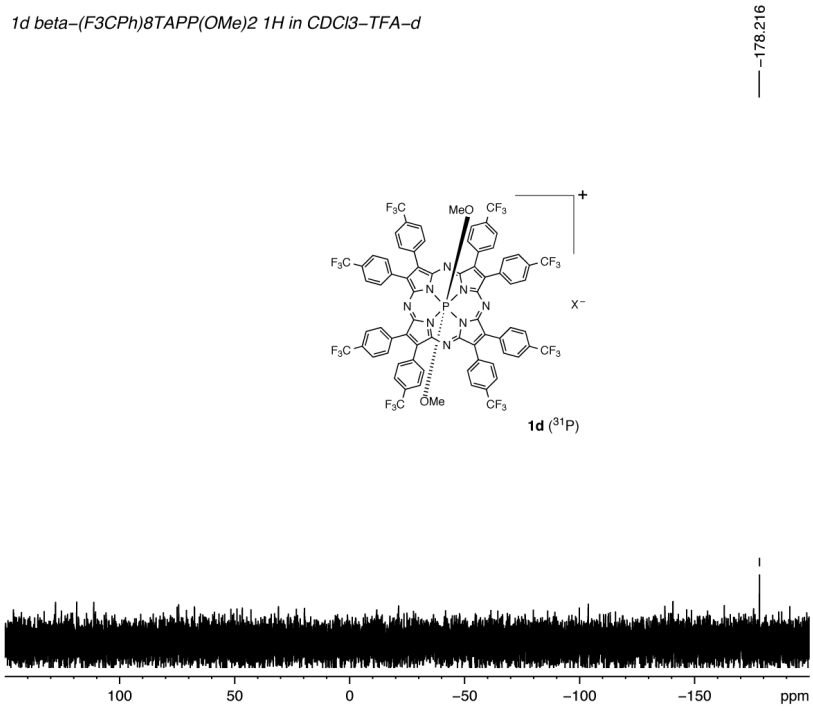

```
Current Data Parameters
NAME      31P NMR (FPh)8TAPP(OMe)2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131112
Time              15.38
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                 339
DS                   4
SWH           81521.742 Hz
FIDRES         1.243923 Hz
AQ            0.4019541 sec
RG               188.42
DW               6.133 usec
DE               6.50 usec
TE               298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        202.4462121 MHz
NUC1               31P
P1              14.00 usec
PLW1        46.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2        17.50000000 W
PLW12        0.23367999 W
PLW13        0.18928000 W

F2 - Processing parameters
SI                32768
SF          202.4562071 MHz
WDW                EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

1d beta–(F3CPh)8TAPP(OMe)2 1H in CDCl3–TFA–d



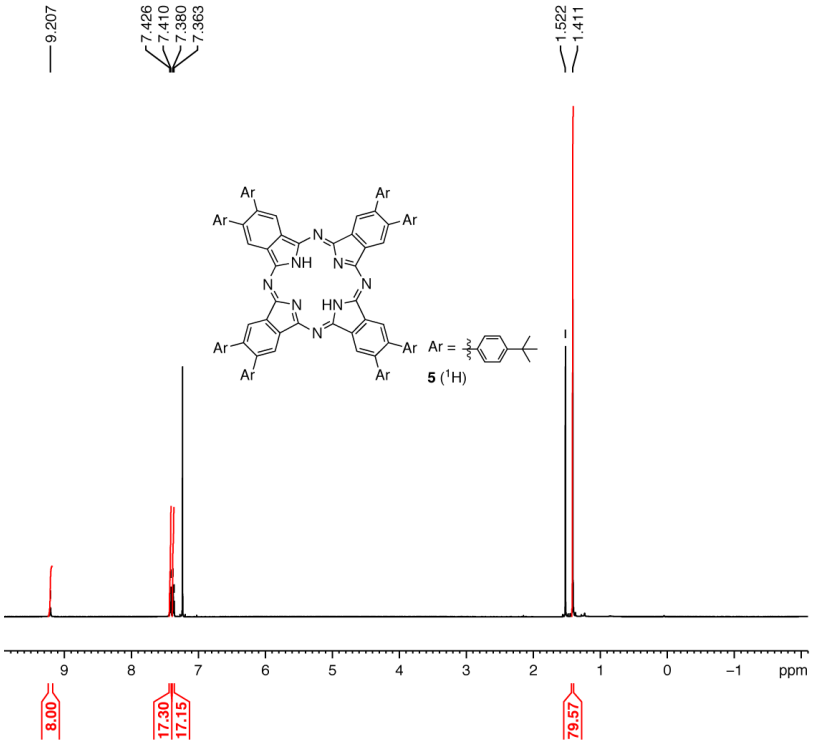

```
Current Data Parameters
NAME      1H NMR (CF3Ph)8TAPP(OMe)2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20130404
Time              20.35
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                 302
DS                   2
SWH          10000.000 Hz
FIDRES           0.152588 Hz
AQ            3.2767999 sec
RG                188.42
DW               50.000 usec
DE                6.50 usec
TE               300.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                 1H
P1                10.40 usec
PLW1         17.50000000 W

F2 - Processing parameters
SI                65536
SF           500.1300140 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

1d beta–(F3CPh)8TAPP(OMe)2 1H in CDCl3–TFA–d



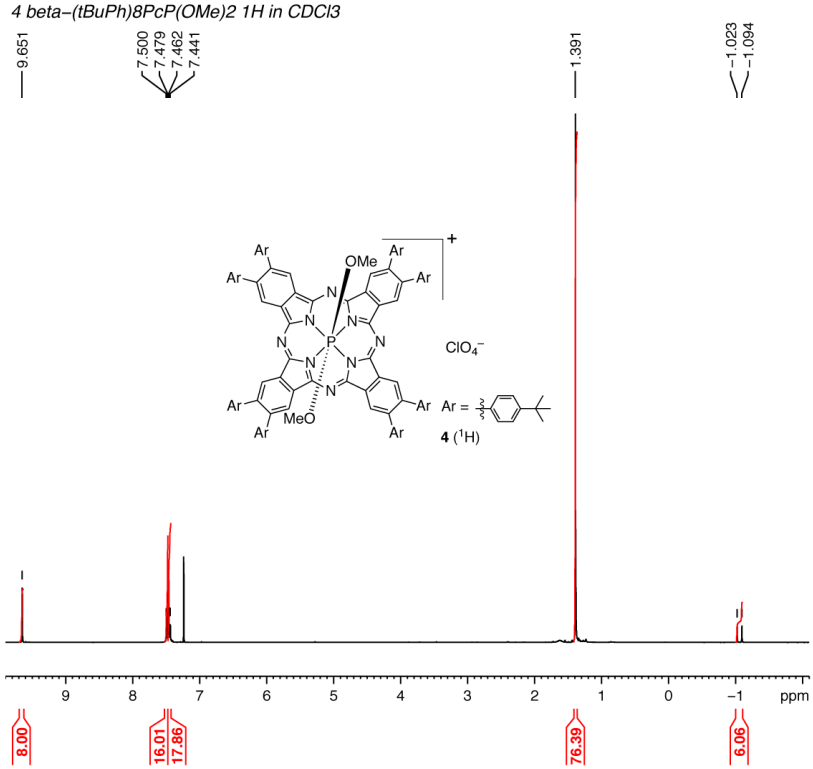

```
Current Data Parameters
NAME      31P NMR (CF3Ph)8TAPP(OMe)2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20131112
Time              19.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 683
DS                   4
SWH          81521.742 Hz
FIDRES           1.243923 Hz
AQ            0.4019541 sec
RG                188.42
DW               6.133 usec
DE                6.50 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         202.4462121 MHz
NUC1                 31P
P1                14.00 usec
PLW1         46.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                 1H
CPDPRG[2          waltz65
PCPD2             90.00 usec
PLW2         17.50000000 W
PLW12         0.23367999 W
PLW13         0.18928000 W

F2 - Processing parameters
SI                32768
SF           202.4562046 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

5 beta-(tBuPh)8PcH2 1H in CDCl3



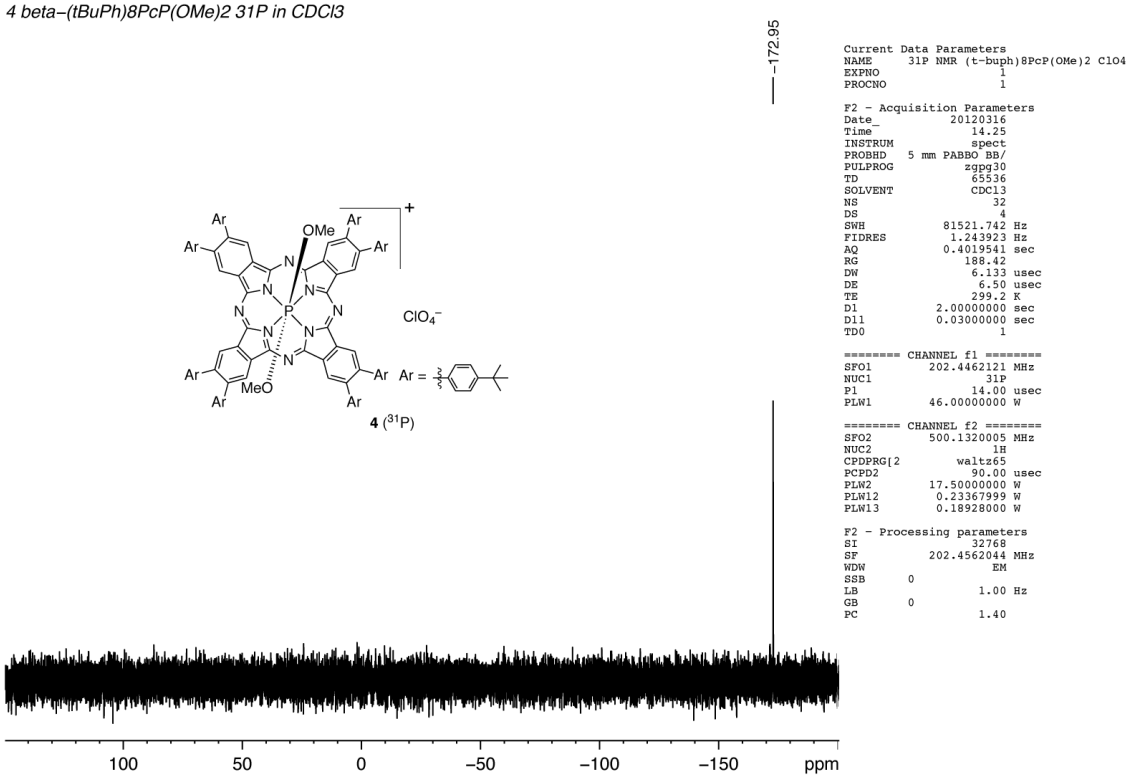

```
Current Data Parameters
NAME      1H NMR (t-buph)8PcH2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20120514
Time                15.12
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2767999 sec
RG                   188.42
DW                   50.000 usec
DE                     6.50 usec
TE                   298.9 K
D1              1.00000000 sec
TD0                         1

========= CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                     1H
P1                    10.40 usec
PLW1          17.50000000 W

F2 - Processing parameters
SI                   65536
SF            500.1300254 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

4 beta-(tBuPh)8PcP(OMe)2 1H in CDCl3

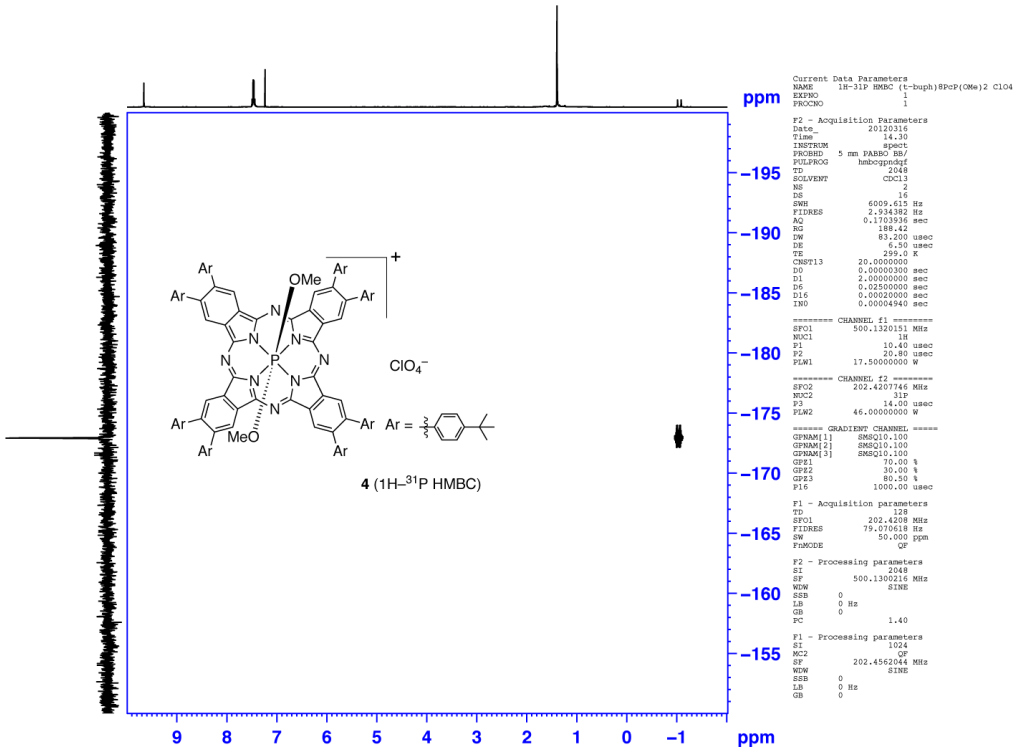



```
Current Data Parameters
NAME      1H NMR (t-buph)8PcP(OMe)2 ClO4
EXPNO                       5
PROCNO                      1

F2 - Acquisition Parameters
Date_            20120225
Time                14.49
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              8278.146 Hz
FIDRES              0.126314 Hz
AQ                3.9583745 sec
RG                   406.4
DW                   60.400 usec
DE                     6.00 usec
TE                   299.0 K
D1              1.00000000 sec
MCREST    0 sec
MCWRK          0.00999999 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    13.00 usec
PL1                    3.00 dB
SFO1          400.0324703 MHz

F2 - Processing parameters
SI                   32768
SF            400.0300149 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

4 beta–(tBuPh)8PcP(OMe)2 31P in CDCl3



4 beta–(tBuPh)8PcP(OMe)2 1H–31P HMBC in CDCl3



Full Computational Details

Computational Details

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

$[Ph_8TAPP(OMe)_2]^+$ (1e)

SCF Done: E(RB3LYP) = -3472.34273366 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.787972	0.807504	0.232128
2	6	0	-3.628076	1.989492	0.221019
3	6	0	-2.796316	3.059684	-0.064010
4	6	0	-1.452527	2.525821	-0.167753
5	7	0	-1.462383	1.148438	0.011874
6	7	0	-3.276289	-0.413630	0.301624
7	6	0	-2.515582	-1.471658	0.127123
8	6	0	-3.056093	-2.815541	0.040746
9	7	0	-1.136242	-1.489250	-0.033151
10	6	0	-1.984181	-3.658803	-0.183055
11	6	0	-0.792829	-2.826646	-0.177717
12	7	0	0.425381	-3.320549	-0.245027
13	7	0	-0.386110	3.287860	-0.299721
14	6	0	1.483735	-2.549889	-0.103442
15	6	0	2.833903	-3.079249	-0.046186
16	7	0	1.496861	-1.170247	0.025161
17	6	0	3.677865	-2.003261	0.122127
18	6	0	2.828205	-0.820491	0.162938
19	6	0	0.827857	2.793743	-0.186029
20	6	0	2.011803	3.630204	-0.163740
21	7	0	1.167042	1.465268	0.053466
22	6	0	3.079272	2.800899	0.126080
23	6	0	2.541998	1.455117	0.210223
24	7	0	3.315110	0.392729	0.296174
25	15	0	0.016765	-0.012523	0.014697
26	8	0	0.144843	0.058316	-1.656810
27	8	0	-0.037473	-0.146192	1.685930
28	6	0	-0.897737	-0.193508	-2.596136
29	1	0	-1.191397	-1.248198	-2.610258
30	1	0	-1.779955	0.429156	-2.408540
31	1	0	-0.482126	0.070652	-3.571026
32	6	0	-0.019102	0.929433	2.621812
33	1	0	-0.207498	0.472100	3.595607
34	1	0	-0.805363	1.665568	2.420344
35	1	0	0.952474	1.433649	2.647682

36	6	0	4.511488	3.119113	0.235298
37	6	0	5.110253	4.011944	-0.673678
38	6	0	5.308170	2.535397	1.237163
39	6	0	6.467107	4.309850	-0.581638
40	1	0	4.511094	4.459869	-1.459567
41	6	0	6.663732	2.845586	1.331864
42	1	0	4.862758	1.843747	1.943503
43	6	0	7.247241	3.731549	0.423791
44	1	0	6.916742	4.993399	-1.296041
45	1	0	7.263663	2.393620	2.116332
46	6	0	1.986344	5.091860	-0.340245
47	6	0	1.305116	5.674720	-1.422286
48	6	0	2.651313	5.927802	0.574643
49	6	0	1.297776	7.058430	-1.589327
