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Cationic Axial Ligands on Sulfur Substituted Silicon(IV) Phthalocyanines: Improved Hydrophilicity and Exceptionally Red-shifted Absorption into the NIR Region

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Supporting information

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General Comments

NMR spectra were obtained on a JEOL ECA-500 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra were referenced to the tetramethylsilane (TMS) or the residual solvent as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet, and brs = broad singlet. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics solariX spectrometer (MALDI). Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. CV measurements were recorded with a Hokuto Denko HZ5000 potentiostat under nitrogen atmosphere in *o*-dichlorobenzene (*o*-DCB) solutions with 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Measurements were made with a glassy carbon electrode (area = 0.07 cm^2), an Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were set to 100 mV/s. The ferrocenium/ferrocene (Fc^+/Fc) couple was used as an internal standard.

Crystallographic data collection

Data collection for αα-$(SPh)_8PcSi(OMe)_2$ was carried out on a Bruker APEXIII CCD diffractometer with Bruker Helios multilayered confocal mirror monochromatized Cu*K*α radiation (λ = 1.54178 Å) at –183°C. The structures were solved by a direct method (SIR2004)[i] and refined using a full-matrix least square technique (SHELXL-2014).[ii] Yadokari-XG 2009 software was used as a GUI for SHELXL-2014.[iii] All non-hydrogen atoms were refined anisotropically. Positions of all hydrogen atoms were calculated geometrically, and refined by applying riding models. CCDC-1905332 contains the supplementary crystallographic data. Their data can be obtained free of charge from Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of $^{1}O_2$ generation efficiency

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using a steady-state method[iv] with methylene blue (Φ_Δ = 0.52 in DMSO[v]) as reference. 1,3-diphenylisobenzofuran (DPBF) was used as the chemical quencher for single oxygen in $CHCl_3$. Irradiation was carried out with a halogen lamp

(ALA-100, Asahi Spectra). A band path filter (680 nm, band width at 0.5 peak = 12.00 nm, Asahi Spectra) was placed in the light beam path of the lamp. The light intensity was measured with an illuminometer (T-10A, KONICA MINOLTA) and adjusted to 1.5 lx at 680 nm. Equation (1) was employed for the calculations:

$$\Phi_{\Delta} = \Phi_{\Delta}^{\mathrm{Std}} \frac{R \bullet I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \bullet I_{\mathrm{abs}}} \qquad (1)$$

where $\Phi^{\mathrm{Std}}_{\Delta}$ is the singlet oxygen quantum yield for the standard ($\Phi^{\mathrm{Std}}_{\Delta}$ = 0.52 in DMSO). R and R_{Std} are the DPBF photobleaching rates in the presence of the samples and standard, respectively. I_{abs} and $I^{\mathrm{Std}}_{\mathrm{abs}}$ are the rates of light absorption at 680 nm by the samples and standard, respectively.

Evaluation of photocytotoxicity

HEK293T cells were plated at initial densities of 5,000 cells/well (100 μL/well) in 96-well plates (2 plates) in Dulbecco's modified Eagle's medium containing Ma^{2+} and Ca^{2+} (DMEM) in the presence of 5Q (10 μM) and allowed to attach overnight. The cells were exposed to 810 nm light irradiation (CL-H1-810-9-1, Asahi Spectra). WST-8 (10 μL/well, CK-04, Dojindo, Japan) was added to one of the plates and incubated with the cells for 3 hrs before absorbance values of control wells and test wells were measured at 450 nm to determine the cell viability. The other plate was further incubated for 48 hr at 37°C in 5% CO_2 incubator, and the cell viability was determined by WST-8 as same as above.

Table S1. Crystal data and structure refinement for αα-$(SPh)_8PcSi(OMe)_2$.

Empirical formula	$C_{82}H_{54}N_8O_2S_8Si$	
Formula weight	1467.90	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.3066(4) Å	α = 90°
	b = 17.3214(6) Å	β = 99.5940(10)°
	c = 15.9077(5) Å	γ = 90°
Volume	3343.58(19) $Å^3$	
Z	2	
Density (Calcd.)	1.458 Mg/m^3	
Absorption coefficient	3.118 mm^{-1}	
F(000)	1520	
Crystal size	0.400 x 0.100 x 0.100 mm^3	
Theta range for data collection	4.218 to 66.500°	
Index ranges	-14<=h<=14, -20<=k<=20, -18<=l<=18	
Reflections collected	22981	
Independent reflections	5856 [R(int) = 0.0303]	
Completeness to theta = 66.500°	99.3%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints /parameters	5856 / 0 / 458	
Goodness-of-fit on F^2	1.080	
Final R indices [I > 2sigma(I)]	R_1 = 0.0734, wR_2 = 0.1884	
R indices (all data)	R_1 = 0.0791, wR_2 = 0.1950	
Largest diff. peak and hole	1.170 and -0.663 e.$Å^{-3}$	
CCDC No.	1905332	

Additional Experimental and Computational Results

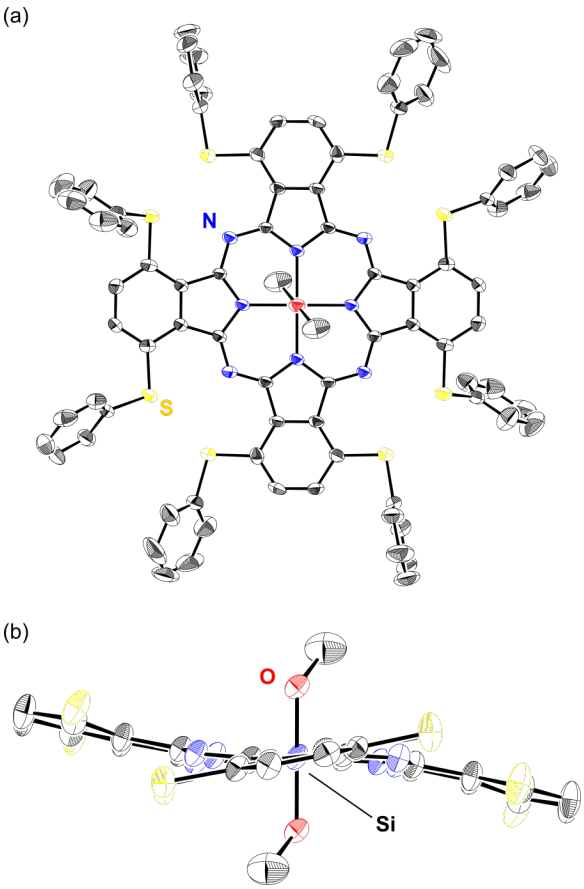


Fig. S1 Molecular structure of αα-$(SPh)_8PcSi(OMe)_2$ with thermal ellipsoids at 50% probability: (a) Top view; (b) side view (peripheral substituents have been omitted for clarity). Hydrogen atoms have been omitted for clarity and only selected atoms have been labeled. Single crystals were obtained by diffusion of methanol into a chloroform solution of **4**. During the recrystallization, the axial ligands of **4** were replaced by methoxy groups from methanol.

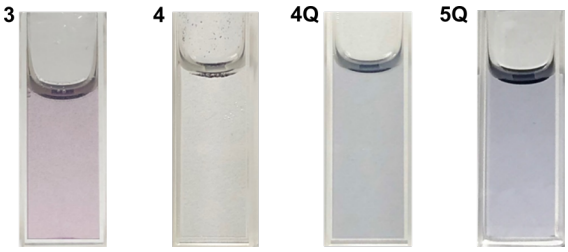


Fig. S2 Photographs of DMSO/PBS buffer = 1:1 (v/v) solutions of **3**, **4**, **4Q**, and **5Q** (~ 1.0×10^{-5} M). Compounds **4** and **5** are insoluble in this medium.

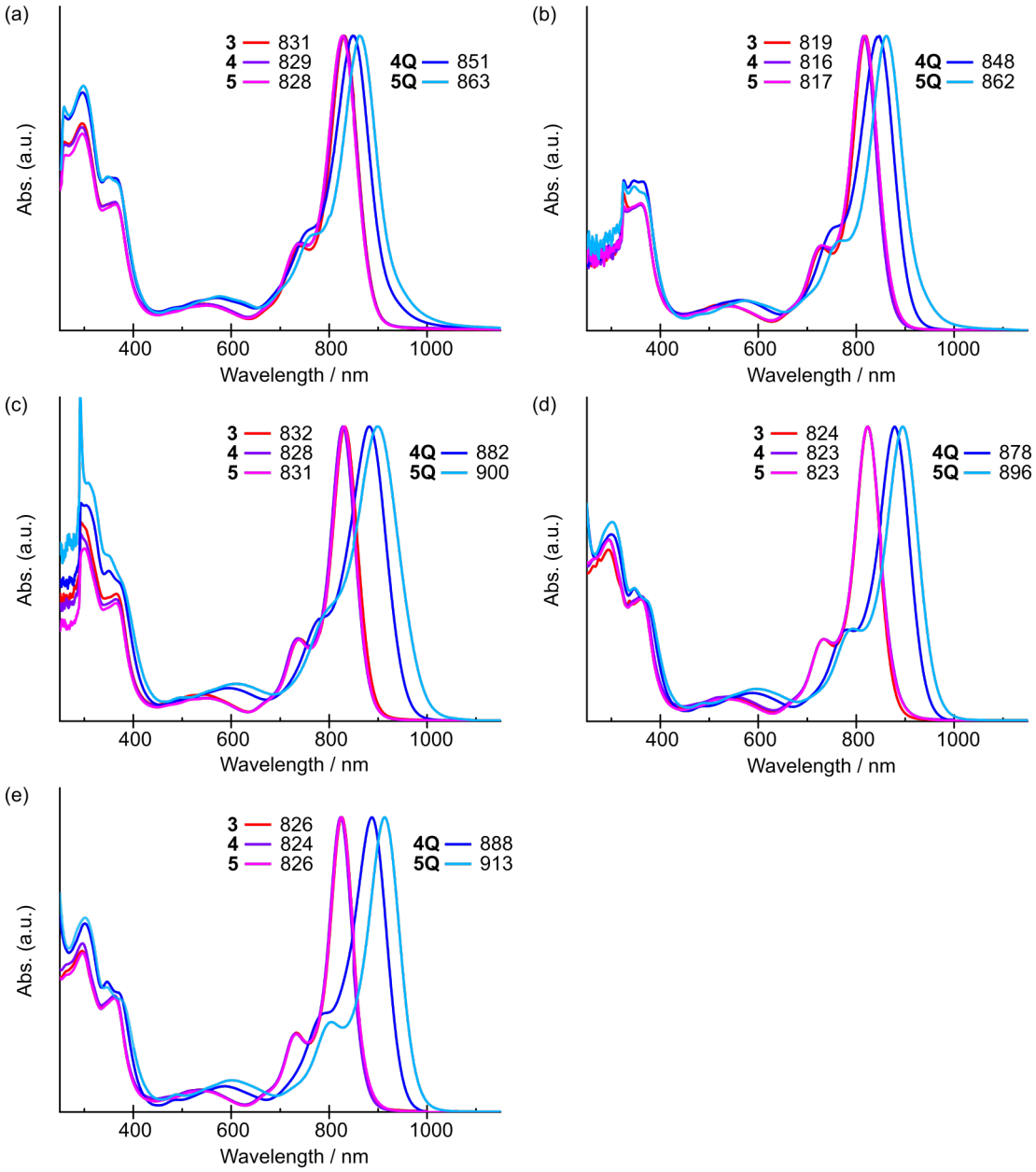


Fig. S3 UV-vis-NIR absorption spectra of **3** (red), **4** (purple), **4Q** (blue), **5** (pink), and **5Q** (light blue) in (a) acetone, (b) DMSO, (c) *o*-DCB, (d) CH_2Cl_2, and (e) $CHCl_3$ (~ 1.0×10^{-5} M).

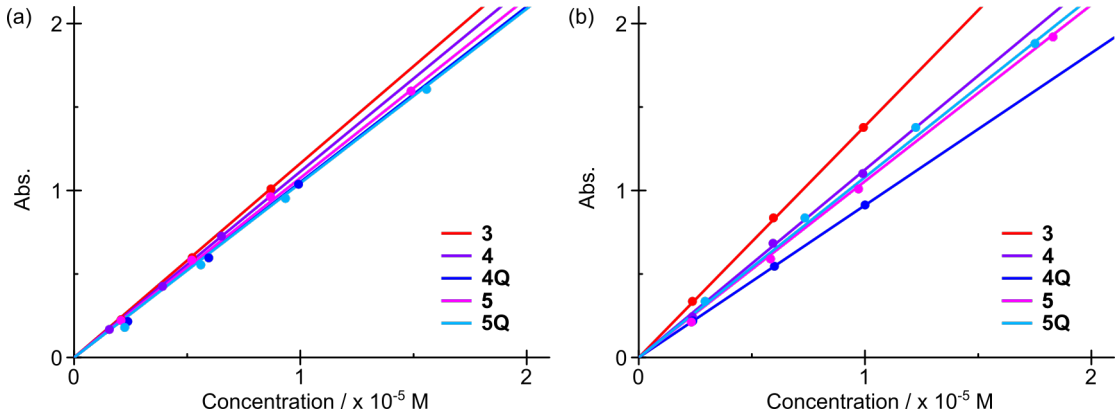


Fig. S4 Beer-Lambert plots of **3** (red), **4** (purple), **4Q** (blue), **5** (pink), and **5Q** (light blue) in (a) DMSO and (b) CH_2Cl_2. Absorbances were measured at the peaks of Q bands (820-900 nm region). All correlation coefficients were over 0.99 in these concentrations.

