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Supporting Information

Carbenaporphyrins: No Longer Missing Ligands in N-Heterocyclic Carbene Chemistry

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1. General Information

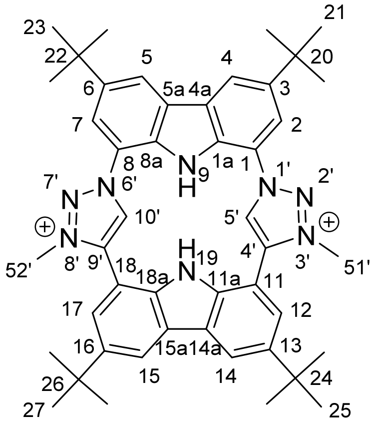
Unless otherwise stated, all reactions were carried out under an argon atmosphere in dried and degassed solvents using Schlenk technique. Toluene, tetrahydrofuran, dichloromethane and diethyl ether were purchased from Sigma Aldrich and dried using an MBraun SPS-800 solvent purification system. Deuterated solvents were dried with standard purification methods and degassed.[1] Chemicals from commercial suppliers were degassed through freeze-pump-thaw cycles prior to use. The precursors **2**[2] and **3**[3] were synthesized according to the literature. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE II+ 400 spectrometer, a Bruker AVANCE AVII+ 500 or a Bruker Avance III HDX 600 or a Bruker Avance III HDX 700. Chemical shifts δ (ppm) are given relative to the solvent's residual proton and carbon signal respectively: THF-d$_8$: 3.58 ppm (^{1}H NMR) and 67.57 ppm (^{13}C NMR); CD_3CN: 1.94 ppm (^{1}H NMR) and 1.32 ppm (^{13}C NMR); DMSO-d_6: 2.50 ppm (^{1}H NMR) and 39.51 ppm (^{13}C NMR), $CDCl_3$: 7.27 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR), CD_2Cl_2: 5.32 ppm (^{1}H NMR) and 53.84 ppm (^{13}C NMR). Coupling constants (*J*) are expressed in Hz. Signals were assigned as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and variations thereof. Assignment of the peaks was made using 2D NMR correlation spectra. The mass spectra were recorded on a Bruker amazon SL mass spectrometer. UV/VIS spectra were measured using a Jasco V-770 UV-Visible/NIR spectrophotometer. Fluorescence spectra were recorded with a PTI Quantamaster QM4 spectrofluorometer equipped with a 75 W continuous xenon short arc lamp as excitation source. Spectral selection was achieved by a single grating monochromator with 1200 grooves/mm (300 nm blaze). The emission was monitored using a single grating monochromator at 1200 grooves/mm (500 nm blaze) and detected with the equipped standard detector module. Samples were prepared under inert atmosphere and measured in quartz fluorescence cuvettes (pathlength of 10 mm) with dry solvents. Solid state samples were measured under inert atmosphere in a glass tube. The elemental analysis was determined using a varioMICRO cube by the elemental analysis section of the Institut für Anorganische Chemie at the University of Tübingen and the high-resolution mass spectra were recorded using a Bruker Daltronics maXis 4G by the mass spectra section of the Institut für Organische Chemie at the University of Tübingen. The melting point was measured with a Büchi Melting Point M-560 apparatus.

X-ray structure analysis. Crystallographic data collection was carried out on a Bruker APEX Duo CCD with an Incoatec I*µ*S Microsource with a Quazar MX mirror using Mo K_α radiation (λ = 0.71073 Å) or using Cu K_α radiation (λ = 1.54056 Å) and a graphite monochromator. Corrections for absorption effects were applied using SADABS.[4] All structures were solved by direct methods using SHELXS and refined using SHELXL.[5] CCDC 2022047 (**5**), 2022048 (**8**) and 2022049 (**6**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations. All calculations were carried out using the ORCA[6] software package. The RI approximation was used for GGA calculations, whereas the RIJCOSX approximation was used for hybrid-DFT calculations.[7] All structures were optimized using the BP86 functional[8] and the def2-TZVP[7] basis set with convergence criteria for minimum energy change of 10^{-8} Hartree for the SCF part and 10^{-6} Hartree for the geometry optimization. TD-DFT[9] calculations were carried out using the *in vacuo* optimized geometry with the B3LYP functional and the def2-TZVP basis set with solvent effects being applied with the conductor-like polarizable continuum model for THF. The cartesian coordinates of the geometry optimized structures are provided as the supplementary file DFT_coordinates.xyz.

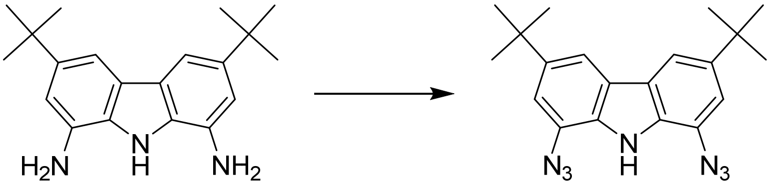
2. Numbering Scheme

For the assignment of the atoms in the X-ray molecular structure and the peaks in NMR spectra, the following numbering scheme was used:



3. Experimental Details and Characterization

Synthesis of 1,8-Diazido-3,6-di-*tert*-butyl-carbazole (**4**)



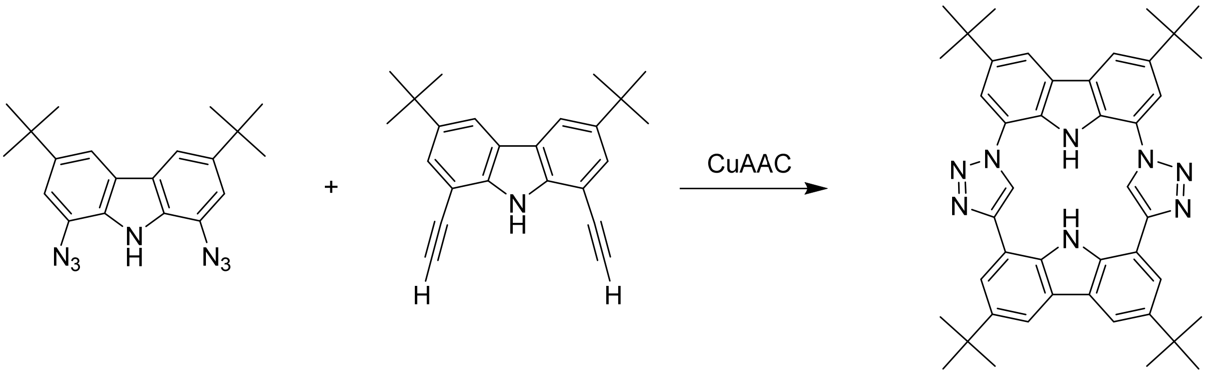
According to a general procedure,[10] 1,8-diamino-3,6-di-*tert*-butyl-carbazol (666 mg, 2.15 mmol, 1.0 eq) was dissolved in a mixture of 8 mL hydrochloric acid (37 %), 8 mL water and 50 mL ethanol. After cooling in an ice bath at 0 °C a solution of sodium nitrite (446 mg, 6.46 mmol, 3.0 eq) in 1 mL of water was added over a period of 10 min so that the temperature stayed below 5 °C. After stirring for 30 min a solution of sodium azide (420 mg, 6.46 mmol, 3.0 eq) in 2 mL of water was added slowly over a period of 10 min so that the temperature stayed below 5 °C. The reaction mixture was stirred for 1 h at 0 °C and another 2 h at room temperature. After addition of 75 mL of water and 150 mL of ethyl acetate the organic layer was separated, and the aqueous phase was extracted three times with 75 mL of ethyl acetate. The combined organic phases were washed two times each with 50 mL of saturated sodium hydrogen carbonate solution and 50 mL of brine. After drying over magnesium sulfate and removing the solvent *in vacuo*, the crude product was purified by means of column chromatography (silica; dichloromethane:petroleum ether (40/60) 1:3) yielding 722 mg (93 %) of product **4** as a light yellow, light sensitive solid.

^{1}H NMR (DMSO-d$_6$, 400.11 MHz): δ 11.15 (s, 1H, H-9), 8.03 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-4/5 or H-2/7), 7.28 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-4/5 or H-2/7), 1.41 (s, 18H, $C(CH_3)_3$).

^{1}H NMR (CD_2Cl_2, 400.11 MHz): δ 8.16 (s, 1H, H-9), 7.86 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-4/5), 7.28 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-2/7), 1.45 (s, 18H, $C(CH_3)_3$).

^{13}C NMR (DMSO-d$_6$, 100.61 MHz): δ 143.0 (C3/6), 130.3, 124.5, 122.8 (C1/8, C1a/8a, C4a/5a), 113.85, 113.0 (C2/7, C4/5), 34.7 ($\mathit{C}(CH_3)_3$), 31.7 ($C(\mathit{C}H_3)_3$).

Synthesis of macrocycle **5**

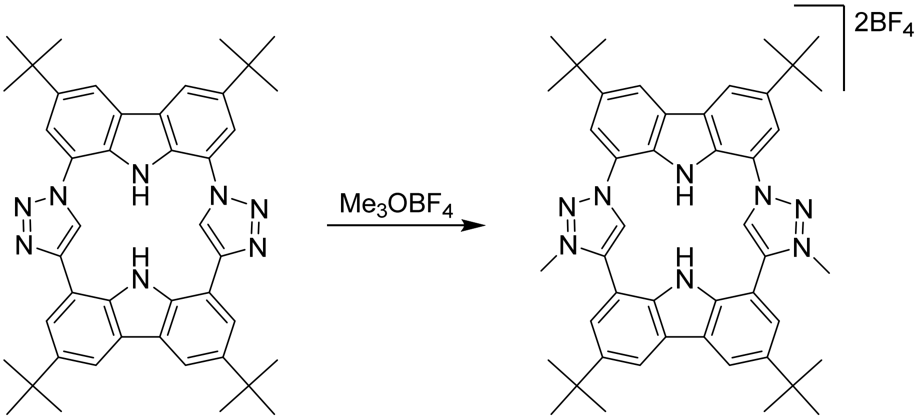


In a modified procedure,[11] a round bottom flask with copper sulfate pentahydrate (6.0 mg, 22 μmol, 0.1 eq), TBTA (12 mg, 22 μmol, 0.1 eq) and sodium ascorbate (1.2 mg, 66 μmol, 0.3 eq) were put under argon. 0.5 mL of triethyl amine and 30 mL of degassed tetrahydrofuran were added. The flask was covered with a septum and heated to 60 °C. Then a solution of 1,8 -diazido-3,6-di-*tert*-butyl-carbazole (80.0 mg, 220 μmol, 1 eq) and 1,8 -diethinyl-3,6-di-*tert*-butyl-carbazole (72.0 mg, 220 μmol, 1 eq) in 10 mL degassed tetrahydrofuran was added with a syringe pump at 10 μL/min. After completion, the reaction was stirred at 60 °C for 3 h. After concentration of the suspension *in vacuo* to 2 mL, 5 mL of methanol were added and the precipitate was filtered off and washed with 1 mL of methanol to yield 79.0 mg (52 %) of the product **5** as a white solid.

^{1}H NMR (THF-d$_8$, 500.11 MHz): δ 10.19 (s, 1H, H-9), 9.79 (s, 2H, H-5'/10), 9.43 (s, 1H, H-19), 8.41 (d, $^4J_{HH}$=1.7 Hz, 2H, H-2/7 or H-4/5), 8.24 (d, $^4J_{HH}$ = 1.9 Hz, 2H, H-14/15), 8.19 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-2/7 or H-4/5), 8.10 (d, $^4J_{HH}$ = 1.9 Hz, 2H, H-12/17), 1.57 (s, 18H, H-25/27), 1.55 (s, 18H, H-21/23).

^{13}C NMR (THF-d$_8$, 125.11 MHz): δ 146.53, 146.48 (C3/6, C4'/9'), 144.7 (C13/16), 139.4 (C14a/15a), 133.4 (C4a/5a), 128.6 (C1/C8), 126.8 (C11/18), 124.8 (C5'/10'), 124.3 (C1a/8a), 122.6 (C12/17), 118.9, 118.5, 118.3 (C2/7, C4/5, C14/15), 116.1 (C11a/18a), 36.1 (C20/22), 35.8 (C24/26), 32.6 (C25/27), 32.4 (C21/23).

Synthesis of macrocycle **6**



A suspension of macrocycle **5** (100 mg, 145 *μ*mol, 1 eq) and trimethyloxonium tetrafluoroborate (42.9 mg, 290 *μ*mol, 2 eq) in 20 mL of dichloromethane was stirred over night at room temperature. After concentration *in vacuo* to about 1 mL, 25 mL of diethyl ether were added and the precipitate was filtered off and washed twice with 5 mL diethyl ether to give 129 mg (99 %) of product **6** as an off-white solid.

^{1}H NMR (THF-d$_8$, 400.11 MHz): δ 10.01 (br s, 2H). 9.77 (br s, 2H), 8.60 (br s, 2H), 8.51 (br s, 2H), 8.07 (br s, 2H), 7.99 (br s, 2H), 4.55 (s, 6H), 1.53 (br s, 36H).

^{1}H NMR (CD$_3$CN, 400.11 MHz): δ 9.58 (br s, 2H), 9.51 (s, 2H), 8.67 (s, 2H), 8.62 (d, $^4J_{HH}$ = 1.3 Hz, 2H), 8.07 (s, 2H), 7.94 (d, $^4J_{HH}$ = 1.3 Hz, 2H), 4.52 (s, 6H), 1.56 (s, 18H), 1.55 (s, 18H).

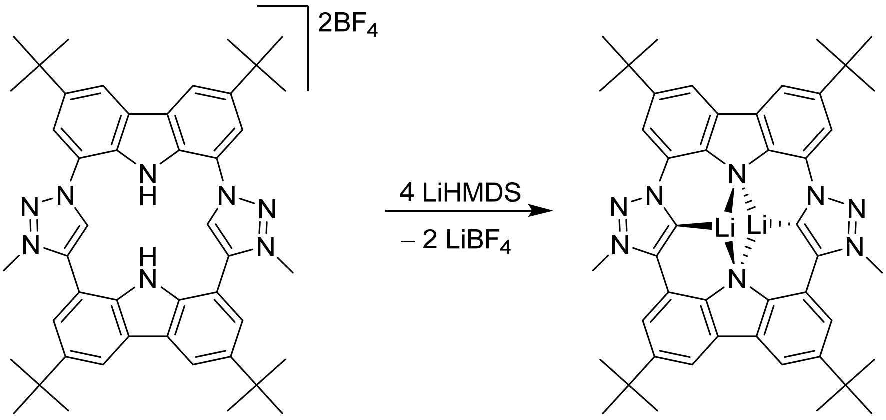
^{1}H NMR (CD$_2$Cl$_2$, 400.11 MHz): δ 9.92 (s, 2H, H-5'/10'), 9.40 (br s, 2H, H-9, H-19), 8.48 (d, $^4J_{HH}$ = 1.3 Hz, 2H, H-4/5), 8.47 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-14/15), 7.97 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-2/7), 7.73 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-12/17), 4.51 (s, 6H, Me), 1.56 (s, 18H, H-25/27), 1.55 (s, 18H, H-21/23).

^{13}C-NMR (CD$_2$Cl$_2$, 100.61 MHz): δ 146.8 (C3/6), 145.4 (C13/16), 142.1 (C4'/9'), 140.0 (C11a/18a), 134.7 (C1/8 or C1a/8a or C4a/5a), 132.2 (C5'/10'), 128.3 (C1/8 or C1a/8a or C4a/5a), 126.3 (C14a/C15a), 124.3 (C12/17), 122.5, 122.4 (C4/5, C14/15), 121.0 (C1/8 or C1a/8a or C4a/5a), 119.7 (C2/7), 106.1 (C11/18), 39.2 (Me), 35.9, 35.7 (C(CH$_3$)$_3$), 32.2, 32.1 (C(CH$_3$)$_3$).

HR-ESI$^+$ (MeCN): $[C_{46}H_{54}N_8]^{2+}$ m/z = 359.22361 – calculated: 359.22302.

m.p.: 340 °C (dec.)

Synthesis of the dilithium complex **7**



A solution of lithium bis(trimethylsilyl)amide (6.7 mg, 40 *μ*mol, 4 eq) in 0.3 mL tetrahydrofuran-d_8 was added to a suspension of macrocycle **6** (9.0 mg, 10 *μ*mol, 1 eq) in 0.2 mL tetrahydrofuran-d_8 to give the product **7** in 99 % yield (NMR) as a yellow solution.

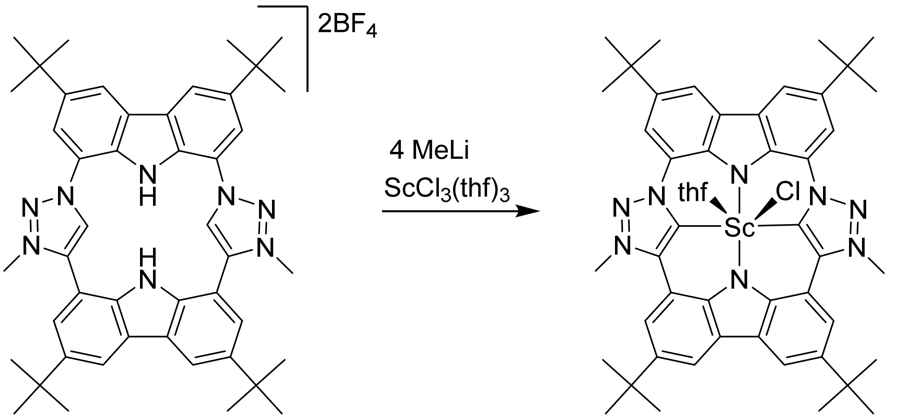
^{1}H NMR (THF-d_8, 300.11 MHz): δ 8.22 (d, $^4J_{HH}$ = 2.0 Hz, 2H, H-4/5 or H-14/15), 8.23 (d, $^4J_{HH}$ = 1.8 Hz, 2H, H-4/5 or H-14/15), 8.04 (d, $^4J_{HH}$ = 1.8 Hz, 2H, H-2/7), 7.69 (d, $^4J_{HH}$ = 2.0 Hz, 2H, H-12/17), 4.48 (s, 6H, Me), 1.57 (s, 18H, C(CH$_3$)$_3$), 1.56 (s, 18H, C(CH$_3$)$_3$).

^{13}C NMR (THF-d_8, 125.11 MHz): δ 187.9 (C5'/C10'), 151.7 (C11a/18a), 149.2 (C4'/C9'), 146.0 (C1a/C8a), 137.2 (C3/6), 136.1 (C13/16), 129.5, 128.7, 128.0 (C1/8 or C4a/5a or C11/C18 or C14a/15a), 120.5 (C12/17), 117.0, 116.8 (C4/5, C14/15), 116.1 (C1/8 or C4a/5a or C11/C18 or C14a/15a), 113.7 (C2/7), 37.3 (Me), 35.5 (C20/22), 35.4 (C24/26), 33.0 (C21/23 + C25/27).

^{7}Li NMR (THF-d_8, 116.6 MHz): δ 0.57 (br s).

^{7}Li NMR (THF-d_8, 116.6 MHz, −80 °C): δ 1.90 (br s).

Synthesis of complex **8**



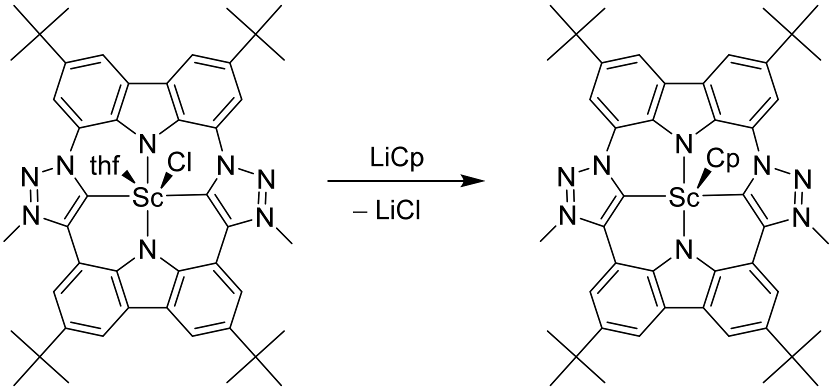
After *in situ* deprotonation of macrocycle **6** (8.9 mg, 10 *μ*mol) in 0.5 mL of tetrahydrofuran-d$_8$ with methyl lithium (1.0 mg, 45 *μ*mol), [ScCl$_3$(thf)$_3$] (3.6 mg, 10 *μ*mol) was added to obtain the product **8** quantitatively (NMR) as an orange solution, which shows an orange fluorescence (excitation at λ = 366 nm).

^{1}H NMR (THF-d$_8$, 400.11 MHz): δ 8.32 (s, 4H, H-4/5 + H-12/17 or H-14/15), 8.28 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-12/17 or H-14/15), 7.98 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-2/7), 4.64 (s, 6H, Me), 1.59 (s, 18H, C(CH$_3$)$_3$), 1.57 (s, 18H, C(CH$_3$)$_3$).

^{13}C NMR (THF-d$_8$, 125.76 MHz): δ 148.0 (C1a/8a), 145.7 (C12/17), 141.6 (C11a/18a), 140.2, 139.2 (C3/6 and C13/16), 129.0, 127.5 (C4a/5a and C14a/15a), 126.5 (C11/18), 120.5 (C2/7), 117.8, 117.7 (C4/5 and C14/15), 114.4 (C1/8), 113.1 (C12/17), 38.8 (Me), 35.3, 35.2 (*C*(CH$_3$)$_3$), 32.4(C(*C*H$_3$)$_3$).

^{45}Sc NMR (121.5 MHz, THF-d$_8$): δ 285.0.

Synthesis of complex **9**



Lithium cyclopentadienide (1.6 mg, 22 *μ*mol) was added to an *in situ* prepared solution of complex **8** (from **6** (20 mg, 22 *μ*mol) and LiHMDS (15 mg, 90 *μ*mol) in 1.5 mL tetrahydrofuran). After removing all volatiles *in vacuo,* the solid was extracted two times with 1.5 mL toluene, and the combined extracts were dried *in vacuo*. The resulting orange residue was washed with pentane (2x 1.5 mL) and yielded 14.6 mg (80%) of complex **9** after drying *in vacuo* as an orange solid.

^{1}H NMR (THF-d_8, 400.11 MHz): δ 8.36 (d, $^4J_{HH}$ = 1.9 Hz, 2H, H-4/5), 8.35 (d, $^4J_{HH}$ = 1.8 Hz, 2H, H-12/17 or H-14/15), 8.33 (d, $^4J_{HH}$ = 1.8 Hz, 2H, H-12/17 or H-14/15), 8.03 (d, $^4J_{HH}$ = 1.9 Hz, 2H, H-2/7), 5.21 (s, 5H, Cp), 4.66 (s, 6H, Me), 1.61 (s, 18H, $C(CH_3)_3$), 1.59 (s, 18H, $C(CH_3)_3$).

^{1}H NMR (C_6D_6, 400.11 MHz): δ 8.75 (d, $^4J_{HH}$ = 1.8 Hz, H-14/15, 2H), 8.71 (d, $^4J_{HH}$ = 1.8 Hz, H-2/7 or H-4/5, 2 H), 8.68 (d, $^4J_{HH}$ = 1.8 Hz, H-2/7 or H-4/5, 2H), 7.64 (d, $^4J_{HH}$ = 1.8 Hz, H-12/17, 2H), 5.69 (s, 5H, Cp), 3.34 (s, 6H, Me), 1.61 (s, 18H, $C(CH_3)_3$),1.60 (s, 18H, $C(CH_3)_3$).

^{13}C NMR (THF-d_8, 125.76 MHz): δ 147.1 (C1a/8a), 145.3 (C12/17), 140.8 (C11a/18a), 140.4, 139.2 (C3/6, C13/16), 129.4 (C14a/15a), 127.9 (C4a/5a), 126.5 (C11/C18), 120.5 (C2/7), 118.0 (C4/5, C12/17 or C14/15), 114.2 (C1/8), 113.3 (C12/17 or C14/15), 110.4 (Cp), 38.9 (Me), 35.4, 35.3 (*C*(CH_3)$_3$), 32.4 (C(*C*H_3)$_3$).

^{45}Sc NMR (121.5 MHz, THF-d_8): δ 132.0.

HR-ESI$^+$ (MeCN): [$C_{51}H_{56}N_8Sc$]$^+$ m/z = 825.41709 – calculated: 825.41816.

EA: Calcd for $C_{51}H_{55}N_8Sc$*0.33 $LiBF_4$: C, 71.54; N, 13.09; H, 6.47; found: C, 71.53; N, 12.91; H, 6.52.

4. X-ray Crystal Structure Analysis

Table S1. Crystallographic data and structure refinement for compounds **5**, **6**, and **8**.

Compound	**5**	**6**	**8**
CCDC	2022047	2022049	2022048
Empirical formula	$C_{62}H_{84}N_8O_{4.50}$	$C_{58}H_{78}B_2F_8N_8O_3$	$C_{50}H_{58}ClN_8OSc$
Formula weight	1013.37	1108.90	867.45
Temperature	100(2) K	100(2) K	100(2) K
Radiation wavelength	MoK$_\alpha$ (λ = 0.71073 Å)	CuK$_\alpha$ (λ = 1.54178 Å)	MoK$_\alpha$ (λ = 0.71073 Å)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions	a = 13.358(2) Å	a = 13.3579(5) Å	a = 10.5932(3) Å
	b = 13.426(2) Å	b = 13.5935(5) Å	b = 15.9956(5) Å
	c = 15.830(3) Å	c = 18.6723(8) Å	c = 16.5273(5) Å
	α = 78.382(3)°	α = 98.686(3)°	α = 88.4420(10)°
	β = 85.129(3)°	β = 95.781(3)°	β = 72.5520(10)°
	γ = 88.732(3)°	γ = 95.576(3)°	γ = 88.0000(10)°
Volume	2770.8(8) Å^3	3312.8(2) Å^3	2669.57(14) Å^3
Z	2	2	2
Density (calculated)	1.215 Mg/m^3	1.112 Mg/m^3	1.079 Mg/m^3
Absorption coefficient	0.077 mm^{-1}	0.702 mm^{-1}	0.228 mm^{-1}
F(000)	1096	1176	920
Crystal size	0.277 x 0.198 x 0.122 mm^3	0.243 x 0.159 x 0.128 mm^3	0.273 x 0.155 x 0.101 mm^3
Theta range for data collection	1.318 to 28.322°.	2.410 to 69.240°.	1.292 to 30.333°.
Index ranges	-17<=h<=17, -17<=k<=17, -21<=l<=21	-16<=h<=16, -16<=k<=16, -22<=l<=22	-15<=h<=15, -22<=k<=22, -23<=l<=23
Reflections collected	66037	65562	142739
Independent reflections	13775 [R(int) = 0.0810]	11840 [R(int) = 0.1213]	15990 [R(int) = 0.0576]
Completeness to theta = 25.242°	100.0 %	96.5 %	99.9 %
Absorption correction	Numerical	Numerical	Numerical
Data / restraints / parameters	13775 / 162 / 751	11840 / 310 / 840	15990 / 66 / 628
Goodness-of-fit on F2	1.031	1.037	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1487	R1 = 0.0818, wR2 = 0.2196	R1 = 0.0591, wR2 = 0.1712
R indices (all data)	R1 = 0.0931, wR2 = 0.1715	R1 = 0.1155, wR2 = 0.2505	R1 = 0.0758, wR2 = 0.1859
Largest diff. peak and hole	0.732 and -0.628 e·Å^{-3}	0.876 and -0.637 e·Å^{-3}	0.667 and -0.798 e·Å^{-3}

5. UV/Vis and Fluorescence Spectra

*a) Experimental and calculated UV/Vis, and fluorescence spectra of **6** and **9**.*

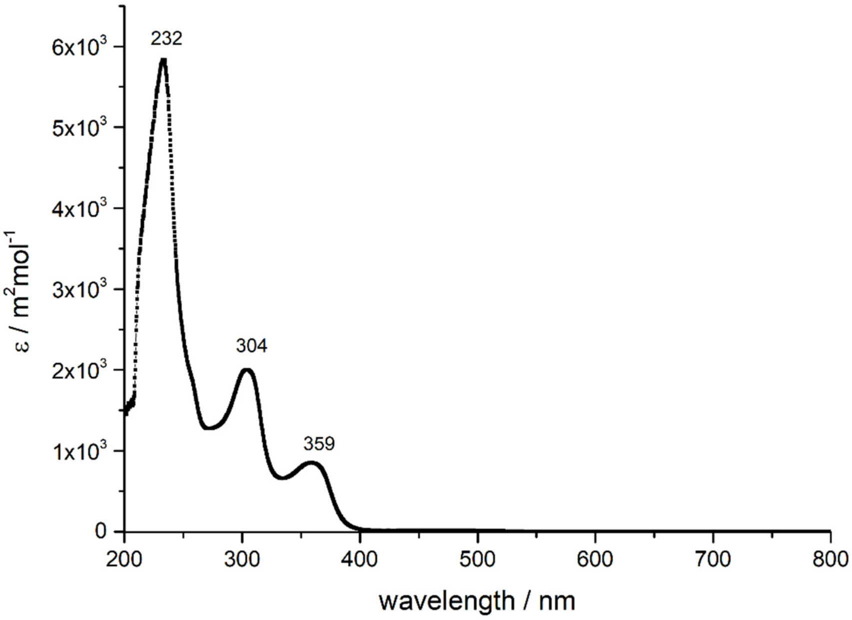


Figure S1. Absorption spectrum of **6** (tetrahydrofuran, c = $6*10^{-5}$ M).

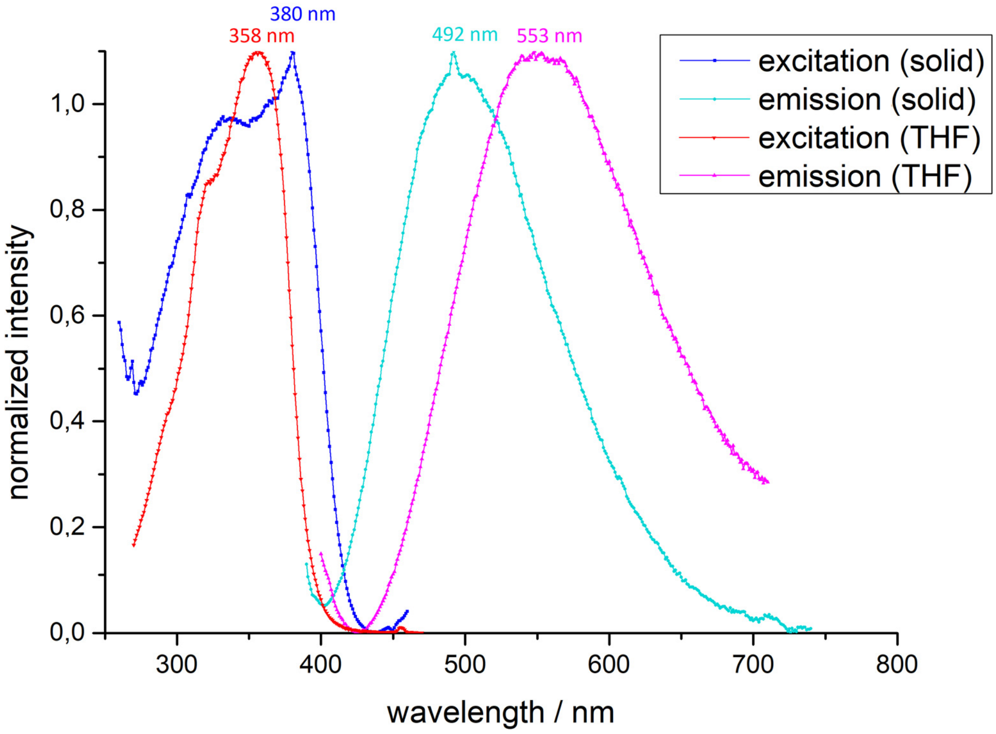


Figure S2. Excitation and emission spectra of **6** in the solid and in solution (tetrahydrofuran, c = $5*10^{-5}$ M).

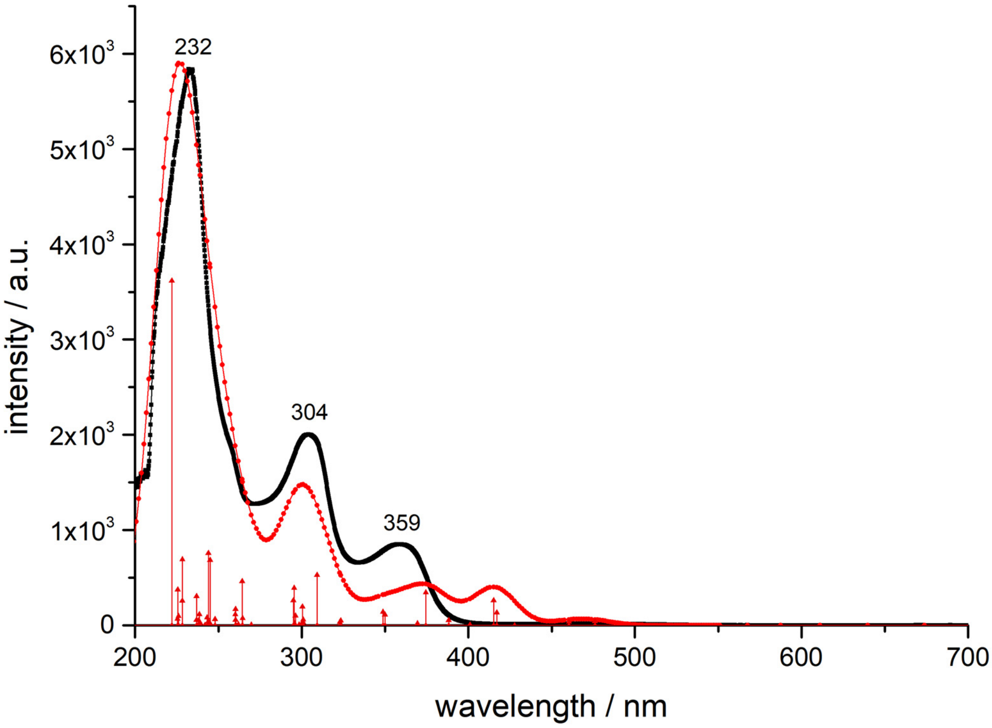


Figure S3. Comparison of the measured (black) and the calculated (red) absorption spectrum of **6** (calculated with TD-DFT B3LYP/def2-TZVP, CPCM(thf)).

Table S2. Calculated states of the absorption spectrum of compound **6** via transition electric dipole moments (TD-DFT: B3LYP/def2-TZVP, RIJCOSX, CPCM (thf)).