50	1	0	0.796370	5.038996	-2.139367
51	6	0	2.629830	7.310733	0.411708
52	1	0	3.174796	5.490116	1.418846
53	6	0	1.956586	7.880105	-0.672454
54	1	0	0.779523	7.495383	-2.438185
55	1	0	3.139243	7.944789	1.131551
56	6	0	5.138315	-1.985594	0.297249
57	6	0	5.758895	-2.964286	1.097596
58	6	0	5.940120	-1.007184	-0.319483
59	6	0	7.139145	-2.960506	1.277826
60	1	0	5.153495	-3.718209	1.589527
61	6	0	7.322637	-1.014596	-0.143441
62	1	0	5.480511	-0.247363	-0.939954
63	6	0	7.926344	-1.987936	0.655178
64	1	0	7.600834	-3.716518	1.906367
65	1	0	7.927760	-0.256665	-0.632302
66	6	0	3.171879	-4.507889	-0.196357
67	6	0	2.626912	-5.474048	0.664429
68	6	0	4.070678	-4.915108	-1.196318
69	6	0	2.975612	-6.817415	0.528919
70	1	0	1.950215	-5.165295	1.455110
71	6	0	4.405888	-6.260316	-1.337901
72	1	0	4.498182	-4.174654	-1.865563
73	6	0	3.861276	-7.214540	-0.475072
74	1	0	2.560638	-7.553300	1.212109
75	1	0	5.094579	-6.563258	-2.121269
76	6	0	-1.995665	-5.104729	-0.466024
77	6	0	-1.080889	-5.985628	0.134409
78	6	0	-2.941405	-5.622943	-1.371176
79	6	0	-1.116337	-7.347952	-0.158387
80	1	0	-0.346578	-5.601672	0.831257
81	6	0	-2.967011	-6.982842	-1.667503
82	1	0	-3.648109	-4.952987	-1.850350
83	6	0	-2.056275	-7.851061	-1.059495
84	1	0	-0.404482	-8.016659	0.316737
85	1	0	-3.696849	-7.364967	-2.375368
86	6	0	-4.476903	-3.148905	0.238390
87	6	0	-4.826706	-4.251595	1.041226
88	6	0	-5.502690	-2.384665	-0.346623
89	6	0	-6.163310	-4.576510	1.254254
90	1	0	-4.045763	-4.843860	1.506915
91	6	0	-6.839627	-2.720696	-0.138163
92	1	0	-5.252628	-1.532575	-0.967421
93	6	0	-7.174492	-3.814262	0.662311
94	1	0	-6.416400	-5.424510	1.884025
95	1	0	-7.619618	-2.124442	-0.602616
96	6	0	-5.090605	1.954873	0.378512
97	6	0	-5.694567	1.151477	1.362872
98	6	0	-5.912275	2.722701	-0.468759
99	6	0	-7.081392	1.126547	1.500959
100	1	0	-5.076264	0.551933	2.021407
101	6	0	-7.297274	2.686108	-0.333583
102	1	0	-5.460992	3.338381	-1.239801

103	6	0	-7.886265	1.891770	0.654534
104	1	0	-7.532273	0.507792	2.271277
105	1	0	-7.918159	3.277443	-1.000376
106	6	0	-3.119989	4.493539	-0.151981
107	6	0	-3.946651	5.090129	0.817734
108	6	0	-2.610776	5.289473	-1.192120
109	6	0	-4.251672	6.446951	0.748082
110	1	0	-4.339067	4.488643	1.631577
111	6	0	-2.928697	6.644466	-1.264921
112	1	0	-1.974345	4.841275	-1.947425
113	6	0	-3.747191	7.227560	-0.295469
114	1	0	-4.882921	6.895811	1.509504
115	1	0	-2.536480	7.245786	-2.080012
116	1	0	-2.078802	-8.912578	-1.288876
117	1	0	4.129303	-8.261697	-0.582373
118	1	0	9.004040	-1.989974	0.792086
119	1	0	8.304263	3.970929	0.498188
120	1	0	1.946898	8.958567	-0.801800
121	1	0	-3.990624	8.284672	-0.351658
122	1	0	-8.966941	1.870205	0.763146
123	1	0	-8.217095	-4.072552	0.824809

TD–DFT output

HOMO**: 264**, LUMO**: 265**

Excited State 1:	Singlet-A	1.8403 eV	673.72 nm	f=0.1984	<S**2>=0.000
247 -> 265	0.15929				
247 -> 266	0.10335				
263 -> 265	-0.16793				
264 -> 265	-0.35119				
264 -> 266	0.55138				

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3462.77818693
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:	Singlet-A	1.8516 eV	669.59 nm	f=0.2076	<S**2>=0.000
247 -> 265	0.10392				
247 -> 266	-0.15499				
263 -> 266	0.16980				
