

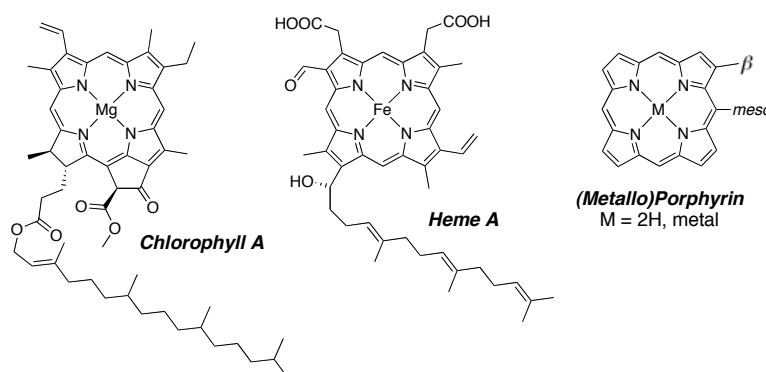
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Merging Porphyrins with Organometallics: Synthesis and Applications

1.1 Introduction

The chlorophyll and heme pigments (Chart 1) are the heart of the energy supply chain of life on Earth and therefore have been the focus of scientific attention for a number of decades.^{1,2} Much of the synthetic research has been conducted on closely related tetrapyrrolic structures, *i.e.* porphyrins, because of their synthetic accessibility and modularity.^{1,2} Porphyrins and their metal chelates have been used as functional building blocks in materials that are of interest for, amongst others, photodynamic therapy,³ photophysical applications,^{4,6} coordination chemistry,⁷ and catalysis.^{8,9} Two distinct sites of substitution on the porphyrin ring are the four *meso*- and the eight β -positions (see Chart 1). This review will focus on a relatively new area of porphyrin research, namely porphyrins that bear organometallic centers at *extra-annular* positions, mostly through connection *via* the *meso*- or β -position(s).

Chart 1



Ever since the metalloporphyrins were discovered, a great deal of research has been devoted to the exploration of their axial coordination¹⁰⁻¹² and organometallic¹³⁻¹⁵ chemistry due in part to the fact that a key organometallic structure occurring in nature is vitamin B₁₂, cyanocobalamin, which is a tetrapyrrolic cobalt compound. Later, it was realized that the metalloligand chemistry of (metallo)porphyrins is not necessarily restricted to the tetrapyrrolic core, but can also occur at its periphery. Numerous ligand sites have been attached to or incorporated into porphyrin systems. Porphyrins have been functionalized with, for instance, crown ethers,¹⁶ phosphines,¹⁷⁻²⁰ pyridines,²¹⁻³⁰ bipyridines³¹⁻³³/phenantrolines,³⁴⁻³⁸ terpyridines,³⁹⁻⁴³ carboxylates,^{44,45} imidazoles,⁴⁶ and other ligand sites, including other porphyrins^{21,47,48}.⁴⁹⁻⁵² Another interesting contribution came from the so-called N-confused porphyrins, in which one pyrrole ring is turned inside out. These compounds can accommodate a metal within the porphyrin cycle while simultaneously acting as a monodentate group by virtue of the peripheral nitrogen atom.⁵³⁻⁵⁷ In all cases, the peripheral metal sites were introduced for their inherent electronic, photophysical and/or coordination properties, which enhance or complement those of the (metallo)porphyrin. This field of porphyrin research has delivered some very exciting results. Sauvage and co-workers, for example, complexed two (metallo)porphyrin-linked terpyridyl groups to several metal centers

(Ir, Ru, Rh) and accomplished photo-induced charge separation mediated by the bis(terpy)metal unit.^{40-42,58} Pyridine- and imidazole-substituted (metallo)porphyrins have also been used to construct multi-porphyrin assemblies through intermolecular coordination of complementary Lewis-acidic and -basic sites. More recently, Reek and co-workers used zinc porphyrins in combination with nitrogen ligand-appended phosphines for the development of supramolecular catalysts and libraries thereof.^{59,60}

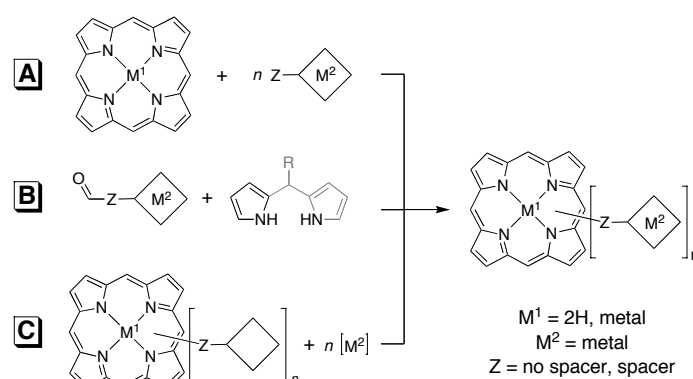
Within the group of porphyrins with peripheral metal centers, the interest in porphyrins with covalently attached metal centers connected *via* one or multiple carbon-to-metal bonds, *i.e.* with organometallic substituents, is gradually increasing. These bonds endow the organometallic complexes with different stabilities, modified intramolecular electronic coupling, dynamics, and coordination chemistry compared to the traditional coordination complexes. Although a number of these complexes have been prepared to date, a general review has, to the best of our knowledge, not yet appeared. Several reviews have appeared that treat the synthesis and applications of porphyrins with peripheral metal centers through coordination of peripheral ligands, in particular to other metalloporphyrins.⁶¹⁻⁶³ This chapter aims at reviewing the majority of the publications on porphyrins that bear peripheral organometallic units, *i.e.* incorporating one or more carbon-metal bonds. It will start with some general synthetic considerations as to when during the synthetic process an organometallic group might be introduced or attached to the porphyrin system. In the remainder, the compounds are categorized with respect to the organometallic constituent and emphasis has been placed on the synthetic routes towards the compounds with special attention for the step in which the organometallic and porphyrin are merged or joined. In most cases, the applications of these compounds will be briefly dealt with. In the section on ring-metallated porphyrins, not only the isolated organometallic compounds as such are treated, but also the transient organometallic species present during the catalytic functionalization of a porphyrin are concisely treated within this context. The large amount of reported peripherally-metallated porphyrins and their structural differences did not allow us to include structural representations of all compounds. Therefore, a selection was made that, in our opinion, reflects the synthetic, structural, and functional diversity encountered in this field of research.

1.2 Synthetic Considerations

There are three general ways to arrive at peripherally-metallated porphyrins (Chart 2). Route A relies on the attachment of organometallic groups to a (metallo)porphyrin skeleton. In a number of cases this has been accomplished by a (metal-mediated) coupling of the organometallic to the porphyrin. However, besides stability of both substrates under the (often basic) reaction conditions, this requires reagents that do not metallate or transmetallate the (metallo)porphyrin group. One example of how to avoid this was explored by Lindsey. His group developed a copper-free Sonogashira protocol for free-base porphyrin modification to counteract the copper insertion that occurs when co-catalytic CuI is used.⁶⁴ Since almost all

porphyrin syntheses rely on an acid-catalyzed condensation of (poly)pyrroles with aldehydes, porphyrins with peripheral carbon-to-metal bonds can also be obtained by appropriate functionalization of either or both reaction partners (Route B, Chart 2). For this approach to succeed, the organometallic building block has to be resistant towards Lewis or Brønsted acid, a property that is not often encountered in organometallic complexes. Functionalized benzaldehydes have often been used in this context (*vide infra*), but to the best of our knowledge, no procedures have been published that use organometallic-functionalized pyrrole. There are, however, some examples of [2 + 2] procedures that employ 5-(organometallic)-dipyrrromethanes as a source of the metalloligand group (*vide infra*).

Chart 2



The third route, Route C, uses porphyrins with previously attached ligands. These ligands can be part of the tetrapyrrolic macrocycle itself, they can be fused to the porphyrin ring, or attached *via* a tether. Subsequent metalation then leads to the desired peripherally-metalated complex. If the porphyrin is in a free-base form, a point of major importance is the order of metalation: the starting material bears multiple ligand sites and, therefore, orthogonal metalation procedures should be used to ensure selectivity of either metalation step for the targeted site. If this is not an option, one should start with the most discriminative metalation step, which concomitantly protects one type of ligand site, after which the other can be metalated. This is well illustrated by, for instance, the ring-mercuration of deuteroporphyrin IX (*vide infra*).⁶⁵ Prior to treatment of the latter porphyrin with HgOAc, its center should be “protected” with Cu(II) or Zn(II) (as the chelate), in order to avoid mercury introduction, which is effected by the same reagent.^{66,67} The reagents used for insertion of copper and zinc in turn do not add in an electrophilic manner to the porphyrin periphery.

The sensitivity and lability towards cleavage of the C-M bond usually associated with organometallics demands careful planning of the synthetic route towards the desired products.⁶⁸ In this chapter, we hope to provide the reader with some useful suggestions on the basis of procedures followed in literature.

1.3 Peripherally-Metalated Porphyrins

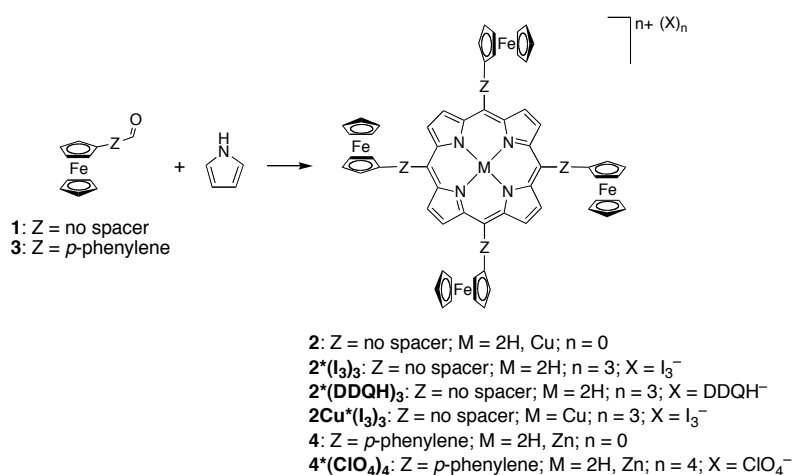
1.3.1 Ferrocene-Porphyrin Hybrids

Ferrocene-substituted porphyrins are undoubtedly the most intensively studied class of peripherally metalated porphyrins. Although ferrocene and porphyrin units have been often covalently combined (even through the axial positions of metalloporphyrins)^{69,70} the underlying rationales are diverse. Since both ferrocenyl and porphyrin groups have a rich and reversible electrochemistry, the merger of the two groups in one molecule can lead to interesting electrochemical devices, provided that ground-state electronic communication between the components is substantial.⁷¹ Linking ferrocene moieties to porphyrins is also of interest because the former are, according to thermodynamic considerations, able to reduce the porphyrins' singlet excited state. Hence, porphyrin-ferrocene hybrid molecules can be used in various photochemical devices, including donor-acceptor molecules that mimic the initial stages in the photosynthetic process at the molecular level. Yet another advantage of the ferrocenyl unit is the comparative effortlessness with which the two cyclopentadienyl rings can rotate about the Cp–Fe–Cp axis.⁷² The interconnection of a porphyrin to another functional moiety *via* a ferrocenyl linker thus leads to high degrees of freedom for both moieties to adopt relative spatial positions and orientations that can be of benefit for their applications. The inertness of the ferrocenyl group in ferrocene-porphyrin constructs furthermore allows for completely selective metalation of the porphyrin part without affecting the ferrocenyl groups. Efforts have been made to categorize the literature according to the functions of the ferrocene as listed above. It should be clear, however, that much of the research in this area is conducted across the boundaries set by these categories.

1.3.1.1 Synthesis and Electronic Communication

The obvious starting point in ferrocene-substituted porphyrins, *meso*-tetraferrocenylporphyrin **2**, was prepared by Wollmann and Hendrickson in 1977,⁷³ using pyrrole and formylferrocene (**1**) in refluxing propionic acid (Adler's procedure)⁷⁴ to furnish 40% of an atropisomeric mixture of the desired product after chromatographic purification (Scheme 1). Although the spectral data did not evidently point to the desired product, thorough analysis of the ¹H and ¹³C NMR, IR, and UV/Vis spectra, with the atropisomeric nature of the product mixture taken into account, led the authors to conclude that its synthesis had been successful. The corresponding Cu(II) complex, **2Cu**, was also synthesized by metalation of **2** with copper acetate.⁷³ From UV/Vis spectroscopy and low temperature ⁵⁷Fe Mössbauer spectroscopy data on the di- or trioxidized species **2*(I₃)₃**, **2Cu*(I₃)₂**, and **2*(DDQH)₃** it was concluded that there is a rather strong π -electron interaction between the porphyrin and *meso*-ferrocenyl groups. This is probably caused by the relative co-planarity of the porphyrin and the *meso*-cyclopentadienyl group, which in turn is enforced by the steric interactions between the β -hydrogen atoms and the ferrocenyl groups. It was later found that the fluorescence of the porphyrin in **2** is almost completely quenched by the peripheral ferrocenyl groups.^{75,76}

Meso-tetrakis(4-ferrocenylphenyl)porphyrin **4**, which was synthesized in 15% yield from 4-ferrocenylbenzaldehyde (**3**) and pyrrole using the same procedure as Hendrickson (Scheme 1), exhibits a UV/Vis spectrum very similar to that of *meso*-tetraphenylporphyrin.⁷⁷ The corresponding zinc(II) complex (**4Zn**), obtained in 67% yield by treatment of **4** with zinc acetate dihydrate in a boiling mixture of chloroform and methanol, neither shows ground-state electronic communication.

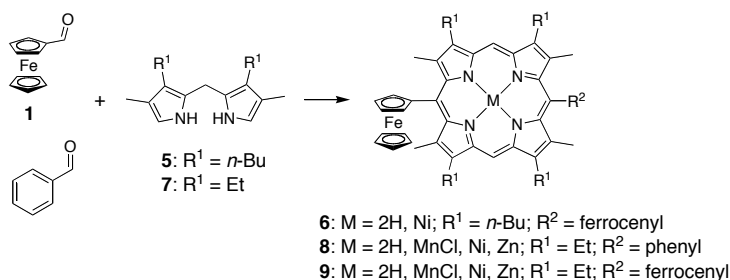


Scheme 1. *Meso*-tetraferrocenylporphyrins by Hendrickson (**2**) and Bruce (**4**).

