Dipyrrinphenol-Mn(III) complex: synthesis, electrochemistry and spectroscopy characterisation and reactivity

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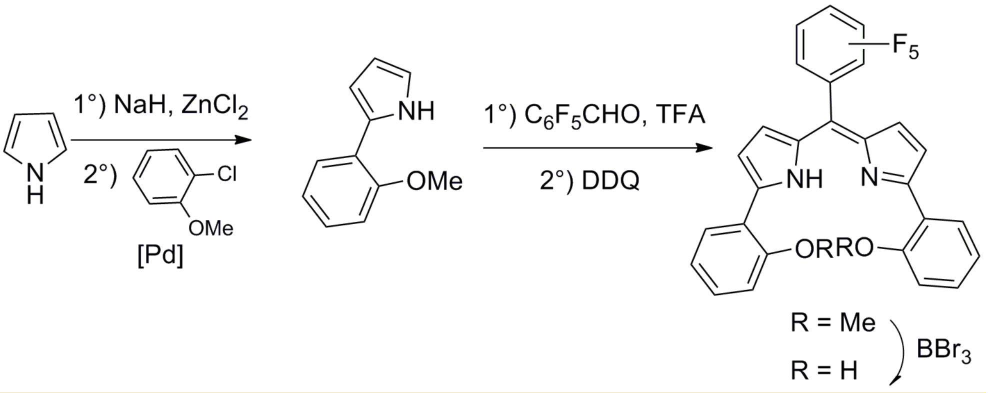
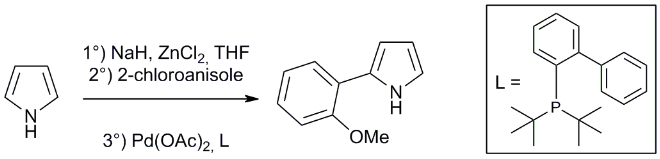
I. SYNTHESIS

I-1. Ligand synthesis:

Scheme S1: ligand *DPPH$_3$*



I-1-1. Synthesis of 2-(2’-Methoxyphenyl)-1H-pyrrole

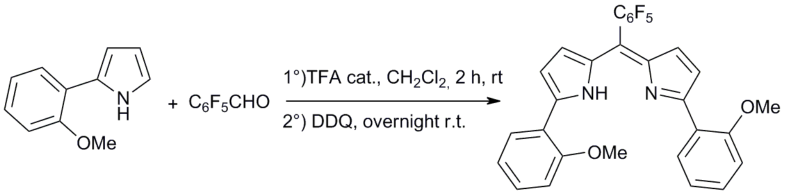


2-(2’-Methoxyphenyl)-1H-pyrrole was prepared according to the procedure described in the literature.[1]

^{1}H NMR (CDCl$_3$): δ = 3.88 (s, 3H, CH$_3$), 6.27 (td, 1H, J=2.7, J=3.4Hz), 6.61 (ddd, 1H, J=1.5, J=2.5, J=3.8Hz), 6.83 (dt, 1H, J=1.5, J=2.6Hz), 6.89-6.99 (m, 2H), 7.12 (ddd, 1H, J=1.7, J=7.5, J=8.2Hz), 7.64 (dd, 1H, J=1.7, J=7.7Hz), 9.77 (bs, 1H, NH).

^{13}C NMR (CDCl$_3$): δ = 55.6, 106.0, 108.8, 111.6, 117.7, 121.0, 121.4, 126.5, 126.6, 129.8, 154.6, in agreement with literature data.[1]

I-1-2. Synthesis of DPPHMe$_2$ [2]



To a stirred solution containing 2-(2-methoxyphenyl)pyrrole (2.0 g, 11.9 mmol, 1.0eq) and the pentafluorobenzaldehyde (1.19 g, 5.95 mmol, 0.5eq.) in CH$_2$Cl$_2$ (80 mL), trifluoroacetic acid (140 μL, 0.86 mmol, 0.15eq) was added under inert atmosphere and the mixture was stirred for 2 h at room temperature. Then, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.35 g, 5.96 mmol) was added and the resulting solution was stirred overnight at rt. The reaction mixture was washed with saturated $NaHCO_3$ aqueous solution, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated to a small volume that was loaded directly on a short alumina pad to remove the salts. The filtrate was then evaporated to dryness, taken in the minimum of CH_2Cl_2 and purified over a silica gel column, using a 1:1:0.1 mixture of CH_2Cl_2: EtOAc: NEt_3 as eluent. R_f = 0.28 in CH_2Cl_2: Cyclohexane 1: 1. Yield 60%; mp = 104-105°C.

