

Multiporphyrin coordination arrays based on complexation of magnesium(II) porphyrins with porphyrinylphosphine oxides†

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Di- and triporphyrin arrays consisting of 5,15-diphenylporphyrinatomagnesium(II) (MgDPP) coordinated to free-base and Ni(II) porphyrinyl mono- and bis-phosphine oxides, as well as the self-coordinating diphenyl[10,20-diphenylporphyrinatomagnesium(II)-5-yl]phosphine oxide [MgDPP(Ph₂PO)], were synthesised in excellent yields and characterised by various spectroscopic techniques. Phosphine oxides stabilise Mg(II) coordination to porphyrins and the resulting complexes have convenient solubilities, while the Ni(II) complexes exhibit interesting intramolecular fluorescence quenching behaviour. The binding constant of MgDPP to triphenylphosphine oxide ($5.3 \pm 0.1 \times 10^5 \text{ M}^{-1}$) and the very high self-association constant of [MgDPP(Ph₂PO)] ($5.5 \pm 0.5 \times 10^8 \text{ M}^{-1}$) demonstrate the strong affinity of phosphine oxides towards Mg(II) porphyrins. These complexes are the first strongly bound synthetic Mg(II) multiporphyrin complexes and could potentially mimic the “special pair” in the photosynthetic reaction centre.

Introduction

The formation of multiporphyrin arrays has received considerable attention in recent years, not only due to their critical role in the biological light harvesting process of plants and bacteria, but also because of their potential applications in diverse fields such as molecular wires, non-linear optics and photodynamic therapy.¹ As the majority of metals form equatorial complexes with porphyrins, the study of multiporphyrinic systems obtained through the coordination of this central metal ion with an axial ligand attached to a second porphyrinic macrocycle is a very fast growing area of research.² Such molecules have been developed in recent years to mimic the primary electron donor in photosynthetic reaction centres of bacteria.³ This so-called “special pair” consists of two bacteriochlorophylls, which are noncovalently held apart by 3.2 Å and the central metal atom of these porphyrinic macrocycles is Mg(II).⁴

Magnesium porphyrins have long singlet excited state lifetimes, large fluorescence quantum yields and low oxidation potentials.⁵ However most examples of Mg(II) porphyrins incorporated in self-assembled synthetic multiporphyrin systems are concerned with aggregation behaviour of chlorophyll based dimers which are weakly bound to each other.⁶ Recently some theoretical studies of chlorophyll and its aggregation behaviour have also been reported.⁷ There is one example of a synthetic Mg(II) porphyrin dimer in which an imidazole moiety attached to the porphyrin periphery coordinates to the central Mg(II) centre of a neighbouring macrocycle.⁸ Although the authors did not

report any self-association constant for their dimer, it has been established that N-ligands bind very weakly to Mg(II) porphyrins.⁹ The vast majority of self-complexed metalloporphyrin oligomers involve zinc porphyrins, which have a shorter singlet state excited lifetime than their Mg(II) analogues but are synthetically more accessible.^{1a,2,3,10} Until the mid 1990's magnesium(II) porphyrins have been avoided by synthetic chemists due to the problems associated with the insertion of Mg(II) into the inner core of porphyrinic macrocycles. This obstacle has been removed by the heterogeneous and homogeneous Mg(II) insertion methods of Lindsey and co-workers.^{5,11} However, suitable ligands that show a high affinity towards magnesium porphyrins have not been reported so far. There is only one example of triphenylphosphine oxide as a ligand for chlorophyll a and b.¹² This IR spectroscopic study showed that the phosphine oxide forms a strong complex with the chlorophylls and thus breaks the self-aggregation that depends on the keto group of a neighbouring chlorophyll molecule.⁴ Triphenylphosphine oxide has also been used as a ligand for other metalloporphyrins such as Os(II),¹³ Cr(III),¹⁴ Fe(III),¹⁵ Ru(IV)¹⁶ and Sn(IV)¹⁷ porphyrins.

During our systematic studies of the formation and reactions of η¹-palladioporphyryns,¹⁸ we recently reported the synthesis and characterisation of *meso*-porphyrinylphosphine oxides.¹⁹ These pentavalent phosphorus compounds can be isolated in high yields under mild reaction conditions either from the direct reaction of η¹-palladioporphyryns or from a Pd(0) catalysed reaction of haloporphyryns with diphenylphosphine oxide. Our results showed a weak affinity of the phosphorus-oxo ligand towards Zn(II) porphyrins. A Japanese group prepared similar phosphine oxides and quantified the self-coordination of the Zn(II) species.²⁰ Both reports^{19b,20} show only a weak reciprocal interaction between the phosphine oxide ligand and the neighbouring zinc(II) porphyrin, which is not surprising due to the low binding strength of oxo ligands towards zinc(II). In earlier reports it has been well established that zinc(II) porphyrins show a larger affinity towards

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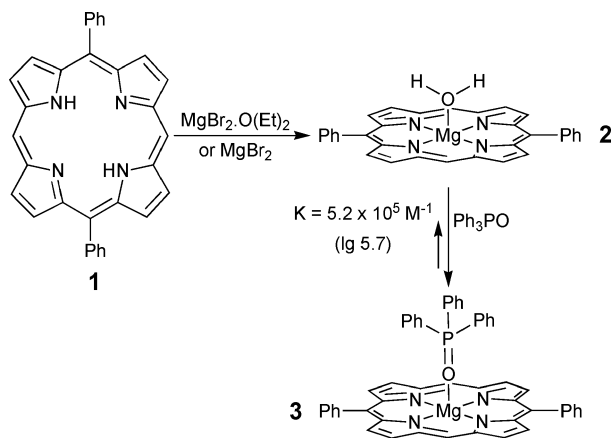
N-donor ligands than hydroxy or carbonyl ligands.^{2a} Magnesium porphyrins on the other hand show very weak coordination capabilities towards nitrogen bases.