Compared to **2**, the *meso*-phenylene groups of **4** are expected to adopt a perpendicular orientation with respect to the porphyrin ring, which, in combination with the expected non-co-planarity of the ferrocenyl groups and *meso*-phenylene groups, leads to a strong decrease in orbital overlap between the porphyrin and ferrocene systems. This was further corroborated by cyclic voltammetry, which also indicated a weak ground state interaction. The corresponding tetrakis-ferricenium derivatives, **4**⁺(ClO₄)₄ and **4Zn**⁺(ClO₄)₄, were synthesized electrochemically and their electronic spectra are virtually the same as those of **4** and **4Zn**, respectively. Fluorescence measurements indicated that fluorescence decay of the porphyrin-centered excited state is much faster than electron transfer from the singlet excited porphyrin to the ferricenium ions.

The findings of Hendrickson *et al.* prompted a number of researchers to attach ferrocenyl fragments directly to the porphyrin *meso*-position. In order to maximize the mutual co-planarity and thus interaction, it was later discovered that the use of β -octa-alkylporphyrins can greatly enhance this interaction. This enhancement is due to the juxtaposition of the alkyl groups and the *meso*-ferrocenyl groups, which sterically forces the ferrocenyl group as a whole, and the *meso*-cyclopentadienyl ring in particular, to be more co-planar with the porphyrin ring, as was evidenced by X-ray crystallographic studies.^{71,78-80} By a condensation of tetra-alkyl dipyrromethane **5** with formylferrocene, Burrell *et al.* obtained a single atropisomer of bis(ferrocenyl)porphyrin **6** in a high yield of 58% (Scheme 2).⁷¹ Two reversible, ferrocene-based redox waves were observed in the cyclic voltammogram of the free base compound ($\Delta V = 190$ mV) and its Ni(II) complex **6Ni** ($\Delta V = 410$ mV) due to

electronic interaction of the two ferrocenyl groups across the porphyrin spacer. Do and Kim *et al.* synthesized an analogous *meso*-ferrocenylporphyrin having ethyl substituents at the 2, 8, 12, and 18 positions by condensation of dipyrromethane **7** with formylferrocene in the presence of *p*-toluenesulfonic acid in methanol, followed by oxidation with *p*-chloranil, to yield **9** in 49% yield (Scheme 2).⁷⁹

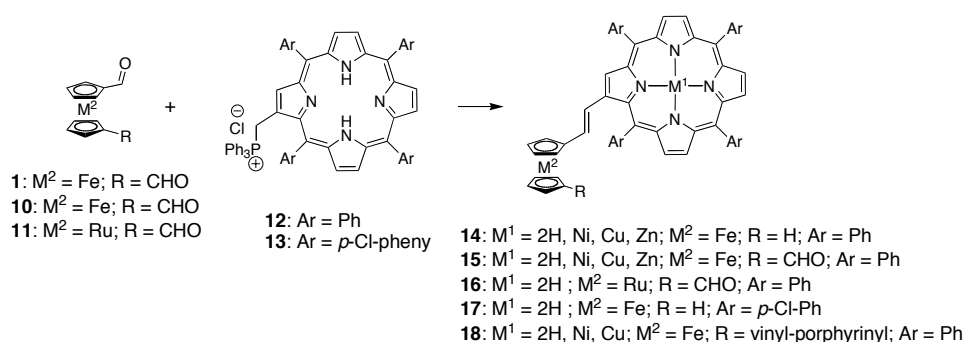


Scheme 2. Mono- and bis(ferrocenyl)porphyrins reported by Burrell (**6**) and Do and Kim (**8**, **9**).

To obtain the related mono-ferrocenylporphyrin **8**, a 1:1 mixture of formylferrocene and benzaldehyde was condensed with 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrromethane in acetonitrile with a stoichiometric amount of trichloroacetic acid, followed by oxidation with *p*-chloranil, to give the desired porphyrin in 27% yield, after column chromatography (Scheme 2).⁸⁰ The relatively inert ferrocene moiety allowed for facile metalation with several metals. Mn(III), Ni(II), and Zn(II) were introduced by treating a refluxing solution of the porphyrin precursor (**8** or **9**) in CHCl₃ with a saturated, methanolic solution of the respective metalating agent (MnCl₂·4H₂O, Ni(OAc)₂·4H₂O or Zn(OAc)₂·2H₂O) to give the corresponding metalloporphyrins **8M** and **9M** in 58%, 95%, and 77% yield, respectively.⁷⁸ The relative coplanarity of the ferrocene and porphyrin constituents in these compounds was manifested in their cyclic voltammograms. These voltammograms showed that, in the mono-compounds, the ferrocenyl groups are more susceptible to oxidation than ferrocene itself, which indicated a strong electron-donating ability of the porphyrin. More interestingly, it was observed that the redox potential of the ferrocenyl moieties changes as a function of the porphyrin metal. Whereas the *meso*-ferrocenyl group was less amenable to oxidation in the electron poor **8MnCl**, oxidation of the ferrocenyl group was facilitated in the more electron-donating nickel(II) and zinc(II) complexes **8Ni** and **8Zn**. The bis(ferrocenyl)(metallo)porphyrins **9M**, in analogy with the systems of Burrell (**6**), also showed a strong communication between the 5,15-ferrocenyl groups, mediated by the porphyrin spacer. The coupling is the strongest in the nickel complex **9Ni** and the weakest in the corresponding manganese chelate **9MnCl**. Similar mono-ferrocenyl-bis(vinyl)porphyrins were later synthesized with the objective to use them as monomers for porphyrin polymers.⁸¹ They were able to insert Co(II) and Ni(II) but unfortunately, the complexes did not seem to form the desired films.

Burrell and co-workers also devoted a significant amount of research to porphyrins linked to metallocenes through conjugated linkers. Employing a Wittig-type reaction to 1,1'-

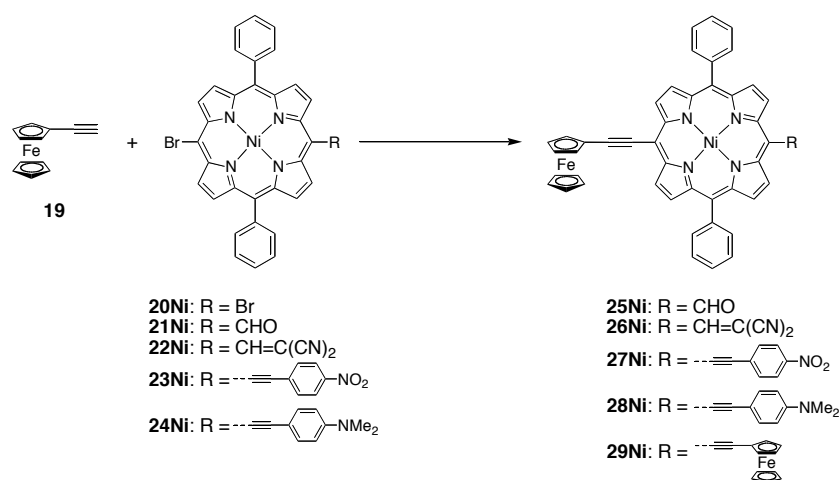
diformylferrocene **10** with 0.25 equivalents of a tetraphenylporphyrin-derived β -vinyllic phosphonium salt **12**, a *cis/trans* mixture of mono- β -porphyrinyl ferrocene (**15**) was obtained in high yield (Scheme 3).⁸² This compound was reacted with another equivalent of **12** to give bis(porphyrin) ferrocene **18**. Later, this work was extended by using several derivatized ferrocenes and a ruthenocene in the same reaction thus obtaining the corresponding β -allylic metallocenyl-tetraphenylporphyrins **14–18** (Scheme 3).⁸³



Scheme 3. β -vinyl metallocenylporphyrin synthesized by Burrell *et al.*

The corresponding Cu(II), Ni(II), and Zn(II) complexes were also synthesized by treatment of **14–18** with the corresponding acetates in yields close to 90%. In spite of the conjugated link between the peripheral metallocene redox unit and the β -positions of the porphyrin, they found only little mutual electronic influence in the ground state as evidenced by both CV and UV/Vis spectroscopy.

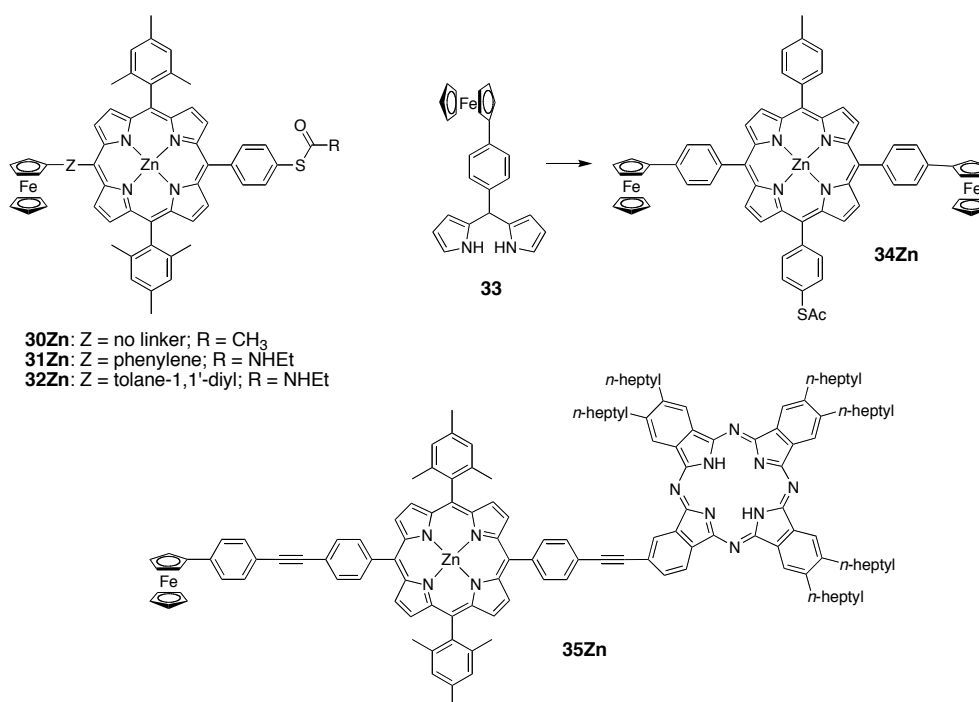
The effect of an ethynyl spacer between the porphyrin *meso*-position and a ferrocenyl group was explored by Ng (Scheme 4).^{84,85} Bis(ferrocenylethynyl)porphyrin **29Ni** was first synthesized by a Sonogashira coupling of dibromoporphyrin **20Ni** with ferrocenylethyne **19**, catalyzed by $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI in a mixture of triethylamine and THF. The desired compound was obtained in 66% yield.⁸⁵



Scheme 4. *Meso*-ferrocenylethylporphyrin synthesized by Ng *et al.*

Later, push-pull porphyrins **25Ni–28Ni** were synthesized from **19** and monobromoporphyrins **21Ni–24Ni** using similar procedures in good yields (36–78%).⁸⁴ Despite the alkyne linker in between the porphyrin and the ferrocene groups, no significant electronic communication was noted between the porphyrin and the ferrocene, and between ferrocene groups across the porphyrin spacer. The structure obtained from single crystal X-ray data revealed that the lack of communication may be attributed to an almost orthogonal orientation of the ferrocenyl cyclopentadienyl ring and the porphyrin. Unfortunately, no direct methods were applied to acquire information about the structure in solution, which could corroborate this assumption.

In a number of publications, Lindsey *et al.* showed their interest in ferrocene-appended porphyrins,⁸⁶ due in large part to their potential application in information storage devices. Following an approach to multiple bit-storage at the molecular level, Bocian, Kuhr, and Lindsey devoted several articles to ferrocene-spacer-porphyrin molecules that contain (protected) thiol groups for making SAMs on gold surfaces. Using mixed condensations between a dipyrromethane, a thiophenol-functionalized aldehyde and ferrocene-bearing aldehydes (ferrocene carboxaldehyde, 4-ferrocenylbenzaldehyde, or a diphenylethyne-linked ferrocene aldehyde) the desired *trans*-ferrocenyl-thiophenyl porphyrins were obtained as their zinc(II) chelates **30Zn–32Zn** in yields of 37, 19, and 7%, respectively (Scheme 5).



Scheme 5. Ferrocenyl-porphyrins synthesized by Lindsey and co-workers.

In these syntheses, the oxidation of the porphyrinogen intermediate under acidic conditions using 2,3-dicyano-5,6-dichloro-benzoquinone (DDQ) was replaced by a neutral oxidation

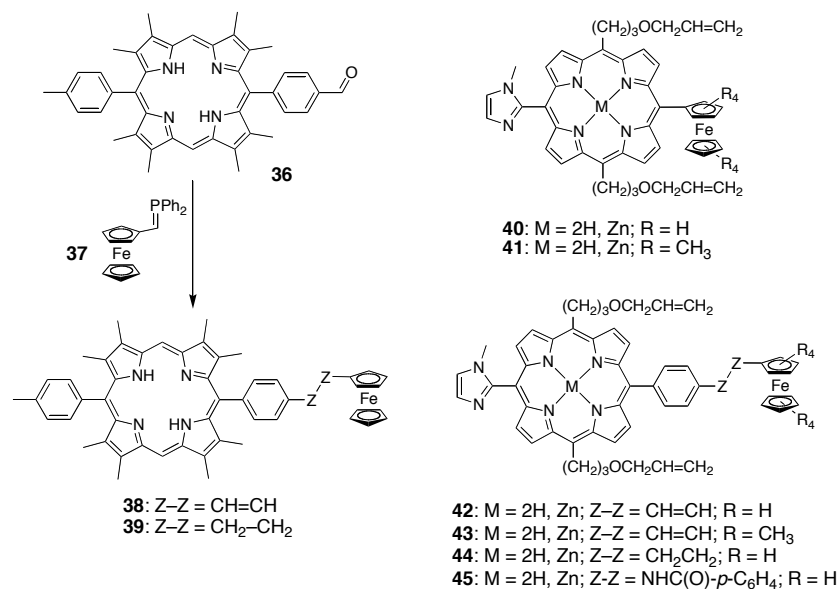
with *p*-chloranil because of the presence of the easily oxidizable ferrocenyl groups. Cyclovoltammetric measurements indicated that in the ground state the ferrocene and porphyrin parts are not electronically coupled except for the case when the ferrocene is directly linked to the porphyrin. More recently, these researchers used tripodal thiol-bearing groups to make more tightly assembled SAMs. Again, a ferrocene was attached to such a tripodal thiol-containing porphyrin to store information electronically.⁸⁷ A similar porphyrin lacking a thiol group (**34Zn**) was also prepared from ferrocene-dipyrrromethane **33** and *p*-tolualdehyde to investigate the possibility of optoelectronic gating.⁸⁸ In yet another example, the ferrocene group was attached by means of a Sonogashira-type coupling of an ethyne-appended porphyrin with 4-ferrocenyl-iodobenzene to give ferrocene-porphyrin-phthalocyanine triad **35Zn** in 15% yield (Scheme 5). Also in this case, ground state interactions were absent, but fluorescence measurements showed significant quenching of the porphyrin fluorescence. When the ferrocenyl group was oxidized prior to excitation, a complete quenching of the fluorescence was observed. According to the authors, these ferrocenyl appended constructs are highly promising for optoelectronic gating.