^{1}H NMR ($CDCl_3$): δ = 3.87 (s, 6H, 2 x CH_3), 6.47 (d, 2H, J=4.3Hz), 6.94 (d, 2H, J=4.3Hz), 7.02 (m, 4H), 7.34 (ddd, 2H, J=1.7Hz, J=7.4Hz, J=8.3Hz), 8.03 (dd, 2H, J=1.7Hz, J=7.7Hz).

^{13}C NMR ($CDCl_3$): δ = 26.9 (2 x CH_3), 55.9, 111.6, 119.6, 120.9, 121.9, 126.5, 129.1, 130.3, 140.3, 153.9, 157.4

ESI-HRMS calculated for $C_{29}H_{20}F_5N_2O_2$ = 523.1439, found 523.1438 [MH^+]

I-1-3. Synthesis of $DPPH_3$[2]

The experimental procedure was adapted from the methodology described in the literature for the preparation of the phenyl analogue.

To a stirred solution of $DPPHMe_2$ (0.400 g, 0.72 mmol) in CH_2Cl_2 (7 mL), BBr_3 (2.17 mL, 2.17 mmol, 3.0 eq) was added at 0 °C under argon atmosphere. The reaction mixture was stirred and allowed to warm up to room temperature and left for 4 days before quenching with methanol. The mixture was evaporated and dissolved again with methanol. To the resulting mixture, conc. HCl (37%) was added and the reaction mixture was refluxed for 3 hrs. After cooling, the mixture was neutralized with a saturated $NaHCO_3$ aqueous solution and extracted with ethylacetate. The organic layer was dried over Na_2SO_4, evaporated to dryness and purified by column chromatography using a 1: 1 mixture of CH_2Cl_2/hexane as eluent. The expected compound was isolated as a dark purple solid (0.186 g) in 49% of yield. mp = 227-230°C

^{1}H NMR ($CDCl_3$): δ = 6.62 (d, 2H, J=4.4Hz), 6.83 (m, 2H), 6.93 (m, 4H), 7.01 (m, 2H), 7.61 (dd, 2H, J=1.3Hz, J=7.8Hz).

^{19}F NMR ($CDCl_3$): δ = -161.38 (dq, 2F, J=3.4, J=10.1Hz), -152.79 (t, 1F, J=20.8Hz), -138.87 (dt, 2F, J=3.4, J=10.1Hz).

^{13}C NMR ($CDCl_3$): δ = 27.1, 53.6, 112.9, 116.8, 116.9, 117.1, 120.4, 121.1, 127.9, 128.5, 130.8, 135.9, 138.4, 139.2, 140.0, 143.7, 146.9, 155.9, 156.3.

ESI-MS observed *m/z* 495.0 [$M+H^+$].

I-2. Complex synthesis:

[MnDPP]$_2$: To a stirred solution containing DPPH$_3$ (0.060 g, 0.12 mmol, 1.0 eq) in a 1:1 mixture of EtOH/toluene (3.0 mL), Et$_3$N (37 µL, 0.26 mmol, 2.17 eq) was added followed by Mn(OAc)$_2$ (0.043 g, 0.25 mmol, 2.08 eq). The reaction mixture was stirred at 85°C for 1 hour and monitored by TLC. After completion, the solvents were evaporated and the resulting complex was purified over a silicagel column chromatography using an increasing amount of ethylacetate in CH$_2$Cl$_2$ (0 to 10%) as eluent. The expected complex was isolated as a green solid (0.046 g) in 68% of yield.

