

Use of Ag(II) as a removable template in porphyrin chemistry: diol cleavage products of [*meso*-tetraphenyl-2,3-*cis*-diolchlorinato]silver(II)

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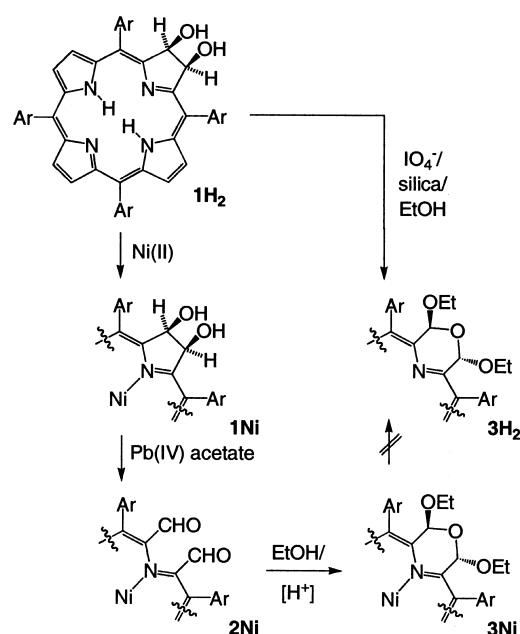
Abstract—The use of Ag^{II} as a removable template in synthetic porphyrin chemistry is described. Mild procedures for the insertion of Ag^{II} into chlorins and the demetallation of the [chlorinato]Ag^{II} complexes are delineated. The UV–vis spectra of the novel [chlorinato]Ag^{II} complexes are discussed. The diol cleavage products of [*meso*-tetraphenyl-2,3-diolchlorinato]silver(II) under a number of conditions are characterized and compared to those resulting from the cleavage of the corresponding free base diol chlorin or its Ni^{II} complex, highlighting the unique templating effect of Ag^{II}. The scopes and limits of electrospray ionization mass spectrometry (ESI-MS) for the analysis of Ag^{II} chlorins is described. The use of Ag^{II} as a templating metal is superior over Ni^{II} or Zn^{II} for the preparation of free base pyrrole-modified porphyrins along metal templated pathways.
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1. Introduction

Porphyrins form complexes with most metals.¹ Some of these metal ions have found use in porphyrin chemistry as protecting groups for the central nitrogens or serve as activating groups. For instance, the nitration, chlorination, and formylation of the β -positions of *meso*-tetraarylporphyrins proceeds smoothly only in the form of their Cu^{II}, Ni^{II}, or Pd^{II} derivatives.² Central metals can also act as directing groups. For example, the OsO₄-mediated dihydroxylation of free base chlorins results specifically in the formation of bacteriochlorin chromophores, while dihydroxylation of the corresponding [chlorinato]Zn^{II} complexes results exclusively in the formation of iso-bacteriochlorins.³ This directing effect is general.⁴ Lastly, central metals can act as templates. For instance, Ni^{II} is known to induce non-planar conformations in inherently planar free base porphyrinic macrocycles and it increases the degree of distortion of non-planar free base porphyrins.⁵

We have demonstrated that Pb^{IV}-induced diol cleavage of chlorin **1**, as its Ni^{II} complex **1Ni**, produces [secochlorinato]Ni^{II} **2Ni** (Scheme 1).⁶ This bisaldehyde can be ring-closed to form the pyrrole-modified metallochlorin-like

chromophore **3Ni**.⁶ [Secochlorinato]Ni^{II} **2Ni** and [morpholinochlorinato]Ni^{II} **3Ni** were shown to possess similar extremely non-planar conformations.^{6,7} On the other hand, the conformation of the corresponding free base **3H₂** proved to be near-planar.⁸ This further supported earlier findings which attributed the non-planarity of chromophores such as **3Ni** and **2Ni** solely to the effect of the small central ion Ni^{II}.⁷



Scheme 1.

Keywords: chlorins; silver chlorin complexes; pyrrole-modified porphyrins; diol oxidation; metal template.

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In fact, the central metal ion pre-organized the ligand in **2Ni** for the facile formation of **3Ni**. Next to this templating effect, Ni^{II} has also a stabilizing effect on the secochlorin. While **2Ni** can be chromatographed, isolated and crystallized, the corresponding free base **2H₂** decomposes rapidly.⁶ Similar stabilizing effects were also reported for β-octaethyl secochlorinato derivatives.⁹

The general disadvantage of Ni^{II} and Cu^{II} porphyrin complexes is, however, that the preparation of the free base chromophores by demetallation requires extremely harsh conditions, such as concentrated sulfuric acid–TFA mixtures.¹⁰ These conditions are often incommensurate with the stability of the porphyrin derivative. This circumstance prevented us from preparing the free base morpholinochlorin **3H₂** by demetallation of **3Ni** without concomitant destruction of the macrocycle (Scheme 1).⁶ Much of the driving force behind contemporary porphyrin chemistry is the search for long wavelength absorbing and fluorescing chromophores suitable for use as imaging agents or photosensitizers in photomedicine.¹¹ In that context, the Ni^{II} or Cu^{II} complexes of porphyrins or chlorins cannot be utilized: Their UV–vis spectra are hypsochromically shifted relative to that of their free bases, they are non-fluorescing, and they do not photosensitize oxygen.

The Zn^{II} complexes of porphyrins and chlorins are often chosen to circumvent the synthetic problems associated with the Ni^{II} or Cu^{II} complexes. The Zn^{II} complexes are readily prepared and require only relatively mild conditions for their demetallation such as 1% TFA or a CHCl₃ solution of the zinc porphyrin or chlorin shaken with 6N HCl.¹² This lability, however, may lead to undesired demetallation in the course of acid-catalyzed reactions, obliterating the templating, directing or stabilizing qualities that the metal ion imparts onto the macrocycle.¹³ Also, Zn^{II} does not have the same stabilization effects as Ni^{II}. For instance, the zinc complex of diol chlorin **1** produces upon diol cleavage a complex mixture of products from which no [secochlorinato]Zn^{II} complex could be isolated.⁷ This lack of stabilization of the Zn^{II} complex compared to the corresponding Ni^{II} complex has precedence.⁹

The inadequacy of the common metal ions Ni^{II}, Cu^{II} and Zn^{II} for the synthesis of free base morpholinochlorin **3H₂** led us to a systematic search for an alternative metal ion. We defined a metal ion to be potentially suitable to serve as a practical and versatile protecting, directing, or templating group if it fulfilled the following criteria: (1) Metal insertion should occur under mild conditions. (2) Demetallation conditions should also be mild, however, they must be selective enough to allow the modification of the porphyrin framework without adventitious demetallation. (3) The metal ion should preferably be divalent and form square planar complexes with porphyrins. This allows for flash chromatographic isolation and purification of the metalloporphyrin without any interference by salt formations, axial ligation or counter ion exchange reactions.¹⁴ (4) Lastly, a diamagnetic metal complex would allow for straightforward NMR-spectroscopic analysis of the complexes.

