Facile Tuning Strong Near-IR Absorption Wavelengths in Manganese(III) Phthalocyanines via Axial Ligand Exchange

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Supporting Information

Experimental:

All cyclization reactions were carried out under a nitrogen atmosphere using standard Schlenk and vacuum-line techniques, with glassware dried overnight at 160 ˚C prior to use and dry solvents were purchased under a Sure/Seal from Sigma Aldrich and used as received. 2,3-dicyanohydroquinone was purchased from Oakwood Products Inc. and used as received.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) data were collected with a Bruker Autoflex Speed spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 1 kHz smartbeam-II laser. Positive ion mass spectra were acquired typically within the 300–7000 m/z range. The mass spectrometer was operated in the reflection mode and the mass spectrum obtained for each image position corresponds to the averaged mass spectra of a minimum of 5000 consecutive laser shots. Flex Control 3.4 and flexAnalysis 3.4 software packages (Bruker Daltonics, Bremen, Germany) were used to control the mass spectrometer, set spectrum parameters and visualize spectral data. For sample preparation, approximately 2–3 mg of the sample was added to 0.5 mL of CH_2Cl_2 and 2 µL of the solution was then pipetted onto a ground steel plate, dried by evaporation and irradiated without a matrix.

Electronic spectra were recorded on a Cary 5000 spectrophotometer at 20 ^{o}C. Solutions were analyzed in a 0.1 cm quartz UV-Vis-NIR cell in CH_2Cl_2 with a baseline recorded prior to each measurement. Air and moisture sensitive species were analyzed in a quartz UV-Vis-NIR cell under an inert atmosphere sealed via a Kontes valve. NMR spectra were recorded at 294 K on a 500 MHz Bruker Avance III spectrometer, with a 5 mm QNP cryoprobe. Elemental analyses (C, H, N) were performed at Simon Fraser University by Mr. Paul Mulyk on a Carlo Erba EA 1110 CHN elemental analyser.

Synthetic Procedures:

1,4-dibutoxyphthalonitrile ((^{n}BuO)$_2$Pn) was synthesized by a standard alkylation reaction as reported with 1-bromobutane and 2,3-dicyanohydroquinone.[22] The cyclization of (^{n}BuO)$_2$Pn to (^{n}BuO)$_8$PcH$_2$ was performed by an adjusted literature procedure with Li$_{(s)}$, refluxing in 1-butanol under an inert atmosphere.[18] The 1,4-bis(isopropylthio)phthalonitrile ((^{i}PrS)$_2$Pn) was synthesized via nucleophilic attack of isopropyl thiol on 1,4-ditosylphthalonitrile as reported.[14] (^{i}PrS)$_8$PcH$_2$ was synthesized via a cyclization of (^{i}PrS)$_2$Pn over Li$_{(s)}$, refluxing in 1-hexanol under an inert atmosphere.[14]

1,4,8,11,15,18,22,25-octabutoxyphthalocyanine, (α-^{n}BuO)$_8$PcH$_2$: The free-base (α-^{n}BuO)$_8$PcH$_2$ was synthesized via a modified version of a reported procedure,[18] where the cyclization solvent was 1-butanol to ensure no unsymmetric PcH$_2$ macrocycles were formed as a result of substituent swapping with alcohols in solution. 10 g (36.5 mmol) of 3,6-dibutoxyphthalonitrile was dried under reduced pressure and 100 mL of dry 1-butanol was added to the flask under an inert atmosphere. The solution was heated to reflux after which 2.0 g (51 mmol) of solid Li beads were added to the flask. This mixture was refluxed for 1 h, after which the 1-butanol was removed under reduced pressure. The crude solid was dissolved in 200 mL of CHCl$_3$ and filtered to remove excess Li. Then, 10 mL of glacial acetic acid was added to the resulting CHCl$_3$ solution and this organic layer was washed with 4 X 200 mL of H$_2$O. The organic layer was dried with MgSO$_4$ and purified by column chromatography in silica with a 1:10 (CH$_3$)$_2$CO:CH$_2$Cl$_2$ mobile phase to yield: 7.8 g (78%) of (α-^{n}BuO)$_8$PcH$_2$.