Table S2. Calculated excited wavelengths (λ) and oscillator strengths (*f*) for components of selected transition energies. Calculations were performed at the B3LYP/6-31G* level.

Compd.	λ / nm	*f*	Composition
4'	738	0.30	HOMO→LUMO (71.9%), HOMO→LUMO+1 (24.2%)
	733	0.34	HOMO→LUMO (24.6%), HOMO→LUMO+1 (72.1%)
[4Q']$^{2+}$	858	0.21	HOMO-1→LUMO (2.5%), HOMO→LUMO (74.5%), HOMO→LUMO+1 (19.0%)
	819	0.33	HOMO-1→LUMO (2.2%), HOMO→LUMO (20.5%), HOMO→LUMO+1 (74.9%)
7	603	0.36	HOMO-5→LUMO+1 (5.1%), HOMO→LUMO (93.2%)
	599	0.36	HOMO-5→LUMO+1 (5.8%), HOMO→LUMO+1 (93.1%)
[7Q]$^{2+}$	644	0.33	HOMO-8→LUMO+1 (2.3%), HOMO-4→LUMO+1 (2.1%), HOMO→LUMO (95.9%)
	635	0.32	HOMO-8→LUMO+1 (2.3%), HOMO-4→LUMO (2.4%), HOMO→LUMO+1 (95.2%)

Table S3. Calculated charges of central silicon of SiPcs. Calculations were performed at the B3LYP/6-31G* level.

	4'	**[4Q']$^{2+}$**	**7**	**[7Q]$^{2+}$**
Mulliken charge	1.48	1.44	1.44	1.44
NPA charge	2.38	2.36	2.38	2.36

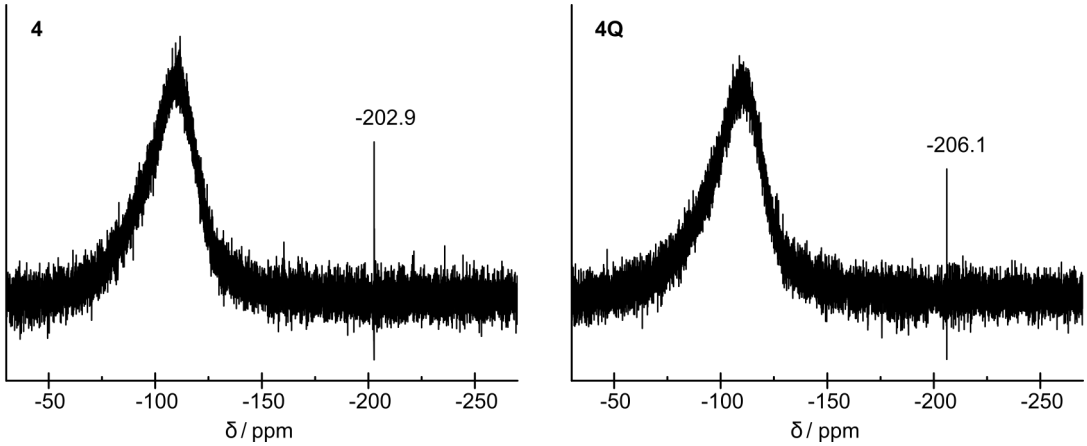


Fig. S5 ^{29}Si NMR spectra of **4** and **4Q** in $CDCl_3$.

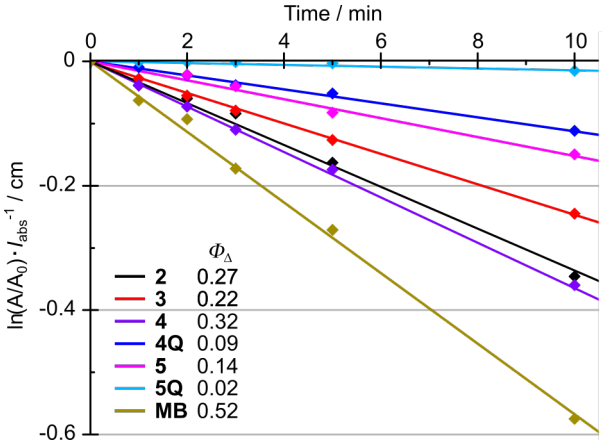


Fig. S6 Comparison of the rate of decay of 1,3-diphenylisobenzofuran (DPBF) sensitized by SiPcs in DMSO (ca. 2.0 x 10^{-5} M) as shown by the decrease in the absorbance at 418 nm. The absorption coefficient was normalized by the rates of the light absorption at 680 nm. The singlet oxygen quantum yields were determined by using methylene blue (**MB**) as the reference. Inset: Singlet oxygen quantum yields (Φ_Δ) of compounds.

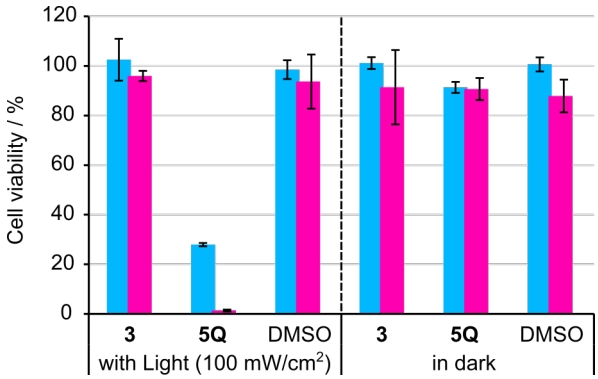


Fig. S7 Photocytotoxicity evaluation of SiPc **3** and **5Q** (10 μM, 0.1% DMSO) on HEK293T cells after 15 min of irradiation (λ_{ex} = 810 nm, 100 mW/cm^2); the CCK array was measured soon after irradiation (blue) and after 2 days of incubation (red). Data are presented as the mean value ± SD (n = 3).

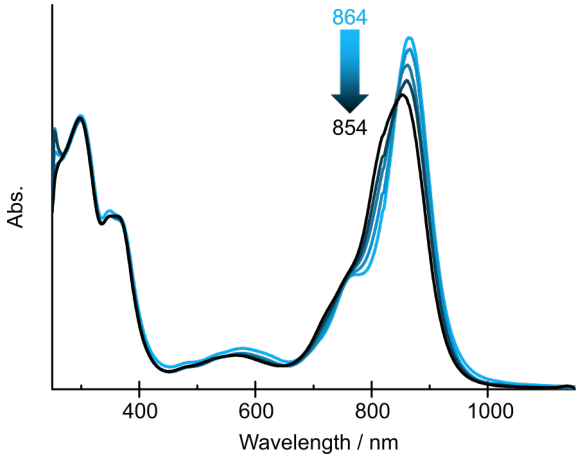


Fig. S8 The change of absorption spectra of DMSO/PBS buffer = 10:1 (v/v) solution of **5Q** for 2 days.

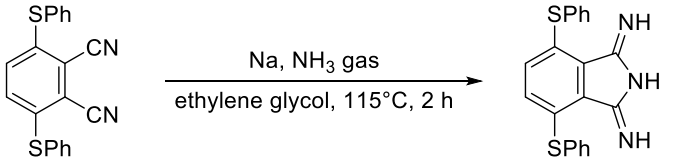
Full Experimental Procedures

Materials

Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation or recrystallization).

3,6-Bis(phenylthio)phthalonitrile was synthesized according to published procedures. [vi] Dichloro(phthalocyaninato)silicon was purchased from Alfa Inorganics Inc.

4,7-bis(phenylthio) isoindoline-1,3-diimine (1)



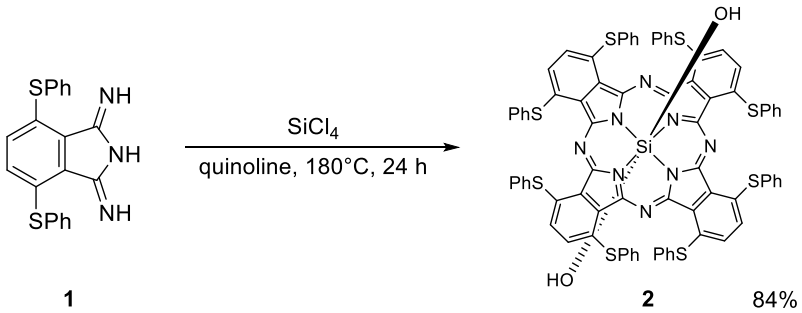
86%

Sodium metal (85 mg) was dissolved in ethylene glycol (25 mL) and 3,6-bis(phenylthio) phthalonitrile (1.01 g, 2.9 mmol) was added to the mixture. After stirred at 115°C for 2 h with passing ammonia gas, the reaction mixture was added to ice water. The precipitate was collected on a Büchner funnel and washed with copious amounts of ice water. The solid was left to dry for 1 h under vacuum. The title compound was obtained (908 mg, 86%) as a yellow powder. The compound contains some impurities, but used for the next reaction without further purification.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 9.01 (br, 1H) 7.60 (br, 2H), 7.46 (br, 4H), 7.30 (br, 4H), 7.19 (br, 3H), 6.72 (br, 1H).

HRMS-ESI Calcd for $C_{20}H_{16}N_3S_2$ $[M+H]^+$: 362.0781. Found: 362.0780.

SiPc 2



1 2 84%

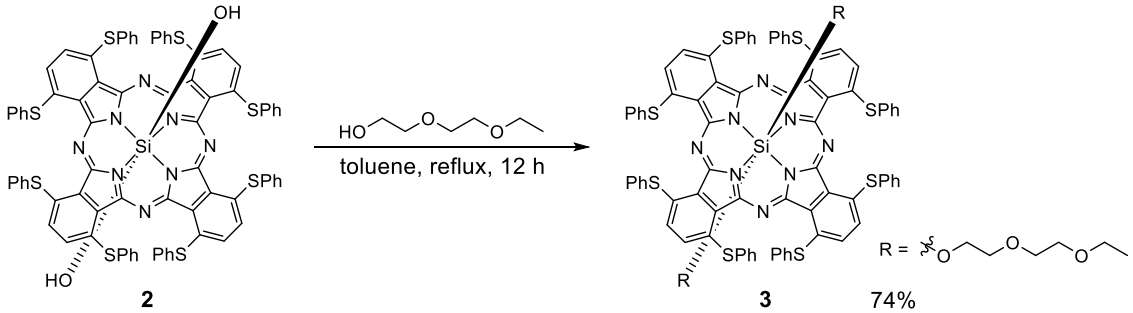
$SiCl_4$ (2.2 mL, 20 mmol) was added to a solution of **1** (492.1 mg, 1.36 mmol) in quinoline (5 mL). After the mixture was refluxed for 24 h under Ar atmosphere, the solution was diluted successively with water (4 mL) and $CHCl_3$ while stirring. The mixture was filtered through a celite pad to remove a purple impurity. The organic layer was washed with water and brine, and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in methanol again, and filtered to afford **2** (411.2 mg, 84%) as a dark purple powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.79-7.77 (m, 16H, PhH), 7.46-7.44 (m, 24H, PhH), 7.21 (s, 8H, βH), -1.10 (s, 2H, OH).

HRMS-MALDI Calcd for $C_{80}H_{49}N_8OS_8Si$ $[M\text{-}OH]^+$: 1421.1559. Found: 1421.1561.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 297 (6.86), 363 (4.54), 533 (0.94), 733 (2.90), 824 (10.74).

SiPc 3



2 3 74%

A mixture of compound **2** (18.0 mg, 13 μmol) and diethylene glycol monoethyl ether (0.30 mL, 2.2 mmol) in dry toluene (1 mL) was refluxed for 12 h under Ar atmosphere. The concentrated organic layer was washed with water and brine, and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in methanol again, and filtered to afford **3** (15.9 mg, 74%) as a dark purple powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.81-7.79 (m, 16H, PhH), 7.47-7.43 (m, 24H, PhH), 7.21 (s, 8H, βH), 3.06 (q, 4H, J = 7.1 Hz, CH_2), 2.75 (t, 4H, J = 5.2 Hz, CH_2), 2.03 (t, 4H, J = 5.2 Hz, CH_2), 0.89 (m, 10H, CH_2, CH_3), -1.21 (t, 4H, J = 5.7 Hz, CH_2).

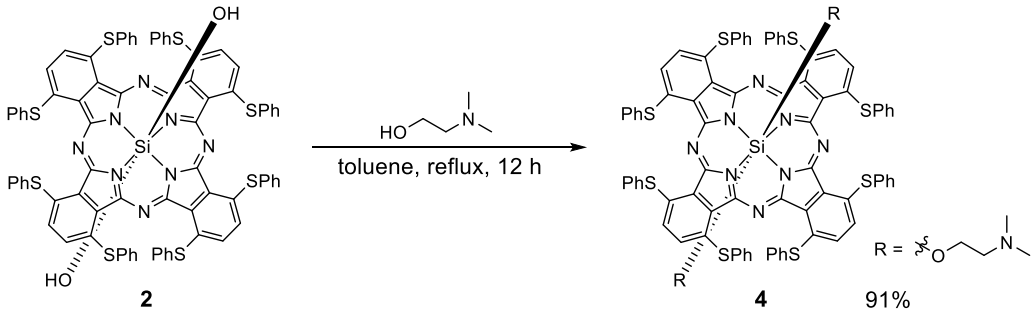
100 MHz ^{29}Si{^{1}H} NMR ($CDCl_3$) δ (ppm): -202.8.