State	**Energy**	**Wavelength**	f_{osc}	T^2	T_X	T_Y	T_Z
	(cm^{-1})	(nm)		(a.u.^{2})	(a.u.)	(a.u.)	(a.u.)
1	21003.0	476.1	0.01384278	0.21698	-0.02016	-0.46490	0.02097
2	21717.4	460.5	0.01337773	0.20279	-0.44678	-0.03877	0.04098
3	24086.6	415.2	0.08630565	1.17961	-0.39016	-0.89879	-0.46859
4	23978.6	417.0	0.04409531	0.60540	-0.68311	0.33272	0.16751
5	23377.0	427.8	0.00028333	0.00399	-0.01463	-0.06145	-0.00047
6	24940.4	401.0	0.00211681	0.02794	0.09492	0.10469	0.08929
7	25759.6	388.2	0.01795857	0.22951	-0.42121	0.20748	0.09513
8	26705.6	374.5	0.11444217	1.41078	-0.31568	-1.05558	-0.44372
9	28669.9	348.8	0.04711680	0.54104	-0.10590	-0.72694	-0.03704
10	27064.1	369.5	0.00696615	0.08474	-0.09590	-0.25146	-0.11095
11	30906.0	323.6	0.01643865	0.17511	0.41728	-0.02172	-0.02261
12	32340.8	309.2	0.17583648	1.78992	-1.30725	0.25990	0.11610
13	28572.8	350.0	0.03699546	0.42626	-0.63693	0.13268	0.05451

14	33228.7	300.9	0.02066903	0.20478	0.44908	-0.05427	-0.01269
15	30966.5	322.9	0.01183935	0.12587	-0.15731	-0.31722	-0.02218
16	33359.1	299.8	0.00430687	0.04250	0.19214	-0.06337	-0.03961
17	33814.2	295.7	0.00706818	0.06882	-0.06891	-0.16753	-0.18974
18	33236.9	300.9	0.01090334	0.10800	0.08367	0.29379	-0.12117
19	33897.8	295.0	0.08675355	0.84254	-0.23486	-0.87144	-0.16728
20	33762.0	296.2	0.03318690	0.32360	0.55518	-0.11748	-0.03976
21	33285.2	300.4	0.06488933	0.64180	0.16996	0.70045	0.34969
22	33838.9	295.5	0.13067945	1.27135	-0.23671	-0.99638	-0.47175
23	33505.0	298.5	0.00254185	0.02498	0.15318	-0.03464	-0.01769
24	37845.5	264.2	0.15302369	1.33113	1.12549	-0.23327	-0.09992
25	38424.8	260.2	0.05712403	0.48942	-0.68560	0.12795	0.05485
26	38171.5	262.0	0.00307970	0.02656	-0.15263	0.05580	-0.01230
27	38411.6	260.3	0.01848100	0.15839	0.07807	0.13684	0.36548
28	37788.9	264.6	0.02521872	0.21970	-0.45905	0.08634	0.03895
29	38432.8	260.2	0.03829531	0.32803	0.55492	-0.12839	-0.06009
30	37066.8	269.8	0.00236965	0.02105	0.00932	-0.13437	0.05388
31	40839.7	244.9	0.00792963	0.06392	-0.20957	-0.14094	-0.01179
32	40989.8	244.0	0.25123572	2.01781	0.27468	1.36166	0.29708
33	41343.4	241.9	0.00106222	0.00846	0.09039	-0.00017	-0.01698
34	40801.8	245.1	0.22749408	1.83555	0.33864	1.20526	0.51790
35	40336.9	247.9	0.02151662	0.17561	-0.41698	0.03777	0.01763
36	38382.8	260.5	0.00094831	0.00813	-0.03751	-0.06994	-0.04284
37	42221.7	236.8	0.10134556	0.79021	0.81045	-0.34038	-0.13237
38	41972.6	238.3	0.01736358	0.13619	0.36441	0.05657	0.01407
39	41917.5	238.6	0.03861064	0.30324	0.13227	0.50136	0.18544
40	41101.9	243.3	0.02773430	0.22214	0.42286	-0.19540	-0.07177
41	43781.6	228.4	0.23029750	1.73170	0.42452	1.19238	0.36016
42	43789.0	228.4	0.08613536	0.64758	-0.28934	-0.73385	-0.15911
43	44346.8	225.5	0.02277526	0.16907	0.31736	0.25270	0.06708
44	40978.5	244.0	0.01391179	0.11176	0.26564	0.20273	0.01001
45	42221.1	236.8	0.01960128	0.15284	0.35591	-0.14341	-0.07485
46	45034.3	222.1	1.19912856	8.76594	-2.85524	0.72639	0.29305
47	42019.9	238.0	0.00208797	0.01636	0.10470	-0.07121	-0.01803
48	44226.3	226.1	0.03285925	0.24460	-0.47914	-0.12253	0.00234
49	44318.0	225.6	0.12466355	0.92605	-0.03687	-0.92347	-0.26813
50	41850.3	238.9	0.00935810	0.07361	-0.01596	-0.26259	-0.06637

Table S3. Orbital contribution to the first 10 excited states (singlets; HOMO = 191; LUMO = 192) in compound **6**.

State	The weight of the individual excitations (printed if larger than 10^{-02})
State 1	190a -> 192a : 0.020308 (c= -0.14250505) 191a -> 192a : 0.948251 (c= -0.97378158) 191a -> 193a : 0.013213 (c= 0.11494996)
State 2	190a -> 193a : 0.102587 (c= -0.32029249) 191a -> 192a : 0.013116 (c= -0.11452432) 191a -> 193a : 0.867916 (c= -0.93161984)
State 3	188a -> 193a : 0.029493 (c= -0.17173637) 190a -> 192a : 0.907056 (c= -0.95239476) 190a -> 193a : 0.015373 (c= 0.12398619) 191a -> 192a : 0.016272 (c= 0.12755996)
State 4	190a -> 192a : 0.016225 (c= 0.12737563) 190a -> 193a : 0.840674 (c= 0.91688252) 191a -> 193a : 0.096729 (c= -0.31101215) 191a -> 195a : 0.010018 (c= -0.10009046)
State 5	189a -> 192a : 0.969575 (c= 0.98467004)
State 6	189a -> 193a : 0.824055 (c= -0.90777463) 191a -> 194a : 0.148828 (c= 0.38578229)
State 7	188a -> 192a : 0.929377 (c= 0.96404203) 188a -> 196a : 0.022191 (c= -0.14896728)
State 8	188a -> 193a : 0.792993 (c= 0.89050177) 190a -> 192a : 0.018915 (c= -0.13753151) 191a -> 194a : 0.138492 (c= -0.37214503)
State 9	188a -> 193a : 0.136284 (c= -0.36916610) 189a -> 193a : 0.148993 (c= -0.38599568) 189a -> 195a : 0.016680 (c= -0.12914919) 189a -> 200a : 0.010315 (c= -0.10156449) 190a -> 192a : 0.011785 (c= 0.10855971) 191a -> 194a : 0.627826 (c= -0.79235441)
State 10	190a -> 194a : 0.965211 (c= 0.98245176)

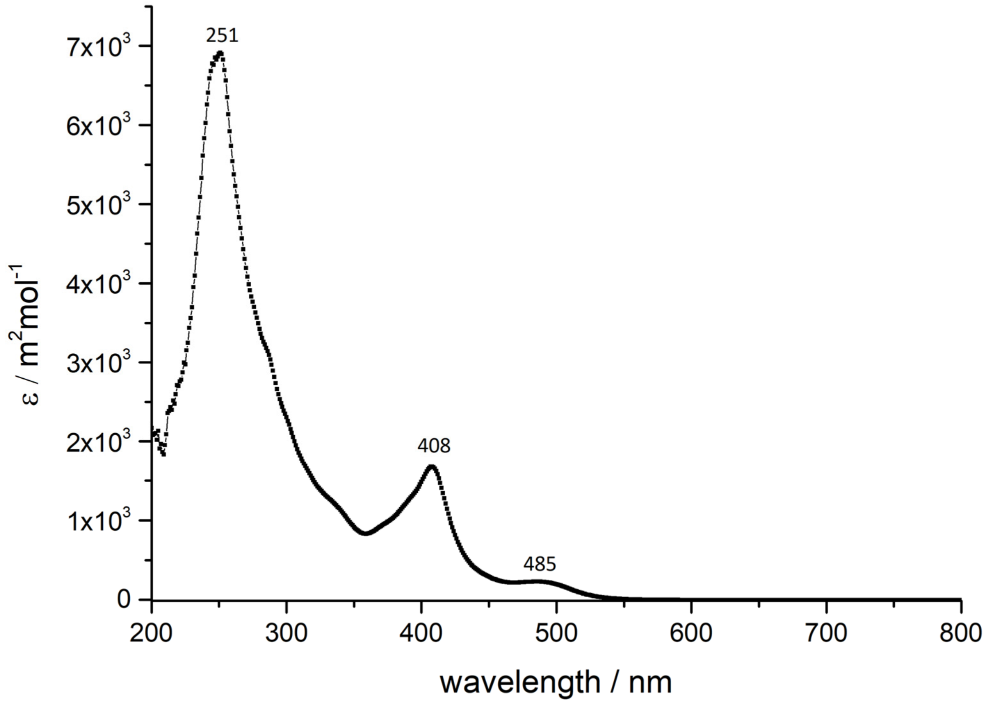


Figure S4. Absorption spectrum of complex **9** (tetrahydrofuran, c = 5*10^{-5} M).

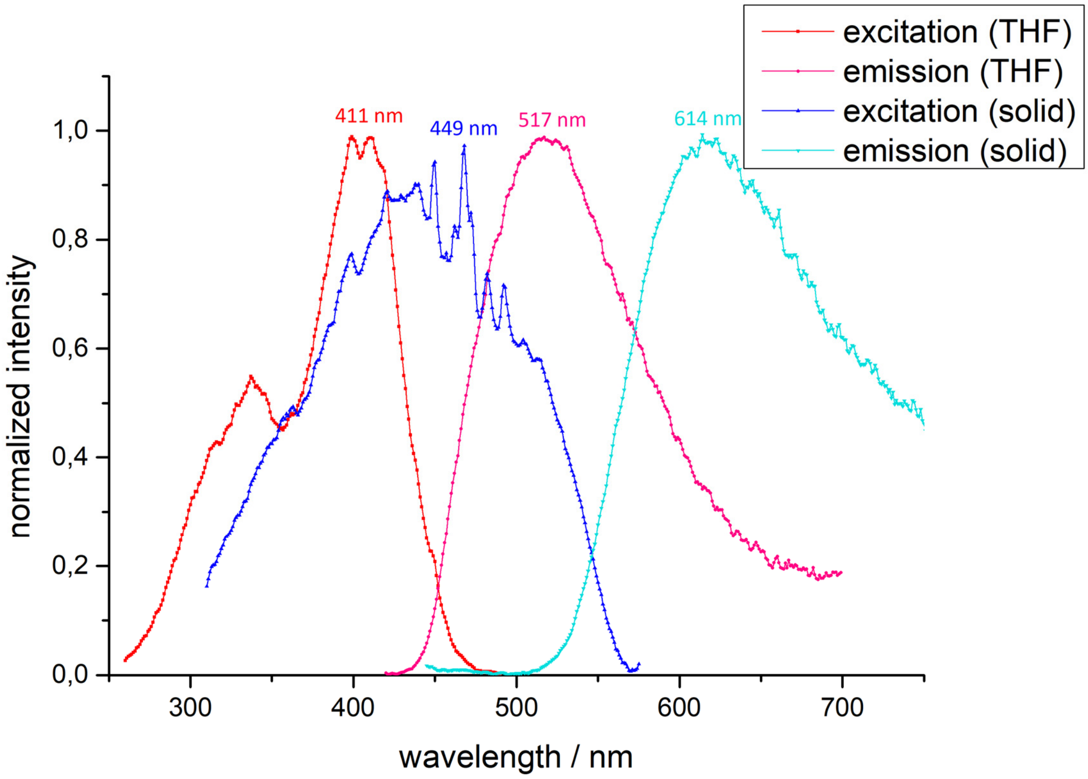


Figure S5. Excitation and emission spectra of complex **9** in the solid and in solution (tetrahydrofuran, c = 5*10^{-5} M).

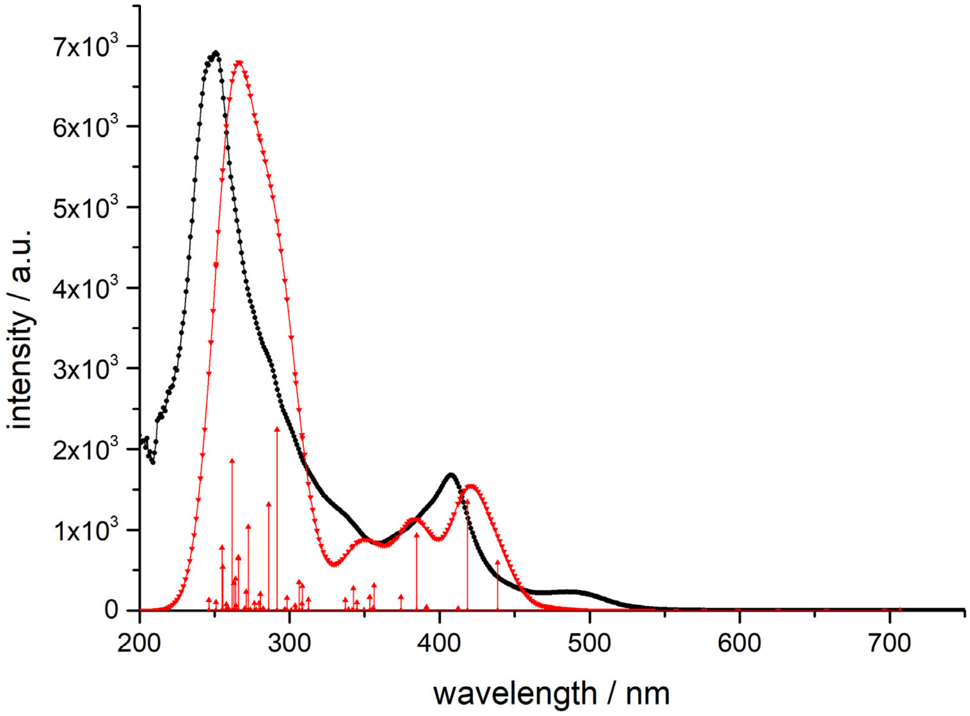


Figure S6. Comparison of the measured (black) and the calculated (red) absorption spectrum of complex **9** (calculated with TD-DFT B3LYP/def2-TZVP, CPCM (thf)).

Table S4. Calculated states of the absorption spectrum of complex **9** via transition electric dipole moments (TD-DFT: B3LYP/def2-TZVP, RIJCOSX, CPCM (thf)).

State	Energy	Wavelength	f_{osc}	T^2	T_X	T_Y	T_Z
	(cm^{-1})	(nm)		(a.u.^{2})	(a.u.)	(a.u.)	(a.u.)
1	21213.8	471.4	0.004630023	0.07185	0.00986	-0.24939	0.09777
2	22797.2	438.7	0.082934879	1.19765	-0.01073	0.36573	1.03140
3	23889.0	418.6	0.188579920	2.59881	0.99908	1.19196	-0.42410
4	24251.1	412.4	0.003409883	0.04629	0.01337	0.08950	0.19519
5	25991.3	384.7	0.131015360	1.65947	0.79075	0.96223	-0.32910
6	25561.2	391.2	0.005532032	0.07125	0.00643	-0.08755	-0.25208
7	28301.2	353.3	0.022701202	0.26407	-0.00478	0.17315	0.48381
8	28593.4	349.7	0.000496688	0.00572	0.07296	-0.01820	0.00798
9	29271.0	341.6	0.000001764	0.00002	-0.00400	-0.00066	-0.00185
10	28064.4	356.3	0.043515293	0.51046	-0.00456	-0.24249	-0.67204
11	26724.0	374.2	0.022901103	0.28212	0.40676	0.32252	-0.11243
12	29657.0	337.2	0.017778180	0.19735	0.00581	0.15580	0.41598
13	28105.8	355.8	0.003733698	0.04373	-0.09517	-0.17738	0.05668
14	29000.3	344.8	0.013426521	0.15242	0.28060	0.25255	-0.09950
15	29196.6	342.5	0.038134435	0.42999	-0.60602	-0.23562	0.08496
16	29474.4	339.3	0.001437383	0.01605	0.00210	-0.04101	-0.11987
17	31988.5	312.6	0.018937376	0.19490	0.00453	0.15525	0.41324
18	32414.5	308.5	0.041888976	0.42544	0.00444	-0.21768	-0.61485

19	32931.4	303.7	0.008021513	0.08019	-0.01062	0.08487	0.26995
20	32650.8	306.3	0.048762361	0.49166	-0.39031	-0.55207	0.18583
21	33220.2	301.0	0.000206102	0.00204	-0.00120	0.01548	0.04244
22	32866.4	304.3	0.000720196	0.00721	-0.00146	-0.03025	-0.07935
23	34299.0	291.6	0.315304368	3.02639	-0.02337	0.57250	1.64258
24	33529.5	298.2	0.021790577	0.21395	0.31381	0.33302	-0.06758
25	32440.2	308.3	0.011857876	0.12034	-0.21346	-0.25097	0.10855
26	33691.1	296.8	0.001954004	0.01909	0.00321	-0.04770	-0.12965
27	35420.1	282.3	0.003113313	0.02894	-0.08083	-0.14599	0.03302
28	35659.1	280.4	0.028639201	0.26440	-0.28469	-0.40521	0.13843
29	34962.0	286.0	0.184232511	1.73478	-0.77518	-1.00729	0.34533
30	36149.4	276.6	0.012427340	0.11318	-0.08066	0.30321	-0.12137
31	36002.7	277.8	0.000577434	0.00528	0.01670	0.05968	0.03794
32	36514.0	273.9	0.001184153	0.01068	0.09945	0.02803	0.00091
33	36699.1	272.5	0.145629860	1.30638	0.79800	0.77292	-0.26866
34	37021.4	270.1	0.003345927	0.02975	0.02915	-0.03189	-0.16699
35	37607.8	265.9	0.089878066	0.78678	0.48438	0.71451	-0.20403
36	37842.7	264.3	0.007903628	0.06876	0.25381	0.06552	-0.00672
37	37882.1	264.0	0.055193691	0.47966	0.01456	-0.23263	-0.65217
38	37625.6	265.8	0.092121367	0.80603	-0.01606	0.28969	0.84962
39	38061.7	262.7	0.047036245	0.40684	-0.60046	-0.20764	0.05634
40	35753.9	279.7	0.012618661	0.11619	0.12368	0.29787	-0.11029
41	38221.6	261.6	0.259299310	2.23341	0.61663	1.27412	-0.47936
42	38771.9	257.9	0.010479685	0.08898	-0.01211	0.09475	0.28259
43	38690.2	258.5	0.004783034	0.04070	0.18489	0.06877	-0.04226
44	36903.1	271.0	0.032211880	0.28736	0.24905	0.44360	-0.16898
45	38477.4	259.9	0.000256617	0.00220	0.00672	0.02661	0.03798
46	39152.5	255.4	0.075414265	0.63412	0.71179	0.33652	-0.11931
47	39838.6	251.0	0.014409692	0.11908	-0.21419	-0.24221	0.12055
48	39852.9	250.9	0.014541422	0.12012	-0.21616	-0.26453	0.05850
49	39227.5	254.9	0.108636588	0.91172	0.00789	-0.31939	-0.89980
50	40628.8	246.1	0.018292183	0.14822	0.23461	0.27100	-0.14048

Table S5. Orbital contribution to the first 10 excited states (singlets; HOMO = 218; LUMO = 219) in complex **9**.