We report here the formation and characterisation of di- and triporphyrin complexes consisting of porphyrinylphosphine oxides and magnesium(II) porphyrins. We have studied these complexes with various techniques, namely ¹H and ³¹P NMR, UV-visible and fluorescence spectroscopies and cyclic voltammetry. The phosphorus-oxo ligands indeed show a strong affinity towards the Mg(II) porphyrins. These novel complexes have potential as synthetic mimics for the “special pair” in photosynthetic reaction centres.

Results and discussion

Synthesis and NMR characterisation

Due to the known low solubility of Mg(II) porphyrins in organic solvents, we decided at first to utilise 5,15-bis(3,5-di-*t*-butylphenyl)porphyrin (H₂DAP) as substrate for the formation of a Mg(II) porphyrin. To our surprise we discovered that the resulting 5,15-bis(3,5-di-*t*-butylphenyl)porphyrinatomagnesium(II) (MgDAP) has a very low solubility in organic solvents (<10⁻⁵ M). 5,5-Diphenylporphyrinatomagnesium(II) (MgDPP, **2**) on the other hand can be dissolved in concentrations of up to 10⁻⁴ M in CDCl₃, CH₂Cl₂ and toluene without the aid of sonication, which is not the case for MgDAP. Porphyrin **2** can be isolated in almost quantitative yield from the reaction of 5,15-diphenylporphyrin (H₂DPP) **1** with either MgBr₂·O(Et)₂ (homogeneous method) or with freshly prepared anhydrous MgBr₂ (heterogeneous method) as shown in Scheme 1.^{5,11} The advantage of the heterogeneous method in this case is the absence of any axial ligand except water in **2**.



Scheme 1 Formation of MgDPP **2** and MgDPP-PPh₃O complex **3**.

Next we isolated the Ph₃PO complex **3** of Mg(II) porphyrin **2** as shown in Scheme 1. During NMR studies, no six-coordinate Mg(II) species could be observed as the peak representing water coordinated to Mg(II) (~0.1 ppm) disappears and free phosphine oxide can always be observed in the spectra upon addition of excess Ph₃PO. Water displacement by Ph₃PO was measured by UV-visible titration as described by Connors.²¹ The titration spectra (Fig. 1) show an isosbestic point at 415 nm which indicates the formation of a single complex. A Job's plot confirms the

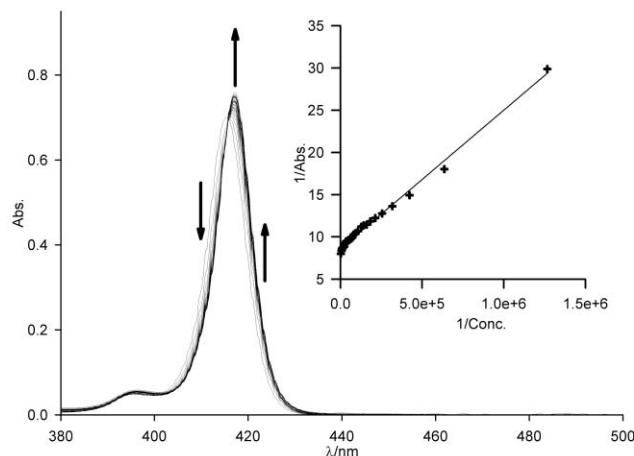
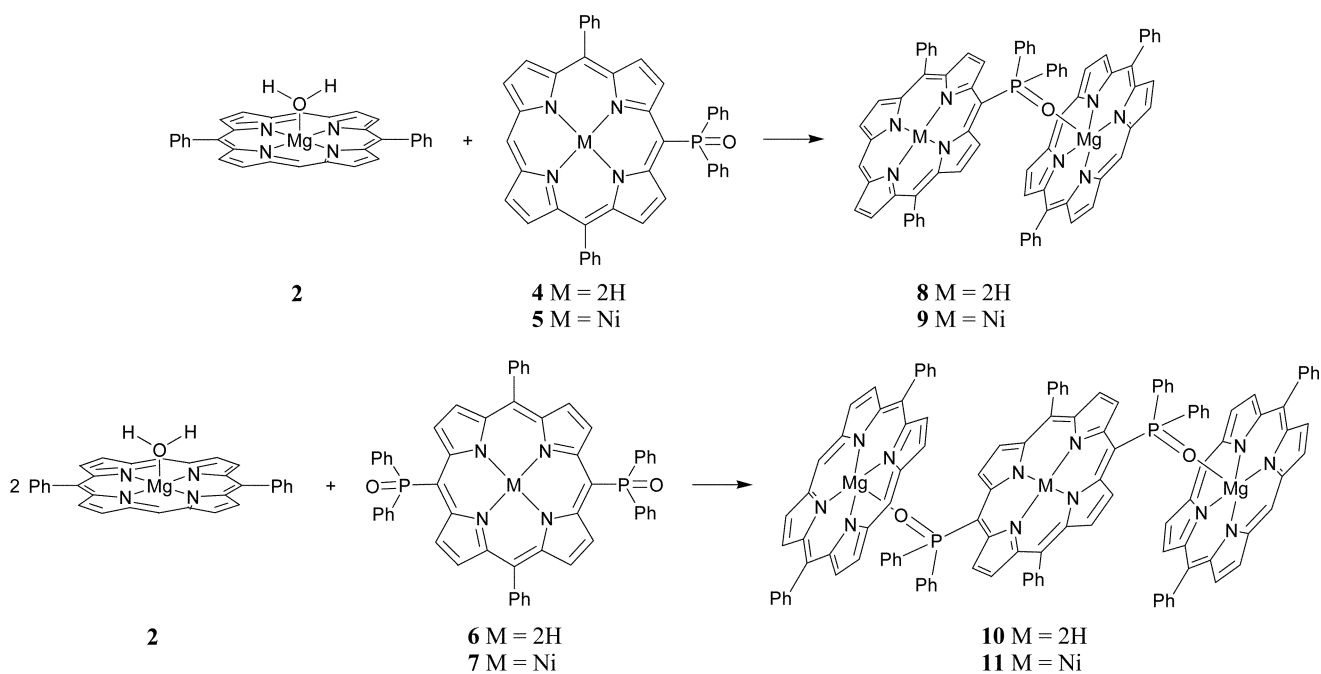


