Electronic supplementary information

Antimony(+5) Ion Induced Tunable Intramolecular Charge Transfer in Hypervalent Antimony(V) Porphyrins

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Physical methods

NMR and mass spectroscopy. NMR spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer using $CDCl_3$ as the solvent. ESI mass spectra were recorded on a Bruker MicroTOF-III mass spectrometer using direct injection from an UltiMate 3000 HPLC and acetonitrile as a solvent.

X-ray crystallography. Single crystal X-ray data for investigated compounds were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source as well as a low-temperature Oxford Cryostream 800 liquid nitrogen cooling system.

Absorption and emission spectroscopy. UV/Vis spectra were recorded with an Agilent Cary 100 UV/Vis spectrometer. The concentration of the samples used for these measurements ranged from 5×10^{-6} M (porphyrin B- band (Soret)) to 5×10^{-5} M (Q-bands) solutions. Steady-state fluorescence spectra were recorded using a Photon Technologies International Quanta Master 8075-11 spectrofluorometer, equipped with a 75 W Xenon lamp, running with FelixGX software. An excitation wavelength of 550 nm was used, and the optical density was

held constant at 0.2 for all the compounds. For phosphorescence studies, samples were prepared to an optical density of 2.0 at their respective excitation wavelength and then were degassed via the freeze-pump-thaw method. The solvent for this experiment consisted of 73% tetrahydrofuran, 12% CH_2Cl_2, and 15% 1,2-dibromoethane; this solvent system forms a glass when flash frozen and contains heavy atoms which facilitate intersystem crossing. Samples were measured at 77K in a liquid nitrogen Dewar. Excitation wavelengths of 426nm were used for Sb(V) porphyrin and 420nm were used for free-base samples.

Electrochemistry. Cyclic and differential pulse voltammetric experiments (CH_3CN, 0.1 M tetrabutylammonium hexafluorophosphate (TBA.PF_6) for Sb porphyrin samples, CH_2Cl_2, 0.1 M tetrabutylammonium perchlorate (TBA.ClO_4) for free base samples, or CH_3CN, 0.1M tetrabutylammonium perchlorate (TBA.ClO_4) for methoxybenzene samples) were performed on a BASi electrochemical analyzer (working electrode: Pt; auxiliary electrode: Pt wire; reference electrode: Ag wire). The Fc^+/Fc (Fc = ferrocene, $E_{1/2}(Fc^+/Fc)$ = 0.40 V *vs*. SCE in CH_3CN, 0.1 M TBA.PF_6; $E_{1/2}(Fc^+/Fc)$ = 0.48 V *vs*. SCE in CH_2Cl_2, 0.1 M TBA.ClO_4 under our experimental conditions)[1] redox couple was used to calibrate the potentials.

DFT calculations. All the antimony(V) porphyrin structures were initially constructed on a local PC using the *GaussView 6* (GV6.0) software. DFT computations were performed on a supercomputer using the *Gaussian 16* software suite.[2] Since the investigation includes the theoretical study of the excited state and charge transfer properties where the highest excitation is to the LUMO+1 the B3LYP method was chosen. The 6-311G(d,p) split-valence polarized basis set was used to model hydrogen and the period 2 elements (C, N, O) in the compounds. Since antimony is a period 5 element, the relativistic effects of the core electrons was modeled using effective core potentials (ECPs). The Stuttgart/Dresden ECPs in combination with the *triple-zeta* polarized basis set (def2TZVPP) was chosen to model antimony for this study. Thus, the B3LYP method was coupled with a GenECP basis to form the B3LYP/GenECP model chemistry which was used to optimize the geometry of all the structures herein to a stationary point on the Born-Oppenheimer surface and calculate the first ten excited singlet states of all chemical species in the current study. The optimization process was followed by a frequency calculation, utilizing the same model chemistry used in the optimization, to ensure that the stationary point to which the molecules were optimized was a minimum. All the structures were optimized *sans* symmetry constraints *in vacuo* as +1 charged cations and closed-shell singlets. The self-consistent field (SCF) convergence constraints and the DFT grid utilized in the calculation were the G16 default values, “Tight” and “UltraFine” respectively. The optimization of the geometrical parameters of each of the chemical species in the study was continued until the maximum force, RMS force, maximum displacement, and RMS displacement reached or was less than, the default *Gaussian 16* minima and the predicted energy change upon a successive optimization cycle of the geometrical parameters was in the range of $–5x10^{-9}$ A.U.

Time-resolved fluorescence spectroscopy. A time-correlated single-photon-counting apparatus utilizing a picosecond-pulsed diode laser was used to measure the porphyrin fluorescence decay. Excitation pulses were delivered at 406 nm by a picosecond diode laser (PicoQuant, PDL 800-B), 54 ps fwhm, at a repetition rate of 10 MHz. The porphyrin fluorescence was measured by a Hamamatsu R3809 microchannel plate photomultiplier screened by a double monochromator. A single-photon-counting PC card (Becker & Hickl, SPC-730) was used for data collection. The instrument response time of the system was 80 ps.

Femtosecond laser flash photolysis. Femtosecond transient absorption spectroscopy. These experiments were performed using an ultrafast femtosecond laser source (Libra) by Coherent incorporating a diode-pumped, mode-locked Ti:sapphire laser (Vitesse) and a diode-pumped intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with a femtosecond harmonics generator, both provided by Ultrafast Systems LLC, was used. The sources for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz; 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with a 290−2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of a white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is ±10%.

Synthesis details

Synthesis of free-base porphyrins. Pyrrole (2.80 mL, 2.708 g, 40.4 mmol) and R-CHO (R = 4-methoxyphenyl, 3,5-dimethoxyphenyl, or 3,4,5-trimethoxyphenyl; 40.1 mmol) were dissolved in 150 mL propionic acid. The resulting solution was refluxed for 1 h. Upon completion of the reaction, the propionic acid was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 and the crude product was precipitated by the addition of hexane. The crude product was collected using vacuum filtration and purified using basic alumina column chromatography.

H_2MP*:* The column was eluted with CH_2Cl_2 to obtain the pure compound. Yield = 1.38 g (19%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 8.86 (8H, s), 8.13 (8H, d, *J* = 8.48 Hz), 7.29 (8H, d, *J* = 8.52 Hz), 4.10 (12H, s), –2.75 (2H, s).

H_2DMP*:* The column was eluted with CH_2Cl_2:hexane (= 75:25) to obtain the pure compound. Yield = 1.51 g (18%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 8.93 (8H, s), 7.40 (8H, d, *J* = 2.28 Hz), 6.90 (4H, t, *J* = 2.30 Hz), 3.96 (24H, s), –2.83 (2H, s).

H_2TMP: Pyrrole (3.73 mL) and 3,4,5-trimethoxybenzaldehyde (10.46 g) were dissolved in 200 mL propionic acid. The resulting solution was refluxed for 1 h. Upon completion of the reaction, the propionic acid was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 and purified using basic alumina column chromatography. The column was eluted with CH_2Cl_2:ethylacetate (= 90:10) to obtain the pure compound. Yield = 4.50 g (8.7%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 8.96 (8H, s), 7.47 (8H, s), 4.19 (12H, s), 3.97 (24H, s), –2.78 (2H, s).

Synthesis of axial dichloroantimony(V) porphyrins. Free-base (1.25 mmol) was dissolved in 60 mL anhydrous pyridine. This solution was flushed with N_2 for 20 min, followed by the dropwise addition of $SbCl_5$ (7.90 mmol). The resulting solution was refluxed for 1 h under a nitrogen atmosphere. Vacuum distillation was used to remove the solvent. The residue was dissolved in CH_2Cl_2 and purified by silica gel column chromatography eluted first with CH_2Cl_2 to remove the free-base and then with CH_2Cl_2:CH_3OH (= 99:1 to 95:5) to elute the product. Some of the porphyrins were converted to PF_6^- salts to remove any additional impurities, see the details below.

***$SbPCl_2.PF_6$*:** CH_2Cl_2:CH_3OH (= 98:2) eluent was used for the column to collect the product. The Cl^- product was converted to PF_6^- salt by dissolving it in 20 mL of CH_3OH and adding 500 mg of NH_4PF_6. The product was precipitated by the addition of 100 mL water and collected via filtration and vacuum dried. Yield = 1.17 g (98%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 9.64 (8H, s), 8.38 (8H, d, *J* = 6.64 Hz), 7.98 (12H, m). ESI MS: *m/z* 803.0441 for $[M - PF_6]^+$, calculated 803.0724 for $C_{44}H_{28}Cl_2N_4Sb^+$.

***$SbMPCl_2.Cl$*:** CH_2Cl_2:CH_3OH (= 99:1) eluent was used for column to collect the product. Yield = 304.5 mg (25%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 9.65 (8H, s), 8.29 (8H, d, *J* = 8.16 Hz), 7.49 (8H, d, *J* = 8.36 Hz), 4.17 (12H, s). ESI MS: *m/z* 923.0920 for $[M - Cl]^+$, calculated 923.1146 for $C_{48}H_{36}Cl_2N_4O_4Sb^+$.

***$SbDMPCl_2.PF_6$*:** CH_2Cl_2:CH_3OH (= 95:5) eluent was used for column to collect the product. PF_6 conversion achieved by using the procedure described for $SbPCl_2.PF_6$. Yield = 1.25 g (84%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 9.68 (8H, s), 7.51 (8H, d, *J* = 2.24 Hz), 7.05 (4H, t, *J* = 2.20 Hz), 4.02 (24H, s). ESI MS: *m/z* 1043.1330 for $[M - PF_6]^+$, calculated 1043.1569 for $C_{52}H_{44}Cl_2N_4O_8Sb^+$.

***$SbTMPCl_2.Cl$*:** CH_2Cl_2:CH_3OH (= 99:1) eluent was used for column to collect the product. Yield = 1.12 g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ, ppm* 9.72 (8H, s), 7.60 (8H, s), 4.24 (12H, s), 4.04 (24H, s). ESI MS: *m/z* 1163.1665 for $[M - Cl]^+$, calculated 1163.1991 for $C_{56}H_{52}Cl_2N_4O_{12}Sb^+$.

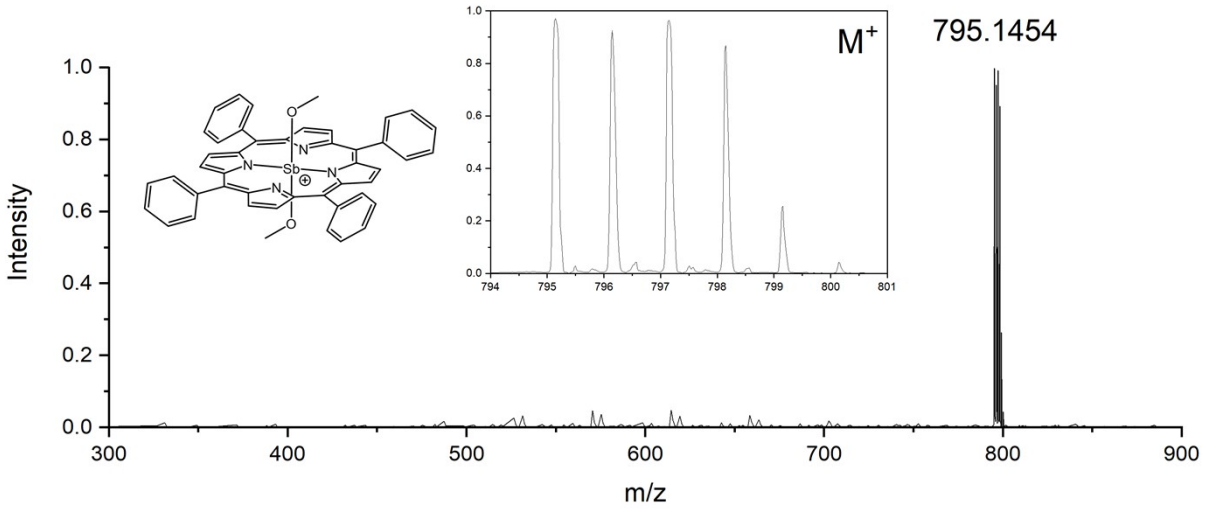


Figure S1: ESI mass spectrum of $SbP(OMe)_2.PF_6$

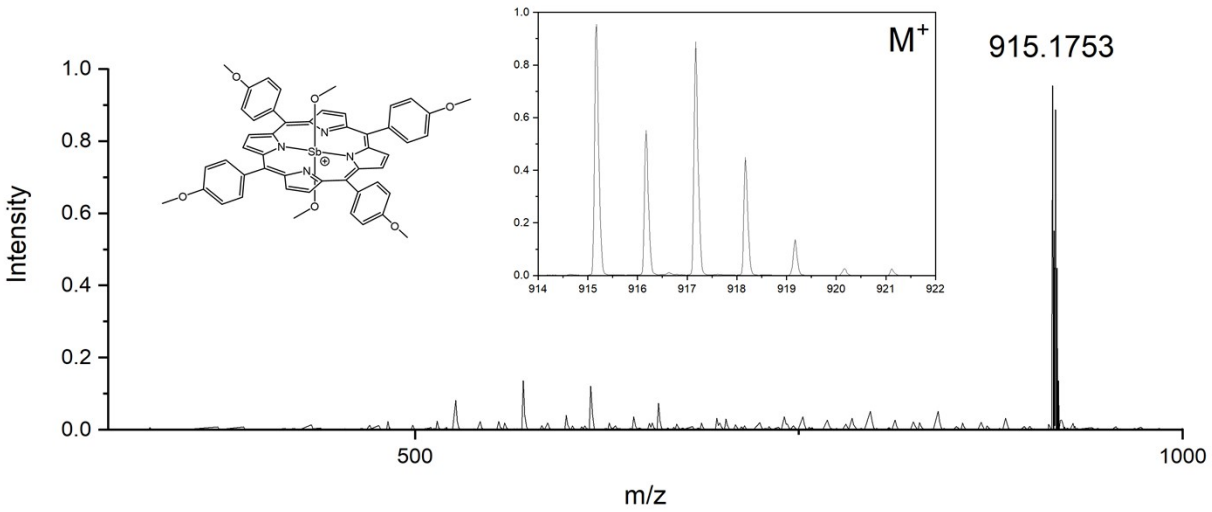


Figure S2: ESI mass spectrum of $SbMP(OMe)_2.PF_6$

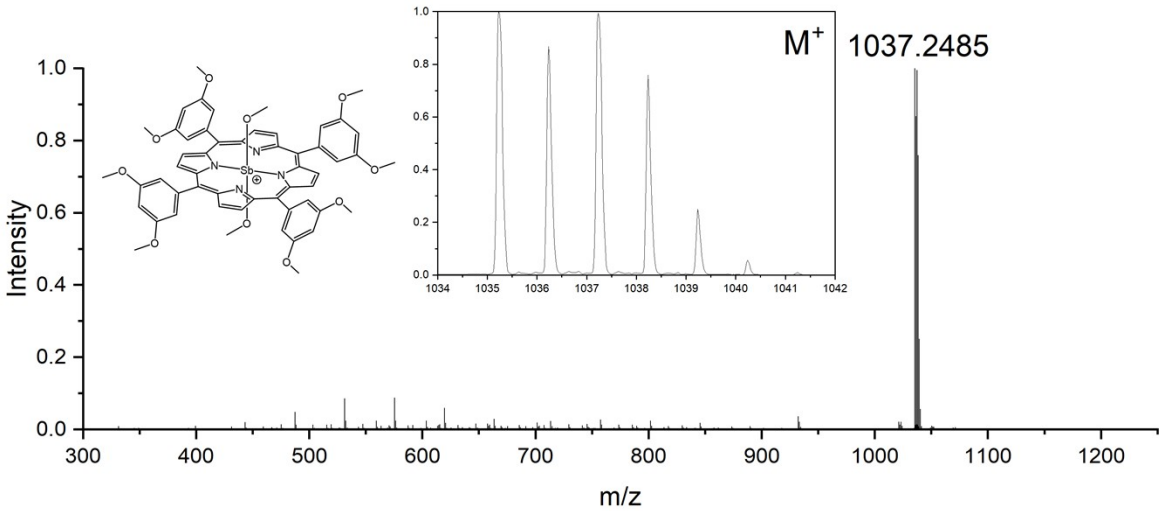


Figure S3: ESI mass spectrum of $SbDMP(OMe)_2.PF_6$

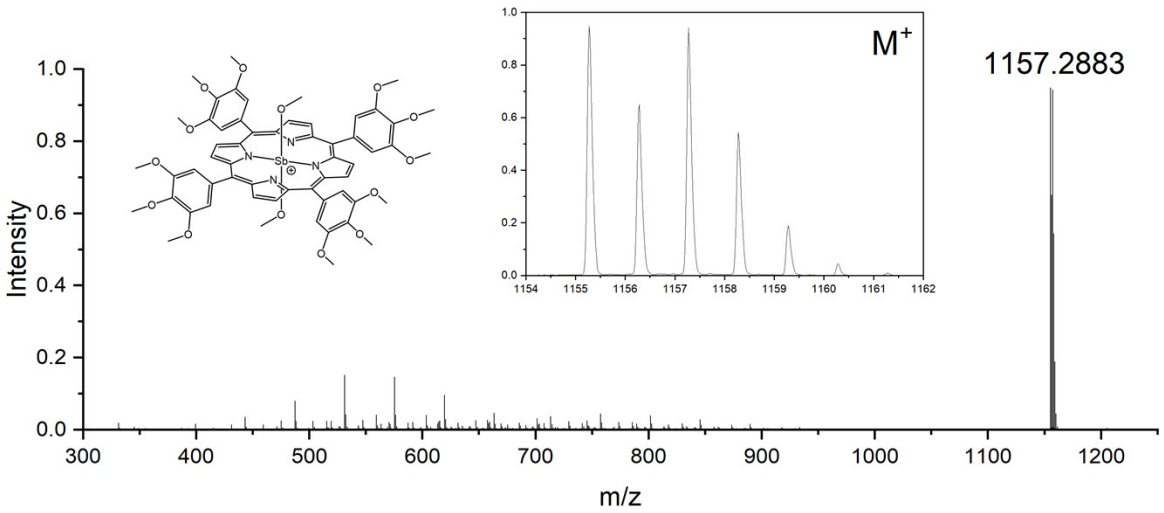
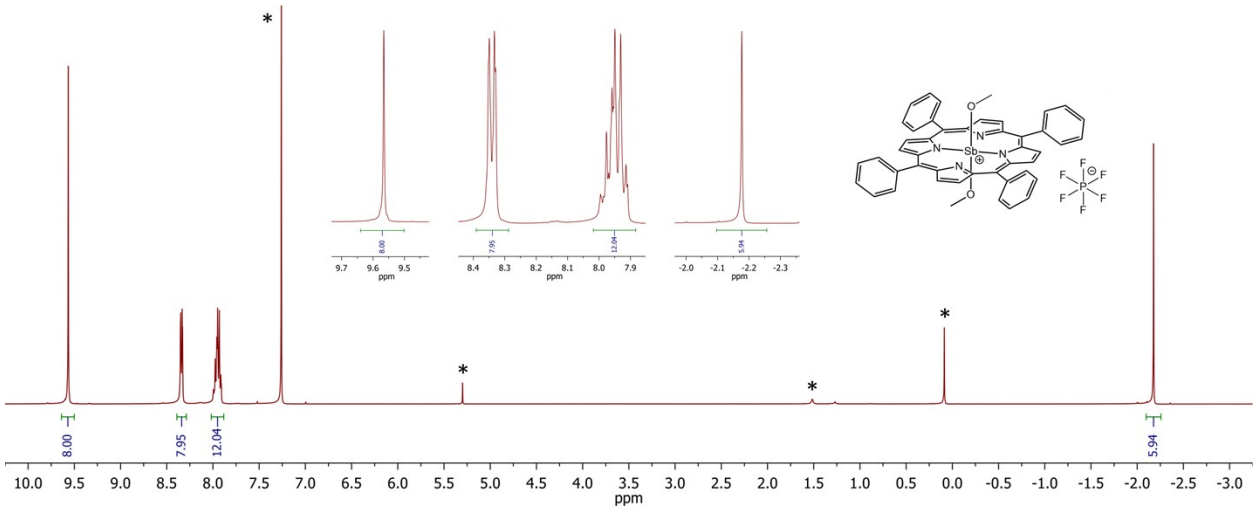