HRMS-MALDI Calcd for $C_{92}H_{74}N_8O_6S_8Si$ $[M]^+$: 1670.3261. Found: 1670.3268.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 294 (8.04), 361 (5.72), 541 (1.11), 733 (3.85), 824 (13.81).

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 296 (8.31), 363 (5.10), 543 (1.07), 741 (3.39), 831 (11.82).

SiPc 4



A mixture of compound **2** (209.1 mg, 145 μmol) and 2-(dimethylamino)ethanol (1.0 mL, 6.2 mmol) in dry toluene (5 mL) was refluxed for 12 h under Ar atmosphere. The residue was dissolved in methanol again, and filtered to afford **4** (209.9 mg, 91%) as a dark violet powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.80-7.78 (m, 16H, PhH), 7.47-7.43 (m, 24H, PhH), 7.19 (s, 8H, βH), 0.83 (s, 12H, CH_3), -0.32 (brs, 4H, CH_2), -1.25 (t, 4H, J = 6.3 Hz, OCH_2).

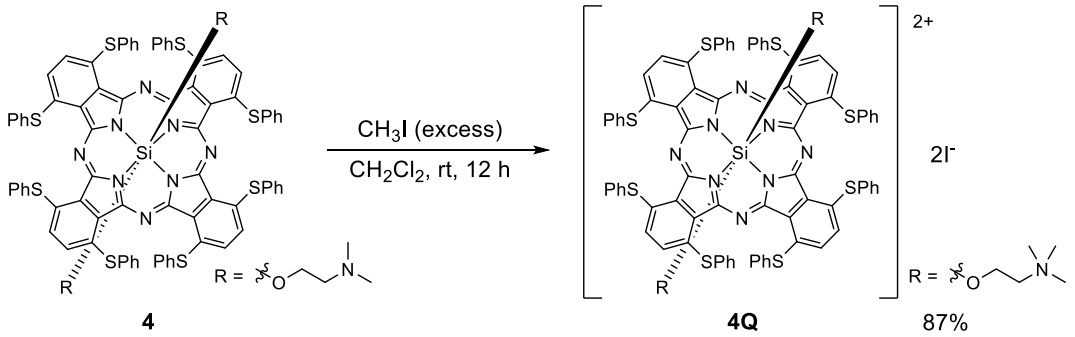
100 MHz ^{29}Si{^{1}H} NMR ($CDCl_3$) δ (ppm): -202.9.

HRMS-MALDI Calcd for $C_{84}H_{58}N_9OS_8Si$ $[M-R]^+$: 1492.2294. Found: 1492.2288.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 295 (7.02), 361 (4.83), 547 (0.96), 736 (3.17), 823 (11.39).

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 295 (7.78), 363 (4.92), 552 (1.01), 741 (3.37), 829 (11.28).

SiPc 4Q



4 **4Q** 87%

A mixture of compound **4** (117.7 mg, 74.4 μmol) and iodomethane (1.0 mL, 16 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 12 h under Ar atmosphere. The residue was dissolved in ethyl acetate again, and filtered to afford **4Q** (120.9 mg, 87%) as a dark navy powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.79-7.77 (m, 16H, PhH), 7.49-7.47 (m, 24H, PhH), 7.24 (s, 8H, βH), 1.72 (s, 18H, CH_3), 1.27 (brs, 4H, CH_2), -0.61 (brs, 4H, OCH_2).

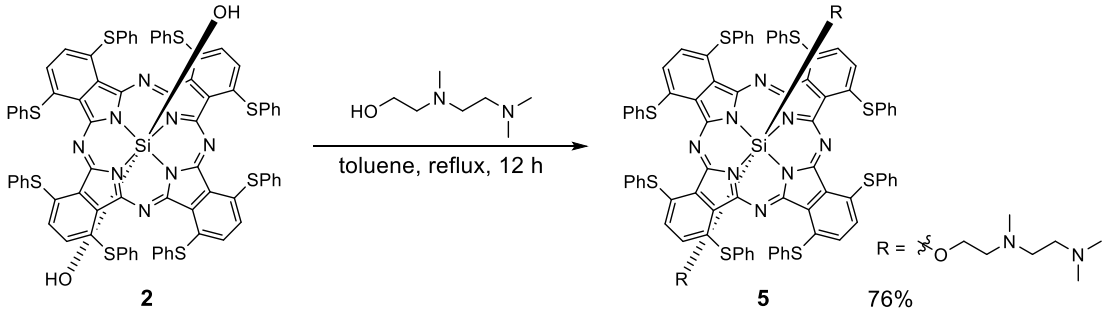
100 MHz ^{29}Si{^{1}H} NMR ($CDCl_3$) δ (ppm): -206.1.

HRMS-MALDI Calcd for $C_{90}H_{74}N_{10}O_2S_8Si$ $[M-2I]^+$: 1610.3526. Found: 1610.3524.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 300 (5.79), 346 (4.11), 589 (0.88), 782 (2.84), 878 (9.13).

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 297 (8.80), 362 (5.63), 570 (1.20), 851 (10.90).

SiPc 5



2 **5** 76%

A mixture of compound **2** (77.9 mg, 54 μmol) and 2-[[2-(dimethylamino)ethyl]methylamino]ethanol (0.50 mL, 3.1 mmol) in dry toluene (3 mL) was refluxed for 12 h under Ar atmosphere. The residue was dissolved in methanol again, and filtered to afford **5** (70.1 mg, 76%) as dark violet powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 7.79-7.78 (m, 16H, PhH), 7.46-7.43 (m, 24H, PhH), 7.20 (s, 8H,

βH), 1.74 (s, 12H, CH_3), 1.37 (t, 4H, *J* = 7.5 Hz, CH_2), 1.06 (t, 4H, *J* = 6.9 Hz, CH_2), 0.77 (s, 6H, CH_3), -0.25 (t, 4H, *J* = 6.9 Hz, CH_2), -1.28 (t, 4H, *J* = 5.8 Hz, OCH_2).

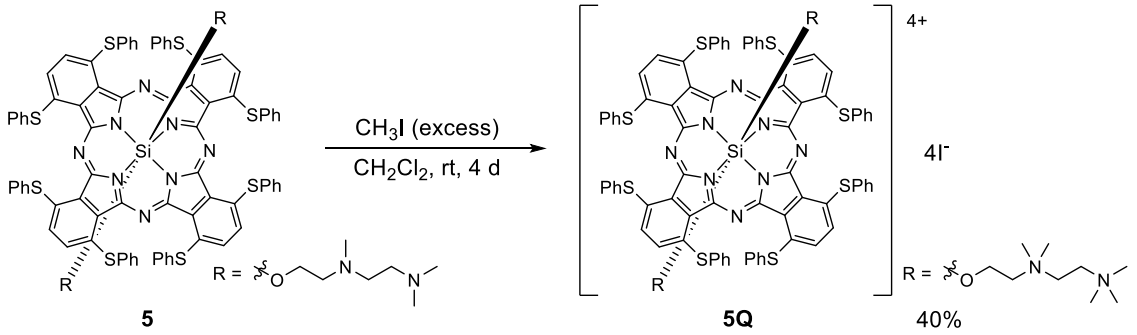
100 MHz $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ (ppm): -201.5.

HRMS-MALDI Calcd for $C_{87}H_{65}N_{10}OS_8Si$ $[M-R]^+$: 1549.2872. Found: 1549.2868.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 295 (6.64), 359 (4.48), 539 (0.80), 734 (3.00), 823 (10.79).

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 297 (7.90), 363 (4.80), 550 (0.95), 741 (3.30), 828 (11.23).

SiPc 5Q



A mixture of compound **5** (50.7 mg, 30 μmol) and iodomethane (2.0 mL, 32 mmol) in CH_2Cl_2 (4 mL) was stirred at room temperature for 4 d under Ar atmosphere. After concentrated under reduced pressure, the residue was diluted with methanol and filtered to remove insoluble impurities, and the filtrate was concentrated under reduced pressure again. Title compound was obtained (27.0 mg, 40%) as a dark navy powder, after the residue was washed with ethyl acetate.

500 MHz ^1H NMR (DMSO-d_6) δ (ppm): 7.78-7.76 (m, 16H, PhH), 7.61-7.59 (m, 24H, PhH), 7.35 (s, 8H, βH), 2.90 (t, 4H, *J* = 6.9 Hz, CH_2), 2.69 (s, 18H, CH_3), 2.44 (t, 4H, *J* = 6.9 Hz, CH_2), 1.25 (s, 12H, CH_3), 1.13 (brs, 4H, CH_2), -0.87 (brs, 4H, OCH_2).

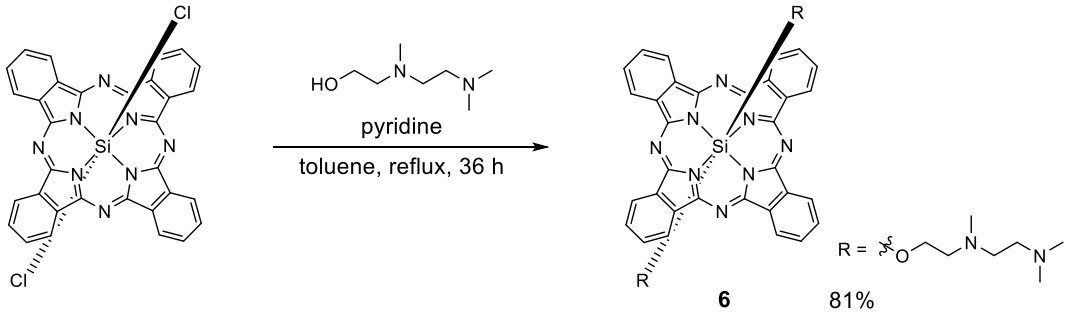
100 MHz $^{29}Si\{^1H\}$ NMR (DMSO-d_6) δ (ppm): -204.4.

HRMS-MALDI Calcd for $C_{98}H_{94}I_2N_{12}O_2S_8Si$ $[M-2I]^+$: 2008.3242. Found: 2008.3248.

UV-vis (CH_2Cl_2) λ_{max} nm (ε x 10^{-4}): 303 (7.57), 347 (5.06), 599 (1.23), 793 (3.52), 896 (11.20).

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 298 (8.85), 349 (5.57), 577 (1.23), 863 (10.65).

SiPc 6[vii]



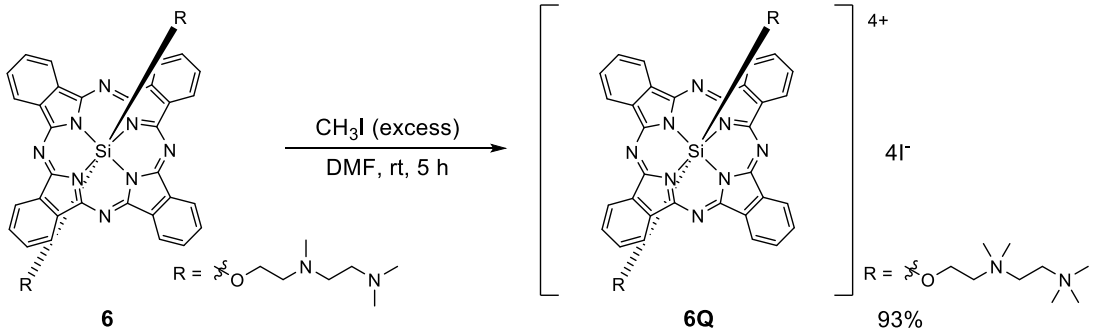
A mixture of dichloro(phthalocyaninato)silicon (42.0 mg, 69 μmol), 2-[[2-(dimethylamino)ethyl]methylamino]ethanol (0.40 mL, 2.5 mmol), and pyridine (0.6 mL) in dry toluene (9 mL) was refluxed for 36 h under Ar atmosphere, then the mixture was concentrated. The residue was dissolved in $CHCl_3$ and washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The title compound was obtained (46.5 mg, 81%) as dark blue powder.

500 MHz ^{1}H NMR ($CDCl_3$) δ (ppm): 9.65-9.63 (m, 8H, αH), 8.34-8.32 (m, 8H, βH), 1.58 (s, 12H, CH_3), 1.09 (t, 4H, J = 7.5 Hz, CH_2), 0.71 (t, 4H, J = 7.5 Hz, CH_2), 0.47 (s, 6H, CH_3), -0.77 (t, 4H, J = 6.9 Hz, CH_2), -1.94 (t, 4H, J = 6.3 Hz, OCH_2).

HRMS-MALDI Calcd for $C_{39}H_{33}N_{10}OSi$ [M-R]$^+$: 685.2603. Found: 685.2600.

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 356 (5.86), 609 (3.10), 677 (18.42).

SiPc 6Q[vii]



A mixture of compound **6** (19.2 mg, 23μmol) and iodomethane (0.50 mL, 8.0 mmol) in DMF (2.5 mL) was stirred at room temperature for 5 h under Ar atmosphere, then diethyl ether was added. The green precipitate was formed and filtered to afford **6Q** (29.9 mg, 93%) as a dark green powder.