1.3.1.2 Photosynthetic Mimics

The ability of ferrocenyl groups to reduce the porphyrin photo-excited state gradually gained more attention. In the early nineties, β -octa-alkylporphyrins to which a ferrocene unit was attached *via* a vinylidene (**38**) or ethylene (**39**) unit were synthesized (Scheme 6).⁸⁹ In contrast to the functional group pattern on the building blocks used by Burrell (see Scheme 3), in this case the ferrocene group was attached to the porphyrin by a Wittig-type reaction between an benzaldehyde-functionalized porphyrin (**36**) and a ferrocene-functionalized phosphorous ylide (**37**) to give the porphyrin-vinylidene-ferrocene product **38** in 82% yield as a mixture of *cis* (73%) and *trans* (27%) isomers. The porphyrin-ethylene-ferrocene construct **39** was obtained by reduction of **38** with H₂ using Pd/C as a catalyst. The inter- and intramolecular quenching of the singlet excited state of the porphyrin by the attached ferrocene was thoroughly investigated by several methods, including transient absorption spectroscopy, cyclic voltammetry, and fluorescence spectroscopy. Whereas relatively little ground-state electronic interaction was observed for **38** and **39** by UV/Vis spectroscopy and cyclic voltammetry, it was found that the fluorescence of both compounds is quenched by 62% and 16% respectively compared to reference compounds that lack the ferrocenyl group. The quenching was attributed to intramolecular reduction of the singlet excited porphyrin by the ferrocenyl centers.

Kobuke *et al.* recently synthesized similar ferrocene-porphyrin constructs (Scheme 6, right).⁹⁰ A different approach was used in which two equivalents of 5-(3-allyloxypropyl)dipyrrromethane were condensed with one equivalent of 1-methyl-2-imidazolecarboxaldehyde and one equivalent of a ferrocene-containing aldehyde. The corresponding *trans*-AB₂C porphyrins **40–44** were obtained in 23, 8, 15, 26, and 17%

respectively. The octamethylferrocene unit was used because of its higher reducing power. Zinc was readily introduced with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in a $\text{MeOH}/\text{CH}_2\text{Cl}_2$ mixture to give zinc(II) porphyrins **40Zn–44Zn** in yields greater than 90%.



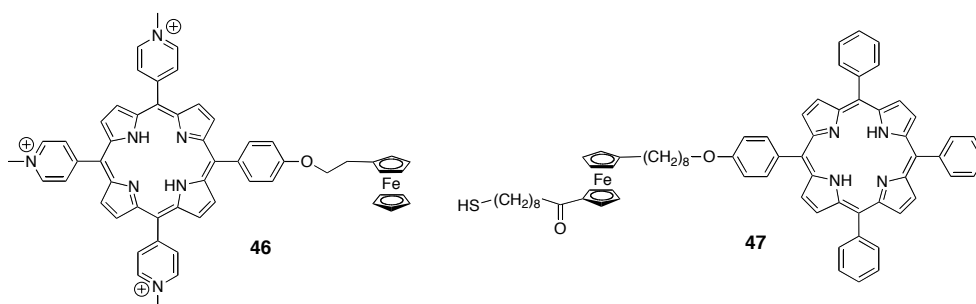
Scheme 6. Ferrocenyl-porphyrins prepared by Wrighton (left) and Kobuke (right).

In the absence of coordinating solvents, these materials self-assemble to give slipped-cofacial dimers. In the ground state, only the directly linked ferrocene-porphyrins **40** and **41** show electronic communication, with an enhanced coupling of the octamethylferrocene-containing compound **41**. This linker-dependent interaction was also observed in the excited state. Whereas the porphyrin fluorescence in **40** and **41** is completely quenched, the quenching efficiency strongly decreases for **42** and **43**. For **44**, the fluorescence is completely recovered, which differs from the results obtained by Wrighton on compound **39** (*vide supra*). The fluorescence of the corresponding zinc complexes **40Zn–44Zn**, which all self-assemble to form complementary dimers, was in all cases, except for **44Zn**, completely quenched. Later, the same group elegantly synthesized a slipped cofacial heterodimer, which consists of **45Zn** (Scheme 6) and a fullerene-appended imidazolylporphyrin. The assembly could be fixed by means of ring-closing metathesis and showed a long-lived $\text{Fc}^+-(\text{ZnP})_2-\text{C}_{60}^-$ charge separated state upon photoexcitation.⁹¹

Fluorescence quenching was also observed for a tricationic porphyrin functionalized with a ferrocene unit that was covalently attached through a phenylethyl ether spacer (**46**, Chart 3).⁹² Upon intercalation of the polar porphyrin part of **46** into DNA, a strong electron transfer from the ferrocene to the porphyrin unit was still noticed. Uosaki elegantly employed the reducing power of the ferrocene moiety to effect light-induced electron transfer at a self-assembled monolayer.⁹³ A molecular architecture was constructed, which combines a porphyrin for light absorption, a ferrocene-unit for reduction of the porphyrin excited state, and a thiol group for attachment to the gold surface (**47**, Chart 3). These compounds form

self-assembled monolayers (SAMs) on gold and are able to efficiently generate a photocurrent using visible light. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) and electrochemical coverage determination showed that the high efficiency is due to a large separation between the porphyrin and the gold layer.⁹⁴

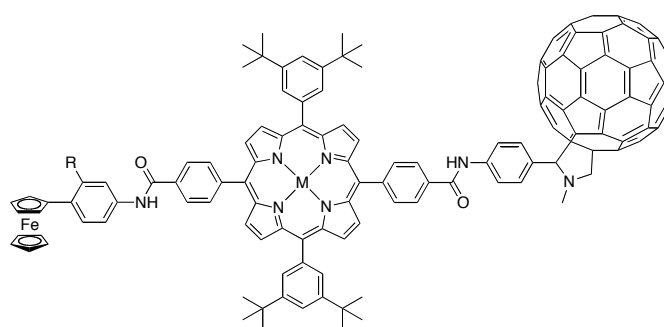
Chart 3



Since the ability of ferrocenyl groups to reduce the porphyrin photo-excited state was fully recognized, ferrocene-porphyrin hybrids have been frequently used in artificial photosynthetic mimics. The ferrocene-(porphyrin)_n-fullerene constructs of Imahori, Ito, Fukuzumi and co-workers deserve special attention. For a complete overview of their work, the reader is referred to accounts by Imahori⁹⁵ and Fukuzumi.⁹⁶

After having synthesized (metallo)porphyrin-fullerene dyads to study light-induced charge transfer processes, Imahori *et al.* tethered an additional electron donor, ferrocene, at the opposite side of the porphyrin relative to the fullerene, thus creating a family of molecular triads.⁹⁷⁻¹⁰² In their synthetic strategies, 5,15-bis(*p*-chlorocarbonylphenyl)-10,20-bis(3,5-bis[*tert*-butyl]phenyl)porphyrin, was reacted with a mixture of appropriately functionalized anilines in pyridine to give the desired mono-ferrocenyl, mono-*p*-formylphenyl porphyrin in 23% yield. After further synthetic elaboration the desired triads (either with (**49** and **49Zn**) or without a thiol functionality (**48** and **48Zn**) at the ferrocene site for additional gold-binding studies) were obtained (Chart 4).

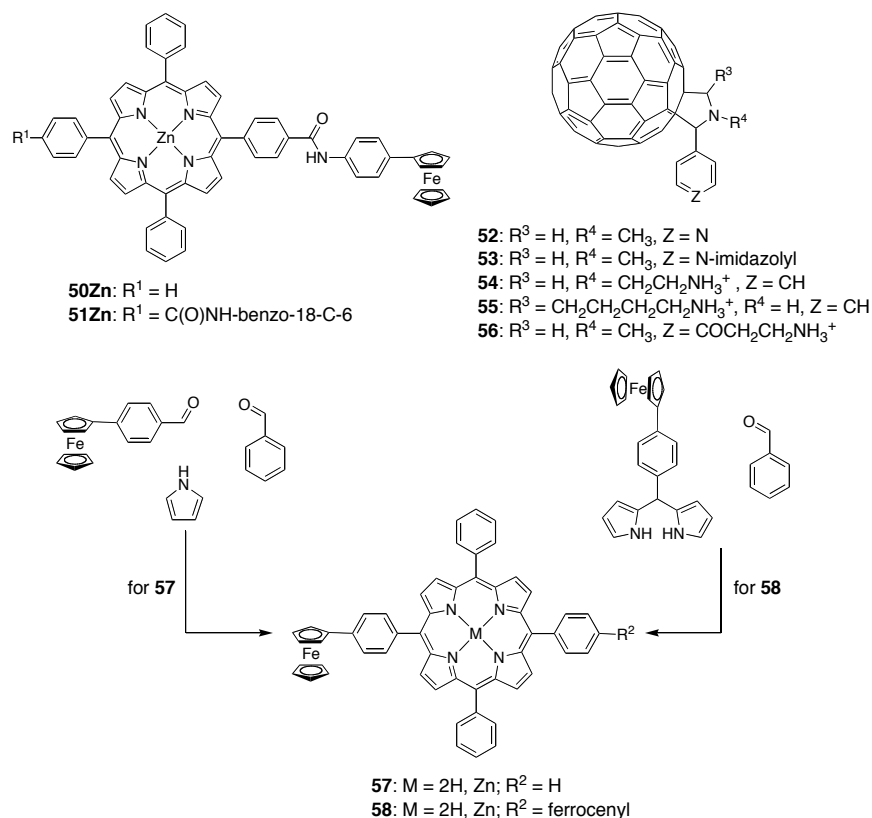
Chart 4



48: M = 2H, Zn; R = H
49: M = 2H, Zn; R = O(CH₂)₁₁SH

After the success of their triads, the researchers focused their research efforts on (a) increasing the distance between the two charges in the charge-separated states, (b) increasing the lifetimes of those charge-separated state, and (c) increasing the quantum yield of this process in pursuit of mimicking the charge-separation processes that continue to endow life on earth with energy coming from the sun as closely as possible. During this more or less evolutionary process, several molecules were synthesized, which all contain a ferrocenyl group (which, at the end of the light-induced charge-separation process, ends up as the ferrocenyl cation) and a fullerene group (eventually reduced to the $C_{60}^{\cdot-}$ radical anion during charge separation) at opposite ends of the multi-ad. Firstly, an extra (metallo)-porphyrin unit was inserted in the porphyrin-ferrocene bond,^{103,104} and subsequently, the novel *meso,meso*-linked porphyrin dimer¹⁰⁵ and trimer¹⁰⁶ structural elements were introduced in between the ferrocenyl and fullerene ends, eventually leading to a long-lived charge-separated state (0.53 s in frozen DMF at 163 K) with an very high quantum yield of 83%. Pertaining to the purpose of this review, it is important to note that the ferrocenyl group in these triads, tetrads and pentads was always introduced using similar chemistry, *i.e.* the reaction of an acid chloride-functionalized porphyrin with an aniline-functionalized ferrocene.

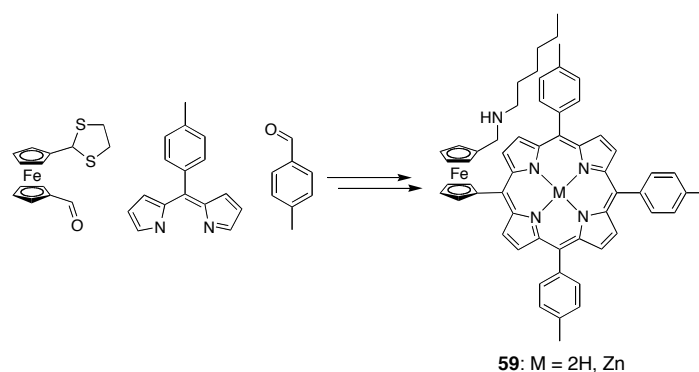
In an analogous manner, D'Souza and Ito *et al.* synthesized a series of zinc(II) porphyrins equipped with ferrocenyl groups (Scheme 7).¹⁰⁷ Whereas the amide-linked dyads **50Zn** and **51Zn** were synthesized in a similar way as porphyrin derivatives **48** and **49**, two novel, phenylene-spaced ferrocene-zinc(II) porphyrin hybrids were synthesized in different ways. Mono-ferrocenyl porphyrin **57** was made *via* a statistical Adler-type condensation of 4-ferrocenyl-benzaldehyde and benzaldehyde (1:3 ratio) with pyrrole in 6.4% yield. The corresponding *trans*-bis(ferrocenyl)porphyrin was synthesized by a [2 + 2] condensation reaction of 5-(*p*-ferrocenyl-phenyl)-dipyrromethane and benzaldehyde in methylene chloride catalyzed by $BF_3 \cdot OEt_2$. After oxidation of the intermediate porphyrinogen, the desired porphyrin **58** was obtained in 45% yield. By using fullerenes appended with Lewis bases such as pyridine or imidazole (**52–56**), supramolecular analogues of the systems of Imahori and Fukuzumi were obtained. Efficient electron transfer from the ferrocene to the singlet excited zinc porphyrin was noted, which, upon axial ligation to **52–56** generated the $Fc^+ \cdot ZnP : C_{60}^{\cdot-}$ species. The supramolecular interaction was expanded by equipping ferrocene-functionalized zinc(II) and magnesium(II) porphyrins with a crown ether moiety.¹⁰⁸ Supramolecular complexes are formed when these compounds are subjected to fullerenes bearing primary ammonium groups and also these complexes are able to form fully charged separated states upon excitation.



Scheme 7. Porphyrins with appended ferrocenes synthesized by D'Souza and co-workers.