We identified Ag^{II} as a suitable metal ion for the reversible metallation of porphyrins and chlorins. While Ag^{II} porphy-

rins have been known for some time,¹⁵ we are not aware of Ag^{II} chlorins or the use of Ag^{II} as a removable template in porphyrin chemistry. We will demonstrate the utility of Ag^{II} using the diol cleavage reaction of diol chlorin **1Ag** under a number of conditions. We will contrast the results obtained for **1Ag** with those obtained for **1Ni** and **1Zn**. We will show that diol chlorin **1Ag** undergoes chemistry similar to that of the Ni^{II} complex **1Ni** but with the advantage of the facile removal of the templating metal from the reaction products. We will also demonstrate the unique reactivity Ag^{II} imparts onto diol chlorin **1**. We will report on the synthesis of a novel pyrrole-modified chlorin, formally derived by replacing one pyrrolic building block of a porphyrin with an oxazole moiety. Lastly, we will highlight the utility of electrospray ionization mass spectrometry (ESI-MS) in the analysis of silver porphyrins and chlorins. Thus, we will delineate here the scope and limits of using Ag^{II} as an alternative to Ni^{II}, Cu^{II}, and Zn^{II}.

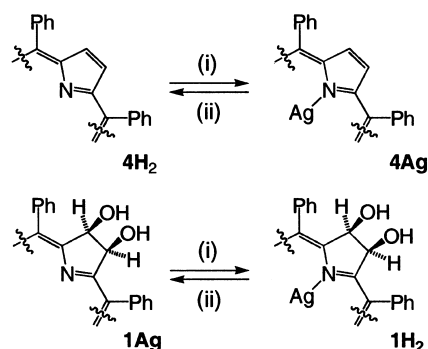
2. Results and discussion

2.1. Insertion of Ag^{II} into porphyrins and chlorins

Reaction of at least 2.2 equiv. Ag^I acetate in warm pyridine inserts the metal quantitatively and within 10 min into *meso*-tetraphenylporphyrin **4H₂** (Scheme 2). The resulting metallated product is identical to that described before.¹⁵ Pyridine is a preferable solvent for this disproportionation reaction (Eq. (1)) compared to the traditionally used hot DMF.



It allows the metallation to take place at lower temperatures and, most importantly, we found this method to be mild enough to metallate diol chlorin **1H₂** (Scheme 2). Using hot DMF conditions we found **1H₂** to be susceptible to oxidation and dehydration.¹⁶ Thus, reaction of red–brown free base **1H₂** with Ag^I in warm pyridine produces within several minutes the forest green product **1Ag**. Filtration of the solution through Celite, followed by removal of the solvent in vacuo, a short silica gel column and crystallization of the product, produces **1Ag** as microcrystalline powder of analytical purity and in near-quantitative yields. We have since found this silver insertion protocol to be applicable to a range of porphyrins, chlorins and corroles.¹⁷



Scheme 2. Reaction conditions: (i) 2.2 equiv. Ag(OAc), pyridine, ~60°C; (ii) THF/20 equiv. aq. HI (0.5N).

2.2. Demetallation of Ag^{II} porphyrins and chlorins

The demetallation of water-soluble Ag^{II} porphyrins using aqueous HNO₃ or of [*meso*-tetraphenylporphyrinato]Ag^{II} (**4Ag**) using electrochemical methods was described before.¹⁸ However, neither method is general nor mild enough to be of wide synthetic use. Utilizing the particular affinity of Ag^I to halogenides, we found that quantitative demetallation of silver porphyrin **4Ag** is affected by treatment with ~20 equiv. of an aq. HI solution in THF (Scheme 2). Alternatively, addition of a concentrated aq. solution of KI to a THF solution of the silver porphyrin or chlorin followed by a trace of conc. aq. HCl is suitable to affect demetallation and precipitation of the corresponding silver halide(s). The demetallation mechanism is likely reduction of Ag^{II} by I⁻, and subsequent acid-induced metal expulsion and precipitation of the insoluble AgX (X=I⁻, Br⁻, Cl⁻). The I₂ formed as the oxidation product from I⁻ is likely bound as I₃⁻ (Eq. (2)).



We have not experienced any undesired iodination or oxidation reactions attributable to the iodine (triiodide) generated.¹⁷ The reaction rates vary with the substrate and its concentration in THF but reaction times of 10 min to 2 h are typically observed (tlc and UV–vis control). Neutralization of the reaction mixtures with Et₃N, followed by filtration through a plug of silica gel is generally sufficient to dry the solution, free it of the precipitates and dissolved salts, and to isolate and purify the free bases.

Experiments using biphasic systems consisting of a CHCl₃ solution of **4Ag** and aq. HCl revealed that 1.5N HCl affects only partial demetallation, even after 48 h, while 3N HCl affects complete demetallation within 24 h. The addition of MeOH or THF to the biphasic systems did not speed the demetallation nor did it allow the use of less concentrated acid solutions. Likely owing to their lower oxidation potentials, the use of aq. HBr or HI allows a decrease in the acid concentration required to affect complete and speedy demetallation, especially when applied in homogeneous systems. Thus, addition of an HBr solution in acetic acid to a CHCl₃ solution of **4Ag** (final HBr conc. 0.25N) affects instantaneous and complete demetallation. Surprising to us, H₂S, under neutral or even weakly acidic conditions (acetic acid), did not cause any demetallation.

Overall we found the use of aq. HI (or KI/HCl) in THF to be the best and most versatile method for the demetallation of Ag^{II} porphyrins. These conditions are also applicable to the demetallation of diol chlorin **1Ag** without any appreciable degradation. The conditions also proved to be suitable for other chlorins, see below. This demonstrates that the lability of the Ag^{II} complexes toward (reducing) acids can be ranked between that of Ni^{II}/Cu^{II} and Zn^{II}.

