# Electronic Supplementary Information

## Electrochemical meso-Functionalization of Magnesium(II) Porphine†

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Experimental Details

Synthesis
Magnesium porphine 1 was synthesized according to known procedures.¹ Data (¹H NMR, ¹³C NMR, UV-Visible absorption, and MALDI-TOF mass spectrum) were consistent with those obtained in reference ¹.

Materials
Pyridine (VWR-BDH-Prolabo, 99.90% on anhydrous product), PPh₃ (Fluka, puriss., >99%), tetraethylammonium hexafluorophosphate (TEAPF₆, Fluka puriss., electrochemical grade, ≥99.0%), 2,6-lutidine (Aldrich, purified by redistillation, ≥99%) and MeOH (Sigma-Aldrich, Chromasolv for HPLC, min. 99.9%) were used as received. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆) was synthesized by mixing stoichiometric amounts of tetra-n-butylammonium hydroxide (Alfa-Aesar, 40% w/w aq. sol.) and hexafluorophosphate acid (Alfa-Aesar, ca 60% w/w aq. sol.). After filtration, the salt was recrystallized three times in ethanol and dried at 80 °C during at least two days. CH₂Cl₂ (Carlo Erba 99.5%) and CH₃CN (SDS, Carlo Erba, HPLC gradient 99.9%) were distilled from P₂O₅ and CaH₂ respectively.

Electrochemistry
All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon at room temperature (T = 20°C ± 3°C). The supporting electrolyte was degassed under vacuum before use and then dissolved to a concentration of 0.1 mol L⁻¹. Voltammetric analyses were carried out in a standard three-electrode cell, with an EG & G Princeton Applied Research (PAR) Model 273 potentiostat, connected to an interfaced computer that employed Electrochemistry Power Suite software. The reference electrode was a saturated calomel electrode (SCE) separated from the analysed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum wire separated from the analysed solution by a sintered glass disk filled with the background solution. For all voltammetric measurements, the working electrode was a platinum electrode (Ø = 2 mm). In these conditions, when operating in pyridine (0.1 M TBAPF₆), the formal potential for the ferrocene (+/0) couple was found to be +0.55 V vs. SCE. When operating in a mixture of CH₂Cl₂/CH₃CN 4/1 (0.1 M TEAPF₆) the formal potential for the ferrocene (+/0) couple was found to be +0.40 V vs. SCE.

Bulk electrolyses were performed in a cell with three compartments separated with glass frits of medium porosity with an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. A platinum wire spiral (l = 53 cm, Ø = 1 mm) was used as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode as the reference electrode. The electrolysis was followed by TLC and UV-visible absorption measurements and was stopped when the pink spot corresponding to 1 disappeared on TLC and when UV-visible absorption spectra and current did not evolve anymore. For pyridinium substitution, 2.0 ± 0.1 faraday per mol of 1 were necessary to exhaust totally the starting product. For the triphenylphosphonium substitution, 3.4 ± 0.2 faraday per mol of 1 were used.
Work-up procedures

$2^+PF_6^-$:
After electrolysis in pyridine, work-up involved evaporating the red solution mixture to dryness under reduce pressure. The resulting crude solid was dissolved in a minimum of cold (ca. −90 °C) MeOH and the precipitated supporting electrolyte was removed by filtration and washed with cooled MeOH. The red filtrate was evaporated to dryness and this precipitation/filtration procedure was repeated one more time. The crude product was then purified by column chromatography ($SiO_2$, 0 to 2% MeOH, 1% pyridine in $CH_2Cl_2$). The first light pink fraction was unreacted $1 (< 1 \text{ mg})$. The second red fraction corresponded to $2^+PF_6^-$. 

$3^+PF_6^-$:
The work-up involved evaporating the blue/green solution mixture to dryness under reduce pressure. The resulting crude solid was dissolved in a minimum of $CH_2Cl_2$ and this solution was washed four times with 250 mL of distilled water to remove the supporting electrolyte. The blue/green organic phase was evaporated to dryness. The crude product was then purified by column chromatography (Alumina, 0 to 1% MeOH in $CH_2Cl_2$). The first colourless fraction was unreacted $PPh_3$, the second blue/purple fraction was $3^+PF_6^-$. 

**Instruments**
UV-visible absorption spectra were obtained with a Varian UV-vis spectrophotometer Cary 50 scan using quartz cells (Hellma).
Mass spectra were obtained on a Bruker ProFLEX III spectrometer (MALDI-TOF) using dithranol as matrix.
NMR spectra were measured on a BRUKER 600 MHz Avance II spectrometer. The reference was the residual non-deuterated solvent ($CH_3COCH_3$ or $CH_3OH$).
Fig. 1 MALDI-TOF mass spectrum of the crude solution resulting from the electrolysis of I in pyridine 0.1 M TBAPF$_6$; $E_{app} = 0.72$ V vs. SCE, $\sim$2 e, working electrode: Pt spiral.