Figure S4: ESI mass spectrum of $SbTMP(OMe)_2.PF_6$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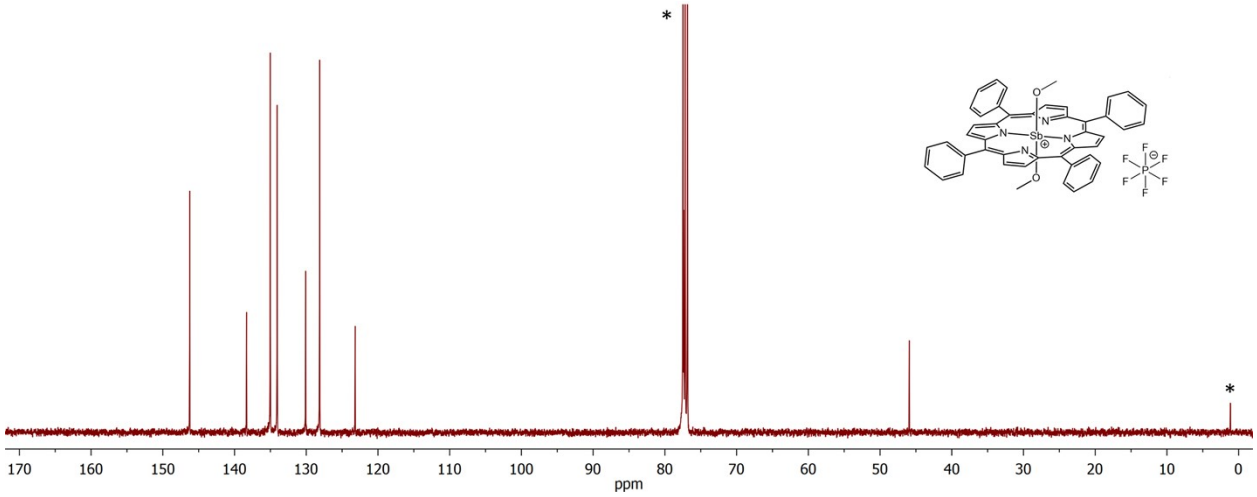
12.04
5.94
ppm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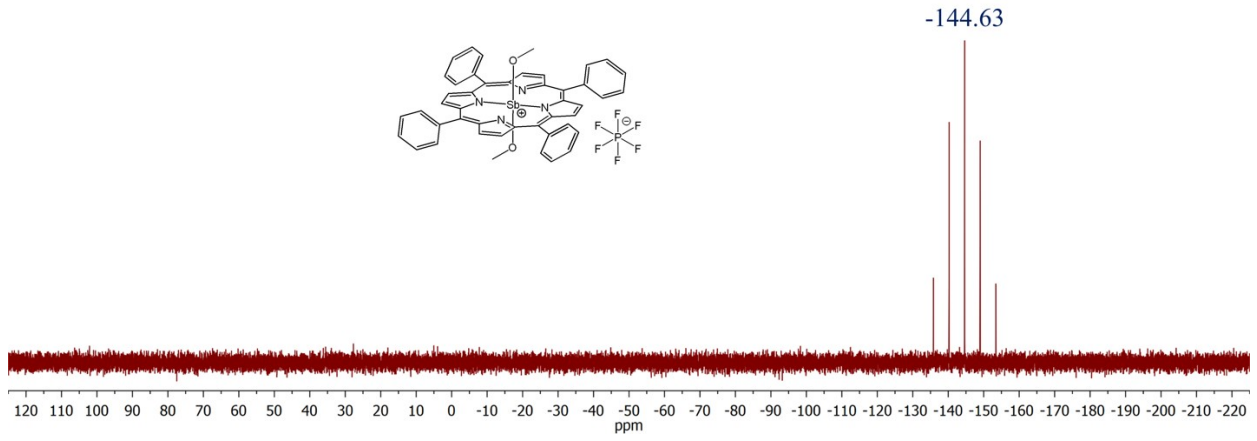
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ppm

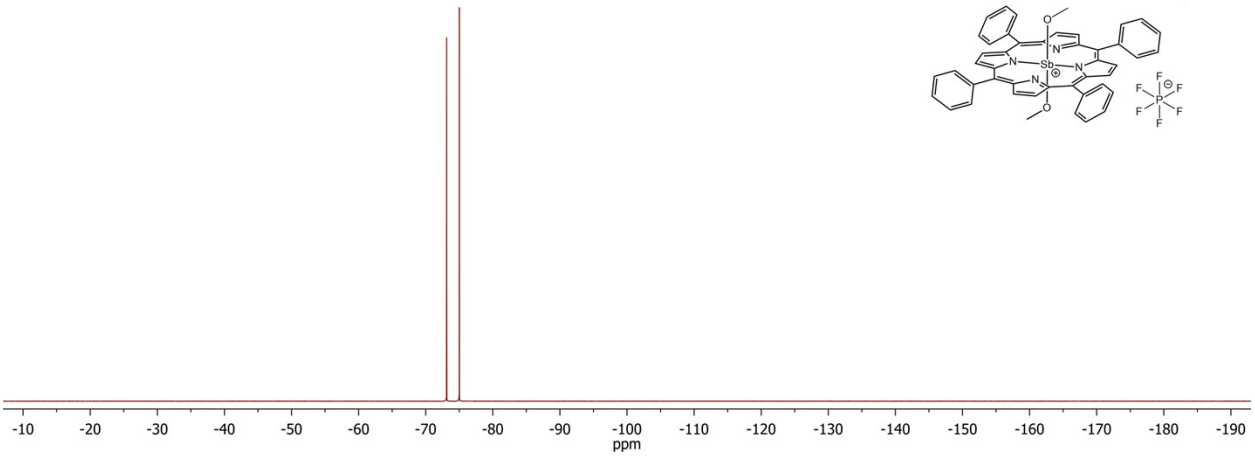
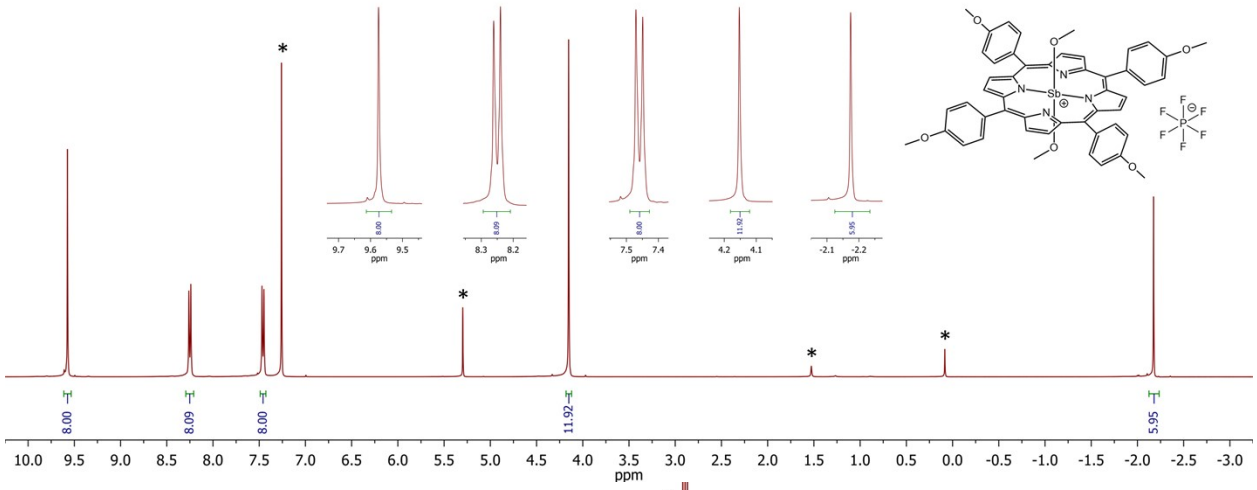
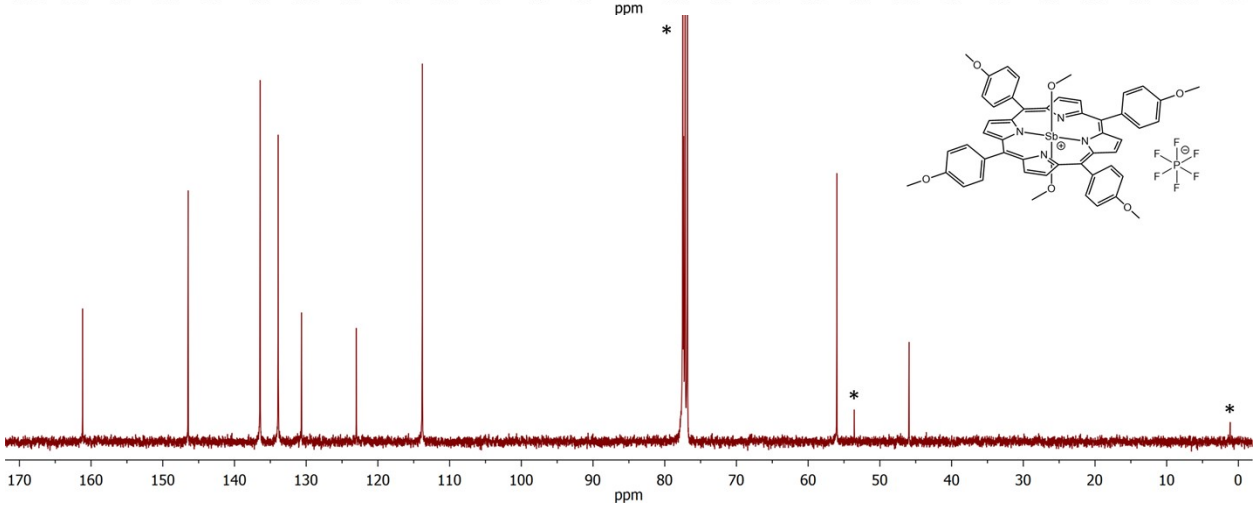


Figure S5: ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR (400 MHz) spectra of $SbP(OMe)_2.PF_6$ in $CDCl_3$. *Indicates solvent impurities.


8.00
8.09
8.00
11.92
5.95
ppm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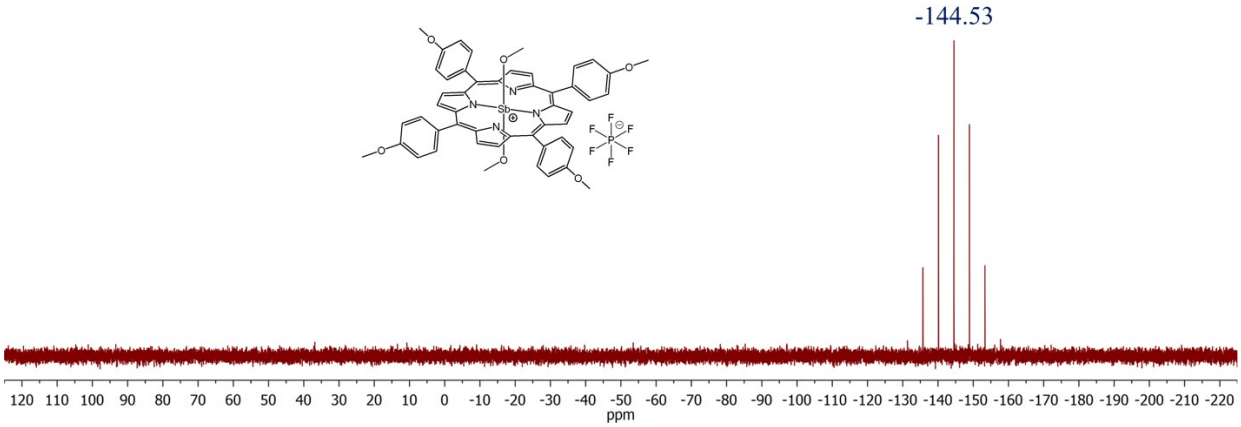
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ppm

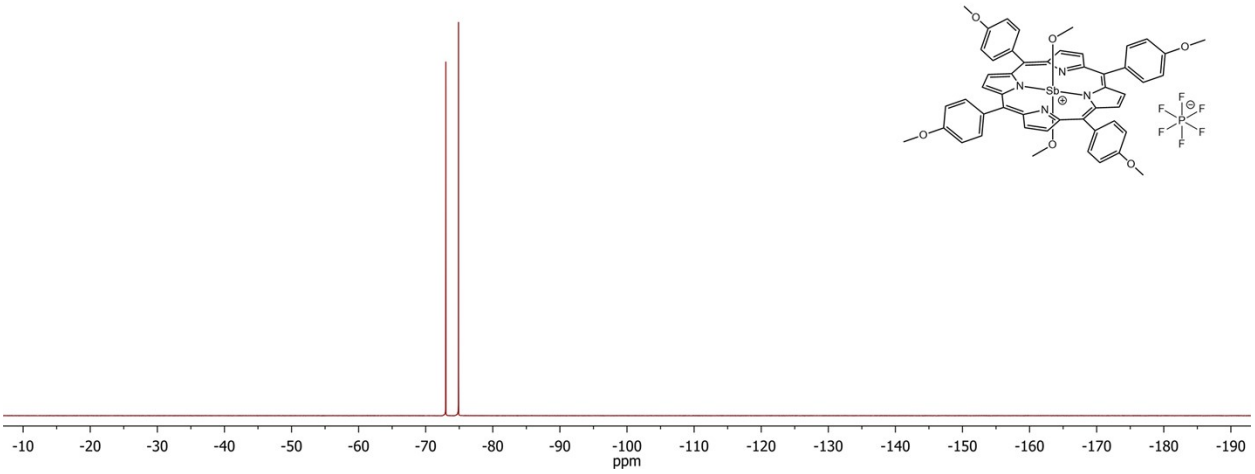
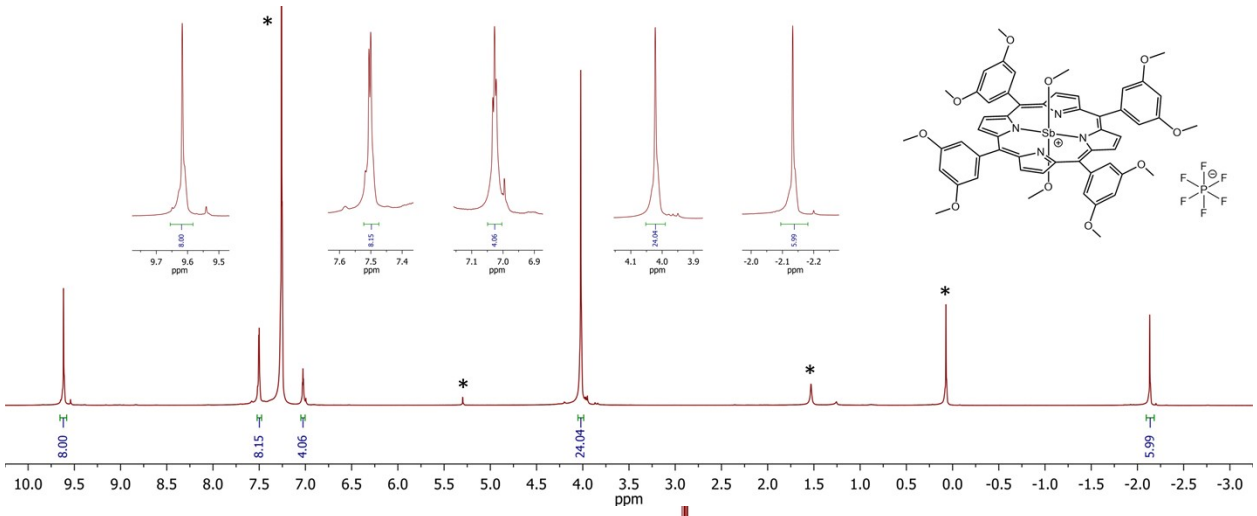


Figure S6: ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR (400 MHz) spectra of $SbMP(OMe)_2.PF_6$ in $CDCl_3$. *Indicates solvent impurities.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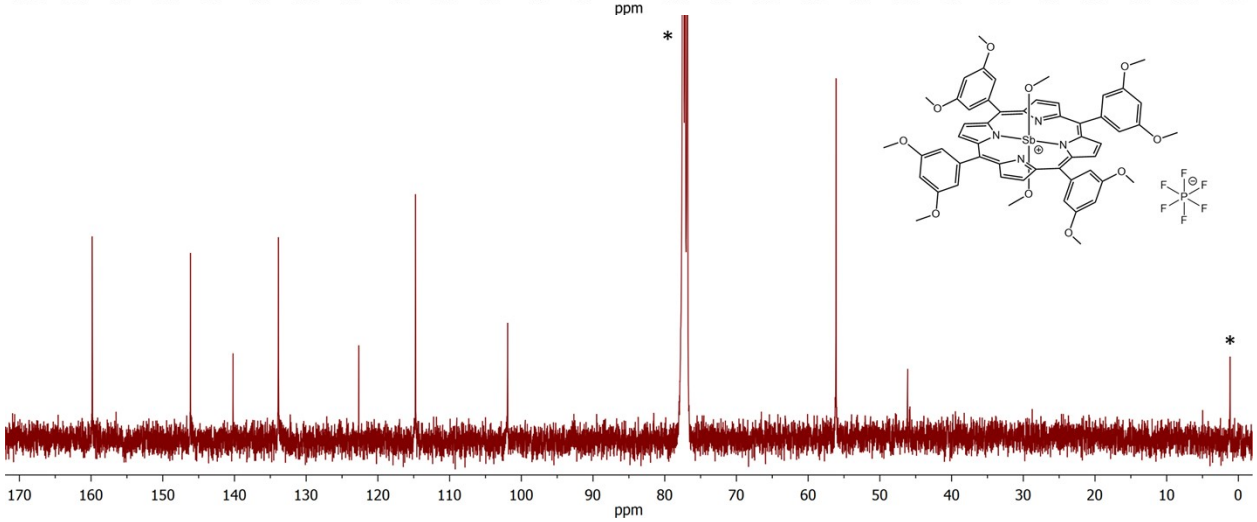
8.15
4.06
24.04
5.99
ppm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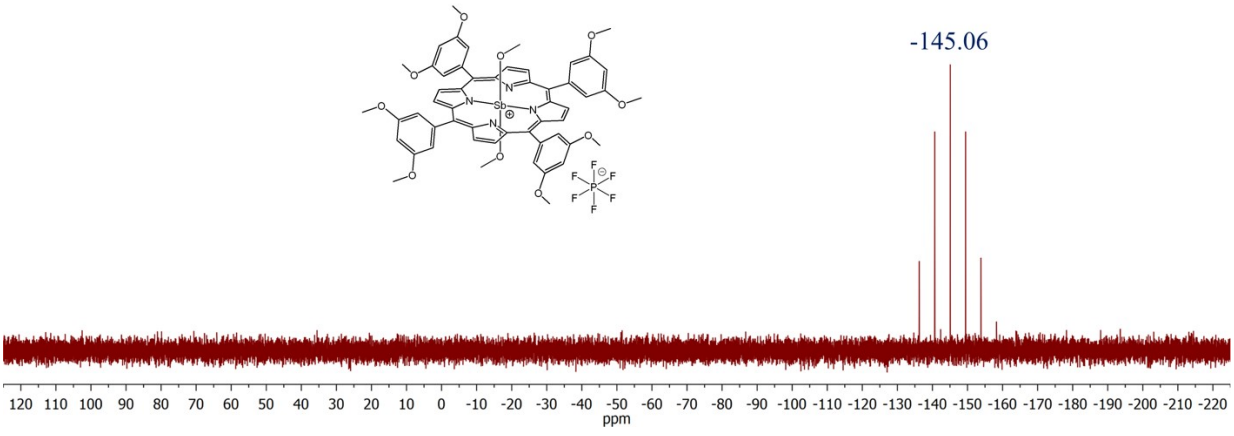
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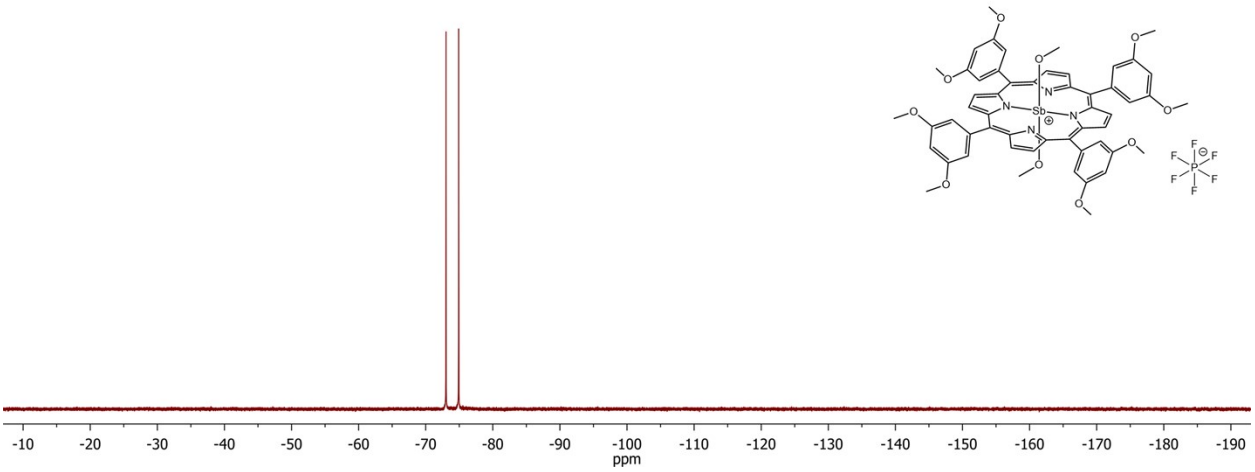
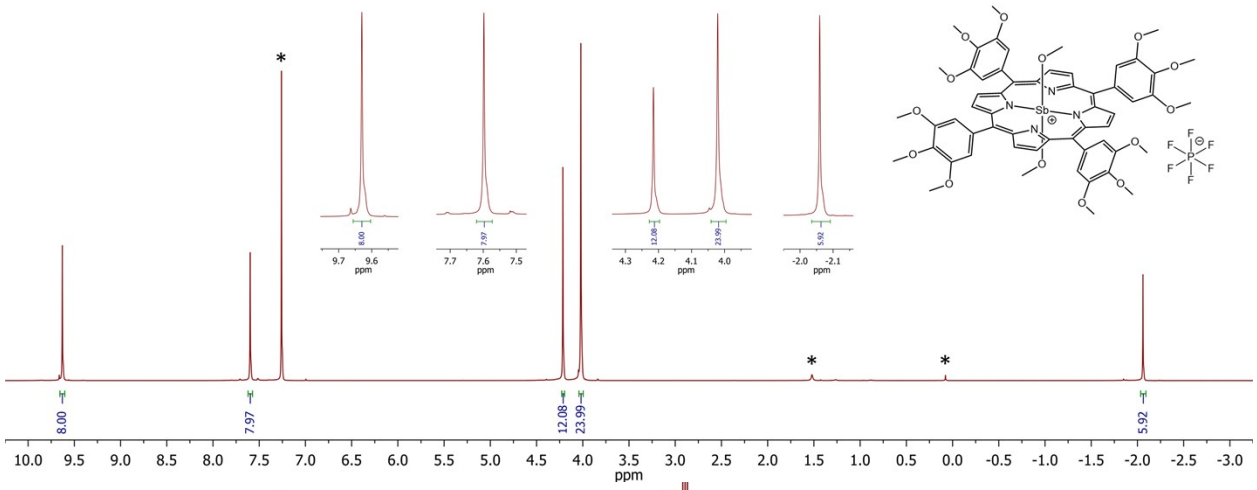