1,4,8,11,15,18,22,25-octabutoxyphthalocyaninemanganese(III) chloride, (α-^{n}BuO)$_8$PcMnCl (1Cl): 3.0 g (2.7 mmol) of (α-^{n}BuO)$_8$PcH$_2$ was added to a 250 mL flask, dissolved in 60 mL of 1-butanol and heated to 80 °C. 2.7 g (11 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ was added to the flask. After 30 min the solution was cooled and 100 mL of $CHCl_3$ was added to the mixture and left to stir overnight. This solution was dried under reduced pressure and purified via column chromatography with a 1:2:10 CH_3OH:$(CH_3)_2CO$:CH_2Cl_2 mobile phase to yield **1Cl**. Yield: 780 mg (24%). Crystals were obtained via slow evaporation of an acetone solution. MALDI-TOF MS: Calc. M$^+$ 1178.52, Found M$^+$ 1178.18 Elemental Analysis Calc. for $C_{64}H_{80}N_8O_8MnCl$: C, 65.16; H, 6.84; N, 9.50; Found: C, 65.34; H, 7.38; N, 9.36; UV-vis: Q-band, 828 nm (ε = 8.3 ± 0.1 x 10^4 M^{-1} cm^{-1}); LMCT, 564 (ε = 1.55 ± 0.02 x 10^4 M^{-1} cm^{-1}); B-band, 349 (ε = 3.31 ± 0.05 x 10^4 M^{-1} cm^{-1})

1,4,8,11,15,18,22,25-octabutoxyphthalocyaninemanganese(III) fluoride, (α-^{n}BuO)$_8$PcMnF (1F): 100 mg (0.085 mmol) of **1Cl** was dissolved in 10 mL of THF under an inert atmosphere. 29 mg (0.085 mmol) of $AgSbF_6$ was added to the solution and it was stirred overnight. The reaction mixture was filtered over Celite and 38 mg (25 mmol) of CsF was added to the filtrate and left to stir for 24 hours, after which the solvent was removed under reduced pressure. The crude solid was washed with heptane, dissolved in a 1:3 hexanes:toluene solution and filtered over celite and dried under reduced pressure to yield **1F**. Yield: 87 mg (88%). MALDI-TOF MS: Calc. M$^+$ 1162.55, Found M$^+$ 1161.43, Elemental analysis Calc. for $C_{64}H_{80}N_8O_8MnF(H_2O)_{2.5}$: C, 63.62; H, 7.09; N, 9.27; Found: C, 63.84; H, 7.32; N, 8.88; UV-vis: Q-band, 815 nm (ε = 9.0 ± 0.5 x 10^4 M^{-1} cm^{-1}); B-band, 345 nm (ε = 3.4 ± 0.2 x 10^4 M^{-1} cm^{-1}).

1,4,8,11,15,18,22,25-octabutoxyphthalocyaninemanganese(III) iodide, (α-^{n}BuO)$_8$PcMnI (1I): 110 mg (0.1 mmol) of (α-^{n}BuO)$_8$PcH$_2$ was added to a 50 mL flask, dissolved in 5.0 mL of 1-