264 -> 265	0.55244				
264 -> 266	0.35053				

Excited State 3:	Singlet-A	3.0369 eV	408.26 nm	f=0.1072	<S**2>=0.000
245 -> 266	-0.11503				
246 -> 265	0.13903				
260 -> 265	0.21579				
260 -> 267	0.12775				
261 -> 265	0.36563				
262 -> 266	0.37630				
262 -> 267	-0.13147				
263 -> 265	-0.10287				
263 -> 266	-0.24691				

Excited State 4:	Singlet-A	3.0783 eV	402.76 nm	f=0.0489	<S**2>=0.000
245 -> 266	-0.11068				
246 -> 265	-0.15896				
260 -> 265	-0.29701				
261 -> 265	-0.29469				
262 -> 265	0.19405				
262 -> 266	0.36114				
263 -> 266	-0.20871				
263 -> 267	0.14082				

Excited State 5:	Singlet-A	3.1443 eV	394.32 nm	f=0.2904	<S**2>=0.000
244 -> 266	0.10700				
260 -> 265	-0.11236				
260 -> 266	0.41997				

260 -> 267	0.11503				
261 -> 265	0.14924				
261 -> 266	-0.14805				
262 -> 266	0.15361				
263 -> 265	0.15382				
263 -> 266	0.33887				
264 -> 265	-0.11824				
Excited State 6:	Singlet-A	3.1975 eV	387.76 nm	f=0.3349	<S**2>=0.000
244 -> 265	-0.12838				
260 -> 265	-0.23571				
260 -> 266	-0.15928				
261 -> 265	0.34062				
261 -> 267	-0.12883				
262 -> 265	0.20204				
262 -> 266	-0.15536				
263 -> 265	0.34548				
263 -> 266	-0.13898				
264 -> 266	0.11986				
Excited State 7:	Singlet-A	3.5513 eV	349.13 nm	f=0.8115	<S**2>=0.000
247 -> 265	-0.12494				
260 -> 265	0.27911				
261 -> 265	-0.17827				
262 -> 265	-0.19389				
263 -> 265	0.50546				
264 -> 266	0.16476				
Excited State 8:	Singlet-A	3.5901 eV	345.35 nm	f=0.7142	<S**2>=0.000
244 -> 266	-0.10344				
247 -> 266	-0.11192				
260 -> 266	-0.29680				
261 -> 266	0.31509				
262 -> 265	0.15554				
262 -> 266	0.22075				
263 -> 266	0.39102				
264 -> 265	-0.14402				
Excited State 9:	Singlet-A	3.6442 eV	340.22 nm	f=0.1123	<S**2>=0.000
245 -> 265	-0.11647				
246 -> 266	0.10319				
260 -> 265	0.27456				
260 -> 266	0.25520				
261 -> 266	0.23808				
262 -> 265	0.43599				
262 -> 266	-0.15414				
Excited State 10:	Singlet-A	3.7343 eV	332.01 nm	f=0.0628	<S**2>=0.000
246 -> 266	0.12198				
260 -> 265	-0.19076				
260 -> 266	0.19556				
261 -> 266	0.50726				
262 -> 265	-0.31356				

Ph_8TAPMg (2e)

SCF Done: E(RB3LYP) = -3101.14307862 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.005304	-1.187239	2.752079
2	6	0	-0.014976	-2.478864	3.458464
3	6	0	0.005398	-3.457809	2.479115
4	6	0	0.033726	-2.759657	1.185793
5	7	0	0.025490	-1.410153	1.405448
6	7	0	0.000000	0.000000	3.364976
7	6	0	0.005304	1.187239	2.752079

8	6	0	0.014976	2.478864	3.458464
9	7	0	-0.025490	1.410153	1.405448
10	6	0	-0.005398	3.457809	2.479115
11	6	0	-0.033726	2.759657	1.185793
12	7	0	-0.034991	3.377392	0.000000
13	7	0	0.034991	-3.377392	0.000000
14	6	0	-0.033726	2.759657	-1.185793
15	6	0	-0.005398	3.457809	-2.479115
16	7	0	-0.025490	1.410153	-1.405448
17	6	0	0.014976	2.478864	-3.458464
18	6	0	0.005304	1.187239	-2.752079
19	6	0	0.033726	-2.759657	-1.185793
20	6	0	0.005398	-3.457809	-2.479115
21	7	0	0.025490	-1.410153	-1.405448
22	6	0	-0.014976	-2.478864	-3.458464
23	6	0	-0.005304	-1.187239	-2.752079
24	7	0	0.000000	0.000000	-3.364976
25	6	0	0.031225	-2.631189	-4.923027
26	6	0	0.848034	-3.614978	-5.512835
27	6	0	-0.717165	-1.789801	-5.766733
28	6	0	0.908728	-3.756156	-6.897007
