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Metalated Porphyrins

Merging Porphyrins with Organometallics: Synthesis and Applications

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organometallic chemistry ·
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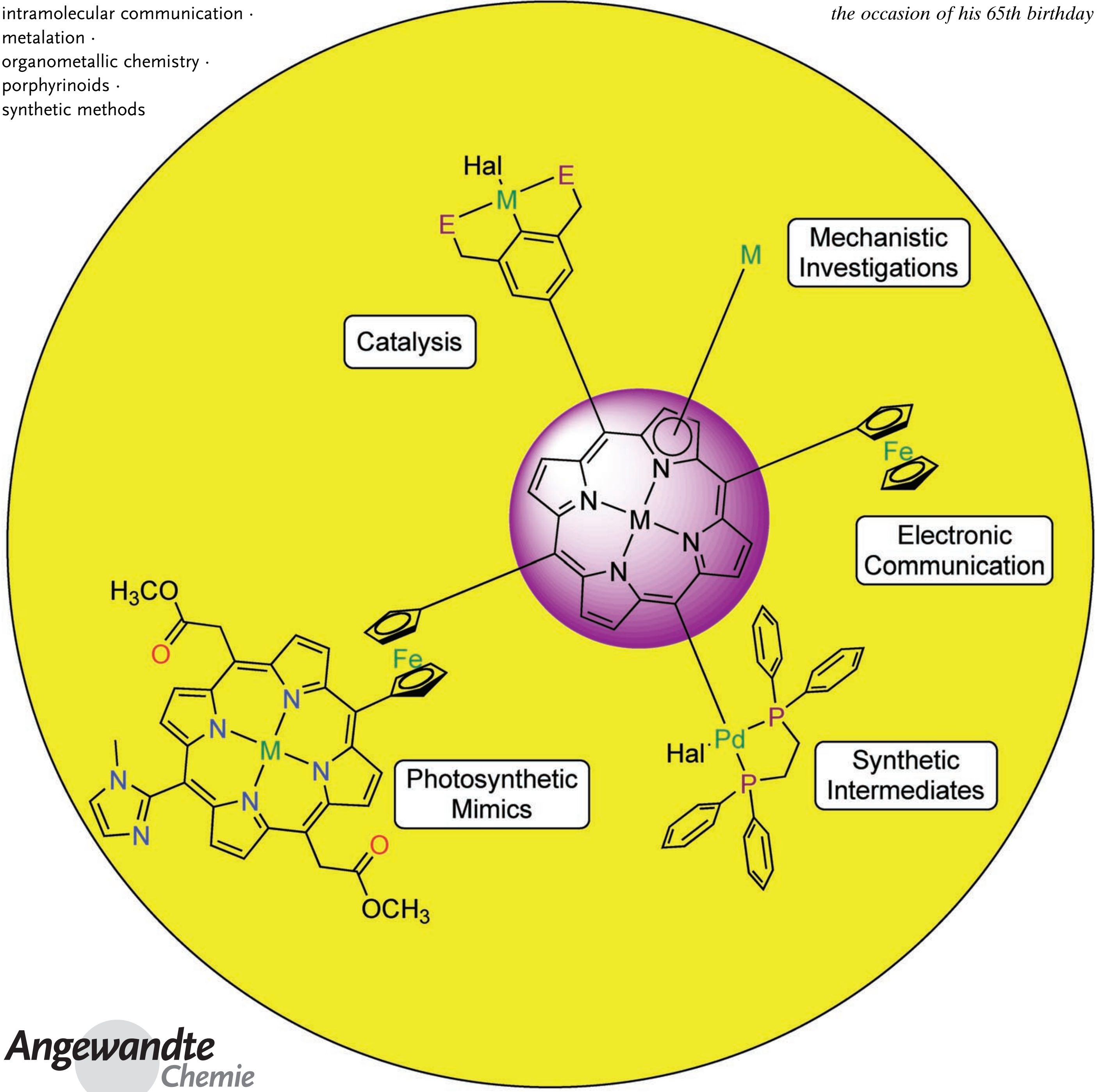
Dedicated to Professor Gerard van Koten on the occasion of his 65th birthday



The coordination chemistry of porphyrins has traditionally involved the ability of the porphyrin's tetrapyrrolic core to accommodate metal ions of varying charges and sizes, and on the organometallic chemistry of the resulting metalloporphyrins. However, the organometallic chemistry of porphyrins is not necessarily restricted to the metal bound in the porphyrin core, but can also be extended to the porphyrin periphery, be it through direct metalation of the porphyrin macrocycle at the meso or β position, or by attachment to or merger of the porphyrin skeleton with ligands, followed by metalation. This Review focuses on the synthetic strategies used for porphyrins with peripheral metal–carbon bonds. The exciting results that have been produced underscore the importance and future potential of this field.

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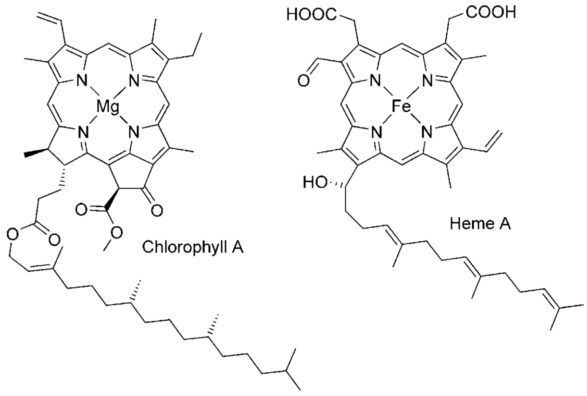
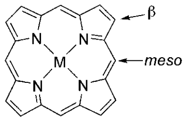
1. Introduction

The chlorophyll and heme pigments are the heart of the energy supply chain of life on Earth and have thus 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, that is, porphyrins, because of their synthetic accessibility and modularity.[1,2] Porphyrins and their metal complexes have been used as functional building blocks in materials that are of interest for, amongst other things, 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. This Review will focus on a relatively new research area, namely porphyrins that bear organometallic centers at extra-annular positions, mostly by linking at the *meso* or β position(s).





(Metallo)Porphyrin
M = 2H, metal

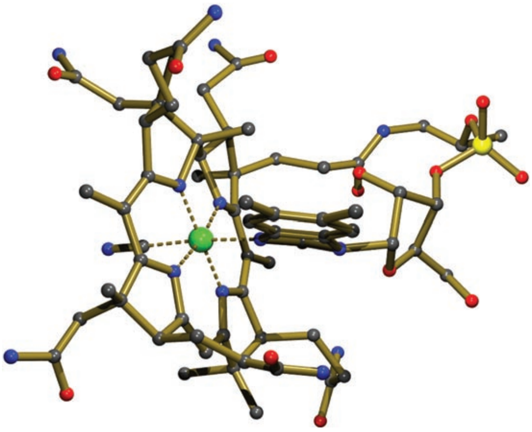


Figure 1. Structure of the organometallic fragment in vitamin B_{12} as determined by X-ray crystallography. Green Co, red O, blue N, yellow P.

Ever since the metalloporphyrins were discovered, a great deal of research has been devoted to the exploration of their axial coordination[10–12] and organometallic[13–15] chemistry, owing in part to the fact that a key organometallic structure occurring in nature is vitamin B_{12}, cyanocobalamin, which is a tetrapyrrolic cobalt complex (Figure 1). Later, it was realized that the coordination chemistry of metalloporphyrins is not necessarily restricted to the tetrapyrrolic core, but can also occur at its periphery. Thus, 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] bipyridines[31–33]/phenanthrolines,[34–38] terpyridines,[39–43] carboxylates,[44,45] imidazoles,[46] and other porphyrins.[21,47–52] Another interesting example is given by the N-confused porphyrins, in which one pyrrole ring is flipped. These compounds can accommodate a metal within the porphyrin system while simultaneously acting as a monodentate ligand 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,

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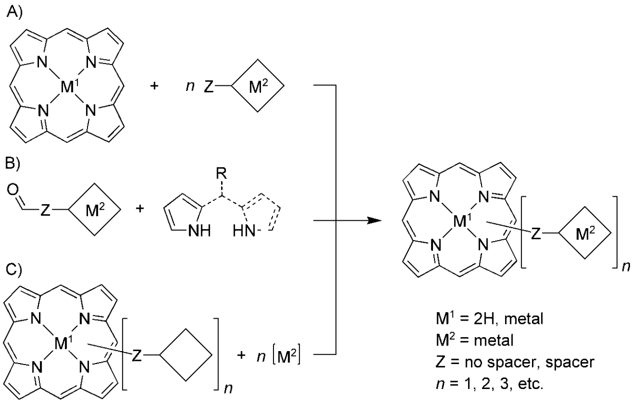
which enhance or complement those of the metalloporphyrin. This field of porphyrin research has delivered some very exciting results. Sauvage and co-workers, for example, complexed two metalloporphyrin-linked terpyridyl groups to several metal centers (iridium, ruthenium, or rhodium), and accomplished photoinduced charge separation mediated by the bis(terpy) metal unit.[40–42,58] Pyridine- and imidazole-substituted metalloporphyrins have also been used to construct multiporphyrin assemblies by intermolecular coordination of complementary Lewis acidic and Lewis basic sites. More recently, Reek and co-workers used zinc porphyrins in combination with P,N ligands in the development of libraries of supramolecular catalysts.[59,60]

There is increasing interest in porphyrins with peripheral metal centers, in which the porphyrins are covalently attached to metal centers by one or several carbon–metal bonds. 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, 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 Review aims at surveying publications on porphyrins that bear peripheral organometallic units, that is, incorporating one or more carbon–metal bonds. First, some general synthetic considerations as to at what stage during the synthetic process an organometallic group might be introduced or attached to the porphyrin system will be discussed. Thereafter, the compounds are categorized with respect to the organometallic constituent. Emphasis is placed on the synthetic step in which the organometallic compound and porphyrin are merged or joined. In most cases, potential applications of these compounds will also be discussed. In Section 3.3 on ring-metalated porphyrins, not only the isolated organometallic compounds as such are presented, but also transient organometallic species present during the catalytic functionalization of a porphyrin. The large number of reports on peripherally-metalated porphyrins does not allow the inclusion of 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.

2. Synthesis

There are three general ways to synthesize peripherally metalated porphyrins (Scheme 1). Route A relies on the attachment of organometallic groups to a (metallo)porphyrin. In a number of cases this has been accomplished by a metal-mediated coupling of the organometallic species to the porphyrin. However, this requires both substrates to be stable under the often basic reaction conditions, and reagents that do not metalate or transmetalate the metalloporphyrin group. To avoid this unwanted reaction, Lindsey et al. developed for example a copper-free Sonogashira reaction for the modification of free-base (i.e., non-metalated) porphyrins to counteract copper coordination that occurs when copper(I) is used as a cocatalyst.[64] As almost all porphyrin syntheses rely on an acid-catalyzed condensation of polypyrroles with aldehydes, porphyrins with peripheral carbon–metal bonds can also be obtained by appropriate functionalization of either or both reaction partners (Route B, Scheme 1). For this approach to succeed, the organometallic building block has to be resistant towards Lewis or Brønsted



Scheme 1. Three general synthetic strategies towards peripherally metalated porphyrins.

Bart Suijkerbuijk was born in Roosendaal (the Netherlands) in 1979. He completed his MSc degree in 2002, and received his PhD in chemistry in 2007 from Utrecht University (the Netherlands) on Pincer–Porphyrin Hybrids with Prof. Gerard van Koten and Prof. Bert Klein Gebbink. He then joined the group of Prof. Caroline Springer at The Institute of Cancer Research in Sutton, London (UK) as a postdoctoral fellow, and is currently working on the design and development of novel kinase inhibitors in the fight against cancer.

Bert Klein Gebbink, born 1969 in Lichtenvoorde (the Netherlands), obtained his PhD in 1998 from Nijmegen University with Prof. R. J. M. Nolte in the field of supramolecular and bioinorganic chemistry. After a postdoctoral stay at Stanford University in the group of Prof. T. D. P. Stack, he joined the group of Prof. van Koten at Utrecht University in 1999 as a postdoctoral fellow. In 2002 he was appointed as an assistant professor, and in 2005 associate professor in the same group. In 2006 he was promoted to full professor at Utrecht University. His current research interests include homogeneous catalysis and bioinorganic chemistry.

acids, a property that is not often encountered in organometallic complexes. Functionalized aryl aldehydes have often been used in this context (see Sections 3.1 and 3.2), but to the best of our knowledge, no procedures have been published that use organometallic-functionalized pyrroles. There are, however, some examples of [2+2] procedures with dipyrromethanes metalated in the 5-position as a source of the metalloligand group (see Section 3.1).

The third route, Route C, uses porphyrins with pre-attached ligands. These ligands can be part of the tetrapyrrolic macrocycle itself, they can be fused to the porphyrin ring, or attached by 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, therefore orthogonal metalation procedures should be used to ensure selectivity of either metalation step for the targeted site. If this is not an option, the most discriminative metalation step should be carried out first, which protects one particular ligand site, and thereafter the other site can be metalated. This approach is well illustrated by, for instance, the ring-mercuration of deuteroporphyrin IX (see Section 3.3.1).[65] Prior to treatment of this porphyrin with mercury(II) acetate, its core is protected with copper(II) or zinc(II) to prevent mercury insertion.[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 organometallic compounds demands careful planning of the synthetic route towards the desired products.[68] In this Review, we hope to provide the reader with some useful suggestions based on several examples.

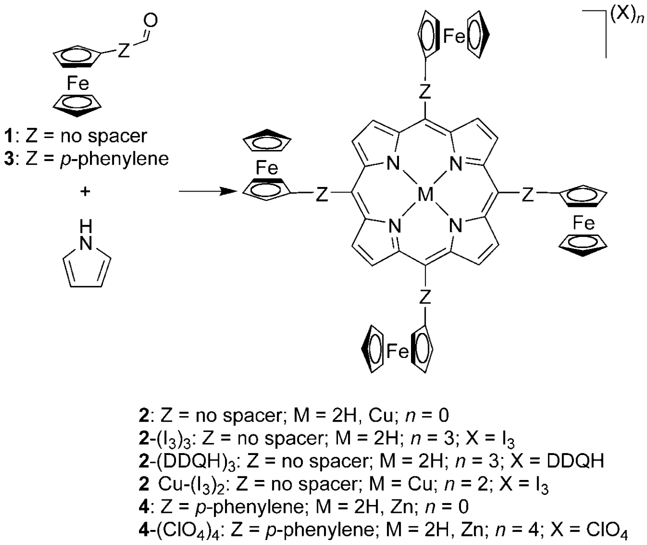
3. Peripherally Metalated Porphyrins

3.1. Porphyrin–Ferrocene Hybrids

Ferrocene-substituted porphyrins are undoubtedly the most intensively studied class of peripherally metalated porphyrins. Ferrocene and porphyrin units have often been combined covalently, even at the axial positions of metalloporphyrins,[69,70] for several reasons. As 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 singlet excited state of porphyrins. Thus, 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 relative ease with which the two cyclopentadienyl rings can rotate about the Cp−Fe−Cp axis.[72] The connection 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. Furthermore, the relative inertness of the ferrocenyl group in porphyrin–ferrocene constructs allows for completely selective metalation of the porphyrin moiety without affecting the ferrocenyl groups. We have attempted to categorize the literature according to the functions of the ferrocene; however, much of the research in this area is conducted across the boundaries set by these categories.