2.3. Diol cleavage reactions of **1Ag**

Method A. The Pb^{IV}-induced diol cleavage of **1Ni** leads to the formation of the stable secochlorin bisaldehyde **2Ni** (Scheme 1). In contrast, the analogous reaction of green **1Ag**, under anaerobic conditions, rapidly leads to the

formation of a blue–green compound with a high resolution mass spectrum indicating its composition to be C₄₃H₂₈N₄O₂Ag (FAB+, *m/z*=739.1221), i.e. corresponding to the loss of one carbon and two hydrogens from the starting material. No C=O stretch could be detected in its IR spectrum. Its metallochlorin-like UV–vis spectrum is very similar to that of the starting diol chlorin **1Ag** (Fig. 2; for further discussions of the electronic spectra of the Ag^{II} chlorins see Section 2.4). Demetallation allowed the recording of a ¹H NMR spectrum. Six doublets attributable to six non-equivalent β-hydrogens were found. This pattern is characteristic of non-symmetrically β,β′-substituted porphyrins. Further, one doublet centered at 3.62 ppm and one broad signal at 8.00 ppm are present. Shaking of the CDCl₃ solution of **5H₂** with D₂O causes the disappearance of the signal at 8.00 ppm and the collapse of the doublet. We thus assign **5H₂** the novel porpholactol structure shown in Scheme 3.

Significantly, the appearance of the lactol **5Ag** is specific to the use of Ag^{II} as the templating metal as it was never observed in the diol cleavage reactions using **1H₂** or its Ni^{II} or Zn^{II} complexes. Lactol **5H₂** can also be prepared independently by reduction of lactone **6H₂**.¹⁹

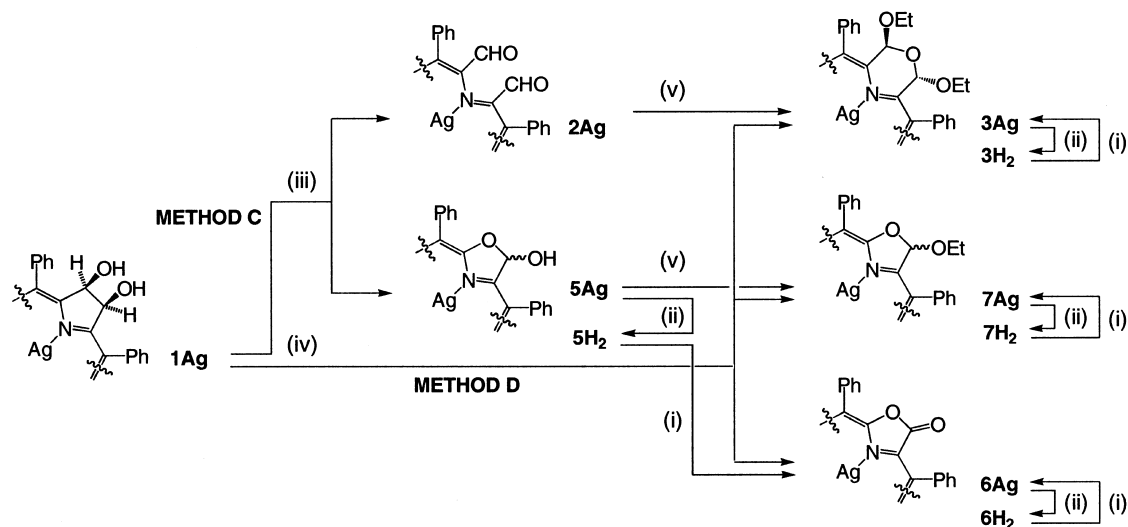
We can only speculate on the mechanism of the simple net reaction (Eq. (3))



The most readily perceivable pathway by which the porphyrin framework could lose a β-carbon is a (radical-induced) decarboxylation reaction. This implies that the diol cleavage reaction is followed by an oxidation and decarboxylation.

Upon reaction of **1Ag** for several hours under aerobic conditions, only one non-polar product is isolated in low yields (~15%) from the ensuing complex mixture. The high resolution mass spectrum of this red product indicates the composition C₄₃H₂₇N₄O₂Ag (FAB+, *m/z*=738.1149), corresponding to the protonated parent ion of porpholactone **6Ag** (Scheme 3). A C=O stretch at 1772 cm⁻¹ can be observed in the IR spectrum of this compound. Demetallation of **6Ag** using the conditions described above produced known porpholactone **6H₂**. Porpholactone was first described as an oxidative degradation product of 2,3-dioxochlorin.²⁰ A number of oxidative methods toward their synthesis have been described since,²¹ notably the MnO₄⁻-induced diol oxidation of **1H₂**.⁸ The ubiquitous appearance of **6** in most ‘failed’ reactions in our laboratories suggests that the porpholactone is a thermodynamic sink in the degradation of porphyrins with activated or cleaved β-positions.

Reaction of **5H₂** with Ag^I acetate under the silver insertion conditions also leads to the formation of **6Ag**. Thus, Ag^I oxidizes the lactol functionality to the corresponding lactone. This reaction highlights one disadvantage of the use of silver as central metal. The mildly oxidizing metallation conditions using Ag^I are not compatible with some functional groups potentially present on the porphyrins or chlorins. Once isolated, though, the lactol is stable. We have not observed any air oxidation of the lactol in



Scheme 3. Reaction conditions: (i) 2.2 equiv. Ag(OAc), pyridine, $\sim 60^\circ\text{C}$; (ii) THF/20 equiv. aq. HI (0.5N); (iii) NaIO₄ heterogenized on silica gel, CH₂Cl₂; (iv) NaIO₄ heterogenized on silica gel, CH₂Cl₂/20% EtOH; (v) CH₂Cl₂/20% EtOH/[H⁺].

solution or in the solid state over the period of several months, as long as **5Ag** was stored in the dark.

Method B. The appearance of the porpholactone **6Ag** in the Pb^{IV}-induced diol cleavage of **1Ag** can be rationalized by oxidation of the intermediate secochlorin bisaldehyde **2Ag**, followed by decarboxylation. We have previously shown that the unstable free base secochlorin **2H₂** can be reacted in situ.⁸ Therefore, we reacted **1Ag** with stoichiometric amounts of Pb^{IV} acetate in a mixture of THF/10% EtOH under anaerobic conditions. This reaction produces one major non-polar green product, **7Ag**, the ethoxy acetal corresponding to hemiacetal **5Ag**. Compound **7Ag** has a UV–vis spectrum slightly bathochromically shifted as compared to that of the starting material (Fig. 2). As expected, **7Ag** can also be formed from **5Ag** by reaction with EtOH in the presence of catalytic amounts of HCl. It is important to note that the central metal Ag^{II} remains in the macrocycle during this reaction. The central metal Zn^{II} would have been, at least partially, lost under these reaction conditions.