29	1	0	1.444325	-4.262195	-4.878127
30	6	0	-0.656230	-1.936285	-7.152345
31	1	0	-1.340527	-1.017741	-5.332051
32	6	0	0.154280	-2.919042	-7.723428
33	1	0	1.550257	-4.518419	-7.331315
34	1	0	-1.243253	-1.276198	-7.785200
35	6	0	-0.069673	-4.922248	-2.634012
36	6	0	0.811529	-5.769503	-1.941684
37	6	0	-1.037162	-5.501584	-3.474434
38	6	0	0.735202	-7.153361	-2.095489
39	1	0	1.559637	-5.335268	-1.287664
40	6	0	-1.117263	-6.884881	-3.619886
41	1	0	-1.732008	-4.859260	-4.006574
42	6	0	-0.229135	-7.716518	-2.933222
43	1	0	1.429891	-7.793066	-1.557537
44	1	0	-1.876055	-7.314141	-4.268778
45	6	0	-0.031225	2.631189	-4.923027
46	6	0	-0.848034	3.614978	-5.512835
47	6	0	0.717165	1.789801	-5.766733
48	6	0	-0.908728	3.756156	-6.897007
49	1	0	-1.444325	4.262195	-4.878127
50	6	0	0.656230	1.936285	-7.152345
51	1	0	1.340527	1.017741	-5.332051
52	6	0	-0.154280	2.919042	-7.723428
53	1	0	-1.550257	4.518419	-7.331315
54	1	0	1.243253	1.276198	-7.785200
55	6	0	0.069673	4.922248	-2.634012
56	6	0	-0.811529	5.769503	-1.941684
57	6	0	1.037162	5.501584	-3.474434
58	6	0	-0.735202	7.153361	-2.095489
59	1	0	-1.559637	5.335268	-1.287664
60	6	0	1.117263	6.884881	-3.619886
61	1	0	1.732008	4.859260	-4.006574
62	6	0	0.229135	7.716518	-2.933222
63	1	0	-1.429891	7.793066	-1.557537
64	1	0	1.876055	7.314141	-4.268778
65	6	0	0.069673	4.922248	2.634012
66	6	0	-0.811529	5.769503	1.941684
67	6	0	1.037162	5.501584	3.474434
68	6	0	-0.735202	7.153361	2.095489
69	1	0	-1.559637	5.335268	1.287664
70	6	0	1.117263	6.884881	3.619886
71	1	0	1.732008	4.859260	4.006574
72	6	0	0.229135	7.716518	2.933222
73	1	0	-1.429891	7.793066	1.557537
74	1	0	1.876055	7.314141	4.268778

75	6	0	-0.031225	2.631189	4.923027
76	6	0	-0.848034	3.614978	5.512835
77	6	0	0.717165	1.789801	5.766733
78	6	0	-0.908728	3.756156	6.897007
79	1	0	-1.444325	4.262195	4.878127
80	6	0	0.656230	1.936285	7.152345
81	1	0	1.340527	1.017741	5.332051
82	6	0	-0.154280	2.919042	7.723428
83	1	0	-1.550257	4.518419	7.331315
84	1	0	1.243253	1.276198	7.785200
85	6	0	0.031225	-2.631189	4.923027
86	6	0	-0.717165	-1.789801	5.766733
87	6	0	0.848034	-3.614978	5.512835
88	6	0	-0.656230	-1.936285	7.152345
89	1	0	-1.340527	-1.017741	5.332051
90	6	0	0.908728	-3.756156	6.897007
91	1	0	1.444325	-4.262195	4.878127
92	6	0	0.154280	-2.919042	7.723428
93	1	0	-1.243253	-1.276198	7.785200
94	1	0	1.550257	-4.518419	7.331315
95	6	0	-0.069673	-4.922248	2.634012
96	6	0	-1.037162	-5.501584	3.474434
97	6	0	0.811529	-5.769503	1.941684
98	6	0	-1.117263	-6.884881	3.619886
99	1	0	-1.732008	-4.859260	4.006574
100	6	0	0.735202	-7.153361	2.095489
101	1	0	1.559637	-5.335268	1.287664
102	6	0	-0.229135	-7.716518	2.933222
103	1	0	-1.876055	-7.314141	4.268778
104	1	0	1.429891	-7.793066	1.557537
105	1	0	0.290525	8.795406	3.048527
106	1	0	0.290525	8.795406	-3.048527
107	1	0	-0.200934	3.030809	-8.803560
108	1	0	0.200934	-3.030809	-8.803560
109	1	0	-0.290525	-8.795406	-3.048527
110	1	0	-0.290525	-8.795406	3.048527
111	1	0	0.200934	-3.030809	8.803560
112	1	0	-0.200934	3.030809	8.803560
113	12	0	0.000000	0.000000	0.000000

TD–DFT output

HOMO**: 246**, LUMO**: 247**

Excited State 1: Singlet-BU 1.8697 eV 663.11 nm f=0.3337 <S**2>=0.000