State	The weight of the individual excitations (printed if larger than 10^{-02})
State 1	218a -> 219a : 0.960932 (c= -0.98027151)
State 2	214a -> 219a : 0.011465 (c= 0.10707332) 218a -> 220a : 0.951401 (c= 0.97539781)
State 3	217a -> 219a : 0.967014 (c= -0.98336847)
State 4	217a -> 220a : 0.945919 (c= -0.97258347) 218a -> 222a : 0.029286 (c= 0.17113152)
State 5	218a -> 221a : 0.948712 (c= 0.97401834)
State 6	212a -> 219a : 0.012664 (c= -0.11253371) 214a -> 219a : 0.020422 (c= 0.14290478) 215a -> 219a : 0.028540 (c= -0.16893831) 216a -> 219a : 0.854188 (c= -0.92422282)

	218a -> 222a : 0.047831 (c= -0.21870189)
State 7	211a -> 219a : 0.018359 (c= 0.13549677)
	212a -> 219a : 0.017196 (c= 0.13113338)
	214a -> 219a : 0.048981 (c= 0.22131541)
	215a -> 219a : 0.639701 (c= -0.79981323)
	216a -> 219a : 0.059836 (c= 0.24461361)
	218a -> 222a : 0.157704 (c= -0.39711950)
	218a -> 223a : 0.021042 (c= -0.14505918)
State 8	215a -> 220a : 0.017268 (c= -0.13140617)
	216a -> 220a : 0.029307 (c= 0.17119418)
	217a -> 221a : 0.893987 (c= -0.94550890)
State 9	211a -> 219a : 0.012899 (c= -0.11357334)
	215a -> 219a : 0.198269 (c= 0.44527416)
	216a -> 219a : 0.015998 (c= 0.12648243)
	216a -> 221a : 0.011684 (c= 0.10809412)
	217a -> 220a : 0.024984 (c= -0.15806215)
	218a -> 222a : 0.687201 (c= -0.82897565)
State 10	212a -> 219a : 0.036845 (c= 0.19195052)
	214a -> 219a : 0.806934 (c= 0.89829499)
	215a -> 219a : 0.028787 (c= 0.16966845)
	218a -> 222a : 0.026087 (c= 0.16151559)
	218a -> 223a : 0.046455 (c= 0.21553373)

*b) Calculated UV/Vis spectra of **1** and **7**.*

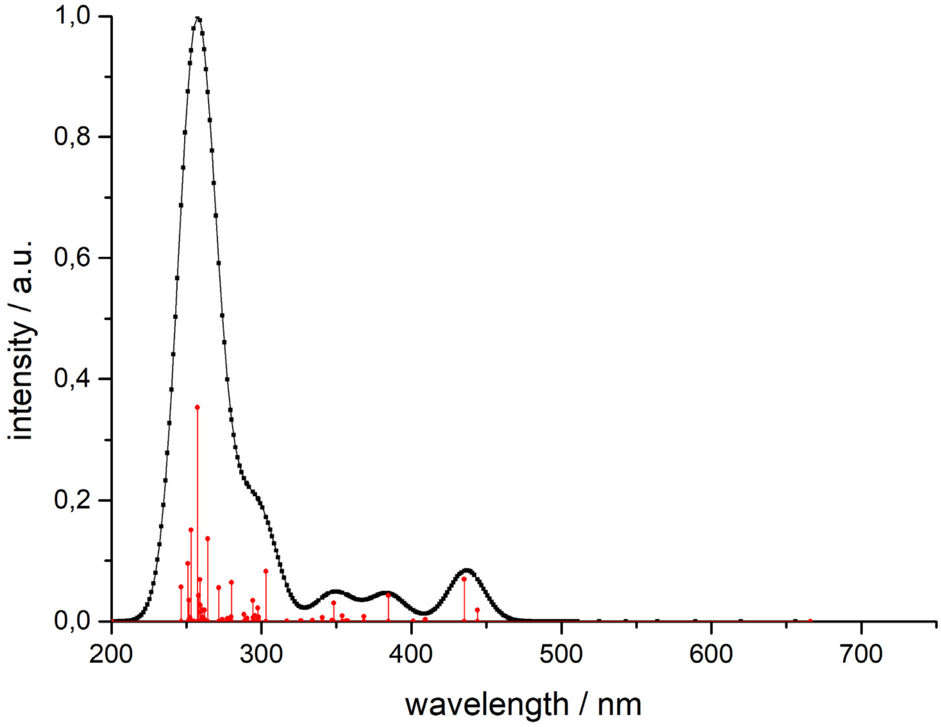


Figure S7. Calculated absorption spectrum of **1** (calculated with TD-DFT B3LYP/def2-TZVP, CPCM (thf)).

Table S6. Calculated states of the absorption spectrum of **1** via transition electric dipole moments (TD-DFT: B3LYP/def2-TZVP, RIJCOSX, CPCM (thf)).

State	Energy	Wavelength	f_{osc}	T^2	T_X	T_Y	T_Z
	(cm^{-1})	(nm)		(a.u.^{2})	(a.u.)	(a.u.)	(a.u.)
1	22520.5	444.0	0.021463756	0.31376	-0.09637	-0.50962	0.21157
2	22977.5	435.2	0.081290261	1.16469	0.25381	0.99941	0.31852
3	24426.3	409.4	0.003600337	0.04852	0.21718	-0.03423	-0.01356
4	24920.1	401.3	0.000748358	0.00989	-0.08795	0.04255	0.01846
5	25999.2	384.6	0.049679517	0.62906	-0.17895	-0.74072	-0.21994
6	27148.2	368.3	0.009621195	0.11667	0.07595	0.22028	0.24976
7	28245.8	354.0	0.011001089	0.12822	0.34877	-0.07516	-0.03049
8	28707.1	348.3	0.035344573	0.40533	0.61814	-0.14118	-0.05750
9	29937.6	334.0	0.001598736	0.01758	0.03127	0.10671	0.07223
10	28048.0	356.5	0.001168578	0.01372	-0.11693	-0.00424	0.00499
11	27964.5	357.6	0.000652178	0.00768	0.02289	-0.08088	-0.02473
12	30600.7	326.8	0.000565748	0.00609	0.02657	0.06870	-0.02570
13	30650.0	326.3	0.001273871	0.01368	-0.11319	0.02793	0.00952
14	31556.1	316.9	0.000220871	0.00230	-0.04135	0.02192	0.01066
15	28823.0	346.9	0.001564054	0.01786	-0.03271	-0.12099	-0.04643
16	29364.0	340.6	0.007586449	0.08505	-0.07232	-0.26217	-0.10531
17	33613.2	297.5	0.026100159	0.25563	-0.49344	0.10173	0.04235
18	34439.2	290.4	0.006303647	0.06026	-0.23783	0.05550	0.02479

19	34686.5	288.3	0.013741678	0.13042	0.04838	0.35095	0.07011
20	33965.3	294.4	0.007642454	0.07408	-0.26599	-0.05733	-0.00602
21	33818.0	295.7	0.011356403	0.11055	0.01856	0.31912	0.09149
22	33559.4	298.0	0.008933228	0.08763	0.28979	-0.05576	-0.02335
23	33557.6	298.0	0.005486470	0.05382	0.08255	-0.20935	-0.05640
24	35701.4	280.1	0.074883345	0.69052	0.81588	-0.14302	-0.06632
25	33979.7	294.3	0.040488738	0.39227	-0.60587	0.14806	0.05722
26	32989.8	303.1	0.096404903	0.96205	-0.95342	0.21177	0.09046
27	35747.5	279.7	0.008782486	0.08088	0.06515	0.25613	0.10504
28	36817.6	271.6	0.064774537	0.57919	-0.74191	0.15753	0.06283
29	36059.8	277.3	0.005361414	0.04895	-0.03459	-0.10456	-0.19188
30	37837.3	264.3	0.159729042	1.38976	1.14275	-0.26665	-0.11301
31	38328.3	260.9	0.022094328	0.18977	-0.14818	-0.40231	-0.07720
32	38187.8	261.9	0.004903693	0.04227	0.19095	-0.07140	-0.02675
33	35797.9	279.3	0.004372049	0.04021	0.06594	0.10753	-0.15587
34	38606.7	259.0	0.080612708	0.68741	-0.81051	0.15540	0.07957
35	38618.0	258.9	0.017693129	0.15083	-0.28422	0.26464	-0.00401
36	38140.4	262.2	0.021501607	0.18559	0.39034	-0.18045	-0.02578
37	38865.7	257.3	0.413264034	3.50056	-1.82948	0.35225	0.17167
38	38748.4	258.1	0.049593615	0.42135	-0.13401	-0.61348	-0.16443
39	38008.6	263.1	0.000572069	0.00495	-0.06644	0.02159	0.00862
40	38569.3	259.3	0.031584344	0.26959	0.12594	0.50370	0.00388
41	36506.3	273.9	0.003657240	0.03298	0.13713	-0.10887	-0.04820
42	39733.6	251.7	0.041236866	0.34167	0.17930	0.51220	0.21720
43	39514.2	253.1	0.177268395	1.47691	-0.25398	-1.18414	0.10112
44	39636.4	252.3	0.007621371	0.06330	0.12707	0.20442	0.07325
45	39697.2	251.9	0.003908774	0.03242	-0.06960	0.13415	0.09786
46	39243.9	254.8	0.000620941	0.00521	-0.01275	-0.04489	0.05506
47	38372.1	260.6	0.007769103	0.06665	0.00456	0.25442	-0.04365
48	34494.1	289.9	0.003632616	0.03467	0.00730	-0.18519	0.01788
49	40575.4	246.5	0.066556408	0.54001	0.72193	-0.11847	-0.06924
50	39860.7	250.9	0.111607597	0.92177	-0.92818	0.22837	0.09004

Table S7. Orbital contribution to the first 10 excited states (singlets; HOMO = 191; LUMO = 192) in **1**.

State	The weight of the individual excitations (printed if larger than 10^{-02})
State 1	190a -> 192a : 0.010703 (c= 0.10345527) 191a -> 192a : 0.956871 (c= 0.97819758)
State 2	190a -> 192a : 0.950483 (c= 0.97492713) 191a -> 192a : 0.010905 (c= -0.10442616) 191a -> 193a : 0.011527 (c= -0.10736397)
State 3	190a -> 194a : 0.027868 (c= -0.16693576) 191a -> 194a : 0.958181 (c= -0.97886696)
State 4	190a -> 194a : 0.953767 (c= -0.97660975) 191a -> 194a : 0.028324 (c= 0.16829848)
State 5	190a -> 192a : 0.012805 (c= 0.11315775) 190a -> 195a : 0.010193 (c= -0.10095912)

	191a -> 193a : 0.941346 (c= 0.97023001)
State 6	190a -> 193a : 0.926029 (c= -0.96230390) 191a -> 195a : 0.021208 (c= 0.14563006)
State 7	186a -> 194a : 0.010592 (c= 0.10291972) 188a -> 192a : 0.036733 (c= 0.19165956) 189a -> 192a : 0.811913 (c= 0.90106225) 190a -> 197a : 0.014698 (c= 0.12123417) 191a -> 196a : 0.052220 (c= 0.22851728) 191a -> 197a : 0.022569 (c= -0.15022995)
State 8	188a -> 192a : 0.819504 (c= -0.90526472) 189a -> 192a : 0.028815 (c= 0.16975039) 190a -> 196a : 0.065553 (c= -0.25603390) 190a -> 197a : 0.016654 (c= -0.12905196) 191a -> 197a : 0.039952 (c= -0.19987908)
State 9	186a -> 192a : 0.062514 (c= -0.25002762) 187a -> 194a : 0.029783 (c= -0.17257682) 190a -> 193a : 0.027926 (c= -0.16710942) 190a -> 195a : 0.017246 (c= -0.13132380) 191a -> 195a : 0.823812 (c= -0.90764103)
State 10	186a -> 192a : 0.092633 (c= 0.30435660) 186a -> 194a : 0.192544 (c= 0.43879788) 187a -> 192a : 0.543614 (c= 0.73730195) 187a -> 194a : 0.038572 (c= 0.19639638) 187a -> 195a : 0.028456 (c= -0.16869026) 189a -> 192a : 0.012660 (c= -0.11251616) 191a -> 195a : 0.037067 (c= -0.19252733)

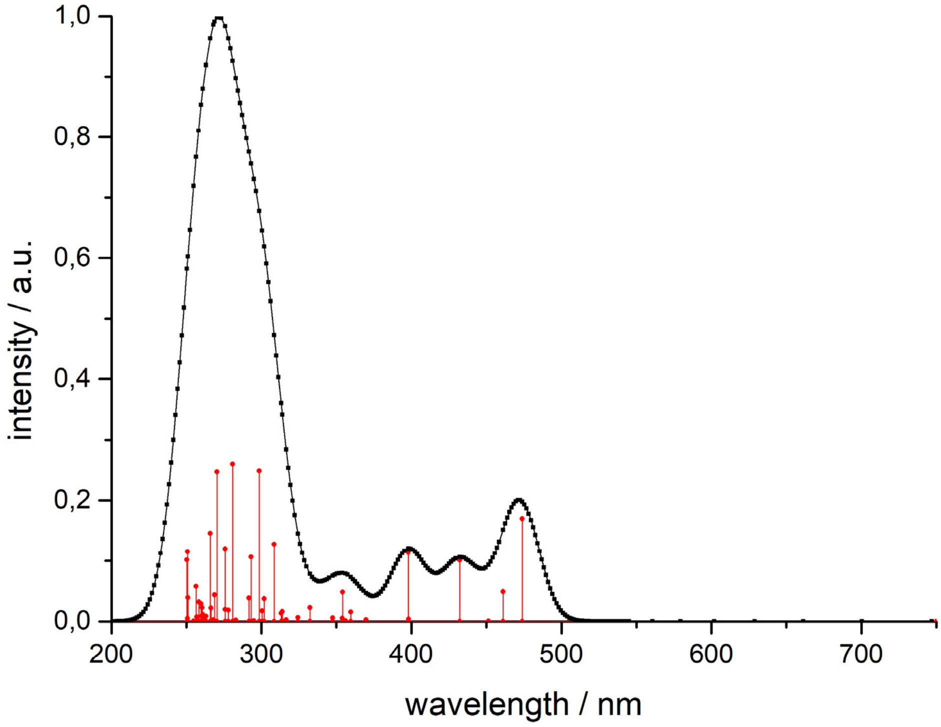


Figure S8. Calculated absorption spectrum of complex **7** (calculated with TD-DFT B3LYP/def2-TZVP, CPCM (thf)).

Table S8. Calculated states of the absorption spectrum of complex **7** via transition electric dipole moments (TD-DFT: B3LYP/def2-TZVP, RIJCOSX, CPCM (thf)).

State	Energy	Wavelength	f_{osc}	T^2	T_X	T_Y	T_Z
	(cm^{-1})	(nm)		(a.u.^{2})	(a.u.)	(a.u.)	(a.u.)
1	21100.2	473.9	0.125229874	1.95387	-0.87524	-1.03072	0.35416
2	21687.1	461.1	0.036046633	0.54719	0.46305	0.54495	-0.18924
3	22161.1	451.2	0.000131382	0.00195	-0.02475	0.00238	-0.03651
4	23133.9	432.3	0.074344664	1.05798	0.16693	-0.46353	-0.90291
5	25123.8	398.0	0.084242364	1.10388	-0.66132	-0.76994	0.27153
6	25111.9	398.2	0.002709402	0.03552	-0.11882	-0.13683	0.05175
7	27051.3	369.7	0.002116646	0.02576	0.00496	-0.05451	-0.15088
8	28092.1	356.0	0.000913813	0.01071	0.06364	0.07723	-0.02635
9	27804.9	359.6	0.011620377	0.13759	-0.01838	0.13891	0.34344
10	28236.2	354.2	0.035756346	0.41689	-0.02499	0.22969	0.60292
11	30093.1	332.3	0.016574106	0.18132	-0.00264	-0.14385	-0.40077
12	28253.1	353.9	0.003566984	0.04156	0.12901	0.14450	-0.06357
13	28775.7	347.5	0.004210318	0.04817	0.13772	0.15970	-0.06080
14	30836.2	324.3	0.004483385	0.04787	0.00575	-0.07714	-0.20465
15	31932.3	313.2	0.009669206	0.09969	0.19838	0.23054	-0.08474
16	31599.8	316.5	0.002068387	0.02155	0.09089	-0.05991	0.09848
17	32408.2	308.6	0.093797739	0.95282	-0.12827	0.38871	0.88616
18	31852.5	313.9	0.012173697	0.12582	-0.21138	-0.28188	0.04103

19	33276.5	300.5	0.012892679	0.12755	0.18072	-0.23136	-0.20337
20	33490.0	298.6	0.183338516	1.80225	0.02830	0.43308	1.27039
21	33117.8	302.0	0.027721549	0.27557	0.32910	0.37887	-0.15402
22	33893.6	295.0	0.000811485	0.00788	-0.01641	0.03334	0.08063
23	34284.5	291.7	0.028356920	0.27229	0.11689	-0.21356	-0.46154
24	34114.4	293.1	0.078245351	0.75509	0.53999	0.65069	-0.20024
25	35351.1	282.9	0.001766800	0.01645	-0.01201	0.05531	0.11511
26	35993.2	277.8	0.013832874	0.12652	-0.02900	-0.08622	-0.34387
27	36270.9	275.7	0.014469548	0.13133	-0.22483	-0.27107	0.08548
28	35609.6	280.8	0.191508617	1.77050	-0.83259	-0.98192	0.33633
29	36248.1	275.9	0.088282608	0.80180	0.04398	-0.31991	-0.83518
30	36991.7	270.3	0.182061472	1.62028	-0.00803	0.42704	1.19910
31	37210.2	268.7	0.032301035	0.28578	0.03471	-0.18459	-0.50050
32	37552.3	266.3	0.016326520	0.14313	-0.23314	-0.28210	0.09589
33	37627.2	265.8	0.107316531	0.93895	-0.60456	-0.71446	0.25100
34	37321.3	267.9	0.002251094	0.01986	-0.08789	-0.04710	-0.09957
35	38035.5	262.9	0.000469599	0.00406	-0.03771	-0.05034	0.01044
36	38407.4	260.4	0.016902241	0.14488	-0.05219	0.15772	0.34246
37	38320.7	261.0	0.002667000	0.02291	-0.09318	-0.10534	0.05596
38	38026.2	263.0	0.006471820	0.05603	0.02565	0.02618	0.23385
39	38450.8	260.1	0.006378825	0.05461	-0.14511	-0.17820	0.04245
40	38489.2	259.8	0.021388019	0.18294	-0.26588	-0.31763	0.10657
41	38724.2	258.2	0.023493508	0.19973	0.28495	0.31570	-0.13736
42	38993.1	256.5	0.042733438	0.36079	-0.10872	0.30322	0.50698
43	38318.0	261.0	0.008467366	0.07275	-0.17146	0.05370	-0.20116
44	38746.9	258.1	0.000273104	0.00232	-0.01165	0.04283	0.01871
45	38931.7	256.9	0.005485039	0.04638	0.11894	-0.12994	-0.12390
46	39248.8	254.8	0.000352130	0.00295	0.02809	0.04377	-0.01577
47	39882.6	250.7	0.003715958	0.03067	0.10629	-0.09128	0.10509
48	39899.8	250.6	0.084752270	0.69929	0.10452	-0.09360	-0.82438
49	39944.7	250.3	0.074822219	0.61666	-0.42321	-0.62699	-0.21081
50	39846.3	251.0	0.028721602	0.23730	0.20003	0.02926	-0.44321

Table S9. Orbital contribution to the first 10 excited states (singlets; HOMO = 273; LUMO = 274) in complex **7**.