Method C. We recently reported the NaIO₄-induced diol cleavage of **1H₂**.⁸ The oxidant was heterogenized on silica gel and suspended in a CHCl₃ solution of the diol. Periodate treatment of **1Ni** smoothly produces secochlorin **2Ni**. In comparison, periodate treatment of **1Ag** produces, under anaerobic conditions, brown secochlorin bisaldehyde **2Ag** and the more polar blue–green **5Ag**, in an approximately 3:1 ratio (**5Ag**:**2Ag**). This ratio is variable, presumably depending on the amount of oxygen adhered to the silica gel. Secochlorin **2Ag** is identified based upon its mass ($m/z=751.1245$, corresponding to C₄₄H₂₈N₄O₂Ag), a $\nu_{\text{C=O}}$ band of 1712 cm⁻¹, and the similarity of its UV–vis spectrum with that of **2Ni** (broad, double-Soret feature at 414 and 464 nm).⁶ Unlike its Ni^{II}-analogue, and similar to the free base bisaldehyde **2H₂**, **2Ag** is very reactive but it can be isolated. Compound **2Ag** cannot be demetallated without decomposition.

Performance of the IO₄⁻ diol cleavage reaction under aerobic conditions leads to the formation of lactone **6Ag**

as the major product. This underscores the catalytic role of the silica gel-based oxidant in these transformations as periodate alone is generally not known to cause the oxidation of lactols to lactones.

Method D. If the NaIO₄-induced diol cleavage reaction of **1Ag** is performed in the presence of EtOH, **7Ag** is formed along with morpholinochlorin **3Ag** and porpholactone **6Ag**. The formation of the lactone can be largely suppressed if the reaction mixture is carefully purged of oxygen. The ratio of **7Ag** to **3Ag** depends on the quantity of oxidant added and the reaction time. The amount of **7Ag** increases with the addition of more oxidant and with longer reaction times. This again underlines the role of the silica gel-based oxidant. Presumably, the formation of the morpholinochlorin is reversible, regenerating the bisaldehyde, which then converts, under the influence of the silica-gel based oxidant, to the oxazole-based species **7Ag**. Demetallation of **3Ag** with HI proceeds without any decomposition and produces the known free base morpholinochlorin **3H₂** in quantitative yields.⁸

We initially developed the Ag^{II}-templated porphyrin chemistry to gain access to long elusive free base morpholinochlorin **3H₂**. Parallel to this route, however, we succeeded in developing a one pot route toward **3H₂** directly from free base **1H₂** (Scheme 1).⁸ As judged by the simplicity and overall yields of this route, it is clearly preferable over the Ag^{II}-route for the synthesis of derivatives of **3H₂** which cannot be formed in the one-pot reaction. For instance, the use of carbohydrates as nucleophiles in the conversion of secochlorin **2** to the corresponding morpholinochlorin **3** may give rise to the formation of carbohydrate-appended chlorin-like chromophores. However, these nucleophiles are incompatible with the reaction conditions, notably the presence of the diol cleavage reagent IO₄⁻. Thus, the isolation of the secochlorin bisaldehyde **2Ag** and subsequent reaction with the carbohydrates, followed by demetallation, is one way to access these intriguing molecules. These reactions and products are currently being studied by our group.

2.4. UV–vis spectroscopic characterization of the novel chromophores

The UV–vis spectra of lactol **5H₂** and diol chlorin **1H₂** are shown in Figure 1. The spectrum of **5H₂** is chlorin-like. Evidently, dihydroxylation of the β,β' -double bond of a porphyrin has the same electronic consequences as its replacement with a lactol moiety. This is not surprising considering that both chromophores carry sp^3 -hybridized atoms at their β -positions. The conformation of both chromophores is also expected to be planar. In comparison, the UV–vis spectrum of porpholactone **6H₂** is porphyrin-like,^{19,20} demonstrating the electronic influence of an sp^2 -hybridized β -atom.

A comparison of the UV–vis spectra of the silver(II) derivatives is shown in Figure 2. The spectra of [diolchlorinato]Ag^{II} **1Ag**, the oxazole-derived complexes **5Ag** and **7Ag**, and the [morpholinochlorinato]Ag^{II} complex **3Ag** are all similar and typical for metallochlorins. In comparison to the hypso-type irregular metalloporphyrin spectrum of **4Ag**, they are bathochromically shifted, the side bands are more intense, and the longest wavelength side bands are the most intense. Unexpected is the relative similarity of the spectra for the morpholinochlorin complex **3Ag** and the diol chlorin **1Ag** (λ_{\max} separation of 5 nm). The observed λ_{\max} separation for the two corresponding free bases **1H₂** and **3H₂** and Ni^{II} complexes **1Ni** and **3Ni** is about 30 nm. This separation is the result of the non-planarity of **3Ni** in comparison to the assumed planar chlorin **1Ni** and the inferred larger conformational flexibility of **3H₂** in comparison to the more rigid **1H₂**.⁸

Inversely, the small separation between the **1Ag** and **3Ag** may indicate that **3Ag** is largely planar. Unlike the porphyrin-like spectrum of free base porpholactone,^{20,21} its Ag^{II} complex has a chlorin-like spectrum, albeit a hypsochromically shifted one as compared to the spectrum of diol chlorin **1Ag**.

2.5. ESI-MS characterization of the [chlorinato]Ag^{II} complexes

The largest practical disadvantage of complexes with the d⁹ metal Ag^{II} is their paramagnetism, disallowing the recording of regular, well resolved NMR spectra.²² We therefore expanded our analytical arsenal to include ESI-MS. While EI, CI, FAB and MALDI-TOEF are well established

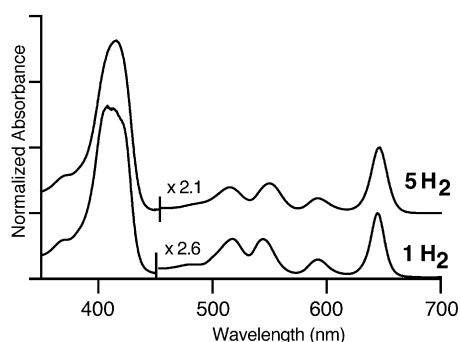


Figure 1. Normalized UV–vis spectra (CH₂Cl₂) of free base chlorins **1H₂** and **5H₂**. Trace above 450 nm is amplified by the factor indicated.