Fig. 1 UV-visible titration of MgDPP **2** (1.4×10^{-6} M) in toluene at 25 °C upon successive addition of Ph₃PO (7.9×10^{-7} – 1.5×10^{-4} M). Inset: Benesi–Hildebrand plot (solid line: fitted curve).²¹

formation of a 1 : 1 complex between Ph₃PO and porphyrin **2**.²¹ The displacement constant of $5.3 \pm 0.1 \times 10^5 \text{ M}^{-1}$ calculated by the Benesi–Hildebrand method is two orders of magnitude larger than any other Mg(II) porphyrin–ligand binding constant reported thus far.²²

Encouraged by this result, we then isolated di- and triporphyrin Mg(II) complexes with free-base and Ni(II) porphyrinyl phosphine oxides as ligands (Scheme 2). Complexes **8–11** were isolated in a similar fashion. Porphyrin **2** and the appropriate ligand (**4–7**) were first dissolved in CDCl₃ in a 1 : 1 stoichiometry and the ¹H NMR spectra of the complexes were recorded. Afterwards the solvent was removed and the products recrystallised from toluene–pentane. The complexes all form in quantitative yield and losses are due only to the recrystallisation process. We discovered that these complexes are remarkably robust. The solid samples were subjected to high resolution ESI, LDI or LSI mass spectrometry and molecular ions were observed for the respective complexes. The solubility of the complexes **8–11** also drastically increases in comparison to uncoordinated **2**, as concentrations of 10⁻³ M in CDCl₃, CH₂Cl₂ and toluene can be easily achieved. The phosphine oxide ligands also stabilise the basal coordination of the Mg(II) centre to DPP. While partial demetalation of **2** in CDCl₃ was observed after only 8 h, complexes **8–11** are stable in CDCl₃ for months. All products were analysed by various 1D and 2D ¹H NMR techniques (see ESI†) as well as ³¹P NMR, and similar features could be observed for all complexes. Again no peaks representing water coordinated to the Mg(II) fragment were observed. If an excess of ligand **4–7** is present, three different kinds of porphyrinyl units can be discerned, namely excess uncomplexed ligand **4–7** and both the metalloporphyrin **2** and the phosphine oxide components of the di- or tri-porphyrin complexes **8–11** in the appropriate integral ratios. Likewise when excess metalloporphyrin **2** is present, the peaks representing both complexed and uncomplexed MgDPP are apparent. This indicates that exchange between complexed and uncomplexed species is slow enough to enable the observation of sharp spectra. Exchange between complexed and uncomplexed species was only observed by elevated temperature experiments.



Scheme 2 Formation of di-porphyrin complexes **8**, **9** (above) and tri-porphyrin complexes **10**, **11** (below).

Fig. 2 shows the ^1H NMR spectra of complexes **8** (left) and **11** (right) in CDCl_3 at 23°C . The arrows indicate some of the differences between the spectra of the complexes (**8**, **11**) and uncomplexed porphyrins **2**, **4** and **7**. One can readily appreciate the large effect the two macrocycles have on each other upon complexation. The most evident features are the differences in chemical shifts of the peaks representing the *o*-Ph protons on the phosphorus (H^3 : shifted upfield by more than 2.5 ppm) and the peaks representing the β -protons next to the P–C bond (H^2 : shifted upfield by more than 3 ppm). These results indicate that the two porphyrin macrocycles are in close proximity, as the influence of the respective ring currents can be observed in a large upfield shift of the ^1H NMR peaks. Even the peak associated with the *meso*-proton on the metalloporphyrin (H^1) and the inner nitrogen protons of the free-base phosphine oxide (H^4) are shifted upfield.

The ^{31}P NMR spectra of the complexes also show peaks in the expected region (**3**: 25.5 ppm, **8–11**: 26.4–31.5 ppm) and these differ only slightly from the values of the uncomplexed ligands (Ph_3PO : 29.6 ppm; **4–7**: 29.2–34.2 ppm).^{19b} This stems from the fact that the P–O–Mg coordination leads to a downfield shift while the ring current from an adjacent porphyrin causes an upfield shift of similar magnitude.

We also isolated Mg(II) phosphine oxide **12** as shown in Scheme 3 and in this case only the heterogeneous Mg(II) insertion method was successful. The complex adheres very strongly to glassware and accumulates between the organic and the water phases during the work up. Nevertheless we could isolate **12** in a satisfactory yield of 75%. Due to its low solubility (10^{-5} M) in organic solvents (CDCl_3 , CH_2Cl_2 and toluene) the ^{31}P NMR and the ^1H NOESY NMR of porphyrin **12** were of poor quality.