ESI-MS calculated for $C_{29}H_{15}F_5N_2O_2Na$ = 569.0, found 569.1 [M+Na$^+$]

II. INSTRUMENTATION.

Electrospray Ionization Mass Spectrometry. Mass spectra were recorded with a Finnigan MAT95S in a BE configuration at low resolution on micromolar acetonitrile solution or with a Spectrometer MicroTof-Q Bruker from the *Centre Commun de Spectrométrie de Masse*, UCBL.

NMR spectroscopy: ^{1}H-NMR, spectra were recorded on a Bruker ALS 300 MHz with a QNP probe at room temperature in CDCl$_3$ (δ = 7.26 ppm); ^{13}C spectra were recorded on a Bruker ALS 300 MHz with a QNP probe at room temperature and referenced to the CDCl$_3$ solvent peak at δ = 77.7 ppm; 19F spectra were recorded on a Bruker ALS 300 MHz with a QNP probe at room temperature and referenced to CFCl$_3$.

EPR spectroscopy: X-band spectra were recorded on a Bruker ELEXSYS 500 spectrometer. Perpendicular mode CW- EPR spectra were recorded with a Bruker HSW4119 cavity and parallel mode CW- EPR spectra were recorded with a Bruker ER4116DM dual mode cavity. Cryogenic temperatures were obtained with an Oxford ESR 900 liquid helium cryostat. The temperature was controlled with an Oxford ITC 503 temperature and gas flow controller. Solutions spectra were recorded in acetonitrile containing 0.2 M NBu$_4$PF$_6$.

Cyclic voltammetry and bulk electrolysis. All electrochemical experiments were run under Argon atmosphere. Cyclic voltammetry and coulometry measurements were recorded either on an EGG PAR potentiostat (M273 model) or a Metrohm potentiostat (AUTOLAB model). For cyclic voltammetry, the counter electrode used was a Pt wire and the working electrode a glassy carbon disk carefully polished before each voltammogram with a 1 μm diamond paste, sonicated in ethanol bath and then washed with ethanol. The reference electrode used was an Ag/$AgClO_4$ electrode with acetonitrile as solvent (0.3 V *vs.* SCE electrode), isolated from the rest of the solution by a fritted bridge. For bulk electrolysis, the counter electrode used was a piece of Pt, separated from the rest of the solution with a fritted bridge. The working electrode was a cylinder of glassy carbon. Supporting electrolyte NBu_4PF_6 (Aldrich, puriss) was 0.1 M (273 K) or a 0.2 M (low temperature) in acetonitrile (Aldrich, puriss). Low temperature regulation was ensured by a Julabo circulation cryostat.

Spetroelectrochemistry: Spectroelectrochemical data were obtained by a combination of a three electrode thin cell (optical length = 0.5 mm) mounted in a UV/Vis/NIR Varian Cary 5E Spectrophotometer. The two-part spectroelectrochemical 0.5 mm quartz cell has been described elsewhere.[3] The working electrode is a Pt grid, the reference and the counter electrodes (Pt wire) are located on the top of the cell. The entire solution was under argon.

X-ray diffraction. The diffraction intensities were collected with graphite-monochromatized Mo Kα radiation. Data collection and cell refinement were carried out using a Brucker Kappa X8 APEX II diffractometer. The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. Intensity data were corrected for Lorenz-polarization and absorption factors. The structures were solved by direct methods using[4], and refined against F^2 by full-matrix least-squares methods using[5] with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed by using the Crystal Structure crystallographic software package[6]. The structures were drawn using ORTEP3. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations with isotropic thermal parameters.

CCDC 811013 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

III. CRYTALLOGRAPHIC DATA

Table S1. Selected bond lengths [Å] and angles [°] for **[MnDPP]$_2$**.