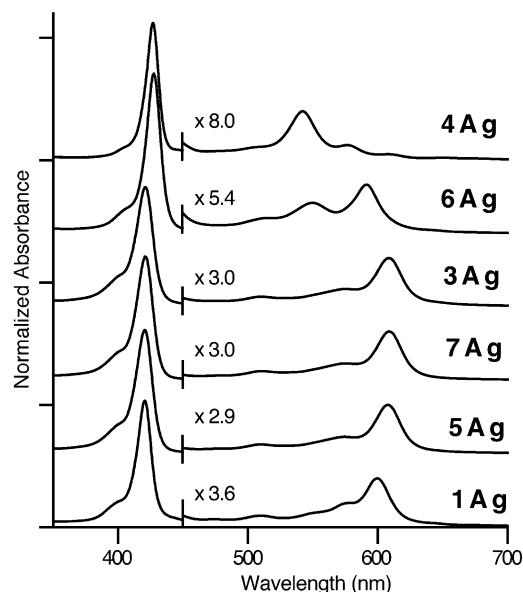


Figure 2. Normalized UV–vis spectra (CH₂Cl₂) of silver(II) chlorins **1Ag**, **3Ag**, **5Ag**, **6Ag**, **7Ag**, and porphyrin **4Ag**. Trace above 450 nm is amplified by the factor indicated.

ionization methods for the analysis of porphyrins,²³ data on the ESI-MS of metalloporphyrins are more rare.^{24,25} However, ESI is potentially a very useful ionization method because it produces a high abundance of molecular ions with little fragmentation, and is therefore also useful in the analysis of mixtures. Typically, ionic molecules or molecules which can be readily protonated are susceptible to investigation by ESI-MS. However, because the electrospray ionization source is a controlled current electrolytic cell, neutral species which can undergo electrochemical ionizations, such as metalloporphyrins, can also be analyzed by ESI-MS.²⁵ This implies that the observed ion abundance is dependent on the ionization potential of the analyte, the needle voltage and polarization, and the chemical stability of the electrochemically generated species. Furthermore, electrochemical ionization mechanisms compete with ionizations through protonation. The latter process is in itself strongly dependent on the solvent and the presence of additional electrolytes. This variability requires the optimization of the ESI-MS conditions for a particular compound class. Within carefully adjusted experimental parameters, however, we found ESI-MS to be a suitable and convenient technique to analyze Ag^{II} chlorins.

The electrochemistry of Ag^{II} porphyrins was studied.²⁶ Ag^{II} porphyrins are susceptible to a reversible one-electron oxidation to produce the corresponding Ag^{III} systems. Figure 3 shows the +ESI-MS spectra of **1Ag** and **7Ag** and their dependence of the cone voltage applied. At 30 V, the positive ion mass spectrum of **1Ag** shows only a peak cluster corresponding to the expected isotope distribution for **1Ag⁺**, i.e. the one-electron-oxidized species, likely the [chlorinato]Ag^{III} species. No signs for extensive ionization through protonation are visible. Upon increase of the cone voltage to 60 V, the isotope pattern for this species erodes and shows evidence for the formation of the protonated species [**1Ag-H**]⁺. Concomitantly, demetallation sets in as evidenced by the appearance of the protonated free base

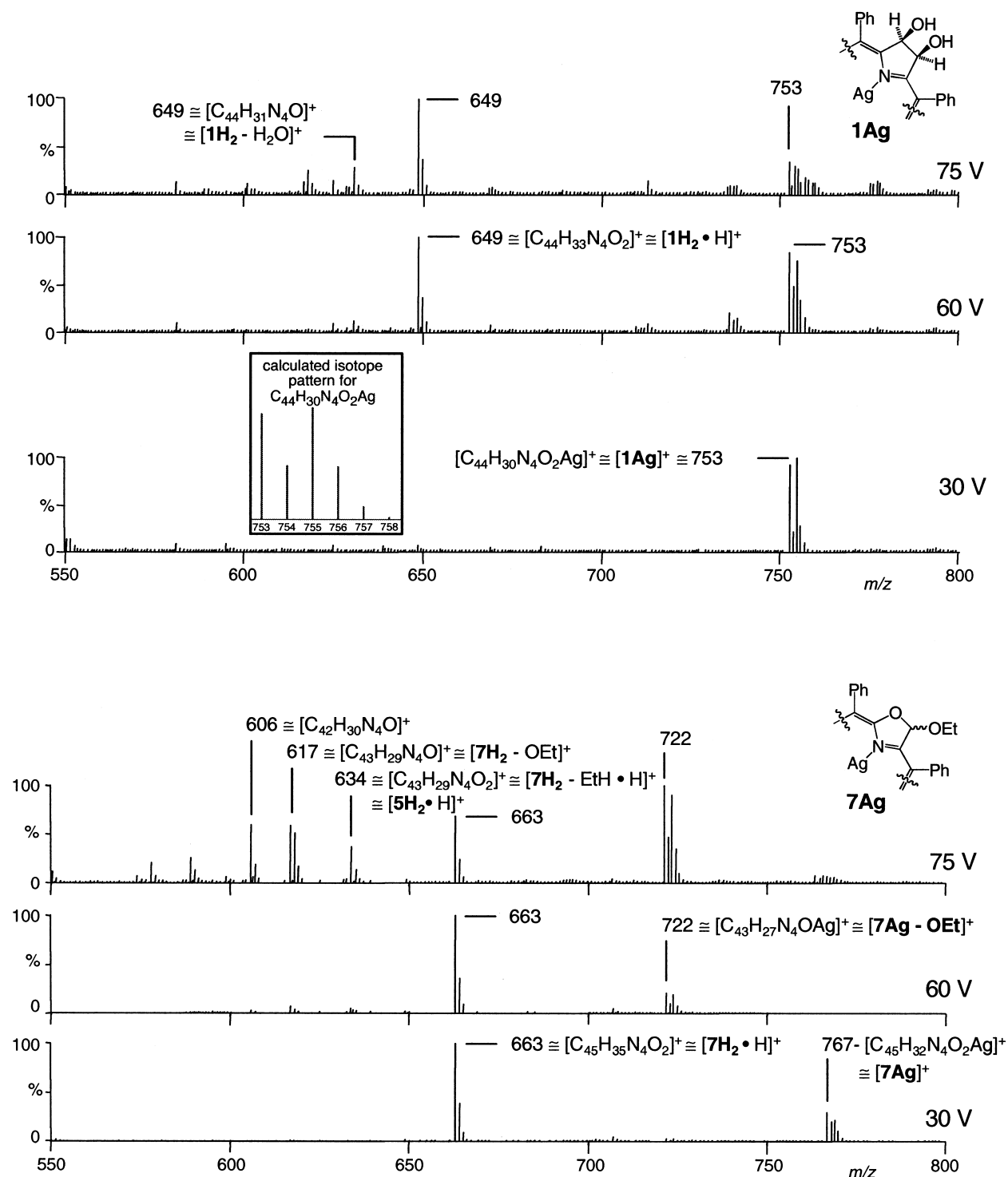


Figure 3. Positive ion detection ESI mass spectra (100% CH₃CN) of **1Ag** (top) and **7Ag** (bottom) recorded at the cone voltages indicated. Insert in top spectrum shows the calculated isotope pattern for the molecular ion species. Injection of a 10 μ L of a \sim 0.2 μ M sample into a continuous stream of CH₃CN.