Figure S7: ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR (400 MHz) spectra of $SbDMP(OMe)_2.PF_6$ in $CDCl_3$. *Indicates solvent impurities.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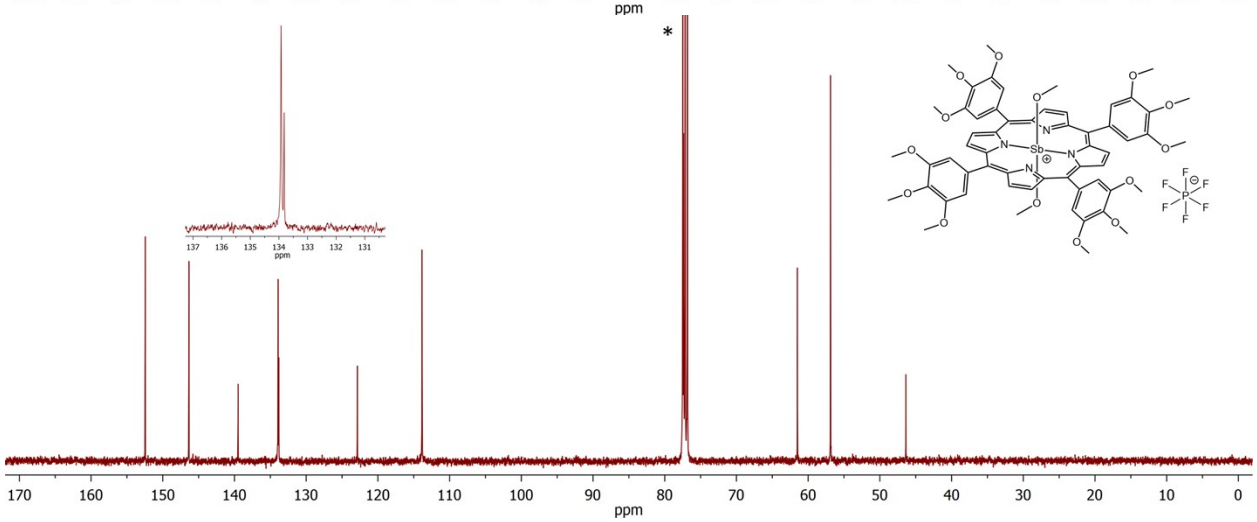
12.08
23.99
5.92
ppm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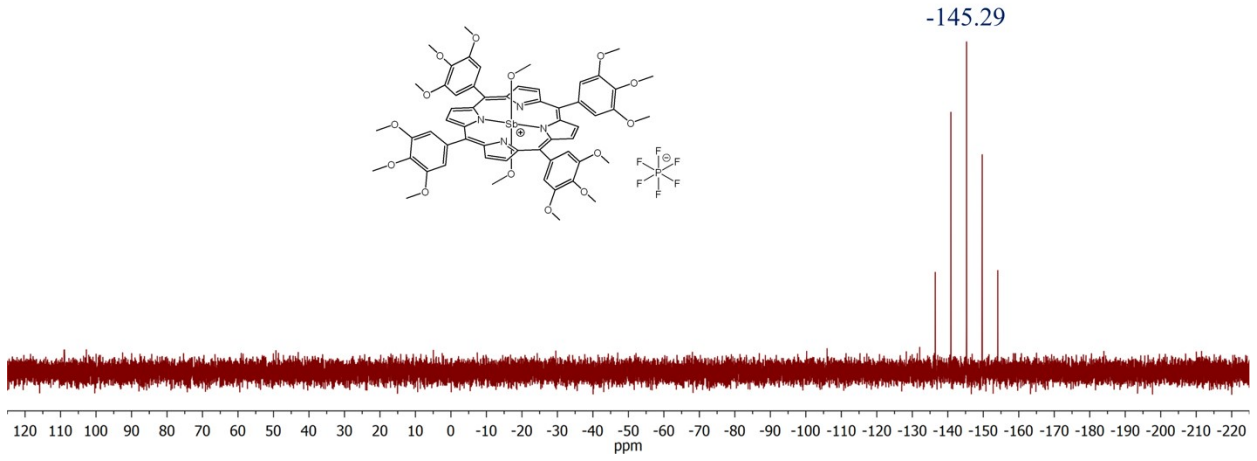
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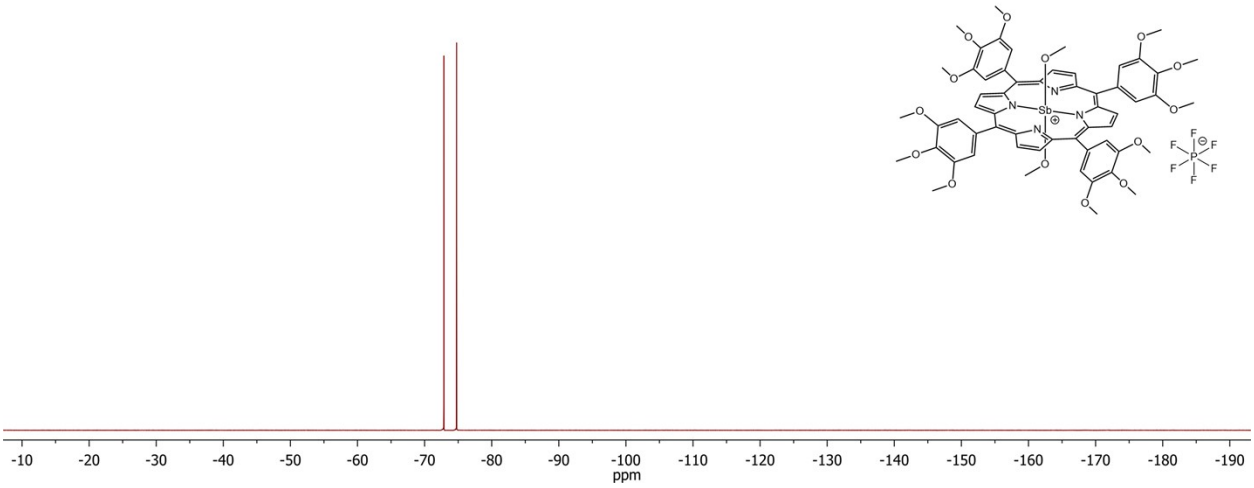

Figure S8: ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR (400 MHz) spectra of $SbTMP(OMe)_2.PF_6$ in $CDCl_3$. *Indicates solvent impurities.

Table S1. Crystallographic data of investigated compounds.

Compound	$SbP(OMe)_2 \cdot PF_6$	$SbMP(OMe)_2.PF_6$	$SbDMP(OMe)_2^+$	$SbTMP(OMe)_2^+$
Formula	$C_{46}H_{34}F_6N_4O_2PSb.3(CHCl_3)$	$C_{50}H_{42}F_6N_4O_6PSb.2(CH_3COCH_3)$	$C_{54}H_{50}F_6N_4O_{10}PSb.3(C_5H_{12})$	$C_{58}H_{58}F_6N_4O_{14}PSb.2(CHCl_3)$
CCDC number	2130977	2130978	2130979	2130980
$D_{calc.}$/ g cm^{-3}	1.614	1.528	1.571	1.594
μ/mm^{-1}	9.068	5.277	4.694	6.680
Formula Weight	1299.59	1177.75	1398.13	1540.54
Size/mm^3	0.04x0.03x0.02	0.07x0.04x0.03	0.07 x 0.04 x 0.01	0.04x0.03x0.02
***T*/K**	229.99(12)	219.99(11)	150.00(10)	229.99(11)
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$C2/c$	$C2/c$	P-1
***a*/Å**	12.4250(2)	30.6284(7)	15.21938(12)	8.52553(12)
***b*/Å**	26.1150(5)	10.75280(10)	25.80070(18)	14.3097(2)
***c*/Å**	17.3913(4)	20.9262(5)	45.1560(4)	14.55804(17)
α/°	90	90	90	104.0630(11)
β/°	108.590(2)	132.011(4)	90.6426(8)	103.8304(11)
γ/°	90	90	90	102.0038(12)
V/Å^3	5348.67(19)	5120.8(3)	17730.3(2)	1604.74(4)
Z	4	4	12	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Measured Refl.	48200	40217	73318	24477
Independent Refl.	11477	5552	18893	6858
R_{int}	0.0471	0.0376	0.0423	0.0529
Largest Peak	0.725	0.783	1.580	1.337
Deepest Hole	–1.196	–1.162	–1.135	-1.446
GooF	1.082	1.095	1.062	1.038
R_1	0.0746	0.0369	0.0471	0.0618
wR_2	0.1771	0.1038	0.1225	0.1642
R_1 **(all data)**	0.0959	0.0396	0.0500	0.0623
wR_2 **(all data)**	0.1890	0.1060	0.1243	0.1647

Table S2. Bond lengths in crystal structure of **$SbP(OMe)_2.PF_6$**

Atom 1	Atom 2	Length/Å
Sb1	O1	1.967(4)
Sb1	O1[1]	1.967(4)
Sb1	N1[1]	2.079(4)
Sb1	N1	2.079(4)
Sb1	N2[1]	2.077(4)
Sb1	N2	2.077(4)
O1	C23	1.376(8)
N1	C1	1.373(6)
N1	C4	1.375(6)
N2	C6	1.378(6)
N2	C9	1.374(6)
C1	C2	1.427(8)
C1	C10	1.403(7)
C2	C3	1.351(8)
C3	C4	1.435(8)
C4	C5	1.406(7)
C5	C6	1.392(7)
C5	C17	1.500(7)
C6	C7	1.446(7)
C7	C8	1.346(8)
C8	C9	1.432(7)
C9	C10[1]	1.409(8)
C10	C11	1.492(7)
C11	C12	1.368(10)
C11	C16	1.379(10)
C12	C13	1.388(10)
C13	C14	1.353(16)
C14	C15	1.374(16)
C15	C16	1.394(11)
C17	C18	1.394(9)
C17	C22	1.376(9)
C18	C19	1.385(9)
C19	C20	1.349(13)
C20	C21	1.389(14)
C21	C22	1.382(10)
Sb2	O1A[2]	1.950(4)
Sb2	O1A	1.950(4)
Sb2	N1A[2]	2.070(4)
Sb2	N1A	2.070(4)
Sb2	N2A	2.079(4)
Sb2	N2A[2]	2.079(4)
O1A	C23A	1.385(8)
N1A	C1A	1.383(7)
N1A	C4A	1.389(6)

Atom 1	Atom 2	Length/Å
N2A	C6A	1.387(7)
N2A	C9A	1.371(7)
C1A	C2A	1.418(8)
C1A	C10A[2]	1.417(7)
C2A	C3A	1.346(8)
C3A	C4A	1.424(8)
C4A	C5A	1.393(8)
C5A	C6A	1.394(8)
C5A	C17A	1.498(7)
C6A	C7A	1.430(8)
C7A	C8A	1.345(9)
C8A	C9A	1.432(8)
C9A	C10A	1.409(8)
C10A	C11A	1.479(8)
C11A	C12A	1.375(9)
C11A	C16A	1.392(9)
C12A	C13A	1.400(10)
C13A	C14A	1.369(13)
C14A	C15A	1.370(13)
C15A	C16A	1.362(11)
C17A	C18A	1.390(9)
C17A	C22A	1.368(9)
C18A	C19A	1.382(10)
C19A	C20A	1.356(13)
C20A	C21A	1.371(12)
C21A	C22A	1.386(9)
Cl1	C24	1.713(10)
Cl2	C24	1.759(12)
Cl3	C24	1.726(12)
Cl4	C25	1.728(10)
Cl5	C25	1.762(11)
Cl6	C25	1.721(10)
P1	F1	1.570(8)
P1	F2	1.533(9)
P1	F3	1.552(8)
P1	F4	1.523(9)
P1	F5	1.479(8)
P1	F6	1.576(9)
Cl8	C26	1.773(9)
Cl7	C26	1.767(9)
C26	Cl9	1.782(10)
Cl7A	C27	1.794(10)
Cl8A	C27	1.783(10)
C27	Cl9A	1.775(10)

Table S3. Bond angles in crystal structure of **$SbP(OMe)_2.PF_6$**

Atom 1	Atom 2	Atom 3	Angle/°
O1	Sb1	O1[1]	180.00(14)
O1[1]	Sb1	N1	90.62(17)
O1	Sb1	N1[1]	90.62(17)
O1[1]	Sb1	N1[1]	89.38(17)
O1	Sb1	N1	89.38(17)
O1	Sb1	N2	93.38(16)
O1[1]	Sb1	N2	86.61(16)
O1	Sb1	N2[1]	86.61(16)
O1[1]	Sb1	N2[1]	93.39(16)
N1[1]	Sb1	N1	180.00(19)
N2	Sb1	N1[1]	89.75(16)
N2[1]	Sb1	N1[1]	90.24(16)
N2	Sb1	N1	90.25(16)
N2[1]	Sb1	N1	89.76(16)
N2	Sb1	N2[1]	180.0
C23	O1	Sb1	123.6(4)
C1	N1	Sb1	125.9(3)
C1	N1	C4	108.5(4)
C4	N1	Sb1	125.6(3)
C6	N2	Sb1	125.0(3)
C9	N2	Sb1	125.9(3)
C9	N2	C6	109.1(4)
N1	C1	C2	107.6(4)
N1	C1	C10	126.8(5)
C10	C1	C2	125.6(5)
C3	C2	C1	108.7(5)
C2	C3	C4	107.0(5)
N1	C4	C3	108.1(4)
N1	C4	C5	126.4(5)
C5	C4	C3	125.4(5)
C4	C5	C17	116.2(5)
C6	C5	C4	125.4(5)
C6	C5	C17	118.4(4)
N2	C6	C5	127.4(4)
N2	C6	C7	107.1(4)
C5	C6	C7	125.5(5)
C8	C7	C6	107.8(5)
C7	C8	C9	108.5(5)
N2	C9	C8	107.5(4)
N2	C9	C10[1]	126.7(4)
C10[1]	C9	C8	125.8(5)
C1	C10	C9[1]	124.9(5)
C1	C10	C11	117.6(5)
C9[1]	C10	C11	117.5(5)
C12	C11	C10	120.8(6)
C12	C11	C16	118.5(6)
C16	C11	C10	120.7(6)
C11	C12	C13	121.2(9)
C14	C13	C12	120.4(10)
C13	C14	C15	119.5(8)
C14	C15	C16	120.4(9)
C11	C16	C15	120.1(9)
C18	C17	C5	120.9(6)
C22	C17	C5	120.0(6)
C22	C17	C18	119.1(6)
C19	C18	C17	119.5(7)
C20	C19	C18	121.3(8)
C19	C20	C21	119.7(7)
C22	C21	C20	119.8(8)
C17	C22	C21	120.5(8)
O1A	Sb2	O1A[2]	180.00(18)
O1A	Sb2	N1A[2]	87.34(17)
O1A	Sb2	N1A	92.66(17)
O1A[2]	Sb2	N1A[2]	92.66(17)
O1A[2]	Sb2	N1A	87.34(17)
O1A[2]	Sb2	N2A	88.18(18)
O1A[2]	Sb2	N2A[2]	91.82(18)
O1A	Sb2	N2A[2]	88.18(18)
O1A	Sb2	N2A	91.82(18)
N1A[2]	Sb2	N1A	180.0(2)
N1A	Sb2	N2A[2]	90.56(18)
N1A	Sb2	N2A	89.43(18)
N1A[2]	Sb2	N2A	90.57(18)
N1A[2]	Sb2	N2A[2]	89.44(18)
N2A	Sb2	N2A[2]	180.0
C23A	O1A	Sb2	123.7(4)
C1A	N1A	Sb2	125.5(3)
C1A	N1A	C4A	108.2(4)
C4A	N1A	Sb2	126.2(4)
C6A	N2A	Sb2	126.0(4)
C9A	N2A	Sb2	125.4(3)
C9A	N2A	C6A	108.1(4)
N1A	C1A	C2A	108.1(5)
N1A	C1A	C10A[2]	126.4(5)
C10A[2]	C1A	C2A	125.6(5)
C3A	C2A	C1A	107.8(5)
C2A	C3A	C4A	109.1(5)
N1A	C4A	C3A	106.8(5)
N1A	C4A	C5A	126.1(5)
C5A	C4A	C3A	127.0(5)
C4A	C5A	C6A	125.8(5)
C4A	C5A	C17A	117.3(5)
C6A	C5A	C17A	116.8(5)
N2A	C6A	C5A	125.9(5)
N2A	C6A	C7A	107.3(5)
C5A	C6A	C7A	126.8(5)
C8A	C7A	C6A	108.7(5)
C7A	C8A	C9A	107.5(6)
N2A	C9A	C8A	108.4(5)
N2A	C9A	C10A	126.9(5)
C10A	C9A	C8A	124.6(6)
C1A[2]	C10A	C11A	117.4(5)
C9A	C10A	C1A[2]	125.1(5)
C9A	C10A	C11A	117.5(5)
C12A	C11A	C10A	121.9(6)
C12A	C11A	C16A	117.7(6)
C16A	C11A	C10A	120.4(6)
C11A	C12A	C13A	120.5(7)
C14A	C13A	C12A	120.2(8)
C13A	C14A	C15A	119.4(8)
C16A	C15A	C14A	120.5(8)
C15A	C16A	C11A	121.7(8)
C18A	C17A	C5A	120.1(6)
C22A	C17A	C5A	121.1(6)
C22A	C17A	C18A	118.7(6)
C19A	C18A	C17A	119.7(7)
C20A	C19A	C18A	121.2(8)
C19A	C20A	C21A	119.4(7)
C20A	C21A	C22A	120.1(8)
C17A	C22A	C21A	120.8(7)
Cl1	C24	Cl2	109.0(6)
Cl1	C24	Cl3	109.3(6)
Cl3	C24	Cl2	111.5(6)
Cl4	C25	Cl5	108.5(6)
Cl6	C25	Cl4	111.5(6)
Cl6	C25	Cl5	109.2(6)
F1	P1	F6	88.2(5)
F2	P1	F1	90.7(6)
F2	P1	F3	94.7(5)
F2	P1	F6	81.5(6)
F3	P1	F1	173.4(6)
F3	P1	F6	88.9(5)
F4	P1	F1	86.7(6)
F4	P1	F2	172.6(7)
F4	P1	F3	87.5(6)
F4	P1	F6	91.5(7)
F5	P1	F1	92.0(6)
F5	P1	F2	95.4(8)
F5	P1	F3	91.3(6)
F5	P1	F4	91.5(8)
F5	P1	F6	177.0(9)
Cl8	C26	Cl9	99.4(6)
Cl7	C26	Cl8	113.6(9)
Cl7	C26	Cl9	99.7(6)
Cl8A	C27	Cl7A	107.4(9)
Cl9A	C27	Cl7A	98.1(7)
Cl9A	C27	Cl8A	103.4(13)

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[1]1-x,1-y,1-z; [2]-x,1-y,-z

Table S4. Dihedral angles in crystal structure of **$SbP(OMe)_2.PF_6$**

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
Sb1	N1	C1	C2	178.6(4)
Sb1	N1	C1	C10	-1.1(9)
Sb1	N1	C4	C3	-178.0(4)
Sb1	N1	C4	C5	0.3(8)
Sb1	N2	C6	C5	-1.6(8)
Sb1	N2	C6	C7	179.8(4)
Sb1	N2	C9	C8	-179.4(4)
Sb1	N2	C9	C10[1]	0.2(8)
N1	C1	C2	C3	-0.1(7)
N1	C1	C10	C9[1]	0.8(10)
N1	C1	C10	C11	-178.8(6)
N1	C4	C5	C6	-1.1(10)
N1	C4	C5	C17	178.4(5)
N2	C6	C7	C8	-0.7(7)
C1	N1	C4	C3	1.3(6)
C1	N1	C4	C5	179.7(6)
C1	C2	C3	C4	0.9(7)
C1	C10	C11	C12	66.4(8)
C1	C10	C11	C16	-112.4(7)
C2	C1	C10	C9[1]	-178.8(6)
C2	C1	C10	C11	1.6(9)
C2	C3	C4	N1	-1.4(7)
C2	C3	C4	C5	-179.8(6)
C3	C4	C5	C6	177.0(6)
C3	C4	C5	C17	-3.5(9)
C4	N1	C1	C2	-0.8(7)
C4	N1	C1	C10	179.5(6)
C4	C5	C6	N2	1.8(9)
C4	C5	C6	C7	-179.9(6)
C4	C5	C17	C18	109.0(6)
C4	C5	C17	C22	-70.1(8)
C5	C6	C7	C8	-179.3(6)
C5	C17	C18	C19	-177.7(6)
C5	C17	C22	C21	178.3(7)
C6	N2	C9	C8	0.0(6)
C6	N2	C9	C10[1]	179.6(5)
C6	C5	C17	C18	-71.5(7)
C6	C5	C17	C22	109.4(7)
C6	C7	C8	C9	0.7(7)
C7	C8	C9	N2	-0.5(7)
C7	C8	C9	C10[1]	180.0(6)
C9	N2	C6	C5	178.9(5)
C9	N2	C6	C7	0.4(6)
C9[1]	C10	C11	C12	-113.3(7)
C9[1]	C10	C11	C16	67.9(8)
C10	C1	C2	C3	179.6(6)
C10	C11	C12	C13	179.8(7)
C10	C11	C16	C15	179.9(6)
C11	C12	C13	C14	1.1(12)
C12	C11	C16	C15	1.1(10)
C12	C13	C14	C15	-0.6(13)
C13	C14	C15	C16	0.4(13)
C14	C15	C16	C11	-0.6(11)
C16	C11	C12	C13	-1.3(10)
C17	C5	C6	N2	-177.6(5)
C17	C5	C6	C7	0.7(9)
C17	C18	C19	C20	-1.0(12)
C18	C17	C22	C21	-0.8(11)
C18	C19	C20	C21	0.1(13)
C19	C20	C21	C22	0.5(14)
C20	C21	C22	C17	-0.2(13)
C22	C17	C18	C19	1.4(10)
Sb2	N1A	C1A	C2A	175.8(4)
Sb2	N1A	C1A	C10A[2]	-3.8(8)
Sb2	N1A	C4A	C3A	-175.4(4)
Sb2	N1A	C4A	C5A	5.2(8)
Sb2	N2A	C6A	C5A	7.0(8)
Sb2	N2A	C6A	C7A	-172.7(4)
Sb2	N2A	C9A	C8A	173.1(4)
Sb2	N2A	C9A	C10A	-3.1(9)
N1A	C1A	C2A	C3A	-0.1(7)
N1A	C4A	C5A	C6A	-4.3(9)
N1A	C4A	C5A	C17A	177.4(5)
N2A	C6A	C7A	C8A	-0.8(7)
N2A	C9A	C10A	C1A[2]	2.1(10)
N2A	C9A	C10A	C11A	-177.2(6)
C1A	N1A	C4A	C3A	0.9(6)
C1A	N1A	C4A	C5A	-178.5(5)
C1A	C2A	C3A	C4A	0.7(7)
C1A[2]	C10A	C11A	C12A	64.0(8)
C1A[2]	C10A	C11A	C16A	-114.8(7)
C2A	C3A	C4A	N1A	-1.0(7)
C2A	C3A	C4A	C5A	178.4(6)
C3A	C4A	C5A	C6A	176.4(6)
C3A	C4A	C5A	C17A	-1.8(9)
C4A	N1A	C1A	C2A	-0.5(6)
C4A	N1A	C1A	C10A[2]	179.9(5)
C4A	C5A	C6A	N2A	-2.3(9)
C4A	C5A	C6A	C7A	177.3(6)
C4A	C5A	C17A	C18A	-62.4(8)
C4A	C5A	C17A	C22A	116.9(7)
C5A	C6A	C7A	C8A	179.6(6)
C5A	C17A	C18A	C19A	178.9(7)
C5A	C17A	C22A	C21A	-179.2(6)
C6A	N2A	C9A	C8A	-0.3(7)
C6A	N2A	C9A	C10A	-176.4(6)
C6A	C5A	C17A	C18A	119.1(7)
C6A	C5A	C17A	C22A	-61.6(8)
C6A	C7A	C8A	C9A	0.6(8)
C7A	C8A	C9A	N2A	-0.2(7)
C7A	C8A	C9A	C10A	176.1(6)
C8A	C9A	C10A	C1A[2]	-173.4(6)
C8A	C9A	C10A	C11A	7.3(9)
C9A	N2A	C6A	C5A	-179.7(6)
C9A	N2A	C6A	C7A	0.6(6)
C9A	C10A	C11A	C12A	-116.7(6)
C9A	C10A	C11A	C16A	64.6(8)
C10A[2]	C1A	C2A	C3A	179.5(6)
C10A	C11A	C12A	C13A	-178.7(6)
C10A	C11A	C16A	C15A	178.9(6)
C11A	C12A	C13A	C14A	-0.2(10)
C12A	C11A	C16A	C15A	0.1(10)
C12A	C13A	C14A	C15A	0.1(11)
C13A	C14A	C15A	C16A	0.0(12)
C14A	C15A	C16A	C11A	-0.1(12)
C16A	C11A	C12A	C13A	0.1(9)
C17A	C5A	C6A	N2A	176.0(5)
C17A	C5A	C6A	C7A	-4.4(9)
C17A	C18A	C19A	C20A	-0.3(13)
C18A	C17A	C22A	C21A	0.1(10)
C18A	C19A	C20A	C21A	1.3(14)
C19A	C20A	C21A	C22A	-1.6(13)
C20A	C21A	C22A	C17A	0.9(12)
C22A	C17A	C18A	C19A	-0.4(11)