1.3.1.3 The Ferrocenyl Group as a Hinge

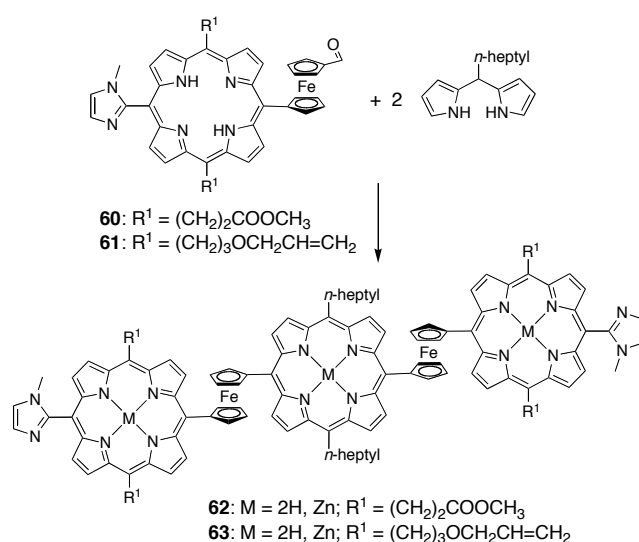
Ferrocenes are increasingly being used as hinges to mediate the changes in mutual arrangements of their substituents. Their structural flexibility was applied by Bucher, Moutet, and co-workers in ferrocenyl-porphyrin electrochemical sensors and they additionally used the electrochemical properties of the ferrocenyl group.¹⁰⁹ Ferrocene was functionalized at the 1- and 1'-positions with a *meso*-zinc(II) porphyrinyl group and a secondary benzylic amine group, respectively in a number of steps, involving the selective assembly of a porphyrin on a mono-protected bis(formyl)ferrocene using Lindsey's conditions (trifluoroacetic acid in dichloromethane)) (Scheme 8).



Scheme 8. Anion sensors described by Moutet *et al.*

The resulting porphyrin **59Zn** self-assembles through amine-Zn coordination in solution, forming supramolecular coordination dimers.¹¹⁰ As a result of the efficient electronic communication between the π -systems of the porphyrin and ferrocene moieties, coordination of a Lewis base to the zinc porphyrin brings about characteristic shifts in the redox potential of the ferrocene, which enables the electrochemical sensing of neutral, amine-containing species. When the secondary amine group of **59Zn** was quaternized with methyl iodide, the resulting cationic zinc porphyrin species is an effective anion sensor through ditopic binding *via* the zinc center and the quaternary ammonium group.¹¹¹ The binding of anions (NO_3^- , HSO_4^- , H_2PO_4^- , Cl^- , Br^- or F^-) to this sensor leads to anion-dependent changes in the redox potentials of both the ferrocenyl and porphyrin moiety.

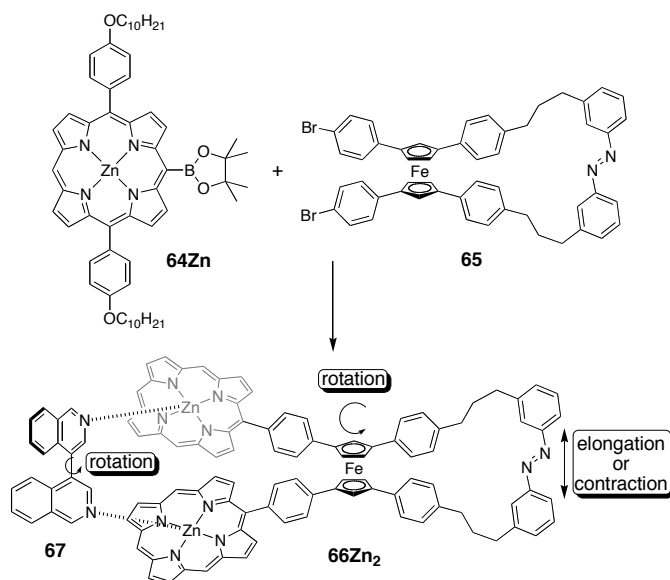
Kobuke and co-workers utilized the unique rotational motion of the two cyclopentadienyl parts of the ferrocenyl-group with respect to each other in supramolecular porphyrin structures arising from complementary dimer formation.¹¹² 1,1'-Diformylferrocene was used as the organometallic building block in the porphyrin synthesis of **62** and **63**, *via* mono-(1'-formylferrocenyl)porphyrins **60** and **61**, to provide these in 5.1% and 2.1% yield, respectively (Scheme 9). In contrast to the corresponding *meso*-(*m*-phenylene)-linked tris(porphyrin)s that were synthesized before,¹¹³ these molecules do not form polymeric mixtures following zinc insertion. Instead, **62Zn** and **63Zn** form dimers, which was attributed to the freely rotating ferrocene hinge. When these dimers are disassembled with pyridine and re-dissolved in chloroform containing 0.5% ethanol, the mixture initially consists of cyclic oligomers, but these reconvert to the dimers owing to the flexibility of the ferrocenyl linkage. A similar principle was used to allow an ferrocene-appended porphyrin and fullerene unit to acquire favorable mutual position for electronic interaction.¹¹⁴



Scheme 9. Hinge porphyrin designed and synthesized by Kobuke.

Very recently, Aida *et al.* reported two systems in which the photoresponsive *cis/trans* isomerization of an azobenzene^{115,116} or a 1,2-bis(pyridyl)ethylene¹¹⁷ unit was coupled to the

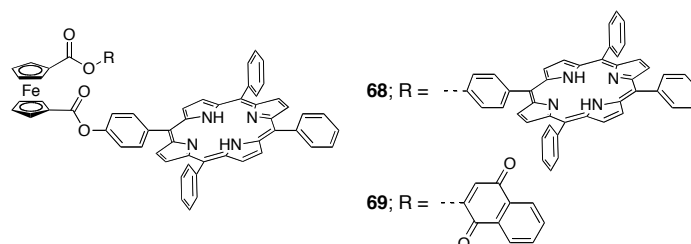
twisting of porphyrin units connected *via* a ferrocene unit. Again, the capability of the ferrocene moiety to rotate around the η^5 -cyclopentadienyl-iron bond was crucial for the success of this strategy. The two cyclopentadienyl rings of a ferrocene unit were interconnected at the 1,1' positions *via* an azobenzene strap (**65**).¹¹⁵ At the 3,3' positions two independent zinc porphyrins were attached by a Suzuki cross-coupling reaction with two equivalents of mono-*meso*-boronate-porphyrin **64Zn** in the presence of Pd(PPh₃)₄ and Cs₂CO₃ in a mixture of toluene and H₂O to give bis(porphyrin) **66Zn₂** in 20% yield (see Scheme 10).



Scheme 10. Ferrocenylporphyrin-based mechanical twisting reported by Aida *et al.*

The *cis/trans* isomerization of the azobenzene unit induces a rotation of the two cyclopentadienyl fragments around the C₅-Fe bond, which in turn leads to a change in the spatial separation of the porphyrin units. Bis(isoquinolinyl) guest **67** was ligated to this host to give a 1:1 complex. Using several techniques, including UV/Vis spectroscopy and circular dichroism (CD), in combination with the fact that ligand dissociation is much slower than the rotational moment, conclusive evidence was provided that the rotation around the ferrocene bond brought about by the contraction and elongation of the azobenzene unit changes the conformation of the guest through the non-covalent interaction with the zinc porphyrins.^{115,116} Subsequently, a similar rotary host was synthesized which also comprised a 1,1'-bis(porphyrin)ferrocene unit similar to that in **66Zn₂**, but now with two *meta*-aniline functionalities on the opposite ends of the ferrocenyl linker.¹¹⁷ By virtue of rotation around the ferrocene group, this molecule can self-ligate through zinc-nitrogen bonds. With a *cis*-1,2-bispyridylethylene guest present, the self-ligated molecule adopts an externally locked conformation, with either zinc porphyrin coordinated to the guest. When this species is irradiated with UV light, the guest isomerizes to the corresponding *trans*-compound and is released from the bis(zinc porphyrin) host upon self-ligation.

Molecules in which a ferrocene unit bridges between two porphyrin units (**68**)¹¹⁸ or between a naphthoquinone and a porphyrin (**69**)¹¹⁹ were developed by Beer *et al.* (Scheme 11). The former molecule was synthesized by reacting two equivalents of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin with one equivalent of 1,1'-bis(chlorocarbonyl)ferrocene in the presence of triethylamine. Cyclic voltammetry and differential pulse voltammetry were employed to probe the electrochemical properties of the compound. It was found that there is no electronic communication between the components.¹¹⁸

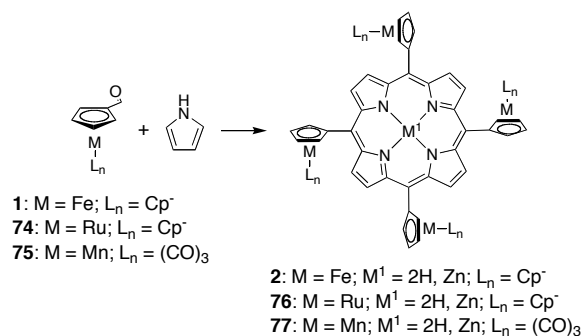


Scheme 11. Porphyrin-ferrocenes developed by Beer and co-workers.

The porphyrin-ferrocene-quinone linked molecule **69** was prepared in a one pot, two step reaction. 1,1'-Bis(chlorocarbonyl)ferrocene was first reacted with one equivalent of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin and the resulting mono-porphyrin-mono-chlorocarbonyl-ferrocene was reacted *in situ* with one equivalent of 2-hydroxynaphthoquinone yielding **69** in a non-optimized yield of 35%. Voltammetric measurements showed negligible ground state interactions between the constituents. Fluorescence measurements, however, revealed a 90% quenching of the porphyrin fluorescence (*vs.* tetraphenylporphyrin reference), which is ascribed to a rapid, intramolecular reduction of the naphthoquinone unit by the singlet excited state of the porphyrin.¹¹⁹ The authors did not elaborate on whether the ferrocene linker actively mediates in this process or is merely a spectator unit. The same group later synthesized different atropoisomers of *meso*-tetrakis(*ortho*-ferrocenylcarbonyl-aminophenyl)porphyrin by reaction of the appropriate atropoisomer of *meso*-tetrakis(2-aminophenyl)porphyrin with 5 equivalents of (chlorocarbonyl)ferrocene in Et₃N/CH₂Cl₂ with yields in the range of 67-72%.¹²⁰ The corresponding zinc complexes were readily obtained in yields > 90% by the zinc acetate in methanol/methylene chloride procedure. The zinc complexes strongly bind to anionic guests (Cl⁻, Br⁻, NO₃⁻, HSO₄⁻), and the anion-selectivity depends on the atropoisomeric nature of the host. The host behavior was evaluated by cyclic voltammetry and showed guest-selective sensing.

Smith has very elegantly shown that metallocene-appended porphyrins can also be synthesized from cyclopentadienide-functionalized porphyrins, despite the fact that this strategy has not found broad application due to the inherent synthetic challenges. A 1-methylcyclopentadiene moiety was fused to a pyrrole subunit of *meso*-tetraarylporphyrin to give porphyrins **70Ni** and **70Cu**. Deprotonation with lithium diisopropyl amide (LDA) followed

organometallic cymantrenyl-carboxaldehyde **75** and reacted it with pyrrole in boiling acetic acid. The targeted tetrakis(cymantrenyl)porphyrin **77** was obtained in an impressive yield of 27% as a mixture of atropoisomers.¹³² Later, it was reported that the use of Lindsey conditions¹³³ enhances the yield of these reactions by more than 200%.¹²⁸ An interesting extension was made by introducing planar chiral (+)-(1*S*)-2-methylcymantrene groups at the four *meso*-positions.¹²⁹ Both positive and negative Cotton effects in the absorption region of the resulting porphyrin chromophore demonstrated the chirality of the molecule as a whole. Separation of the atropoisomers was not reported. During the course of this work, the analogous tetrakis(ferrocenyl)- and tetrakis(ruthenocenyl)porphyrin, **2** and **76** were also synthesized.¹³⁴ The electronic impact of these *meso*-metallocenyl group on the corresponding zinc(II) chelates **2Zn**, **76Zn**, and **77Zn**, synthesized in 85–90% by metalation with zinc acetate or zinc chloride in DMF, was assessed by the determination of their binding constants with imidazole.¹³⁰ The effects of *meso*-ferrocenyl ($K_{\text{ass}} = 3.8 \pm 0.9 \times 10^4 \text{ M}^{-1}$) and -ruthenocyl ($K_{\text{ass}} = 3.0 \pm 0.7 \times 10^4 \text{ M}^{-1}$) only differed marginally from the corresponding phenyl groups ($K_{\text{ass}} = 3.0 \pm 0.7 \times 10^4 \text{ M}^{-1}$). Interestingly, the affinity of the zinc atom for imidazole was remarkably enhanced by *meso*-cymantrenyl groups ($K_{\text{ass}} = 7.7 \pm 0.5 \times 10^6 \text{ M}^{-1}$).

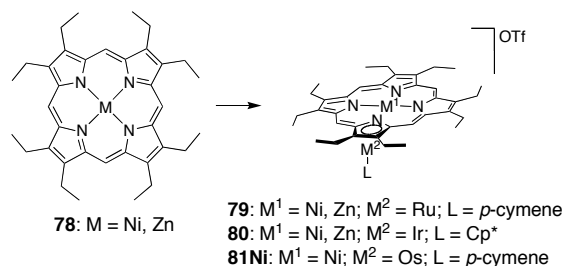


Scheme 13. *Meso*-tetrakis(metallocenyl)porphyrin synthesized by Loim.

This effect is contributed to the electron-withdrawing nature of the cymantrenyl moiety. These results are consistent with the σ_p Hammett parameters for the four substituents, which follow approximately the same trend. The Loim group subsequently focused their attention on the synthesis of mixed systems containing *meso*-phenyl-, ferrocenyl- and/or cymantrenyl-groups.¹³¹ For this, they applied different synthetic strategies, including mixed condensations of aldehydes with pyrrole under Lindsey conditions ($\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2) and reactions of different 5-substituted dipyrromethanes with metallocene- and benzaldehydes. ^1H NMR and UV/Vis spectroscopy showed that in *meso*-metallocenylporphyrins, the degree of distortion of the macrocycle as a function of the metallocenyl group increases in the series cymantrene < ruthenocene < ferrocene.

In an effort to obtain new insights into hydrodemetalation catalysis, Rauchfuss realized that the pyrrole rings of the tetrapyrrolic macrocycles could act as η^5 -pyrrolide ligands for π -complexes.¹³⁵⁻¹³⁷ Treatment of solutions of $[(\text{cymene})\text{Ru}(\text{OTf})_2]$, $[(\text{Cp}^*)\text{Ir}(\text{OTf})_2]$, or

[(cymene)Os(OTf)₂] with either NiOEP (**78Ni**) or ZnOEP (**78Zn**) (OEP = dianion of β -octaethylporphyrine) in dichloromethane gave the corresponding π -complexes **79–81** in which one of the pyrrole rings acts as an η^5 -pyrrolide ligand in 60–67% yield (Scheme 14).



Scheme 14. Porphyrinocenes made by Rauchfuss.