3.1.1. Synthesis and Electronic Communication

The first ferrocenyl-substituted porphyrin, *meso*-tetraferrocenylporphyrin (**2**), was prepared by Wollmann and Hendrickson in 1977,[73] using Adler's procedure[74] with pyrrole and formylferrocene (**1**) in refluxing propionic acid to furnish an atropoisomeric mixture of the desired product in 40% yield after chromatographic purification (Scheme 2). A thorough analysis of the ^{1}H and ^{13}C NMR, IR, and UV/Vis spectra led the authors to conclude that its synthesis had been successful. The copper(II) complex, **2** Cu, was also synthesized by metalation of **2** with copper acetate.[73] From UV/Vis spectroscopy and low-temperature ^{57}Fe Mössbauer spectroscopy data on the doubly or triply oxidized species **2**-$(I_3)_3$, **2** Cu-$(I_3)_2$, and **2**-(DDQH)$_3$, it was concluded that there is a rather strong π-electron interaction between the porphyrin and *meso* ferrocenyl groups. This interaction is probably caused by the relative coplanarity 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]



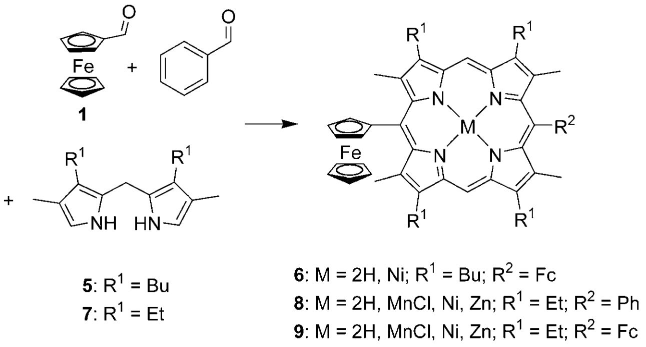
Scheme 2. *Meso*-tetraferrocenylporphyrins from Hendrickson (**2**)[73] and Bruice (**4**).[77]

Meso-tetrakis(4-ferrocenylphenyl)porphyrin (**4**) was synthesized in 15% yield from 4-ferrocenylbenzaldehyde (**3**) and pyrrole using the same procedure as Hendrickson

(Scheme 2). The UV/Vis spectrum is very similar to that of *meso*-tetraphenylporphyrin.[77] The corresponding zinc(II) complex **4**Zn, obtained in 67% yield by treatment of **4** with zinc acetate dihydrate in a boiling chloroform/methanol mixture, shows no ground-state electronic communication.

The *meso* phenylene groups of **4** are expected to adopt a perpendicular orientation relative to the porphyrin ring, which, in combination with the expected lack of coplanarity of the ferrocenyl groups and *meso* phenylene groups, leads to a strong decrease in orbital overlap between the porphyrin and ferrocene systems. This assumption was further corroborated by cyclic voltammetry (CV), which indicated a weak ground-state interaction. The corresponding tetrakis(ferrocenium) derivatives **4**-$(ClO_4)_4$ and **4**Zn-$(ClO_4)_4$ were synthesized electrochemically, and their electronic spectra are virtually the same as those of **4** and **4**Zn, respectively. Fluorescence decay of the porphyrin-centered excited state is much faster than electron transfer from the excited singlet-state porphyrin to the ferricenium ions.

The findings of Hendrickson et al. prompted a number of researchers to attach ferrocenyl fragments directly at the porphyrin *meso* positions. It was later discovered that the use of β-octaalkylporphyrins to maximize the mutual coplanarity can greatly enhance this interaction. This effect 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 coplanar with the porphyrin ring, as shown by X-ray crystallographic studies.[71,78–80] By a condensation of tetraalkyldipyrromethane **5** with formylferrocene, Burrell et al. obtained a single atropisomer of bis(ferrocenyl)porphyrin **6** in 58% yield (Scheme 3, Figure 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 nickel(II) complex **6**Ni ($\Delta V = 410$ mV) owing 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 3).[79]



Scheme 3. Mono- and bis(ferrocenyl)porphyrins reported by Burrell (**6**)[71] and Do and Kim (**8**, **9**).[78–80]

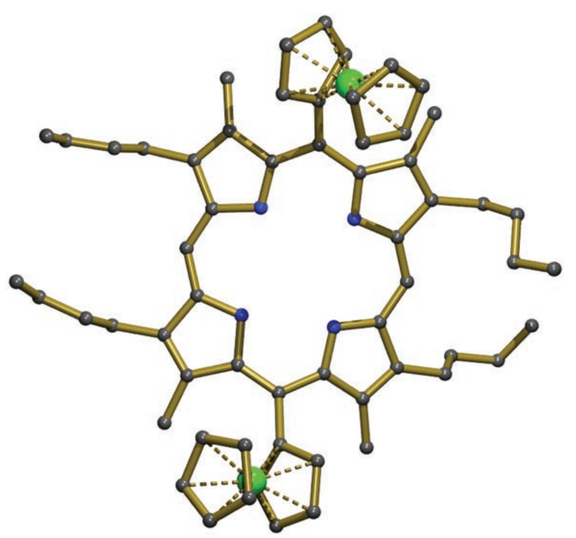
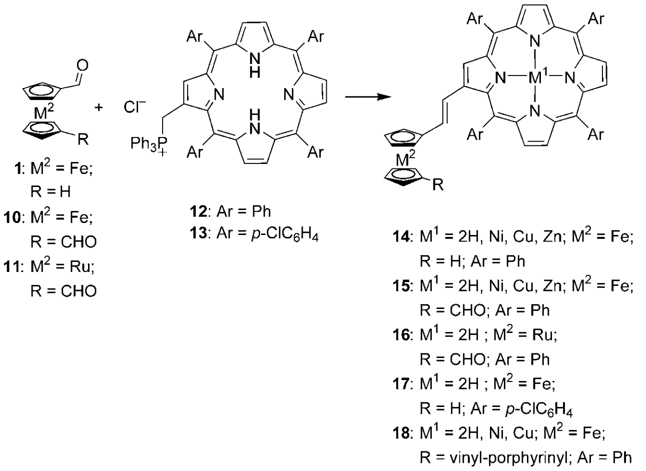


Figure 2. X-ray structure of free-base compound **6**. Green Fe, blue N.

To obtain the related monoferrocenylporphyrin **8**, a 1:1 mixture of formylferrocene and benzaldehyde was reacted with 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane in acetonitrile with a stoichiometric amount of trichloroacetic acid, followed by oxidation with *p*-choranil, to give the desired porphyrin in 27% yield after column chromatography (Scheme 3).[80] The relatively inert ferrocene moiety allowed facile metalation with manganese(III), nickel(II), and zinc(II), which were introduced by treating a refluxing solution of the porphyrin precursor (**8** or **9**) in $CHCl_3$ with a saturated, methanolic solution of the metalating agent ($MnCl_2{\cdot}4H_2O$, $Ni(OAc)_2{\cdot}4H_2O$ or $Zn(OAc)_2{\cdot}2H_2O$) to give the corresponding metalloporphyrins **8**M and **9**M in 58%, 95%, and 77% yield, respectively.[78] The relative coplanarity of the ferrocene and porphyrin components in these compounds is manifested in their cyclic voltammograms. The ferrocenyl groups in the monosubstituted compounds are more susceptible to oxidation than ferrocene itself, which indicates a strong electron-donating ability of the porphyrin. Furthermore, the redox potential of the ferrocenyl moieties changes with the metal coordinated to the porphyrin. Whereas the *meso* ferrocenyl group was less amenable to oxidation in the electron-poor **8**MnCl, oxidation of the ferrocenyl group was facilitated in the more electron-donating nickel(II) and zinc(II) complexes **8**Ni and **8**Zn. The bis(ferrocenyl)metalloporphyrins **9**M also showed strong communication between the 5,15-ferrocenyl groups mediated by the porphyrin spacer, in analogy with the systems of Burrell (**6**). The coupling is strongest in the nickel complex **9**Ni and weakest in the manganese complex **9**MnCl. Similar monoferrocenylbis(vinyl)porphyrins were later synthesized as monomers for potential porphyrin polymers.[81] The insertion of both cobalt(II) and nickel(II) was successful, but unfortunately the complexes did not form the desired polymer films.

Burrell and co-workers also researched 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-vinylic phosphonium salt **12**, a *cis*/*trans* mixture of mono-β-porphyrinyl ferrocene (**15**) was obtained in high yield (Scheme 4).[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, to give the corresponding β-vinylic metallocenyl-tetraphenylporphyrins **14**, **15**, and **18** (Scheme 4).[83]

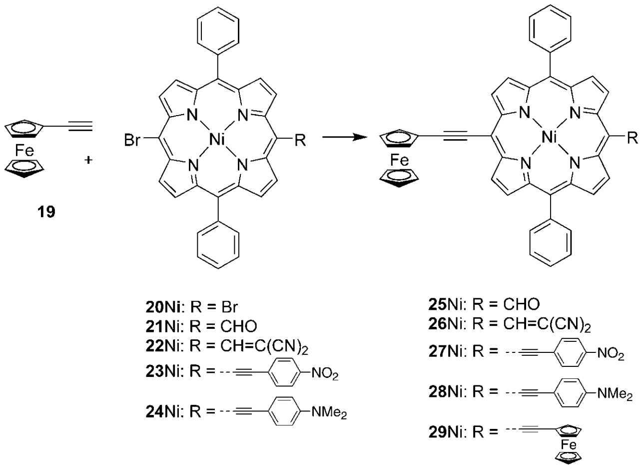


Scheme 4. β-Vinylmetallocenylporphyrins synthesized by Burrell et al.[82,83]

The copper(II), nickel(II), and zinc(II) complexes were also synthesized by treatment of **14**–**18** with the corresponding acetates in yields of up to 90%. Despite the conjugated link between the peripheral metallocene redox unit and the β positions of the porphyrin, only little mutual electronic influence in the ground state was found, as shown 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 et al. (Scheme 5).[84,85] Bis(ferrocenylethynyl)porphyrin **29** Ni was first synthesized by a Sonogashira coupling of dibromoporphyrin **20** Ni with ferrocenylethyne **19** catalyzed by [$PdCl_2(PPh_3)_2$] and CuI in a mixture of triethylamine and THF. The desired compound was obtained in 66% yield.[85]

Later, push-pull porphyrins **25** Ni–**28** Ni were synthesized in good yields (36–78%) from **19** and monobromoporphyrins **21** Ni–**24** Ni using similar procedures.[84] Despite the alkyne linker in between the porphyrin and the ferrocene groups, no significant electronic communication was observed between the porphyrin and the ferrocene, or between ferrocene groups across the porphyrin spacer. The single-crystal X-ray structure of **27** Ni revealed that the lack of communication may be attributed to an almost orthogonal orientation of the ferrocenyl cyclopentadienyl ring and the porphyrin (Figure 3). Unfortunately, no information about the structure in solution, which could corroborate this assumption, is available.



Scheme 5. *Meso*-ferrocenylethynylporphyrins synthesized by Ng et al.[84,85]

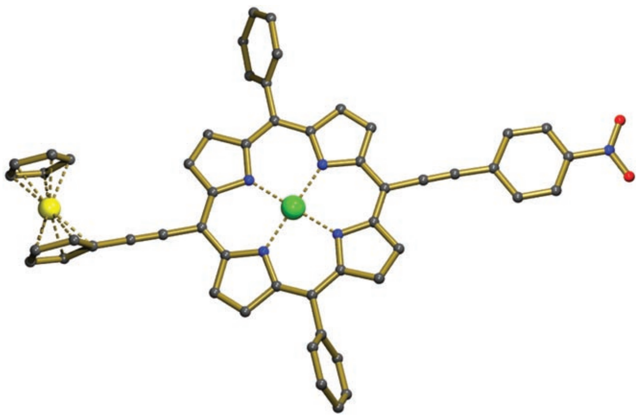
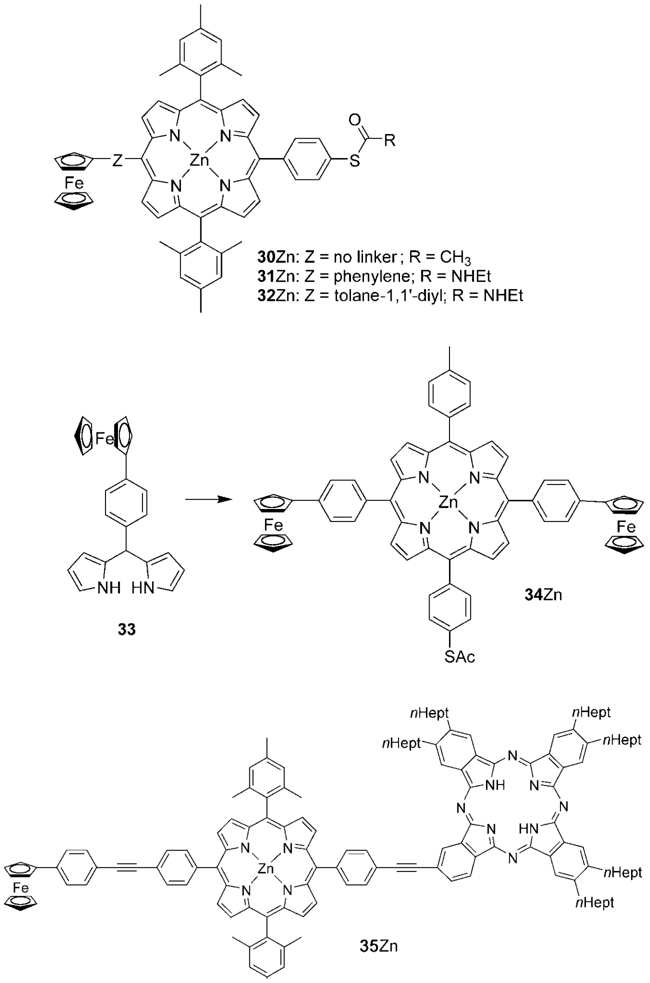


Figure 3. X-ray structure of **27** Ni, showing the orthogonal orientation of the ferrocenyl cyclopentadienyl ring and the porphyrin ring in the solid state. Green Ni, yellow Fe, blue N, red O.

Lindsey et al. studied ferrocene-appended porphyrins,[86–89] owing 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 synthesized ferrocene-spacer porphyrin molecules that contain protected thiol groups for producing self-assembled monolayers (SAMs) on gold surfaces. Using mixed condensations between a dipyrromethane, a thiophenol-functionalized aldehyde, and ferrocenecarboxaldehyde, 4-ferrocenylbenzaldehyde, or a diphenylethyne-linked ferrocene aldehyde, the desired *trans*-ferrocenylthiophenylporphyrins were obtained as their zinc(II) complexes **30** Zn–**32** Zn in yields of 37, 19, and 7%, respectively (Scheme 6).

In these syntheses, the oxidation of the porphyrinogen intermediate under acidic conditions using 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) was replaced by a neutral oxidation with *p*-chloranil to prevent oxidation of the ferrocenyl groups. Cyclovoltammetric measurements indicated that, in the ground state, the ferrocene and porphyrin moieties are not electronically coupled, except for the case when the ferrocene is directly linked to the porphyrin. A similar porphyrin bearing two ferrocenyl groups and one acetylthio functionality (**34** Zn) was also prepared from ferrocenedipyrromethane **33**, *p*-tolualdehyde, and 4-(*S*-acetylthio)benzaldehyde, but this did not influence the extent of

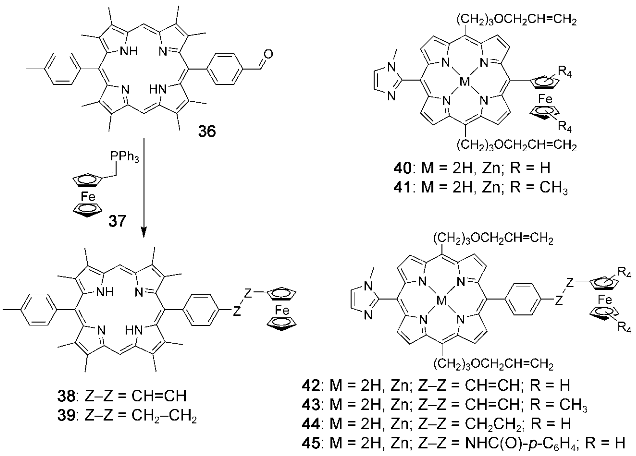


Scheme 6. Ferrocenylporphyrins synthesized by Lindsey and co-workers.[87–89]

electronic coupling between the porphyrin and the ferrocenyl groups.[87] More recently, this research group used tripodal thiol-bearing groups to make more tightly assembled SAMs. Again, a ferrocene group was attached to a tripodal thiol-containing porphyrin to store information electronically.[88] In yet another example, the ferrocene group was attached by means of a Sonogashira-type coupling of an ethynyl-appended porphyrin with 4-ferrocenyl-iodobenzene to give the ferrocene–porphyrin–phthalocyanine triad **35**Zn in 15% yield (Scheme 6).[89] Ground-state interactions were also absent in this case, 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.