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[1]1-x,1-y,1-z; [2]-x,1-y,-z

Table S5. Bond lengths in crystal structure of **$SbMP(OMe)_2.PF_6$**

Atom 1	Atom 2	Length/Å
Sb1	O3	1.9500(17)
Sb1	O3[1]	1.9501(17)
Sb1	N1[1]	2.0640(17)
Sb1	N1	2.0640(18)
Sb1	N2[1]	2.0808(18)
Sb1	N2	2.0809(18)
O1	C14	1.372(3)
O1	C23	1.424(3)
O2	C20	1.368(3)
O2	C24	1.429(3)
O3	C25	1.423(3)
N1	C1	1.384(3)
N1	C4	1.386(3)
N2	C6	1.383(3)
N2	C9	1.383(3)
C1	C2	1.430(3)
C1	C10[1]	1.404(3)
C2	C3	1.358(3)
C3	C4	1.430(3)
C4	C5	1.403(3)
C5	C6	1.402(3)
C5	C11	1.494(3)
C6	C7	1.433(3)
C7	C8	1.353(3)
C8	C9	1.434(3)
C9	C10	1.403(3)
C10	C17	1.499(3)
C11	C12	1.393(3)
C11	C16	1.389(4)
C12	C13	1.385(4)
C13	C14	1.385(4)
C14	C15	1.386(4)
C15	C16	1.390(4)
C17	C18	1.393(3)
C17	C22	1.388(4)
C18	C19	1.387(3)
C19	C20	1.384(3)
C20	C21	1.387(4)
C21	C22	1.389(4)
P1	F1	1.516(9)
P1	F2	1.569(8)
P1	F3	1.511(9)
P1	F4	1.506(8)
P1	F5	1.527(7)
P1	F6	1.501(7)
O1A	C1A	1.208(5)
C1A	C2A	1.508(6)
C1A	C3A	1.473(6)

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[1]1-x,2-y,1-z

Table S6. Bond angles in crystal structure of **$SbMP(OMe)_2.PF_6$**

Atom 1	Atom 2	Atom 3	Angle/°
O3	Sb1	O3[1]	180.0
O3[1]	Sb1	N1[1]	93.55(7)
O3[1]	Sb1	N1	86.44(7)
O3	Sb1	N1[1]	86.45(7)
O3	Sb1	N1	93.56(7)
O3	Sb1	N2[1]	89.94(8)
O3[1]	Sb1	N2	89.93(8)
O3	Sb1	N2	90.06(8)
O3[1]	Sb1	N2[1]	90.07(8)
N1[1]	Sb1	N1	180.0
N1	Sb1	N2	89.73(7)
N1	Sb1	N2[1]	90.27(7)
N1[1]	Sb1	N2[1]	89.73(7)
N1[1]	Sb1	N2	90.27(7)
N2[1]	Sb1	N2	180.0
C14	O1	C23	117.4(2)
C20	O2	C24	117.4(2)
C25	O3	Sb1	122.13(16)
C1	N1	Sb1	125.45(15)
C1	N1	C4	108.37(18)
C4	N1	Sb1	125.74(14)
C6	N2	Sb1	126.30(14)
C9	N2	Sb1	125.63(15)
C9	N2	C6	108.03(18)
N1	C1	C2	107.7(2)
N1	C1	C10[1]	126.5(2)
C10[1]	C1	C2	125.7(2)
C3	C2	C1	108.1(2)
C2	C3	C4	108.1(2)
N1	C4	C3	107.64(19)
N1	C4	C5	126.6(2)
C5	C4	C3	125.7(2)
C4	C5	C11	116.42(19)
C6	C5	C4	125.1(2)
C6	C5	C11	118.4(2)
N2	C6	C5	125.9(2)
N2	C6	C7	108.05(19)
C5	C6	C7	126.1(2)
C8	C7	C6	108.0(2)
C7	C8	C9	108.0(2)
N2	C9	C8	107.96(19)
N2	C9	C10	126.2(2)
C10	C9	C8	125.8(2)
C1[1]	C10	C17	116.0(2)
C9	C10	C1[1]	125.4(2)
C9	C10	C17	118.6(2)
C12	C11	C5	121.9(2)
C16	C11	C5	119.4(2)
C16	C11	C12	118.7(2)
C13	C12	C11	120.5(2)
C12	C13	C14	120.2(2)
O1	C14	C13	115.6(2)
O1	C14	C15	124.4(2)
C13	C14	C15	120.1(2)
C14	C15	C16	119.4(2)
C11	C16	C15	121.1(3)
C18	C17	C10	121.9(2)
C22	C17	C10	119.7(2)
C22	C17	C18	118.4(2)
C19	C18	C17	120.9(2)
C20	C19	C18	119.8(2)
O2	C20	C19	115.6(2)
O2	C20	C21	124.2(2)
C19	C20	C21	120.2(2)
C20	C21	C22	119.4(2)
C17	C22	C21	121.3(2)
F1	P1	F2	78.6(7)
F1	P1	F5	75.6(7)
F3	P1	F1	153.2(9)
F3	P1	F2	80.1(7)
F3	P1	F5	90.3(6)
F4	P1	F1	89.7(8)
F4	P1	F2	167.4(10)
F4	P1	F3	112.4(8)
F4	P1	F5	86.8(6)
F5	P1	F2	94.8(7)
F6	P1	F1	105.9(8)
F6	P1	F2	83.5(6)
F6	P1	F3	87.5(7)
F6	P1	F4	95.3(9)
F6	P1	F5	177.3(8)
O1A	C1A	C2A	121.6(4)
O1A	C1A	C3A	120.2(4)
C3A	C1A	C2A	118.2(4)

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[1]1-x,2-y,1-z

Table S7. Dihedral angles in crystal structure of **$SbMP(OMe)_2.PF_6$**

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
Sb1	N1	C1	C2	-170.36(17)
Sb1	N1	C1	C10[1]	9.4(4)
Sb1	N1	C4	C3	170.31(17)
Sb1	N1	C4	C5	-9.0(4)
Sb1	N2	C6	C5	-3.0(4)
Sb1	N2	C6	C7	177.54(17)
Sb1	N2	C9	C8	-178.66(16)
Sb1	N2	C9	C10	-1.3(3)
O1	C14	C15	C16	179.5(3)
O2	C20	C21	C22	177.1(3)
N1	C1	C2	C3	-1.5(3)
N1	C4	C5	C6	9.1(4)
N1	C4	C5	C11	-169.5(2)
N2	C6	C7	C8	1.2(3)
N2	C9	C10	C1[1]	-1.4(4)
N2	C9	C10	C17	179.2(2)
C1	N1	C4	C3	-2.4(3)
C1	N1	C4	C5	178.3(2)
C1	C2	C3	C4	0.0(3)
C1[1]	C10	C17	C18	-113.3(3)
C1[1]	C10	C17	C22	64.1(3)
C2	C3	C4	N1	1.5(3)
C2	C3	C4	C5	-179.2(3)
C3	C4	C5	C6	-170.0(3)
C3	C4	C5	C11	11.3(4)
C4	N1	C1	C2	2.4(3)
C4	N1	C1	C10[1]	-177.8(2)
C4	C5	C6	N2	-2.6(4)
C4	C5	C6	C7	176.8(3)
C4	C5	C11	C12	-114.7(3)
C4	C5	C11	C16	65.1(3)
C5	C6	C7	C8	-178.3(3)
C5	C11	C12	C13	179.1(2)
C5	C11	C16	C15	180.0(3)
C6	N2	C9	C8	-1.1(3)
C6	N2	C9	C10	176.3(2)
C6	C5	C11	C12	66.6(3)
C6	C5	C11	C16	-113.6(3)
C6	C7	C8	C9	-1.8(3)
C7	C8	C9	N2	1.8(3)
C7	C8	C9	C10	-175.6(2)
C8	C9	C10	C1[1]	175.6(3)
C8	C9	C10	C17	-3.8(4)
C9	N2	C6	C5	179.5(2)
C9	N2	C6	C7	0.0(3)
C9	C10	C17	C18	66.2(3)
C9	C10	C17	C22	-116.4(3)
C10[1]	C1	C2	C3	178.7(3)
C10	C17	C18	C19	174.8(2)
C10	C17	C22	C21	-175.8(3)
C11	C5	C6	N2	176.0(2)
C11	C5	C6	C7	-4.6(4)
C11	C12	C13	C14	1.2(4)
C12	C11	C16	C15	-0.2(4)
C12	C13	C14	O1	179.5(2)
C12	C13	C14	C15	-0.7(4)
C13	C14	C15	C16	-0.2(4)
C14	C15	C16	C11	0.7(4)
C16	C11	C12	C13	-0.7(4)
C17	C18	C19	C20	0.8(4)
C18	C17	C22	C21	1.8(4)
C18	C19	C20	O2	-177.9(2)
C18	C19	C20	C21	2.0(4)
C19	C20	C21	C22	-2.8(4)
C20	C21	C22	C17	0.9(4)
C22	C17	C18	C19	-2.6(4)
C23	O1	C14	C13	178.4(2)
C23	O1	C14	C15	-1.4(4)
C24	O2	C20	C19	175.2(2)
C24	O2	C20	C21	-4.7(4)

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[1]1-x,2-y,1-z

Table S8. Bond lengths in crystal structure of **SbDMP(OMe)$_2$.PF$_6$**

Atom 1	Atom 2	Length/Å
Sb1	O9	1.942(2)
Sb1	O10	1.954(2)
Sb1	N1	2.074(2)
Sb1	N2	2.074(2)
Sb1	N3	2.071(2)
Sb1	N4	2.079(3)
O1	C23	1.361(4)
O1	C45	1.433(5)
O2	C25	1.359(4)
O2	C46	1.425(5)
O3	C29	1.356(4)
O3	C47	1.431(5)
O4	C31	1.361(4)
O4	C48	1.428(4)
O5	C35	1.365(5)
O5	C49	1.421(5)
O6	C37	1.366(4)
O6	C50	1.431(5)
O7	C41	1.350(5)
O7	C51	1.478(8)
O8	C43	1.361(5)
O8	C52	1.408(5)
O9	C53	1.399(5)
O10	C54	1.454(6)
O10	C54C	1.342(8)
N1	C1	1.373(4)
N1	C4	1.378(4)
N2	C6	1.389(4)
N2	C9	1.381(4)
N3	C11	1.375(4)
N3	C14	1.379(4)
N4	C16	1.382(4)
N4	C19	1.379(4)
C1	C2	1.433(4)
C1	C20	1.401(5)
C2	H2	0.95
C2	C3	1.354(5)
C3	H3	0.95
C3	C4	1.442(4)
C4	C5	1.396(4)
C5	C6	1.400(4)
C5	C21	1.498(4)
C6	C7	1.429(4)
C7	H7	0.95
C7	C8	1.354(4)
C8	H8	0.95
C8	C9	1.424(4)
C9	C10	1.402(4)
C10	C11	1.398(5)
C10	C27	1.496(4)
C11	C12	1.430(4)
C12	H12	0.95
C12	C13	1.357(5)
C13	H13	0.95
C13	C14	1.444(5)
C14	C15	1.403(5)
C15	C16	1.404(5)
C15	C33	1.500(4)
C16	C17	1.438(5)
C17	H17	0.95
C17	C18	1.361(5)
C18	H18	0.95
C18	C19	1.427(5)
C19	C20	1.393(4)
C20	C39	1.501(5)
C21	C22	1.388(5)
C21	C26	1.397(5)
C22	H22	0.95
C22	C23	1.395(4)
C23	C24	1.390(5)
C24	H24	0.95
C24	C25	1.389(5)
C25	C26	1.392(4)
C26	H26	0.95
C27	C28	1.383(5)
C27	C32	1.396(4)
C28	H28	0.95
C28	C29	1.393(5)
C29	C30	1.388(5)
C30	H30	0.95
C30	C31	1.396(4)
C31	C32	1.390(4)
C32	H32	0.95
C33	C34	1.397(5)
C33	C38	1.393(5)
C34	H34	0.95
C34	C35	1.389(5)
C35	C36	1.391(5)
C36	H36	0.95
C36	C37	1.383(5)
C37	C38	1.386(4)
C38	H38	0.95
C39	C40	1.385(5)
C39	C44	1.385(6)
C40	H40	0.95
C40	C41	1.401(6)
C41	C42	1.398(7)
C42	H42	0.95
C42	C43	1.368(6)
C43	C44	1.401(5)
C44	H44	0.95
C45	H45A	0.98
C45	H45B	0.98
C45	H45C	0.98
C46	H46A	0.98
C46	H46B	0.98
C46	H46C	0.98
C47	H47A	0.98
C47	H47B	0.98
C47	H47C	0.98
C48	H48A	0.98
C48	H48B	0.98
C48	H48C	0.98
C49	H49A	0.98
C49	H49B	0.98
C49	H49C	0.98
C50	H50A	0.98
C50	H50B	0.98
C50	H50C	0.98
C51	H51A	0.98
C51	H51B	0.98
C51	H51C	0.98
C52	H52A	0.98
C52	H52B	0.98
C52	H52C	0.98
C53	H53A	0.98
C53	H53B	0.98
C53	H53C	0.98
C54	H54A	0.98
C54	H54B	0.98
C54	H54C	0.98
Sb1A	O5A	1.954(2)
Sb1A	O5A^1	1.954(2)
Sb1A	N1A	2.071(2)
Sb1A	N1A^1	2.071(2)
Sb1A	N2A^1	2.076(2)
Sb1A	N2A	2.076(2)
O1A	C13A	1.364(4)
O1A	C23A	1.418(5)
O2A	C15A	1.355(4)
O2A	C24A	1.290(7)
O2A	C24B	1.329(7)
O3A	C19A	1.366(3)
O3A	C25A	1.422(4)
O4A	C21A	1.360(4)
O4A	C26A	1.435(4)
O5A	C27A	1.388(5)
N1A	C1A	1.379(3)
N1A	C4A	1.373(4)
N2A	C6A	1.374(4)
N2A	C9A	1.373(3)
C1A	C2A	1.428(4)
C1A	C10A	1.399(4)
C2A	H2A	0.95
C2A	C3A	1.367(4)
C3A	H3A	0.95
C3A	C4A	1.432(4)
C4A	C5A^1	1.397(4)
C5A	C6A	1.396(4)
C5A	C11A	1.505(4)
C6A	C7A	1.439(4)
C7A	H7A	0.95
C7A	C8A	1.352(4)
C8A	H8A	0.95
C8A	C9A	1.437(4)
C9A	C10A	1.399(4)
C10A	C17A	1.497(4)
C11A	C12A	1.387(5)
C11A	C16A	1.379(5)
C12A	H12A	0.95
C12A	C13A	1.389(4)
C13A	C14A	1.391(5)
C14A	H14A	0.95
C14A	C15A	1.384(5)
C15A	C16A	1.396(4)
C16A	H16A	0.95
C17A	C18A	1.397(4)
C17A	C22A	1.378(5)
C18A	H18A	0.95
C18A	C19A	1.387(4)
C19A	C20A	1.401(5)
C20A	H20A	0.95
C20A	C21A	1.376(5)
C21A	C22A	1.407(4)
C22A	H22A	0.95
C23A	H23A	0.98
C23A	H23B	0.98
C23A	H23C	0.98
C24A	H24A	0.98
C24A	H24B	0.98
C24A	H24C	0.98
C25A	H25A	0.98
C25A	H25B	0.98
C25A	H25C	0.98
C26A	H26A	0.98
C26A	H26B	0.98
C26A	H26C	0.98
C27A	H27A	0.98
C27A	H27B	0.98
C27A	H27C	0.98
P1	F1	1.583(4)
P1	F2	1.602(4)
P1	F3	1.602(4)
P1	F4	1.542(4)
P1	F5	1.590(3)
P1	F6	1.599(4)
P2	F7	1.597(3)
P2	F7^2	1.597(3)
P2	F8^2	1.598(2)
P2	F8	1.598(2)
P2	F9^2	1.598(2)
P2	F9	1.598(3)
C24B	H24D	0.98
C24B	H24E	0.98
C24B	H24F	0.98
C54C	H54D	0.98
C54C	H54E	0.98
C54C	H54F	0.98

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^{1} -x+1/2,-y+1/2,-z+1 ^{2} -x,y,-z+1/2