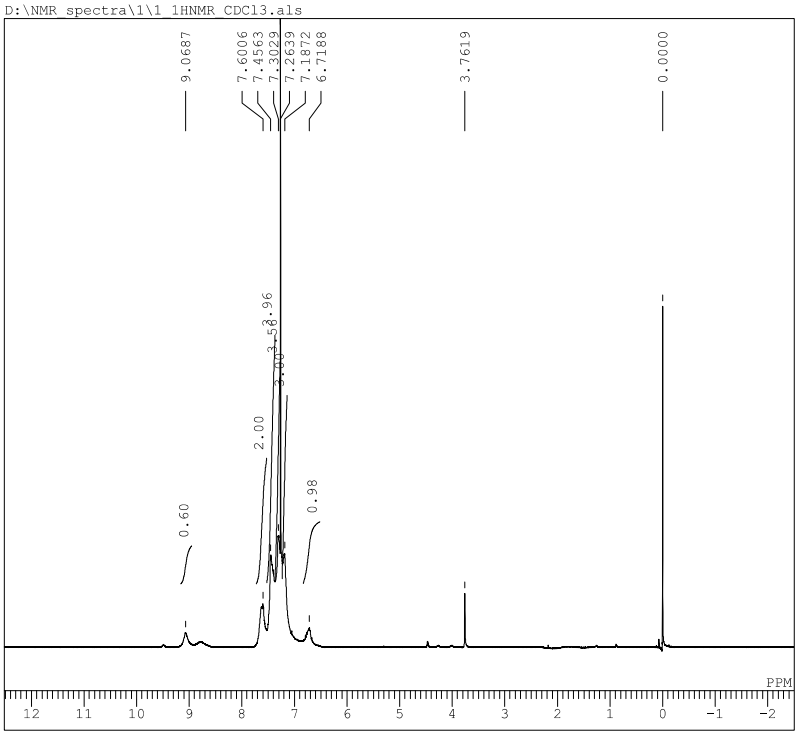
500 MHz ^{1}H NMR (DMSO-d_6) δ (ppm): 9.75-9.73 (m, 8H, αH), 8.60-8.58 (m, 8H, βH), 2.59 (t, 4H, J = 8.1 Hz, CH_2), 2.44 (s, 18H, CH_3), 2.05 (t, 4H, J = 7.5 Hz, CH_2), 0.75 (s, 12H, CH_3), -0.55 (brs, 4H, CH_2), -1.73 (brs, 4H, OCH_2).

100 MHz ^{29}Si{^{1}H} NMR (DMSO-d_6) δ (ppm): -206.4.

HRMS-MALDI Calcd for $C_{50}H_{62}I_2N_{12}O_2Si$ $[M\text{-}2I]^+$: 1144.2972. Found: 1144.2973.

UV-vis (DMSO) λ_{max} nm (ε x 10^{-4}): 356 (5.95), 612 (2.93), 681 (16.74).

Copies of the NMR Spectra of Studied Compounds

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OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            5.80 usec
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CTEMP         20.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
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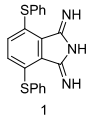
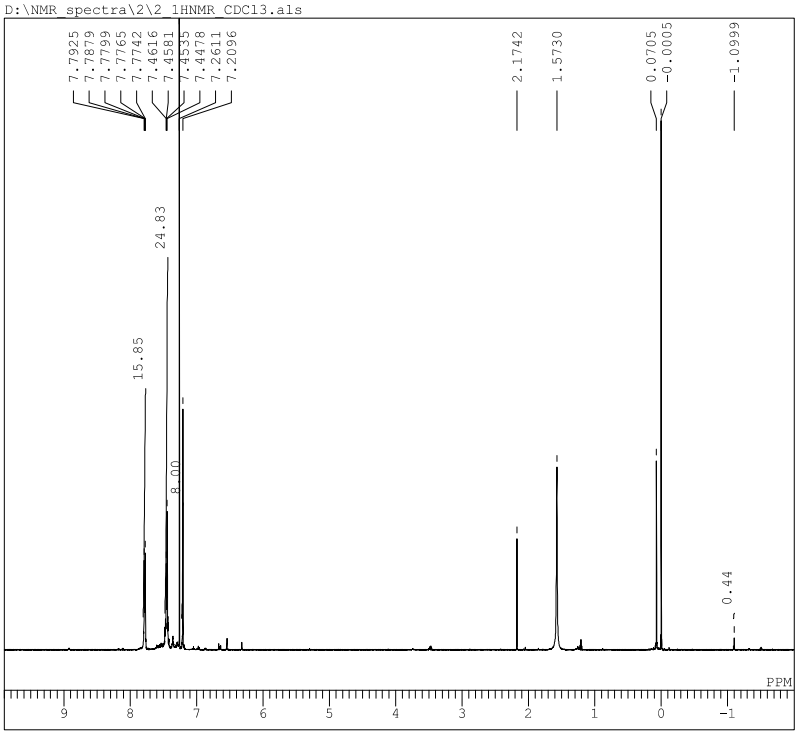


1

Figure. S9 ^{1}H NMR spectra of 4,7-bis(phenylthio) isoindoline-1,3-diimine (**1**) in $CDCl_3$.