State	The weight of the individual excitations (printed if larger than 10^{-02})
State 1	272a -> 274a : 0.716466 (c= 0.84644305) 273a -> 274a : 0.265014 (c= 0.51479541)
State 2	272a -> 274a : 0.261694 (c= -0.51156068) 273a -> 274a : 0.707008 (c= 0.84083757)
State 3	272a -> 275a : 0.948735 (c= 0.97403051) 273a -> 275a : 0.032684 (c= 0.18078813)
State 4	272a -> 275a : 0.029276 (c= 0.17110196) 273a -> 275a : 0.934200 (c= -0.96654003)
State 5	273a -> 276a : 0.952436 (c= -0.97592829)
State 6	272a -> 276a : 0.957613 (c= 0.97857691)

State 7	266a -> 275a : 0.067519 (c= 0.25984482) 268a -> 274a : 0.064257 (c= -0.25348928) 269a -> 274a : 0.462138 (c= -0.67980753) 270a -> 274a : 0.062745 (c= 0.25049006) 271a -> 274a : 0.316034 (c= -0.56216881)
State 8	266a -> 274a : 0.149798 (c= 0.38703699) 266a -> 278a : 0.010517 (c= 0.10255383) 268a -> 275a : 0.067171 (c= -0.25917367) 269a -> 275a : 0.452935 (c= -0.67300434) 270a -> 275a : 0.057871 (c= 0.24056316) 271a -> 275a : 0.246196 (c= -0.49618114)
State 9	269a -> 274a : 0.282615 (c= 0.53161531) 270a -> 274a : 0.026776 (c= -0.16363382) 271a -> 274a : 0.534493 (c= -0.73109038) 272a -> 277a : 0.015638 (c= -0.12505016) 273a -> 277a : 0.091594 (c= -0.30264433)
State 10	267a -> 274a : 0.018424 (c= 0.13573374) 269a -> 274a : 0.095908 (c= -0.30969050) 270a -> 274a : 0.774440 (c= -0.88002255) 272a -> 277a : 0.053363 (c= -0.23100537) 272a -> 279a : 0.014952 (c= -0.12227734) 273a -> 279a : 0.011683 (c= 0.10808831)

6. NMR Spectra

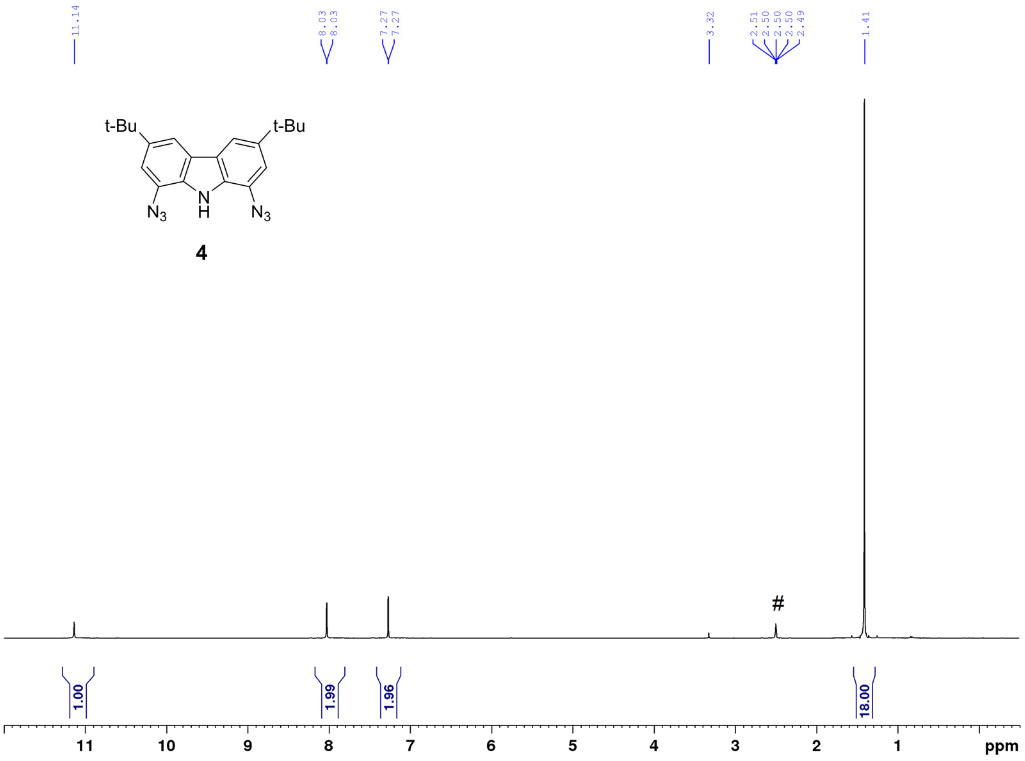


Figure S9. ^{1}H NMR (DMSO-d$_6$ (#), 400 MHz) spectrum of **4**.

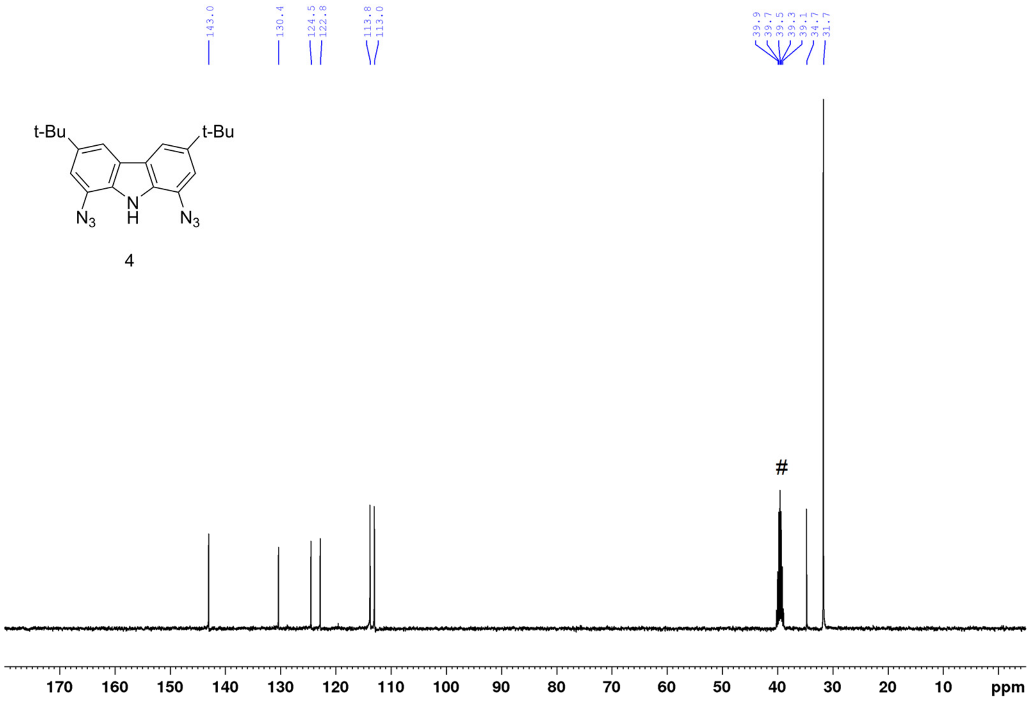


Figure S10. ^{13}C NMR (DMSO-d$_6$ (#), 100 MHz) spectrum of **4**.

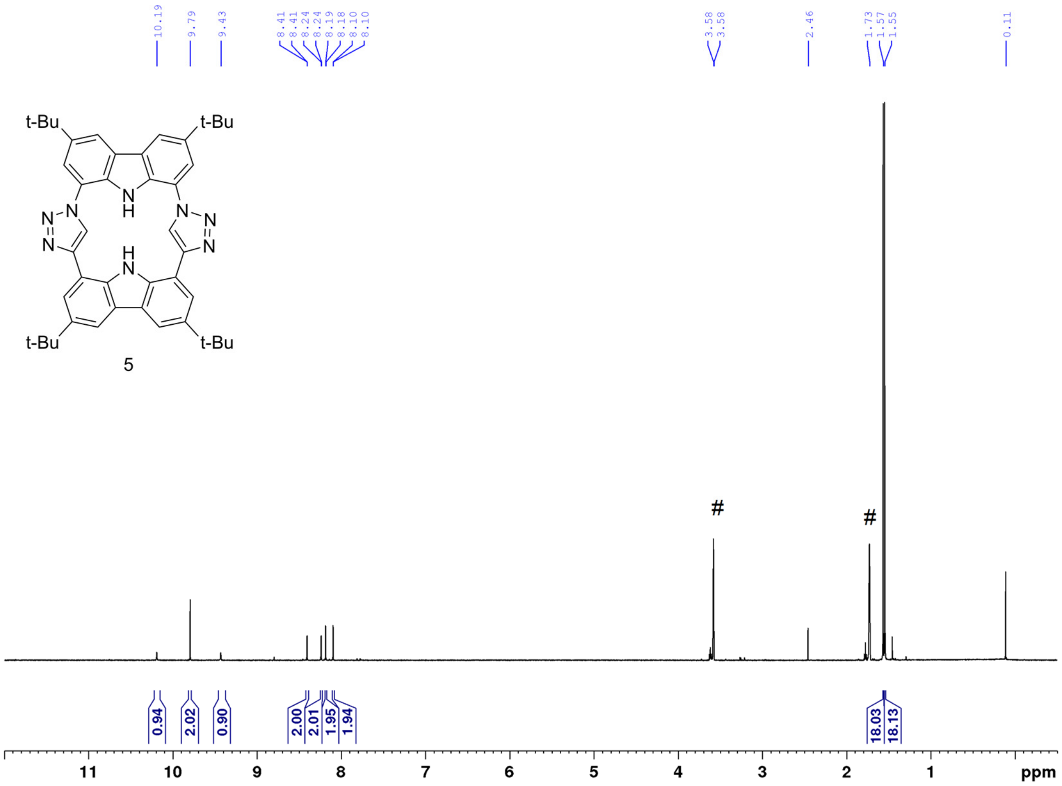


Figure S11. ^{1}H NMR (THF-d_8 (#), 500 MHz) spectrum of **5**.

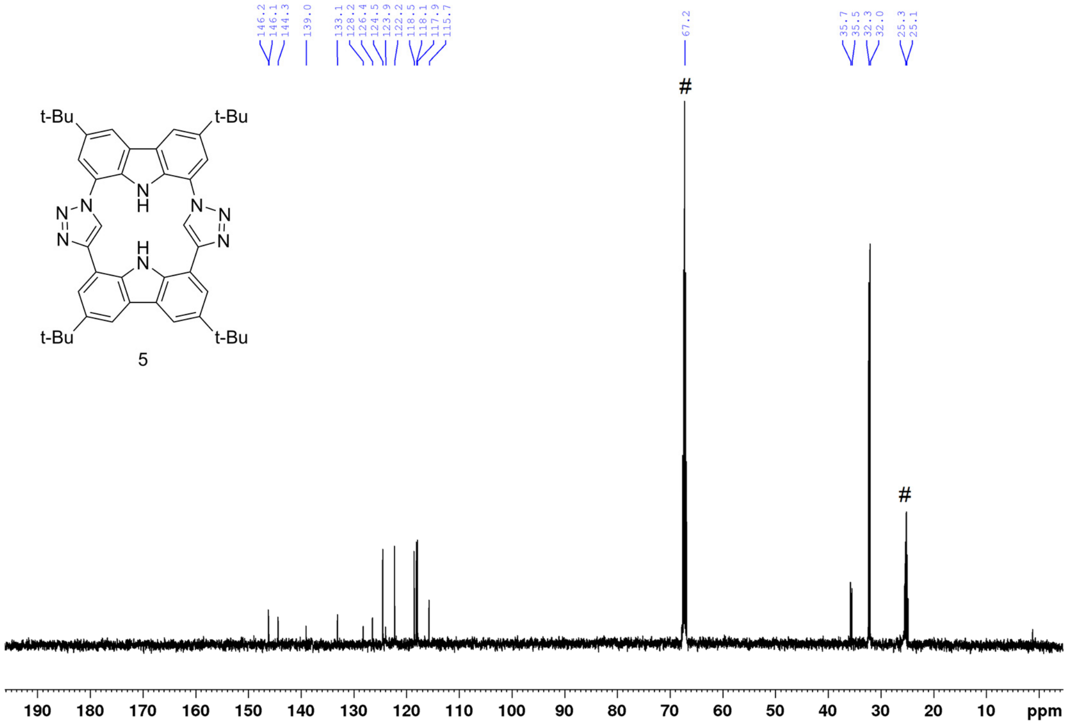


Figure S12. ^{13}C NMR (THF-d_8 (#), 125 MHz) spectrum of **5**.

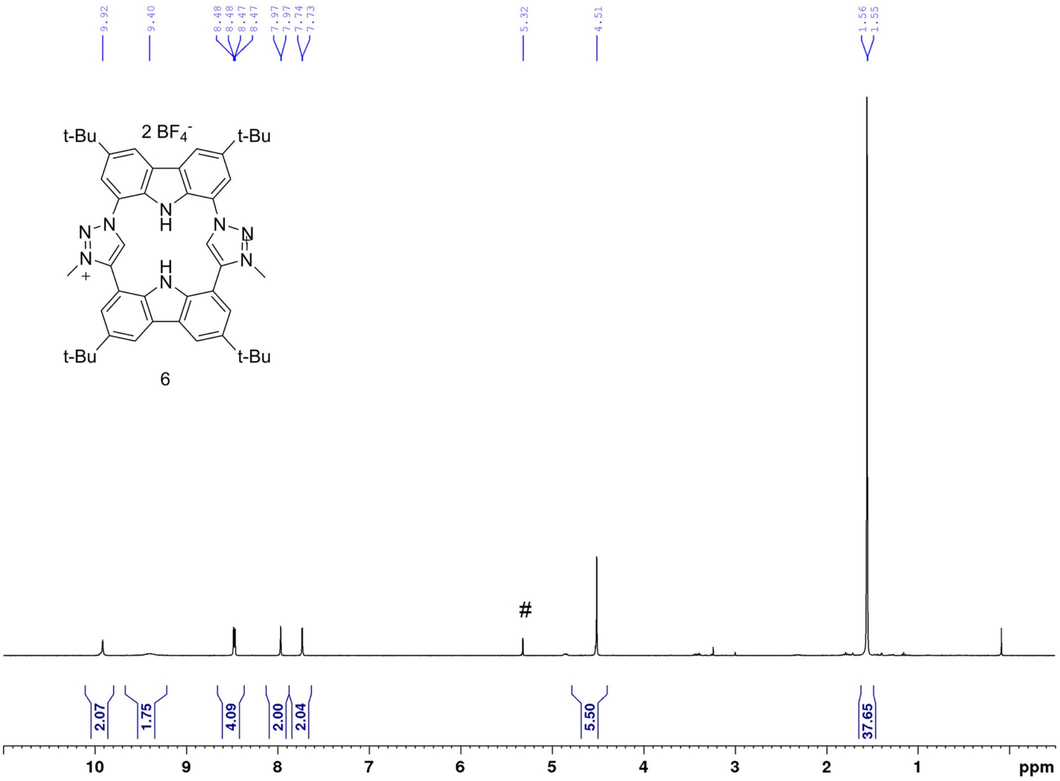


Figure S13. ^{1}H NMR (CD_2Cl_2 (#), 400 MHz) spectrum of **6**.