Table S9. Bond angles in crystal structure of **SbDMP(OMe)$_2$.PF$_6$**

Atom 1	Atom 2	Atom 3	Angle/°
O9	Sb1	O10	175.74(10)
O9	Sb1	N1	92.84(10)
O9	Sb1	N2	89.34(10)
O9	Sb1	N3	86.70(10)
O9	Sb1	N4	91.25(11)
O10	Sb1	N1	90.72(11)
O10	Sb1	N2	93.03(10)
O10	Sb1	N3	89.75(10)
O10	Sb1	N4	86.40(11)
N1	Sb1	N4	90.08(10)
N2	Sb1	N1	89.59(10)
N2	Sb1	N4	179.33(11)
N3	Sb1	N1	179.41(11)
N3	Sb1	N2	90.04(10)
N3	Sb1	N4	90.29(10)
C23	O1	C45	118.0(3)
C25	O2	C46	117.5(3)
C29	O3	C47	117.3(3)
C31	O4	C48	118.3(3)
C35	O5	C49	117.9(3)
C37	O6	C50	117.5(3)
C41	O7	C51	117.0(4)
C43	O8	C52	119.6(4)
C53	O9	Sb1	124.0(3)
C54	O10	Sb1	123.5(3)
C54C	O10	Sb1	118.2(5)
C1	N1	Sb1	125.2(2)
C1	N1	C4	108.8(2)
C4	N1	Sb1	126.0(2)
C6	N2	Sb1	126.11(19)
C9	N2	Sb1	126.02(19)
C9	N2	C6	107.9(2)
C11	N3	Sb1	125.6(2)
C11	N3	C14	109.1(2)
C14	N3	Sb1	125.1(2)
C16	N4	Sb1	125.7(2)
C19	N4	Sb1	125.6(2)
C19	N4	C16	108.7(3)
N1	C1	C2	107.7(3)
N1	C1	C20	126.8(3)
C20	C1	C2	125.5(3)
C1	C2	H2	125.8
C3	C2	C1	108.4(3)
C3	C2	H2	125.8
C2	C3	H3	126.3
C2	C3	C4	107.4(3)
C4	C3	H3	126.3
N1	C4	C3	107.7(3)
N1	C4	C5	126.7(3)
C5	C4	C3	125.5(3)
C4	C5	C6	125.4(3)
C4	C5	C21	117.0(3)
C6	C5	C21	117.6(3)
N2	C6	C5	126.0(3)
N2	C6	C7	107.8(3)
C5	C6	C7	126.2(3)
C6	C7	H7	126
C8	C7	C6	107.9(3)
C8	C7	H7	126
C7	C8	H8	125.9
C7	C8	C9	108.2(3)
C9	C8	H8	125.9
N2	C9	C8	108.2(3)
N2	C9	C10	125.7(3)
C10	C9	C8	126.1(3)
C9	C10	C27	115.8(3)
C11	C10	C9	125.9(3)
C11	C10	C27	118.3(3)
N3	C11	C10	126.6(3)
N3	C11	C12	107.5(3)
C10	C11	C12	125.9(3)
C11	C12	H12	125.7
C13	C12	C11	108.6(3)
C13	C12	H12	125.7
C12	C13	H13	126.3
C12	C13	C14	107.4(3)
C14	C13	H13	126.3
N3	C14	C13	107.4(3)
N3	C14	C15	127.1(3)
C15	C14	C13	125.5(3)
C14	C15	C16	125.3(3)
C14	C15	C33	117.6(3)
C16	C15	C33	116.9(3)
N4	C16	C15	126.2(3)
N4	C16	C17	107.6(3)
C15	C16	C17	126.2(3)
C16	C17	H17	126.2
C18	C17	C16	107.7(3)
C18	C17	H17	126.2
C17	C18	H18	125.9
C17	C18	C19	108.2(3)
C19	C18	H18	125.9
N4	C19	C18	107.9(3)
N4	C19	C20	126.0(3)
C20	C19	C18	126.2(3)
C1	C20	C39	115.4(3)
C19	C20	C1	126.0(3)
C19	C20	C39	118.7(3)
C22	C21	C5	119.3(3)
C22	C21	C26	121.6(3)
C26	C21	C5	119.1(3)
C21	C22	H22	120.5
C21	C22	C23	118.9(3)
C23	C22	H22	120.5
O1	C23	C22	124.6(3)
O1	C23	C24	115.3(3)
C24	C23	C22	120.1(3)
C23	C24	H24	119.9
C25	C24	C23	120.3(3)
C25	C24	H24	119.9
O2	C25	C24	115.2(3)
O2	C25	C26	124.3(3)
C24	C25	C26	120.5(3)
C21	C26	H26	120.7
C25	C26	C21	118.6(3)
C25	C26	H26	120.7
C28	C27	C10	119.4(3)
C28	C27	C32	120.1(3)
C32	C27	C10	120.4(3)
C27	C28	H28	120.1
C27	C28	C29	119.9(3)
C29	C28	H28	120.1
O3	C29	C28	115.8(3)
O3	C29	C30	123.2(3)
C30	C29	C28	121.1(3)
C29	C30	H30	120.8
C29	C30	C31	118.3(3)
C31	C30	H30	120.8
O4	C31	C30	123.2(3)
O4	C31	C32	115.5(3)
C32	C31	C30	121.4(3)
C27	C32	H32	120.4
C31	C32	C27	119.2(3)
C31	C32	H32	120.4
C34	C33	C15	120.8(3)
C38	C33	C15	118.5(3)
C38	C33	C34	120.6(3)
C33	C34	H34	120.3
C35	C34	C33	119.3(3)
C35	C34	H34	120.3
O5	C35	C34	124.5(4)
O5	C35	C36	115.2(3)
C34	C35	C36	120.3(3)
C35	C36	H36	120.2
C37	C36	C35	119.6(3)
C37	C36	H36	120.2
O6	C37	C36	114.9(3)
O6	C37	C38	124.1(3)
C36	C37	C38	121.1(3)
C33	C38	H38	120.5
C37	C38	C33	119.0(3)
C37	C38	H38	120.5
C40	C39	C20	118.3(4)
C44	C39	C20	119.8(3)
C44	C39	C40	121.8(3)
C39	C40	H40	120.8
C39	C40	C41	118.3(4)
C41	C40	H40	120.8
O7	C41	C40	123.7(5)
O7	C41	C42	116.0(4)
C42	C41	C40	120.3(4)
C41	C42	H42	119.8
C43	C42	C41	120.3(4)
C43	C42	H42	119.8
O8	C43	C42	124.8(4)
O8	C43	C44	115.0(4)
C42	C43	C44	120.2(4)
C39	C44	C43	119.1(4)
C39	C44	H44	120.5
C43	C44	H44	120.5
O1	C45	H45A	109.5
O1	C45	H45B	109.5
O1	C45	H45C	109.5
H45A	C45	H45B	109.5
H45A	C45	H45C	109.5
H45B	C45	H45C	109.5
O2	C46	H46A	109.5
O2	C46	H46B	109.5
O2	C46	H46C	109.5
H46A	C46	H46B	109.5
H46A	C46	H46C	109.5
H46B	C46	H46C	109.5
O3	C47	H47A	109.5
O3	C47	H47B	109.5
O3	C47	H47C	109.5
H47A	C47	H47B	109.5
H47A	C47	H47C	109.5
H47B	C47	H47C	109.5
O4	C48	H48A	109.5
O4	C48	H48B	109.5
O4	C48	H48C	109.5
H48A	C48	H48B	109.5
H48A	C48	H48C	109.5
H48B	C48	H48C	109.5
O5	C49	H49A	109.5
O5	C49	H49B	109.5
O5	C49	H49C	109.5
H49A	C49	H49B	109.5
H49A	C49	H49C	109.5
H49B	C49	H49C	109.5
O6	C50	H50A	109.5
O6	C50	H50B	109.5
O6	C50	H50C	109.5
H50A	C50	H50B	109.5
H50A	C50	H50C	109.5
H50B	C50	H50C	109.5
O7	C51	H51A	109.5
O7	C51	H51B	109.5
O7	C51	H51C	109.5
H51A	C51	H51B	109.5
H51A	C51	H51C	109.5
H51B	C51	H51C	109.5
O8	C52	H52A	109.5
O8	C52	H52B	109.5
O8	C52	H52C	109.5
H52A	C52	H52B	109.5
H52A	C52	H52C	109.5
H52B	C52	H52C	109.5
O9	C53	H53A	109.5
O9	C53	H53B	109.5
O9	C53	H53C	109.5
H53A	C53	H53B	109.5

Atom 1	Atom 2	Atom 3	Angle/°
H53A	C53	H53C	109.5
H53B	C53	H53C	109.5
O10	C54	H54A	109.5
O10	C54	H54B	109.5
O10	C54	H54C	109.5
H54A	C54	H54B	109.5
H54A	C54	H54C	109.5
H54B	C54	H54C	109.5
O5A	Sb1A	O5A[1]	180.00(14)
O5A[1]	Sb1A	N1A[1]	91.33(10)
O5A	Sb1A	N1A[1]	88.67(10)
O5A	Sb1A	N1A	91.33(10)
O5A[1]	Sb1A	N1A	88.67(10)
O5A	Sb1A	N2A[1]	93.37(10)
O5A	Sb1A	N2A	86.63(10)
O5A[1]	Sb1A	N2A	93.37(10)
O5A[1]	Sb1A	N2A[1]	86.63(10)
N1A	Sb1A	N1A[1]	180
N1A	Sb1A	N2A[1]	89.22(9)
N1A[1]	Sb1A	N2A[1]	90.78(9)
N1A[1]	Sb1A	N2A	89.22(9)
N1A	Sb1A	N2A	90.78(9)
N2A[1]	Sb1A	N2A	180
C13A	O1A	C23A	117.7(3)
C24A	O2A	C15A	120.8(4)
C24B	O2A	C15A	132.8(7)
C19A	O3A	C25A	117.5(2)
C21A	O4A	C26A	117.6(3)
C27A	O5A	Sb1A	121.7(2)
C1A	N1A	Sb1A	124.61(18)
C4A	N1A	Sb1A	126.59(18)
C4A	N1A	C1A	108.7(2)
C6A	N2A	Sb1A	126.04(18)
C9A	N2A	Sb1A	124.80(18)
C9A	N2A	C6A	108.5(2)
N1A	C1A	C2A	108.1(2)
N1A	C1A	C10A	126.8(3)
C10A	C1A	C2A	125.1(3)
C1A	C2A	H2A	126.3
C3A	C2A	C1A	107.4(3)
C3A	C2A	H2A	126.3
C2A	C3A	H3A	126
C2A	C3A	C4A	108.0(3)
C4A	C3A	H3A	126
N1A	C4A	C3A	107.7(2)
N1A	C4A	C5A[1]	126.1(3)
C5A[1]	C4A	C3A	126.1(3)
C4A[1]	C5A	C11A	118.0(3)
C6A	C5A	C4A[1]	125.4(3)
C6A	C5A	C11A	116.6(2)
N2A	C6A	C5A	126.6(3)
N2A	C6A	C7A	107.8(2)
C5A	C6A	C7A	125.6(3)
C6A	C7A	H7A	126
C8A	C7A	C6A	107.9(2)
C8A	C7A	H7A	126
C7A	C8A	H8A	126.2
C7A	C8A	C9A	107.7(2)
C9A	C8A	H8A	126.2

Atom 1	Atom 2	Atom 3	Angle/°
N2A	C9A	C8A	108.1(2)
N2A	C9A	C10A	126.6(2)
C10A	C9A	C8A	125.3(3)
C1A	C10A	C9A	125.8(3)
C1A	C10A	C17A	117.5(2)
C9A	C10A	C17A	116.2(2)
C12A	C11A	C5A	120.0(3)
C16A	C11A	C5A	118.2(3)
C16A	C11A	C12A	121.8(3)
C11A	C12A	H12A	120.6
C11A	C12A	C13A	118.7(3)
C13A	C12A	H12A	120.6
O1A	C13A	C12A	124.7(3)
O1A	C13A	C14A	114.8(3)
C12A	C13A	C14A	120.5(3)
C13A	C14A	H14A	120.2
C15A	C14A	C13A	119.7(3)
C15A	C14A	H14A	120.2
O2A	C15A	C14A	118.0(3)
O2A	C15A	C16A	121.5(3)
C14A	C15A	C16A	120.5(3)
C11A	C16A	C15A	118.8(3)
C11A	C16A	H16A	120.6
C15A	C16A	H16A	120.6
C18A	C17A	C10A	122.0(3)
C22A	C17A	C10A	116.5(3)
C22A	C17A	C18A	121.5(3)
C17A	C18A	H18A	121.1
C19A	C18A	C17A	117.8(3)
C19A	C18A	H18A	121.1
O3A	C19A	C18A	123.8(3)
O3A	C19A	C20A	114.3(3)
C18A	C19A	C20A	121.9(3)
C19A	C20A	H20A	120.5
C21A	C20A	C19A	119.1(3)
C21A	C20A	H20A	120.5
O4A	C21A	C20A	125.1(3)
O4A	C21A	C22A	114.7(3)
C20A	C21A	C22A	120.2(3)
C17A	C22A	C21A	119.6(3)
C17A	C22A	H22A	120.2
C21A	C22A	H22A	120.2
O1A	C23A	H23A	109.5
O1A	C23A	H23B	109.5
O1A	C23A	H23C	109.5
H23A	C23A	H23B	109.5
H23A	C23A	H23C	109.5
H23B	C23A	H23C	109.5
O2A	C24A	H24A	109.5
O2A	C24A	H24B	109.5
O2A	C24A	H24C	109.5
H24A	C24A	H24B	109.5
H24A	C24A	H24C	109.5
H24B	C24A	H24C	109.5
O3A	C25A	H25A	109.5
O3A	C25A	H25B	109.5
O3A	C25A	H25C	109.5
H25A	C25A	H25B	109.5
H25A	C25A	H25C	109.5

Atom 1	Atom 2	Atom 3	Angle/°
H25B	C25A	H25C	109.5
O4A	C26A	H26A	109.5
O4A	C26A	H26B	109.5
O4A	C26A	H26C	109.5
H26A	C26A	H26B	109.5
H26A	C26A	H26C	109.5
H26B	C26A	H26C	109.5
O5A	C27A	H27A	109.5
O5A	C27A	H27B	109.5
O5A	C27A	H27C	109.5
H27A	C27A	H27B	109.5
H27A	C27A	H27C	109.5
H27B	C27A	H27C	109.5
F1	P1	F2	88.1(2)
F1	P1	F3	177.4(3)
F1	P1	F5	90.3(2)
F1	P1	F6	89.9(2)
F2	P1	F3	89.4(3)
F4	P1	F1	95.8(3)
F4	P1	F2	175.9(3)
F4	P1	F3	86.7(3)
F4	P1	F5	92.0(2)
F4	P1	F6	90.4(3)
F5	P1	F2	89.0(2)
F5	P1	F3	90.4(2)
F5	P1	F6	177.5(3)
F6	P1	F2	88.5(3)
F6	P1	F3	89.3(2)
F7	P2	F7[2]	90.1(2)
F7	P2	F8	89.52(14)
F7[2]	P2	F8	90.14(14)
F7	P2	F8[2]	90.14(14)
F7[2]	P2	F8[2]	89.51(14)
F7[2]	P2	F9	179.77(18)
F7[2]	P2	F9[2]	90.17(14)
F7	P2	F9[2]	179.77(18)
F7	P2	F9	90.16(14)
F8	P2	F8[2]	179.5(2)
F9[2]	P2	F8[2]	89.78(14)
F9	P2	F8	89.78(14)
F9	P2	F8[2]	90.56(14)
F9[2]	P2	F8	90.57(14)
F9[2]	P2	F9	89.6(2)
O2A	C24B	H24D	109.5
O2A	C24B	H24E	109.5
O2A	C24B	H24F	109.5
H24D	C24B	H24E	109.5
H24D	C24B	H24F	109.5
H24E	C24B	H24F	109.5
O10	C54C	H54D	109.5
O10	C54C	H54E	109.5
O10	C54C	H54F	109.5
H54D	C54C	H54E	109.5
H54D	C54C	H54F	109.5
H54E	C54C	H54F	109.5

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[1] -x+1/2,-y+1/2,-z+1 [2] -x,y,-z+1/2

Table S10. Dihedral angles in crystal structure of **SbDMP(OMe)$_2$.PF$_6$**

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
Sb1	N1	C1	C2	-178.8(2)
Sb1	N1	C1	C20	2.4(5)
Sb1	N1	C4	C3	178.8(2)
Sb1	N1	C4	C5	1.3(5)
Sb1	N2	C6	C5	0.5(4)
Sb1	N2	C6	C7	179.7(2)
Sb1	N2	C9	C8	179.6(2)
Sb1	N2	C9	C10	-2.7(4)
Sb1	N3	C11	C10	-5.0(5)
Sb1	N3	C11	C12	174.0(2)
Sb1	N3	C14	C13	-173.2(2)
Sb1	N3	C14	C15	7.1(5)
Sb1	N4	C16	C15	0.4(5)
Sb1	N4	C16	C17	-177.9(2)
Sb1	N4	C19	C18	177.7(2)
Sb1	N4	C19	C20	-3.5(5)
O1	C23	C24	C25	176.0(4)
O2	C25	C26	C21	-179.7(3)
O3	C29	C30	C31	-179.2(4)
O4	C31	C32	C27	180.0(3)
O5	C35	C36	C37	-178.6(3)
O6	C37	C38	C33	178.8(3)
O7	C41	C42	C43	-179.1(3)
O8	C43	C44	C39	-179.5(3)
N1	C1	C2	C3	0.7(4)
N1	C1	C20	C19	2.7(6)
N1	C1	C20	C39	-178.1(3)
N1	C4	C5	C6	3.2(5)
N1	C4	C5	C21	-179.1(3)
N2	C6	C7	C8	0.6(4)
N2	C9	C10	C11	-1.3(5)
N2	C9	C10	C27	-179.0(3)
N3	C11	C12	C13	-0.7(4)
N3	C14	C15	C16	-2.8(6)
N3	C14	C15	C33	173.1(3)
N4	C16	C17	C18	0.5(4)
N4	C19	C20	C1	-2.1(6)
N4	C19	C20	C39	178.7(3)
C1	N1	C4	C3	1.1(4)
C1	N1	C4	C5	-176.5(3)
C1	C2	C3	C4	-0.1(4)
C1	C20	C39	C40	-91.9(4)
C1	C20	C39	C44	82.7(4)
C2	C1	C20	C19	-175.9(4)
C2	C1	C20	C39	3.4(5)
C2	C3	C4	N1	-0.6(4)
C2	C3	C4	C5	176.9(3)
C3	C4	C5	C6	-173.9(3)
C3	C4	C5	C21	3.8(5)
C4	N1	C1	C2	-1.1(4)
C4	N1	C1	C20	-179.9(3)
C4	C5	C6	N2	-4.2(5)
C4	C5	C6	C7	176.8(3)
C4	C5	C21	C22	-109.7(4)
C4	C5	C21	C26	69.2(4)
C5	C6	C7	C8	179.8(3)
C5	C21	C22	C23	177.7(3)
C5	C21	C26	C25	-179.1(3)
C6	N2	C9	C8	-0.9(3)
C6	N2	C9	C10	176.8(3)
C6	C5	C21	C22	68.1(4)
C6	C5	C21	C26	-112.9(3)
C6	C7	C8	C9	-1.2(4)
C7	C8	C9	N2	1.3(4)
C7	C8	C9	C10	-176.4(3)
C8	C9	C10	C11	176.1(3)
C8	C9	C10	C27	-1.6(5)
C9	N2	C6	C5	-179.0(3)
C9	N2	C6	C7	0.2(3)
C9	C10	C11	N3	5.5(5)
C9	C10	C11	C12	-173.3(3)
C9	C10	C27	C28	77.0(4)
C9	C10	C27	C32	-100.2(4)
C10	C11	C12	C13	178.3(3)
C10	C27	C28	C29	-177.2(3)
C10	C27	C32	C31	177.5(3)
C11	N3	C14	C13	1.2(4)
C11	N3	C14	C15	-178.5(3)
C11	C10	C27	C28	-100.9(4)
C11	C10	C27	C32	81.9(4)
C11	C12	C13	C14	1.4(4)
C12	C13	C14	N3	-1.6(4)
C12	C13	C14	C15	178.0(3)
C13	C14	C15	C16	177.6(3)
C13	C14	C15	C33	-6.6(5)
C14	N3	C11	C10	-179.3(3)
C14	N3	C11	C12	-0.3(4)
C14	C15	C16	N4	-1.3(6)
C14	C15	C16	C17	176.6(3)
C14	C15	C33	C34	119.0(4)
C14	C15	C33	C38	-64.4(4)
C15	C16	C17	C18	-177.8(3)
C15	C33	C34	C35	176.4(3)
C15	C33	C38	C37	-176.2(3)
C16	N4	C19	C18	0.2(4)
C16	N4	C19	C20	179.0(3)
C16	C15	C33	C34	-64.8(5)
C16	C15	C33	C38	111.8(4)
C16	C17	C18	C19	-0.3(4)
C17	C18	C19	N4	0.1(4)
C17	C18	C19	C20	-178.7(4)
C18	C19	C20	C1	176.5(4)
C18	C19	C20	C39	-2.7(6)
C19	N4	C16	C15	177.9(3)
C19	N4	C16	C17	-0.4(4)
C19	C20	C39	C40	87.4(4)
C19	C20	C39	C44	-98.0(4)
C20	C1	C2	C3	179.5(3)
C20	C39	C40	C41	173.5(3)
C20	C39	C44	C43	-173.7(3)
C21	C5	C6	N2	178.2(3)
C21	C5	C6	C7	-0.9(5)
C21	C22	C23	O1	-176.1(4)
C21	C22	C23	C24	2.7(5)
C22	C21	C26	C25	-0.2(5)
C22	C23	C24	C25	-2.9(6)
C23	C24	C25	O2	-178.7(3)
C23	C24	C25	C26	1.5(6)
C24	C25	C26	C21	0.0(5)
C26	C21	C22	C23	-1.2(5)
C27	C10	C11	N3	-176.8(3)
C27	C10	C11	C12	4.3(5)
C27	C28	C29	O3	179.5(4)
C27	C28	C29	C30	-0.8(6)
C28	C27	C32	C31	0.3(5)
C28	C29	C30	C31	1.1(5)