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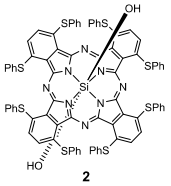
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            5.80 usec
IRNUC  1H
CTEMP         19.6 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.02 Hz
RGAIN            50
```



2

Figure. S10 ^{1}H NMR spectra of **SiPc 2** in $CDCl_3$.

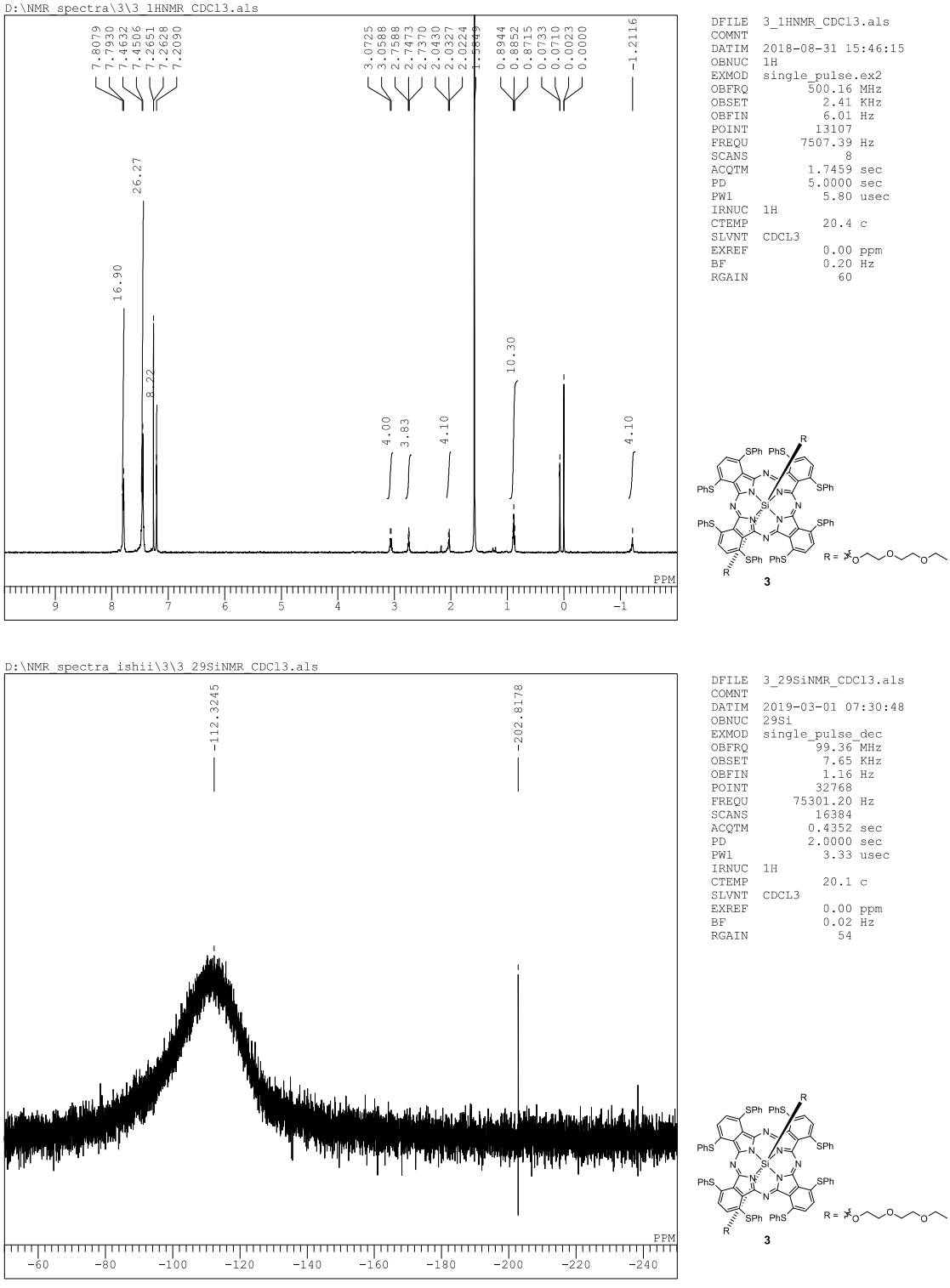


Figure. S11 ^{1}H (top) and ^{29}Si{^{1}H} (bottom) NMR spectra of SiPc **3** in $CDCl_3$.

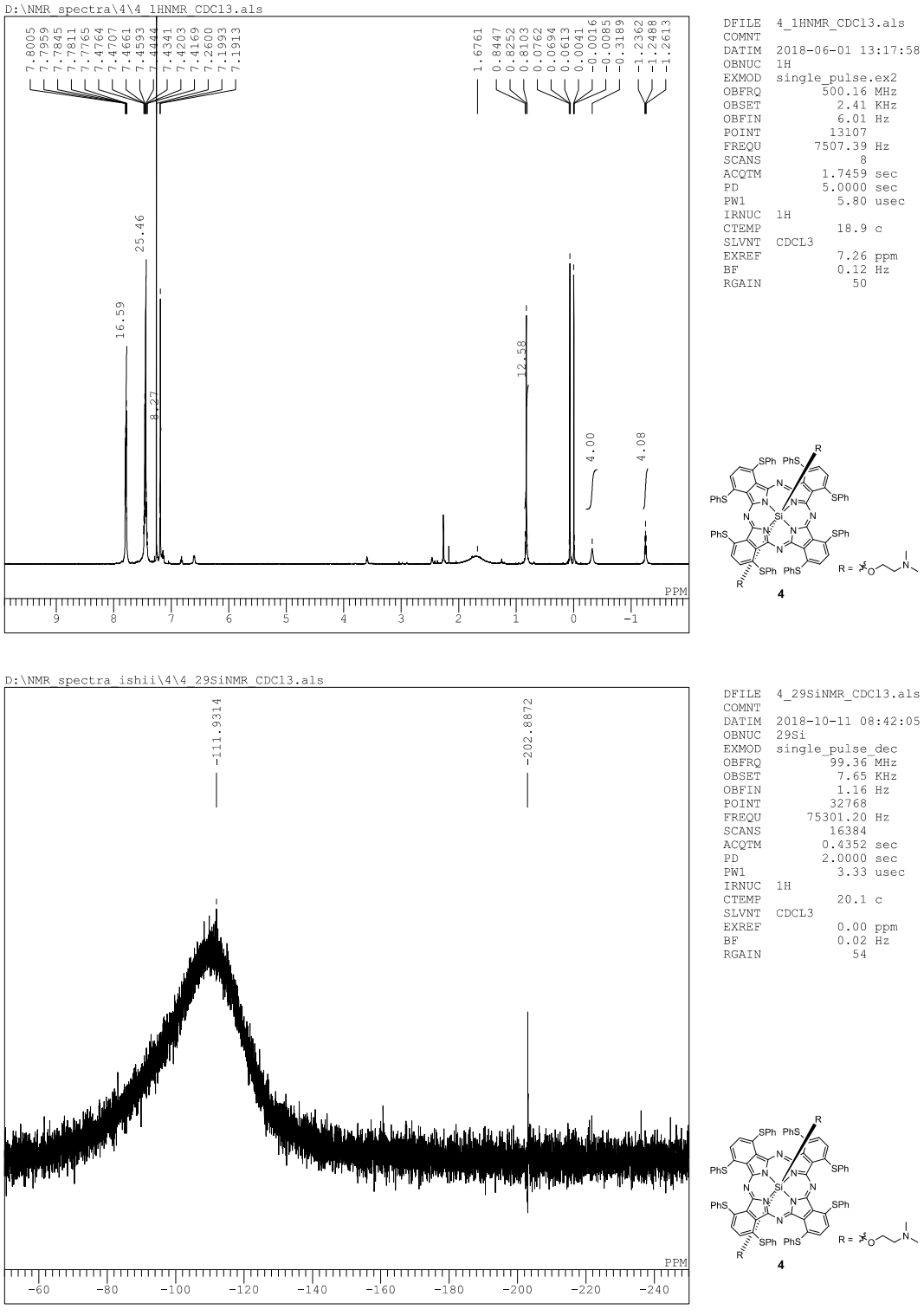


Figure. S12 ^{1}H (top) and $^{29}Si\{^{1}H\}$ (bottom) NMR spectra of SiPc **4** in $CDCl_3$.

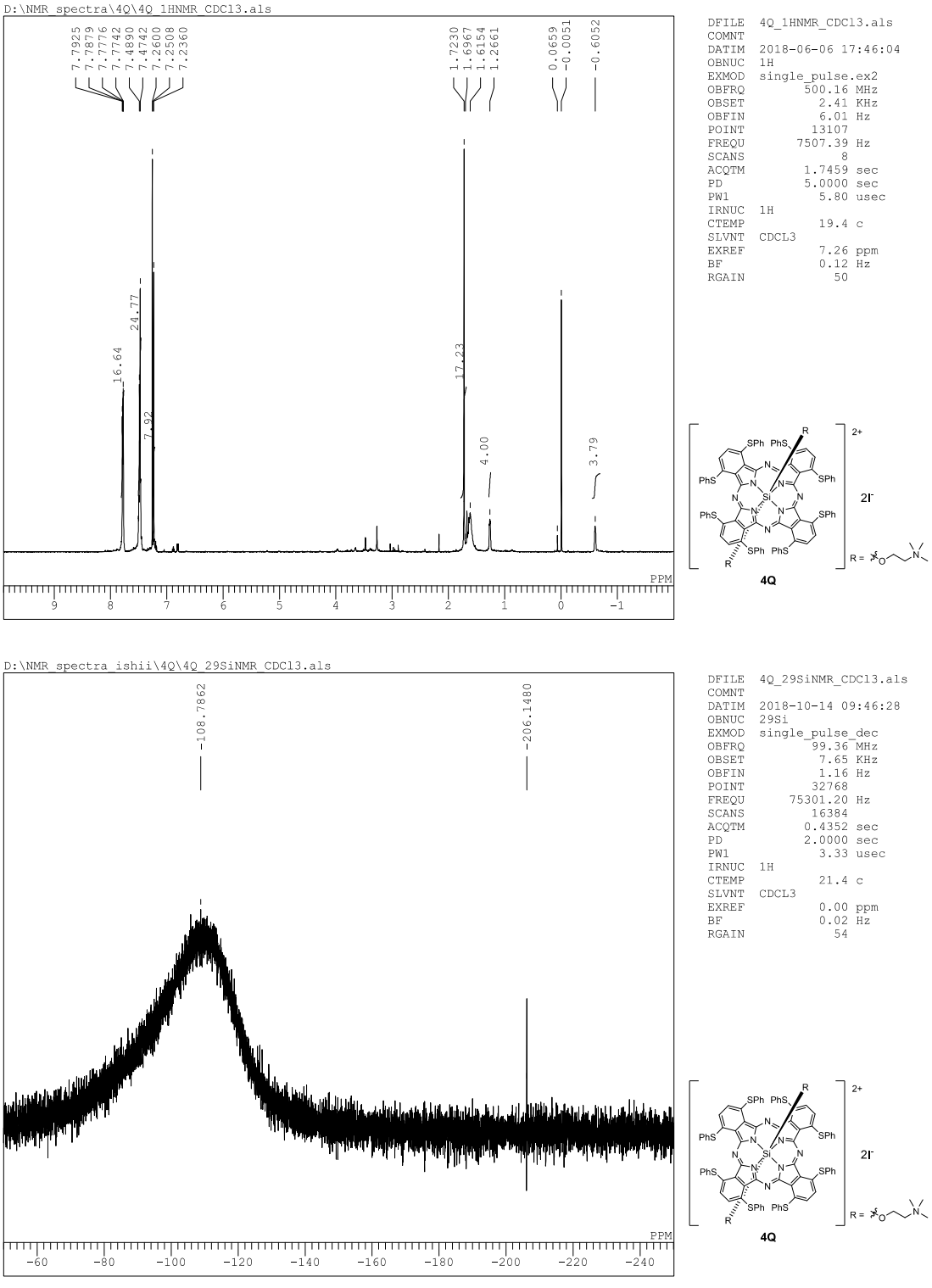


Figure. S13 ^{1}H (top) and ^{29}Si{^{1}H} (bottom) NMR spectra of SiPc **4Q** in $CDCl_3$.

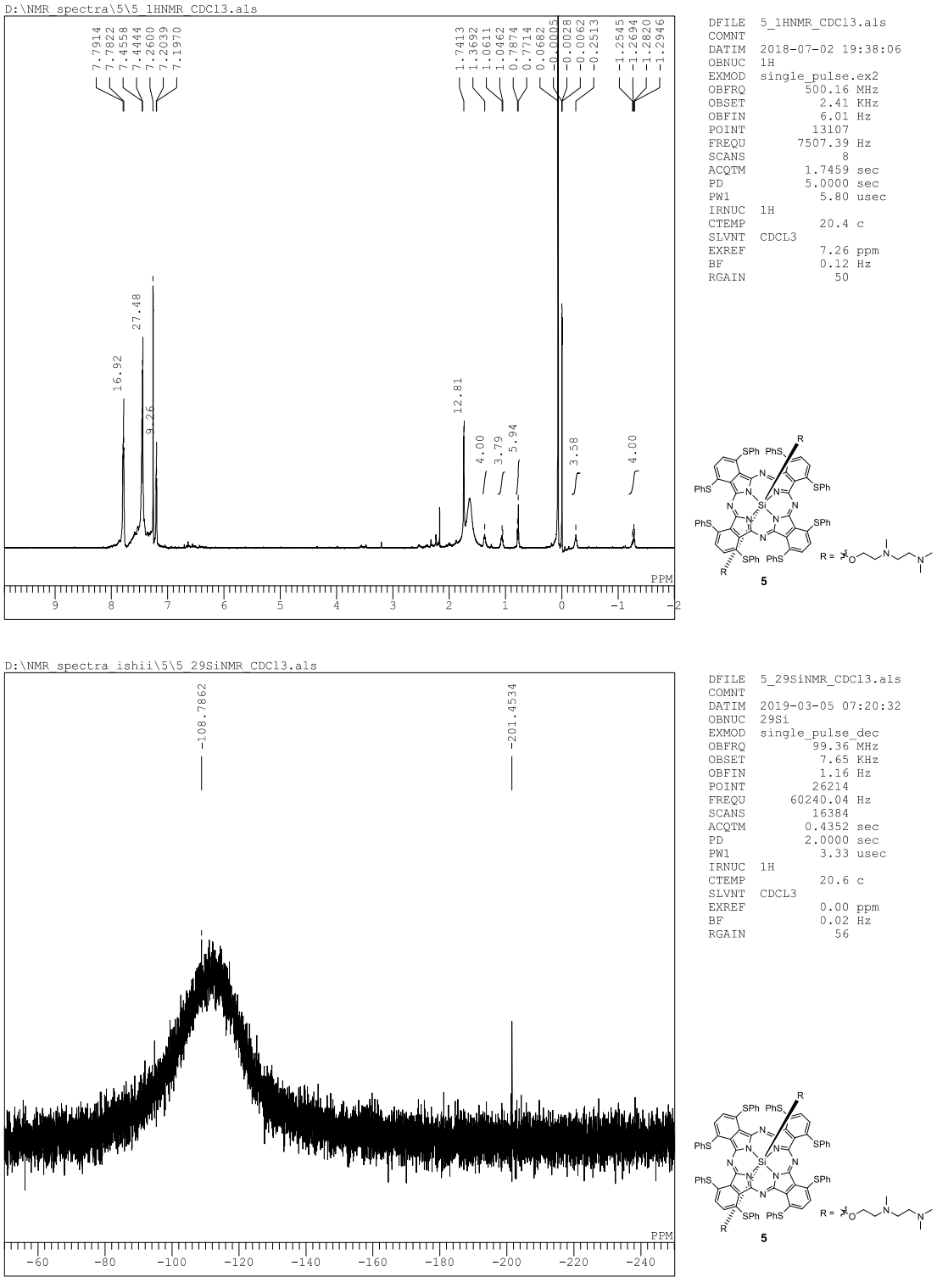


Figure. S14 ^{1}H (top) and $^{29}Si\{^{1}H\}$ (bottom) NMR spectra of SiPc **5** in $CDCl_3$.

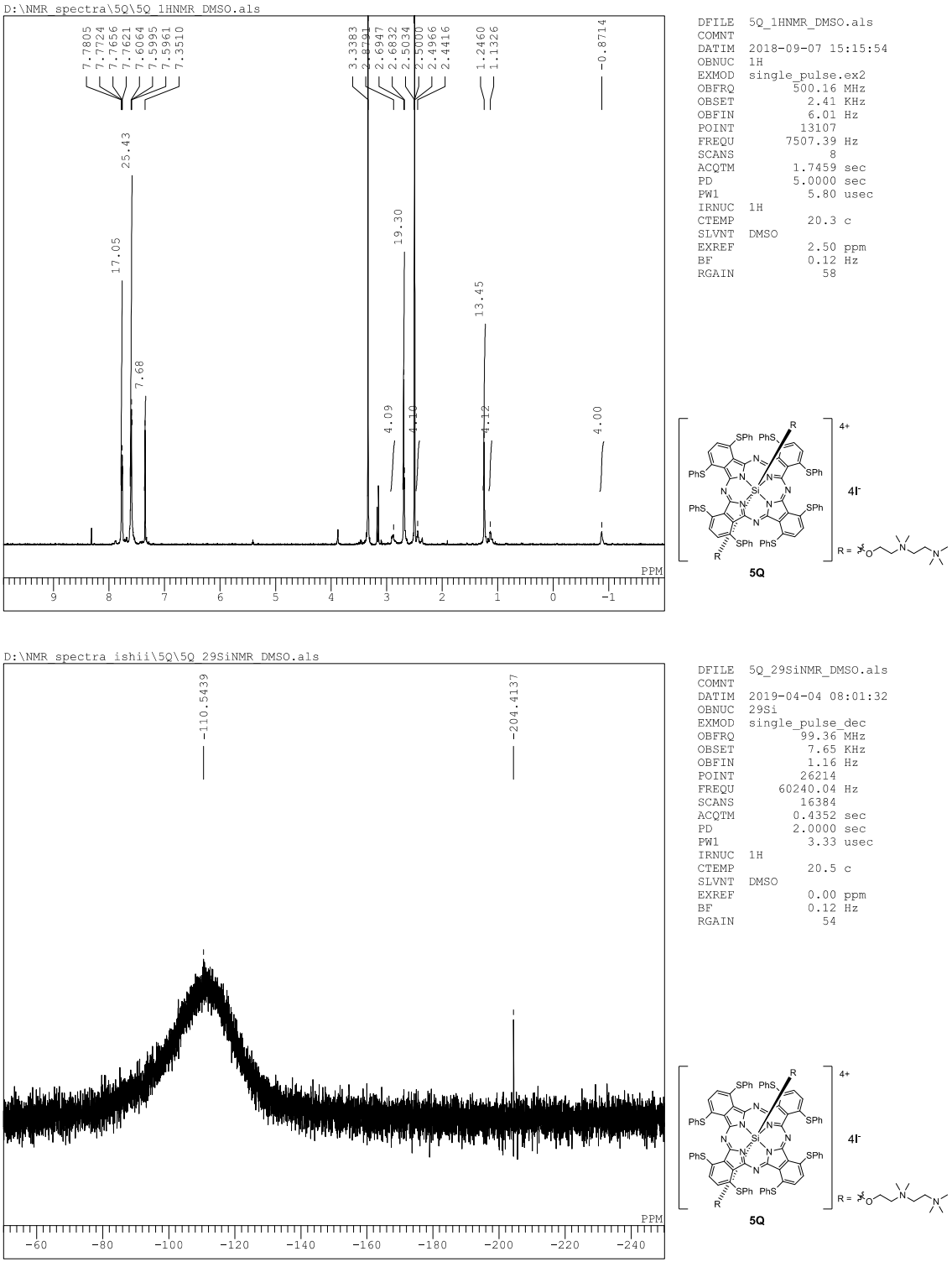


Figure. S15 ^{1}H (top) and ^{29}Si{^{1}H} (bottom) NMR spectra of SiPc **5Q** in DMSO-*d*$_6$.

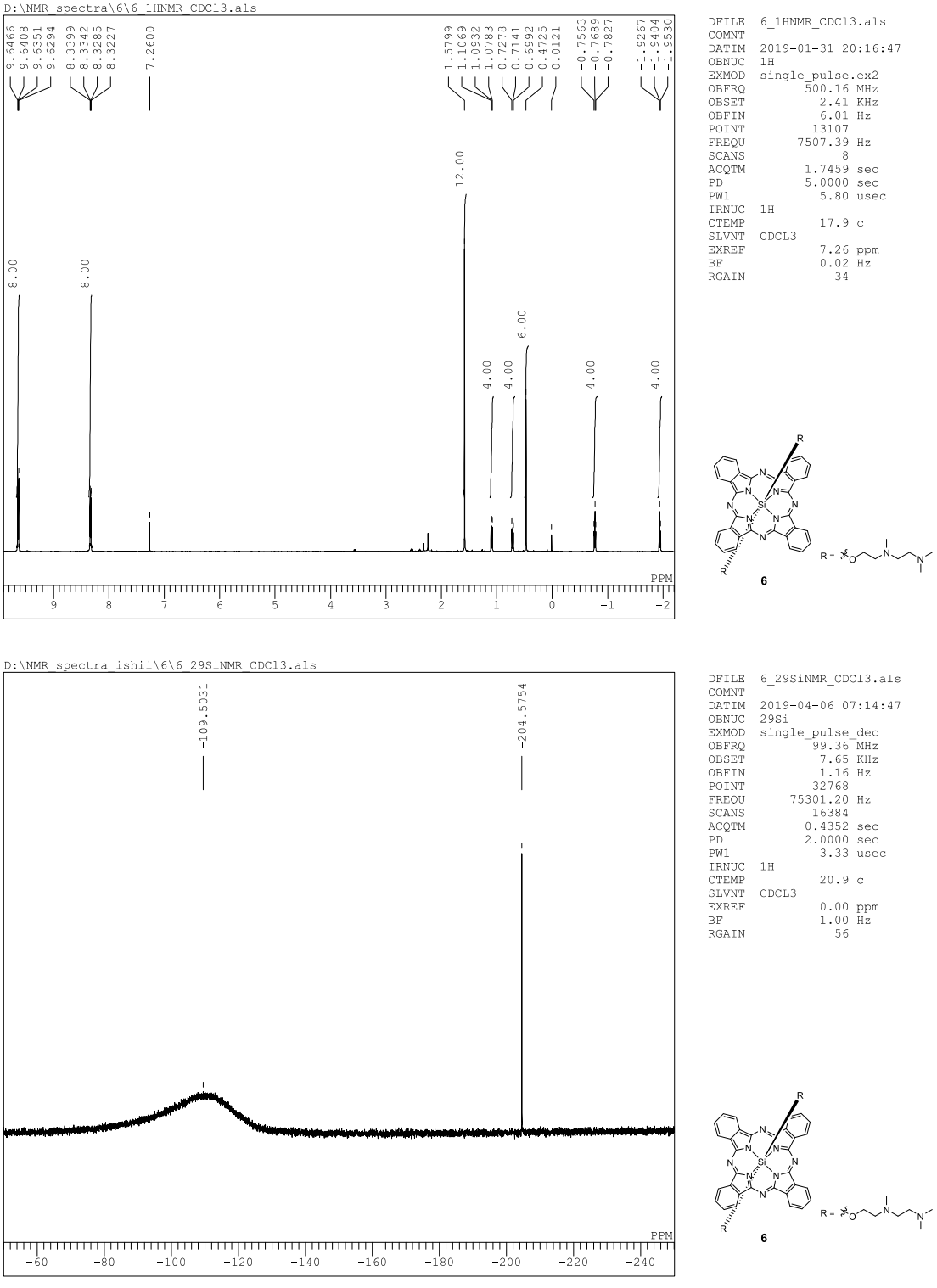


Figure. S16 ^{1}H (top) and $^{29}Si\{^{1}H\}$ (bottom) NMR spectra of SiPc **6** in $CDCl_3$.

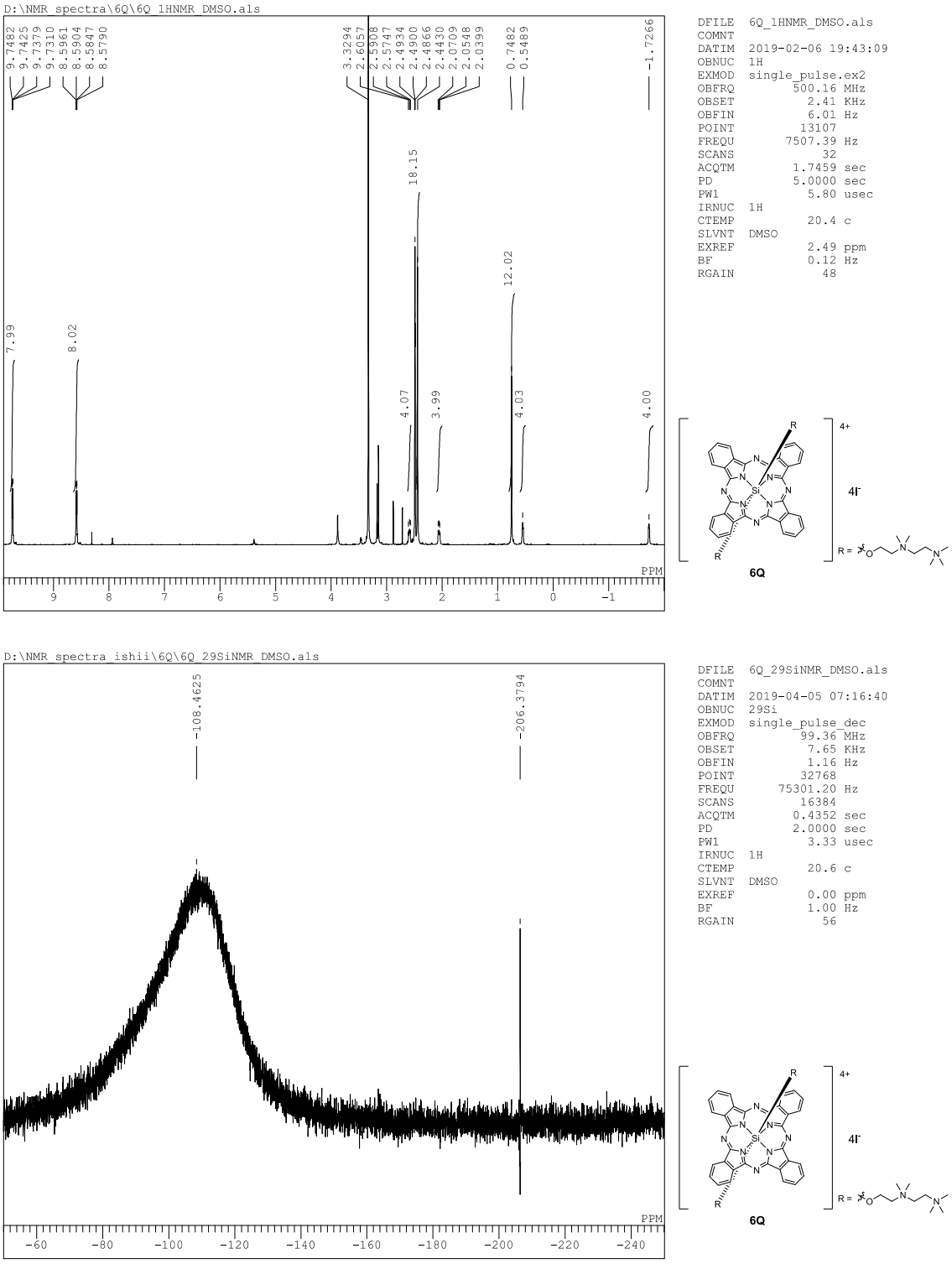


Figure. S17 ^{1}H (top) and ^{29}Si{^{1}H} (bottom) NMR spectra of SiPc **6Q** in DMSO-*d*$_6$.

Full Computational Details

Computational Details

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

Cartesian Coordinates and Total Electron Energies

4'

SCF Done: E(RB3LYP) = -6033.48130377 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	-4.112374	0.744640	-0.285953
3	6	0	-2.962676	-0.086515	0.043806
4	7	0	-1.821737	0.677923	0.014601
5	6	0	-2.182670	1.982929	-0.222321
6	6	0	2.085795	3.543796	0.487625
7	6	0	0.769536	4.054941	0.434828
8	6	0	-0.087333	2.938849	0.062630
9	7	0	0.669374	1.800193	-0.077756
10	6	0	1.992681	2.141165	0.110808
11	7	0	-1.394856	3.044419	-0.127410
12	6	0	3.490349	-2.095367	-0.919493
13	6	0	4.002527	-0.775814	-0.846723
14	6	0	2.916497	0.064768	-0.372184
15	7	0	1.788637	-0.696807	-0.191111
16	6	0	2.107096	-2.013695	-0.455049
17	7	0	3.039270	1.362187	-0.109703
18	6	0	-2.061150	-3.587953	0.786942
19	6	0	-0.758940	-4.106411	0.550852
20	6	0	0.064099	-2.968898	0.144026
21	7	0	-0.699171	-1.827181	0.150608
22	6	0	-1.995456	-2.164990	0.460411
23	7	0	-3.051871	-1.371405	0.350387
24	7	0	1.333313	-3.061070	-0.227777
25	6	0	4.291420	-3.159186	-1.384408
26	6	0	5.615002	-2.841475	-1.712638
27	6	0	6.125607	-1.544760	-1.627075
28	6	0	5.329121	-0.466629	-1.219316
29	6	0	3.174704	4.338585	0.898678
30	6	0	2.875766	5.673404	1.203430
31	6	0	1.576461	6.182348	1.139576
32	6	0	0.478156	5.392423	0.772826
33	6	0	-3.111043	-4.427915	1.214835
34	6	0	-2.830338	-5.797819	1.297379
35	6	0	-1.559529	-6.309225	1.036478
36	6	0	-0.481741	-5.481814	0.697146
37	6	0	-4.449492	3.109087	-0.892437

38	6	0	-5.805646	2.789767	-1.051108
39	6	0	-6.300279	1.500059	-0.843743
40	6	0	-5.473444	0.430836	-0.470984
41	14	0	-0.029358	-0.021109	-0.022440
42	16	0	4.798758	3.645865	1.058604
43	6	0	5.722543	4.990225	1.878787
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45	6	0	-1.007975	7.687028	1.404194
46	16	0	-3.784047	4.717112	-1.229932
47	16	0	-6.050554	-1.232060	-0.264289
48	16	0	-4.772262	-3.958180	1.652666
49	16	0	1.083670	-6.298539	0.438690
50	16	0	3.824160	-4.870805	-1.561444
51	16	0	5.906930	1.206771	-1.191329
52	6	0	7.575646	1.063543	-1.918342
53	6	0	2.412751	-4.803080	-2.723954
54	6	0	2.165211	-5.517930	1.691238
55	6	0	-4.533761	-2.637105	2.895063
56	6	0	-7.816945	-1.094268	-0.705139
57	6	0	-5.196123	5.573224	-2.008522
58	8	0	-0.006478	0.102381	1.697244
59	8	0	-0.190960	-0.206645	-1.732061
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61	6	0	0.375026	-0.224064	4.021233
62	7	0	1.195844	-0.852203	5.056795
63	6	0	2.458724	-0.156273	5.271815
64	6	0	0.467556	-0.989267	6.310395
65	6	0	0.351720	0.603635	-2.751669
66	6	0	0.287308	-0.083641	-4.118459
67	7	0	-1.034632	-0.093335	-4.743011