239 -> 248 0.12004
241 -> 248 0.16167
245 -> 248 -0.16381
246 -> 247 0.66326
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3092.13696430
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-AU 1.8788 eV 659.93 nm f=0.3330 <S**2>=0.000
239 -> 247 -0.12690
241 -> 247 -0.16418
245 -> 247 0.16276
246 -> 248 0.66198

Excited State 3: Singlet-BG 3.4042 eV 364.20 nm f=0.0000 <S**2>=0.000
225 -> 248 -0.15497
226 -> 247 -0.15502
242 -> 247 0.43798
243 -> 248 0.43444
244 -> 249 0.21971

Excited State 4: Singlet-BU 3.4464 eV 359.75 nm f=0.0703 <S**2>=0.000
222 -> 248 0.11664

227 -> 247	-0.16506					
239 -> 248	0.13897					
241 -> 248	0.15840					
242 -> 249	0.20410					
244 -> 247	0.52219					
245 -> 248	0.27144					
Excited State 5:	Singlet-AU	3.4492 eV	359.46 nm	f=0.1421	<S**2>=0.000	
222 -> 247	0.11720					
227 -> 248	-0.16556					
239 -> 247	0.13078					
241 -> 247	0.13580					
243 -> 249	0.20808					
244 -> 248	0.50891					
245 -> 247	0.31148					
Excited State 6:	Singlet-AG	3.4648 eV	357.84 nm	f=0.0000	<S**2>=0.000	
225 -> 247	-0.15529					
226 -> 248	-0.15490					
242 -> 248	0.42912					
243 -> 247	0.45152					
245 -> 249	0.17370					
Excited State 7:	Singlet-AU	4.0101 eV	309.18 nm	f=1.7414	<S**2>=0.000	
239 -> 247	-0.18309					
241 -> 247	-0.28362					
244 -> 248	-0.18395					
245 -> 247	0.52029					
246 -> 248	-0.23776					
246 <- 248	0.12001					
Excited State 8:	Singlet-BU	4.0280 eV	307.81 nm	f=1.6362	<S**2>=0.000	
239 -> 248	-0.21097					
241 -> 248	-0.25664					
244 -> 247	-0.13933					
245 -> 248	0.54228					
246 -> 247	0.24124					
246 <- 247	-0.11993					
Excited State 9:	Singlet-BG	4.1255 eV	300.53 nm	f=0.0000	<S**2>=0.000	
224 -> 249	0.13738					
226 -> 247	0.10848					
228 -> 247	0.42338					
236 -> 247	-0.21041					
242 -> 247	-0.30768					
243 -> 248	0.31904					
Excited State 10:	Singlet-AG	4.1536 eV	298.50 nm	f=0.0000	<S**2>=0.000	
223 -> 249	-0.15649					
228 -> 248	0.47955					
236 -> 248	-0.22081					
242 -> 248	-0.25805					
243 -> 247	0.26159					

$[Ph_8PcP(OMe)_2]^+$ (4')

SCF Done: E(RB3LYP) = -4075.51041298 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.722046	1.086884	0.191679
2	6	0	4.096373	0.659235	0.132177
3	6	0	4.086884	-0.715444	-0.140300
4	6	0	2.706509	-1.124568	-0.196047
5	7	0	1.884448	-0.013099	-0.002203
6	7	0	2.362378	2.346263	0.315712
7	6	0	1.109610	2.714905	0.177859

8	6	0	0.696423	4.095898	0.130914
9	7	0	0.002088	1.891260	-0.042763
10	6	0	-0.674933	4.103183	-0.149495
11	6	0	-1.097204	2.726141	-0.222787
12	7	0	-2.356881	2.371303	-0.352394
13	7	0	2.329236	-2.379112	-0.316757
14	6	0	-2.724210	1.118775	-0.206864
15	6	0	-4.108841	0.712732	-0.145010
16	7	0	-1.904111	0.013325	0.001290
17	6	0	-4.118654	-0.655346	0.143991
18	6	0	-2.740041	-1.080468	0.208459
19	6	0	1.071652	-2.729984	-0.175181
20	6	0	0.639717	-4.104731	-0.125438
21	7	0	-0.024064	-1.890141	0.045763
22	6	0	-0.731785	-4.092793	0.153877
23	6	0	-1.134967	-2.709832	0.225074
24	7	0	-2.389773	-2.337970	0.354235
25	15	0	-0.012340	0.001563	0.000575
26	8	0	-0.081597	-0.118841	-1.665372
27	8	0	-0.064252	0.135144	1.666486
28	6	0	0.666283	0.651157	-2.606322
29	1	0	0.421702	1.716863	-2.549503
30	1	0	1.745574	0.516086	-2.480863