Fig. 2 RDE voltammogram before (black/solid line) and after (red/dashed line) electrolysis of I in pyridine containing 0.1 M TBAPF$_6$ (WE: Pt, $\Theta = 2$ mm, 10 mV s$^{-1}$, $\omega = 500$ rpm, [I] = 5.0×10$^{-4}$ M).
Fig. 3 $^1$H NMR spectrum of $2^\prime,PF_6^-$ in CD$_3$COCD$_3$, 600 MHz, 298 K.
Fig. 4 $^{13}$C NMR spectrum of $2^+, PF_6^-$ in CD$_3$COCD$_3$, 150 MHz, 298 K.
(*): non attributed signals. These signals could be:
m, n, o, p or q (these 5 C are uncoupled with proton signals in the \(^1\)H-\(^{13}\)C HSQC experiment)

Fig. 5 Partial \(^{13}\)C NMR spectrum of \(2^+\cdot\text{PF}_6^-\) in CD\(_3\)COCD\(_3\), 150 MHz, 298 K.
Fig. 6 $^1$H-$^1$H COSY NMR spectrum of $2^+PF_6^-$ in CD$_3$COCD$_3$, 600 MHz, 298 K.
Fig. 7 $^1$H-$^1$H NOESY NMR spectrum of $2^i$PF$_6$-$^i$Py in CD$_3$COCD$_3$, 600 MHz, 298 K.
Fig. 8 $^1$H-$^{13}$C HSQC NMR spectrum of $2\text{'},\text{PF}_6^-$ in CD$_3$COCD$_3$, 600 MHz, 298 K.
Experimental spectrum of $2^+,PF_6^-$

Theoretical isotopic pattern for $C_{25}H_{16}MgN_5$+  

Chemical Formula: $C_{25}H_{16}MgN_5^+$

Exact Mass: 410.13

Fig. 9 Partial MALDI-TOF mass spectrum of $2^+,PF_6^-$ centered on its isotopic pattern (red/solid curve) and simulated isotopic pattern for a formula corresponding to $2^+$ (black/dotted curve).
Fig. 10 $^1$H NMR spectrum of $3^+\text{PF}_6^-$ in CD$_3$OD, 600 MHz, 298 K.
Fig. 11 $^{13}$C NMR spectrum of $3', PF_6^-$ in CD$_3$OD, 150 MHz, 298 K.
Fig. 12 Partial $^{13}$C NMR spectrum of $3^'+PF_6^-$ in CD$_3$OD, 150 MHz, 298 K. (*): non attributed signals. These signals could be: m, l, k, j, n or o (these 6 C are uncoupled with proton signals in $^1$H-$^{13}$C HSQC experiment). The “o” signal is attributed thanks to its coupling constant in comparison with phosphonium compounds reported in the literature, see for example ref 2.

$^{13}$C-$^{31}$P coupling constants:
- g: d, $^3J = 10.2$ Hz
- i: d, $^3J = 2.6$ Hz
- h: d, $^3J = 13.0$ Hz
- f: d, $^3J = 4.5$ Hz
- o: d, $^3J = 88.0$ Hz
- 154.3 ppm: d, $J = 15.4$ Hz (m ?)
Fig. 13 $^{31}$P NMR spectrum of $3^+PF_6^-$ in CD$_3$OD, 243 MHz, 298 K.
Fig. 14 $^1$H-$^1$H COSY NMR spectrum of $3^\beta$,[PF$_6$]$^{-}$ in CD$_3$OD. 600 MHz, 298 K.
Fig. 15 $^1$H–$^1$H NOESY NMR spectrum of 3$^\text{PF}_6$ in CD$_3$OD, 600 MHz, 298 K.
Fig. 16 $^1$H-$^{13}$C HSQC NMR spectrum of 3+,PF$_6^-$ in CD$_3$OD, 600 MHz, 298 K.
Fig. 17 MALDI-TOF mass spectrum of $3^+,\text{PF}_6^-$.

Fig. 18 Partial MALDI-TOF mass spectrum of $3^+,\text{PF}_6^-$ centered on its isotopic pattern (red/solid curve) and simulated isotopic pattern for a formula corresponding to $3^+$ (black/dotted curve).
Fig. 19 UV-Visible spectra of 1 in pyridine (black/solid line), 2',PF$_6^-$ in pyridine (red/dashed line) and 3',PF$_6^-$ in CH$_2$Cl$_2$ (blue/dotted line).

References