68	6	0	-1.955390	-1.043472	-4.125818
69	6	0	-0.942935	-0.328897	-6.176684
70	1	0	-1.379475	-7.373182	1.154152
71	1	0	-3.616363	-6.470600	1.626426
72	1	0	3.662990	6.350008	1.513521
73	1	0	1.434495	7.223727	1.401827
74	1	0	6.260779	-3.635391	-2.075390
75	1	0	7.156577	-1.385077	-1.917727
76	1	0	-7.360702	1.340122	-0.997370
77	1	0	-6.511619	3.553185	-1.355278
78	1	0	6.713072	4.571651	2.076700
79	1	0	5.266245	5.277997	2.830322
80	1	0	5.838905	5.868449	1.237108
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82	1	0	-0.579916	7.698960	2.410799
83	1	0	-2.027566	8.078798	1.453302
84	1	0	3.096792	-6.089191	1.670225
85	1	0	2.373962	-4.481755	1.426115
86	1	0	1.715939	-5.591026	2.684798
87	1	0	-4.187144	-1.716995	2.424900
88	1	0	-3.841725	-2.964677	3.675040
89	1	0	-5.519981	-2.471069	3.337227
90	1	0	-8.367788	-0.445585	-0.017764
91	1	0	-8.208422	-2.111034	-0.614137
92	1	0	-7.957950	-0.756022	-1.735809
93	1	0	-4.800635	6.544031	-2.319424
94	1	0	-5.557124	5.041300	-2.893434
95	1	0	-6.020131	5.742069	-1.309130
96	1	0	0.952550	-1.588041	2.462698
97	1	0	1.904103	-0.094369	2.476062
98	1	0	0.279295	0.869999	4.164931
99	1	0	-0.636914	-0.639412	4.085380
100	1	0	1.088314	-1.521746	7.040342
101	1	0	0.176075	-0.017969	6.759101
102	1	0	-0.444211	-1.574639	6.149443
103	1	0	3.055774	-0.701004	6.011926
104	1	0	2.322819	0.881654	5.638240

105	1	0	3.037615	-0.112167	4.345134
106	1	0	-0.180842	1.564134	-2.820226
107	1	0	1.411962	0.826526	-2.549573
108	1	0	0.715169	-1.102626	-4.024486
109	1	0	0.953354	0.481581	-4.783260
110	1	0	-2.032742	-0.846310	-3.056978
111	1	0	-1.631873	-2.096500	-4.255516
112	1	0	-2.946654	-0.936072	-4.581548
113	1	0	-0.523234	-1.322885	-6.435486
114	1	0	-0.313350	0.436538	-6.644778
115	1	0	-1.942242	-0.264668	-6.622565
116	1	0	2.686109	-4.251586	-3.627121
117	1	0	1.538321	-4.365736	-2.242555
118	1	0	2.198638	-5.842897	-2.984505
119	1	0	7.947610	2.090399	-1.970186
120	1	0	8.253864	0.478785	-1.290290
121	1	0	7.548533	0.648955	-2.930089

TD–DFT output

HOMO**: 284**, LUMO**: 285**

Excited State 1: Singlet-A 1.6803 eV 737.86 nm f=0.3031 <S**2>=0.000
284 -> 285 0.59967
284 -> 286 -0.34776
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -6033.41955298
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.6905 eV 733.40 nm f=0.3380 <S**2>=0.000
284 -> 285 0.35057
284 -> 286 0.60030

Excited State 3: Singlet-A 1.8818 eV 658.84 nm f=0.0006 <S**2>=0.000
283 -> 285 0.61865
283 -> 286 0.34128

Excited State 4: Singlet-A 1.9081 eV 649.79 nm f=0.0009 <S**2>=0.000
283 -> 285 -0.34146
283 -> 286 0.61882

Excited State 5: Singlet-A 2.0464 eV 605.87 nm f=0.0778 <S**2>=0.000
282 -> 285 0.69260

Excited State 6: Singlet-A 2.0647 eV 600.49 nm f=0.0731 <S**2>=0.000
282 -> 286 0.68538

Excited State 7: Singlet-A 2.0941 eV 592.06 nm f=0.0058 <S**2>=0.000
281 -> 285 0.66501
281 -> 286 -0.20387

Excited State 8: Singlet-A 2.1314 eV 581.70 nm f=0.0064 <S**2>=0.000
279 -> 285 -0.28172
280 -> 285 0.23124
281 -> 285 0.12794
281 -> 286 0.57969

Excited State 9: Singlet-A 2.1511 eV 576.39 nm f=0.0002 <S**2>=0.000
279 -> 285 0.17201
280 -> 285 0.58931
280 -> 286 -0.28162
281 -> 286 -0.16174

Excited State 10: Singlet-A 2.1702 eV 571.31 nm f=0.0081 <S**2>=0.000
279 -> 285 -0.17535
279 -> 286 -0.23539
280 -> 285 0.25238
280 -> 286 0.57293

281 -> 285 -0.10329

[4Q']$^{2+}$

SCF Done: E(RB3LYP) = -6112.85550012 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.905727	1.549605	0.316465
2	6	0	4.192931	0.166399	0.228772
3	6	0	2.937015	-0.493234	-0.071750
4	7	0	1.913672	0.436997	-0.085155
5	6	0	2.483298	1.687635	0.073931
6	6	0	-1.530489	3.923697	-0.229666
7	6	0	-0.150973	4.224026	-0.365383
8	6	0	0.555681	2.966023	-0.147490
9	7	0	-0.360121	1.941754	0.030770
10	6	0	-1.621101	2.505570	0.062899
11	7	0	1.868005	2.853772	-0.047843
12	6	0	-3.690381	-1.514251	0.918719
13	6	0	-3.973694	-0.132494	1.052490
14	6	0	-2.815005	0.572477	0.538308
15	7	0	-1.842244	-0.336574	0.165526
16	6	0	-2.367936	-1.605446	0.330972