species $[1H_2 \cdot H]^+$. The addition of 0.1% formic acid to the solvent amplified the degree of protonation and demetallation. Upon further increase of the cone voltage to 75 V, the protonated free base becomes the major ion species, and peaks corresponding to the dehydrated free base appear. The formation of Ag^{III} species and the cone voltage-dependant degree of protonation with concurrent demetallation and fragmentation was observed for all Ag^{II} chlorins investi-

gated. However, the extent of these processes is strongly species-dependant as the spectra for **7Ag** demonstrate. Under the same conditions as used for the analysis of **1Ag**, protonation, demetallation, and fragmentation are much more prevalent than in the case of the diol chlorin. In comparison, the corresponding Ni^{II} complexes form the single electron oxidized species but they are not prone to demetallation.

3. Conclusions

In conclusion, Ag^{II} proves to be a useful template in the synthesis of pyrrole-modified porphyrins. It can be readily inserted and removed from chlorins. The stability of the Ag^{II} complexes can be ranked to lie between that of the Ni^{II} and the Zn^{II} complexes. We expect Ag^{II} to fill a role in synthetic porphyrin chemistry in reactions in which the central metal Zn^{II} is too labile but in which the metal template should be removed from the product under relatively mild conditions. The preparation of the novel oxazole-based chromophores **5** and **7** demonstrated that Ag^{II} has unique templating properties. The major practical disadvantage of Ag^{II}, its paramagnetism, is alleviated by the fact that the metal can be removed quickly under relatively selective conditions. Further, +ESI-MS was shown to be useful in the analysis of Ag^{II} chlorins. Thus, a wider use of Ag(II) as central metal in synthetic porphyrin chemistry can be anticipated.

4. Experimental

4.1. Materials and instrumentation

All solvents and reagents used were reagent grade or better and were used as received. The analytical TLC plates were Silicycle ultra pure silica gel 60 (aluminum backed, 250 μm); preparative TLC plates (500 μm silica gel on glass) and the flash column silica gel (standard grade, 60 Å, 32–63 mm) used were provided by Sorbent Technologies, Atlanta, GA. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX400 and were referenced to residual solvent peaks. UV–vis spectra were recorded on a Cary 50 spectrophotometer, fluorescence spectra on a Cary Eclipse, and IR spectra on a Perkin–Elmer Model 834 FT-IR. ESI mass spectra were recorded on a Micromass Quattro II at the conditions indicated. High-resolution FAB mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, University of Notre-Dame (Bill Boggess). Elemental analyses were provided by Numega Resonance Labs Inc., San Diego, CA.

Diol **1H₂** was prepared by OsO₄-mediated dihydroxylation of **4H₂** as described before.⁶ The silica gel-supported NaIO₄ was prepared according to a procedure adopted from the literature.²⁷ NaIO₄ (2.57 g, 12.0 mmol) was dissolved in hot H₂O (5 mL, ~70°C) in a 25 mL round-bottom flask. To the hot solution was added silica gel (10 g, 40 μ flash grade) under vigorous swirling. The resulting product was dried in an open vessel at 50°C for 12 h, resulting in a free flowing powder.

Some of the reactions are characterized by variable yields, depending on the batch of the heterogeneous oxidant, the level of moisture and/or oxygen present in the reaction flask. The yields provided are average yields from a number of experiments whereby the yields of the single runs did not vary more than about ±10% points.

4.1.1. [*meso*-Tetraphenyl-2,3-dihydroxy-2,3-chlorinato]-silver(II) (1Ag**). General silver(II) insertion procedure.** To a solution of **1H₂** (275 mg, 4.24×10⁻¹ mmol) in pyridine (50 mL) was added Ag(OAc) (155 mg, 2.2 equiv.). The solution was warmed for 10 min to 60–80°C, allowed to

cool to ambient temperature, and evaporated to dryness in vacuo. The residue was triturated with CHCl₃ and filtered through a plug of Celite. The volume of the resulting solution was reduced in vacuo and purified by flash chromatography (CH₂Cl₂). The main green product is crystallized by slow solvent exchange with MeOH. Yield: 90% (320 mg). *R_f* (silica—CH₂Cl₂)=0.16; UV–vis (CH₂Cl₂) λ_{max} (log ε): 420 (5.17), 509 (3.85), 576 (4.14), 600 (4.44) nm; IR (KBr) ν_{max} (rel. intensity): 420 (m), 438 (w), 457 (w), 471 (w), 485 (w), 518 (w), 612 (w), 701 (m), 752 (m), 789 (m), 1005 (s), 1070 (m), 1104 (m), 1298 (w), 1340 (m), 1396 (w), 1419 (w), 1436 (w), 1456 (m), 1473 (w), 1496 (s), 1507 (s), 1521 (s), 1540 (s), 1558 (s), 3420 (w) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): *m/z*=753 (M⁺); HR-MS (+FAB of M⁺, PEG) *m/z* calcd for C₄₄H₃₀N₄O₂Ag: 753.1420, found: 753.1428. Anal. calcd for C₄₄H₃₀N₄O₂Ag (CH₃OH)_{0.5}: C, 69.36; H, 4.19; N, 7.27%; Found: C, 69.52; H, 3.96; N, 7.31%.

4.1.2. [*meso*-Tetraphenyl-2,3-dialdehyde-2,3-secochlorinato]silver(II) (2Ag**). Method C.** Under an atmosphere of N₂, silica gel-heterogenized NaIO₄ was added to a stirring solution of **1Ag** in CH₂Cl₂. The reaction proceeded until the starting material was consumed, at which point the reaction mixture was filtered to remove the silica gel. The volume of the solution was reduced to ~5 mL and loaded onto a flash chromatography column (CH₂Cl₂/33% pet ether 30–60). Compound **2Ag** and **5Ag** were isolated in varying yields and ratios, depending on the reaction time and the relative amount of oxidant used.