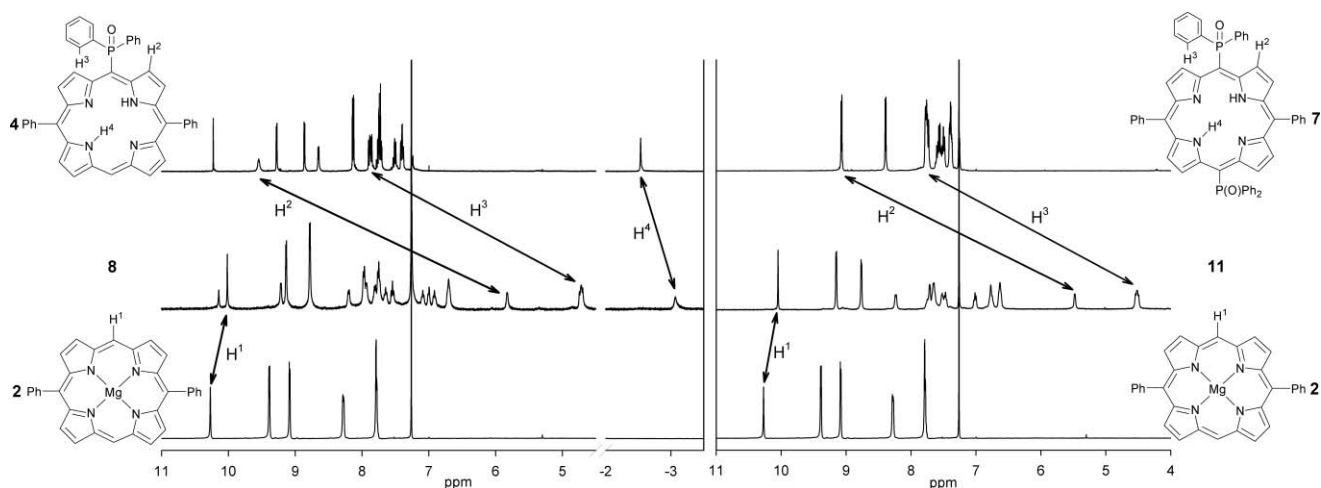
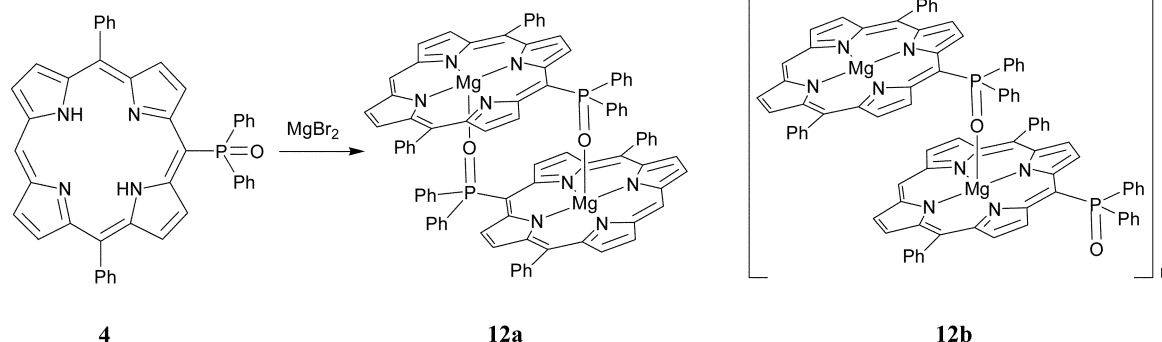


Fig. 2 (Left) ^1H NMR spectra of MgDPP **2** (bottom), complex **8** (middle) and ligand **4** (top); (right) ^1H NMR spectra of MgDPP **2** (bottom), complex **11** (middle) and ligand **7** (top).



Scheme 3 Formation of Mg(II) phosphine oxide **12** and possible polymeric form.

The UV-visible and fluorescence spectra (discussed below) show that the complex exists in its dimeric form **12a** in solution. The previously reported single crystal X-ray structures of the polymeric Zn(II) phosphine oxides^{19b,20} suggest that a polymeric structure **12b** is likely for complex **12** in the solid state. The ¹H NMR spectrum is similar to the spectra already discussed above. Even the addition of large amounts of coordinating solvents (MeOH, pyridine) does not improve the solubility, indicating a very stable self-coordinated complex.

Electronic absorption spectra, emission spectra and redox properties

The UV-visible spectra of the complexes (**3**, **8–11**) were recorded in toluene at 25 °C at various concentrations (1×10^{-4} to 5×10^{-6} M) in order to gain some insight into the complexation properties in solution. High concentrations (10^{-4} – 10^{-5} M) were measured in 1 mm pathlength cells while lower concentrations were recorded in a 10 mm cell. As one example, Fig. 3 shows the spectral changes of complex **8**. High concentrations show the same spectral profiles, while at 10^{-6} M a small deviation of the spectral properties can be observed. At these low concentrations the complexes show some dissociation into their monomeric forms. A splitting of the Soret bands due to excitonic coupling can be observed for the multi-porphyrin complexes. This feature is most prominent in complex **12**, as in the other cases (**8–11**) the Soret bands of the monomers overlap with those of the complexes. The self-association constant of **12** was measured by UV-visible

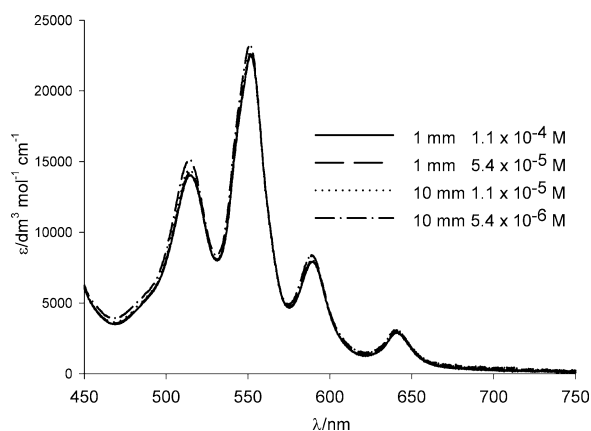


Fig. 3 UV-visible spectra of **8** (1.1×10^{-4} to 5.4×10^{-6} M; 10 mm and 1 mm cells).

displacement titration by successive addition of Ph_3PO , to obtain the data displayed in Fig. 4 that indicate the expected 1 : 2 complex formation.²³ With the reasonable assumption that the binding constants for the complexation of Ph_3PO to MgDPP **2** and MgDPP(Ph_3PO) **12** are the same, the self-association constant was calculated to be $5.5 \pm 0.5 \times 10^8 \text{ M}^{-1}$ (lg 8.7), showing that very little dissociation will occur at 10^{-5} M monomer concentration. The stability and solubility of complexes such as **8–12** in organic solvents are encouraging for further studies of these aggregates.