butanol and heated to 80 ^{o}C. 98 mg (0.4 mmol) of $Mn(OAc)_2•4H_2O$ was added to the flask. After 30 min the solution was cooled and 1.2 g (3.04 mmol) iodoform was added and the solution was stirred overnight. The solvent was removed under reduced pressure and the crude solid was purified through column chromatography over silica with a 1:1:3 hexanes:$(CH_3)_2CO$:EtOAc mobile phase to yield **1I**. Yield: 46 mg (36%). Crystals were obtained via slow evaporation of a toluene solution. MALDI-TOF MS: Calc. M^+ 1270.45, Found M^+ 1271.0. Elemental analysis Calc. for $C_{64}H_{80}N_8O_8MnI(C_7H_8)_{0.5}$: C, 61.55; H, 6.42; N, 8.51; Found: C, 61.61; H, 6.64; N, 8.82; UV-Vis-NIR: Q-band, λ_{max} = 839 nm ($\varepsilon = 8.7 \pm 0.1 \times 10^4$ M^{-1} cm^{-1}); λ_{max} = LMCT, 587 nm ($\varepsilon = 1.81 \pm 0.02 \times 10^4$ M^{-1} cm^{-1}); λ_{max} = B-band, 353 nm ($\varepsilon = 3.34 \pm 0.05 \times 10^4$ M^{-1} cm^{-1}).

1,4,8,11,15,18,22,25-octabutoxyphthalocyanine-bis(X)manganese(III), $[(\alpha\text{-}^{n}BuO)_8PcMnX_2]SbF_6$ (X = Py, DMAP): In order to produce the significant quantities of 6-coordinate complexes, 20 mg (0.017 mmol) of **1Cl** was dissolved in 8 mL of o-dichlorobenzene (DCB) under an N_2 atmosphere. 5.8 mg (0.017 mmol) of $AgSbF_6$ was added to the solution and stirred for 20 minutes. Pyridine (3 g) for **$[1Py_2]^+$** or DMAP (50 mg) for **$[1DMAP_2]^+$** was added to the reaction mixture. The DCB solution was transferred to a 125 mL flask and layered, heptane and left to recrystallize, yielding crystalline **$[1Py_2]^+$** (Yield: 16 mg, 62%) or **$[1DMAP_2]^+$** (Yield: 14 mg, 51 %). In order to obtain UV-Vis spectra of **$[1Py_2]^+$** and **$[1DMAP_2]^+$**, under an N_2 atmosphere, 0.4 mL of each solution was diluted to 10 mL and the electronic spectrum of each solution was recorded. Single crystal X-ray quality crystals of **$[1Py_2]^+$** and **$[1DMAP_2]^+$** were obtained by the solvent diffusion of heptane into DCB. **$[1Py_2]^+$** Elemental analysis Calc. for $C_{64}H_{80}N_8O_8Mn(C_5H_5N)_2(C_6H_4Cl_2)_{0.5}$: C, 57.38; H, 5.75; N, 8.69; Found: C, 56.96; H, 6.07; N, 8.85; UV-Vis-NIR: Q-band, λ_{max} = 868 nm ($\varepsilon = 1.04 \pm 0.06 \times 10^5$ M^{-1} cm^{-1}); LMCT, 581 nm ($\varepsilon = 2.7 \pm 0.02 \times 10^4$ M^{-1} cm^{-1}); B-band, λ_{max} = 370 nm (ε = 4.7 ± 0.03 x 10^4 M^{-1} cm^{-1}); **$[1DMAP_2]^+$** Elemental analysis Calc. for $C_{64}H_{80}N_8O_8Mn((CH_3)_2NC_5H_4N)_2(C_6H_4Cl_2)_{0.5}$: C, 57.30; H, 6.06; N, 9.90; Found: C, 56.71; H, 6.19; N, 10.18; UV-Vis-NIR: Q-band, λ_{max} = 850 nm (ε = 1.04 ± 0.04 x 10^5 M^{-1} cm^{-1}); LMCT, λ_{max} = 557 nm (ε = 1.89 ± 0.07 x 10^4 M^{-1} cm^{-1}); B-band, λ_{max} = 365 nm (ε = 4.0 ± 0.2 x 10^4 M^{-1} cm^{-1}).