Compound 2Ag. Prepared in 20% yield according to Method C using **1Ag** (84 mg, 1.1×10⁻¹ mmol) dissolved in CH₂Cl₂ (15 mL), silica gel-heterogenized NaIO₄ (1.0 g) and a reaction time of <30 min. After chromatography, the solution of **2Ag** is precipitated by solvent exchange with cyclohexane. *R_f* (silica—CH₂Cl₂)=0.67; UV–vis (CH₂Cl₂) λ_{max} (rel. intensity): 395 (sh), 428 (1), 472 (sh), 509 (sh), 617 (sh), 668 (0.21) nm; IR (KBr) ν_{max} (rel. intensity): 702 (m), 754 (w), 791 (w), 931 (w), 1008 (m), 1070 (w), 1263 (w), 1439 (w), 1664 (m), 1712 (s), 3434 (s) cm⁻¹; HR-MS (+FAB of M⁺, PEG) *m/z* calcd for C₄₄H₂₈N₄O₂Ag: 751.1263, found: 751.1245.

4.1.3. [*meso*-Tetraphenyl-2-hydroxy-3-oxa-porphyrinato]silver(II) (5Ag**).** Synthesized in yields up to 50% according to Method C using **1Ag** (84 mg, 1.1×10⁻¹ mmol) dissolved in CH₂Cl₂ (15 mL), silica gel-heterogenized NaIO₄ (0.5 g) and a reaction time of ~2 h. Alternatively, it was prepared in 30% yield according to Method A. The fractions of **5Ag** resulting from the column chromatographic separations following either method were crystallized by slow solvent exchange with cyclohexane to produce a dark-purple powder.

Method A. To a stirring solution of **1Ag** (63 mg, 8.3×10⁻² mmol) in THF (15 mL) under N₂ were added 3 equiv. Pb(OAc)₄ (111 mg, 2.51×10⁻¹ mmol). The reaction was monitored by tlc for the disappearance of **1Ag**. Upon completion (~2 h), the solution was evaporated to dryness, re-dissolved in CH₂Cl₂, and purified by flash chromatography (CH₂Cl₂). The reaction produced two products, **2Ag** (traces) and **5Ag** (major, up to 30% yield).

R_f (silica—CH₂Cl₂)=0.74; UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 420 (5.05), 510 (3.48), 575 (3.75), 607 (4.20) nm; IR (KBr) ν_{\max} (rel. intensity): 516 (w), 632 (w), 703 (m), 752 (m), 786 (m), 838 (w), 1009 (s), 1068 (m), 1172 (w), 1208 (w), 1294 (w), 1342 (w), 1405 (w), 1435 (w), 1494 (m), 1528 (m), 1572 (m), 3433 (m) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): m/z =740.8 (MH⁺); HR-MS (+FAB of MH⁺, PEG) m/z calcd for C₄₃H₂₈N₄O₂Ag: 739.1263, found: 739.1221.

4.1.4. [*meso*-Tetraphenyl-2,3-diethoxymorpholinochlorinato]silver(II) (3Ag). *Method D.* To a stirring solution of **1Ag** in CH₂Cl₂/20% EtOH was added, under anaerobic conditions, silica gel-heterogenized NaIO₄. The reaction was monitored by tlc for the disappearance of **1Ag**. Upon completion, the mixture was filtered to remove the silica gel and submitted to flash chromatography (CH₂Cl₂/33% pet ether 30–60). The reaction produced three products in variable yields, depending on the reaction time and the quantity of oxidant used: **3Ag** (major, up to 50%), **6Ag** (up to 20%), and **7Ag** (up to 60%).

Compound 3Ag. Prepared in 50% yield according to *Method D* using **1Ag** (156 mg, 2.10×10⁻¹ mmol) dissolved in CH₂Cl₂/20% EtOH (25 mL), silica gel-heterogenized NaIO₄ (0.5 g), and a reaction times of <30 min. The compound was recovered from the corresponding chromatography fractions by solvent exchange to EtOH. R_f (silica—CH₂Cl₂)=0.84; UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 425 (4.90), 515 (3.47), 554 (sh), 605 (4.02) nm; IR (KBr) ν_{\max} (rel. intensity): 668 (w), 702 (m), 754 (w), 791 (m), 1007 (s), 1044 (m), 1069 (m), 1262 (m), 1269 (w), 1296 (w), 1352 (w), 1380 (w), 1439 (w), 1491 (w), 1522 (w), 1596 (w), 2343 (w), 2361 (w), 2923 (w), 2965 (w), 3435 (m) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): m/z =826.3 (MH⁺); HR-MS (+FAB of M⁺, PEG) m/z calcd for C₄₈H₃₈N₄O₃Ag: 825.1994, found: 825.1978.

4.1.5. [*meso*-Tetraphenyl-2-oxa-3-oxoporphyrinato]silver(II) (6Ag). Synthesized in up to 20% yields according to *Method D* using **1Ag** (156 mg, 2.10×10⁻¹ mmol) dissolved in CH₂Cl₂/20% EtOH (25 mL), silica gel-heterogenized NaIO₄ (1.0 g), and reaction times of up to 120 min. The fractions containing **6Ag** were crystallized by solvent exchange with EtOH to provide a purplish powder. R_f (silica—CH₂Cl₂)=0.80; UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 427 (6.54), 514 (4.76), 549 (5.06), 591 (5.26) nm; IR (KBr) ν_{\max} (rel. intensity): 438 (w), 701 (m), 753 (w), 789 (w), 845 (w), 918 (w), 1010 (m), 1069 (w), 1213 (w), 1288 (w), 1350 (w), 1435 (w), 1494 (w), 1598 (w), 1772 (s), 3444 (s) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): m/z =739.2 (MH⁺); HR-MS (+FAB of MH⁺, PEG) m/z calcd for C₄₃H₂₇N₄O₂Ag: 738.1185, found: 738.1149. Anal. calcd for C₄₃H₂₆N₄O₂Ag: C, 69.93; H, 3.55; N, 7.59%. Found: C, 69.76; H, 3.62; N, 7.62%.

4.1.6. [*meso*-Tetraphenyl-2-ethoxy-3-oxoporphyrinato]silver(II) (7Ag). Compound **7Ag** was prepared in up to 60% according to *Method D* using **1Ag** (156 mg, 2.10×10⁻¹ mmol) dissolved in CH₂Cl₂/20% EtOH (25 mL), silica gel-heterogenized NaIO₄ (1.0 g), and a reaction times of up to 120 min. Alternatively, it could be prepared in yields up to 50% as the main product according to *Method B* or in quantitative yield from **5Ag**.

Method B. To a stirring solution of **1Ag** (59 mg, 7.8×10⁻² mmol) in THF/10% EtOH under N₂ was added Pb(OAc)₄ (111 mg, 2.51×10⁻¹ mmol, 3 equiv.). The reaction was monitored by tlc for the disappearance of **1Ag**. Upon completion (~120 min), the solution was evaporated to dryness, re-dissolved in CH₂Cl₂, and purified by flash chromatography (silica gel—CH₂Cl₂). The main product **7Ag** is crystallized by slow solvent exchange with EtOH to produce a purplish powder in 50% yields.