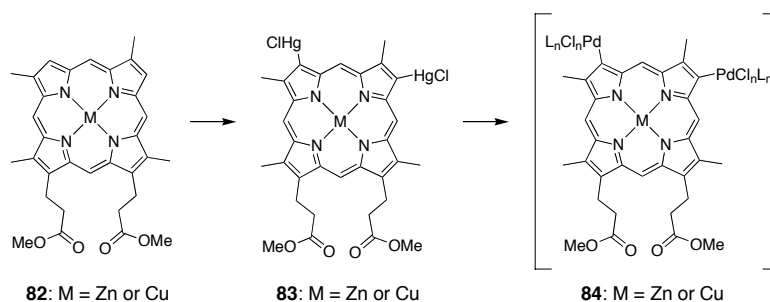
The stability of these complexes is related to the electron-donating ability of the porphyrin ring. **78Zn** forms the most stable complexes, while those of **78Ni** are less stable and the related vanadium compounds were not formed at all. Unfortunately, these results have not led to additional research in this area.

1.3.3 Ring-Metalated Porphyrins

The preparation of porphyrins that bear (transient) peripheral σ -bonded metal centers has mainly been stimulated by two objectives. The most important one is the ability of these peripheral metal centers to take part in a metal-mediated catalytic cycle to functionalize the parent porphyrin in a desired way.¹³⁸ Secondly, ring-metalated porphyrins have also been studied as such rather than as synthetic intermediates. In that case, the metal centers can be used for electronic communication with the porphyrin center and as anchoring points for the coordination of other functional ligands. With respect to the first category, this review will only cover those cases wherein the transient metal complexes are directly bonded to the porphyrin *meso*- or β -positions and they will be discussed in combination with the second group.

1.3.3.1 Ring-Metalated Porphyrins as Synthetic Intermediates

Smith and co-workers found that partially β -unsubstituted porphyrins reacted with Hg(OAc)₂ to form the corresponding mercurated porphyrins.^{65,139,140} Since free-base porphyrins can react with Hg(OAc)₂ to form the corresponding mercury(II) chelates, the starting materials were converted into their zinc(II) or copper(II) complexes **82Zn** and **82Cu** prior to the mercuration reaction. The electrophilic mercuration takes place nearly selectively at the unsubstituted β -positions of the porphyrin substrates with only a minor extent of *meso*-mercuration, to give bis(β,β) and tris(mercurated) ($\beta,\beta,meso$) porphyrin species **83Zn** and **83Cu** in nearly quantitative yields (Scheme 15).

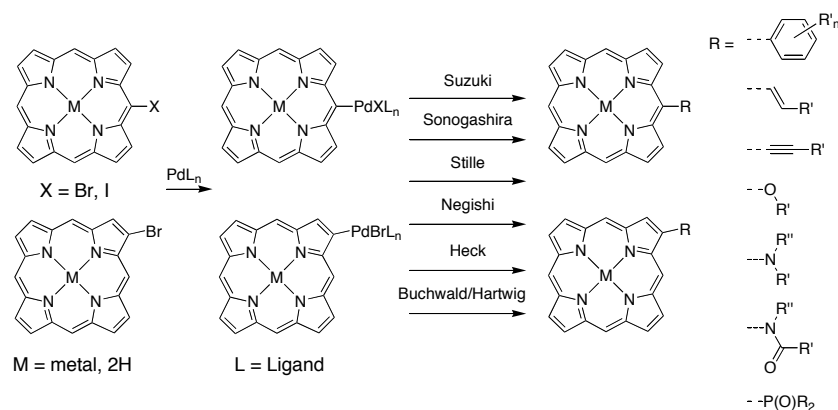


Scheme 15. Mercurated and palladated porphyrins used by Smith and co-workers.

When brought together in solution with LiPdCl_3 and methyl acrylate, these mercurated porphyrins undergo a Heck reaction sequence *via* intermediate species **84** to give the desired methyl acrylate-porphyrins. In this way coproporphyrin III tetramethyl ester, harderoporphyrin trimethyl ester, isoharderoporphyrin trimethyl ester, and S-411 porphyrin could be obtained in good yields. An advantage of this methodology is that it circumvents the need for complex, lengthy synthetic routes to the appropriate pyrrolic building blocks. Later, the scope of this work was expanded by introducing a myriad of alkenyl- and styryl-fragments onto the porphyrin framework.¹⁴¹ Further research revealed that the β,β ,*meso*-tris(mercurated) porphyrin can react further to give species with one methyl acrylate-substituent and one fused five-membered isocyclic ring bridging the β - and *meso*-positions.¹⁴² The researchers found that these compounds probably originate from a species with two β -(methyl acrylate) groups and one *meso*-mercuric chloride substituent. In this reaction, the starting material most probably transmetalates with LiPdCl_3 and the double bond of the methyl acrylate fragment which was at the β -position adjacent to the *meso*-Pd moiety subsequently inserts into the Pd–C bond followed by protio-depalladation to form the isolated products. This reaction sequence gives access to deoxyphylloerythroetioporphyrin and deoxyphylloerythrin methyl ester *via* relatively short routes. The same authors showed later that iodinated and brominated porphyrins can be obtained from the reaction of the appropriately mercurated porphyrins with iodine and bromine, respectively, in high yields.¹⁴³

Direct ring-metalation of porphyrins *via* oxidative addition of ring-halogenated porphyrins to appropriate metal centers has been known since the late 80's when Smith *et al.* reported the use of a Stille-type coupling between 2,4-dibromodeuteroporphyrin IX dimethyl ester with tri-*n*-butylethynylstannane catalyzed by tetrakis(triphenylphosphine)-palladium(0) to give protoporphyrin IX dimethyl ester in 85% yield.¹⁴³ Therien and co-workers later synthetically extended [5,15-dibromo-10,20-diphenyl-porphinato]zinc(II) and [2-bromotetraphenylporphinato]zinc(II) using palladium-mediated Negishi- and Stille-type couplings to give the desired substituted porphyrins in 90% isolated yield.^{144,145} With respect to the nature of the transient organopalladium(II) in the former case, it should be noted that a mono-palladated compound is probably most abundant, as Arnold and co-workers showed later that the first metalation pronouncedly reduces the activity of the opposite *meso*-bromine atom in a subsequent oxidative addition reaction.¹⁴⁶⁻¹⁴⁸ Later, *meso*-brominated and iodinated

porphyrins were also employed as substrates in palladium-catalyzed Sonogashira reactions^{138,149} and Therien and coworkers applied *meso*-brominated porphyrins in Suzuki reactions, thereby making “Suzuki porphyrins” which could be utilized in further functionalization reactions (Scheme 16).¹⁵⁰



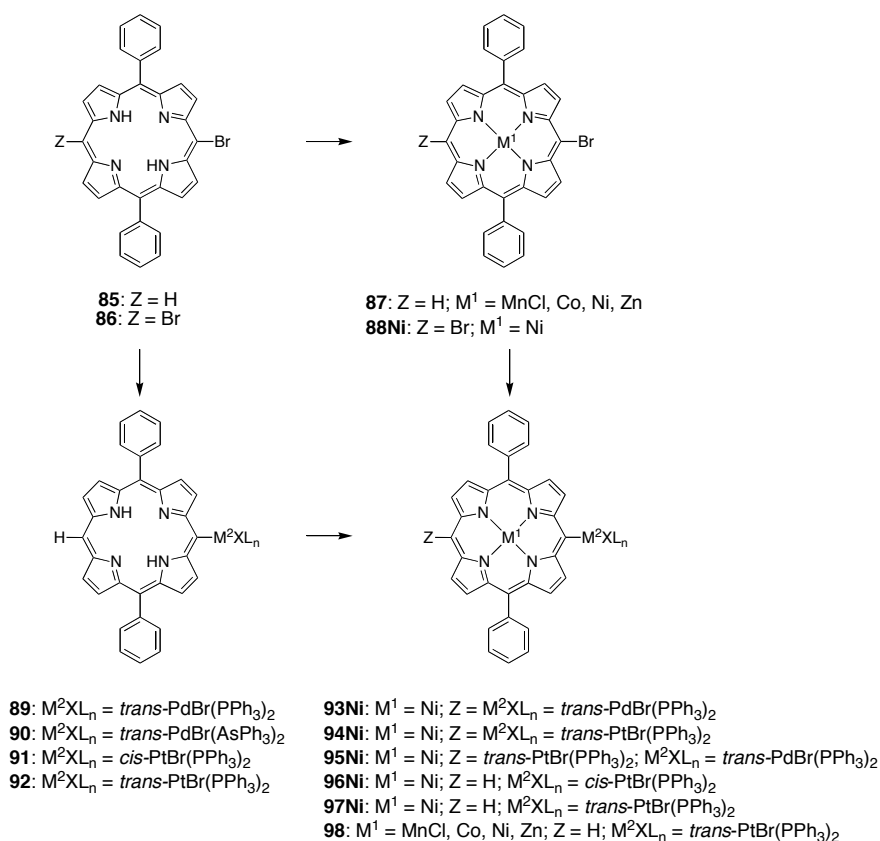
Scheme 16. Overview of the porphyrin products that can be obtained by palladium-mediated coupling on the β - or *meso*-position(s).

When boron is considered a metal, the latter molecules can actually be considered as *meso*-metalated porphyrins. Zhang and co-workers used transient *meso*-palladated porphyrins in the high-yielding syntheses of *meso*-arylamino- and -alkylamino-porphyrins,^{151,152} *meso*-aryloxy and -alkoxy,¹⁵³ and *meso*-amidoporphyrins.¹⁵⁴ Suda and co-workers reported a more general procedure for *meso*-amination and amidation of porphyrins by which they could also couple aliphatic secondary amines with *meso*-bromo porphyrins.¹⁵⁵ They found that a nickel-porphyrin is a far more reactive substrate than its free-base precursor under the applied reaction conditions. Arnold and co-workers did not note a big difference in completion time between the reactions of 5-bromo-10,20-diphenylporphyrin and (5-bromo-10,20-diphenylporphyrinato)nickel(II) with $\text{Pd}(\text{PPh}_3)_4$,¹⁴⁶ which might suggest that the oxidative addition of the bromo-porphyrin to Pd in their case is not rate-limiting.¹⁴⁵ Moreover, it was also found that during the reactions toward *meso*- η^1 -platinio(II)porphyrins the oxidative addition of the *meso*-bromoporphyrins to Pt(0) was faster for the free base compound than for its Ni(II) and Zn(II) complexes.¹⁵⁶ In a recent example, Arnold showed that *meso*-phosphine oxide groups could also be introduced using palladium-catalyzed couplings.¹⁵⁷

1.3.3.2 Ring-Metalated Porphyrins

In 1998, Arnold and co-workers reported the serendipitous isolation of *meso*- η^1 -metalloporphyrins **89–93** (Scheme 17).^{147,158} Instead of regarding them as mere synthetic intermediates, they began studying these organometallic porphyrins in their own right. The first examples of these *meso*- η^1 -metalloporphyrins were synthesized by treating free-base and nickel complexes of 5-bromo-10,20-diphenylporphyrin (**85**, **87Ni**) and 5,15-dibromo-10,20-diphenylporphyrin (**86**, **88Ni**) with equimolar amounts of a Pd(0) and Pt(0) source.¹⁴⁷

$\text{Pd}(\text{PPh}_3)_4$ or a mixture of Pd_2dba_3 and PPh_3 , AsPh_3 or dppe was used for palladation and $\text{Pt}(\text{PPh}_3)_4$ for platination, and the reactions were performed in argon-purged toluene at 105 °C. In this way, the first step in the catalytic processes described above was carried out on a preparative scale and the resulting complexes were isolated in high yields.

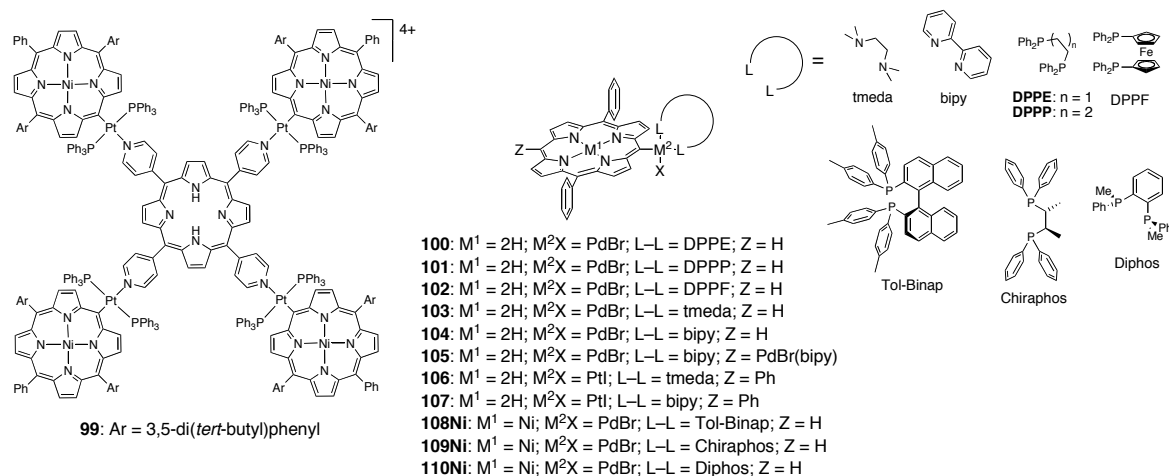


Scheme 17. *Meso*- η^1 -metalloporphyrins investigated by Arnold *et al.*

It was furthermore found that the kinetic *cis*-products **91** and **96** of the oxidative addition of 5-bromo-10,20-diphenylporphyrin and (5-bromo-10,20-diphenylporphyrinato)nickel(II) to $\text{Pt}(0)$ precursors gradually transform in the thermodynamically more stable *trans*-analogues **92** and **97**, respectively.¹⁴⁶ Later, however, the authors were able to readily isolate *cis*-complexes by using *cis*-bischelating ligands such as *tmeda* and *bipy* (Chart 6).¹⁵⁶ In chlorinated solvents some halide exchange between the synthesized palladium(II) and platinum(II) complexes and the solvent takes place, but it was not mentioned whether the rate of this reaction is unusual and or influenced by the (photophysical) properties of the porphyrin. In addition, the expansion of the bimetallic porphyrin arsenal by introducing Mn(III), Co(II), and Zn(II) into the porphyrin ring was reported, next to the earlier reported free-base and nickel(II) compounds (**87MnCl–87Zn** and **98MnCl–98Zn**, Scheme 17).¹⁴⁸ In order to synthesize these hetero-multimetallic compounds, two procedures can be followed: (1) metalation of the porphyrin followed by oxidative addition to a metal(0) source ($\text{Pt}(\text{PPh}_3)_4$) or (2) oxidative addition of the *meso*-C–Br bond to a metal(0) source prior to

metalation of the porphyrin moiety. Procedure (2) is preferred over (1) since the latter is hampered by a low solubility of the metalloporphyrin species. When employing procedure (2), the liberated acid does not protio-deplatinate the *meso*-position in the second step indicating that in these complexes the C-Pt bond is quite robust. It was furthermore found that insertion of Pt(II) in the carbon-bromine bond deactivates the opposite carbon-bromine bond towards oxidative addition, allowing the isolation of the bis-platinum species **93Ni** in low yields only. From ^1H NMR, UV/Vis, and CV measurements, the authors concluded that the $-\text{Pt}(\text{PPh}_3)_2\text{Br}$ group is a strong electron donor and that the introduction of an extra $-\text{Pt}(\text{PPh}_3)_2\text{Br}$ moiety has an additive effect. In subsequent research, the researchers used AgOTf to synthesize cationic porphyrin [**97Ni**]**OTf** from nickel(II) porphyrin **97Ni**. Having one vacant coordination site, the $-\text{Pt}(\text{PPh}_3)^+$ moiety could be used for coordination to functionalized Lewis bases to give supramolecular multi-porphyrin assemblies (for an example, see **99** in Chart 6).¹⁵⁹ Assemblies of 2, 3, and 5 porphyrins could be created by using 5-(4-pyridyl)-10,15,20-tris(*p*-tolyl)porphyrin, 5,15-bis(4-pyridyl)-10,20-bis(*p*-tolyl)porphyrin, and tetrakis(4-pyridyl)porphyrin as the Lewis base in appropriate stoichiometries. The electronic spectra of the assemblies showed some through-space electronic communication between the porphyrins.