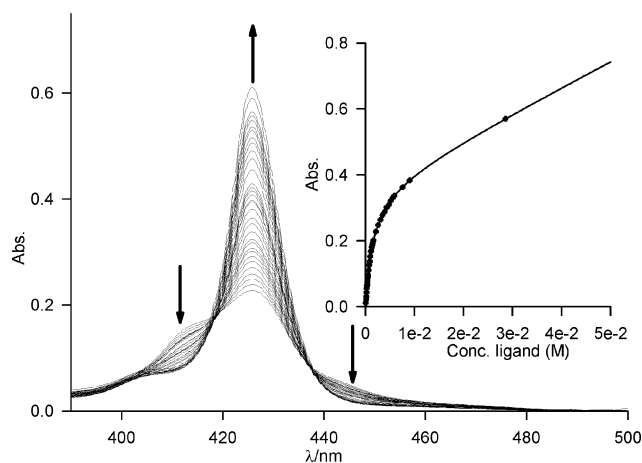


Fig. 4 UV-visible titration of **12** (3.1×10^{-6} M) in toluene at 25 °C upon successive addition of Ph_3PO (5.7×10^{-5} to 2.9×10^{-2} M). Inset: Binding isotherm (solid line: fitted curve for 1 : 2 complex).

The fluorescence spectra of the complexes **8–12** were recorded in toluene at 25 °C (10^{-5} M, except for **12**: 10^{-6} M). We excited at 485 nm (minimum between Soret and Q-bands) in order to avoid any effects due to internal absorption. The spectrum of **9** was compared to the spectra of free MgDPP **2** and a solution containing **2** and 5,15-diphenylporphyrinatonicel(II) (NiDPP, **13**). Nickel(II) porphyrins are non-fluorescent due to radiationless decay pathways associated with the unfilled d orbitals.²⁴ As shown in Fig. 5, the fluorescence profiles for MgDPP **2** and a mixture of **2** with NiDPP **13** differ only slightly. Therefore no significant intermolecular fluorescence quenching due to the presence of the Ni(II) porphyrin can be detected. However, the spectrum of complex **9** shows a large quenching ($\sim 80\%$) due to intramolecular energy transfer between the Ni(II) and Mg(II) macrocycles, which indicates effective electronic communication in the excited state. The fluorescence for complex **11** is less efficiently quenched, as

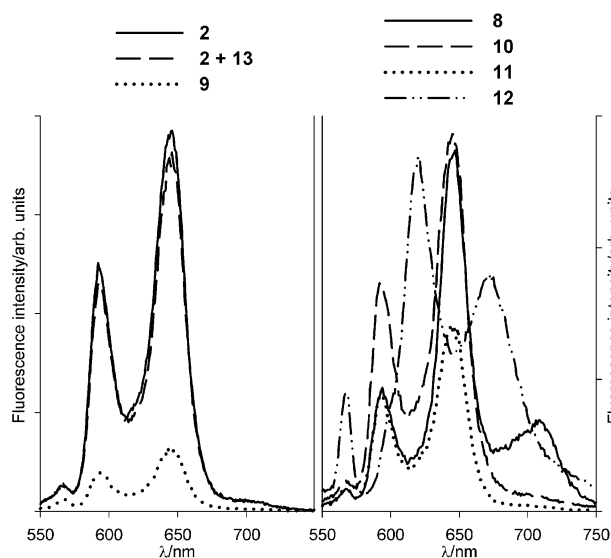


Fig. 5 Fluorescence spectra of **2**, **2 + 13** and **9** (left); **8**, **10–12** (right) excited at 485 nm in toluene at 25 °C and normalised to 10^{-5} M (except for **12**: measured at 10^{-6} M on a more sensitive detector setting).

there is only one Ni(II) for two Mg(II) centres present. Due to the low solubility of dimer **12**, the spectrum for this complex was recorded at 10^{-6} M. Both maxima for **12** are red-shifted by ~ 25 nm compared with the other species. This indicates a more rigid face-to-face geometry in comparison to the other complexes.²⁵ These preliminary empirical studies indicate that measurements of excited state lifetimes and intramolecular energy transfer rates are warranted in the future.

The oxidation properties of MgDPP **2** and complexes **3**, **8** and **10** were briefly studied by cyclic and square wave voltammetry and compared to values for H₂DPP **1** and free-base ligands **4** and **6**. The measurements were conducted in CH₂Cl₂ (10^{-3} M) containing 0.1 M Bu₄NPF₆ at a Pt working electrode (*vs* Ag/Ag⁺; ferrocene/ferrocinium at +0.55 V). The values for the first oxidation potential (Table 1) show, as expected, the electron donating properties of Mg(II) in **2** (+0.78 V) in comparison to free-base porphyrin **1** (+1.16 V). The first oxidation potentials of the complexes show only a slight further cathodic shift in comparison to MgDPP **2**, which is largest for complex **3** (+0.73 V). The second oxidation wave of complexes **8** and **10** comprises overlapped waves due to the second oxidation of **2** and the first oxidation of the free-base phosphine oxide ligands **4** and **6**. Relative areas from square wave measurements support this being an overall two-electron process.

Table 1 Oxidation potentials for **1–4**, **6**, **8** and **10** (10^{-3} M) measured in CH₂Cl₂ containing 0.1 M Bu₄NPF₆

Compound	Ox(1)/V	Ox(2)/V
1 ^{18c}	+1.16	
2	+0.78	1.12
3	+0.73	1.20
4 ^{19b}	+1.24	
6 ^{19b}	+1.33	
8	+0.76	+1.2 ^a
10	+0.77	+1.2 ^a

^a Ox(2) of Mg(II) and Ox(1) of free-base part of complex overlap.