31	1	0	0.373748	0.271844	-3.587593
32	6	0	0.616276	-0.693917	2.608294
33	1	0	0.436153	-0.233467	3.581953
34	1	0	1.695730	-0.723531	2.425540
35	1	0	0.218546	-1.713663	2.616726
36	6	0	-5.318177	-1.350644	0.274046
37	1	0	-5.319515	-2.420295	0.453697
38	6	0	-6.529814	-0.660029	0.125827
39	6	0	-6.519631	0.752256	-0.135240
40	6	0	-5.297565	1.425347	-0.278804
41	1	0	-5.282389	2.494890	-0.458364
42	6	0	-1.375828	5.302537	-0.263572
43	1	0	-2.447009	5.300594	-0.433842
44	6	0	-0.689607	6.514501	-0.110069
45	6	0	0.726320	6.507567	0.139724
46	6	0	1.404857	5.288199	0.268553
47	1	0	2.475708	5.276059	0.440538
48	6	0	5.299116	1.355828	0.250993
49	1	0	5.300207	2.428030	0.414979
50	6	0	6.508755	0.664388	0.112354
51	6	0	6.499009	-0.754459	-0.127289
52	6	0	5.279264	-1.429027	-0.261763
53	1	0	5.264515	-2.501262	-0.424719
54	6	0	1.331164	-5.307560	-0.259677
55	1	0	2.402153	-5.311527	-0.431257
56	6	0	0.635368	-6.516542	-0.127172
57	6	0	-0.780853	-6.503714	0.121085
58	6	0	-1.449990	-5.281627	0.269976
59	1	0	-2.521251	-5.263483	0.438684
60	6	0	1.429611	-7.774967	-0.210235
61	6	0	1.358117	-8.749467	0.799634
62	6	0	2.322429	-7.974774	-1.276245
63	6	0	2.158249	-9.888803	0.742845
64	1	0	0.681547	-8.608075	1.636523
65	6	0	3.114618	-9.121743	-1.337465
66	1	0	2.380215	-7.235619	-2.071148
67	6	0	3.036403	-10.081135	-0.326725
68	1	0	2.097176	-10.627564	1.536996
69	1	0	3.790224	-9.265336	-2.176101
70	1	0	3.654595	-10.973239	-0.371567
71	6	0	-1.601080	-7.745992	0.188808
72	6	0	-2.503048	-7.935875	1.249190
73	6	0	-1.545184	-8.713991	-0.828289
74	6	0	-3.319569	-9.066097	1.297505

75	1	0	-2.549161	-7.202380	2.050084
76	6	0	-2.369466	-9.836580	-0.784380
77	1	0	-0.862284	-8.579968	-1.661139
78	6	0	-3.256684	-10.018893	0.279445
79	1	0	-4.002260	-9.201981	2.131672
80	1	0	-2.320144	-10.569932	-1.584325
81	1	0	-3.893904	-10.897958	0.314122
82	6	0	-7.785853	-1.458232	0.206963
83	6	0	-8.754716	-1.397462	-0.809011
84	6	0	-7.989113	-2.343546	1.278575
85	6	0	-9.891870	-2.200725	-0.752670
86	1	0	-8.610361	-0.727006	-1.650276
87	6	0	-9.133828	-3.138999	1.339161
88	1	0	-7.254383	-2.393030	2.078146
89	6	0	-10.087664	-3.071351	0.322394
90	1	0	-10.626109	-2.148155	-1.551612
91	1	0	-9.280074	-3.808860	2.181950
92	1	0	-10.978031	-3.692094	0.366724
93	6	0	-7.763769	1.567630	-0.223723
94	6	0	-8.740858	1.520482	0.785033
95	6	0	-7.947048	2.455686	-1.296910
96	6	0	-9.865972	2.339992	0.720702
97	1	0	-8.611831	0.848138	1.627234
98	6	0	-9.079841	3.267124	-1.365747
99	1	0	-7.206337	2.494417	-2.091528
100	6	0	-10.041713	3.213269	-0.355718
101	1	0	-10.606543	2.297709	1.514388
102	1	0	-9.210642	3.938833	-2.209599
103	1	0	-10.922789	3.846650	-0.406364
104	6	0	-1.493160	7.768135	-0.173780
105	6	0	-1.429377	8.727736	0.850761
106	6	0	-2.387400	7.977248	-1.236838
107	6	0	-2.238274	9.861604	0.810872
108	1	0	-0.752506	8.578561	1.686023
109	6	0	-3.188499	9.118738	-1.281001
110	1	0	-2.439753	7.249629	-2.042707
111	6	0	-3.117662	10.063390	-0.255941
112	1	0	-2.183269	10.588565	1.616272
113	1	0	-3.865363	9.269568	-2.117349
114	1	0	-3.742805	10.951212	-0.287366
115	6	0	1.537595	7.754351	0.229687
116	6	0	1.477128	8.738471	-0.771544
117	6	0	2.435980	7.932866	1.295066