Chart 6. Example of a supramolecular complex (left) and *meso*-metalated porphyrins with chelating ligands (right), synthesized by Arnold and co-workers.



The exclusive product of the reaction between a 5-bromo-porphyrin and a Pd(0) source (Pd_2dba_3 , $\text{Pd}(\text{PPh}_3)_4$) is a *trans*-[Pd(porph)Br(PPh_3)₂] compound, whereas both *cis*- and *trans*-products can be isolated in the case of Pt. In the former case, the *cis*-products **100–102** can be readily obtained by addition of chelating diphosphines (dppe, dppp, dppf) to the palladium source prior to addition of the bromoporphyrin.¹⁴⁶ For the corresponding platinum compounds, this is not an option due to *in situ* formation of highly stable [Pt(diphosphine)₂] species, which will not react further with the haloporphyrin. In order to overcome this problem, diamines were used instead of diphosphines.¹⁵⁶ For the *cis*-palladium complexes **103–105** this works equally well as when the chelating phosphines were used (one equivalent

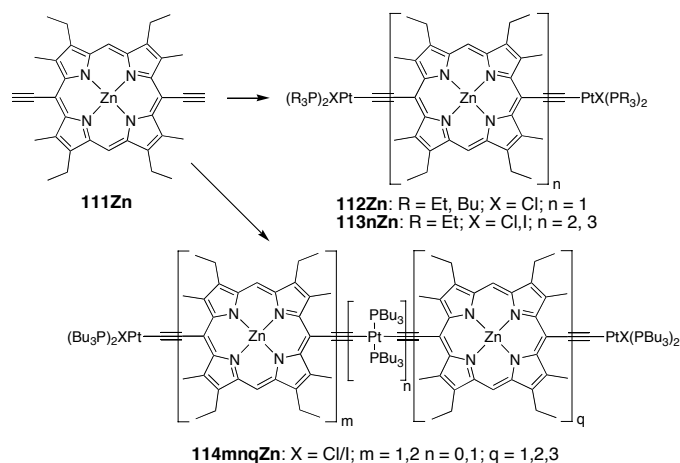
of Pd, excess diamine, toluene 105 °C).¹⁵⁶ Interestingly, this route proved to be even useful for the platinum complexes, since the corresponding *cis*-compounds **106**, **107** were obtained in high yields using the same procedure as for their palladium analogues. A *meso*-iodinated porphyrin was used because reactions with the *meso*-bromo analogues failed. Later it was realized that these “normal” chelating ligands, which do not have a substantial effect on the porphyrin, can be replaced by chiral, bidentate ligands to give chiral complexes **108Ni**–**110Ni**,¹⁶⁰ which can eventually lead to interesting catalytic applications.

1.3.3.3 Semi-Metallic Examples

Not only transition metals have been attached to the porphyrin ring. Several main-group semi-metals have also been appended to tetrapyrrole systems. Instead of using electrophilic aromatic metalation or oxidative addition for these reactions, Shine and co-workers used the zinc(II) tetraphenylporphyrin (**ZnTPP**) cation radical to react with several nucleophiles.¹⁶¹ Reaction with triphenylarsine in acetonitrile gave 39 % of [(2-triphenylarsonium-5,10,15,20-tetrakis(phenyl)porphyrinato)-zinc(II)] perchlorate. In a similar method, **ZnTPP** was oxidized *in situ* in the presence of several group 15 nucleophiles (EPh_nR_{3-n}, E = P, As) using 2,6-lutidine as a proton trap in mixtures of apolar (CH₂Cl₂, C₂H₄Cl₂) and apolar solvents (MeOH, MeCN).¹⁶² The corresponding β-arsonium compounds show bathochromic shifts of the UV/Vis bands. While pursuing the synthesis of a *meso*-trichlorotellurio(IV)porphyrin, Sugiura and Sakata and co-workers unexpectedly found a new oligomerization reaction. Upon treatment of nickel 5,15-diarylporphyrin with TeCl₄ in dry methylene chloride at room temperature, they found that multiply fused dimers and associated higher oligomers are formed. A mechanism involving attack at the *meso*-position, followed by β-attack of the intermediate *meso*-trichlorotellurio(IV) group on another porphyrin with a final detelluration reaction, was postulated by the authors to account for this reaction.

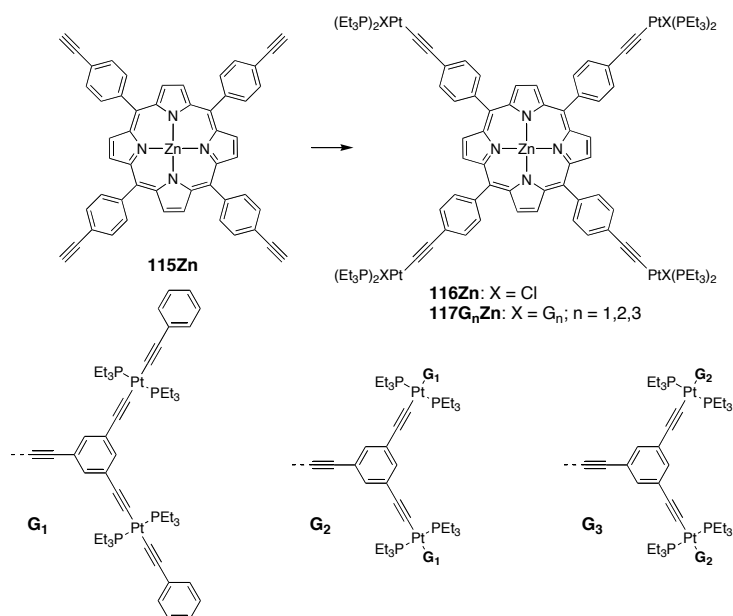
1.3.4 Porphyrins with Platinum-Acetylide Units

Due to the rich photophysical and photochemical properties of platinum-acetylides¹⁶³ they have been attached to porphyrins for electronic reasons. Pt-acetylide linkages were used by Paolesse *et al.* to synthesize conjugated organometallic porphyrin polymers.¹⁶⁴ A zinc β-octa-alkyl-5,15-bis(acetylene)porphyrin **111Zn** was reacted with several Pt complexes of the general formula [PtClZ(PR₃)₂] (*cis* and *trans*; Z = Cl or H; R = Bu or Ph), in the presence of essential, catalytic amounts of CuI with diethylamine/methylene chloride as the solvent (Scheme 18). Reaction of **111Zn** with one equivalent of *trans*-[PtCl₂(PBu₃)₂] furnished 15% of a mixture of *cis* and *trans* 5,15-bis[halidoplatino(II)-bis(PBu₃)ethynyl]porphyrins **112Zn** in which the platinum-bound halide can be either Cl or I as a result of halide scrambling at Pt (CuI as the iodide source). In addition, a mixture of the oligomeric products **113nZn** was formed as evidenced by MALDI-TOF MS. This mixture consists of different oligomeric multiporphyrin compounds, which are interconnected by butadiyne- or *trans*-[bis(acetylide)(PBu₃)₂] units.



Scheme 18. Porphyrin-Pt-bis(acetylide) porphyrins of Paolesse and co-workers.

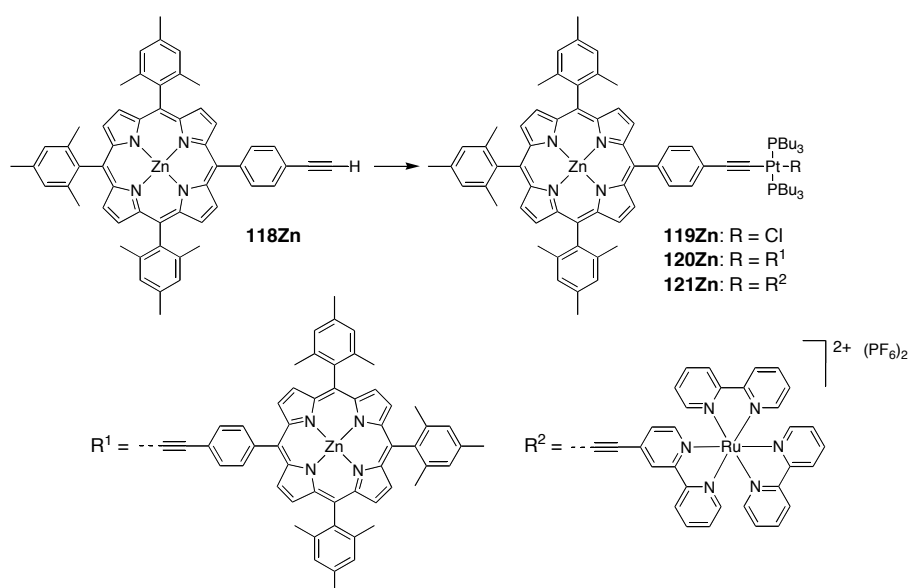
On the contrary, reaction of **111Zn** with *cis*-[PtCl₂(PPh₃)₂] or *trans*-[PtHCl(PPh₃)₂] under the same reaction conditions gave different product distributions. The major product of this reaction is a mixture of bi/trinuclear products consisting of two peripheral platinum centers interconnected by a free base or zinc(II) porphyrin, respectively (15%). As a by-product, a mixture of multinuclear, bis-platinum, bis-zinc(II) porphyrin compound was formed, the platinum centers of which are located at both extremes (**114mnqZn**). These platinum groups are linked to each other by a bis(5,15-bis(acetylene)porphyrin) spacer, which was supposedly the product of a Glaser/Hay type coupling. The reported structures were also analyzed by using X-ray photoelectron spectroscopy (XPS)¹⁶⁵ and NEXAFS¹⁶⁶ and these techniques showed that the pendant peripheral platinum centers acquire electron density at the expense of electron density of the core N 1s orbitals and that both chromophores communicate intramolecularly.



Scheme 19. Porphyrin-cored platinum-bis(acetylide) dendrimers synthesized by Takahashi.

Takahashi and co-workers used Sonogashira/Hagihara coupling methodology (6 equivalents of *trans*-[PtCl₂(PEt₃)₂], CuCl, piperidine/dioxane) to equip *meso*-tetrakis(*p*-ethynylphenyl)porphyrin (**115Zn**) with four -PtCl(PEt₃)₂ centers to serve as a dendrimer core (**116Zn**) (Scheme 19).¹⁶⁷ (Platinum-acetylide)acetylene dendrons of generation one (**G**₁), two (**G**₂), and three (**G**₃) were synthesized in the same way and finally attached (convergent approach, CuCl in Et₃N/THF) to **116Zn** to give organometallic porphyrin dendrimers **117G**₁₋₃**Zn** in yields of 73%, 67%, and 41%. Electronic studies revealed that the ϵ values of the porphyrin part as well as its fluorescence at 617 nm (excitation in the platinum-acetylide MLCT band) decrease with an increase in the generation, which indicates efficient energy transfer from the periphery to the core.

A similar *trans*-bis(acetylide)Pt(II)(PBU₃)₂ moiety was employed by Harriman and Ziessel to interconnect a zinc(II) porphyrin fragment to a [Ru(bipy)₃]²⁺ group.¹⁶⁸ *meso*-Tris(mesityl)-(*p*-ethynylphenyl)porphyrin (**118Zn**) was reacted with one or half an equivalent of *trans*-[PtCl₂(PBU₃)₂] in the presence of catalytic amounts (1%) of CuI in a *iso*-Pr₂NH/THF mixture to give dyad **119Zn** and triad **120Zn** in 72% and 20%, respectively (Scheme 20). A [Ru(bipy)₃]²⁺ fragment was attached to **118Zn** by a similar methodology using [Ru(bipy)₂(4-ethynyl-2,2'-bipyridyl)]²⁺ to give triad **121Zn** in a yield of 51%. Hardly any electronic interaction between the chromophores is observed within these systems in the ground state. In the triad, the Pt moiety neither influences the reduction potential of the zinc(II) porphyrin nor that of the [Ru(bipy)₃]²⁺ moiety, although it makes each terminal moiety more difficult to reduce as a result of charge donation from the Pt(II) center to the alkyne-bridged ligands.

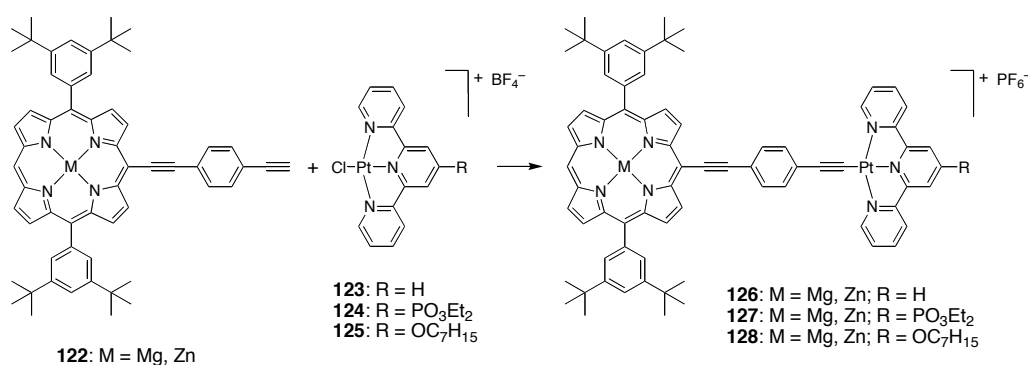


Scheme 20. Triads consisting of a zinc porphyrin, a platinum bis(acetylide) unit, and either another zinc porphyrin or a Ru(bipy)₃ unit, synthesized by Ziessel and Harriman.