Conclusions

We have prepared several representatives of a new class of multiporphyrin complexes containing Mg(II) porphyrins and our recently reported porphyrinylphosphine oxides.¹⁹ These compounds can be obtained in excellent yield by complexation in organic solvents. Inter-porphyrin electronic interaction can be observed with various spectroscopic techniques and the complexes are remarkably robust in solution. The large self-association constant ($5.5 \pm 0.5 \times 10^8$ M⁻¹) of complex **12** is a very good indication of this behaviour. In comparison the self-association constant of the Zn(II) dimer reported by the Japanese group is two orders of magnitude lower (5.9×10^{-6} M⁻¹).²⁰ The presence of Ni(II) in the phosphine oxide ligands leads to intramolecular fluorescence quenching of the complexes. Although no X-ray quality single crystal for any of the complexes has been obtained so far, the comparison with zinc(II) porphyrinylphosphine oxide polymers^{19b,20} leads us to expect very interesting porphyrin–porphyrin interactions in the solid state. We have shown that Mg(II) porphyrins have a very high affinity towards oxo-ligands, especially phosphine oxides, and our complexes are the first strongly bound synthetic Mg(II) porphyrin analogues of the “special pair” of the photosynthetic reaction centre.

Experimental

General remarks

Chemical reagents were of laboratory reagent (LR) or analytical reagent (AR) grade, received from Sigma-Aldrich and used without further purification. Toluene was stored over sodium wire and CH₂Cl₂ was stored over anhydrous sodium carbonate. MgBr₂,²⁶ H₂DPP²⁷ and phosphine oxides **4–7**^{19b} were synthesised according to literature procedures. Recrystallisation from two solvents was accomplished by dissolving the product in a minimum amount of the first solvent (or solvent mixture) and carefully layering the solution with a tenfold excess of the solvent in which the product is less soluble. Analytical TLC was performed using aluminium backed Merck silica gel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 400 MHz instrument and *J* values are given in Hz. Quantitative UV-visible spectra were recorded on a Cary 3 spectrometer in toluene solutions. UV-visible titrations were performed by adding aliquots of a solution containing excess Ph₃PO and the Mg(II) porphyrin to a solution of the same concentration containing only the Mg(II) porphyrin. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a standard multicell Peltier thermostatted sample holder in toluene solutions. Accurate mass electrospray ionisation (ESI) mass spectra were recorded at Monash University, Australia on a Bruker BioApex 47e FTMS fitted with an Analytical Electrospray source. Dichloromethane was used as a solvent and the samples were diluted either with methanol or dichloromethane–methanol. The samples were introduced into the source by direct infusion (syringe pump) at 60 μL h⁻¹ with a capillary voltage of 80 V. Sodium iodide clusters were used as internal standard for mass calibration. Laser desorption/ionization (LDI) MS analysis was performed at Monash University, Australia with an Applied Biosystems Voyager-DE STR BioSpectrometry Workstation. The instrument

was operated in positive polarity in reflecton mode. Samples were spotted on a stainless steel sample plate and allowed to air dry. Data from 500 laser shots (337 nm nitrogen laser) were collected, signal averaged, and processed with the instrument manufacturer's Data Explorer software. Liquid secondary ion (LSI) MS measurements were collected at the University of Tasmania, Australia using *m*-nitrobenzyl alcohol as proton donor and CsI/TEG mixture for external reference on a Kratos Concept ISQ double focussing Magnetic/Electrostatic Mass Spectrometer. Isotopic modelling was performed by MassLynx V3.5 Software by Micromass Limited.

5,15-Diphenylporphyrinatomagnesium(II) 2

Homogeneous method. H₂DPP **1** (50 mg, 0.11 mmol) was dried under high vacuum. After the addition of freshly distilled CH₂Cl₂ (10 cm³) and triethylamine (TEA) (0.3 cm³, 2.2 mmol), freshly ground MgBr₂·OEt₂ (280 mg, 1.1 mmol) was added and the mixture was stirred for 2 h. The reaction was monitored by TLC (CH₂Cl₂–TEA = 200 : 1) and a new more polar spot could be observed. The reaction mixture was diluted with 25 cm³ of CH₂Cl₂, washed with 2 × 25 cm³ NaHCO₃, 5 × 50 cm³ water, dried over sodium sulfate, filtered and the residue was recrystallised from CH₂Cl₂–TEA–hexane to obtain 52 mg (0.11 mmol, 99%) of a bright red crystalline powder.

Heterogeneous method. The desired Mg(II) porphyrin can also be obtained under the same reaction conditions and with the same reactants as above by using freshly prepared MgBr₂ (203 mg, 1.1 mmol) instead of MgBr₂·OEt₂. δ_H (400 MHz, CDCl₃, CHCl₃) 10.24 (2H, s, *meso*-H), 9.35 (4H, br d, β-H), 9.05 (4H, br d, β-H), 8.29–8.21 (4H, br, *o*-H 5,15-phenyl), 7.79–7.77 (6H, m, *m*, *p*-H 5,15-phenyl), 0.05 (br s, H₂O coordinated to Mg, variable according to amount of water in solvent); UV/Vis (toluene) λ_{max}/nm 416 (ε/10³ dm³ mol⁻¹ cm⁻¹ 336), 514 (2.2), 551 (19), 588 (3.1); *m/z* (High-resolution ESI) 507.1430 (C₃₂H₂₀MgN₄ + Na⁺ requires 507.1436).

5,15-Diphenylporphyrinatomagnesium(II)–triphenylphosphine oxide complex 3

Mg(II)DPP **2** (15 mg, 0.030 mmol) and triphenylphosphine oxide (8 mg, 0.030 mmol) were dissolved in 5 cm³ of CDCl₃ and the ¹H NMR spectrum of the mixture was recorded. The solvent was removed under vacuum and the complex was recrystallised from toluene–pentane to obtain 22 mg (0.029 mmol, 97%) of a purple crystalline powder. The ¹H NMR spectrum of the redissolved solid after recrystallisation agreed with the one recorded of the initial solution. δ_H (400 MHz, CDCl₃, CHCl₃) 10.13 (2H, s, *meso*-H), 9.28 (4H, d, ³*J* 4.0, β-H), 8.98 (4H, d, ³*J* 4.1, β-H), 8.35–8.30 (2H, br, *o*-H 5,15 Ph), 7.93 (2H, br d, ³*J* 6.4, *o*-H 5,15 Ph), 7.78–7.72 (4H, br, *m*, *p*-H 5,15 Ph), 7.70–7.66 (2H, br, *m*-H 5,15 Ph), 7.06 (2H, t, ³*J* 6.3, *p*-H PPh₃), 6.77–6.70 (4H, br, *m*-H PPh₃), 4.65–4.60 (4H, m, *o*-H PPh₃); δ_P (162 MHz, CDCl₃, 85% H₃PO₄ in H₂O) 25.5; UV/Vis (toluene) λ_{max}/nm 416 (ε/10³ dm³ mol⁻¹ cm⁻¹ 524), 552 (19), 589 (3.6); *m/z* (High-resolution ESI) 785.2277 (C₅₀H₃₅MgN₄OP + Na⁺ requires 785.2297).