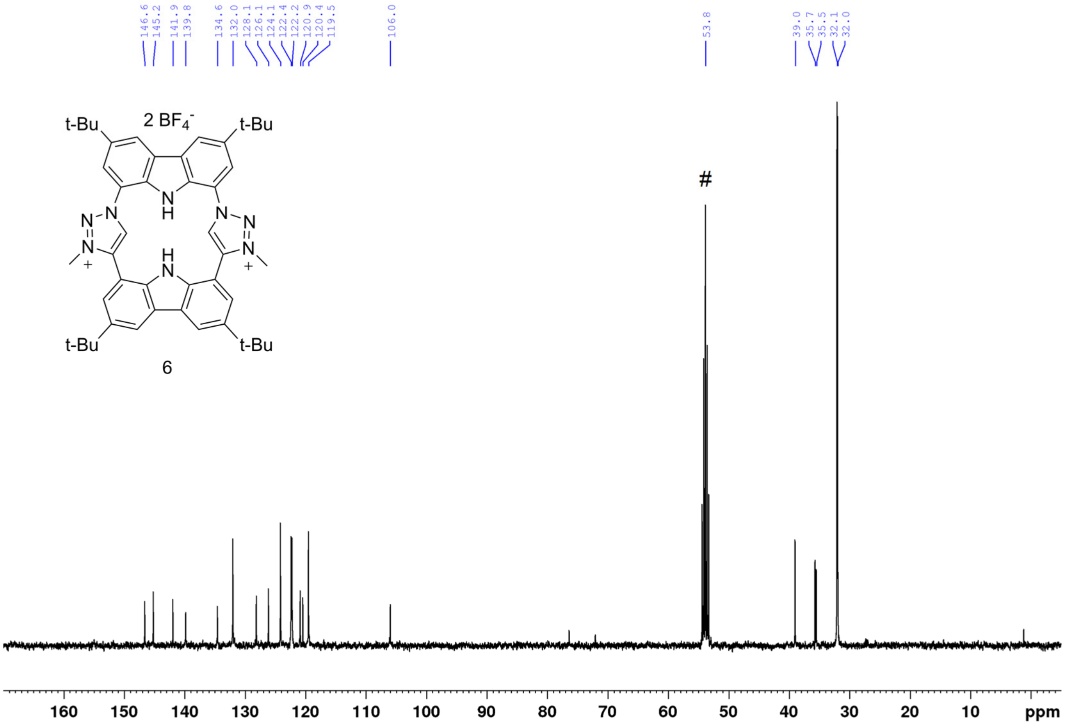


Figure S14. ^{13}C NMR (CD_2Cl_2 (#), 100 MHz) spectrum of **6**.

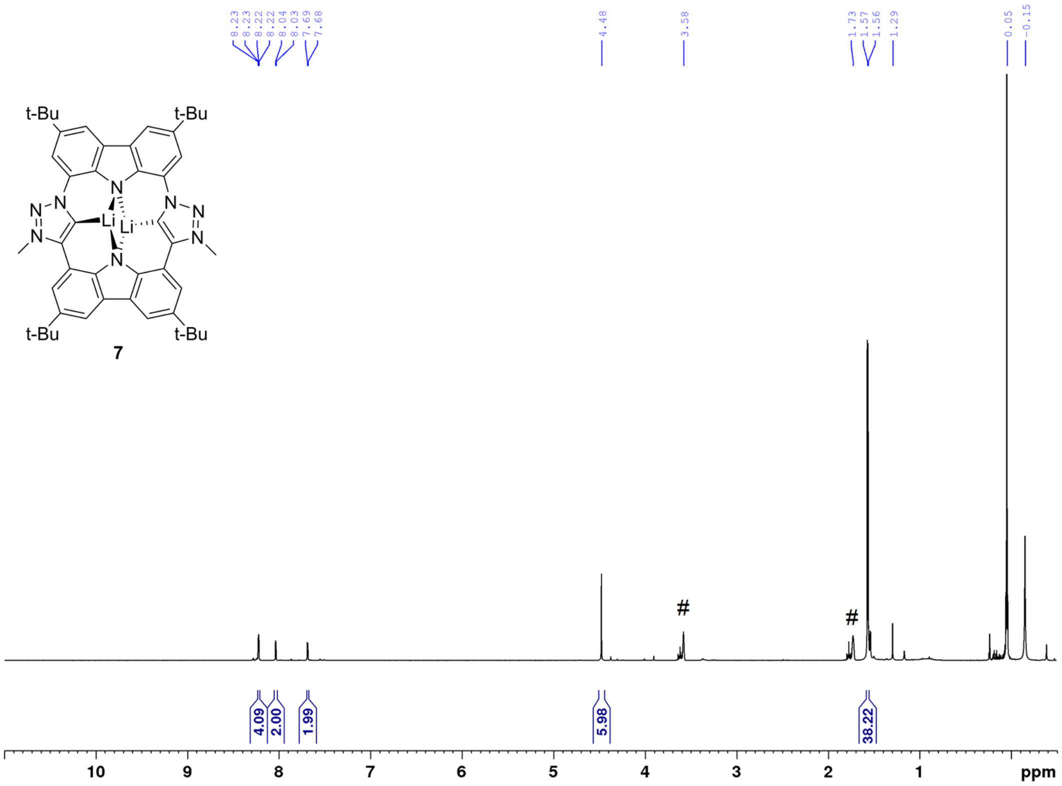


Figure S15. ^{1}H NMR (THF-d$_8$ (#), 400 MHz) spectrum of **7**.

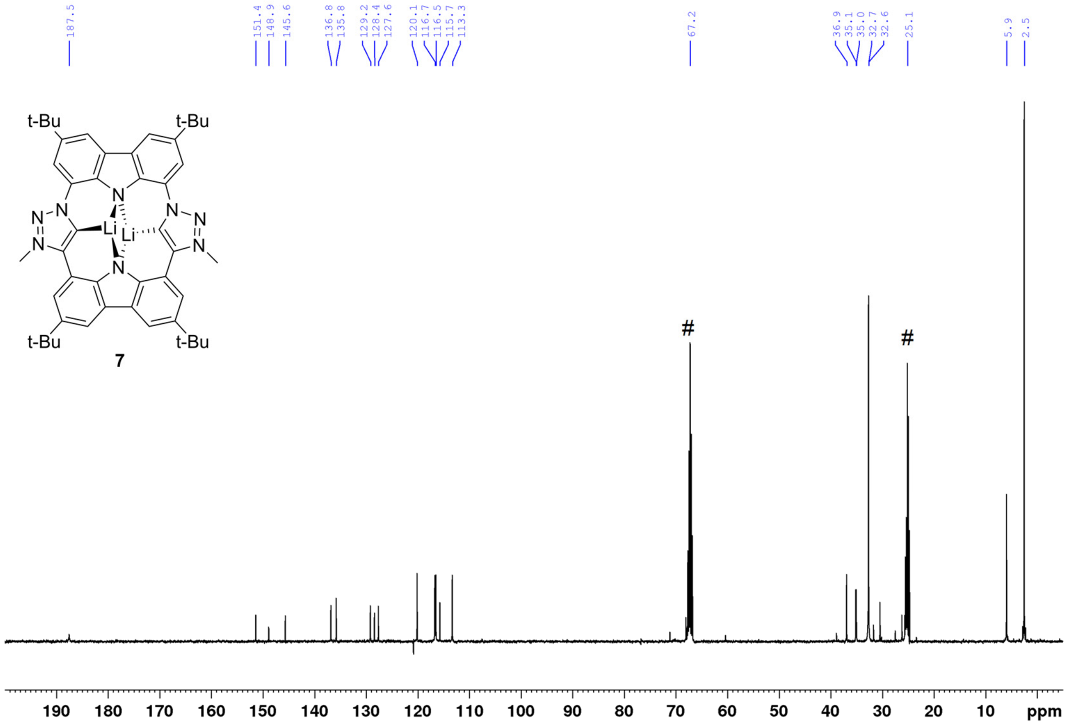


Figure S16. ^{13}C NMR (THF-d$_8$ (#), 100 MHz) spectrum of **7** at 26 °C.

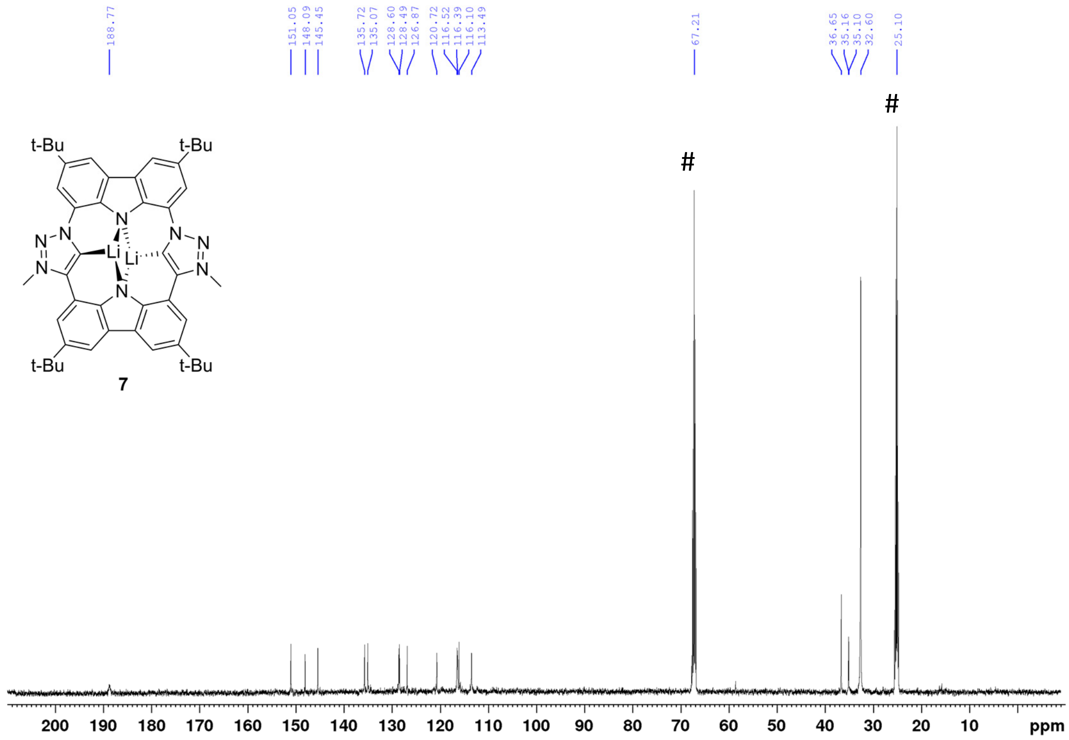


Figure S17. ^{13}C NMR (THF-d$_8$ (#), 125 MHz) spectrum of complex **7** at -80 °C.

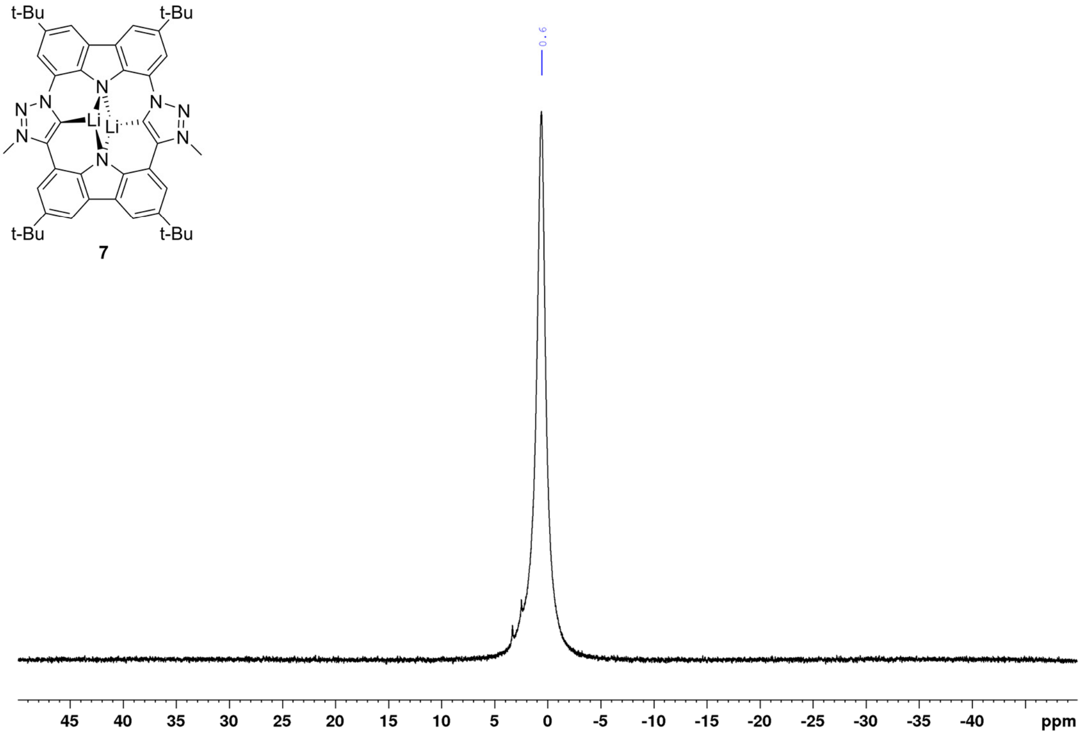


Figure S18. ^{7}Li NMR (THF-d$_8$, 117 MHz) spectrum of **7** at 26 °C.

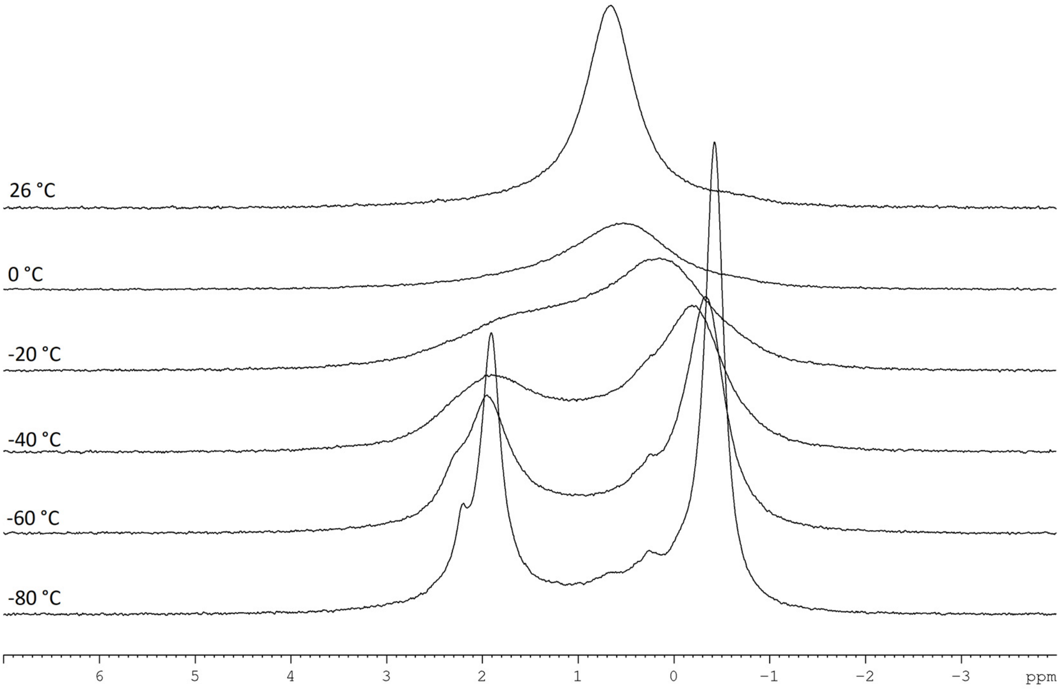


Figure S19. ^{7}Li NMR (THF-d_8, 117 MHz) spectra of complex **7** at various temperatures. Peak at 1.90 ppm for the lithium complex **7** and at -0.43 ppm for LiBF$_4$.

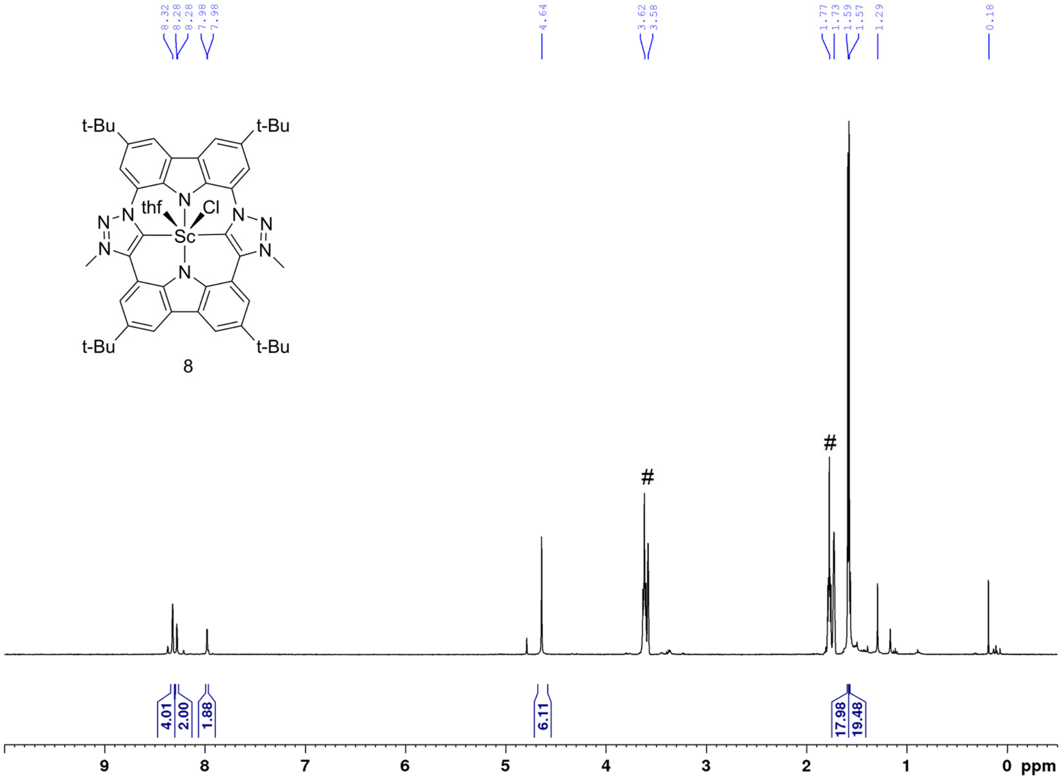


Figure S20. ^{1}H NMR (THF-d_8 (#), 400 MHz) spectrum of complex **8**.