3.1.2. Photosynthetic Mimics

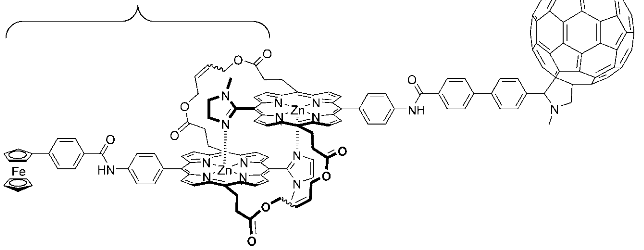
Ferrocenyl groups are able to reduce the photoexcited state of porphyrin systems. In the early nineties, *meso*-diaryl-β-octaalkylporphyrins were synthesized to which a ferrocene unit is attached by a vinylidene (**38**) or ethylene (**39**) unit (Scheme 7).[90] In contrast to the functional group pattern on the building blocks used by Burrell et al. (Scheme 4), in this case the ferrocene group was attached to the porphyrin by a Wittig-type reaction between an arylaldehyde-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* and *trans* isomers (73:27). The porphyrin–ethylene–ferrocene construct **39** was obtained by reduction of **38** with H_2 using Pd/C as a catalyst. The inter- and intramolecular quenching of the singlet excited state of the porphyrin system 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, the fluorescence of both compounds is quenched by 62% and 16%, respectively, relative to reference compounds that lack the ferrocenyl group. The fluorescence quenching was attributed to intramolecular reduction of the singlet excited porphyrin by the ferrocenyl centers.



Scheme 7. Ferrocenylporphyrins prepared by Wrighton[90] (left) and Kobuke[91–93] (right).

Kobuke et al. recently synthesized similar porphyrin–ferrocene constructs (Scheme 7, right).[91] A different approach was used, in which two equivalents of 5-(3-allyloxypropyl)dipyrromethane were condensed with one equivalent of 1-methyl-2-imidazolecarboxaldehyde and one equivalent of a ferrocene-containing aldehyde. The corresponding *trans*-AB_2C porphyrins **40**–**44** were obtained in yields of 23, 8, 15, 26, and 17%, respectively. The octamethylferrocene unit was used because of its higher reducing power. Zinc was readily introduced with $Zn(OAc)_2\cdot 2H_2O$ in a $MeOH/CH_2Cl_2$ mixture to give zinc(II) porphyrins **40**Zn–**44**Zn in yields greater than 90%.

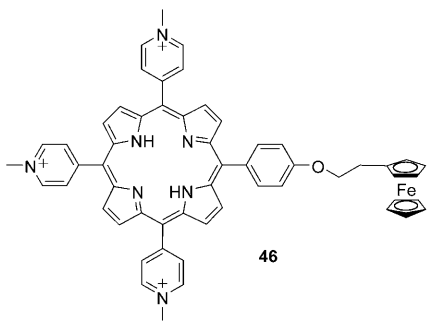
In the absence of coordinating solvents, these materials self-assemble to give slipped-cofacial dimers. In the ground state, only the directly linked ferrocenylporphyrins **40** and **41** show electronic communication, with enhanced coupling for the octamethylferrocene-containing compound **41**. This 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 completely recovered, which differs from the results obtained by Wrighton on compound **39**. The fluorescence of the corresponding zinc complexes **40** Zn–**44** Zn, which all self-assemble to form complementary dimers, was, with the exception of **44** Zn, completely quenched. Later, the same group synthesized a slipped cofacial heterodimer, which consists of **45** Zn (Scheme 7, right) and a fullerene-appended imidazolylporphyrin. The assembly was fixed by means of ring-closing metathesis, and showed a long-lived Fc$^+$–{Zn(porph)}$_2$–C$_{60}^{\bullet-}$ charge-separated state upon photoexcitation.[93] Furthermore, the heterodimerization of **40** Zn–**44** Zn with an indium tin oxide (ITO)-linked imidazolylporphyrin, followed by fixation by olefin metathesis, furnished systems that generated anodic photocurrents.[92]


45 Zn

Fluorescence quenching was also observed for tricationic porphyrin **46**, which is functionalized with a ferrocene unit covalently attached by a phenylethyl ether spacer.[94] Upon intercalation of the polar porphyrin part of **46** into DNA, a strong electron transfer from the ferrocene to the porphyrin unit was still observed. Uosaki et al. employed the reducing power of the ferrocenyl moiety to accomplish light-induced electron transfer at a self-assembled monolayer.[95] A molecule 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. Such compounds, for example **47**, 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.[96]

As ferrocenyl groups are able to reduce the porphyrin photoexcited state, porphyrin–ferrocene hybrids have been frequently used in artificial photosynthesis mimics. The ferrocene–(porphyrin)$_n$–fullerene constructs of Imahori, Ito, Fukuzumi and co-workers deserve special attention (for an overview, see the accounts by Imahori[97] and Fukuzumi[98]).

After having synthesized metalloporphyrin–fullerene diads 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.[99–104] In their syntheses, 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 monoferrocenylmono(*p*-formylphenyl)porphyrin in 23% yield. After further synthetic elaboration, the desired triads were obtained, either with (**49** and **49** Zn) or without (**48** and **48** Zn) a thiol functionality at the ferrocene site for additional gold-binding studies.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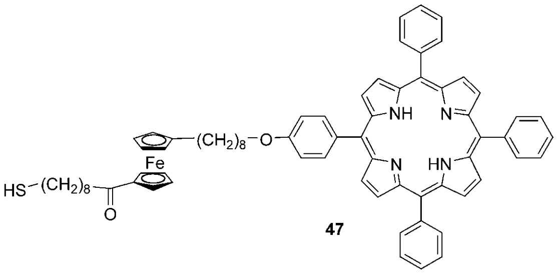
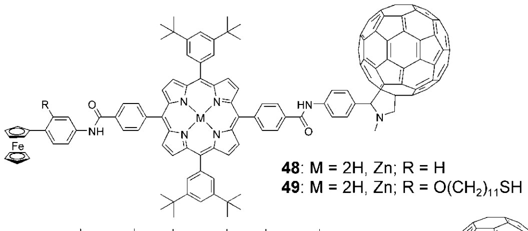
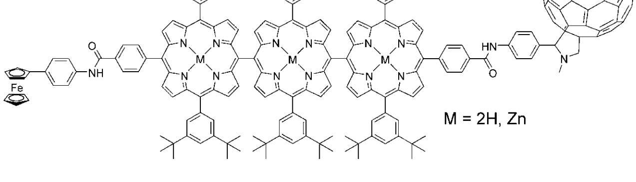

47

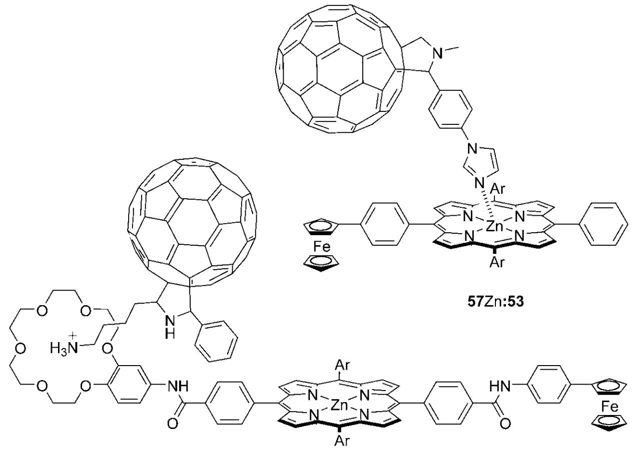
Owing to the promising photophysical properties of the triads, research efforts focused on increasing 1) the distance between the two charges in the charge-separated states, 2) the lifetimes of those charge-separated states, and 3) the quantum yield of this process to mimic as closely as possible the charge-separation processes that allow solar energy to be harnessed in nature. During this "evolutionary" process, several molecules were synthesized that 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 (which is reduced to the radical anion C$_{60}^{\bullet-}$ during charge separation) at opposite ends of the molecule. An extra metalloporphyrin


48: M = 2H, Zn; R = H
49: M = 2H, Zn; R = O(CH$_2$)$_{11}$SH


M = 2H, Zn

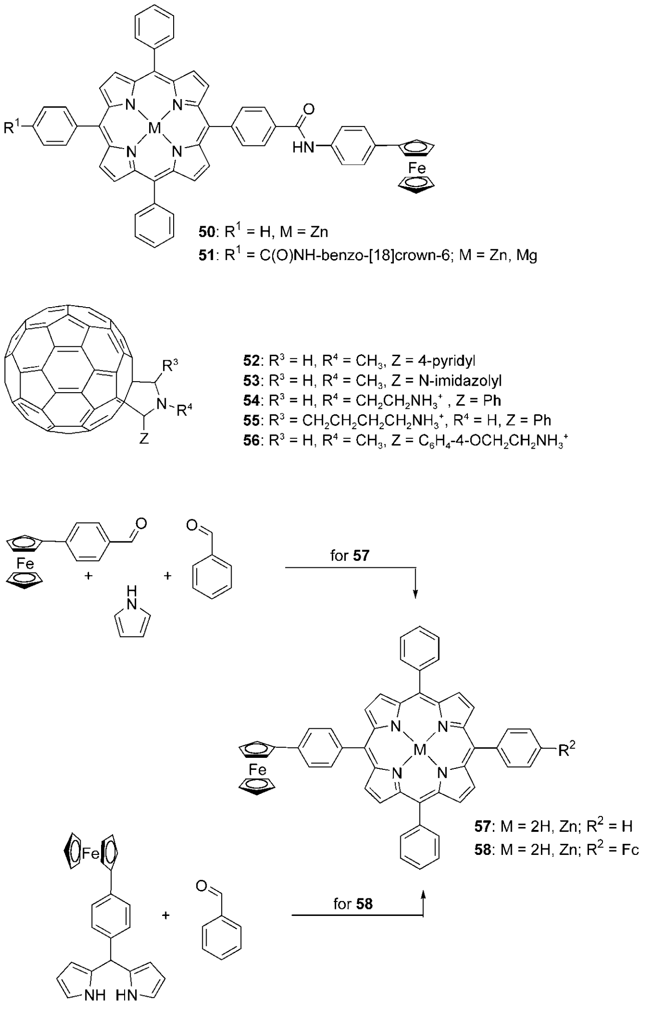
unit was first inserted in the porphyrin–ferrocene link.[105,106] Then the novel *meso,meso*-linked diporphyrin[107] and triporphyrin[108] structural elements were introduced between the ferrocenyl and fullerene ends, eventually leading to a long-lived charge-separated state (0.53 s in frozen DMF at 163 K) with a very high quantum yield (83 %). The ferrocenyl group in these triads, tetrads, and pentads was always introduced by the reaction of an aryl 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 with ferrocenyl groups (Scheme 8).[109] Whereas the amide-linked diads **50**Zn and **51**Zn were synthesized in a similar fashion to porphyrin derivatives **48** and **49**, the two novel, phenylene-spaced ferrocene zinc(II) porphyrin hybrids were synthesized in different ways. Monoferrocenyl porphyrin **57** was formed by a statistical Adler-type condensation of 4-ferrocenylbenzaldehyde and benzaldehyde (1:3 ratio) with pyrrole in 6.4 % yield. The corresponding *trans*-bis(ferrocenyl)porphyrin was synthesized by a [2+2] condensation of 5-(*p*-ferrocenylphenyl)-dipyrromethane and benzaldehyde in dichloromethane, and catalyzed by BF$_3$·OEt$_2$. After oxidation of the intermediate porphyrinogen, the desired porphyrin **58** was obtained in 45 % yield. When these zinc porphyrins were exposed to fullerenes appended with Lewis bases, such as pyridine or imidazole (**52, 53**), supramolecular analogues of the systems of Imahori and Fukuzumi were obtained through coordination of the nitrogen donor of the functionalized fullerene to the zinc atom in the porphyrin cavity. Efficient electron transfer from the ferrocene to the excited singlet zinc porphyrin was observed, which, upon axial ligation to Lewis bases **52**–**56**, generated the Fc$^+$–ZnP:C$_{60}^{\bullet-}$ species. The supramolecular interaction was expanded by equipping ferrocene-functionalized zinc(II) and magnesium(II) porphyrins with a crown ether moiety (**51**).[110] Supramolecular complexes are formed (for instance **51**Zn:**55**) when these compounds are subjected to fullerenes bearing primary ammonium groups (**54**–**56**). These complexes are also able to form fully charge-separated states upon excitation.



57Zn:**53**

51Zn:**55**

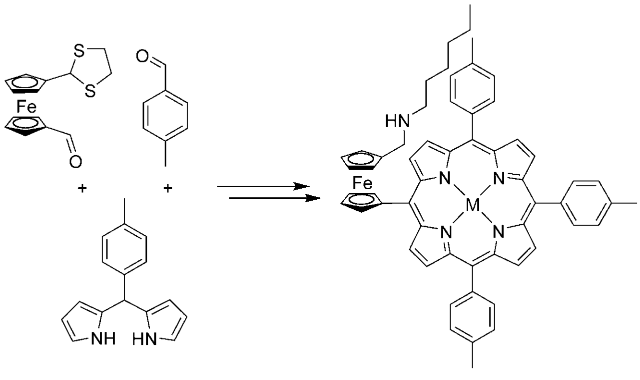


Scheme 8. Porphyrins with appended ferrocene groups synthesized by D'Souza and co-workers.[109,110]

3.1.3. The Ferrocenyl Group as a Hinge

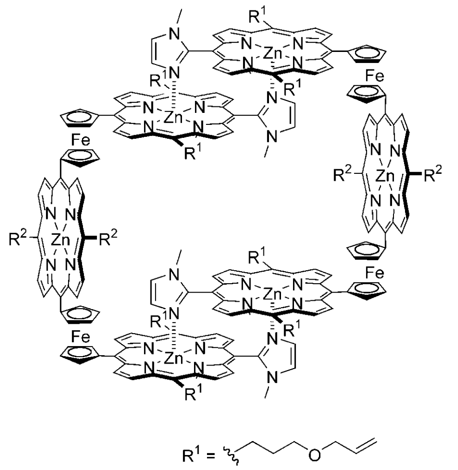
Ferrocene groups have being increasingly used as hinges to mediate the changes in the mutual arrangements of their substituents. Both the structural flexibility of the ferrocenyl group and its electrochemical properties were applied by Bucher, Moutet, and co-workers in ferrocenyl porphyrin electrochemical sensors.[111] Ferrocene was functionalized at the 1- and 1′-positions with a *meso* zinc(II) porphyrinyl group and an *N*-hexylmethyleneamine group, respectively. One of a number of steps involved was the selective assembly of a porphyrin on a mono-protected bis(formyl)ferrocene using Lindsey's conditions, namely trifluoroacetic acid in dichloromethane (Scheme 9).