Upon excitation of the porphyrin part of **121Zn** (565 nm), it was found that the fluorescence is quenched by ca. 50% with respect to a non-peripherally-metalated, reference zinc

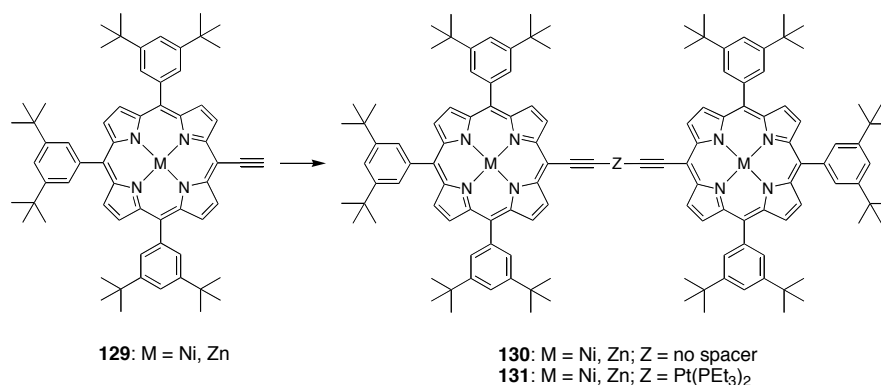
porphyrin. Because the central Pt(II) bis- σ -acetylide imposes a barrier for through-bond electron exchange, it was postulated that the quenching originates from a Förster-type singlet-to-triplet energy transfer. Excitation into the upper vibrational levels of the S_2 state of the zinc(II) porphyrin gives two different decay processes for **120Zn** and **121Zn**. Whereas rapid $S_2 \rightarrow S_1$ internal conversion, followed by $S_1 \rightarrow S_0$ fluorescence takes place in **120Zn**, **121Zn** is involved in an additional photoprocess that competes with this decay, namely the energy transfer from the zinc porphyrin to the [Ru(bipy)₃] fragment.

Another type of Pt(II)-acetylide fragment was employed by Odobel and Hammarström in complexes for photoinduced electron transfer.¹⁶⁹ They hypothesized that the σ -nature of the C-Pt bond could allow large electronic coupling between the substituents. Several derivatized terpy ligands (with hydrogen (**123**), phosphonate (**124**) or ether (**125**) *para*-substituents) were reacted with [Pt(COD)Cl₂] to form the corresponding platinum-acetylide complexes. A zinc(II) porphyrin (**122Zn**) or magnesium(II) porphyrin (**122Mg**) tethered with a terminal alkyne fragment was subsequently attached to these compounds *via* a Sonogashira/Hagihara coupling in the presence of CuI and *iso*-Pr₂NH, yielding the corresponding metalloporphyrin-ethynyl-Pt(terpy) diads in yields ranging from 45% to 71% for the zinc(II) porphyrins and 60% to 90% for the magnesium(II) porphyrins (Scheme 21).



Scheme 21. Metalloporphyrin-(acetylide)terpy Pt dyad developed by Odobel and co-workers.

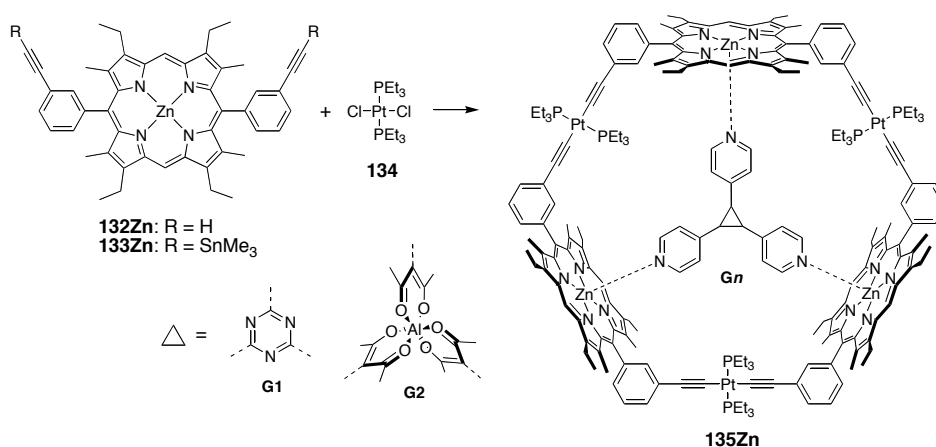
Electrochemical studies (CV) indicated that whereas the metal ion in the porphyrin had little effect on the reduction potential of the platinum center, the *para*-substituent of the terpy fragment has a measurable effect on the reduction potentials of the zinc(II) and magnesium(II) porphyrin and on the oxidation potential of the zinc(II) porphyrin. This effect is most pronounced on the reduction potential of the platinum center with an electron withdrawing substituent (phosphonate), stabilizing the reduced terpyridine and thus facilitating the reduction of this moiety. The absorption spectra of all dyads are virtual superpositions of those of their constituents, but fluorescence measurements showed that the fluorescence of the porphyrin moieties are almost quantitatively quenched in every case, compared to reference porphyrins. The authors found that an electron transfer from the porphyrin to the platinum units is the only reasonable explanation for the very rapid quenching of the S_1 state of the porphyrins.



Scheme 22. Triads prepared by Yeh *et al.*

In order to test the previously postulated hypothesis of beneficial contribution of the platinum-acetylide unit to conjugation of its substituents, Yeh and co-workers synthesized two types of bis(porphyrin) compounds.¹⁷⁰ Mono-acetylene porphyrin precursors **129Ni** and **129Zn** were reacted with either *trans*-[PtCl₂(PEt₃)₂] in diethylamine to yield platinum-bis(acetylidoporphyrin)s **131Ni** and **131Zn** in yields of 66–68% or they were reacted with CuI in air to form butadiyne-linked bis(porphyrin)s **130Ni** and **130Zn** (Scheme 22). The porphyrin subunits are much more strongly coupled in the ground state (as shown by UV/Vis and CV measurements) in **130Ni** and **130Zn** than in their Pt-linked counterparts. Evidence based on UV/Vis measurements on the mono-cations, generated by oxidation with [(*p*-BrC₆H₄)₃N]SbCl₆, supported this even further. The Ni chelates interact more strongly with one another than the corresponding Zn analogues.

In search of novel ways to interconnect porphyrin subunits in cyclic, trimeric porphyrin hosts, Sanders and co-workers used *trans*-bis(acetylide)-platinum(II)¹⁶³ moieties.¹⁷¹ With respect to their butadiyne-linked congeners,¹⁷² the formal insertion of a square-planar Pt center into the ≡C-C≡ single bond was anticipated to lead to a larger central cavity, which would in turn generate different host-behavior in terms of the size of suitable guest molecules.



Scheme 23. Pt-bis(acetylide)-bridged porphyrin trimers of Sanders.

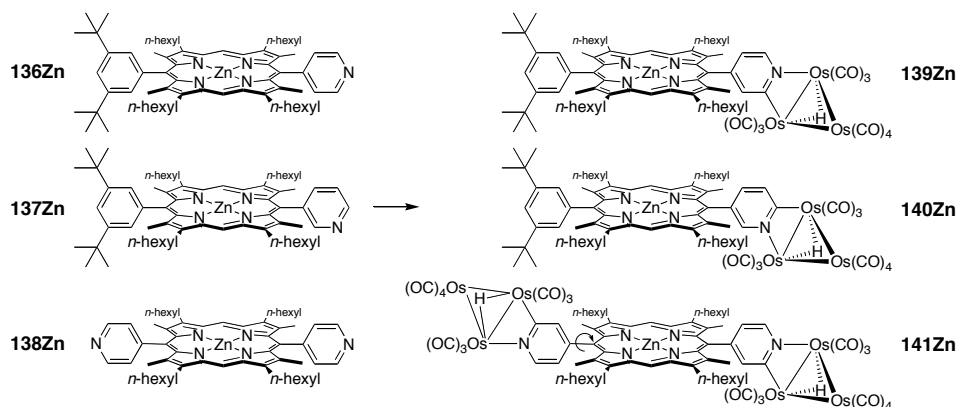
A zinc(II) β -octa-alkyl-5,15-bis(phenyl)-porphyrin, the phenyl groups of which contain acetylene groups at their 3-positions (**132Zn**) was coupled with *trans*-Pt(PEt₃)₂Cl₂ (**134**) in diethylamine using a Sonogashira/Hagihara-type protocol, yielding 16% of the desired trimer **135Zn** (Scheme 23). Unfortunately, this trimer cannot be used for templation. To that end, **132** was converted into the corresponding tin-acetylide **133Zn** and subsequently trimerized using Cu^I catalysis without the use of an amine to give **135Zn** again in 16% yield. As predicted, the increased cavity size leads to a decreased binding constant of 2,4,6-tris(*p*-pyridyl)pyrazine **G1** compared to the corresponding butadiyne-linked trimeric host (3×10^7 vs. 10^9 M⁻¹), whereas a slightly larger guest, **G2**, binds with a high binding constant of 10^{10} M⁻¹. Contrary to the smaller host, the synthesis of **135Zn** is not efficiently templated by its most strongly bound guest, which only increases the yield by 25% to 20%.

The bis(acetylide)platinum group is perfectly suited to function as a construction moiety in (multi)porphyrin systems owing to its relative robustness and inertness. The findings above altogether suggest that, if maximum ground state communication between two molecular constituents is desired, the platinum-acetylide unit should not be the first unit of choice. At the same time, its electronic properties make it an ideal connector for systems that aim at photo-induced energy transfer operating *via* a Förster type mechanism. One drawback of this unit is the synthetic route towards it, which invariably employs Cu(I). This makes the use of free-base porphyrin-containing substrates awkward because of the tendency of copper to form the corresponding Cu(II) complexes. To arrive at free-base porphyrin platinum-acetylide conjugates, metalloporphyrins that are readily demetalated, *e.g.*, magnesium porphyrins, could therefore be used as a valuable synthetic intermediate.

1.3.5 Miscellaneous

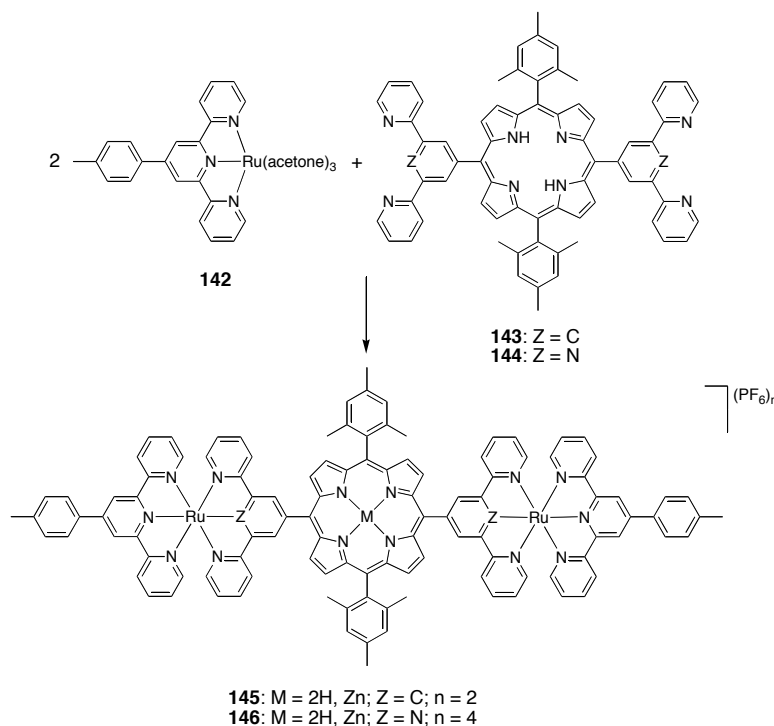
Sanders *et al.* reacted several *meso*-pyridine-substituted zinc porphyrins (**136Zn–138Zn**) with Os₃(CO)₁₀(NCMe)₂ in dichloromethane at room temperature (Scheme 24).¹⁷³ Osmium-to-nitrogen coordination followed by an activation of the *ortho* C–H bond leads to the formation of cyclometalated hydrido complexes **139Zn–141Zn** in yields of 31% (**140Zn**) to 42% (**139Zn**). As a result of steric demands, **137** was only cyclometalated at the pyridyl position *para* with respect to the porphyrin ring rather than at the corresponding *ortho*-position to give **140Zn**. When the 5,15-bis(pyridyl) zinc system **138Zn** was metalated, two different atropoisomers can be envisaged: one with the activated C–H bonds on the same side of the porphyrin plane, **141Zn $\alpha\alpha$** , and **141Zn $\alpha\beta$** , with the activated ends on opposite sides. Indeed, while the room temperature ¹H NMR spectrum only shows evidence for highly dynamic species, at low temperature signals arise that are consistent with the proposed structures. In addition, there is a possibility for both hydrides to be in front, and one of them being in front and the other one in the back. The distance between them, however, makes them spectroscopically indistinguishable. Compared to the parent zinc porphyrins **136Zn–138Zn**, the UV/Vis spectra of **139Zn–141Zn** exhibited slight hypsochromic shifts of 4, 3, and 7 nm, respectively, of the Soret band. While the fluorescence intensities of the metalated complexes

are somewhat quenched with respect to those of the parent compounds, the phosphorescence intensities increase upon metalation. The authors attribute this observation to a heavy atom effect rather than arising from energy- or electron transfer processes within the molecules.



Scheme 24. Organometallic porphyrins prepared by Sanders.