118	6	0	2.293437	9.865901	-0.707364
119	1	0	0.796399	8.613582	-1.607617
120	6	0	3.244305	9.067891	1.363835
121	1	0	2.485080	7.186655	2.083917
122	6	0	3.177030	10.036818	0.361379
123	1	0	2.240507	10.612142	-1.495072
124	1	0	3.923989	9.194963	2.201838
125	1	0	3.807860	10.919714	0.412040
126	6	0	7.744241	-1.569808	-0.199401
127	6	0	8.721395	-1.499907	0.808051
128	6	0	7.928550	-2.480596	-1.253196
129	6	0	9.847283	-2.319558	0.761519
130	1	0	8.592296	-0.809212	1.635268
131	6	0	9.061942	-3.292534	-1.304206
132	1	0	7.188139	-2.537122	-2.047006
133	6	0	10.023679	-3.216039	-0.295514
134	1	0	10.587935	-2.259202	1.553943
135	1	0	9.193414	-3.982198	-2.133322
136	1	0	10.905294	-3.849602	-0.332416
137	6	0	7.765246	1.463085	0.180637
138	6	0	7.968512	2.366310	1.237211
139	6	0	8.734130	1.385350	-0.834196
140	6	0	9.112925	3.163095	1.284221
141	1	0	7.233934	2.429047	2.035976

142	6	0	9.870986	2.189888	-0.791575
143	1	0	8.590215	0.700590	-1.663975
144	6	0	10.066567	3.078733	0.268539
145	1	0	9.259075	3.847051	2.115606
146	1	0	10.605270	2.123919	-1.589477
147	1	0	10.956744	3.700384	0.302275

TD–DFT output

HOMO**: 316**, LUMO**: 317**

Excited State 1: Singlet-A 1.5855 eV 782.01 nm f=0.5706 <S**2>=0.000
299 -> 317 0.13087
316 -> 318 0.68488
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4075.45214837
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.5906 eV 779.46 nm f=0.5785 <S**2>=0.000
299 -> 318 -0.12824
316 -> 317 0.68556

Excited State 3: Singlet-A 3.4841 eV 355.85 nm f=0.0935 <S**2>=0.000
295 -> 317 0.27081
297 -> 317 0.11021
312 -> 317 0.18355
314 -> 317 0.48260
314 -> 319 -0.11116
315 -> 317 0.23997

Excited State 4: Singlet-A 3.5857 eV 345.77 nm f=0.0230 <S**2>=0.000
294 -> 318 0.28411
298 -> 318 -0.11709
305 -> 318 -0.10130
312 -> 317 0.11022
312 -> 319 0.11114
313 -> 318 0.55798

Excited State 5: Singlet-A 3.6051 eV 343.91 nm f=0.3723 <S**2>=0.000
293 -> 318 -0.16867
295 -> 318 -0.11337
299 -> 318 0.15492
312 -> 318 -0.39230
313 -> 319 -0.14298
315 -> 318 0.42091

Excited State 6: Singlet-A 3.6900 eV 336.00 nm f=0.3674 <S**2>=0.000
293 -> 317 0.20973
299 -> 317 0.14944
312 -> 317 0.31100
314 -> 317 -0.29820
315 -> 317 0.40191

Excited State 7: Singlet-A 3.9520 eV 313.73 nm f=1.1123 <S**2>=0.000
293 -> 318 0.18312
299 -> 318 0.20049
310 -> 317 -0.11003
312 -> 318 0.38070
314 -> 318 -0.16926
315 -> 318 0.35963
316 -> 319 -0.10672

Excited State 8: Singlet-A 3.9645 eV 312.73 nm f=1.3494 <S**2>=0.000
292 -> 317 0.10013
293 -> 317 0.15202
299 -> 317 -0.22517
312 -> 317 0.42972
313 -> 320 -0.12225

315 -> 317 -0.36232
316 -> 318 0.10474

Excited State 9: Singlet-A 3.9676 eV 312.49 nm f=0.1096 <S**2>=0.000
294 -> 317 -0.16103
295 -> 318 0.17344
297 -> 318 -0.11985
298 -> 317 -0.10817
301 -> 317 -0.10198
302 -> 318 -0.10921
309 -> 318 0.19879
310 -> 317 0.18815
312 -> 318 0.14397
313 -> 317 -0.10373
315 -> 318 0.13750
316 -> 319 0.42306

Excited State 10: Singlet-A 4.0283 eV 307.78 nm f=0.1157 <S**2>=0.000
297 -> 318 0.16425
298 -> 317 -0.19390
309 -> 318 -0.14467
310 -> 317 0.15732
312 -> 320 -0.11123
313 -> 317 0.43750
314 -> 318 0.26753
315 -> 318 0.15051

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