The resulting porphyrin **59**Zn self-assembles through amine–zinc coordination in solution, forming supramolecular coordination dimers.[113] 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



59: M = 2H, Zn

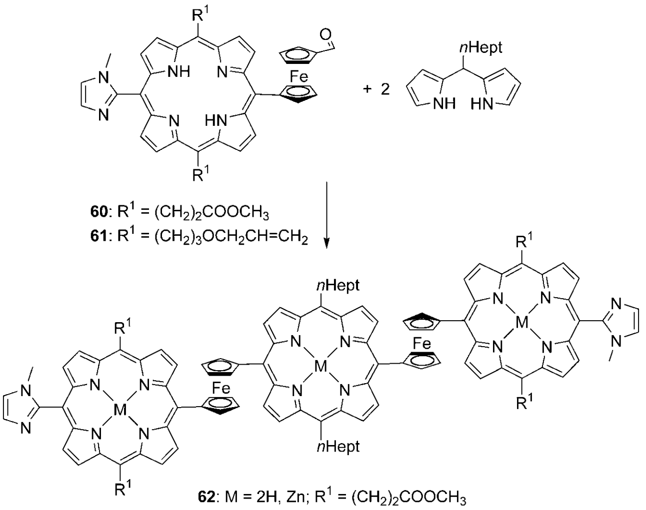
Scheme 9. Anion sensors described by Moutet et al.[111,112]



(**63**Zn)$_2$ R^2 = -(CH$_2$)$_6$CH$_3$

sensing of neutral, amine-containing species. When the secondary amine group of **59**Zn 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.[112] Binding of the 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 rotational motion of both cyclopentadienyl units of the ferrocenyl group in supramolecular porphyrin structures arising from complementary dimer formation.[114] 1,1′-Diformylferrocene was used as the organometallic building block in the porphyrin synthesis of **62** and **63**, with mono(1′-formylferrocenyl)porphyrins **60** and **61**, to give the products in 5.1 % and 2.1 % yield, respectively (Scheme 10). In contrast to the corresponding *meso m*-phenylene-linked triporphyrins,[115] these molecules do not form polymeric mixtures following zinc insertion. Instead, **62**Zn and **63**Zn form coordination dimers, which was attributed to the freely rotating ferrocene hinge. After these dimers are disassembled with pyridine, however, a mixture consisting of cyclic oligomers (from trimers to decamers) is formed, as shown by gel permeation chromatography (GPC). These cyclic oligomers are stable in the absence of coordinating solvents, but reconvert into the dimers in the presence of, for instance, methanol. The oligomerization process was corroborated by subjecting the mixture obtained from **63**Zn to Grubbs' metathesis catalyst, which irreversibly interlinked the individual building blocks of the cyclic oligomers. The hinge behavior of the ferrocenyl group was used by others to allow a ferrocene-appended porphyrin and fullerene unit to achieve a favorable mutual position for electronic interaction.[116]



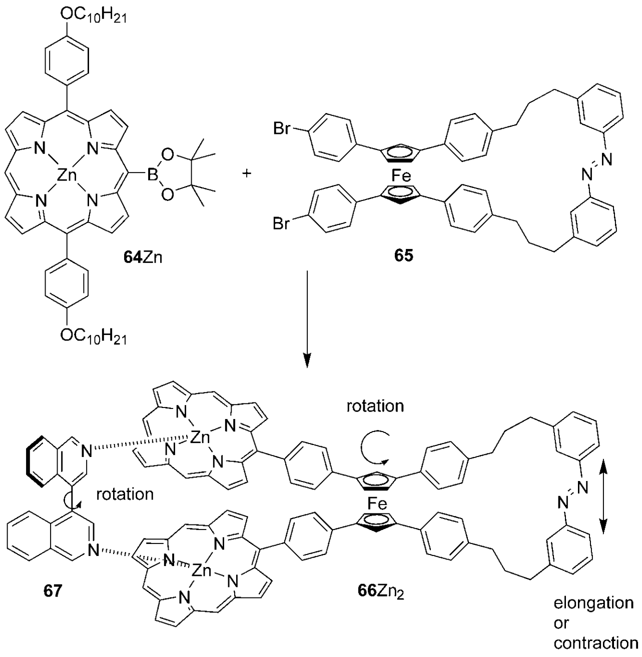
60: R^1 = (CH$_2$)$_2$COOCH$_3$
61: R^1 = (CH$_2$)$_3$OCH$_2$CH=CH$_2$

62: M = 2H, Zn; R^1 = (CH$_2$)$_2$COOCH$_3$
63: M = 2H, Zn; R^1 = (CH$_2$)$_3$OCH$_2$CH=CH$_2$

Scheme 10. Hinge porphyrins designed and synthesized by Kobuke.[114]

Recently, Aida et al. reported two systems in which the photoresponsive *cis*/*trans* isomerization of an azobenzene[117,118] or a 1,2-bis(pyridyl)ethylene[119] unit was coupled to the twisting of porphyrin units connected by 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 by an azobenzene strap (**65**).[117] At the 3,3′ positions, two independent zinc porphyrins were attached by a Suzuki cross-coupling reaction with two equivalents of mono-*meso*-boronateporphyrin **64**Zn in the presence of [Pd(PPh$_3$)$_4$] and Cs$_2$CO$_3$ in a mixture of toluene and H$_2$O to give bis(porphyrin) **66**Zn$_2$ in 20 % yield (Scheme 11).

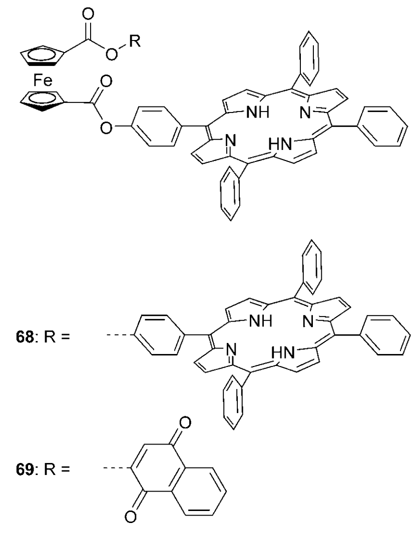
The *cis*/*trans* isomerization of the azobenzene unit induces a rotation of the two cyclopentadienyl fragments around the cyclopentadienyl–iron bond, which in turn leads to a change in the spatial separation of the porphyrin units. Bis(isoquinolinyl) guest **67** was ligated to **66**Zn$_2$ to give a 1:1 complex. Using several techniques, including UV/Vis spectroscopy and circular dichroism (CD), together with the fact that ligand dissociation is much slower than the rotational movement, 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 noncovalent interaction with the zinc porphyrins.[117,118] Subsequently, a rotary host similar to **66**Zn$_2$ was synthesized, which also comprised a 1,1′-bis(porphyrin)-



Scheme 11. Ferrocenylporphyrin-based mechanical twisting reported by Aida et al.[117]

ferrocene unit similar to that in **66** Zn_2, but now with two *meta* aniline groups on the opposite ends of the ferrocenyl linker.[119] By rotation around the ferrocene group, this molecule can self-ligate through zinc–nitrogen bonds. With a *cis*-1,2-bipyridylethylene guest present, the self-ligated molecule adopts an externally locked conformation, with one of the zinc porphyrin units 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, which then undergoes self-ligation.

Compounds in which a ferrocene unit bridges two porphyrin units (**68**)[120] or a naphthoquinone and a porphyrin (**69**)[121] were developed by Beer et al. The former compound 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. No electronic communication was found between the components.[120]

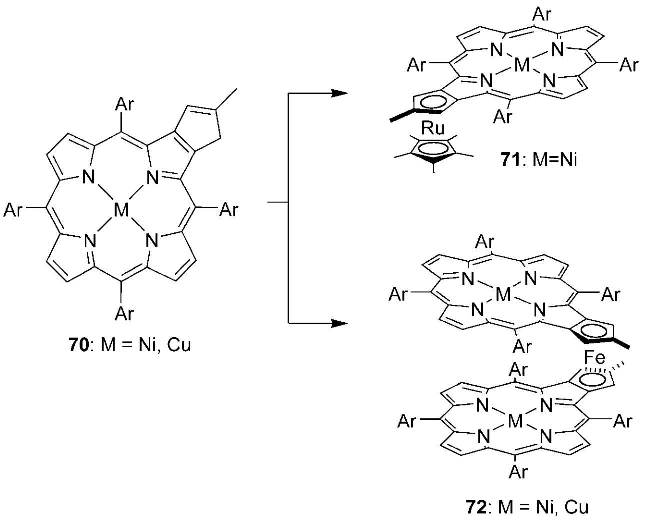


The porphyrin–ferrocene-quinone-linked molecule **69** was prepared in a one-pot, two-step reaction. 1,1′-Bis(chlorocarbonyl)ferrocene was first reacted with one equivalent of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin, and the resulting mono(porphyrin)mono(chlorocarbonyl)ferrocene was reacted in situ with one equivalent of 2-hydroxynaphthoquinone, giving **69** in a nonoptimized yield of 35%. Voltammetric measurements showed negligible ground-state interactions between the constituents. Fluorescence measurements, however, revealed a 90% quenching of the porphyrin fluorescence relative to tetraphenylporphyrin, which is ascribed to a rapid, intramolecular reduction of the naphthoquinone unit by the singlet excited state of the porphyrin.[121] The authors did not elaborate on whether the ferrocene linker actively mediates in this process or is merely a spectator unit. The same research group later synthesized different atropoisomers of *meso*-tetrakis(*ortho*-ferrocenylcarbonylaminophenyl)porphyrin by reaction of the appropriate atropoisomer of *meso*-tetrakis(2-aminophenyl)porphyrin with 5 equivalents of (chlorocarbonyl)ferrocene in Et_3N/CH_2Cl_2, in yields of 67–72%.[122] The corresponding zinc complexes were readily obtained in yields of over 90% with zinc acetate in methanol/dichloromethane. The zinc complexes strongly bind to the anionic guests Cl^-, Br^-, NO_3^-, and HSO_4^-, 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 and co-workers have shown that metallocene-appended porphyrins can also be synthesized from cyclopentadienide-functionalized porphyrins, despite the fact that this strategy has not found broad application owing to the inherent synthetic challenges. A 1-methyl-cyclopentadiene moiety was fused to a pyrrole subunit of *meso*-tetraarylporphyrin to give porphyrins **70** Ni and **70** Cu. Deprotonation with lithium diisopropylamide (LDA) followed by treatment with either [Cp*$RuCl_2$] or $FeCl_2$ furnished the corresponding metalated porphyrins **71** Ni and **72** Ni_2 in 25 and 30% yield, respectively (Scheme 12, Figure 4).[123] The UV/Vis spectrum of **71** Ni exhibits a split Soret band with intense Q bands, whereas **72** Ni_2 shows a broad Soret band and no well-defined Q bands, indicating interaction between the porphyrin units. A related bis(copper porphyrin)ferrocene, **72** Cu_2 was also synthesized by a similar route in 7.5% yield.[124]

3.2. Other π-Complexes

Besides ferrocene-functionalized porphyrins, other metallocene-type complexes of tetrapyrrolic macrocycles have also been studied.[125,126] In the early 1970s, Gogan and Siddiqui conducted their seminal work in this field, in which they reacted several metallotetraphenylporphyrins with $[Cr(CO)_6]$



Scheme 12. Porphyrins with fused metallocenyl groups synthesized by Smith.[123,124]

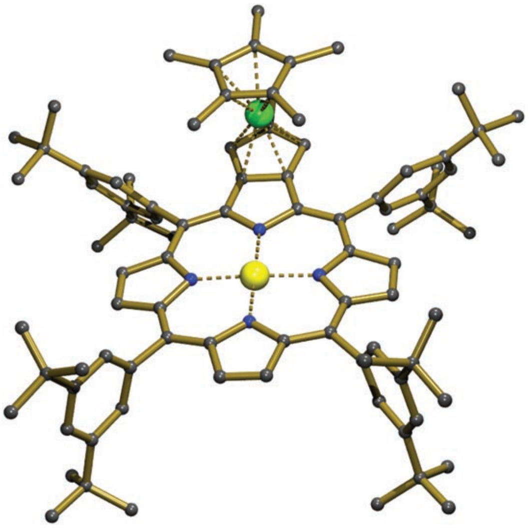
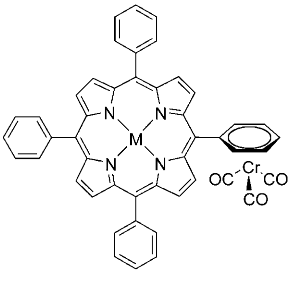


Figure 4. X-ray structure of **71 Ni** in the solid state. Yellow Ni, green Fe, Blue N.

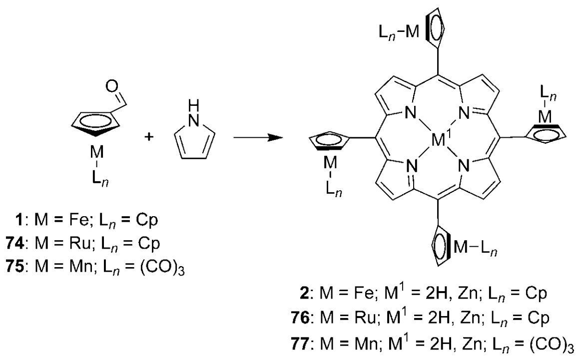
in refluxing di-*n*-butyl ether, which yielded the monosubstituted complexes **73** in good yields.[127]

Owing to their inherent instability, these complexes were not completely analyzed, except for **73** Zn, which is sufficiently stable. By using UV/Vis, IR, and ^{1}H NMR spectroscopy, no high degree of electronic communication between the peripheral metal centers and the porphyrin ring was found, although the exclusive stability of the zinc complex might, at least partially, rebut this claim. The metal affinity of *meso* aryl groups was later exploited by Shinkai for the synthesis of a molecular motor, which consisted of a double-decker cerium porphyrin that can be activated by addition of Ag$^+$ ions.[128,129]



73: M = 2H, Cr, MnCl, Co, Ni, Zn

Loim's group has devoted considerable attention to the synthesis and characterization of *meso*-tetrakis(metallocenyl)porphyrins (Scheme 13).[75,130–134] They used the organometallic cymantrene carboxaldehyde (**75**; cymantrene = $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_3]$) 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.[134] Later, it was reported that the use of Lindsey conditions[135] enhances the yield of these reactions significantly.[130] An interesting extension was made by introducing planar chiral (+)-(1*S*)-2-methylcymantrene groups at the four *meso* positions.[131] 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 the work, the analogous tetrakis(ferrocenyl)- and tetrakis(ruthenocenyl)-porphyrin, **2** and **76**, were also synthesized.[136] The electronic impact of these *meso* metallocenyl groups on the corresponding zinc(II) chelates **2** Zn, **76** Zn, and **77** Zn, 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.[132] The effects of *meso* ferrocenyl ($K_{\text{ass}} = (3.8 \pm 0.9) \times 10^4\,\text{M}^{-1}$) and *meso* ruthenocenyl groups ($K_{\text{ass}} = (3.0 \pm 0.7) \times 10^4\,\text{M}^{-1}$) differed only marginally from that of 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 ($K_{\text{ass}} = (7.7 \pm 0.5) \times 10^6\,\text{M}^{-1}$), which was attributed to the electron-withdrawing nature of the cymantrenyl moiety. These results are consistent with the σ_p Hammett parameters of the four substituents, which follow approximately the same trend of

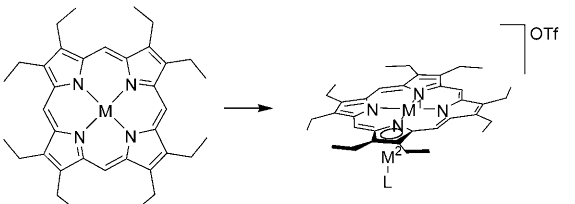


Scheme 13. *Meso*-tetrakis(metallocenyl)porphyrins synthesized by Loim.[130–133,136]

increasing electron negativity (phenyl < ruthenocyl < ferrocenyl < cymantrenyl).

The Loim group subsequently focused their attention on the synthesis of mixed systems containing phenyl, ferrocenyl, and/or cymantrenyl groups in the *meso* position.[133] For this purpose, they applied different synthetic strategies, including mixed condensations of aldehydes with pyrrole under Lindsey conditions ($BF_3{\cdot}OEt_2$, CH_2Cl_2) and reactions of different 5-substituted dipyrromethanes with metallocene aldehydes and benzaldehydes. ^1H NMR and UV/Vis spectroscopy showed that for *meso* metallocenylporphyrins, the degree of distortion of the macrocycle as a function of the metallocenyl group increases in the series cymantrene < ruthenocene < ferrocene.