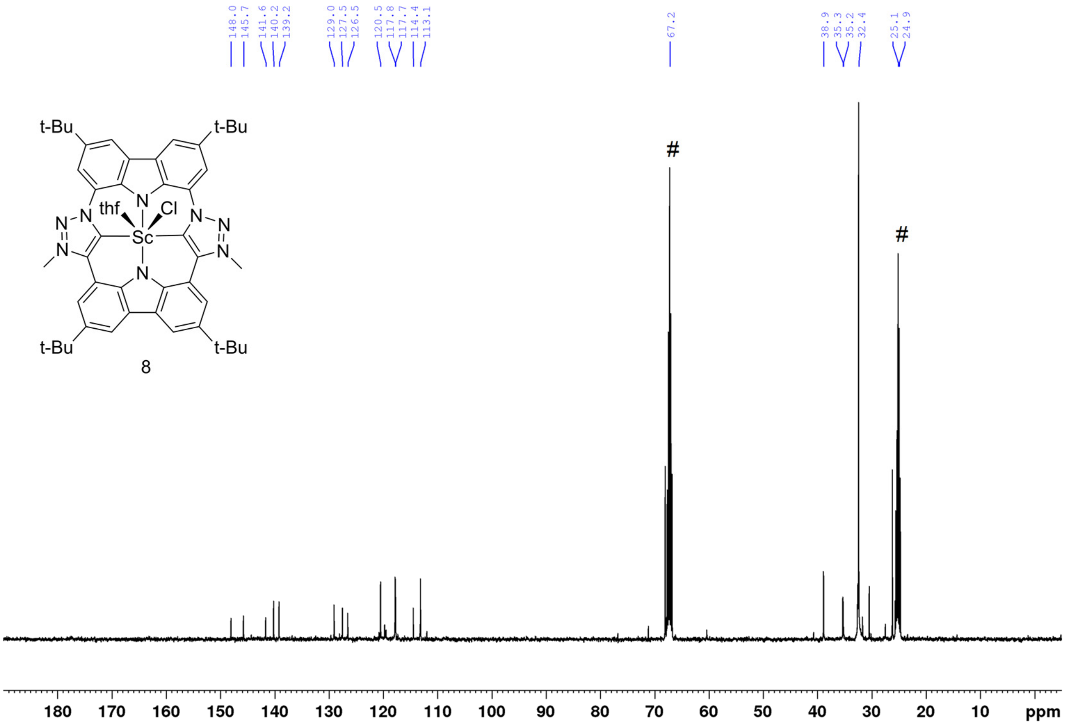


Figure S21. ^{13}C NMR (THF-d_8 (#), 100 MHz) spectrum of complex **8**.

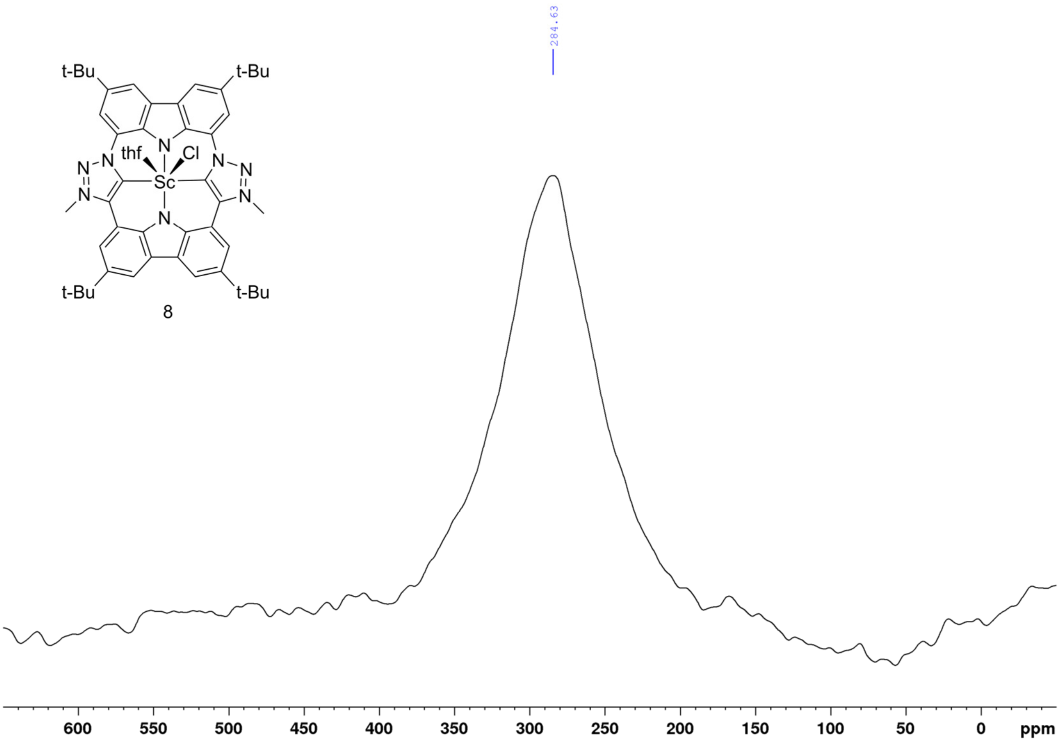


Figure S22. ^{45}Sc NMR (THF-d_8, 121 MHz) spectrum of complex **8**.

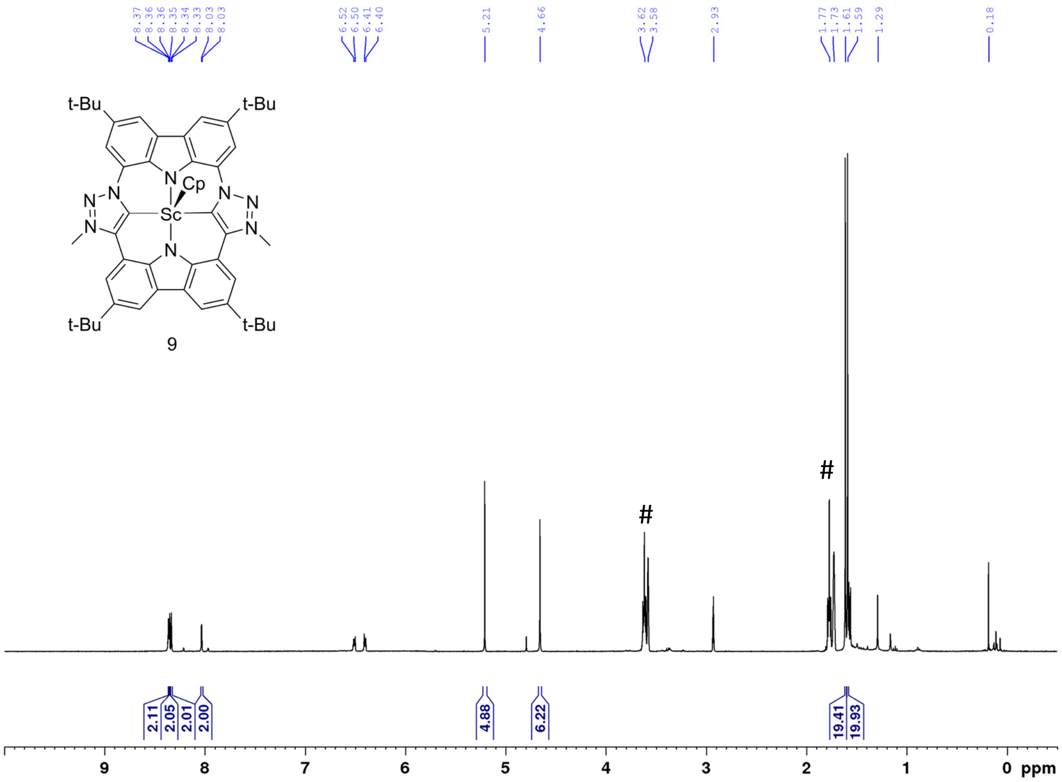


Figure S23. ^{1}H NMR (THF-d_8 (#), 400 MHz) spectrum of complex **9**.

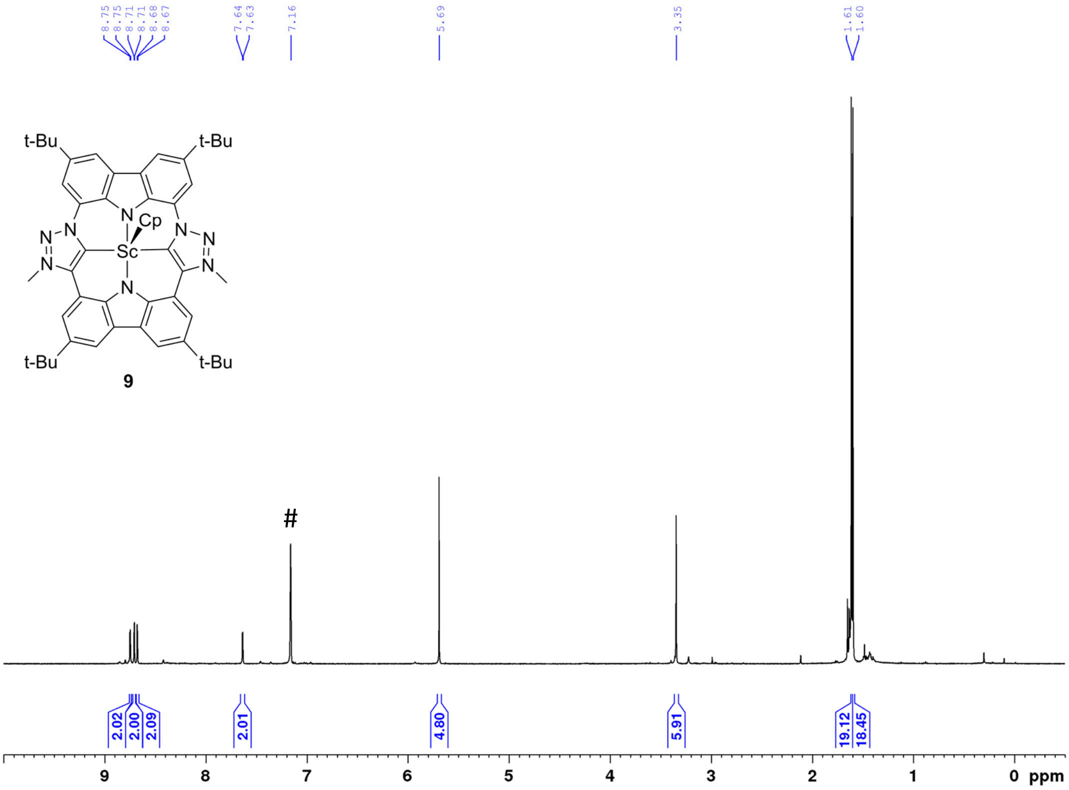


Figure S24. ^{1}H NMR (C_6D_6 (#), 400 MHz) spectrum of complex **9**.

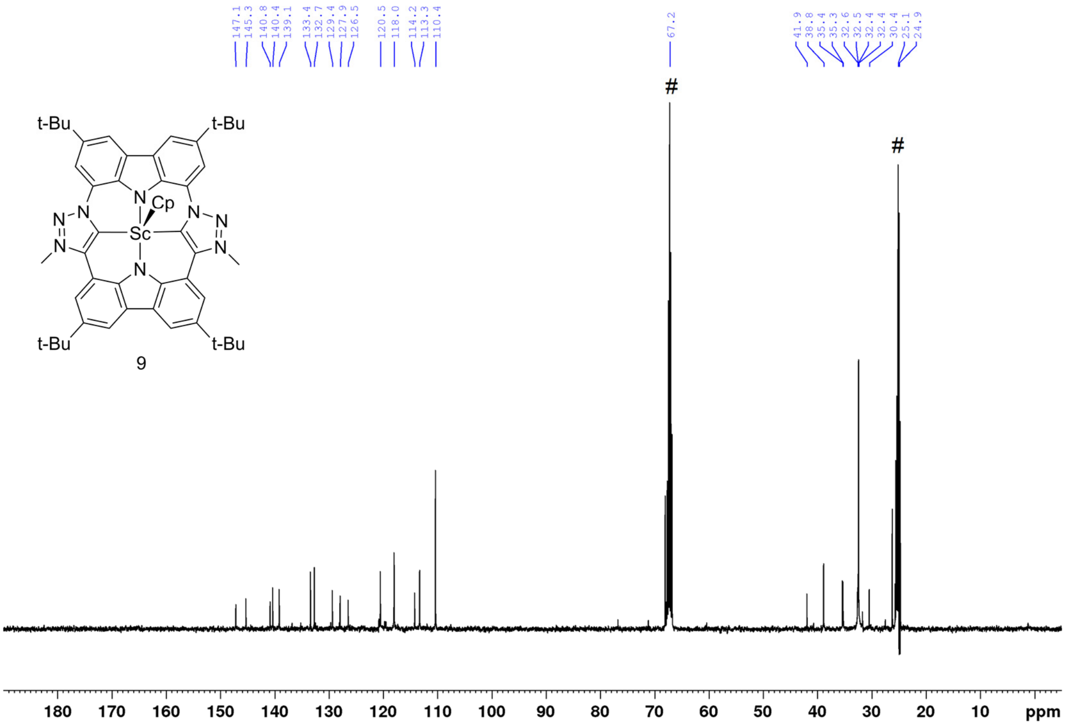


Figure S25. ^{13}C NMR (THF-d$_8$ (#), 100 MHz) spectrum of complex **9**.

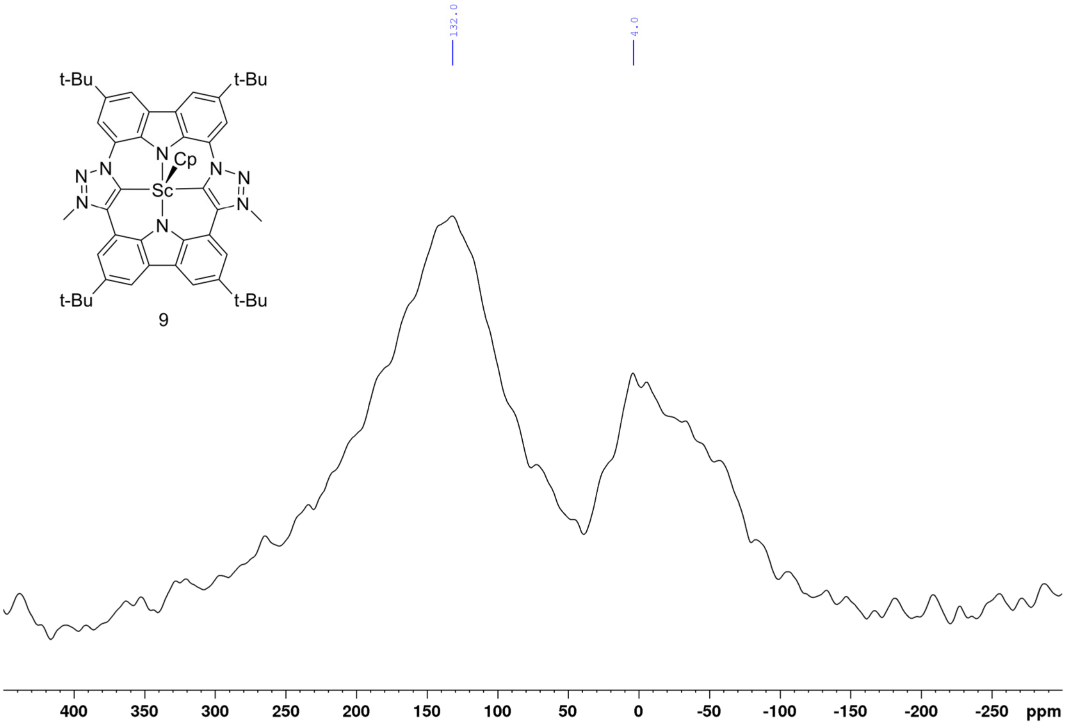


Figure S26. ^{45}Sc NMR (THF-d$_8$, 121 MHz) spectrum of complex **9**.

7. DFT Calculations

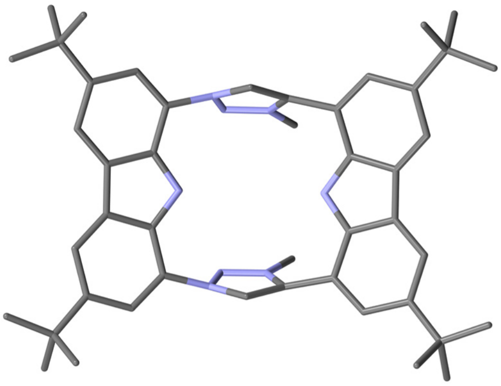


Figure S27. Geometry optimized structure of the “free” ligand **1** (DFT-D3BJ, BP86/def2-TZV).