1,4,8,11,15,18,22,25-octabutoxyphthalocyanine-bis(X)manganese(III), $[(\alpha\text{-}^nBuO)_8PcMnX_2]SbF_6$ (**X** = **FPy**, **THF**): In order to obtain UV-Vis-NIR spectra of other 6-coordinate complexes, 24 mg of **1Cl** was dissolved in 20 ml of o-dichlorobenzene under an N_2 atmosphere. 7 mg of $AgSbF_6$ was added to the solution and stirred for 20 minutes. The solution was diluted to 1/10 of the concentration and divided amongst four UV-Vis cells kept under and N_2 atmosphere. 1 drop of each of the axial ligands (**FPy**, **THF**) was added to each vessel and the electronic spectrum of each solution was recorded. An identical synthetic method was performed to synthesize and obtain UV-Vis-NIR spectra of $[\mathbf{2X_2}]^+$ (**X** = **FPy**, **Py**, **DMAP**).

1,4,8,11,15,18,22,25-octakis(isopropoxy)phthalocyanine, $(\alpha\text{-}^iPrS)_8PcH_2$: $(\alpha\text{-}^iPrS)_8PcH_2$ was synthesized via a modification to Kobayashi's procedure.[14] 1-hexanol (10 mL) was added to 3,6-bis[(1-methylethyl)thiophthalonitrile (1.20 g, 4.38 mmol) in a 3-necked flask equipped with a stir bar, a reflux condenser and a solid addition funnel containing lithium (215 mg, 30.6 mmol). The reaction mixture was heated to 100 ˚C and the lithium was added to the beige solution under N_2. The mixture was then heated to 120 ˚C and maintained at this temperature for 3 h, during which time it turned deep green. The solvent was removed *in vacuo* and the residue was washed with H_2O (10 mL). After silica gel column chromatography ($CHCl_3$) and drying *in vacuo* a black/purple powder of $(\alpha\text{-}^iPrS)_8PcH_2$ was obtained. Yield: 675 mg (56.3%). UV-vis ($CHCl_3$): , Q-band λ_{max} = 799 nm (ε = 1.37 ± 0.05 x 10^5 M^{-1} cm^{-1}); B-band, λ_{max} = 349 nm (ε = 4.3 ± 0.1 x 10^4 M^-

^{1} cm^{-1}), Elemental Analysis Calc. for $C_{56}H_{66}N_8S_8$: C, 60.72; H, 6.01; N, 10.12; S, 23.16. Found C, 60.55; H, 6.01; N, 10.10; S, 25.51. MALDI-TOF MS: Calc. M$^+$ 1106, Found M$^+$ 1105.

1,4,8,11,15,18,22,25-octakis(isopropoxy)phthalocyaninemanganese(III) chloride, (α-^{i}PrS)$_8$PcMnCl (2Cl): To a solution of (α-^{i}PrS)$_8$PcH$_2$ (570 mg, 0.512 mmol) in 10 mL DMF, Mn(OAc)$_2$•4H$_2$O (878 mg, 3.58 mmol) was added. The mixture was heated to 120 ^{o}C and maintained at this temperature for 2 h. The solvent was removed *in vacuo* and CHCl$_3$/methanol (10 mL each) was added to the residue. After stirring for 1 hr, the solvent was removed *in vacuo* again; the residue was washed with methanol (10 mL). Black crystals of (α-^{i}PrS)$_8$PcMnCl were isolated after silica gel column chromatography (CHCl$_3$) (300 mg, 48.7%). UV-vis: (CHCl$_3$) , λ_{max} = 877 nm (ε = 7.7 ± 0.3 x 10^4 M^{-1} cm^{-1}); LMCT, λ_{max} = 562 nm (ε = 1.34 ± 0.05 x 10^4 M^{-1} cm^{-1}); B-band, λ_{max} = 360 nm (ε = 2.8 ± 0.1 x 10^4 M^{-1} cm^{-1}). Elemental Analysis Calc. for $C_{56}H_{64}N_8MnS_8Cl(THF)_2$: C, 57.35; H, 6.02; N, 8.36; S, 19.14. Found: C, 57.25; H, 5.88; N, 8.15; S, 18.98; MALDI-TOF MS: Calc. M$^+$ 1195, Found M$^+$ 1194. Crystals of **1,4,8,11,15,18,22,25-octakis(isopropoxy)phthalocyaninetetrahydrofuranmanganese(III) chloride, [(α-^{i}PrS)$_8$PcMnCl(THF)]** (**2Cl(THF)**) were isolated when THF was used in the silica gel column chromatography step. UV-vis: (CHCl$_3$) , λ_{max} = 910 nm; LMCT, λ_{max} = 564 nm; B-band, λ_{max} = 359 nm.