While studying catalytic hydrodemetalation, Rauchfuss and co-workers realized that the pyrrole rings of the tetrapyrrolic macrocycles could act as η^5-pyrrolide ligands for π complexes.[137–139] Treatment of dichloromethane solutions of $[(cymene)Ru(OTf)_2]$, $[(Cp^*)Ir(OTf)_2]$, or $[(cymene)Os(OTf)_2]$ with either NiOEP (**78** Ni) or ZnOEP (**78** Zn; OEP = dianion of β-octaethylporphyrin) 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, Figure 5). The stability of these complexes is related to the electron-donating ability of the porphyrin ring. **78** Zn forms the most stable complexes, whereas those of **78** Ni are less stable, and the related vanadium compounds did not form at all.



78: M = Ni, Zn

79: M^1 = Ni, Zn; M^2 = Ru; L = *p*-cymene
80: M^1 = Ni, Zn; M^2 = Ir; L = Cp*
81: M^1 = Ni; M^2 = Os; L = *p*-cymene

Scheme 14. Porphyrinocenes developed by Rauchfuss.[138,139]

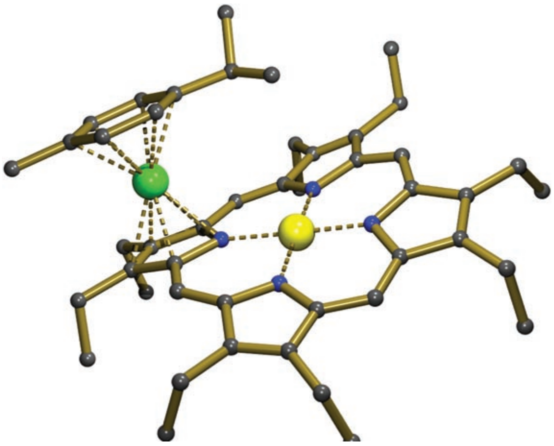


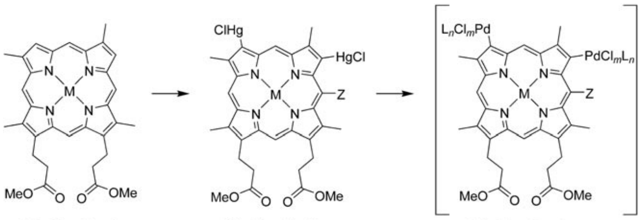
Figure 5. X-ray structure of **79** **Ni** in the solid state. Yellow Ni, green Ru, Blue N.

3.3. *Ring-Metalated Porphyrins*

Preparation of porphyrins that bear transient peripheral σ-bonded metal centers has been stimulated in particular by two objectives. The most important goal 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.[140] Secondly, ring-metalated porphyrins have also been studied as such, rather than as synthetic intermediates. In this case, the metal centers can be used in 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 in which the transient metal complexes are directly bonded to the porphyrin *meso* or β positions, and these will be discussed in combination with examples from the second category.

3.3.1. *Ring-Metalated Porphyrins as Synthetic Intermediates*

Smith and co-workers found that porphyrins that are partially unsubstituted at the β positions reacted with $Hg(OAc)_2$ to form the corresponding mercurated porphyrins.[65,141,142] As free-base porphyrins can form complexes with $Hg(OAc)_2$, the starting materials were converted into their zinc(II) or copper(II) complexes **82** Zn and **82** Cu prior to the mercuration reaction. The electrophilic mercuration takes place almost 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-(β,β,*meso*)-mercurated porphyrin species **83** Zn and **83** Cu in nearly quantitative yields (Scheme 15).



82: M = Zn, Cu

83: M = Zn, Cu
Z = H, HgCl

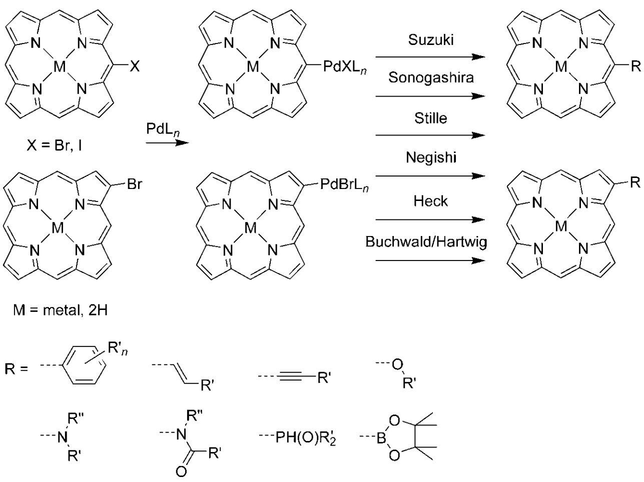
84: M = Zn, Cu
Z = H, $PdCl_mL_n$

Scheme 15. Mercurated and palladated porphyrins used by Smith and co-workers.[65,141,142]

If 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 method is that it circumvents the need for complex, lengthy synthetic routes to the appropriate pyrrolic building blocks. Later, the scope of this method was expanded by introducing a myriad of alkenyl and styryl fragments onto the porphyrin framework.[143] 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.[144] 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* palladium moiety subsequently inserts into the Pd−C bond, followed by protiodepalladation to form the isolated products. This reaction sequence gives access to deoxophylloerythroetioporphyrin and deoxophylloerythrin 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.[145]

Direct ring metalation of porphyrins by oxidative addition of ring-halogenated porphyrins to appropriate metal centers has been known since the late 1980s, when Smith et al. reported the use of a Stille-type coupling between 2,4-dibromodeuteroporphyrin IX dimethyl ester with tri-*n*-butylethenylstannane catalyzed by [Pd(PPh$_3$)$_4$] to give protoporphyrin IX dimethyl ester in 85% yield.[145] Therien and co-workers later synthetically extended [5,15-dibromo-10,20-diphenyl-porphinatozinc(II)] and [2-bromotetraphenylporphinatozinc(II)] using palladium-mediated Negishi and Stille couplings to give the desired substituted porphyrins in 90% yield.[146,147] Regarding the transient organopalladium(II) species, in the first case, 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.[148–150] Later, *meso*-brominated and iodinated porphyrins were also employed as substrates in palladium-catalyzed Sonogashira reactions.[140,151] Therien and co-workers applied *meso*-brominated porphyrins in Suzuki reactions with pinacolborane, thereby forming “Suzuki porphyrins” that could be utilized in further functionalization reactions (Scheme 16).[152] If boron is considered to be a metal, Therien’s Suzuki porphyrins 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,[153,154] *meso*-aryloxy and -alkoxy,[155] and *meso*-amidoporphyrins.[156] 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.[157] They found that, under the reaction conditions used, a nickel porphyrin is a far more reactive substrate than its free-base precursor. Arnold and co-workers did not note a large difference in completion time between the reactions of 5-bromo-10,20-diphenylporphyrin and [5-bromo-10,20-diphenylporphyrinatonickel(II)] with [Pd(PPh$_3$)$_4$],[148] which suggests that the oxidative addition of the bromoporphyrin to palladium is not rate-limiting in their case.[147] Moreover, it was also found that during reactions to form *meso*-η^1-platino(II)porphyrins, the oxidative addition of the *meso*-bromoporphyrins to platinum(0) was faster for the free base compound than for its nickel(II) and zinc(II) complexes.[158] Arnold et al. later showed that *meso* phosphine oxide groups could also be introduced using palladium-catalyzed couplings.[159]

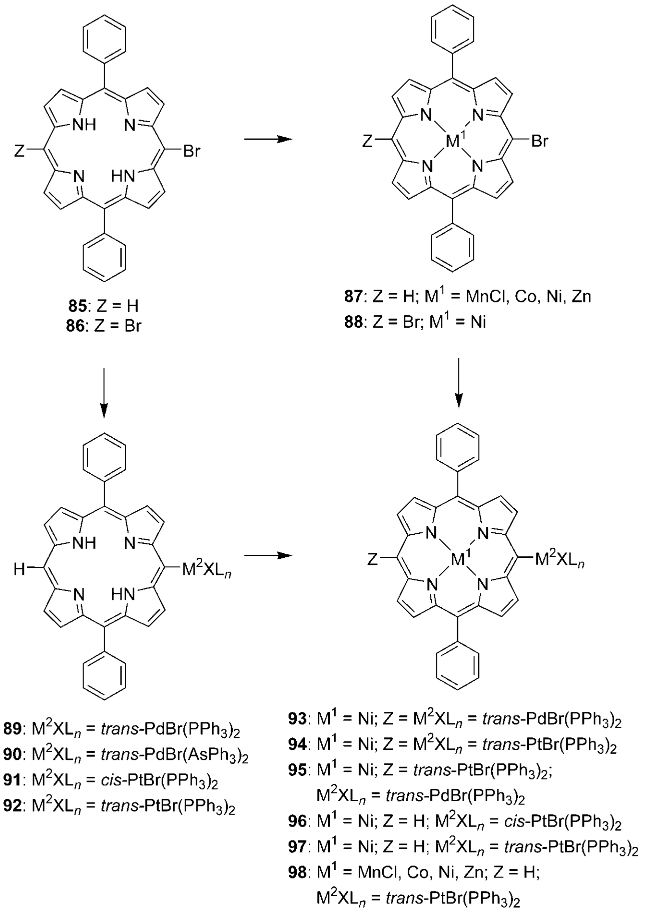


Scheme 16. Overview of the porphyrin products that can be obtained by palladium-mediated coupling on the β or *meso* position(s). For clarity, only monosubstitution is depicted; multi-halogenated porphyrins allow a higher degree of substitution.

3.3.2. *Isolable Ring-Metalated Porphyrins*

In 1998, Arnold and co-workers reported the serendipitous isolation of *meso*-η^1-metalloporphyrins **89**–**93** (Scheme 17).[149,160] 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**, **87** Ni) and 5,15-dibromo-10,20-diphenylporphyrin (**86**, **88** Ni) with equimolar amounts of a palladium(0) and platinum(0) source.[149] [Pd(PPh$_3$)$_4$] or a mixture of [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone) and PPh$_3$, AsPh$_3$, or dppe (dppe = 1,2-bis(diphenylphosphino)ethane) was used for palladation, and [Pt(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 in Section 3.3.1 was carried out on a preparative scale, and the resulting complexes were isolated in high yields (Figure 6).

Furthermore, it was found that the kinetic *cis* products **91** and **96** of the oxidative addition of 5-bromo-10,20-diphenylporphyrin and [5-bromo-10,20-diphenylporphyrinatonickel(II)] to platinum(0) precursors gradually transform into the thermodynamically more stable *trans* analogues **92** and **97**, respectively.[148] Later, however, Arnold et al. were able to readily isolate *cis* complexes by using *cis* bichelating ligands, such as tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and bipy (2,2′-bipyridyl).[158] In chlorinated solvents, some halide exchange between the palladium(II) and platinum(II) complexes synthesized and the solvent takes place, but it was not mentioned whether the rate of this reaction is influenced by the photophysical properties of the porphyrin. Along with the



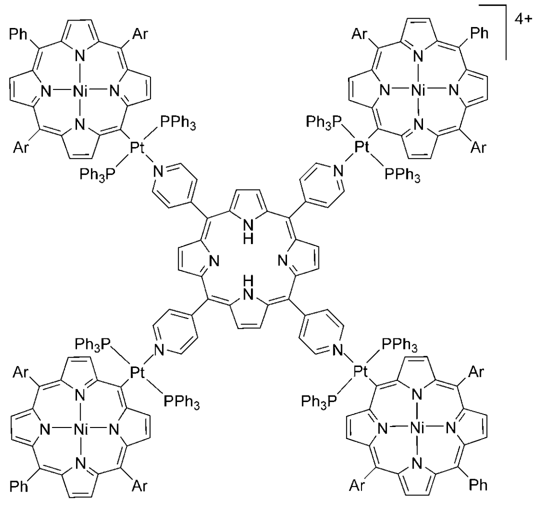
85: Z = H
86: Z = Br

87: Z = H; M^1 = MnCl, Co, Ni, Zn
88: Z = Br; M^1 = Ni

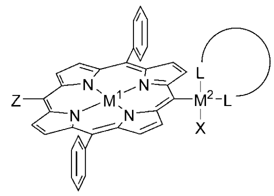
89: M^{2}XL$_n$ = *trans*-PdBr(PPh$_3$)$_2$
90: M^{2}XL$_n$ = *trans*-PdBr(AsPh$_3$)$_2$
91: M^{2}XL$_n$ = *cis*-PtBr(PPh$_3$)$_2$
92: M^{2}XL$_n$ = *trans*-PtBr(PPh$_3$)$_2$

93: M^1 = Ni; Z = M^{2}XL$_n$ = *trans*-PdBr(PPh$_3$)$_2$
94: M^1 = Ni; Z = M^{2}XL$_n$ = *trans*-PtBr(PPh$_3$)$_2$
95: M^1 = Ni; Z = *trans*-PtBr(PPh$_3$)$_2$; M^{2}XL$_n$ = *trans*-PdBr(PPh$_3$)$_2$
96: M^1 = Ni; Z = H; M^{2}XL$_n$ = *cis*-PtBr(PPh$_3$)$_2$
97: M^1 = Ni; Z = H; M^{2}XL$_n$ = *trans*-PtBr(PPh$_3$)$_2$
98: M^1 = MnCl, Co, Ni, Zn; Z = H; M^{2}XL$_n$ = *trans*-PtBr(PPh$_3$)$_2$

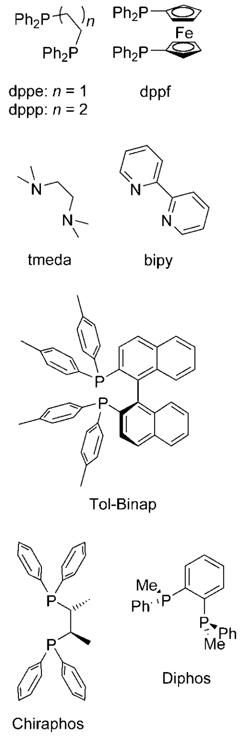
Scheme 17. *Meso*-η^1-metalloporphyrins investigated by Arnold et al.[148–150]



99: Ar = 3,5-*t*Bu$_2$C$_6$H$_3$



100: M^1 = 2H; M^{2}X = PdBr; L⁀L = dppe; Z = H
101: M^1 = 2H; M^{2}X = PdBr; L⁀L = dppp; Z = H
102: M^1 = 2H; M^{2}X = PdBr; L⁀L = dppf; Z = H
103: M^1 = 2H; M^{2}X = PdBr; L⁀L = tmeda; Z = H
104: M^1 = 2H; M^{2}X = PdBr; L⁀L = bipy; Z = H
105: M^1 = 2H; M^{2}X = PdBr; L⁀L = bipy; Z = PdBr(bipy)
106: M^1 = 2H; M^{2}X = PtI; L⁀L = tmeda; Z = Ph
107: M^1 = 2H; M^{2}X = PtI; L⁀L = bipy; Z = Ph
108: M^1 = Ni; M^{2}X = PdBr; L⁀L = Tol-Binap; Z = H
109: M^1 = Ni; M^{2}X = PdBr; L⁀L = Chiraphos; Z = H
110: M^1 = Ni; M^{2}X = PdBr; L⁀L = Diphos; Z = H



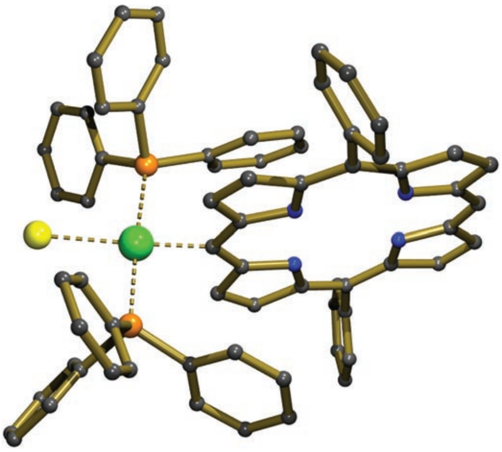


Figure 6. X-ray structure of **89** in the solid state. Green Pd, yellow Br, orange P, blue N.

free-base and nickel(II) compounds reported earlier, the scope of bimetallic porphyrins was increased by introducing manganese(III), cobalt(II), and zinc(II) into the porphyrin ring (**87**MnCl–**87**Zn and **98**MnCl–**98**Zn; Scheme 17).[150] To synthesize these heteromultimetallic compounds, two procedures can be followed: 1) metalation of the porphyrin, followed by oxidative addition to a metal(0) source (for example, [Pt(PPh$_3$)$_4$]), or 2) oxidative addition of the *meso* carbon–bromine bond to a metal(0) source prior to metalation of the porphyrin moiety. Procedure (2) is preferred over (1) as the latter is hampered by a low solubility of the metalloporphyrin species. When employing procedure (2), the liberated acid does not protiodeplatinate the *meso* positon in the second step, indicating that in these complexes the carbon–platinum bond is quite robust. Insertion of platinum(II) into the carbon–bromine bond deactivates the opposite carbon–bromine bond towards oxidative addition, resulting in only low yields of the bis(platinum) species **94**Ni. From ^{1}H NMR and UV/Vis spectroscopy and cyclic voltammetry measurements, the authors concluded that the {Pt(PPh$_3$)$_2$Br} group is a strong electron donor, and that the introduction of an extra {$Pt(PPh_3)_2Br$} moiety has an additive effect.