Lengths [Å]			
Mn – O(1)	1.909(3)	Mn – N(2)	1.941(3)
Mn – O(2)	1.855(3)	Mn – O*(1)	2.207(3)
Mn – N(1)	1.954(3)	Mn ··· M*	3.1460(13)
Angles [°]			
O(1) – Mn - O*(1)	80.54(11)	N(2) – Mn – O*(1)	98.82(11)
Mn - O(1) - Mn*	99.46(11)	N(1) – Mn – O*(1)	101.90(12)
N(1) – Mn – N(2)	91.78(13)	N(1) – Mn – O(1)	90.08(12)
O(2) – Mn – N(2)	90.23(13)	N(1) – Mn – O(2)	158.83(13)
O(1) – Mn – O(2)	98.82(11)	N(2) – Mn – O(1)	176.54(13)

Table S2. Crytallographic Data for **[MnDPP]$_2$.**

Empirical formula	$C_{54}H_{24}F_{10}Mn_2N_4O_4$
Formula weight	1092.65
Temperature (K)	100(1)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions	
a (Å)	11.7563(16)
b (Å)	11.2145(13)
c (Å)	15.6509(18)
α (°)	90.00
β (°)	100.273(4)
γ (°)	90.00
V (Å^3)	2030.4(4)
Z	2
$D_{calc.}$ (Mg.m^{-3})	1.787
Absorption coefficient (mm^{-1})	0.668
F (0 0 0)	1096
Reflection collected	27228
Independent reflections (Rint)	4156 (0.0975)
Observed reflections (I >2σ(I))	2588
Final R indices [$I > 2\sigma I$]	R1=0.0559, wR2=0.1013
S	1.000
$(\Delta\rho)_{max,\,min}$ [e Å^{-3}]	0.495 ; -0.718

IV. PHYSICAL STUDIES

Electrochemistry of MnDPP

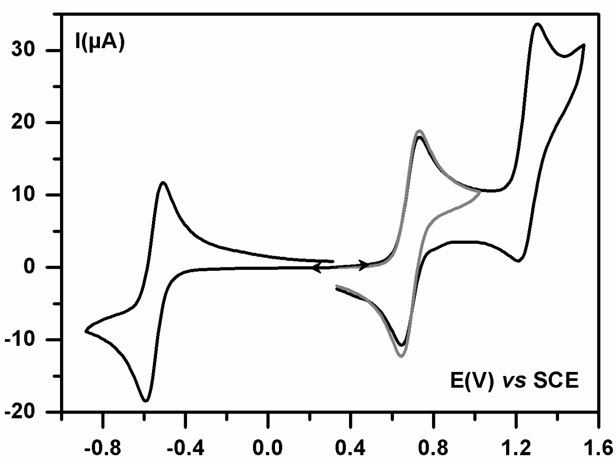


Fig. S1. Cyclic voltammograms of MnDPP (2 mM) in acetonitrile (0.2 M NBu_4PF_6) on a glassy carbon electrode at a scan rate of 0.1 V/s, T=293 K showing the two anodic processes and a cathodic wave at -0.56 V *vs* SCE

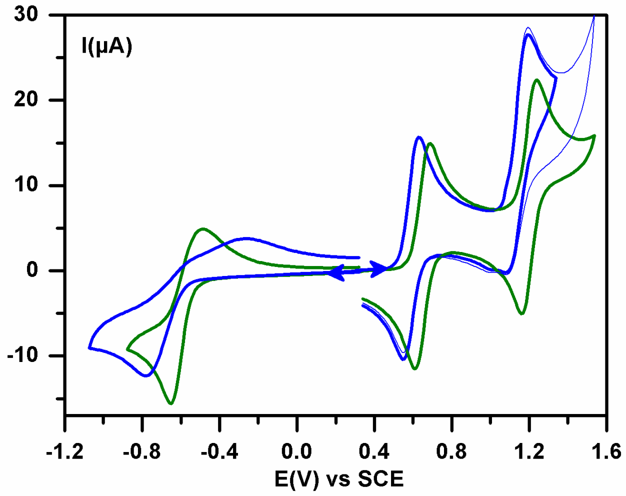


Fig. S2. Cyclic Voltammograms of MnDPP (2 mM) at 0.1 V/s, T = 253 K, on a glassy carbon electrode in acetronitrile (0.2 M NBu_4PF_6), (Green line) and in acetonitrile containing 6 % water (Blue line).