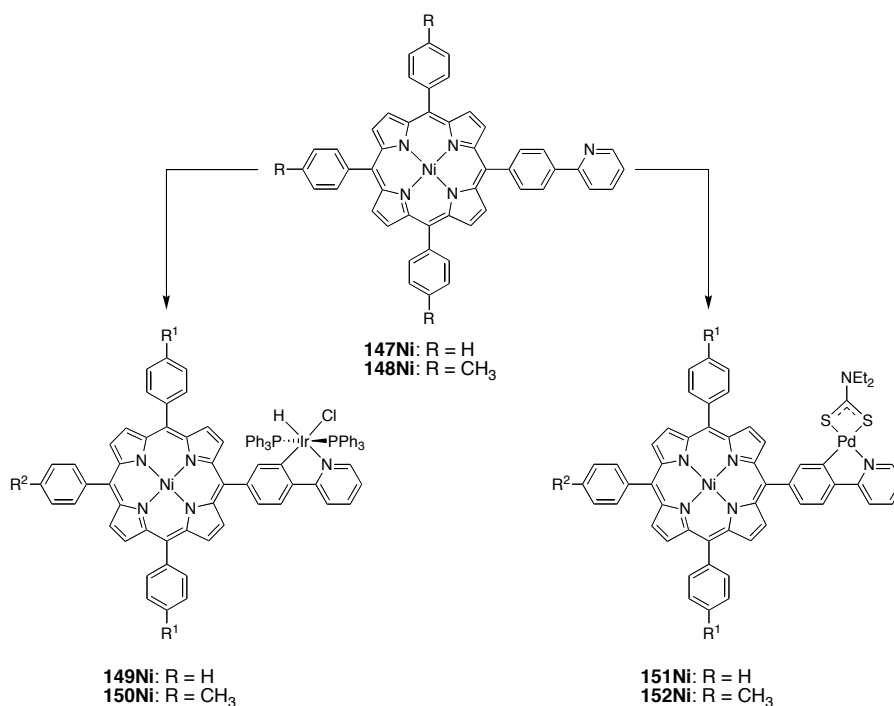
Transition-metal complexes of poly(2-pyridyl)phenyl groups have emerged as interesting optical materials.¹⁷⁴ Their combination with porphyrins, being a highly versatile chromophore itself, has therefore been subject of research. Cycloruthenation was employed by Dixon and Collin as a method to obtain porphyrins with *meso*-linked tridentate NCN moieties.¹⁷⁵ They used a Lindsey/MacDonald [2 + 2] condensation of 5-mesityl-dipyrromethane and 3,5-bis(2-pyridyl)benzaldehyde to give multitopic ligand **143** in 39% yield (Scheme 25).



Scheme 25. Peripherally-ruthenated porphyrins prepared by Collin.

Treatment of **143** with $[\text{Ru}(\text{tterpy})(\text{acetone})_3]^{3+}$ (**142**), generated by treatment of $[\text{RuCl}_3(\text{terpy})]$ with AgBF_4 in acetone, in refluxing *n*-BuOH yielded bis(PF_6) salt **145** in 57% yield after column chromatography and anion exchange. The corresponding zinc chelate **145Zn** was readily prepared in quantitative yield *via* a reaction with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in a methanol/acetonitrile mixture. These two compounds were compared to the analogous *NNN* complexes **146** and **146Zn** with cyclic voltammetry and UV/Vis spectroscopy. The researchers found that there is a larger extent of communication between the porphyrin and the peripheral ruthenium(II) centers in the case of Ru-*NNN* ligation than in the case of Ru-*NCN* ligation. In contrast to some bis(ferrocenyl)porphyrins (*vide supra*), there is no electronic communication between the terminal ruthenium centers in any of these compounds in the ground state.

Another study employed the cyclometalating properties of phenylpyridine groups to peripherally metalate porphyrins. Nickel porphyrins were equipped with *meso*-(*para*-(2-pyridyl)phenyl) groups and subsequently metalated the pyridylphenyl unit with palladium and iridium (Scheme 26).¹⁷⁶

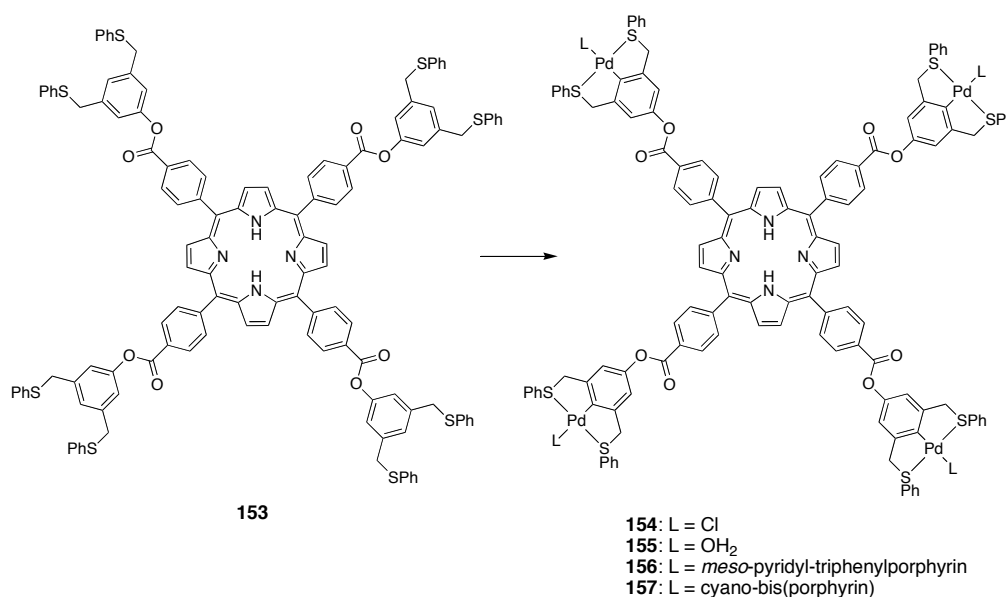


Scheme 26. Cyclometalated porphyrins prepared by Leung.

Reaction of either the *meso*-tris(phenyl) derivative **147Ni** or the analogous *para*-tolyl compound **148Ni** with $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{O}=\text{CMe}_2)_2]\text{BF}_4$ in methylene chloride at room temperature furnished iridium(III) complexes **149Ni** and **150Ni** in moderate yields of 27 and 40%, respectively. Both starting complexes were also shown to react readily under electrophilic palladation conditions with $\text{K}_2[\text{PdCl}_4]$ in a refluxing solvent mixture of MeOH/THF. The initial products of this reaction, assumed to be chloride-bridged dimers, are

insoluble in the reaction mixture and precipitate out. The authors suggested that this may explain why similar bis(phenylpyridine)porphyrins do not undergo double palladation (precipitation occurs after the first metalation step). The insoluble intermediates were converted into mono-palladium complexes **151Ni** and **152Ni** by treatment with $K_2SC(S)NEt_2$ in 27 and 29%. Unfortunately, the authors did not comment as to why the yields are rather low in all cases. It is of note that the peripheral metalation leads to bathochromic shifts of the Soret band for all complexes, while the Q bands remain at the same position. This shift was larger for the Ir complexes (~5 nm) than for their Pd counterparts (~1 nm).

ECE-pincer metal complexes have come under the attention of researchers operating in different fields of chemistry, particularly catalysis and materials chemistry, owing to the multitude of tunable properties *via* its modular characteristics.¹⁷⁷⁻¹⁸⁰ The merger of the properties of these molecules with those of porphyrins has encouraged a few researchers to explore their molecular combinations.^{175,181,182} The rigid four-fold symmetry of the porphyrin was exploited by Reinhoudt and co-workers as an organization precept to non-covalently synthesize multi-porphyrin systems through metal-to-ligand interactions.

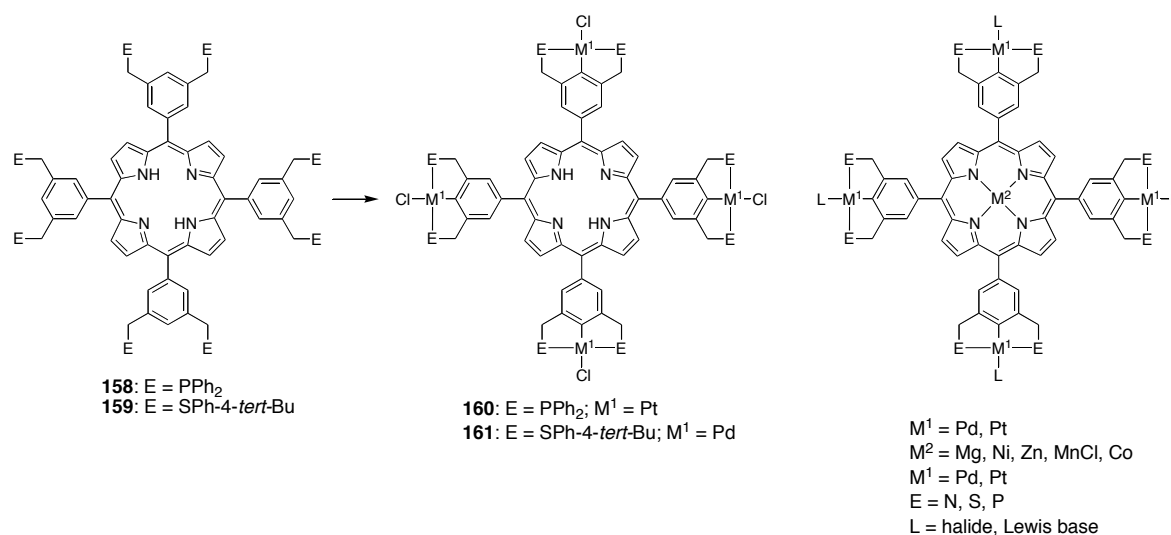


Scheme 27. Peripherally-palladated porphyrins prepared by Reinhoudt *et al.* for self-assembly studies.

A phenolic SCS-pincer ligand, 3,5-bis[(phenylsulfido)methyl]phenol (four equivalents) was reacted with one equivalent of tetrakis(4-chlorocarbonylphenyl)porphyrin and triethylamine in dichloromethane to yield tetrakis(SCS-pincer) porphyrin **153** in 32% yield. The corresponding tetra-SCS-pincer Pd complex **154** was synthesized by treating **153** with 4.04 equivalents of $[Pd(NCMe)_4](BF_4)_2$ in a $CH_2Cl_2/MeCN$ mixture and after treatment with NaCl, the tetrakis(SCS-PdCl)porphyrin product was obtained in 90% yield (Scheme 27). Dehalogenation of **154** with four equivalents of $AgBF_4$ gave the tetra-cationic aqua species **155**, which was subsequently treated with 5-pyridyl-10,15,20-tris-(phenyl)-porphyrin to give the pentameric porphyrin assembly **156** in quantitative yield. A nonameric porphyrin array

(**157**) was also quantitatively assembled from **155** and four equivalents of a cyano-bis(porphyrin). The authors reported that there is no appreciable communication between the porphyrin units in the ground state, but, unfortunately, no excited state measurements were undertaken to probe light-induced electron or energy transfer.

Several ECE-pincer ligand groups were later directly merged with the tetraphenylporphyrin skeleton.¹⁸² A general procedure was developed by Klein Gebbink and co-workers to obtain *meso*-tetrakis(ECE-pincer)porphyrins **158** and **159** in a modular way. The SCS-pincer-porphyrin hybrid could be metalated *via* the same procedure as published earlier by Reinhoudt (*vide supra*) in an impressive yield of 90% (Scheme 28). It is notable that in both cases, palladation of the porphyrin macrocycle was not observed despite the fact that an electrophilic Pd²⁺ complex was used. Another way to effect a selective peripheral metalation was transcyclometalation (TCM) methodology, which relies on an ECE-pincer selective mechanism.¹⁸³ Thus, when tetrakis(PCP-pincer)porphyrin **158** was treated with four equivalents of [PtCl(NCN)] in refluxing toluene, the desired tetra-platinated porphyrin **160** was obtained in quantitative yield. The authors found that peripheral metalation brings about a bathochromic shift of the Soret band with a concomitant broadening. Interestingly, platination leads to much larger red-shifts than palladation (11 vs. 6 nm). It was furthermore found that the porphyrin fluorescence of **161** was quenched by 74% relative to that of **159**. Later, the authors found that hetero-multimetallic complexes (Scheme 28, right)¹⁸⁴ could be obtained by selecting the right order of metalation steps of the parent multitopic ligands. These pincer-porphyrin hybrids have been used as templates in ring-closing metathesis¹⁸⁵ and catalysis.^{186,187}



Scheme 28. Pincer-porphyrin hybrids synthesized by Klein Gebbink *et al.*

1.4 Concluding Remarks

As this chapter underlines, the covalent combination of (metallo)porphyrins with metalloligand groups in general and with organometallic moieties in particular may lead to interesting new materials with special properties. There are many ways to synthesize porphyrins with a peripheral metal-to-carbon bond. Especially the chemical robustness of the organometallic group plays a role of importance in selecting the synthetic route toward the desired molecules, since the reaction conditions used for porphyrin synthesis, *i.e.* employing Lewis or Brønsted acidic catalysts, are often incompatible with the lability of the metal-to-carbon bond.⁶⁸ When the synthetic strategy relies on the selective metalation of a free-base porphyrin with (an) attached ligand group(s), care should be taken to choose mild, orthogonal metalation methods that are capable of addressing either the porphyrin or the peripheral ligand moiety selectively.

Within the peripherally-metalated (metallo)porphyrins, both the (metallo)porphyrin entity and the peripheral organometallic group can serve a multitude of purposes. The porphyrin can be used as a photochemical group, as a redox-active unit or it can function as a functional substituent, whose electronic properties can be readily tuned by virtue of metalation. The axial coordination properties of metalloporphyrins furthermore provide ample opportunities to bind functional groups in a non-covalent way.

Transient peripherally-metalated porphyrins have found wide application in the catalytic functionalization of the porphyrin periphery. Arnold and co-workers, however, were the first to investigate the properties of some of these molecules in their own right and found that these compounds exhibit a number of interesting properties. This fact may be taken as an incentive for further exploration of complexes that are normally viewed as synthetic intermediates.

The inherent mechanical features of the organometallic (*e.g.*, a ferrocenyl group) or its Lewis-acidic nature can be exploited to organize multiple functional groups in a covalent way by virtue of rotation around, for instance, a ferrocene hinge, or in a non-covalent way through coordination of functionalized Lewis bases to the peripheral Lewis acid. The peripheral organometallic unit can be used to influence the porphyrin, but the porphyrin can concomitantly also affect the properties of the organometallic. These combinations can lead to interesting electrochemical and photophysical devices.

Finally, this review reveals the relatively modest extent to which the merger of organometallic entities with porphyrins has been exploited to date. A few organometallic groups such as ferrocenyl groups and Pt-bis(acetylido) complexes have been extensively applied because of their unique properties and robustness. The molecular combination of porphyrins with less-stable, *i.e.* more reactive, organometallic moieties has yet to commence. Research in this area is encouraged, as the amalgamation of the photo- and redox-active properties of the (metallo)porphyrin with those of the organometallic complex may give rise to new reactivity profiles for either or both.

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