Free-base di-porphyrin complex 8

Magnesium porphyrin **2** (10 mg, 0.020 mmol) and ligand **4** (13 mg, 0.020 mmol) were dissolved in 7 cm³ of CDCl₃ and the ¹H NMR spectrum of the mixture was recorded. The solvent was removed under vacuum and the complex was recrystallised from toluene–pentane to obtain 22 mg (0.019 mmol, 96%) of a purple crystalline powder. The ¹H NMR spectrum of the redissolved solid after recrystallisation agreed with the one recorded of the initial solution. δ_H (400 MHz, CDCl₃, CHCl₃) 10.15 (1H, s, *meso*-H P=O), 10.02 (2H, s, *meso*-H Mg), 9.22 (2H, d, ³*J* 4.4, β-H P=O), 9.14 (4H, d, ³*J* 4.3, β-H Mg), 8.78 (6H, d, ³*J* 4.2, β-H P=O, β-H Mg), 8.20 (2H, br d, ³*J* 6.8, *o*-H 5,15 Ph Mg), 7.97 (4H, d, ³*J* 6.4, *m*-H 10,20 Ph P=O), 7.93 (2H, d, ³*J* 4.4, β-H P=O), 7.80 (2H, d, ³*J* 6.4, *p*-H 10,20 Ph P=O), 7.77–7.73 (4H, m, *o*-H 10,20 Ph P=O), 7.65 (2H, t, ³*J* 6.8, *m*-H 5,15 Ph Mg), 7.54 (2H, t, ³*J* 7.3, *p*-H 5,15 Ph Mg), 7.09 (2H, t, ³*J* 6.4, *p*-H PPh₂), 7.01–6.99 (2H, br, *o*-H 5,15 Ph Mg), 6.91 (2H, t, ³*J* 6.3, *m*-H 5,15 Ph Mg), 6.74–6.72 (4H, br, *m*-H PPh₂), 5.84–5.82 (2H, br, β-H P=O), 4.75–4.70 (4H, m, *o*-H PPh₂), –3.07 (2H, br, NH); δ_P (162 MHz, CDCl₃, 85% H₃PO₄ in H₂O) 31.5; UV/Vis (toluene) λ_{max}/nm 416 (ε/10³ dm³ mol⁻¹ cm⁻¹ 655), 514 (14), 551 (23), 589 (7.8), 640 (2.8); *m/z* (High-resolution ESI) 1147.3825 (C₇₆H₅₁MgN₈OP + H⁺ requires 1147.3852).

Nickel(II) di-porphyrin complex 9

Magnesium porphyrin **2** (12 mg, 0.025 mmol) and ligand **5** (18 mg, 0.025 mmol) were dissolved in 7 cm³ of CDCl₃ and the ¹H NMR spectrum of the mixture was recorded. The solvent was removed under vacuum and the complex was recrystallised from toluene–pentane to obtain 29 mg (0.023 mmol, 92%) of a purple crystalline powder. The ¹H NMR spectrum of the redissolved solid after recrystallisation agreed with the one recorded of the initial solution. δ_H (400 MHz, CDCl₃, CHCl₃) 10.03 (2H, s, *meso*-H Mg), 9.68 (1H, s, *meso*-H P=O), 9.15 (4H, d, ³*J* 4.4, β-H Mg), 9.04 (2H, d, ³*J* 4.5, β-H P=O), 8.77 (4H, d, ³*J* 4.2, β-H Mg), 8.69 (2H, d, ³*J* 4.52, β-H P=O), 8.24 (2H, br d, ³*J* 6.8, *o*-H 5,15 Ph Mg), 7.84 (2H, d, ³*J* 4.6, β-H P=O), 7.78–7.64 (12H, br, *o*, *m*, *p*-H, 10,20 Ph P=O; *m*-H 5,15 Ph Mg), 7.54 (2H, br, *p*-H 5,15 Ph Mg), 7.00–6.97 (2H, m, *p*-H PPh₂), 6.85 (4H, br, *m*, *o*-H 5,15 Ph Mg), 6.63–6.57 (4H, br, *m*-H PPh₂), 5.60–5.55 (2H, br, β-H P=O), 4.53–4.47 (4H, m, *o*-H PPh₂); δ_P (162 MHz, CDCl₃, 85% H₃PO₄ in H₂O) 27.2; UV/Vis (toluene) λ_{max}/nm 416 (ε/10³ dm³ mol⁻¹ cm⁻¹ 501), 552 (24), 586 (10); *m/z* (High-resolution LSI) 1202.2920 (C₇₆H₄₉MgN₈NiOP⁺ requires 1202.2971).