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
C29	C30	C31	O4	179.3(3)
C29	C30	C31	C32	-0.8(5)
C30	C31	C32	C27	0.1(5)
C32	C27	C28	C29	0.0(5)
C33	C15	C16	N4	-177.2(3)
C33	C15	C16	C17	0.8(5)
C33	C34	C35	O5	178.7(4)
C33	C34	C35	C36	-0.4(6)
C34	C33	C38	C37	0.3(5)
C34	C35	C36	C37	0.5(6)
C35	C36	C37	O6	-179.3(3)
C35	C36	C37	C38	-0.3(6)
C36	C37	C38	C33	-0.2(5)
C38	C33	C34	C35	-0.1(5)
C39	C40	C41	O7	-179.2(3)
C39	C40	C41	C42	-0.3(5)
C40	C39	C44	C43	0.7(5)
C40	C41	C42	C43	1.9(5)
C41	C42	C43	O8	178.3(4)
C41	C42	C43	C44	-2.3(5)
C42	C43	C44	C39	1.0(5)
C44	C39	C40	C41	-1.1(5)
C45	O1	C23	C22	0.7(6)
C45	O1	C23	C24	-178.2(4)
C46	O2	C25	C24	177.0(4)
C46	O2	C25	C26	-3.3(6)
C47	O3	C29	C28	179.5(4)
C47	O3	C29	C30	-0.2(6)
C48	O4	C31	C30	-5.0(5)
C48	O4	C31	C32	175.1(3)
C49	O5	C35	C34	8.0(6)
C49	O5	C35	C36	-172.9(4)
C50	O6	C37	C36	177.7(3)
C50	O6	C37	C38	-1.3(5)
C51	O7	C41	C40	-1.6(6)
C51	O7	C41	C42	179.4(4)
C52	O8	C43	C42	10.7(6)
C52	O8	C43	C44	-168.8(4)
Sb1A	N1A	C1A	C2A	179.1(2)
Sb1A	N1A	C1A	C10A	-2.0(5)
Sb1A	N1A	C4A	C3A	-179.8(2)
Sb1A	N1A	C4A	C5A[1]	-2.4(5)
Sb1A	N2A	C6A	C5A	-2.0(5)
Sb1A	N2A	C6A	C7A	175.0(2)
Sb1A	N2A	C9A	C8A	-174.6(2)
Sb1A	N2A	C9A	C10A	2.8(5)
O1A	C13A	C14A	C15A	-179.8(3)
O2A	C15A	C16A	C11A	-179.0(3)
O3A	C19A	C20A	C21A	-179.3(3)
O4A	C21A	C22A	C17A	179.8(3)
N1A	C1A	C2A	C3A	-0.3(4)
N1A	C1A	C10A	C9A	-5.7(5)
N1A	C1A	C10A	C17A	165.9(3)
N2A	C6A	C7A	C8A	-3.0(4)
N2A	C9A	C10A	C1A	5.2(5)
N2A	C9A	C10A	C17A	-166.5(3)
C1A	N1A	C4A	C3A	-2.6(4)
C1A	N1A	C4A	C5A[1]	174.8(3)
C1A	C2A	C3A	C4A	-1.3(4)
C1A	C10A	C17A	C18A	104.2(3)
C1A	C10A	C17A	C22A	-79.0(4)
C2A	C1A	C10A	C9A	173.0(3)
C2A	C1A	C10A	C17A	-15.4(5)
C2A	C3A	C4A	N1A	2.4(4)
C2A	C3A	C4A	C5A[1]	-175.0(3)
C4A	N1A	C1A	C2A	1.8(4)
C4A	N1A	C1A	C10A	-179.3(3)
C4A[1]	C5A	C6A	N2A	-0.6(6)
C4A[1]	C5A	C6A	C7A	-177.1(3)
C4A[1]	C5A	C11A	C12A	-81.8(4)
C4A[1]	C5A	C11A	C16A	99.6(4)
C5A	C6A	C7A	C8A	174.1(3)
C5A	C11A	C12A	C13A	-179.5(3)
C5A	C11A	C16A	C15A	178.9(3)
C6A	N2A	C9A	C8A	-3.5(4)
C6A	N2A	C9A	C10A	173.9(3)
C6A	C5A	C11A	C12A	99.9(4)
C6A	C5A	C11A	C16A	-78.7(4)
C6A	C7A	C8A	C9A	0.8(4)
C7A	C8A	C9A	N2A	1.7(4)
C7A	C8A	C9A	C10A	-175.8(3)
C8A	C9A	C10A	C1A	-177.7(3)
C8A	C9A	C10A	C17A	10.6(5)
C9A	N2A	C6A	C5A	-173.0(3)
C9A	N2A	C6A	C7A	4.0(4)
C9A	C10A	C17A	C18A	-83.4(4)
C9A	C10A	C17A	C22A	93.4(3)
C10A	C1A	C2A	C3A	-179.2(3)
C10A	C17A	C18A	C19A	175.4(3)
C10A	C17A	C22A	C21A	-176.1(3)
C11A	C5A	C6A	N2A	177.6(3)
C11A	C5A	C6A	C7A	1.1(5)
C11A	C12A	C13A	O1A	-178.5(3)
C11A	C12A	C13A	C14A	-0.1(4)
C12A	C11A	C16A	C15A	0.3(5)
C12A	C13A	C14A	C15A	1.7(5)
C13A	C14A	C15A	O2A	178.0(3)
C13A	C14A	C15A	C16A	-2.2(5)
C14A	C15A	C16A	C11A	1.2(5)
C16A	C11A	C12A	C13A	-0.9(4)
C17A	C18A	C19A	O3A	180.0(3)
C17A	C18A	C19A	C20A	1.0(4)
C18A	C17A	C22A	C21A	0.7(5)
C18A	C19A	C20A	C21A	-0.2(5)
C19A	C20A	C21A	O4A	180.0(3)
C19A	C20A	C21A	C22A	-0.3(5)
C20A	C21A	C22A	C17A	0.1(5)
C22A	C17A	C18A	C19A	-1.2(4)
C23A	O1A	C13A	C12A	-2.4(5)
C23A	O1A	C13A	C14A	179.2(3)
C24A	O2A	C15A	C14A	-176.7(4)
C24A	O2A	C15A	C16A	3.5(6)
C25A	O3A	C19A	C18A	0.2(5)
C25A	O3A	C19A	C20A	179.3(3)
C26A	O4A	C21A	C20A	1.9(5)
C26A	O4A	C21A	C22A	-177.8(3)
C24B	O2A	C15A	C14A	5.1(9)
C24B	O2A	C15A	C16A	-174.7(8)

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[1] -x+1/2,-y+1/2,-z+1 [2] -x,y,-z+1/2

Table S11. Bond lengths in crystal structure of **SbTMP(OMe)$_2$.PF$_6$**

Atom 1	Atom 2	Length/Å
Sb1	O7[1]	1.955(3)
Sb1	O7	1.955(3)
Sb1	N1[1]	2.086(3)
Sb1	N1	2.086(3)
Sb1	N2[1]	2.076(3)
Sb1	N2	2.076(3)
O1	C13	1.362(5)
O1	C23	1.415(7)
O2	C14	1.376(5)
O2	C24	1.411(7)
O3	C15	1.360(5)
O3	C25	1.428(7)
O4	C19	1.371(16)
O4	C26	1.410(14)
O5	C20	1.384(5)
O5	C27	1.403(10)
O6	C21	1.362(9)
O6	C28	1.388(16)
O7	C29	1.380(8)
O7	C29A	1.365(10)
N1	C1	1.378(5)
N1	C4	1.380(5)
N2	C6	1.377(5)
N2	C9	1.378(5)
C1	C2	1.441(6)
C1	C10[1]	1.402(5)
C2	C3	1.357(6)
C3	C4	1.433(6)
C4	C5	1.401(5)
C5	C6	1.398(6)
C5	C11	1.499(5)
C6	C7	1.432(5)
C7	C8	1.349(6)
C8	C9	1.429(5)
C9	C10	1.406(5)
C10	C17	1.504(5)
C10	C17A	1.490(11)
C11	C12	1.389(6)
C11	C16	1.383(6)
C12	C13	1.394(6)
C13	C14	1.399(6)
C14	C15	1.387(6)
C15	C16	1.397(5)
C17	C18	1.3900
C17	C22	1.3900
C18	C19	1.3900
C19	C20	1.3900
C20	C21	1.3900
C21	C22	1.3900
Cl1	C30	1.761(13)
Cl2	C30	1.749(14)
Cl3	C30	1.752(14)
P1	F1[2]	1.558(6)
P1	F1	1.558(6)
P1	F2[2]	1.567(6)
P1	F2	1.567(6)
P1	F3[2]	1.521(7)
P1	F3	1.521(7)
Cl3A	C30A	1.803(10)
Cl1A	C30A	1.803(10)
C30A	Cl2A	1.803(10)
O6A	C21A	1.33(4)
O6A	C28A	1.447(19)
C17A	C22A	1.3900
C17A	C18A	1.3900
C22A	C21A	1.3900
C21A	C20A	1.3900
C20A	C19A	1.3900
C20A	O5A	1.382(16)
C19A	C18A	1.3900
C19A	O4A	1.36(3)
O5A	C27A	1.39(2)
O4A	C26A	1.45(3)

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[1]1-x,1-y,1-z; [2]2-x,2-y,-z

Table S12. Bond angles in crystal structure of **SbTMP(OMe)$_2$.PF$_6$**

Atom 1	Atom 2	Atom 3	Angle/°
O7[1]	Sb1	O7	180.0
O7	Sb1	N1[1]	90.68(15)
O7[1]	Sb1	N1[1]	89.31(15)
O7	Sb1	N1	89.32(15)
O7[1]	Sb1	N1	90.69(15)
O7[1]	Sb1	N2	87.27(14)
O7[1]	Sb1	N2[1]	92.73(14)
O7	Sb1	N2	92.73(14)
O7	Sb1	N2[1]	87.27(14)
N1[1]	Sb1	N1	180.0
N2	Sb1	N1	90.59(13)
N2[1]	Sb1	N1[1]	90.59(13)
N2	Sb1	N1[1]	89.41(13)
N2[1]	Sb1	N1	89.41(13)
N2	Sb1	N2[1]	180.00(13)
C13	O1	C23	117.5(4)
C14	O2	C24	114.0(4)
C15	O3	C25	117.3(4)
C19	O4	C26	117.7(12)
C20	O5	C27	115.1(6)
C21	O6	C28	119.3(8)
C29	O7	Sb1	125.6(4)
C29A	O7	Sb1	126.7(18)
C1	N1	Sb1	125.9(3)
C1	N1	C4	108.9(3)
C4	N1	Sb1	124.8(3)
C6	N2	Sb1	124.8(3)
C6	N2	C9	108.8(3)
C9	N2	Sb1	126.1(2)
N1	C1	C2	107.3(3)
N1	C1	C10[1]	126.8(4)
C10[1]	C1	C2	125.8(4)
C3	C2	C1	108.1(4)
C2	C3	C4	107.8(4)
N1	C4	C3	107.8(3)
N1	C4	C5	126.6(4)
C5	C4	C3	125.5(4)
C4	C5	C11	117.9(3)
C6	C5	C4	125.8(4)
C6	C5	C11	116.3(3)
N2	C6	C5	127.1(3)
N2	C6	C7	107.5(3)
C5	C6	C7	125.4(3)
C8	C7	C6	108.0(3)
C7	C8	C9	108.4(4)
N2	C9	C8	107.4(3)
N2	C9	C10	126.9(3)
C10	C9	C8	125.7(4)
C1[1]	C10	C9	124.6(4)
C1[1]	C10	C17	118.0(4)
C1[1]	C10	C17A	119.2(10)
C9	C10	C17	117.4(4)
C9	C10	C17A	116.2(10)
C12	C11	C5	119.6(4)
C16	C11	C5	119.1(4)
C16	C11	C12	121.2(4)
C11	C12	C13	119.5(4)
O1	C13	C12	124.7(4)
O1	C13	C14	115.4(4)
C12	C13	C14	119.9(4)
O2	C14	C13	120.3(4)
O2	C14	C15	119.8(4)
C15	C14	C13	119.9(4)
O3	C15	C14	115.2(4)
O3	C15	C16	124.4(4)
C14	C15	C16	120.4(4)
C11	C16	C15	119.3(4)
C18	C17	C10	118.2(5)
C18	C17	C22	120.0
C22	C17	C10	121.3(4)
C19	C18	C17	120.0
O4	C19	C18	124.2(6)
O4	C19	C20	115.7(6)
C18	C19	C20	120.0
O5	C20	C19	119.9(4)
O5	C20	C21	119.3(4)
C19	C20	C21	120.0
O6	C21	C20	115.6(5)
O6	C21	C22	124.4(5)
C20	C21	C22	120.0
C21	C22	C17	120.0
Cl2	C30	Cl1	111.1(9)
Cl2	C30	Cl3	108.4(8)
Cl3	C30	Cl1	106.6(7)
F1[2]	P1	F1	180.0(3)
F1[2]	P1	F2[2]	91.7(4)
F1[2]	P1	F2	88.3(4)
F1	P1	F2	91.7(4)
F1	P1	F2[2]	88.3(4)
F2	P1	F2[2]	180.0
F3	P1	F1[2]	92.0(6)
F3	P1	F1	88.0(6)
F3[2]	P1	F1[2]	88.0(6)
F3[2]	P1	F1	92.0(6)
F3[2]	P1	F2	89.3(6)
F3	P1	F2[2]	89.3(6)
F3	P1	F2	90.7(6)
F3[2]	P1	F2[2]	90.7(6)
F3	P1	F3[2]	180.0
Cl1A	C30A	Cl3A	97.9(12)
Cl1A	C30A	Cl2A	102.9(14)
Cl2A	C30A	Cl3A	150(3)
C21A	O6A	C28A	120(3)
C22A	C17A	C10	122.6(13)
C22A	C17A	C18A	120.0
C18A	C17A	C10	117.0(13)
C17A	C22A	C21A	120.0
O6A	C21A	C22A	124.5(16)
O6A	C21A	C20A	115.3(17)
C20A	C21A	C22A	120.0
C21A	C20A	C19A	120.0
O5A	C20A	C21A	117.3(11)
O5A	C20A	C19A	122.6(11)
C20A	C19A	C18A	120.0
O4A	C19A	C20A	113.4(14)
O4A	C19A	C18A	126.5(14)
C19A	C18A	C17A	120.0
C20A	O5A	C27A	118.8(15)
C19A	O4A	C26A	115(2)

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[1]1-x,1-y,1-z; [2]2-x,2-y,-z

Table S13. Dihedral angles in crystal structure of **SbTMP(OMe)$_2$.PF**

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
Sb1	N1	C1	C2	172.8(3)
Sb1	N1	C1	C10[1]	-5.8(6)
Sb1	N1	C4	C3	-173.5(3)
Sb1	N1	C4	C5	4.6(6)
Sb1	N2	C6	C5	-4.3(6)
Sb1	N2	C6	C7	174.6(3)
Sb1	N2	C9	C8	-174.0(3)
Sb1	N2	C9	C10	4.9(6)
O1	C13	C14	O2	1.5(6)
O1	C13	C14	C15	-179.9(4)
O2	C14	C15	O3	-1.2(6)
O2	C14	C15	C16	177.8(4)
O3	C15	C16	C11	179.3(4)
O4	C19	C20	O5	-13.6(9)
O4	C19	C20	C21	176.3(8)
O5	C20	C21	O6	11.0(6)
O5	C20	C21	C22	-170.2(6)
O6	C21	C22	C17	178.7(6)
N1	C1	C2	C3	0.7(6)
N1	C4	C5	C6	-1.8(7)
N1	C4	C5	C11	179.9(4)
N2	C6	C7	C8	-0.8(5)
N2	C9	C10	C1[1]	-2.9(7)
N2	C9	C10	C17	178.6(5)
N2	C9	C10	C17A	178.8(11)
C1	N1	C4	C3	-0.6(5)
C1	N1	C4	C5	177.6(4)
C1	C2	C3	C4	-1.1(6)
C1[1]	C10	C17	C18	-61.4(6)
C1[1]	C10	C17	C22	126.1(4)
C1[1]	C10	C17A	C22A	-55.1(15)
C1[1]	C10	C17A	C18A	117.3(9)
C2	C3	C4	N1	1.0(6)
C2	C3	C4	C5	-177.1(5)
C3	C4	C5	C6	176.0(4)
C3	C4	C5	C11	-2.2(7)
C4	N1	C1	C2	-0.1(5)
C4	N1	C1	C10[1]	-178.7(4)
C4	C5	C6	N2	1.6(7)
C4	C5	C6	C7	-177.0(4)
C4	C5	C11	C12	105.5(5)
C4	C5	C11	C16	-78.2(5)
C5	C6	C7	C8	178.1(4)
C5	C11	C12	C13	176.8(4)
C5	C11	C16	C15	-176.5(4)
C6	N2	C9	C8	0.0(5)
C6	N2	C9	C10	179.0(4)
C6	C5	C11	C12	-72.9(5)
C6	C5	C11	C16	103.4(5)
C6	C7	C8	C9	0.9(5)
C7	C8	C9	N2	-0.6(5)
C7	C8	C9	C10	-179.5(4)
C8	C9	C10	C1[1]	175.9(4)
C8	C9	C10	C17	-2.6(7)
C8	C9	C10	C17A	-2.4(12)
C9	N2	C6	C5	-178.4(4)
C9	N2	C6	C7	0.5(5)
C9	C10	C17	C18	117.2(4)
C9	C10	C17	C22	-55.3(7)
C9	C10	C17A	C22A	123.3(9)
C9	C10	C17A	C18A	-64.3(13)
C10[1]	C1	C2	C3	179.3(5)
C10	C17	C18	C19	-172.6(7)
C10	C17	C22	C21	172.4(7)
C10	C17A	C22A	C21A	172.2(19)
C10	C17A	C18A	C19A	-172.6(18)
C11	C5	C6	N2	179.9(4)
C11	C5	C6	C7	1.2(6)
C11	C12	C13	O1	-179.9(4)
C11	C12	C13	C14	-1.1(7)
C12	C11	C16	C15	-0.3(6)
C12	C13	C14	O2	-177.5(4)
C12	C13	C14	C15	1.1(7)
C13	C14	C15	O3	-179.8(4)
C13	C14	C15	C16	-0.7(7)
C14	C15	C16	C11	0.3(6)
C16	C11	C12	C13	0.6(7)
C17	C18	C19	O4	-175.9(9)
C17	C18	C19	C20	0.0
C18	C17	C22	C21	0.0
C18	C19	C20	O5	170.1(6)
C18	C19	C20	C21	0.0
C19	C20	C21	O6	-178.8(6)
C19	C20	C21	C22	0.0
C20	C21	C22	C17	0.0
C22	C17	C18	C19	0.0
C23	O1	C13	C12	-5.3(8)
C23	O1	C13	C14	175.8(5)
C24	O2	C14	C13	-81.7(6)
C24	O2	C14	C15	99.7(6)
C25	O3	C15	C14	176.5(5)
C25	O3	C15	C16	-2.5(7)
C26	O4	C19	C18	-1.9(16)
C26	O4	C19	C20	-178.0(9)
C28	O6	C21	C20	-179.4(9)
C28	O6	C21	C22	1.9(13)
C27	O5	C20	C19	90.7(7)
C27	O5	C20	C21	-99.1(6)
O6A	C21A	C20A	C19A	-175(3)
O6A	C21A	C20A	O5A	9(3)
C17A	C22A	C21A	O6A	174(3)
C17A	C22A	C21A	C20A	0.0
C22A	C17A	C18A	C19A	0.0
C22A	C21A	C20A	C19A	0.0
C22A	C21A	C20A	O5A	-176.5(15)
C21A	C20A	C19A	C18A	0.0
C21A	C20A	C19A	O4A	177.8(15)
C21A	C20A	O5A	C27A	-98.6(18)
C20A	C19A	C18A	C17A	0.0
C20A	C19A	O4A	C26A	-173.1(18)
C19A	C20A	O5A	C27A	85.0(19)
C18A	C17A	C22A	C21A	0.0
C18A	C19A	O4A	C26A	4(3)
C28A	O6A	C21A	C22A	10(5)
C28A	O6A	C21A	C20A	-175(3)
O5A	C20A	C19A	C18A	176.3(16)
O5A	C20A	C19A	O4A	-5.9(17)
O4A	C19A	C18A	C17A	-177.4(17)

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[1]1-x,1-y,1-z

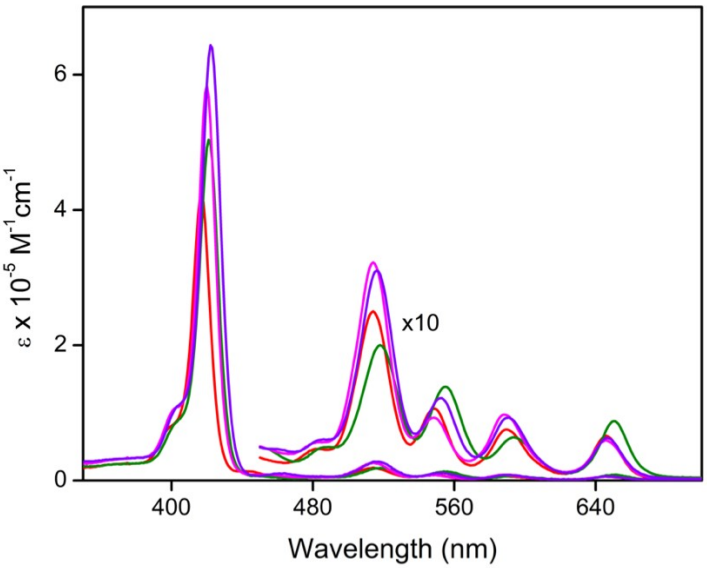


Figure S9: UV-visible absorption spectra of H_2P (red), H_2MP (green), H_2DMP (magenta), and H_2TMP (violet) in CH_2Cl_2.

Table S14. Optical and redox data of investigated compounds

Porphyrin	Absorption λ in nm (logε in $M^{-1}cm^{-1}$)
In CH_3CN	
H_2P	644 (3.63), 588(3.72), 546 (3.86), 512 (4.23), 413 (5.63)
H_2MP	Insoluble
H_2DMP	645 (3.49), 589 (3.73), 549 (3.73), 514 (4.44), 417 (4.67)
H_2TMP	645 (3.63), 589 (3.77), 549 (3.91), 514 (4.37), 419 (5.73)
In CH_2Cl_2	
H_2P	646 (3.77), 589 (3.78), 548 (3.94), 514 (4.28), 417 (5.63)
H_2MP	650 (3.93), 593 (3.84), 555 (4.12), 518 (4.27), 421 (5.70)
H_2DMP	646 (3.76), 588 (3.92), 548 (3.91), 514 (4.42), 420 (5.77)
H_2TMP	646 (3.80), 590 (3.93), 552 (4.05), 516 (4.44), 422 (5.81)
In Toluene	
H_2P	649 (3.85), 591 (3.91), 548 (4.05), 514 (4.36), 419 (5.64)
H_2MP	Insoluble
H_2DMP	649 (3.68), 590 (3.88), 548 (3.90), 514 (4.38), 421 (5.70)
H_2TMP	649 (3.77), 593 (3.92), 552 (4.06), 516 (4.41), 424 (5.74)

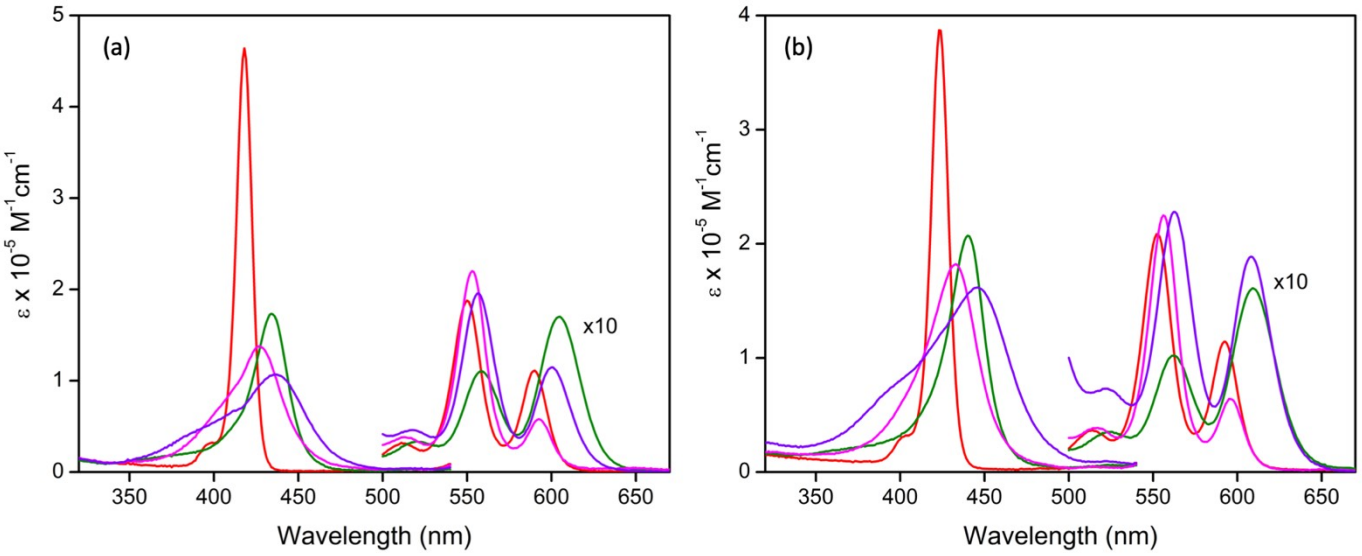


Figure S10: UV-visible absorption spectra of $SbP(OMe)_2.PF_6$ (red), $SbMP(OMe)_2.PF_6$ (green), $SbDMP(OMe)_2.PF_6$ (magenta), and $SbTMP(OMe)_2.PF_6$ (violet) in (a) acetonitrile and (b) toluene.