1,4,8,11,15,18,22,25-octakisisopropoxyphthalocyanine-bisdimethoxyethanemanganese(III) hexafluoroantimonate, [(α-^{i}PrS)$_8$PcMn(DME)$_2$]$^+$SbF$_6^-$ [2(DME)$_2$]SbF$_6$: To a solution of (α-^{i}PrS)$_8$PcMnCl (60 mg, 0.050 mmol) in 15 ml THF, AgSbF$_6$ (17.0 mg, 0.050 mmol) was added slowly, causing the solution to become dark green. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 4 mL DME/ 2 mL hexane, and then the extracts were filtered through Celite. Black crystals of $[(\alpha\text{-}^{i}PrS)_8PcMn(DME)_2]^{+}SbF_6^{-}$ were isolated. Yield: 52.7 mg (75.1%). UV-vis: (DME) λ_{max} 375, 586, 920 nm; UV-vis (THF): λ_{max} = 925 nm ($\varepsilon = 6.5 \pm 0.3 \times 10^4$ M^{-1} cm^{-1}); LMCT, λ_{max} = 562 nm ($\varepsilon = 1.67 \pm 0.07 \times 10^4$ M^{-1} cm^{-1}); B-band, λ_{max} = 360 nm ($\varepsilon = 2.9 \pm 0.1 \times 10^4$ M^{-1} cm^{-1}), Elemental Analysis Calc. for $C_{56}H_{64}N_8MnSbF_6(C_4H_{10}O_2)(C_6H_{14})$: C, 50.40; H, 5.64; N, 7.13; S, 16.31. Found: C, 50.07; H, 5.27; N, 7.39; S, 15.93.

Table S1: Energy separations of molecular orbitals represented in Figure 2 (energy in E*10^{-19} J).

Compound	HOMO-LUMO	HOMO-d(eg)	LUMO-d(eg)	(HOMO-1)-HOMO	(HOMO-1)-LUMO	(HOMO-1)-d(eg)
1Cl	2.42	0.23	2.19	3.32	5.73	3.55
1I	2.39	0.13	2.26	3.28	5.67	3.41
$[1THF_2]^+$	2.32	0.38	1.94	3.09	5.41	3.47
$[1DMAP_2]^+$	2.35	0.46	1.90	3.13	5.48	3.59
$[1Py_2]^+$	2.31	0.32	1.98	3.12	5.42	3.44
$[1Fpy_2]^+$	2.28	0.27	2.00	3.10	5.38	3.37

The values in Table S1 were obtained by converting the wavelengths of the Q-band, B-band and LMCT λ_{max} absorptions which correspond to the $E_{HOMO\text{-}LUMO}$, $E_{(HOMO\text{-}1)\text{-}LUMO}$ and $E_{(HOMO\text{-}1)\text{-}d(eg)}$ energy separations respectively. The other energy separations were calculated by subtractions of these energies from each other represented in equations **1-3** below.

$$E_{(HOMO\text{-}1)\text{-}HOMO} = E_{(HOMO\text{-}1)\text{-}LUMO} - E_{HOMO\text{-}LUMO} \quad \textbf{(1)}$$

$$E_{d(eg)\text{-}LUMO} = E_{(HOMO\text{-}1)\text{-}LUMO} - E_{(HOMO\text{-}1)\text{-}d(eg)} \quad \textbf{(2)}$$

$$E_{HOMO\text{-}d(eg)} = E_{HOMO\text{-}LUMO} - E_{d(eg)\text{-}LUMO} \quad \textbf{(3)}$$