17	7	0	-2.748035	1.886416	0.382911
18	6	0	1.492639	-3.751410	-0.992753
19	6	0	0.100730	-4.014595	-0.921773
20	6	0	-0.522564	-2.817553	-0.394173
21	7	0	0.431442	-1.832660	-0.219206
22	6	0	1.664117	-2.380872	-0.523647
23	7	0	2.831873	-1.782820	-0.355103
24	7	0	-1.797730	-2.740334	-0.043218
25	6	0	-4.589868	-2.505535	1.367065
26	6	0	-5.790427	-2.030907	1.918616
27	6	0	-6.069427	-0.670553	2.049717
28	6	0	-5.171282	0.328317	1.640425
29	6	0	-2.531269	4.910667	-0.378189
30	6	0	-2.077297	6.218502	-0.606013
31	6	0	-0.720408	6.511606	-0.739551
32	6	0	0.282890	5.535242	-0.652537
33	6	0	2.396095	-4.731487	-1.453894
34	6	0	1.838924	-5.972219	-1.794554
35	6	0	0.469213	-6.231576	-1.733154
36	6	0	-0.449142	-5.255194	-1.320618
37	6	0	4.904502	2.500524	0.621897
38	6	0	6.195897	1.982280	0.808726
39	6	0	6.477022	0.616587	0.729175
40	6	0	5.490078	-0.342384	0.452603
41	14	0	0.038130	0.054881	-0.027188
42	16	0	-4.244566	4.481176	-0.324362
43	6	0	-5.076054	6.058695	-0.720707
44	16	0	1.952728	6.113840	-0.868888
45	6	0	2.567388	5.115968	-2.273232
46	16	0	4.502533	4.213360	0.785966
47	16	0	5.795783	-2.085705	0.422547
48	16	0	4.167302	-4.597675	-1.595219
49	16	0	-2.197426	-5.510655	-1.331798
50	16	0	-4.182761	-4.222919	1.266372
51	16	0	-5.471303	2.053807	1.871885
52	6	0	-7.032957	2.075005	2.818781
53	6	0	-5.586454	-5.026894	2.114722
54	6	0	-2.365713	-7.164250	-2.089613
55	6	0	4.384698	-3.256449	-2.821437
56	6	0	7.564240	-2.196525	0.866993
57	6	0	6.095820	4.962070	1.272770
58	8	0	-0.034443	0.087541	-1.790685
59	8	0	0.083306	-0.003216	1.734632

60	6	0	-1.010506	0.689635	-2.576585
61	6	0	-0.915237	-0.035945	-3.927824
62	7	0	-1.843673	0.459894	-5.039450
63	6	0	-1.519680	1.883242	-5.417653
64	6	0	-1.636344	-0.420090	-6.247508
65	6	0	1.064427	-0.577464	2.534859
66	6	0	0.429604	-0.638096	3.932112
67	7	0	1.330880	-1.128095	5.067859
68	6	0	1.882786	-2.498790	4.765052
69	6	0	0.498540	-1.204523	6.323872
70	1	0	0.124679	-7.211055	-2.040391
71	1	0	2.503129	-6.754408	-2.148663
72	1	0	-2.784183	7.031770	-0.712525
73	1	0	-0.425965	7.534748	-0.951533
74	1	0	-6.537932	-2.729801	2.273266
75	1	0	-7.016180	-0.396638	2.498706
76	1	0	7.501009	0.307059	0.899857
77	1	0	7.019038	2.648777	1.035656
78	1	0	-6.141451	5.815141	-0.741566
79	1	0	-4.784369	6.444905	-1.700990
80	1	0	-4.907942	6.814277	0.050942
81	1	0	1.894037	5.201999	-3.130179
82	1	0	2.710698	4.074259	-1.984146
83	1	0	3.534644	5.551247	-2.537598
84	1	0	-3.443768	-7.329918	-2.161577
85	1	0	-1.936033	-7.202166	-3.094116
86	1	0	-1.935180	-7.948787	-1.462064
87	1	0	4.088423	-2.292657	-2.406053
88	1	0	3.832007	-3.480795	-3.737180
89	1	0	5.454244	-3.237496	-3.046308
90	1	0	8.204530	-1.723328	0.118045
91	1	0	7.781839	-3.267557	0.882822
92	1	0	7.768215	-1.781644	1.857813
93	1	0	5.874590	6.023979	1.407142
94	1	0	6.467257	4.559534	2.218975
95	1	0	6.853617	4.860530	0.491472
96	1	0	-2.018300	0.569824	-2.154159
97	1	0	-0.827482	1.769286	-2.699017
98	1	0	0.103343	0.049484	-4.313732
99	1	0	-1.143811	-1.094606	-3.784418
100	1	0	-2.280375	-0.070653	-7.056294
101	1	0	-0.590116	-0.362013	-6.551072
102	1	0	-1.891263	-1.447425	-5.983721
103	1	0	-2.151895	2.174611	-6.258125
104	1	0	-0.468539	1.939569	-5.704810
105	1	0	-1.710459	2.536449	-4.567324
106	1	0	1.336115	-1.588508	2.197057
107	1	0	1.986144	0.025140	2.553922
108	1	0	-0.433982	-1.307026	3.911283
109	1	0	0.088080	0.360310	4.215020
110	1	0	2.552039	-2.439688	3.907321
111	1	0	1.052163	-3.171684	4.546010
112	1	0	2.431371	-2.855085	5.638623
113	1	0	-0.310400	-1.919657	6.168484
114	1	0	0.086873	-0.216475	6.534709
115	1	0	1.132119	-1.530249	7.150595
116	1	0	-6.527436	-4.887154	1.576271
117	1	0	-5.687458	-4.692109	3.150592
118	1	0	-5.340779	-6.091985	2.113139
119	1	0	-7.217821	3.131865	3.027664
120	1	0	-7.873127	1.683342	2.239344
121	1	0	-6.943183	1.541553	3.768821
122	6	0	2.470484	-0.168210	5.303136
123	1	0	3.105206	-0.134737	4.418869
124	1	0	3.048015	-0.515691	6.161424
125	1	0	2.059409	0.821937	5.505723
126	6	0	-3.288346	0.369072	-4.615133