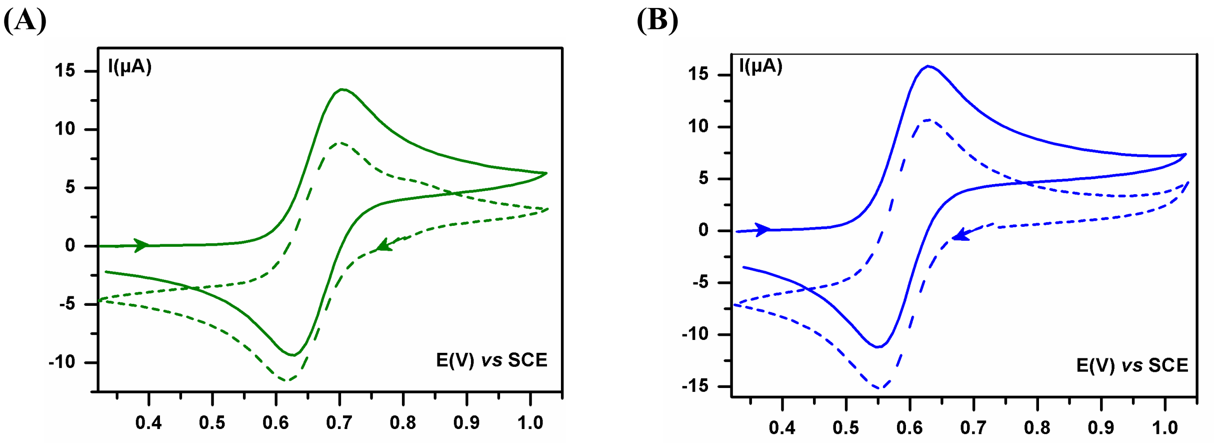


Fig. S3. Cyclic Voltammograms of MnDPP (2 mM) before (solid line) and after (dashed line) exhaustive oxidative electrolysis at 0.8 V vs SCE at 253 K. (A) in acetonitrile (0.2 M NBu_4PF_6), (Green line). (B) in acetonitrile (0.2 M NBu_4PF_6) containing 6 % water (Blue line).

Table S3. $E_{1/2}$[a] values (V *vs* SCE) for complexes MnDPP in acetonitrile and acetonitrile/water (0.2 M NBu_4PF_6) at 0.1 V/s.

MnDPP	$E_{1/2}(\Delta E_p/mV)$		
	Mn^{III}/Mn^{II}	Mn^{IV}/Mn^{III}	Mn^{V}/Mn^{IV}
Acetonitrile	-0.557(114)[b] -0.567(169)[c]	0.675(96)[b] 0.651(79)[c]	1.227(84)[b] 1.200(79)[c]
Acetonitrile/Water	-0.779(irr)[c]	0.590(82)[c]	1.194(irr)[c]

[a] $E_{1/2}$ is defined as $(E_p^a + E_p^c)/2$, where E_p^a is the potential value of the anodic peak and E_p^c is the potential value of the cathodic peak. [b] at 293 K; [c] at 253 K

EPR of MnDPP

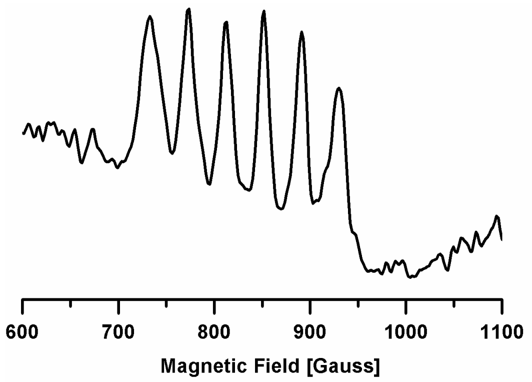


Fig. S4. Parallel mode EPR spectrum of a 2 mM solution of MnDPP in acetonitrile (0.2 M NBu_4PF_6). EPR recording conditions: microwave frequency 9.41 GHz, modulation frequency 100 kHz, microwave power 4 mW, modulation amplitude 0.7 mT, T 5K, time constant 160 ms