Free-base tri-porphyrin complex 10

Magnesium porphyrin **2** (10 mg, 0.020 mmol) and ligand **6** (9 mg, 0.010 mmol) were dissolved in 7 cm³ of CDCl₃ and the ¹H NMR spectrum of the mixture was recorded. The solvent was removed under vacuum and the complex was recrystallised from toluene–pentane to obtain 18 mg (0.0096 mmol, 95%) of a purple crystalline powder. The ¹H NMR spectrum of the redissolved solid after recrystallisation agreed with the one recorded of the initial solution. δ_H (400 MHz, CDCl₃, CHCl₃) 9.99 (4H, s, *meso*-H Mg), 9.11 (8H, d, ³*J* 4.1, β-H Mg), 8.75 (8H, d, ³*J* 4.1, β-H Mg), 8.19 (4H, br d, ³*J* 6.9, *o*-H 5,15 Ph Mg), 7.78 (4H, d, ³*J* 4.6, β-H P=O), 7.72–7.67 (10H, m, *o*, *m*, *p*-H 10,20 Ph P=O), 7.64 (4H, br t, ³*J* 6.8, *m*-H 5,15 Ph Mg), 7.49 (4H, br t, ³*J* 7.7, *p*-H 5,15 Ph

Mg), 7.13 (4H, br t, 3J 6.4, *p*-H PPh₂), 6.89–6.85 (4H, br, *o*-H 5,15 Ph Mg), 6.80–6.70 (12H, m, *m*-H 5,15 Ph Mg, *m*-H PPh₂), 5.72 (4H, br d, 3J 4.1, β -H P=O), 4.74–4.68 (8H, m, *o*-H PPh₂), –3.16 (2H, br, NH); δ_P (162 MHz, CDCl₃, 85% H₃PO₄ in H₂O) 29.9; UV/Vis (toluene) λ_{\max}/nm 416 ($\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1040), 515 (11), 552 (45), 588 (14), 661 (7.1); *m/z* (High-resolution ESI) 938.2732 (C₁₂₀H₈₀Mg₂N₁₂O₂P₂ + Na₂²⁺ requires 938.2750).

Nickel(II) tri-porphyrin Complex 11

Magnesium porphyrin **2** (10 mg, 0.020 mmol) and ligand **7** (9 mg, 0.010 mmol) were dissolved in 7 cm³ of CDCl₃ and the ¹H NMR spectrum of the mixture was recorded. The solvent was removed under vacuum and the complex was recrystallised from toluene–pentane to obtain 18 mg (0.0095 mmol, 95%) of a purple crystalline powder. The ¹H NMR spectrum of the redissolved solid after recrystallisation agreed with the one recorded of the initial solution. δ_H (400 MHz, CDCl₃, CHCl₃) 10.05 (4H, s, *meso*-H Mg), 9.15 (8H, d, 3J 4.1, β -H Mg), 8.76 (8H, d, 3J 4.0, β -H Mg), 8.24 (4H, br d, 3J 7.0, *o*-H 5,15 Ph Mg), 7.71 (4H, d, 3J 4.6, β -H P=O), 7.69–7.61 (12H, m, *o*, *m*-H 10,20 Ph P=O, *m*-H 5,15 Ph Mg), 7.55–7.45 (6H, m, *p*-H 10,20 Ph P=O, *p*-H 5,15 Ph Mg), 7.01 (4H, br t, 3J 6.7, *p*-H PPh₂), 6.81–6.73 (8H, br, *o*, *m*-H 5,15 Ph Mg), 6.67–6.60 (8H, br, *m*-H PPh₂), 5.50–5.46 (4H, br, β -H P=O), 4.56–4.48 (8H, m, *o*-H PPh₂); δ_P (162 MHz, CDCl₃, 85% H₃PO₄ in H₂O) 26.4; UV/Vis (toluene) λ_{\max}/nm 416 ($\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 856), 515 (8.3), 552 (41), 590 (14) 615 (13); *m/z* (High-resolution ESI) 1886.4851 (C₁₂₀H₇₈Mg₂N₁₂NiO₂P₂⁺ requires 1886.4900).

Bis{diphenyl[10,20-diphenylporphyrinatomagnesium(II)-5-yl]phosphine oxide} **12**

Phosphine oxide **4** (13 mg, 0.020 mmol) was dried under high vacuum. After the addition of freshly distilled CH₂Cl₂ (5 cm³) and TEA (0.220 cm³, 1.6 mmol), freshly ground MgBr₂·OEt₂ (204 mg, 0.790 mmol) was added and the mixture was stirred for 7 h. Due to the polarity and insolubility of the resulting product, the reaction could not be monitored by TLC. The reaction mixture was diluted with 50 cm³ of CH₂Cl₂. Even with the aid of sonication the product could not be fully dissolved. The mixture was washed with 50 cm³ of water in the flask. The majority of the water was decanted off and the remaining solvents were removed under vacuum. The solid was dissolved in 30 cm³ of a toluene–MeOH–TEA (100 : 100 : 1) mixture with the aid of sonication and washed with 5 × 50 cm³ water. The solvents were removed under vacuum and the product was dried thoroughly under high vacuum. After recrystallisation from toluene–MeOH–TEA–pentane, 10 mg (0.015 mmol, 75%) of the desired product was obtained as a purple crystalline powder. δ_H (400 MHz, CDCl₃, CHCl₃) 10.27 (1H, s, *meso*-H), 9.26 (2H, d, 3J 4.2, β -H), 8.68 (2H, d, 3J 4.2, β -H), 8.40–8.36 (2H, br, *m*-H 10,20 Ph), 9.05 (2H, d, 3J 4.1, β -H), 7.74–7.59 (4H, m, *m*, *p*-H 10,20 Ph), 7.55–7.51 (2H, m, *m*-H 10,20 Ph), 7.48–7.43 (2H, br, *o*-H 10,20 Ph), 7.23–7.19 (2H, m, *p*-H PPh₂), 6.86–6.80 (4H, m, *m*-H PPh₂), 6.34 (2H, d, 3J 4.4, β -H), 6.53–6.43 (4H, br, *o*-H PPh₂); UV/Vis (toluene) λ_{\max}/nm 414sh ($\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 54), 426 (74), 568 (7), 595 (5); *m/z* (LDI) 685.2 (C₄₄H₂₉MgN₄PO + H⁺ requires 685.2); dimer *m/z* (LDI) 1369.4 (C₈₈H₃₀Mg₂N₈P₂O₂ + H⁺ requires 1369.4)

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