Single crystal X-ray diffraction:

Suitable crystals (**1Cl**, **1I**, **[1Py$_2$]$^+$**, **2Cl**, **2Cl(THF)**, **[2DME$_2$]$^+$**) were suspended in paratone oil in a glovebox under an inert N_2 atmosphere. They were then removed from the glovebox, mounted on a MiTeGen Micro Mount, and transferred to the X-ray diffractometer, which was set to 150 K using an Oxford Cryosystems Cryostream. Data was collected at 150 K on a Bruker Smart instrument equipped with an APEX II CCD area detector fixed at a distance of 5.0 cm from the crystal and a Cu Kα fine focus sealed tube (λ = 1.54178 Å) operated at 1.5 kW (45 kV, 0.65 mA), filtered with a graphite monochromator. Data were collected and integrated using the Bruker SAINT software package and were corrected for absorption effects using the multi-scan technique (SADABS[1] or TWINABS[2]). The structures were solved with direct methods (SIR92) and subsequent refinements were performed using SHELXL[3] and ShelXle.[4] Hydrogen atoms on carbon atoms were included at geometrically idealized positions (C–H bond distance 0.95Å) and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom. Diagrams were prepared using Mercury[5] and POV-RAY.[6] Thermal ellipsoids are shown at the 50% probability level.

Table S2, Crystallographic information table for **1Cl**, **1I**, **[1Py$_2$]$^+$** and **[1DMAP$_2$]$^+$**:

Compound Reference	**1Cl**	**1I**	**[1Py$_2$]$^+$**	**[1DMAP$_2$]$^+$**
Chemical Formula	$C_{64}H_{80}N_8O_8MnCl$	$C_{64}H_{80}N_8O_8MnI$	$C_{74}H_{90}N_{10}O_8Mn$ SbF_6	$C_{78}H_{100}N_{12}O_8Mn$ $SbF_6(C_6H_4Cl_2)_2$
Formula Mass	1179.75	1271.20	1538.24	1918.36
a/Å	11.5975(5)	11.7058(4)	9.5442(2)	25.6866(4)
b/Å	15.2196(7)	15.8078(5)	22.0391(6)	31.2724(5)
c/Å	17.3722(9)	16.9440(5)	33.9345(7)	11.2657(2)
α/°	88.379(4)	89.382(2)	90	90
β/°	75.385(4)	75.678(2)	95.618(2)	90
γ/°	84.439(3)	84.468(2)	90	90

Unit cell volume/Å^3	2953.2(2)	3023.50(17)	7103.7(3)	9049.5(3)
Temperature/K	150(2)	150(2)	150(2)	150(2)
Space group	P-1	P-1	P2$_1$/c	Pnma
Number of formula unit per cell/Z	2	2	4	4
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	2.740	6.279	5.122	5.203
No. of reflections collected	43876	10466	55377	54574
No. unique reflections	10107	10466	12599	8169
R$_{int}$	0.0527	0.0292	0.0867	0.1647
Final R$_1$ values (I>2σ(I))	0.0573	0.0718	0.1247	0.0727
Final wR(F^2) values (I>2σ(I))	0.1482	0.2073	0.2717	0.1605
Final R$_1$ values (all data)	0.0712	0.0793	0.1633	0.1299
Final wR(F^2) (all data)	0.1649	0.2155	0.2962	0.1871
Goodness of fit	1.046	1.089	1.047	1.044

Table S3, Crystallographic information table for **2Cl**, **2Cl(THF)** and **[2DME$_2$]$^+$**:

Compound Reference	**2Cl**	**2Cl(THF)**	**[2DME$_2$]$^+$**
Chemical Formula	$C_{56}H_{64}N_8S_8MnCl$	$[C_{60}H_{72}N_8OS_8MnCl]_4(C_4H_8O)_7$	$[C_{64}H_{84}N_8S_8O_4Mn]_2[SbF_6]_2(C_4H_{10}O_2)_{1.5}$
Formula Mass	1196.03	5577.44	3411.38
a/Å	12.1142(5)	13.5537(6)	16.1626(10)
b/Å	15.6404(6)	23.4630(9)	16.4059(13)
c/Å	16.6869(6)	21.6379(10)	18.7657(17)
α/°	74.248(3)	90	104.879(7)
β/°	81.437(3)	90	110.295(5)
γ/°	71.617(3)	90	103.963(5)
Unit cell volume/Å^3	2880.7(2)	6881.1(5)	4200.3(6)
Temperature/K	150.0(2)	150.0(2)	150.0(2)
Space group	P-1	P n a 21	P-1
Number of formula unit per cell/Z	2	1	1
Radiation type	Cu Kα	Cu Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	5.350	4.586	6.176

No. of reflections collected	28459	57480	50638
No. unique reflections	8944	11135	14356
R_{int}	0.0629	0.0344	0.1491
Final R_1 values ($I>2\sigma(I)$)	0.0466	0.0530	0.2499
Final $wR(F^2)$ values ($I>2\sigma(I)$)	0.0977	0.1371	0.5851
Final R_1 values (all data)	0. 762	0.0627	0.2999
Final $wR(F^2)$ (all data)	0.1139	0.1464	0.6259
Goodness of fit	1.056	1.098	2.354

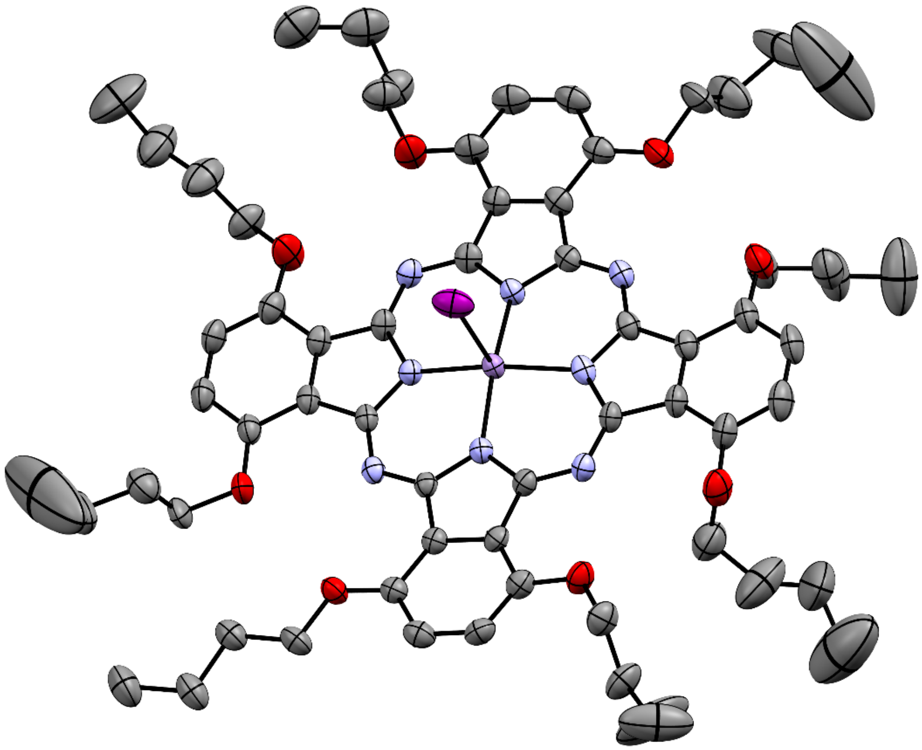

Figure S1: Single crystal X-ray structure of **1I** (carbon: grey, nitrogen: blue, oxygen: red, manganese: light purple, iodide: magenta).