Table S15. Optical and redox data of investigated compounds.

Porphyrin	**Absorption λ in nm (logε in $M^{-1}cm^{-1}$)**	**FWHM of B-band (nm)**
In CH_3CN		
ZnTPP	595 (3.82), 555 (4.24), 420 (5.74)	12
$SbP(OMe)_2.PF_6$	590 (4.40), 550 (4.61), 511 (3.91), 418 (6.01)	12
$SbMP(OMe)_2.PF_6$	605 (4.83), 558 (4.63), 520 (4.16), 434 (5.84)	26
$SbDMP(OMe)_2.PF_6$	593 (4.39, 553 (4.97), 513 (4.21), 4.26 (5.79)	37
$SbTMP(OMe)_2.PF_6$	600 (4.67), 556 (4.90), 518 (4.30), 437 (5.68)	68
In Toluene		
ZnTPP	588 (3.58), 549 (4.32), 422 (5.68)	10
$SbP(OMe)_2.PF_6$	593 (4.40), 552 (5.61), 514 (4.06), 423 (5.94)	10
$SbMP(OMe)_2.PF_6$	609 (4.96), 562 (4.78), 523 (4.41), 440 (5.92)	24
$SbDMP(OMe)_2.PF_6$	5.96 (4.43), 556 (4.98), 517 (4.22), 432 (5.81)	40
$SbTMP(OMe)_2.PF_6$	608 (5.01), 562 (5.09), 523 (4.63), 446 (5.86)	58

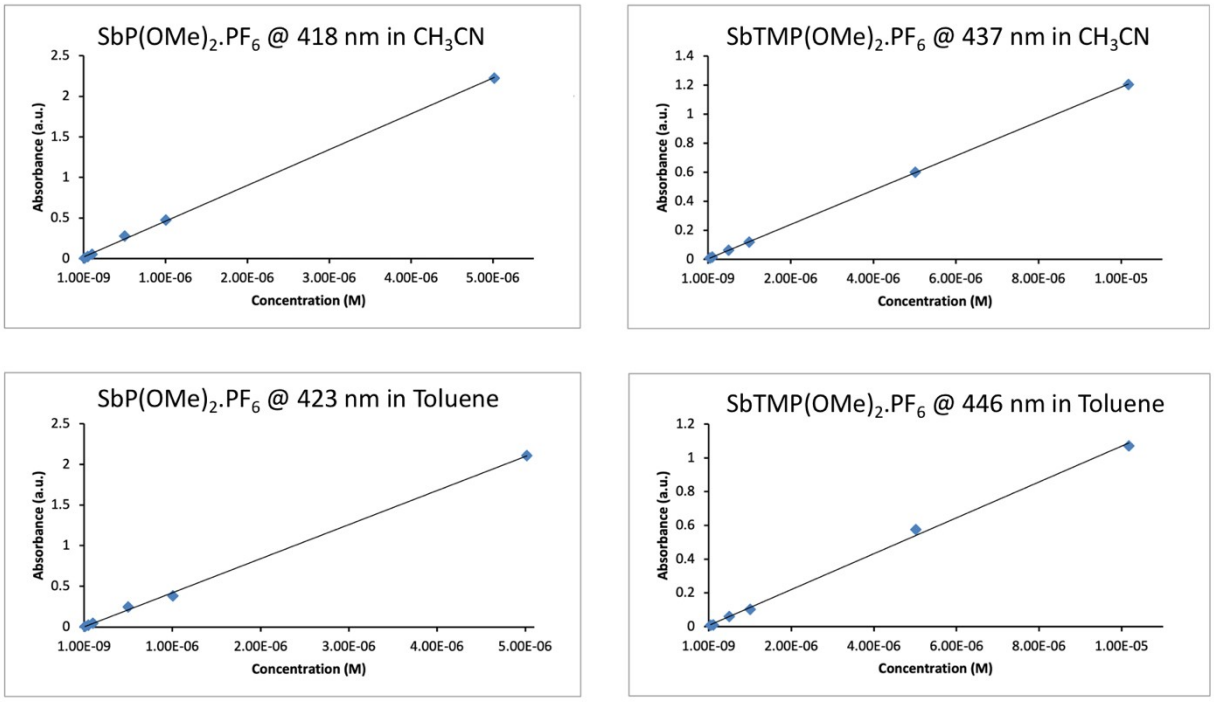


Figure S11. The Beer-Lambert plots in CH_3CN and toluene.

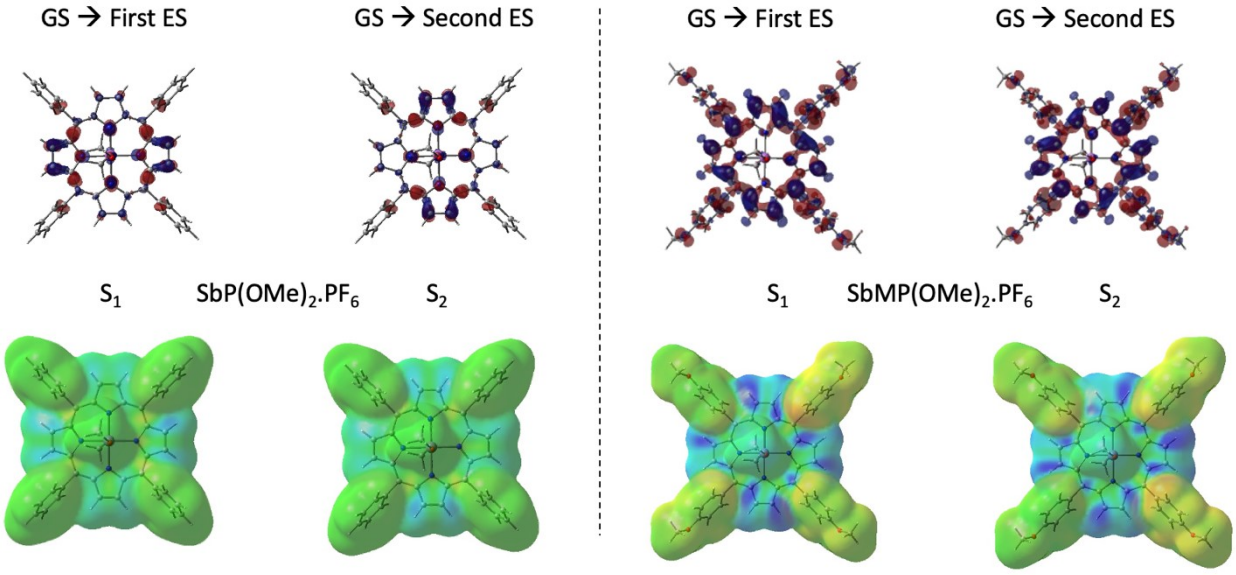


Figure S12. Top row: Charge transfer state density difference between ground and first and second excited states. Cyan, ground-state density; purple, excited-state density. Bottom row: Electrostatic potential surface. Green indicates no CT; GS, ground state; ES, excited state.

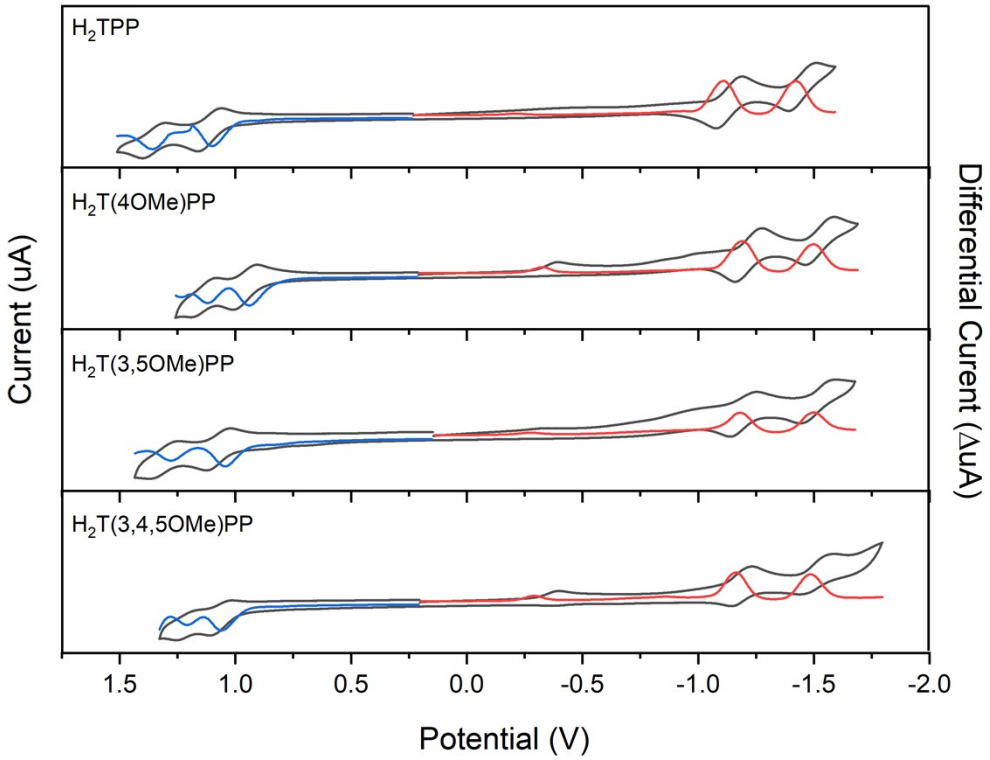


Figure S13: Cyclic and differential voltammograms of the investigated free-base porphyrins in CH_2Cl_2 with 0.1 M TBA.ClO_4. Scan rate 100 mV/s. Pulse period 200 ms Pulse amplitude 50 mV, Pulse width 50 ms.

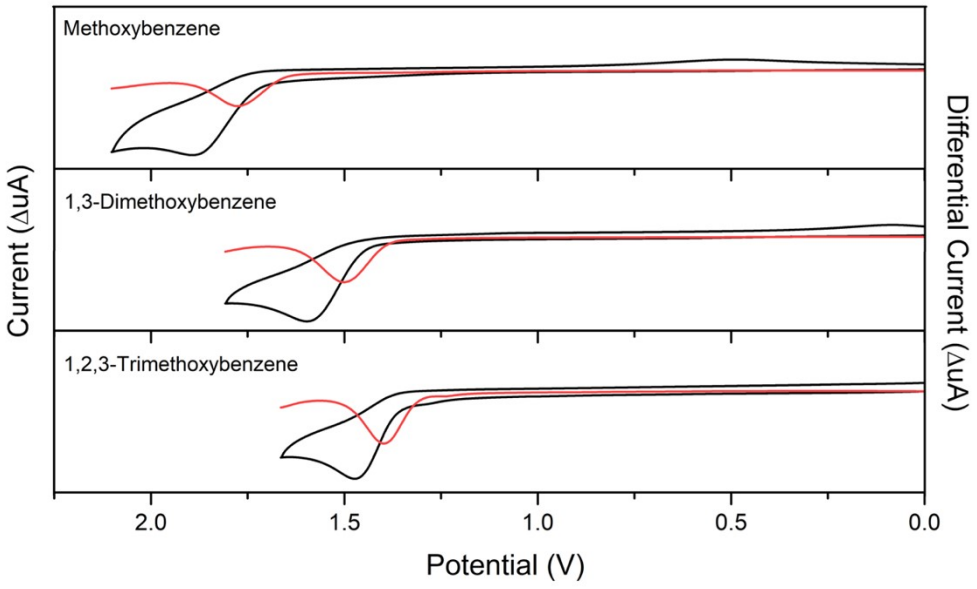
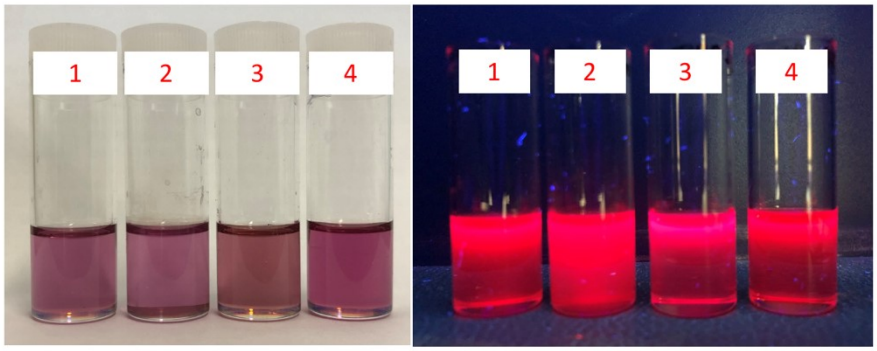


Figure S14. Cyclic and differential voltammograms of methoxybenzenes in CH_3CN with 0.1 M TBA.ClO_4.



*Same appearance in acetonitrile, DCM, and toluene

Figure S15. Visual comparison of the free-base porphyrins in CH_3CN. Samples left to right in each image: H_2P, H_2MP, H_2DMP, H_2TMP. The left image is under ambient light and the right is under UV (365nm). The samples had the same coloration in CH_3CN, CH_2Cl_2, and toluene.

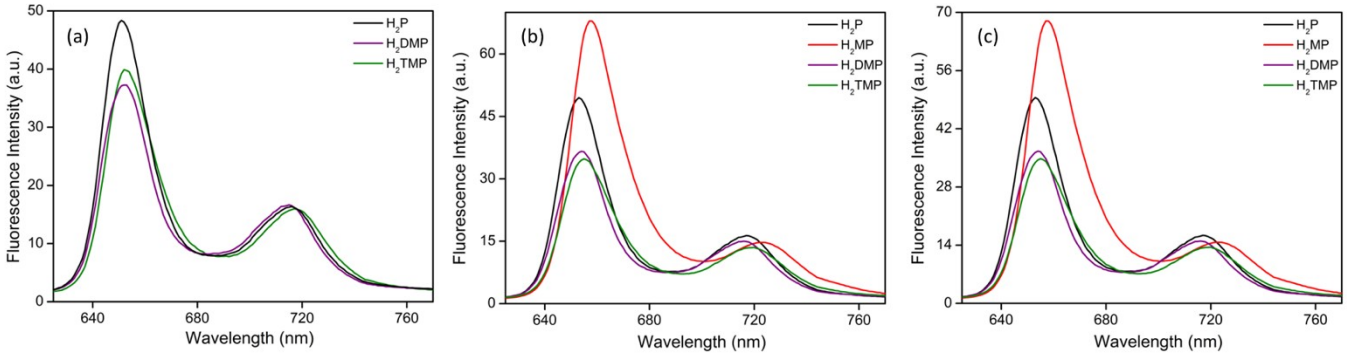


Figure S16. Fluorescence spectra of free-base porphyrins in (a) CH_3CN, (b) CH_2Cl_2, and (c) toluene. Excitation wavelength was used 550 nm.

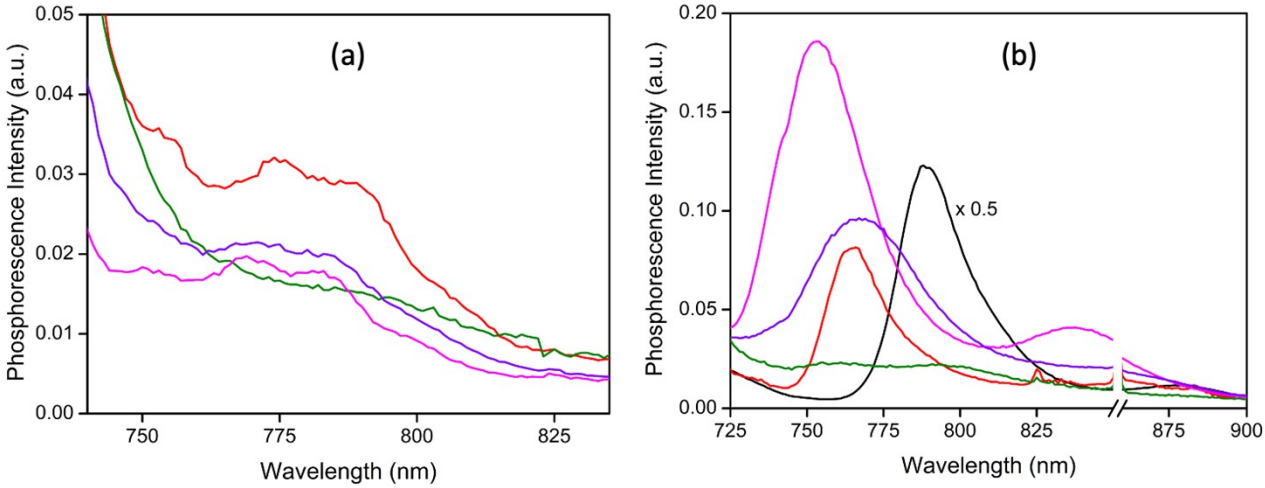


Figure S17. Phosphorescence spectra of (a) free-base porphyrins (Exc. 420nm) and (b) dimethoxyantimony(V) porphyrins (Exc. 426nm) in THF:CH_2Cl_2:1,2-dibromoethane = 73%:12%:15% at 77K. Red: H_2P / $SbP(OMe)_2.PF_6$, Green: H_2MP / $SbMP(OMe)_2.PF_6$, Magenta: H_2DMP / $SbDMP(OMe)_2.PF_6$, Violet: H_2TMP / $SbTMP(OMe)_2.PF_6$, Black: ZnTPP.

Table S16. Fluorescence data, quantum yields (Φ_{flu}) phosphorescence data, first excited singlet state energy ($E_{0\text{-}0}$) and triplet state energy (E_T) of the free-base porphyrins.

Porphyrin	Fluorescence (nm) (Φ_{flu})			Phosphorescence[a] (nm)	$E_{0\text{-}0}$[b] (eV)	E_T[a] (eV)
	CH_3CN	CH_2Cl_2	Toluene			
H_2P	651, 716 (0.130)	653, 717 (0.130)*	655, 719 (0.148)	782	1.91	1.59
H_2MP	Insoluble	658, 723 (0.176)	Insoluble	787	1.90	1.58
H_2DMP	652, 715 (0.116)	654, 716 (0.110)	656, 718 (0.130)	777	1.91	1.60
H_2TMP	652, 717 (0.123)	655, 719 (0.109)	657, 721 (0.137)	778	1.90	1.59

[a]THF:CH_2Cl_2:1,2-dibromoethane = 73%:12%:15% at 77K. [b]in CH_2Cl_2. *Adopted from *J. Chem. Sci.* **2005**, *117*, 193-201.

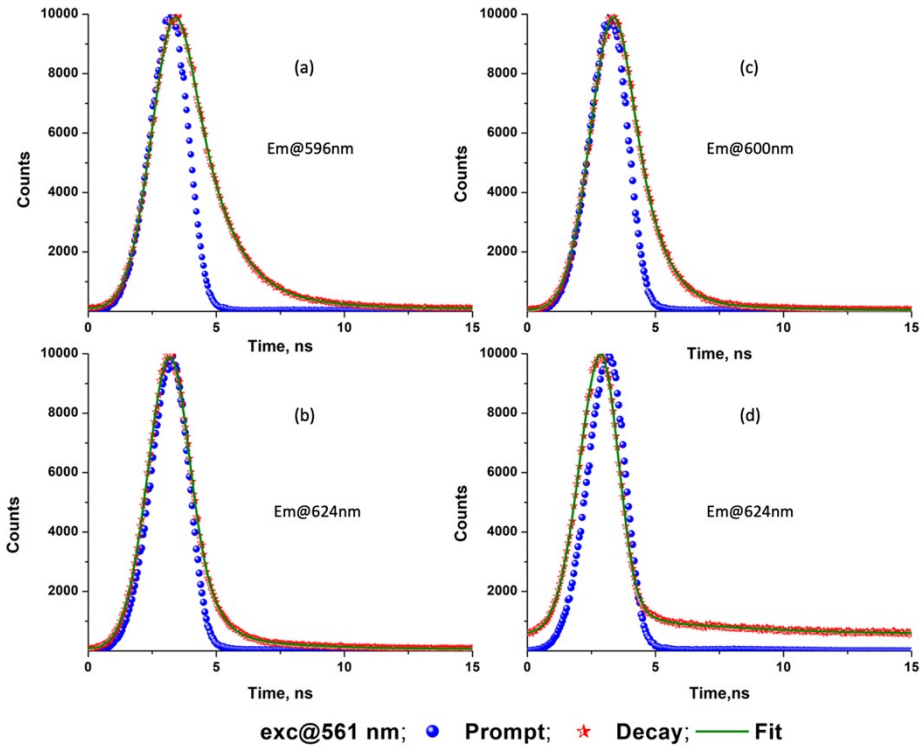


Figure S18. Singlet state decay profiles of (a) $SbP(OMe)_2.PF_6$, (b) $SbMP(OMe)_2.PF_6$ (c) $SbDMP(OMe)_2.PF_6$, and (d) $SbTMP(OMe)_2.PF_6$ in toluene.