In subsequent work, the researchers reacted nickel(II) porphyrin **97** Ni with AgOTf, abstracting the bromine ligand at platinum and replacing it with OH_2, to synthesize cationic porphyrin [**97** Ni]OTf. Having one vacant coordination site, the {$Pt(PPh_3)_2$}$^+$ moiety could be used for coordination to functionalized Lewis bases to give supramolecular multi-porphyrin assemblies (for example, **99**).[161] Assemblies of two, three, and five porphyrin units 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.

The exclusive product of the reaction between a 5-bromoporphyrin and a palladium(0) source ([$Pd_2(dba)_3$], [$Pd(PPh_3)_4$]) is *trans*-[Pd(porph)Br(PPh_3)$_2$], whereas both *cis* and *trans* products can be isolated with platinum(0). 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 (Figure 7).[149] For the corresponding platinum compounds, this is not an option owing to formation of highly stable [Pt(diphosphine)$_2$] species in situ, which will not react further with the haloporphyrin. To overcome this problem, diamines were used instead of diphosphines.[158] For the *cis* palladium complexes **103**–**105**, this method works equally well as when chelating phosphines were used (one equivalent of palladium, excess diamine, toluene, 105 °C).[158] Interestingly, this route proved to be even useful for the platinum complexes, as the corresponding *cis* compounds **106** and **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 **108** Ni–**110** Ni,[162] which could lead to interesting catalytic applications.

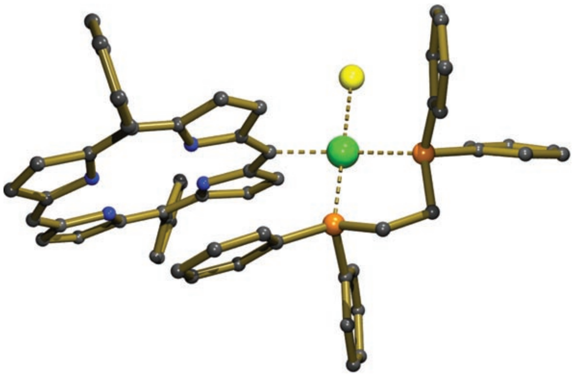


Figure 7. X-ray structure of **100** in the solid state. Green Pd, yellow Br, orange P, blue N.

3.3.3. Main-Group Examples

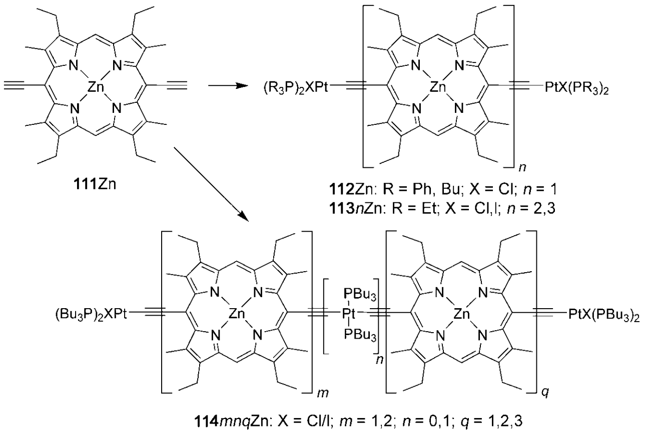
Apart from transition metals, several main group semi-metallic elements have also been appended to tetrapyrrole systems; for example, boron in Therien's Suzuki porphyrins described in Section 3.3.1. Instead of using electrophilic aromatic metalation or oxidative addition for these reactions, Shine and co-workers used the zinc(II) tetraphenylporphyrin (ZnTPP) cation radical to react with several nucleophiles.[163] Reaction with triphenylarsine in acetonitrile gave [(2-triphenylarsonium-5,10,15,20-tetrakis-(phenyl)porphyrinato)zinc(II)] perchlorate in 39 % yield. ZnTPP was also oxidized in situ by a similar procedure in the presence of several Group 15 nucleophiles (EPh_nR_{3-n}, E = P,As) with 2,6-lutidine as a proton trap in mixtures of apolar (CH_2Cl_2, $C_2H_4Cl_2$) and polar solvents (MeOH, MeCN). The β-arsonium compounds thus obtained show bathochromic shifts of the UV/Vis bands.[164]

While pursuing the synthesis of a *meso*-trichlorotellurium(IV) porphyrin, Sugiura, Sakata and co-workers unexpectedly discovered a new oligomerization reaction.[191] Upon treatment of a nickel 5,15-diarylporphyrin with $TeCl_4$ in dry dichloromethane at room temperature, they found that multiply fused dimers and associated higher oligomers formed. A mechanism involving attack at the *meso* position, followed by β attack of the intermediate *meso*-trichlorotellurium(IV) group on another porphyrin and a subsequent detelluration reaction was postulated by the authors to account for this reaction.

3.4. Porphyrins with Platinum Acetylide Units

Platinum acetylides have been attached to porphyrins to make use of their photophysical and photochemical properties.[165] Paolesse et al. used platinum acetylide linkages to synthesize conjugated organometallic porphyrin polymers.[166] The zinc β-octaalkyl-5,15-bis(acetylene)porphyrin **111** Zn was reacted with several platinum complexes with the general formula [PtClZ(PR_3)$_2$] (*cis* and *trans*; Z = Cl or H; R = Bu or Ph) in the presence of catalytic amounts of CuI and with diethylamine/dichloromethane as the solvent (Scheme 18). Reaction of **111** Zn with one equivalent of *trans*-[$PtCl_2$(PBu_3)$_2$] furnished **112** Zn as a mixture of *cis* and *trans* isomers in 15 % yield, in which the platinum-bound halide can be either chlorine or iodine as a result of halide scrambling at platinum, where CuI is the iodide source. A mixture of the oligomeric products **113** *n*Zn was also formed, as shown by MALDI-TOF mass spectrometry. This mixture consists of different oligomeric multiporphyrin compounds which are interconnected by butadiyne or *trans*-{(C≡C)Pt(PBu_3)$_2$-(C≡C)} units.

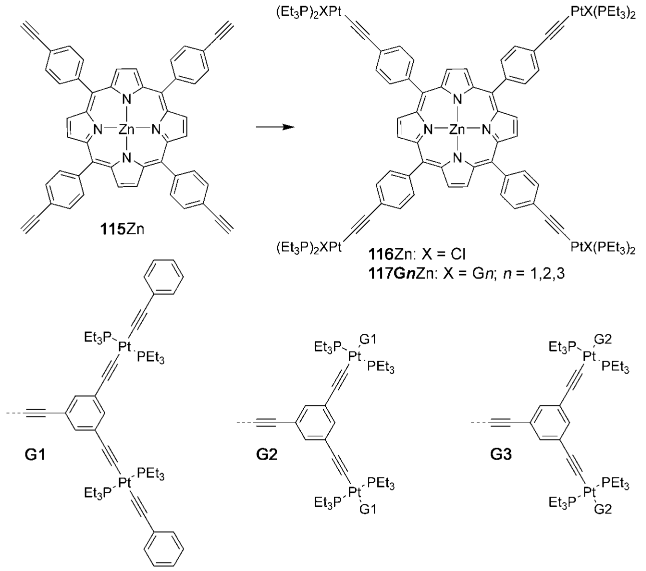
In contrast, reaction of **111** Zn with *cis*-[$PtCl_2$(PPh_3)$_2$] or *trans*-[Pt(H)Cl(PPh_3)$_2$] under the same reaction conditions led to different product distributions. The major product of this reaction is a mixture of bi/trinuclear products consisting of two peripheral platinum centers interconnected by a free-base or zinc(II) porphyrin, respectively (15 %). A mixture of multinuclear, bisplatinum–biszinc(II) porphyrin compounds



Scheme 18. Platinum bis(acetylide)–porphyrin polymers from Paolesse and co-workers.[166]

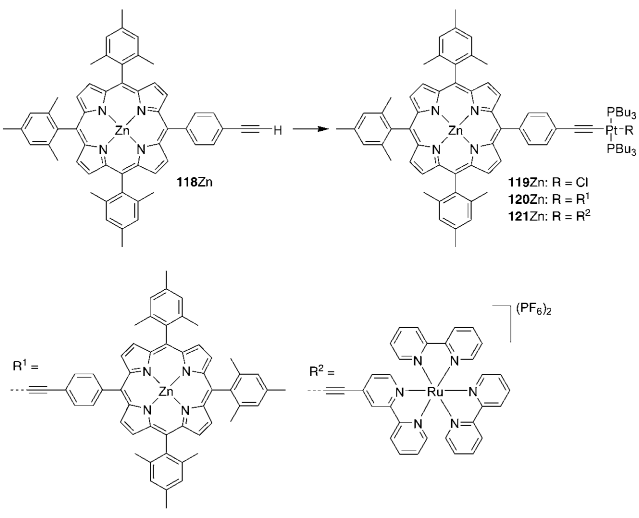
was formed as a byproduct, in which the platinum centers are located at both extremes (**114***mnq*Zn, with $m=1$, $n=0$, $q=1$). These platinum groups are linked to each other by a bis[5,15-bis(acetylene)porphyrin] spacer, which was supposedly the product of a Glaser–Hay coupling. The structures were also analyzed by using X-ray photoelectron spectroscopy (XPS)[167] and NEXAFS;[168] these techniques showed that the peripheral platinum centers acquire electron density at the expense of electron density of the core N 1*s* orbitals, and that both chromophores communicate intramolecularly.

Takahashi and co-workers used Sonogashira–Hagihara coupling (six equivalents of *trans*-[$PtCl_2(PEt_3)_2$], CuCl, piperidine/dioxane) to furnish *meso*-tetrakis(*p*-ethynylphenyl)porphyrin (**115**Zn) with four {$PtCl(PEt_3)_2$} units to serve as a dendrimer core (**116**Zn; Scheme 19).[169] (Platinumacetylide)acetylene dendrons of generation one (**G1**), two (**G2**), and three (**G3**) were synthesized in the same way, and then attached (convergent approach, CuCl in Et_3N/THF) to **116**Zn to give organometallic porphyrin dendrimers **117G*n***Zn ($n=1$–3) in yields of 73 %, 67 %, and 41 %. Electronic studies revealed that the extinction coefficients of the porphyrin as well as its fluorescence at 617 nm (excitation in the platinumacetylide MLCT band) decrease with an increase in the generation, which indicates efficient energy transfer from the periphery to the core.



Scheme 19. Porphyrin-cored platinum bis(acetylide) dendrimers synthesized by Takahashi.[169]

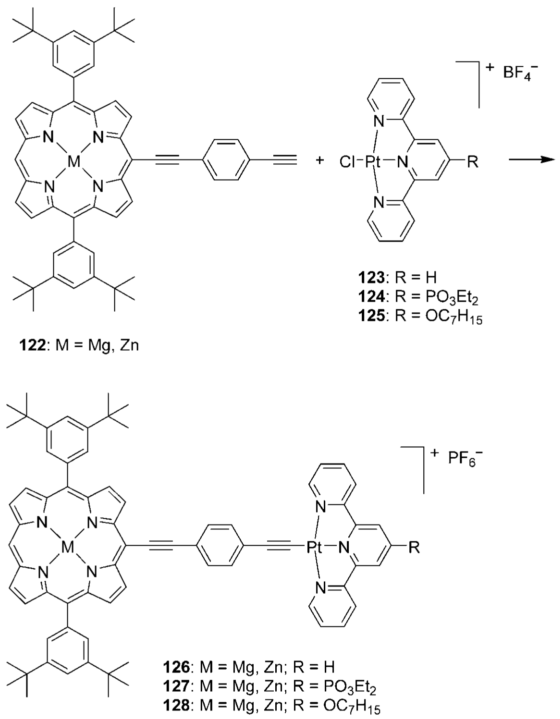
A similar *trans*-{(C≡C)$Pt^{II}(PBu_3)_2$(C≡C)} moiety was employed by Harriman, Ziessel and co-workers to connect a zinc(II) porphyrin fragment to a $[Ru(bipy)_3]^{2+}$ ion.[170] *Meso*-trimesityl(*p*-ethynylphenyl)porphyrin (**118**Zn) was reacted with one equivalent of *trans*-[$PtCl_2(PBu_3)_2$] in the presence of catalytic amounts (1 %) of CuI in *i*Pr_2NH/THF to give diad **119**Zn in 72 % yield, and with half an equivalent to give triad **120**Zn in 20 % yield (Scheme 20). A $[Ru(bipy)_3]^{2+}$ moiety was attached to **118**Zn by a similar methodology using [Ru(bipy)$_2$(4-ethynyl-2,2′-bipyridyl)]$^{2+}$ to give triad **121**Zn in 51 % yield. Hardly any electronic interaction between the chromophores is observed within these systems in the ground state. The platinum moiety in **121**Zn 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 platinum(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, as described by Ziessel and Harriman.[170]

Upon excitation of the porphyrin part of **121**Zn (565 nm), the fluorescence is quenched by circa 50 % with respect to a reference zinc porphyrin that was not peripherally metalated. Because the central platinum(II) diacetylide unit imposes a barrier for through-bond electron exchange, it was postulated that the quenching originates from a Förster-type singlet–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 **120**Zn and **121**Zn. Whereas rapid $S_2 \rightarrow S_1$ internal conversion, followed by $S_1 \rightarrow S_0$ fluorescence, takes place in **120**Zn, **121**Zn 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 platinum(II) acetylide fragment was employed by Odobel, Hammarström and co-workers in complexes for photoinduced electron transfer.[171] They hypothesized that the carbon–platinum σ bond could allow large electronic coupling between the substituents. The ligand terpy (2,2′,6′,2″-terpyridine) and derivatives with phosphonate or ether *para* substituents were reacted with [Pt(cod)Cl$_2$] (cod = 1,5-cyclooctadiene) to form the corresponding platinum acetylide complexes **123**–**125**. A zinc(II) porphyrin (**122**Zn) or magnesium(II) porphyrin (**122**Mg) tethered with a terminal alkyne fragment was then attached to these compounds by a Sonogashira–Hagihara coupling in the presence of CuI and *i*Pr$_2$NH. The metalloporphyrin–acetylide(terpy)platinum diads were obtained in yields ranging from 45 to 71 % for the zinc(II) porphyrins, and 60 to 90 % for the magnesium(II) porphyrins (Scheme 21).