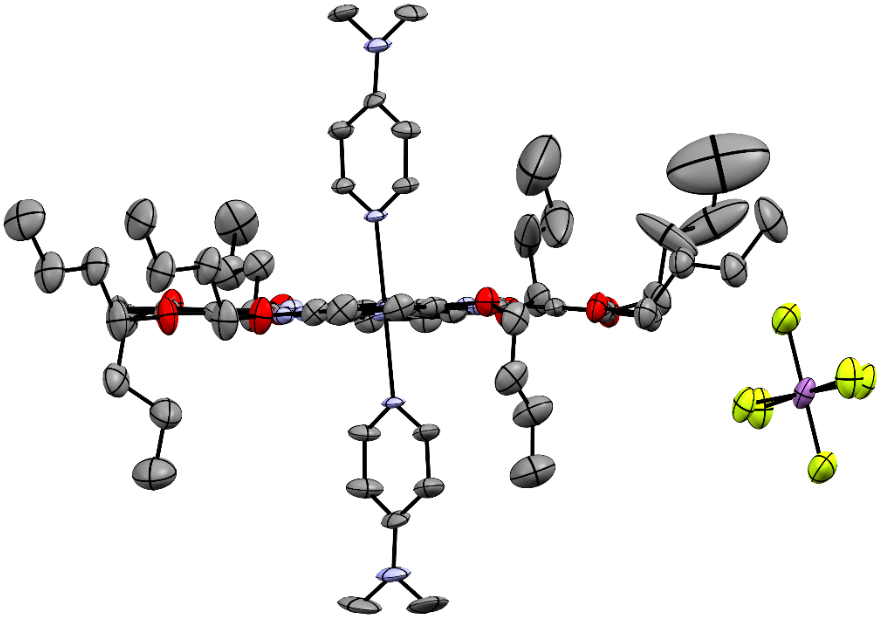

Figure S2: Single crystal X-ray structure of **[1DMAP$_2$]**$^+$ (carbon: grey, nitrogen: blue, oxygen: red, manganese: light purple, fluorine: yellow/green, antimony: purple). Hydrogens and DCB molecules excluded for clarity.

Molecular Modeling:

All calculations on the compounds studied were performed on Gaussian 09.[7] Molecular coordinates were imported from the crystallographic data and all atoms except the hydrogens were frozen in the constrained optimizations. The optimizations were computed using density functional theory (DFT)[8] using the Becke three parameter Lee-Yang-Parr (B3LYP) method[9,10] at the 6-31G(d) level[11]. The molecular orbitals for all three structures were obtained from the optimized structure (only hydrogens were optimized).

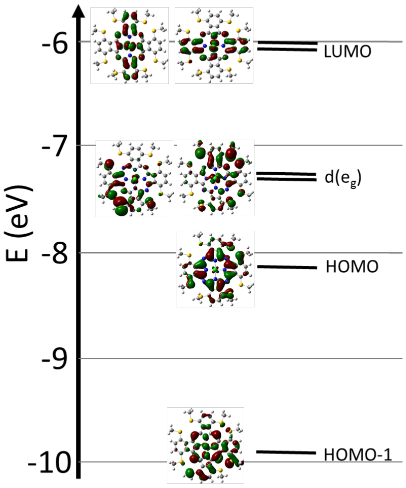

Figure S3: Calculated MO energy levels participating in the Q-band, B-band and LMCT electronic transitions for **2Cl**.

References:

1. Bruker, APEX3, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
2. G. M. Sheldrick, TWINABS (Version 2012/1), University of Gçttingen, Germany, 1996.
3. G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
4. C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.
5. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.* **2008**, *41*, 466-470.
6. T. D. Fenn, D. Ringe, G. A. Petsko, *J. Appl. Crystallogr.* **2003**, *36*, 944-947.
7. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian, Inc.: Wallingford CT 2016.
8. Parr, R. G.; Yang, W. Y. *Density Functional Theory of Atoms and Molecules*; Oxford

University Press: New York, 1989.

9. Becke, A. D. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.

10. Lee, C.; Hill, C.; Carolina, N. *Chem. Phys. Lett.* **1989**, *162* (3), 165–169.

11. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77* (7), 3654–3665.