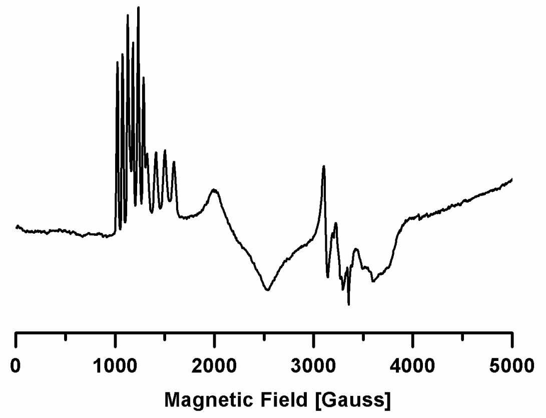


Fig. S5. Perpendicular mode EPR spectrum of a 2 mM solution of MnDPP in acetonitrile (0.2 M NBu_4PF_6) recorded after exhaustive reduction at 0.8 V vs SCE; T=253 K; working electrode: glassy carbon crucible; auxiliary electrode: Pt grid separated from the rest of the solution with a fritted glass. EPR recording conditions: microwave frequency 9.38 GHz; modulation frequency 100 kHz; microwave power 2 mW; modulation amplitude 1 mT; T 5K; time constant 160 ms.

Perpendicular mode X-band EPR data obtained at 5 K on the electrolysed solution in acetonitrile, indicate well-resolved signals with g values at g 5.8, 4,9, 3, and 1,8. The presence of two series of hyperfine lines detected at g 5.8 and 4.9 splitting with 52 and 91 G respectively. We interpret these findings by the concomitant presence of two Mn(IV) species differing by the nature of the axial ligand. As discussed in the text, the signal with A value of 91 G is attributed to the presence of a bound water molecule and the one with A of 52 G is assigned to the presence of an acetonitrile molecule.

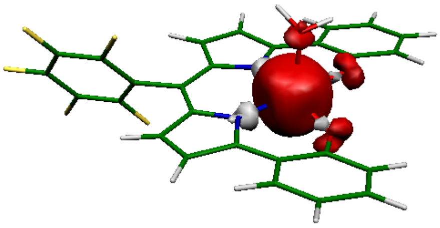
V. DFT CALCULATIONS.

Computational details

All calculations reported in this paper were done with the program package ORCA.[8] DFT calculations were carried out using the B3LYP/G hybrid functional[9,10] with 20% HF exchange and the same defintion as in the Gaussian package. The all-electron basis sets of Ahlrichs group[11] were used : the 3-ζ basis set with one polarisation function (TZVP) for cobalt, the 2-ζ split valence set with one polarisation function (SVP) for oxygen and nitogen atoms and the 2-ζ set (SV) for other atoms. Geometry optimisations were performed for the isolated molecule. Calculations on these open-shell systems are unrestricted ones.

DFT calculations on [MnDPP(OH$_2$)]

The geometry of the putative pentacoordinated monomer [MnDPP(OH$_2$)] was fully optimised in gas phase in the spin state (S = 2) expected for Mn^{III} (d^4) in this surrounding. The calculated Mn-O$_W$ distance between the manganese and the oxygen of the water molecule is 2.27 Å. The other distances in the coordination sphere are Mn-O = 1.87 and 1.87 Å. and Mn-N = 1.99 and 2.00 Å. The Mulliken atomic spin on manganese ρ_{Mn} = 3.88 and the map of the spin density distribution are characteristic of the occupation of four spin-up d orbitals as expected for high-spin Mn^{III}.



VI. Catalysis

Under argon, a Schlenk tube was charged with the catalyst and PhIO. Then, 2 mL of degassed MeCN was added. The reaction mixture was stirred at room temperature for 3 minute before the alkene was added. The reaction was allowed to proceed at room temperature and was monitored by GC-analyses. Typically, a sample was taken, and filtered though a pad of celite. The eluate was diluted in Et$_2$O and directly injected on the GC column (Zebron phase 2B1 from Phenomenex; L = 30 m x ID = 0.32 mm x di = 0.25 μm).

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