```
   127          1          0      -3.469860    1.060778   -3.793323
   128          1          0      -3.497383   -0.653464   -4.296684
   129          1          0      -3.919174    0.631660   -5.466070
 -----------------------------------------------------------------
```

TD–DFT output

HOMO**: 292**, LUMO**: 293**

Excited State 1: Singlet-A 1.4443 eV 858.42 nm f=0.2054 <S**2>=0.000
291 -> 293 0.11123
292 -> 293 0.61040
292 -> 294 -0.30790
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -6112.80242195
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.5133 eV 819.27 nm f=0.3262 <S**2>=0.000
291 -> 293 -0.10550
292 -> 293 0.32048
292 -> 294 0.61204

Excited State 3: Singlet-A 1.7189 eV 721.29 nm f=0.0931 <S**2>=0.000
290 -> 293 0.18695
290 -> 294 -0.13266
291 -> 293 0.63762
291 -> 294 -0.13269
292 -> 294 0.12250

Excited State 4: Singlet-A 1.7622 eV 703.59 nm f=0.0651 <S**2>=0.000
290 -> 293 -0.28231
291 -> 293 0.21692
291 -> 294 0.59436

Excited State 5: Singlet-A 1.7982 eV 689.51 nm f=0.0875 <S**2>=0.000
290 -> 293 0.51507
290 -> 294 -0.29546
291 -> 293 -0.13270
291 -> 294 0.32445

Excited State 6: Singlet-A 1.8643 eV 665.06 nm f=0.0169 <S**2>=0.000
289 -> 293 0.57909
289 -> 294 0.14488
290 -> 293 0.10102
290 -> 294 0.36158

Excited State 7: Singlet-A 1.8884 eV 656.56 nm f=0.0152 <S**2>=0.000
289 -> 293 0.10727
289 -> 294 0.56652
290 -> 293 -0.22785
290 -> 294 -0.33466

Excited State 8: Singlet-A 1.9840 eV 624.92 nm f=0.0021 <S**2>=0.000
289 -> 293 -0.36809
289 -> 294 0.38934
290 -> 293 0.23190
290 -> 294 0.37632

Excited State 9: Singlet-A 2.4018 eV 516.22 nm f=0.0391 <S**2>=0.000
286 -> 293 -0.12299
288 -> 293 0.65885
288 -> 294 -0.17597

Excited State 10: Singlet-A 2.4522 eV 505.60 nm f=0.0078 <S**2>=0.000
287 -> 293 -0.11425
288 -> 293 0.18380
288 -> 294 0.65367

7

SCF Done: E(RB3LYP) = -2533.54379766 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.168936	0.225742	0.847418
2	6	0	-3.996991	-1.165749	0.797562
3	6	0	-2.592533	-1.397091	0.492615
4	7	0	-1.943798	-0.189080	0.365188
5	6	0	-2.864916	0.812258	0.574905
6	6	0	0.147750	4.254130	0.135075
7	6	0	-1.223240	4.075711	0.377567
8	6	0	-1.467139	2.642984	0.338013
9	7	0	-0.290292	1.982165	0.066630
10	6	0	0.709622	2.926787	-0.053011
11	7	0	-2.659878	2.116676	0.558419
12	6	0	4.044784	-0.109865	-0.945106
13	6	0	3.892252	1.279980	-0.807433
14	6	0	2.494610	1.512576	-0.487234
15	7	0	1.829442	0.305926	-0.427003
16	6	0	2.738894	-0.695879	-0.697612
17	7	0	1.989450	2.722159	-0.307096
18	6	0	-0.255143	-4.141310	-0.139390
19	6	0	1.097500	-3.962264	-0.469521
20	6	0	1.338375	-2.528576	-0.459369
21	7	0	0.171871	-1.868836	-0.130768
22	6	0	-0.811200	-2.812643	0.059953
23	7	0	-2.082712	-2.608245	0.360550
24	7	0	2.520113	-1.999815	-0.722059
25	6	0	5.283172	-0.675455	-1.258021
26	6	0	6.361116	0.189912	-1.430364
27	6	0	6.207807	1.584990	-1.292942
28	6	0	4.972677	2.148375	-0.980551
29	6	0	0.719663	5.527534	0.108782
30	6	0	-0.122056	6.615613	0.332065
31	6	0	-1.498764	6.436333	0.575440
32	6	0	-2.067773	5.164407	0.602190
33	6	0	-0.819601	-5.415581	-0.059854
34	6	0	0.010707	-6.504505	-0.319414
35	6	0	1.368798	-6.324783	-0.650522
36	6	0	1.930595	-5.051773	-0.729883
37	6	0	-5.414154	0.793347	1.118925
38	6	0	-6.482724	-0.075025	1.339993
39	6	0	-6.309940	-1.472116	1.290739
40	6	0	-5.064240	-2.036815	1.018512
41	14	0	-0.059074	0.055068	-0.030812
42	8	0	0.227130	0.077013	1.667981
43	8	0	-0.447289	-0.003280	-1.711981
44	6	0	1.216051	-0.578197	2.428220
45	6	0	1.008388	-0.195540	3.897011
46	7	0	1.936078	-0.876330	4.800230
47	6	0	3.283936	-0.324691	4.742646
48	6	0	1.443760	-0.883877	6.170892
49	6	0	-0.155532	0.929790	-2.729378
50	6	0	-0.401225	0.346049	-4.123314
51	7	0	-1.806557	0.276133	-4.522598
52	6	0	-2.543889	-0.786393	-3.845528
53	6	0	-1.942126	0.151034	-5.966892
54	1	0	1.986258	-7.196981	-0.846741
55	1	0	-0.393018	-7.511830	-0.266704
56	1	0	0.287010	7.622093	0.319005
57	1	0	-2.124733	7.308016	0.745159
58	1	0	7.339672	-0.213770	-1.675217
59	1	0	7.071301	2.229160	-1.434067
60	1	0	-7.164980	-2.118672	1.467870
61	1	0	-7.467768	0.330119	1.554559

62	1	0	1.144394	-1.672204	2.339767
63	1	0	2.223551	-0.289574	2.092889
64	1	0	1.058667	0.906820	3.994360
65	1	0	-0.012020	-0.489207	4.166764
66	1	0	2.129042	-1.458556	6.804750
67	1	0	1.346951	0.129836	6.609843
68	1	0	0.460669	-1.365131	6.210560
69	1	0	3.945790	-0.905383	5.395026
70	1	0	3.331187	0.735871	5.063844
71	1	0	3.682633	-0.386527	3.726063
72	1	0	-0.767215	1.838021	-2.623883
73	1	0	0.902579	1.233803	-2.685133
74	1	0	0.105268	-0.637791	-4.192433
75	1	0	0.101482	1.014278	-4.834589
76	1	0	-2.451597	-0.672362	-2.765681
77	1	0	-2.177473	-1.798309	-4.113972
78	1	0	-3.602926	-0.725845	-4.122822
79	1	0	-1.506251	-0.785195	-6.372174
80	1	0	-1.452901	0.995625	-6.465533
81	1	0	-3.004231	0.167141	-6.237398
82	1	0	-1.866638	-5.543739	0.195124
83	1	0	2.975159	-4.903591	-0.984237
84	1	0	5.391499	-1.750317	-1.361608
85	1	0	4.845059	3.220729	-0.872842
86	1	0	1.780885	5.655755	-0.078775
87	1	0	-3.126338	5.015956	0.789514
88	1	0	-5.537341	1.870972	1.154834
89	1	0	-4.921344	-3.111850	0.977679

TD–DFT output

HOMO**: 188**, LUMO**: 189**

Excited State 1: Singlet-A 1.9125 eV 648.29 nm f=0.0005 <S**2>=0.000
187 ->189 0.70453
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2533.47351569
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.9280 eV 643.08 nm f=0.0003 <S**2>=0.000
187 ->190 0.70467

Excited State 3: Singlet-A 2.0574 eV 602.62 nm f=0.3575 <S**2>=0.000
183 ->190 0.15951
188 ->189 0.68255

Excited State 4: Singlet-A 2.0688 eV 599.31 nm f=0.3593 <S**2>=0.000
183 ->189 -0.17031
188 ->190 0.68236

Excited State 5: Singlet-A 2.1251 eV 583.42 nm f=0.0012 <S**2>=0.000
186 ->189 0.70639

Excited State 6: Singlet-A 2.1377 eV 579.99 nm f=0.0015 <S**2>=0.000
186 ->190 0.70571

Excited State 7: Singlet-A 2.8190 eV 439.82 nm f=0.0034 <S**2>=0.000
184 ->190 -0.26048
185 ->189 0.63216
185 ->190 -0.16121

Excited State 8: Singlet-A 2.8689 eV 432.16 nm f=0.0023 <S**2>=0.000
184 ->189 -0.45746
184 ->190 -0.16110
185 ->190 0.49383

Excited State 9: Singlet-A 2.9269 eV 423.60 nm f=0.0127 <S**2>=0.000
184 ->190 0.60873

185 ->189 0.29691
185 ->190 0.18531

Excited State 10: Singlet-A 2.9801 eV 416.04 nm f=0.0017 <S**2>=0.000
181 ->189 0.12695
184 ->189 0.50974
184 ->190 -0.17346
185 ->190 0.41915

[7Q]$^{2+}$

SCF Done: E(RB3LYP) = -2612.88099218 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.510781	3.154475	-1.335891
2	6	0	3.239741	2.033960	-1.801184
3	6	0	2.396007	0.876104	-1.577045
4	7	0	1.237434	1.262455	-0.928061
5	6	0	1.249782	2.642805	-0.836636
6	6	0	-2.855461	2.876856	1.235761
7	6	0	-1.996101	3.742827	0.512383
8	6	0	-0.842449	2.934703	0.131028
9	7	0	-1.036803	1.624192	0.536472
10	6	0	-2.205779	1.580125	1.271690
11	7	0	0.251544	3.413633	-0.433356
12	6	0	-1.729093	-2.887338	2.265602
13	6	0	-2.430998	-1.763939	2.768313
14	6	0	-2.095162	-0.651801	1.899814
15	7	0	-1.180636	-1.062070	0.947487
16	6	0	-0.986638	-2.422087	1.110211
17	7	0	-2.651001	0.548455	1.973954
18	6	0	2.135473	-2.729932	-2.269004
19	6	0	1.218741	-3.571474	-1.588472
20	6	0	0.533393	-2.741449	-0.618357
21	7	0	0.952865	-1.430544	-0.746131
22	6	0	1.955085	-1.399518	-1.698654
23	7	0	2.689141	-0.342621	-2.005016
24	7	0	-0.288331	-3.211301	0.308568
25	6	0	-1.786452	-4.146562	2.901053
26	6	0	-2.608605	-4.216273	4.036847
27	6	0	-3.300000	-3.110341	4.531294
28	6	0	-3.226777	-1.842792	3.931391
29	6	0	-4.088604	3.316732	1.768299
30	6	0	-4.384620	4.676975	1.593541
31	6	0	-3.538457	5.526677	0.881568
32	6	0	-2.339046	5.094110	0.296964
33	6	0	2.980712	-3.239037	-3.276882
34	6	0	2.881201	-4.614821	-3.528320
35	6	0	1.974925	-5.443728	-2.865959
36	6	0	1.095035	-4.947077	-1.893327
37	6	0	3.044518	4.461503	-1.379356
38	6	0	4.330067	4.571572	-1.932918
39	6	0	5.051528	3.464553	-2.385113
40	6	0	4.544749	2.157029	-2.324021
41	14	0	-0.006019	0.101814	-0.048421
42	8	0	-0.974254	0.004425	-1.521272
43	8	0	0.950735	0.164291	1.431492
44	6	0	-2.359352	0.075362	-1.617847
45	6	0	-2.685167	-0.606930	-2.955648
46	7	0	-4.157608	-0.628054	-3.374018
47	6	0	-4.675591	0.770887	-3.594436
48	6	0	-4.263144	-1.392181	-4.670835
49	6	0	2.335813	0.121332	1.543017
50	6	0	2.590373	-0.135682	3.035710
51	7	0	4.052123	-0.119904	3.488875
52	6	0	4.867603	-1.124929	2.714270

53	6	0	4.090729	-0.485140	4.952197
54	1	0	1.949312	-6.490171	-3.143050
55	1	0	3.519657	-5.045254	-4.293487
56	1	0	-5.303073	5.091826	1.989495
57	1	0	-3.833430	6.562434	0.745001
58	1	0	-2.715568	-5.151597	4.572309
59	1	0	-3.900886	-3.254647	5.420718
60	1	0	6.041674	3.644057	-2.786209
61	1	0	4.804346	5.542230	-2.011394
62	1	0	-2.862159	-0.450474	-0.793754
63	1	0	-2.716052	1.117899	-1.613807
64	1	0	-2.141719	-0.105267	-3.759842
65	1	0	-2.360833	-1.649432	-2.916011
66	1	0	-5.305969	-1.403938	-4.992387
67	1	0	-3.645668	-0.898534	-5.422602
68	1	0	-3.909992	-2.411615	-4.509524
69	1	0	-5.702288	0.710477	-3.959443
70	1	0	-4.045303	1.265996	-4.334797
71	1	0	-4.648982	1.319456	-2.653958
72	1	0	2.775937	-0.685408	0.938372
73	1	0	2.804635	1.066593	1.227194
74	1	0	2.191487	-1.115129	3.310039
75	1	0	2.074196	0.626197	3.624430
76	1	0	4.915165	-0.825174	1.667857
77	1	0	4.394228	-2.104179	2.801938
78	1	0	5.873650	-1.157610	3.135956
79	1	0	3.683284	-1.489385	5.076396
80	1	0	3.488584	0.232866	5.510812
81	1	0	5.125238	-0.455709	5.298483
82	6	0	4.653566	1.253026	3.319285
83	1	0	4.671613	1.513238	2.261984
84	1	0	5.670291	1.240101	3.715578
85	1	0	4.046820	1.972731	3.870918
86	6	0	-5.003352	-1.318962	-2.333472
87	1	0	-4.999705	-0.733320	-1.414893
88	1	0	-4.589336	-2.311067	-2.146376
89	1	0	-6.022780	-1.405161	-2.713375
90	1	0	-1.212869	-4.974964	2.540981
91	1	0	-3.712987	-0.976754	4.329482
92	1	0	-4.756565	2.631073	2.246420
93	1	0	-1.781756	5.838385	-0.232547
94	1	0	2.493717	5.291256	-0.988167
95	1	0	5.099044	1.291120	-2.620432
96	1	0	3.714061	-2.706020	-3.845207
97	1	0	0.348470	-5.549631	-1.419545

TD–DFT output

HOMO**: 196**, LUMO**: 197**

Excited State 1: Singlet-A 1.9244 eV 644.27 nm f=0.3268 <S**2>=0.000

188 ->198	0.10720
192 ->198	0.10332
196 ->197	0.69235

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

Total Energy, E(TD-HF/TD-DFT) = -2612.81027118

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

Excited State 2: Singlet-A 1.9512 eV 635.43 nm f=0.3198 <S**2>=0.000

188 ->197	-0.10895
192 ->197	-0.10842
196 ->198	0.69009

Excited State 3: Singlet-A 3.0390 eV 407.98 nm f=0.0007 <S**2>=0.000

193 ->198	0.13674
195 ->197	0.66389
195 ->198	0.13929

Excited State	4:	Singlet-A	3.0902 eV	401.22 nm	f=0.0026	<S**2>=0.000
192 ->197		-0.16845				
193 ->197		0.28985				
194 ->197		0.10968				
195 ->197		-0.11531				
195 ->198		0.58613				
Excited State	5:	Singlet-A	3.1953 eV	388.02 nm	f=0.0023	<S**2>=0.000
188 ->198		0.15452				
192 ->197		0.13384				
192 ->198		-0.11807				
193 ->197		-0.12713				
194 ->197		0.62693				
Excited State	6:	Singlet-A	3.2280 eV	384.09 nm	f=0.0009	<S**2>=0.000
188 ->197		0.20949				
192 ->197		-0.19316				
193 ->197		-0.10414				
193 ->198		-0.11674				
194 ->198		0.60233				
Excited State	7:	Singlet-A	3.2833 eV	377.62 nm	f=0.0015	<S**2>=0.000
191 ->197		0.15765				
191 ->198		0.10879				
192 ->197		0.17325				
192 ->198		-0.25556				
193 ->197		-0.22790				
193 ->198		0.47737				
194 ->198		0.12887				
195 ->197		-0.16473				
195 ->198		0.13940				
Excited State	8:	Singlet-A	3.3140 eV	374.12 nm	f=0.0026	<S**2>=0.000
189 ->197		-0.10618				
189 ->198		0.10780				
190 ->197		0.21794				
191 ->198		-0.15496				
192 ->197		-0.23862				
192 ->198		-0.16521				
193 ->197		0.38313				
193 ->198		0.26545				
194 ->197		0.12514				
195 ->198		-0.25613				
Excited State	9:	Singlet-A	3.3379 eV	371.44 nm	f=0.0006	<S**2>=0.000
189 ->197		-0.22285				
190 ->198		0.22094				
191 ->197		0.52223				
193 ->198		-0.14382				
196 ->199		0.26813				
Excited State	10:	Singlet-A	3.3764 eV	367.21 nm	f=0.0026	<S**2>=0.000
189 ->197		-0.13809				
190 ->197		0.10733				
190 ->198		-0.40425				
191 ->198		0.24141				
196 ->199		0.44864				

References for Supporting Information

[i] Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005**, *38*, 381.

[ii] Sheldrick, G. M. *Acta Crystallogr. C, Struct. Chem.* **2015**, *71*, 3-8.

[iii] Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. *J. Cryst. Soc. Jpn.* **2009**, *51*, 218-224.

[iv] Nyokong, T.; Antunes, E. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific: Singspore, 2010; Vol. 7, pp 247-357.

[v] Adarsh, N.; Shanmugasundaram, M.; Avirah, R. R.; Ramaiah, D. *Chem. Eur. J.* **2012**, *18*, 12655-12662.

[vi] Furuyama, T.; Satoh, K.; Kushiya, T.; Kobayashi, N. *J. Am. Chem. Soc.* **2014**, *136*, 765-776.

[vii] Jiang, X.-J.; Lo, P.-C.; Yeung, S.-L.; Fong, W.-P.; Ng, D. K. P. *Chem. Commun.* **2010**, *46*, 3188-3190.

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

[ix] *Gaussian 09*, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

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