From 5Ag. To a solution of **5Ag** in CH₂Cl₂/20% EtOH are added trace amounts of HCl vapor. The reaction is monitored by tlc for consumption of the starting material. Upon completion the product is crystallized by slow solvent exchange into EtOH. R_f (silica—CH₂Cl₂)=0.93; UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 421 (5.06), 510 (3.46), 575 (3.72), 608 (4.18) nm; IR (KBr) ν_{\max} (rel. intensity): 703 (w), 790 (w), 1010 (s), 1105 (w), 1344 (w), 1495 (w), 1633 (m), 3432 (s) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): m/z =766.7; HR-MS (+FAB of M⁺, PEG) m/z calcd for C₄₅H₃₂N₄O₂Ag: 767.1576, found: 767.1612. Anal. calcd for C₄₅H₃₂N₄O₂Ag C₂H₆O: C, 69.29; H, 4.70; N, 6.88%. Found: C, 69.21; H, 4.36; N, 7.62%.

4.2. General demetallation procedure

To a concentrated solution of [porphyrinato-] or [chlorinato]Ag^{II} in THF was added aq. HI (0.5N, 20 equiv.). Demetallation was monitored by tlc and UV–vis, and is complete upon disappearance of the metallo-species (10 min–2 h). The resulting solution was filtered through a plug silica gel to isolate the product in quantitative yields.

4.2.1. *meso*-Tetraphenyl-2-hydroxy-3-oxoporphyrin (5H₂). Compound **5H₂** is prepared by the demetallation of **5Ag** according to the general demetallation procedure (Section 4.2). Compound **5H₂** is crystallized from the resulting solution by slow solvent exchange with cyclohexane to yield a purple powder. R_f =0.54 (silica—CH₂Cl₂); UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 416 (5.26), 515 (4.11), 550 (4.18), 592 (3.87), 646 (4.51) nm; Fl (CH₂Cl₂, λ_{ex} =416 nm) λ_{\max} : 651, 704 nm; ¹H NMR (400 MHz, CDCl₃) δ -1.11 (s, 1H), -0.74 (s, 1H), 3.62 (d, J =3.6 Hz, 1H), 7.71 (m, 12H), 7.87 (m, 2H), 8.11 (m, 6H), 8.18 (d, J =2.3 Hz, 1H), 8.35 (d, J =2.3 Hz, 1H), 8.43 (d, J =2.3 Hz, 1H), 8.43 (d, J =2.3 Hz, 1H), 8.52 (d, J =2.3 Hz, 1H), 8.59 (d, J =2.4 Hz, 1H), 125.3, ¹³C NMR (100 MHz, CDCl₃) δ 100.2, 112.2, 122.1, 125.3, 127.0, 127.1, 127.7, 127.9, 128.0, 128.1, 128.2, 128.2, 129.9, 131.5, 131.9, 133.7, 133.9, 134.1, 135.1, 136.9, 142.0, 151.6, 152.0, 155.1, 164.3 ppm; IR (KBr) ν_{\max} (rel. intensity): 697 (s), 712 (m), 749 (m), 794 (s), 867 (w), 965 (m), 1066 (m), 1052 (m), 1140 (w), 1210 (w), 1269 (w), 1359 (w), 1438 (w), 1489 (w), 1518 (w), 1542 (w), 1592 (m), 2360 (w), 3053 (w), 3338 (w), 3509 (w) cm⁻¹; LR-ESI-MS (30 V, 100% CH₃CN) m/z =635 (MH⁺); HR-MS (+FAB of MH⁺) m/z calcd for C₄₃H₃₁N₄O₂: 635.2447, found: 635.2435. Anal. calcd for C₄₃H₃₀N₄O₂: C, 81.37; H, 4.76; N, 8.83%. Found: C, 81.02; H, 4.84; N, 8.72%.

4.2.2. *meso*-Tetraphenyl-2-ethoxy-3-oxoporphyrin (7H₂). Compound **7H₂** is prepared by the demetallation of **6Ag** according to the general demetallation procedure (Section 4.2). Compound **7H₂** is crystallized from the resulting

solution by slow solvent exchange with cyclohexane to yield a purple powder. R_f (silica—CH₂Cl₂)=0.84; UV–vis (CH₂Cl₂) λ_{\max} (log ϵ): 417 (4.93), 516 (3.77), 550 (3.83), 593 (3.52), 647 (4.18) nm; Fl (CH₂Cl₂, λ_{ex} =420 nm) 652, 710 nm; ¹H NMR (400 MHz, CDCl₃) δ -1.11 (s, 1H), -0.74 (s, 1H), 1.08 (t, J =7.1 Hz, 3H), 3.51 (m, 1H), 3.69 (m, 1H), 7.57 (s, 1H), 7.70 (m, 12H), 7.85 (m, 1H), 7.93 (br s, 1H), 8.10 (m, 6H), 8.19 (dd, J =2.3, 0.9 Hz, 1H), 8.33 (d, J =2.3 Hz, 1H), 8.41 (d, J =2.2 Hz, 1H), 8.43 (dd, J =2.5, 0.8 Hz, 1H), 8.50 (dd, J =2.3, 0.8 Hz, 1H), 8.57 (dd, J =2.5, 0.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 15.4, 65.0, 100.5, 105.9, 112.4, 122.2, 125.3, 127.1, 127.2, 127.7, 127.8, 127.9, 128.1, 128.2, 128.2, 128.2, 131.4, 132.0, 134.2, 134.2, 135.2, 142.2, 143.2, 150.9, 152.1, 155.2, 165.2 ppm; IR (KBr) ν_{\max} (rel. intensity): 429 (m), 513 (w), 654 (w), 704 (s), 741 (s), 799 (s), 874 (w), 972 (s), 1001 (s), 1046 (m), 1103 (m), 1170 (w), 1213 (w), 1288 (w), 1362 (w), 1439 (w), 1517 (w), 1592 (s), 2923 (w), 3446 (m) cm⁻¹; +ESI-MS (30 V, 100% CH₃CN): m/z =663.1 (MH⁺); HR-MS (+FAB of MH⁺, PEG) m/z calcd for C₄₅H₃₅N₄O₂: 663.2760, found: 663.2778. Anal. calcd for C₄₅H₃₄N₄O₂: C, 81.55; H, 5.17; N, 8.45%. Found: C, 81.32; H, 4.99; N, 8.23%.

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