122: M = Mg, Zn

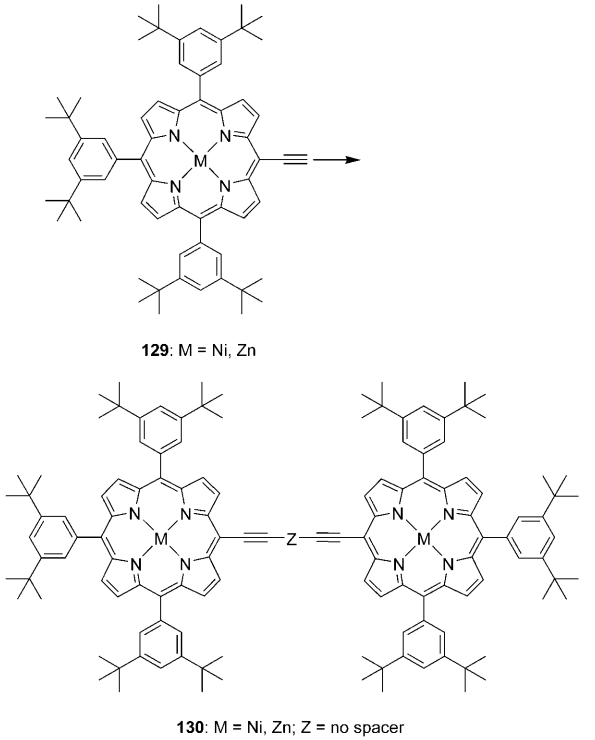
123: R = H
124: R = PO$_3$Et$_2$
125: R = OC$_7$H$_{15}$

126: M = Mg, Zn; R = H
127: M = Mg, Zn; R = PO$_3$Et$_2$
128: M = Mg, Zn; R = OC$_7$H$_{15}$

Scheme 21. Metalloporphyrin–acetylide(terpy)platinum diads developed by Odobel and co-workers.[171]

Cyclic voltammetry studies 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 for the reduction potential of the platinum center with an electron-withdrawing phosphonate substituent, stabilizing the reduced terpyridine and thus facilitating the reduction of this moiety. The absorption spectra of all the diads are virtual superpositions of those of their constituents, but by comparison with reference porphyrins it was shown that the fluorescence of the porphyrin moieties is almost quantitatively quenched in every case. The very rapid quenching of the S$_1$ state was explained by electron transfer to the platinum units.

To test the hypothesis that a platinum acetylide unit contributes beneficially to conjugation of its substituents, Yeh and co-workers synthesized two types of bis(porphyrin) compounds.[172] Monoacetylene precursors **129**Ni and **129**Zn were reacted with either *trans*-[PtCl$_2$(PEt$_3$)$_2$] in diethylamine to yield platinum-linked bis(acetylidoporphyrin)s **131**Ni and **131**Zn in yields of 66–68 %, or with CuI in air to form butadiyne-linked bis(porphyrin)s **130**Ni and **130**Zn (Scheme 22, Figure 8). UV/Vis and CV measurements showed that the porphyrin subunits are much more strongly coupled in the ground state in **130**Ni and **130**Zn than in their platinum-linked counterparts. Evidence based on UV/Vis measurements on the monocations, generated by oxidation with [(p-BrC$_6$H$_4$)$_3$N]SbCl$_6$, gave further support. The nickel complexes interact more strongly with one another than the zinc analogues.



129: M = Ni, Zn

130: M = Ni, Zn; Z = no spacer
131: M = Ni, Zn; Z = Pt(PEt$_3$)$_2$

Scheme 22. Triads prepared by Yeh et al.[172]

In the search for new ways to interconnect porphyrin subunits in cyclic trimeric porphyrin hosts, Sanders and co-workers used *trans*-(diacetylide)platinum(II) moieties.[165,173] The formal insertion of a square-planar-coordinated platinum center into the single bond of the ≡C–C≡ unit was anticipated to lead to a larger central cavity relative to their butadiyne-linked congeners,[174] so that other guest molecules could be incorporated.

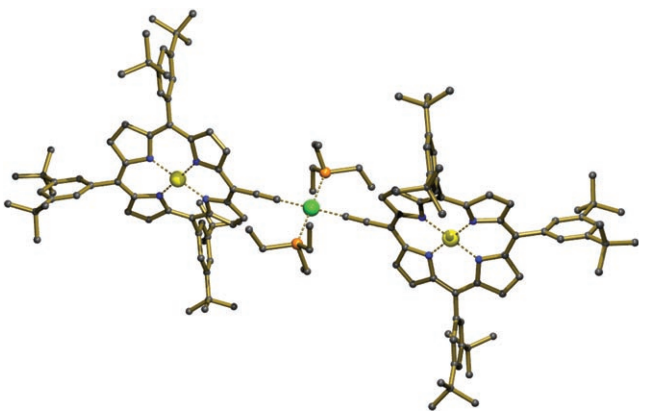
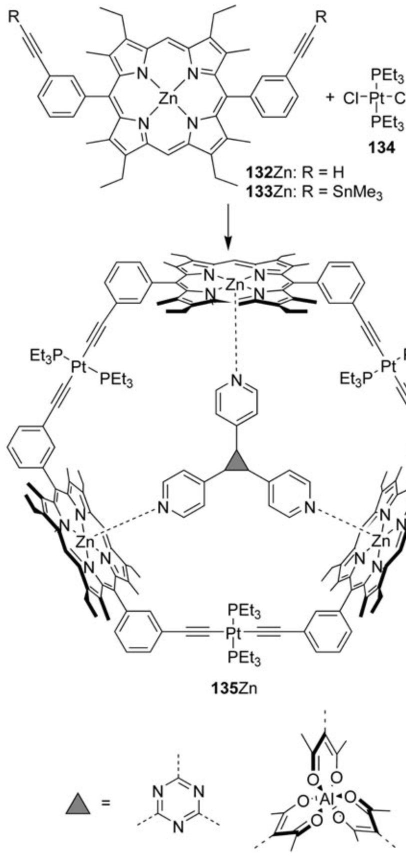


Figure 8. X-ray structure of **131** Zn in the solid state. Green Pt, yellow Zn, orange P, blue N.

A zinc(II) β-octaalkyl-5,15-bis(phenyl)porphyrin, in which the phenyl groups contain acetylene groups at their 3-positions (**132** Zn), was linked to *trans*-[PtCl$_2$(PEt$_3$)$_2$] (**134**) using a Sonogashira–Hagihara coupling in diethylamine, giving the desired trimer **135** Zn in 16% yield (Scheme 23). In contrast to the synthesis of its butadiyne-linked analogue, the synthesis of **135** Zn by cyclotrimerization of **132** Zn could not be templated by a suitable tris(pyridyl) guest, presumably because of the presence of diethylamine, which is a competing ligand for the zinc atoms of the porphyrins. Therefore, **132** Zn was converted into the corresponding tin acetylide **133** Zn, which was trimerized using copper(I) catalysis without the use of an amine to give **135** Zn, again in 16% yield. When using **133** Zn as the monomer for trimerization, the synthesis of **135** Zn could be templated, but the yield was only increased to 20%. As predicted, the increased cavity size leads to a decreased binding constant for 2,4,6-tris(*p*-pyridyl)pyrazine relative to the corresponding butadiyne-linked trimeric host (3×10^7 vs. $10^9\,\mathrm{M}^{-1}$), whereas a slightly larger aluminum complex has a binding constant of $10^{10}\,\mathrm{M}^{-1}$ (Scheme 23).

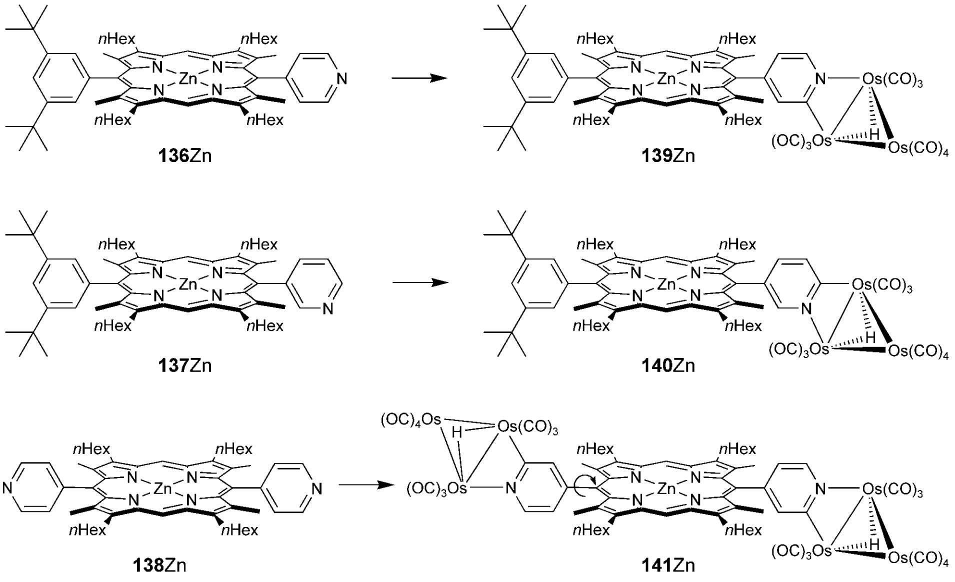


Scheme 23. Bis(acetylide)platinum-bridged porphyrin trimers from Sanders.[173]

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

3.5. Miscellaneous Porphyrins

Sanders et al. reacted the *meso* pyridine-substituted zinc porphyrins **136** Zn–**138** Zn with [Os$_3$(CO)$_{10}$(NCMe)$_2$] in dichloromethane at room temperature (Scheme 24).[175] Coordination of nitrogen to osmium followed by *ortho* metalation leads to the hydrido complexes **139** Zn–**141** Zn in yields of 31–42%. As a result of steric demands, **137** was only cyclometalated at the pyridyl position *para* to the porphyrin ring, rather than at the corresponding *ortho* position, to give **140** Zn (Figure 9). For the metalation of the 5,15-bis(pyridyl) zinc system **138** Zn, two different atropoisomers can be envisaged: one with the activated C–H bonds on the same side of the porphyrin plane (**141** Znαα), and with the activated ends on opposite sides (**141** Znαβ). Indeed, although the room-temperature ^{1}H NMR spectrum only shows evidence for highly dynamic species, signals arise at low temperatures that are consistent with the proposed structures. Regarding the representation in Scheme 24, it is possible for both hydrides to be on the same side of the molecule, or on opposite sides. The distance between them, however, makes them spectroscopically indistinguishable. Compared to the parent zinc porphyrins **136** Zn–**138** Zn, the UV/Vis spectra of **139** Zn–**141** Zn show slight hypsochromic shifts of the Soret band of 4, 3, and 7 nm, respectively. Whereas the fluorescence intensities of the metalated complexes are somewhat quenched with respect to those of the parent compounds, the phosphorescence intensities increase upon metalation. This observation was attributed to a heavy-atom effect rather than arising



Scheme 24. Organometallic porphyrins prepared by Sanders.[175]

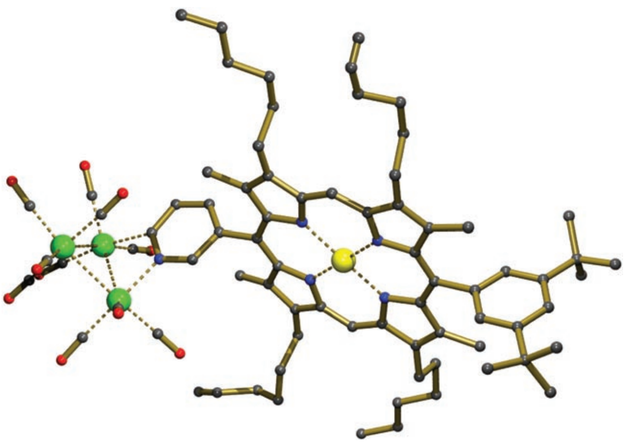


Figure 9. X-ray structure of **140 Zn** in the solid state. Green Os, yellow Zn, blue N, red O.

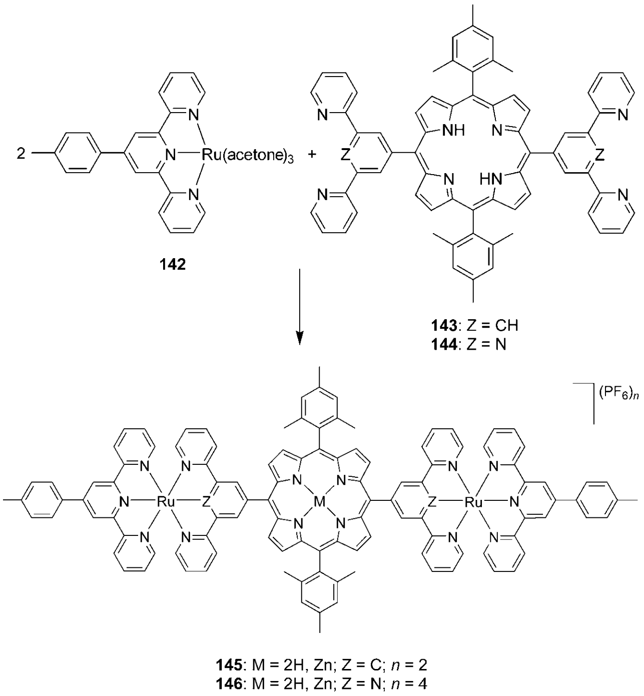
from energy- or electron-transfer processes within the molecules.

Transition-metal complexes of poly(2-pyridyl)phenyl groups have emerged as interesting optical materials.[176] 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 NCN–ruthenium moieties.[177] They used a Lindsey–MacDonald [2+2] condensation of 5-mesityldipyrromethane and 3,5-bis(2-pyridyl)benzaldehyde to give the tritopic ligand **143** in 39 % yield (Scheme 25).