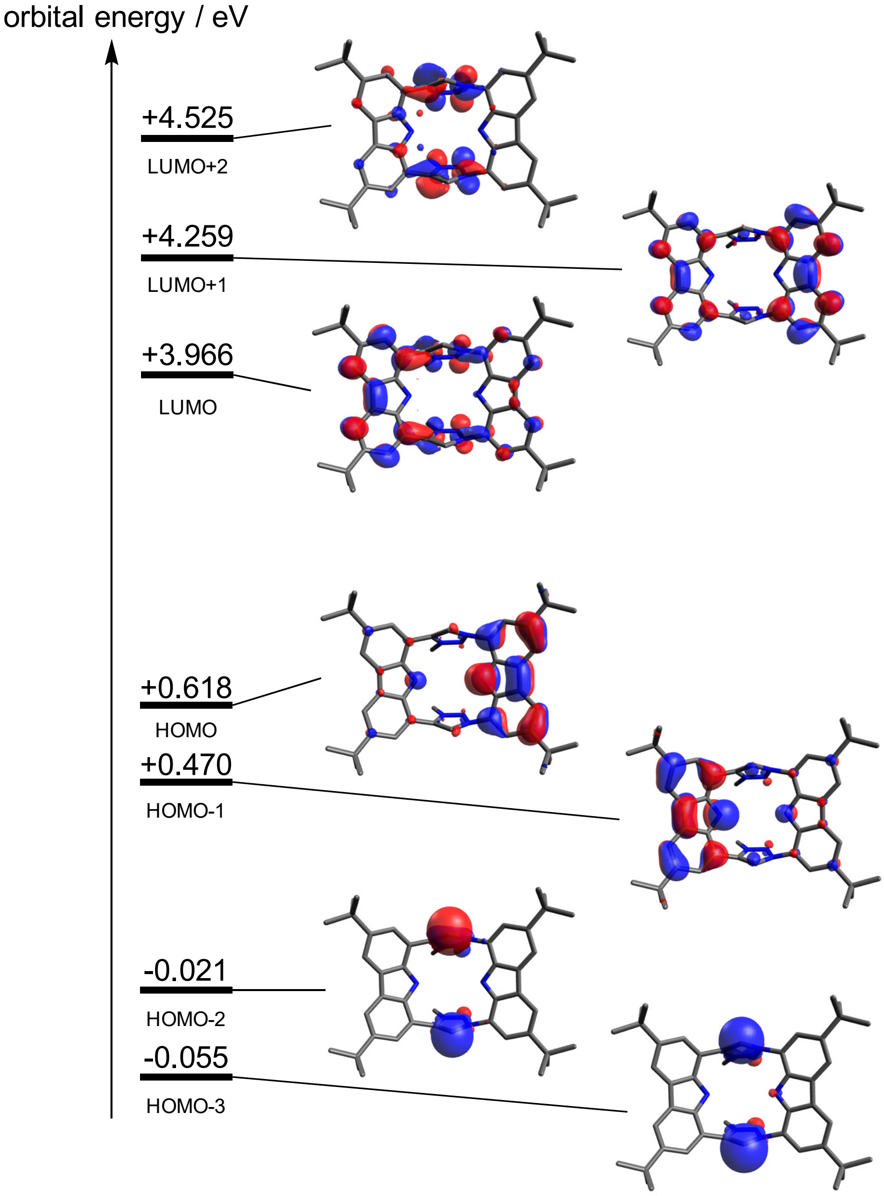


Figure S28. Schematic representation of the orbital energies of **1** at an iso value of 0.03 (DFT-D3BJ, BP86/def2-TZVP).

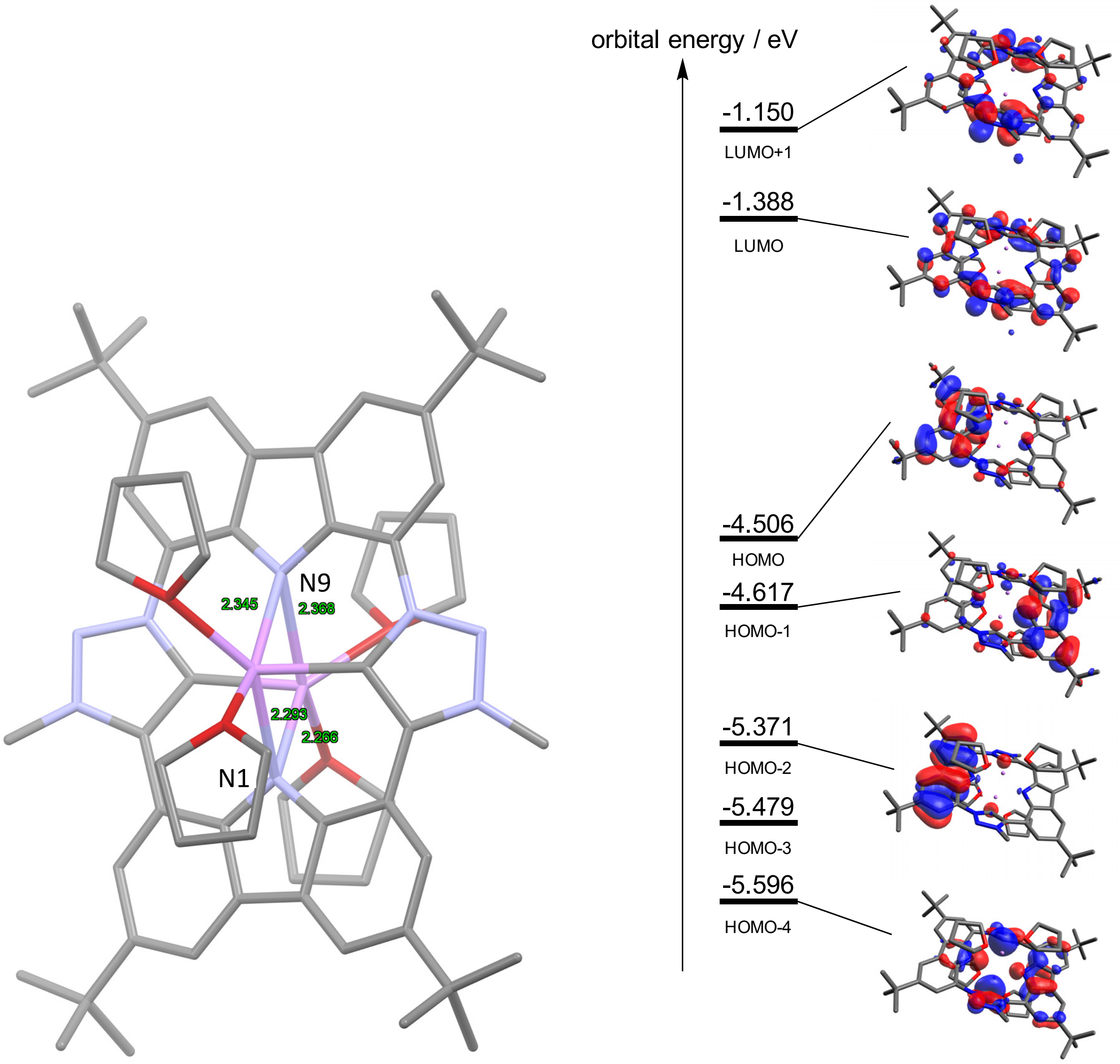


Figure S29. Left: Geometry optimized structure of complex **7** (DFT-D3BJ, BP86/def2-TZVP, CPCM (THF)) showing η^3-coordination of the CTP ligand to each Li$^+$ as well as two THF molecules to each Li$^+$. The Li-N bond lengths (green, in Å) are slightly shorter to N19 than to N9. Right: Schematic representation of the orbital energies at an iso value of 0.03.

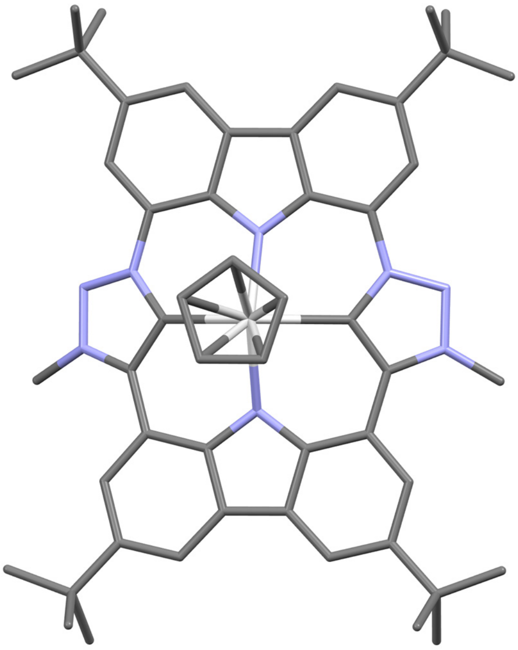


Figure S30. Geometry optimized structure of complex **9** (DFT-D3BJ, BP86/def2-TZV).

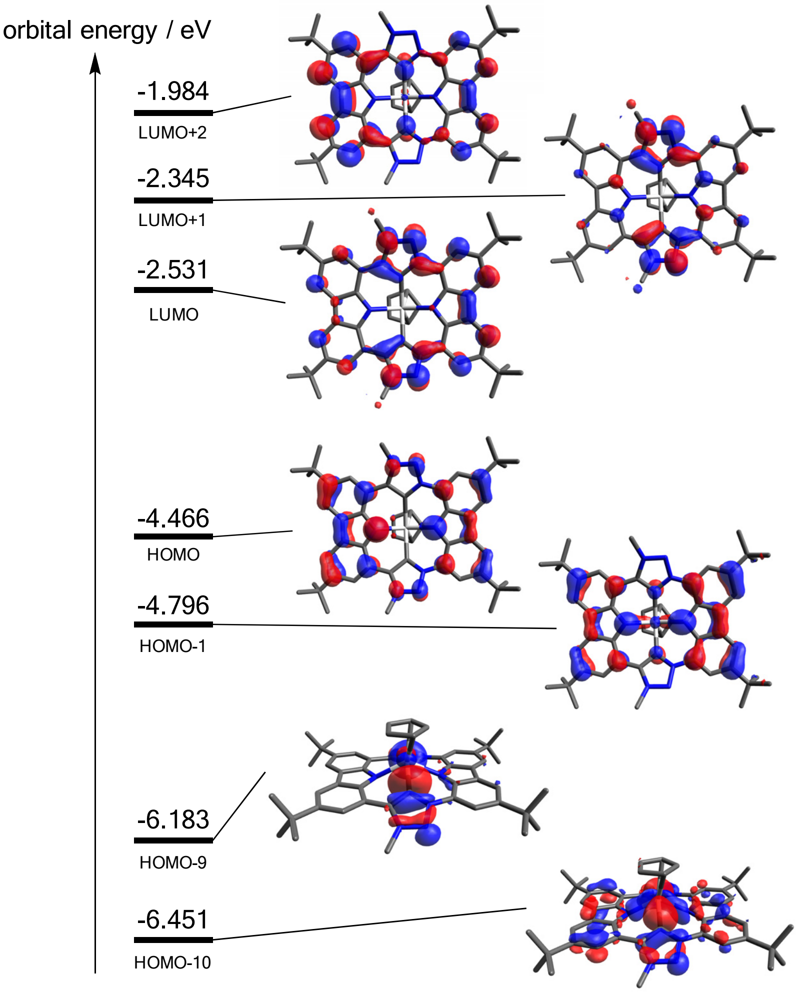
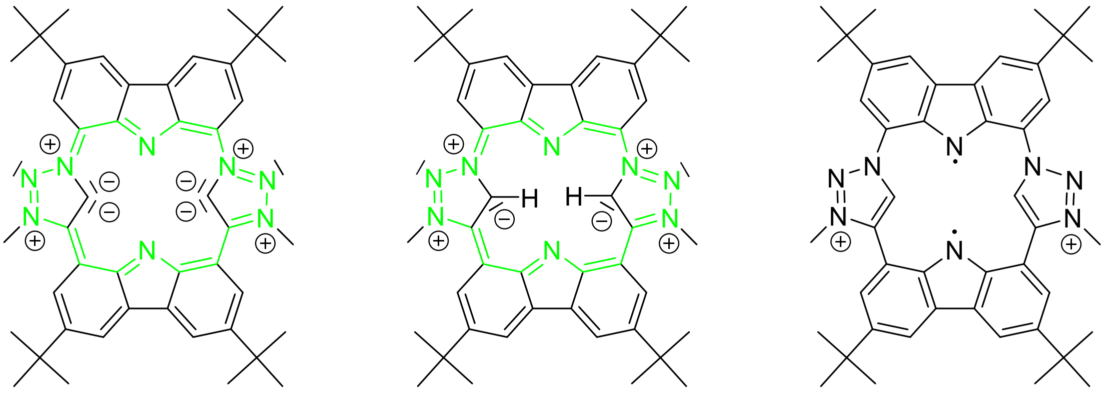


Figure S31. Schematic representation of the orbital energies of **9** at an iso value of 0.03 (DFT-D3BJ, BP86/def2-TZVP).

Oxidization to the formally 18 e⁻ π-system

The oxidation of ligand **1** and its precursor **6** to an 18 πe⁻ macrocycle was investigated theoretically. The geometry optimization of the oxidized ligand **1_{ox}** did not lead to a minimum structure. However, the triazolium system **6_{ox}-2H^{+}**, which is similar to the oxidized pyrrole-carbazole porphyrinoid synthesized by Müllen and coworkers,[12] did converge to the structures **6_{ox}-2H^{+}-(S)** (singlet) and **6_{ox}-2H^{+}-(T)** (triplet) (Figure S33). The triplet state is lower in energy by 1.7 kcal/mol.



1_{ox} **6_{ox}-2H^{+}-(S)** **6_{ox}-2H^{+}-(T)**

Figure S32. Structure of the oxidation products **1_{ox}** and **6_{ox}-2H^{+}** (in singlet **(S)** and triplet **(T)** spin state) with a formal 18 e⁻ π-system.

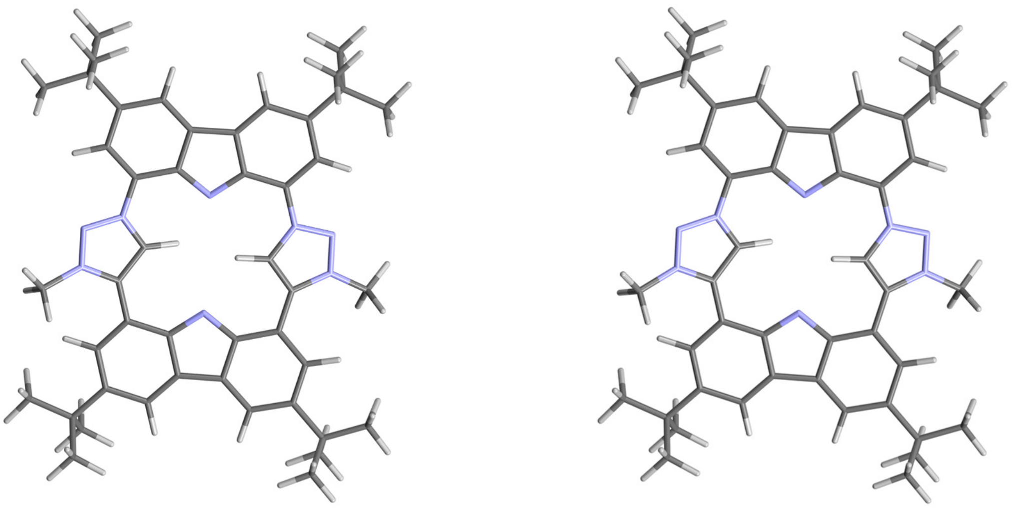


Figure S33. The geometry optimized structures of the oxidation product **6_{ox}-2H^{+}** (in singlet **(S)** and triplet **(T)** spin state) (DFT-D3BJ, BP86/def2-TZVP) show only slight differences in geometry. E_{total} = -1394779.287 kcal/mol (**6_{ox}-2H^{+}-(S)**) and -1394777.606 kcal/mol (**6_{ox}-2H^{+}-(T)**); ΔE = 1.7 kcal/mol in favor of the triplet state.

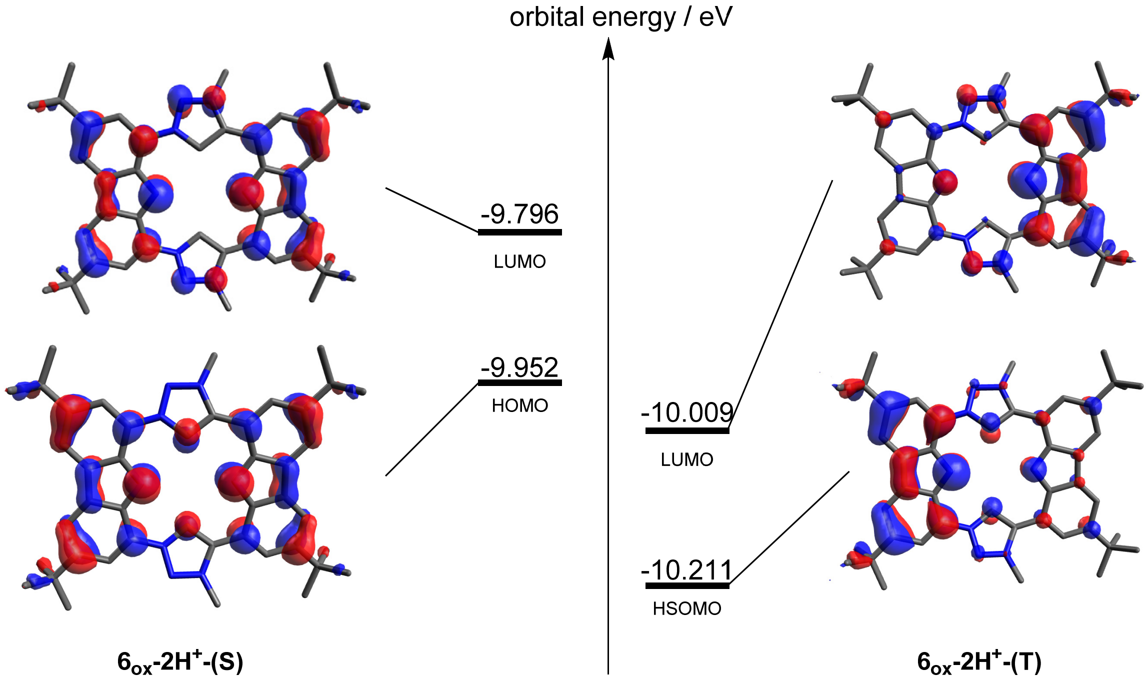


Figure S34. Schematic representation of the orbital energies of the geometry optimized structures of the oxidation product **6_{ox}-2H$^+$** (in singlet **(S)** and triplet **(T)** spin state) at an iso value of 0.03 (DFT-D3BJ, BP86/def2-TZVP).

8. References

[1] W. L. F. Armarego, C. L. L. Chai, Purification of laboratory chemicals, 6th ed.; Elsevier/BH: Oxford, 2009.

[2] Y. Liu, M. Nishiura, Y. Wang, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 5592–5593

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