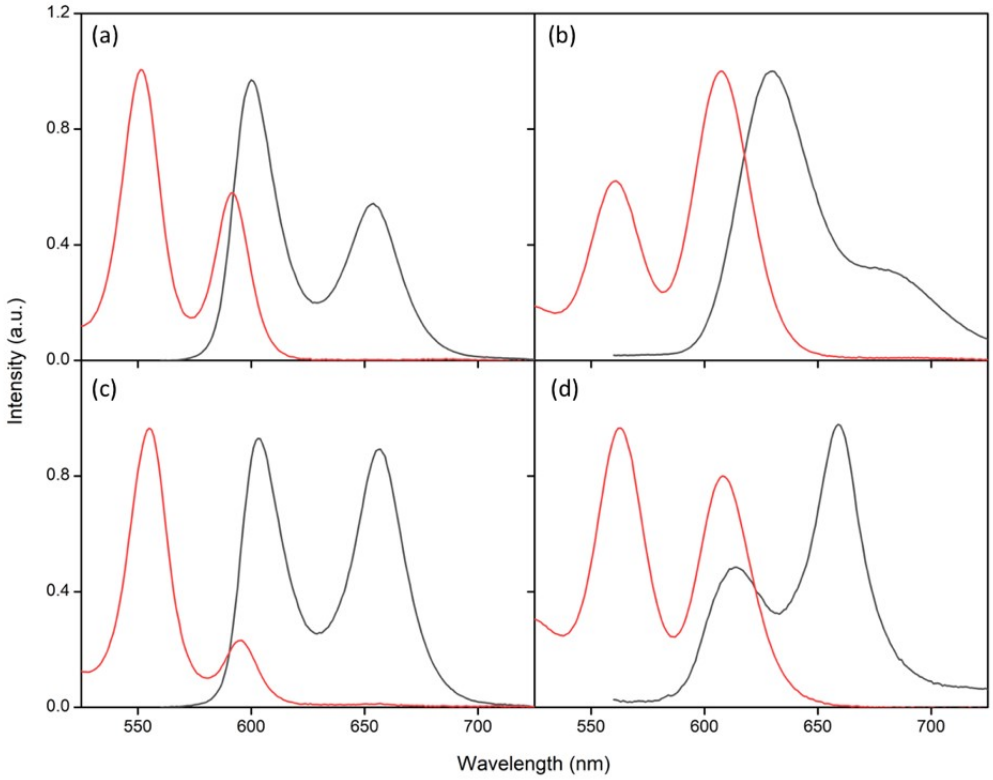


Figure S19. Overlap of absorption (red) and fluorescence (black) spectra of (a) $SbP(OMe)_2.PF_6$ in CH_2Cl_2, (b) $SbMP(OMe)_2.PF_6$ in CH_2Cl_2, (c) $SbDMP(OMe)_2.PF_6$ in CH_2Cl_2, and (d) $SbTMP(OMe)_2.PF_6$ in benzene.

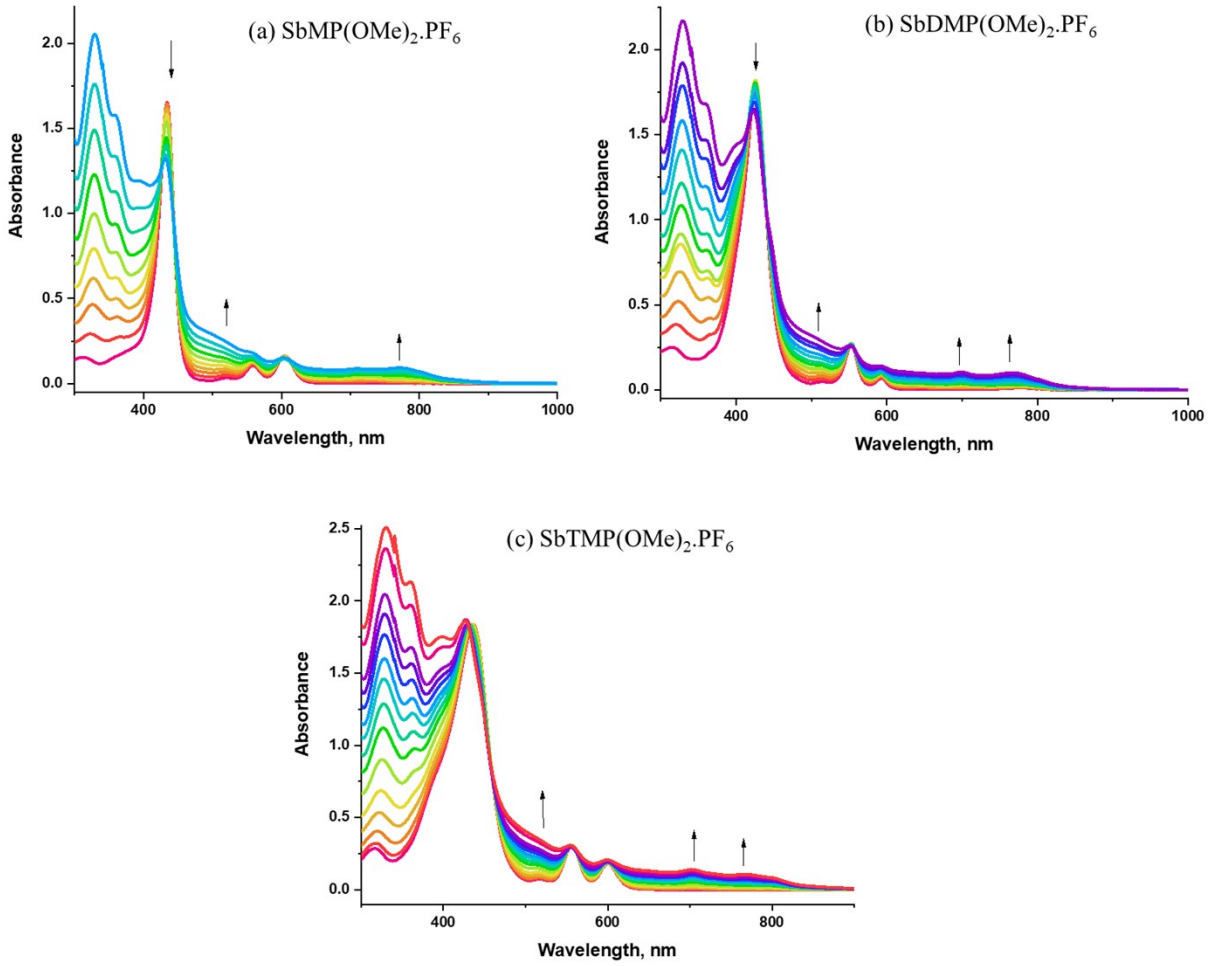


Figure S20. Spectral changes observed during the chemical reduction of the indicated compounds in CH_3CN. Cobaltocene was used as a reducing agent.

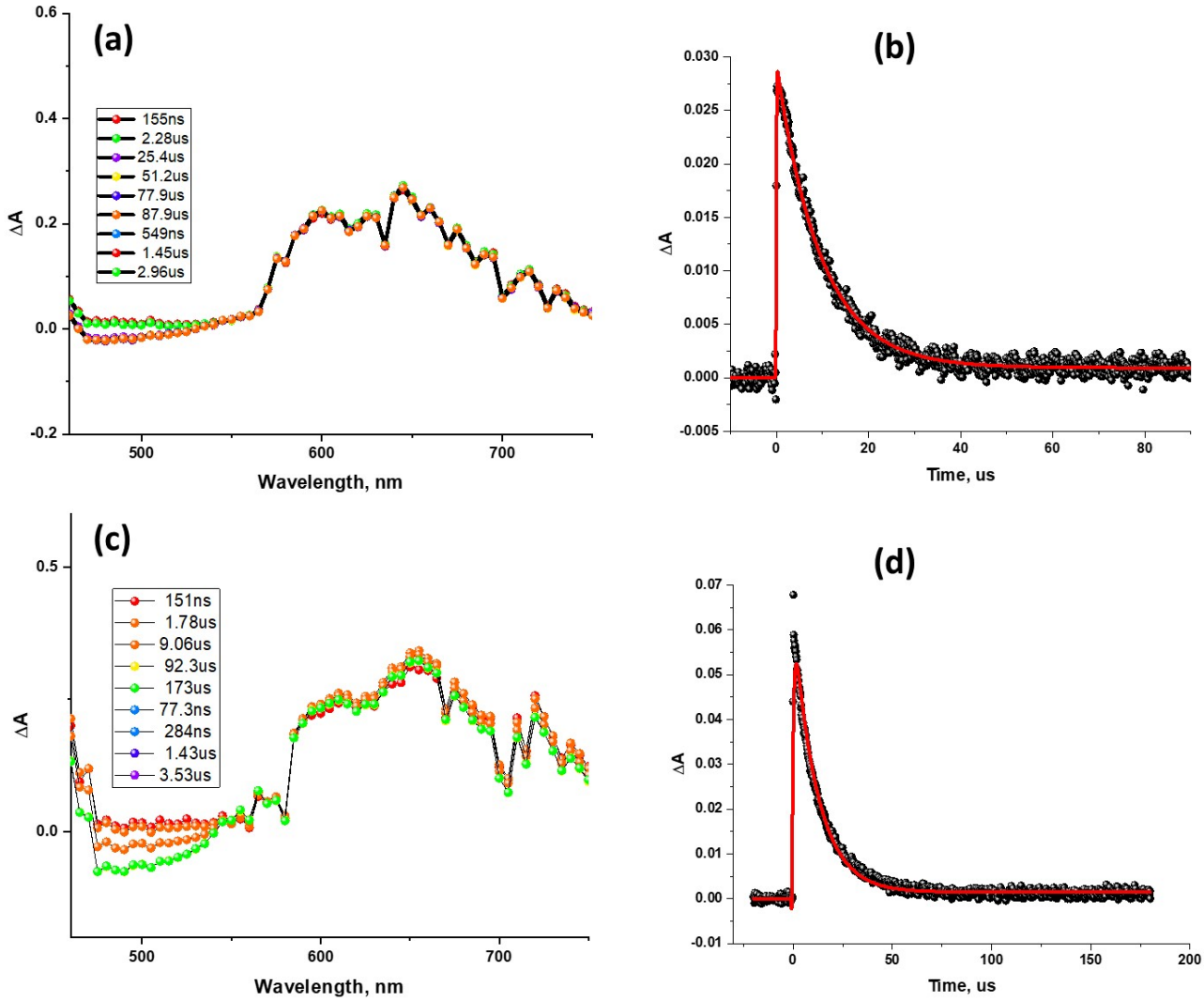


Figure S21. *ns*-TA absorption spectra at the indicated delay times of (a) $SbP(OMe)_2.PF_6$ and (c) $SbDMP(OMe)_2.PF_6$ in oxygen-free toluene at the Soret band excitation. (b and d) show the decay profiles.

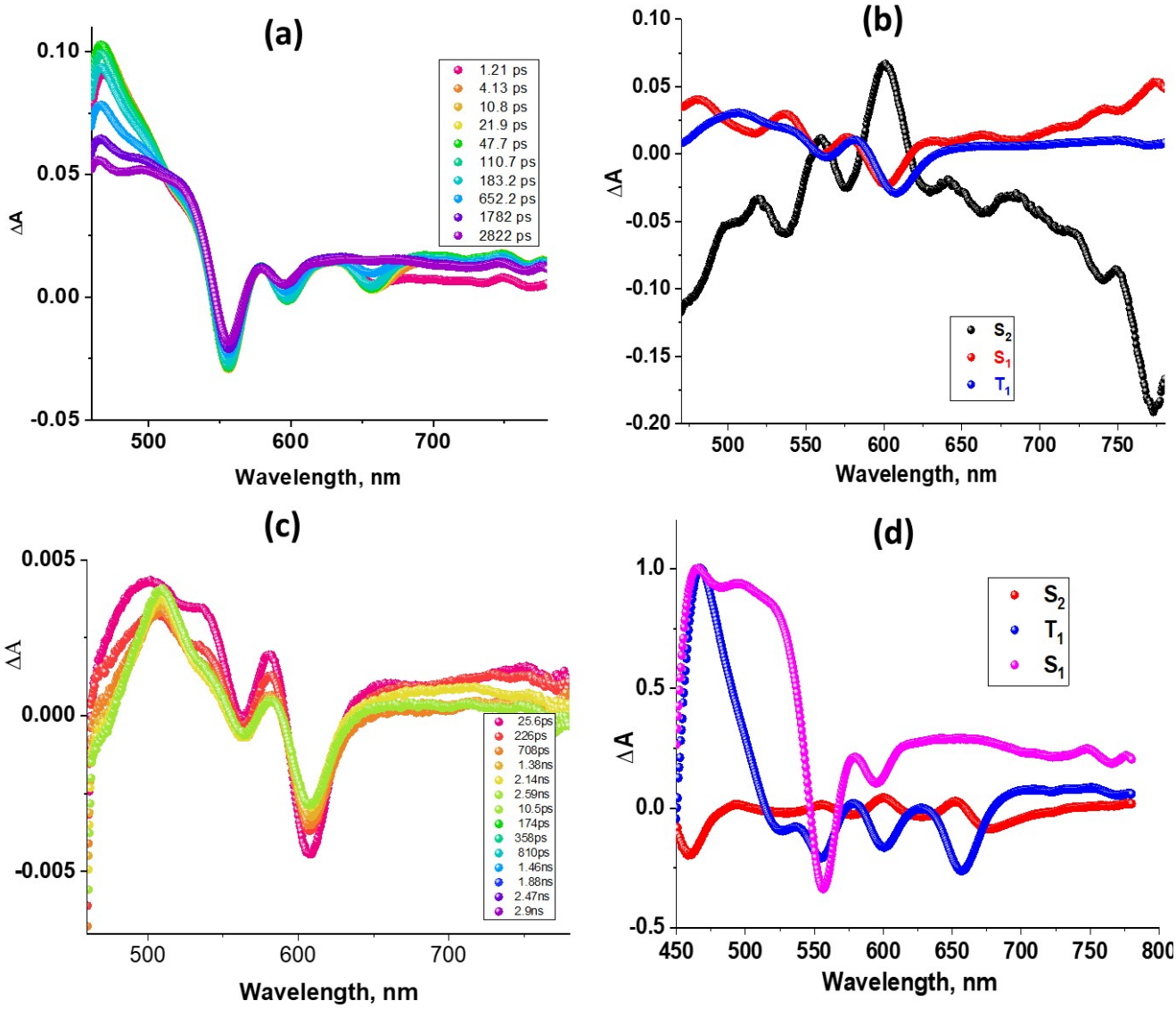


Figure S22. *fs*-TA absorption spectra at the indicated delay times of (a) $SbMP(OMe)_2.PF_6$ and (c) $SbDMP(OMe)_2.PF_6$ in oxygen-free toluene at the Soret band excitation. (b and d) show the corresponding decay associated generated from global analysis.

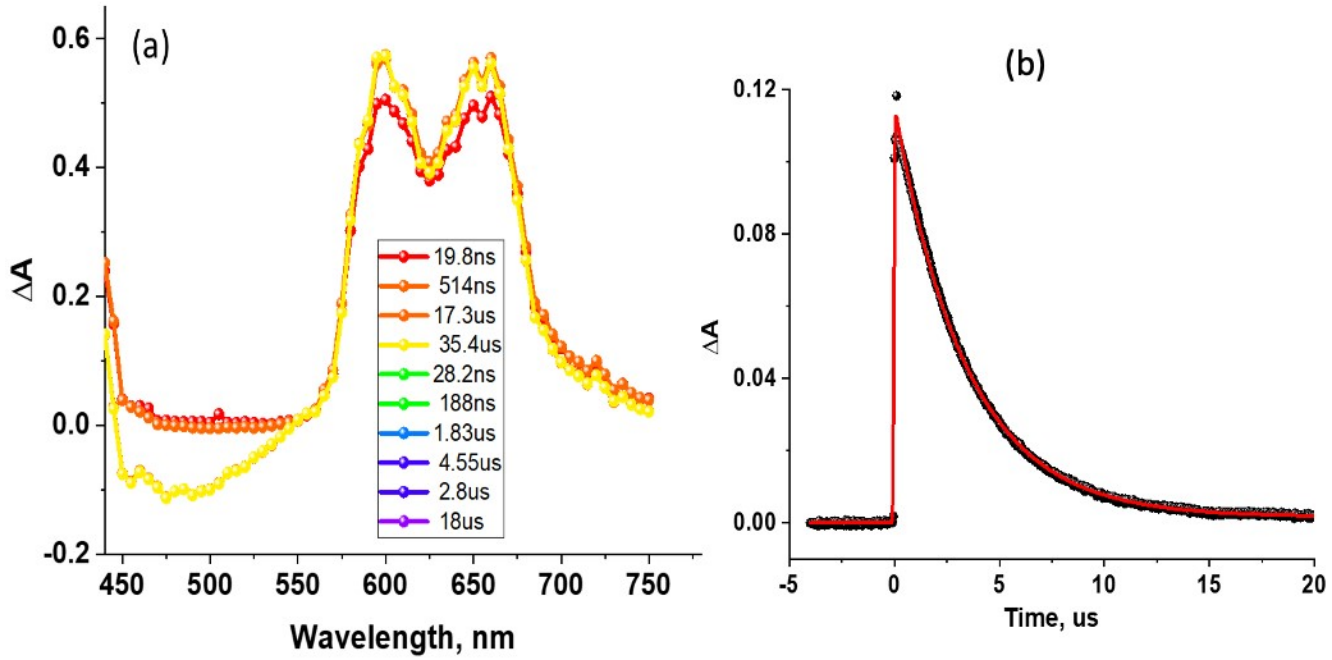


Figure S23. *ns*-TA absorption spectra at the indicated delay times of (a) $SbP(OMe)_2.PF_6$ in oxygen-free CH_3CN at the Soret band excitation. (b) shows the decay profile.

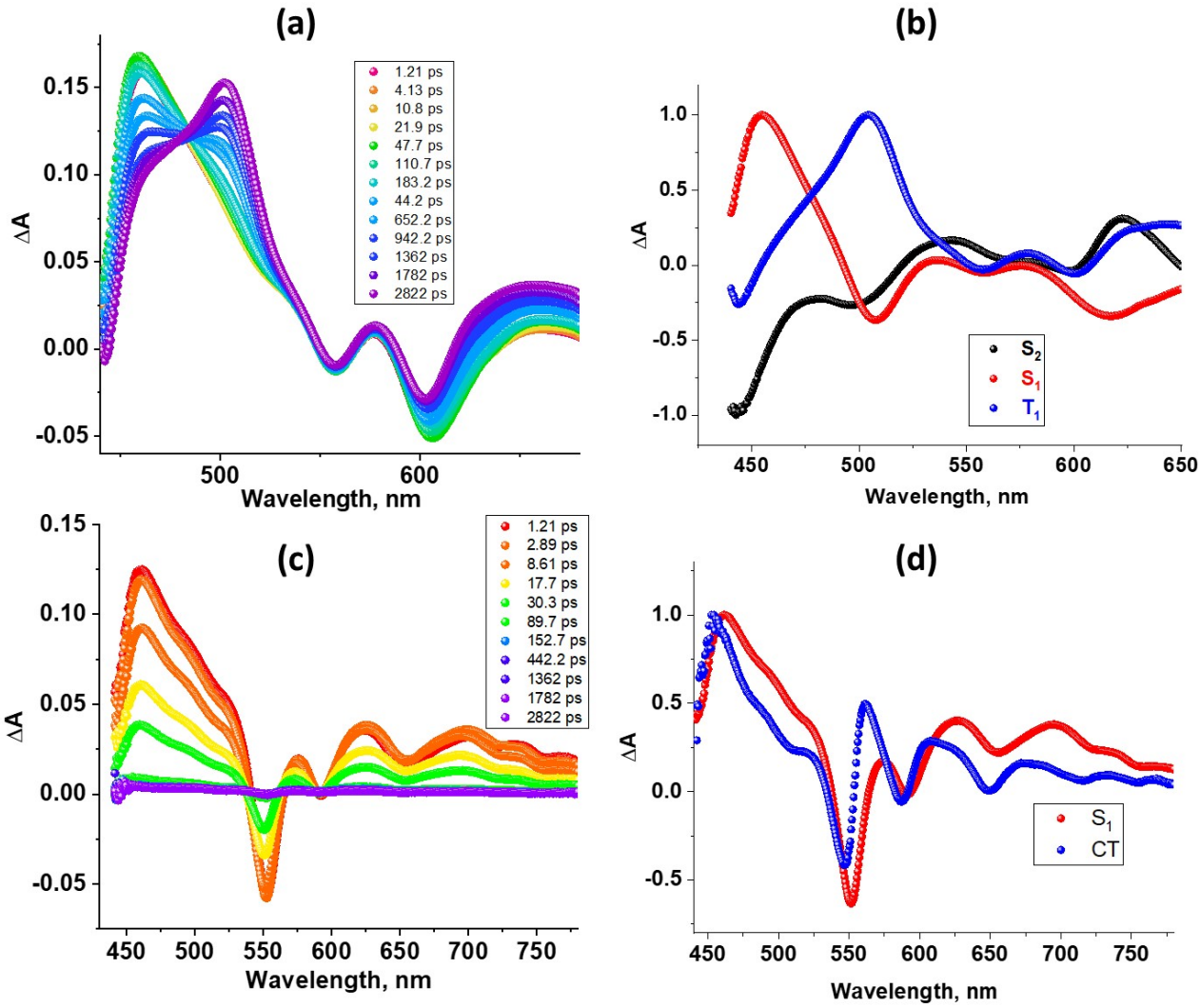


Figure S24. *fs*-TA absorption spectra at the indicated delay times of (a) $SbMP(OMe)_2.PF_6$ and (c) $SbDMP(OMe)_2.PF_6$ in oxygen-free acetonitrile at the Soret band excitation. (b and d) show the corresponding decay associated generated from global analysis.

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