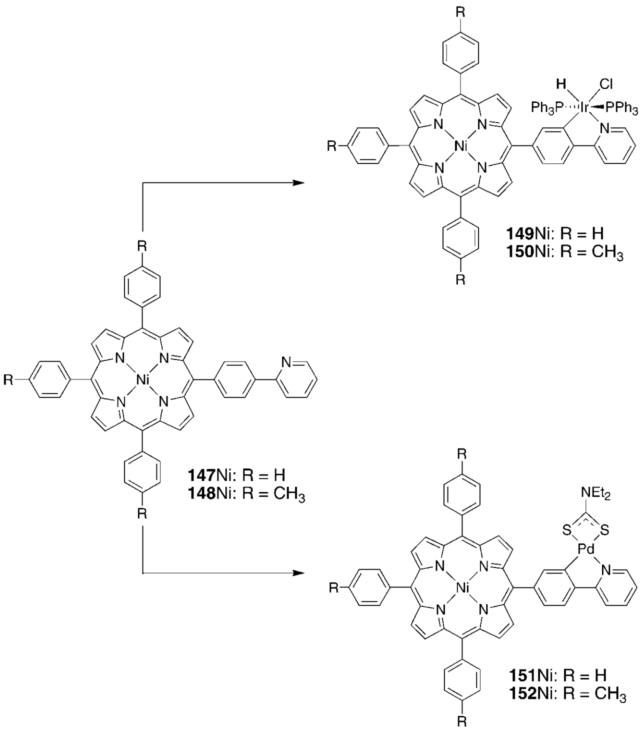
Treatment of **143** with [Ru(tterpy)(acetone)$_3$]$^{3+}$ (**142**; tterpy = 4′-*p*-tolyl-2,2′,6′,2″-terpyridine), generated by treatment of [RuCl$_3$(tterpy)] with AgBF$_4$ in acetone, in refluxing *n*BuOH yielded the PF$_6$ salt **145** in 57 % yield after column chromatography and anion exchange. The corresponding zinc chelate **145** Zn was readily prepared in quantitative yield by a reaction with Zn(OAc)$_2$·2 H$_2$O in a methanol/acetonitrile mixture. These two compounds were compared to the analogous NNN complexes **146** and **146** Zn by cyclic voltammetry and UV/Vis spectroscopy. It was found that there is a larger degree of communication between the porphyrin and the peripheral ruthenium(II) centers for Ru–NNN ligation than for Ru–NCN ligation. In contrast to several bis(ferrocenyl)porphyrins (see Section 3.1), 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 substituted in the meso position with *p*-(2-pyridyl)phenyl groups, and the pyridylphenyl unit was subsequently metalated with palladium and iridium (Scheme 26).[178]

Reaction of either the *meso*-tris(phenyl) derivative **147** Ni or the analogous tris(*p*-tolyl) compound **148** Ni with [Ir(H)$_2$(PPh$_3$)$_2$(O=CMe$_2$)$_2$]BF$_4$ in dichloromethane at room temperature furnished iridium(III) complexes **149** Ni and **150** Ni in moderate yields of 27 and 40 %, respectively. Both starting complexes also react readily under electrophilic palladation conditions with K$_2$[PdCl$_4$] in a refluxing solvent mixture of



Scheme 25. Peripherally ruthenated porphyrins prepared by Collin.[177]

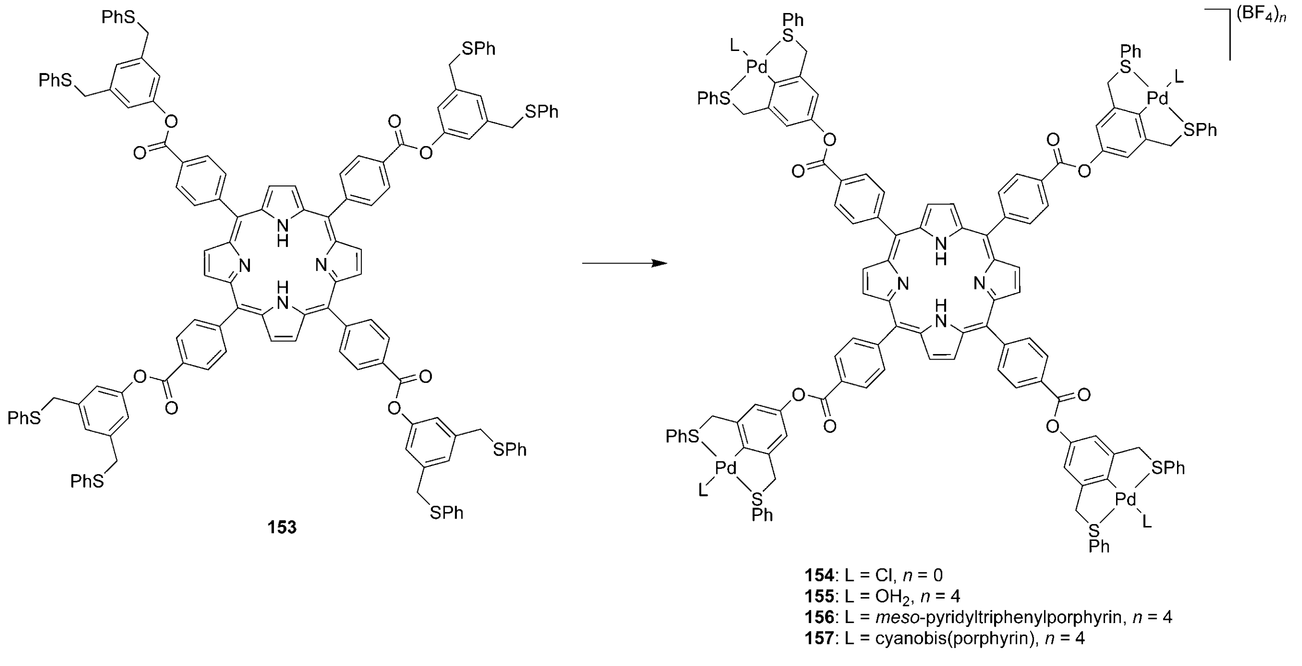


Scheme 26. Cyclometalated porphyrins prepared by Leung.[178]

MeOH/THF. The initial products, which were assumed to be chlorido-bridged dimers, are insoluble in the reaction mixture and precipitate out, which may explain why similar bis(phenylpyridine)porphyrins do not undergo double palladation: precipitation occurs after the first metalation step, which prevents further reaction. The insoluble intermediates were converted into monopalladium complexes **151**Ni and **152**Ni by treatment with $K_2SC(S)NEt_2$ in low yields (27 and 29 %). Remarkably, the peripheral metalation leads to bathochromic shifts of the Soret band for all the complexes, whereas the Q bands remain unchanged. This shift was larger for the iridium complexes (ca. 5 nm) than for their palladium counterparts (ca. 1 nm).

Metal complexes of the potentially tridentate ECE pincer ligand $[2,6\text{-}(ECH_2)_2C_6H_3]^-$ (E = NMe_2, SPh, PPh_2, AsPh) have come to the attention of researchers operating in different fields of chemistry, such as catalysis and materials chemistry, as the properties of the ligand can be tailored by altering its various components.[179–182] The combination of the properties of these molecules with those of porphyrins has led to novel molecular combinations.[177,183,184] The rigid fourfold symmetry of the porphyrin was exploited by Reinhoudt and co-workers[183] as an organization precept in the non-covalent synthesis of multiporphyrin systems through metal–ligand interactions.

Four equivalents of the SCS pincer ligand 3,5-bis[(phenylsulfido)methyl]phenol was reacted with one equivalent of tetrakis(4-chlorocarbonylphenyl)porphyrin and triethylamine in dichloromethane to yield tetrakis(SCS) porphyrin **153** in 32 % yield. The corresponding tetra(SCS-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 **154** was obtained in 90 % yield (Scheme 27). Dehalogenation of **154** with four equivalents of $AgBF_4$ gave the tetracationic aqua species **155**, which was subsequently treated with 5-pyridyl-10,15,20-triphenylporphyrin to give the pentameric porphyrin assembly **156** in quantitative yield. A nonameric porphyrin array (**157**) was also obtained quantitatively from **155** and four equivalents of a cyanobisporphyrin. There is no appreciable communication between

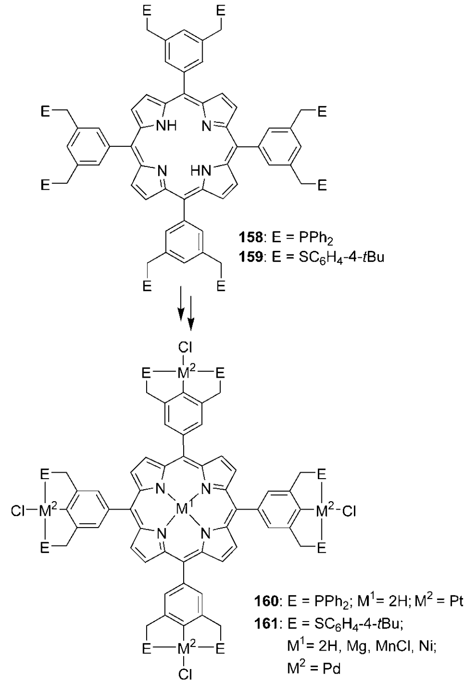


154: L = Cl, $n = 0$
155: L = OH_2, $n = 4$
156: L = *meso*-pyridyltriphenylporphyrin, $n = 4$
157: L = cyanobis(porphyrin), $n = 4$

Scheme 27. Peripherally-palladated porphyrins prepared by Reinhoudt et al.[183]

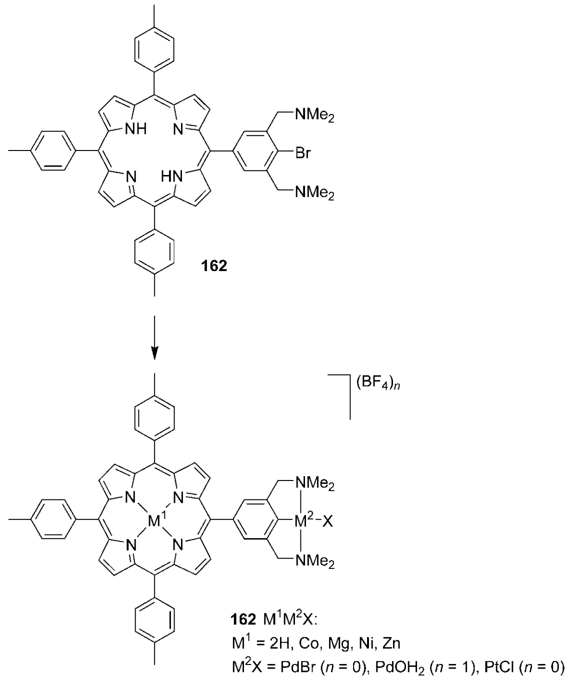
the porphyrin units in the ground state, but no excited-state measurements were undertaken to probe light-induced electron or energy transfer.

Several ECE pincer ligand groups were later directly merged with the tetraphenylporphyrin skeleton.[184] A general procedure was developed by Klein Gebbink and co-workers to obtain *meso*-tetrakis(ECE)porphyrins **158** and **159** in a modular fashion.



Scheme 28. General structure and synthesis of the pincer–porphyrin hybrids synthesized by Klein Gebbink et al.[184,188,189]

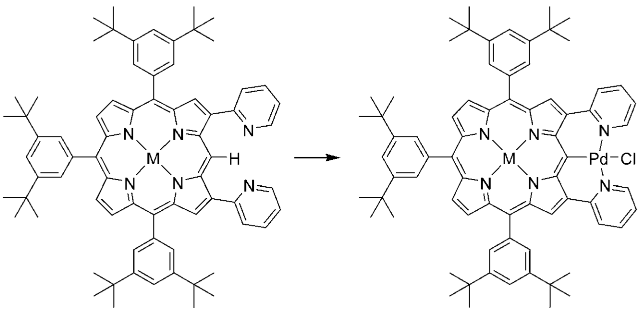
The SCS pincer–porphyrin hybrid could be metalated by the same procedure as published earlier by Reinhoudt to give fourfold peripherally pallidated porphyrin **161** in 90 % yield (Scheme 28). It is notable that in both cases, palladation of the porphyrin macrocycle was not observed, despite the fact that an electrophilic palladium(II) complex was used. Another way to metalate the periphery selectively is an ECE-pincer-selective transcyclometalation (TCM).[185] Thus, when tetrakis(PCP)porphyrin **158** was treated with four equivalents of [2,6-bis[(dimethylamino)methyl]chloridoplatino(II)-benzene], [PtCl(NCN)], in refluxing toluene, the desired tetraplatinated porphyrin **160** was obtained in quantitative yield. 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). Furthermore, it was found that the porphyrin fluorescence of free **161** was quenched by 74 % relative to that of **159**. Later, the authors found that heteromultimetallic complexes[186] could be obtained by selecting the right order of metalation steps of the parent multitopic ligands. These pincer–porphyrin hybrids were subsequently used as templates in ring-closing metathesis,[187] as catalysts,[188] and as catalyst precursors.[189] For example, a series of tetrakis(SCS-PdCl)–metalloporphyrin hybrids was synthesized by two distinct synthetic routes: **161**MnCl and **161**Ni were synthesized by fourfold electrophilic palladation of the corresponding tetrakis(SCS)–metalloporphyrins with $[Pd(NCMe)_4](BF_4)_2$ in $MeCN/CH_2Cl_2$ in yields of circa 90 %, whereas **161**Mg was obtained by treatment of **161** with $MgBr_2{\cdot}OEt_2$. These heteromultimetallic complexes exhibited different catalytic activities when used as precatalysts in the Heck reaction of iodobenzene with styrene in the presence of triethylamine.[189] The catalytic activity increased in the order of $M = MnCl < 2H < Mg$, which suggested an intramolecular electronic influence of the metalloporphyrin on the SCS pincer palladium sites.



Scheme 29. Monopincer–porphyrin hydrids synthesized by Klein Gebbink et al.[188]

A related series of mono(NCN-metal)–metalloporphyrin hybrid complexes **162**M^1M^2X was subsequently synthesized to better quantify intramolecular interaction between the two metal centers (Scheme 29).[188] Pincer metalation after, rather than before, porphyrin metalation was the preferred approach to optimize yields. The metal(0) sources $[Pd_2(dba)_3]{\cdot}CHCl_3$ and $[Pt_2(dipdba)_3]$ (dipdba = 4,4′-diisopropyl dibenzylideneacetone) were used to accomplish palladation and platination of the NCN pincer group. ^{195}Pt NMR spectroscopic investigations revealed that only a modest electronic influence was exerted by the metalloporphyrin on the NCN-PtCl group for the **162**M^1PtCl compounds (M^1 = 2H, Mg, Ni, Zn). In an analogous manner, the catalytic activity of the palladium center in the cationic mono(NCN-Pd)–metalloporphyrin hybrids [**162**$M^1PdOH_2]BF_4$ was determined to be the same within experimental error in the double Michael addition of methyl vinyl ketone to ethyl α-cyanoacetate. The only and remarkable exception was [**162**MgPdOH$_2$]BF$_4$, which exhibited a six-fold increase in the catalytic activity in comparison with its free-base, nickel, and zinc analogues. Further experiments provided evidence for a supramolecular mechanism, in which both the magnesium and palladium centers partake in activation of the substrates.

Very recently, Shinokubo, Osuka and co-workers devised a very elegant method to merge the ECE pincer skeleton with the porphyrin core structure.[190] Two 2-pyridyl fragments were attached to the 2 and 18 positions of a 5,10,15-triaryl nickel(II) porphyrin by a palladium-catalyzed reaction to give porphyrin-based, tridentate ECE-pincer ligands by virtue of the unsubstituted *meso* carbon atom and the two flanking pyridyl nitrogen atoms. The nickel porphyrin could be converted into a free-base porphyrin **163** by reatment with H$_2$SO$_4$, which could subsequently be converted into its zinc(II) and copper(II) complexes. C−H activation of the *meso* position was subsequently performed with K$_2$PdCl$_4$ in a mixture of toluene and DMF to give the corresponding compounds **163**MPd (M = 2H, Ni, Cu, Zn) in yields ranging from 71–92 % (Scheme 30). Compound **163**Pd could be synthesized in 71 % yield by treatment of **163**NiPd with sulfuric acid in refluxing trifluoroacetic acid. Apparently, no attempts were made to synthesize **163**Pd from **163**, or the reaction was not selective enough for the extraannular position. UV/Vis spectroscopic analysis of the palladated compounds showed substantial bathochromic shifts of the Soret band. For **163**Pd and **163**ZnPd, fluorescence from the porphyrin chromophore was completely quenched. The heterobimetallic compounds were used as catalysts in the Heck reaction between butyl acrylate and iodobenzene, and exhibited different activities depending on the porphyrin metal ($2\,\mathrm{H} < \mathrm{Cu} < \mathrm{Ni} < \mathrm{Zn}$).



163M **163**MPd

Scheme 30. Pincer–porphyrin hybrids synthesized by Osuka et al.[190]

4. Concluding Remarks

The covalent linking of metalloporphyrins 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–carbon bond. The chemical robustness of the organometallic group in particular plays an import role in selecting the synthetic route, as the reaction conditions used for porphyrin synthesis, that is, employing Lewis or Brønsted acidic catalysts, are often incompatible with the lability of the metal–carbon bond.[68] When the synthetic strategy relies on the selective metalation of a free-base porphyrin with (an) attached ligand group(s), mild, orthogonal metalation methods should be chosen that are capable of discriminating between the porphyrin and the peripheral ligand moiety.

Both the metalloporphyrin entity and the peripheral organometallic group of the peripherally-metalated metalloporphyrins can have a multitude of functions. The porphyrin can be used as a photochemical group, as a redox-active unit, or it can act 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 fashion.

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 group or its Lewis acidic nature can be exploited to covalently organize multiple functional groups by rotation around, for example, 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 affect the properties of the organometallic group. 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 and platinum bis(acetylido) groups, have been extensively applied because of their unique properties and robustness. The molecular combination of porphyrins with more reactive organometallic moieties has yet to commence. Research in this area will show whether the amalgamation of the photo- and redox-active properties of metalloporphyrins with those of organometallic complexes give rise to new reactivity profiles for either or both.[192]

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