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Chemical Synthesis in Solution and Porphyrin Nanostructures on Surfaces - Similar Concepts, Different Results

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The chemistry of porphyrins is reaching out to more complex and ever larger polyporphyrin arrays. In solution the synthesis of porphyrin arrays is greatly aided by recent advances in organometallic chemistry which now allows the rational construction of selected tetrapyrrole scaffolds. Examples for these are unsymmetrical porphyrin arrays with conjugating and nonconjugating linker groups and the use of presenting scaffolds such as triptycenes. In order to circumvent a laborious and step-wise organic synthesis of porphyrin arrays efforts are underway to utilize principles of self-aggregation and organization for the construction of ordered nanostructural arrays on metal surfaces. Here, even rather simple systems are able to form highly ordered structures. On the other hand, thermal activation can be used to form covalent bonds between individual porphyrin molecules to yield highly ordered, large, and stable arrays. The type of structures formed depends on the porphyrinoid material, the metal surface, and the deposition methods.

Introduction

Mulitporphyrinic arrays are important in nature and much work is being undertaken to create arrays which mimic such biological processes present in light harvesting complexes for applications in solar energy conversion. Artificial models of porphyrin arrays with distinct geometries can provide a useful insight into the mechanisms of electron and energy transfers within these photosynthetic systems and also could duplicate light harvesting and electron transfer characteristics (1). Thus, it is necessary to develop synthetic strategies towards the development of such arrays. Multiporphyrin arrays can be generated by various routes (2) and the strategy adopted will depend on how the array is connected, i.e. whether it is non-covalently linked or covalently linked, and also on the type of linker or spacer group between the porphyrin sub-units which form the array (3). Covalently linked porphyrin arrays, depending on the class of linkage required can be assembled through various organometallic synthetic methods. Multiporphyrin arrays, if exhibiting enhanced delocalized π-conjugation, can serve as materials for NLO, PDT and other optical applications, which require long-wavelength absorption. The electronic properties of these arrays can be fine-tuned via structural modifications of the porphyrin sub-units either at the monomeric stage or through post array construction modifications; for example by variation of the central metal or by alteration of meso and β substituents.

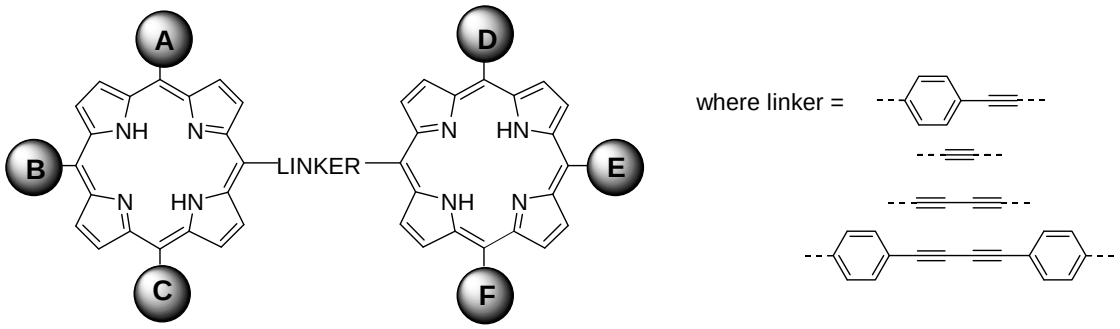


Figure 1: Model compound for unsymmetric conjugated multiporphyrin arrays

Ethynyl linked porphyrin arrays and derivatives of such a conjugated linker such as phenylethyne and butadiyne linkers, are widely known in the literature. As a result of the conjugation through the linker, there is strong excitonic and electronic coupling between the porphyrin units and this causes a pronounced shift in absorption profiles into the visible and near infra-red regions. Directly linked multiporphyrin arrays, both singly and triply fused, have the potential to be utilized in applications such as optoelectronics and nanotechnology. These directly linked arrays exhibit extremely efficient and rapid electron transfer along the array as the porphyrin chromophores interact strongly with one another as they are closer together than arrays connected via covalent linkers. With meso-meso directly linked arrays, the porphyrins lie orthogonal to each other (Figure 2), whereby the electronic delocalization is minimal, in contrast to the conjugatively linked arrays. In contrast, *β-β*, meso-meso, *β-β* triply linked arrays exhibit a substantial increase in electronic delocalization and the π-conjugation is greatly enhanced through the array. Such oligomers are suitable for a wide range of optical applications.

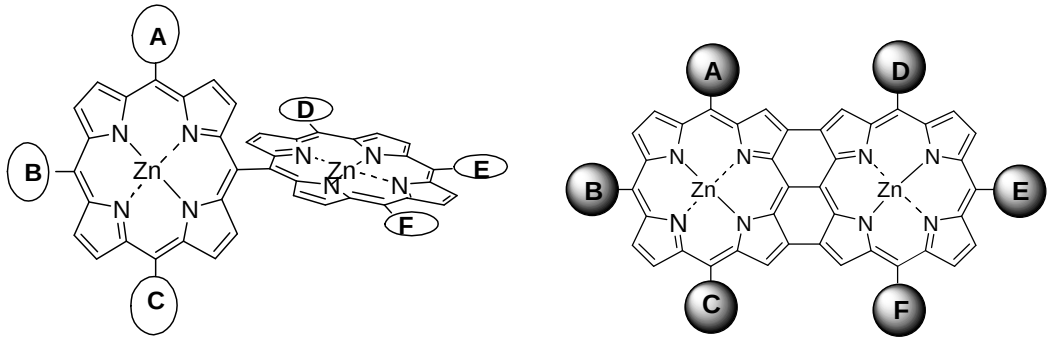


Figure 2: Model compounds for unsymmetrical singly (orthogonal conformation) and triply linked bisporphyrins

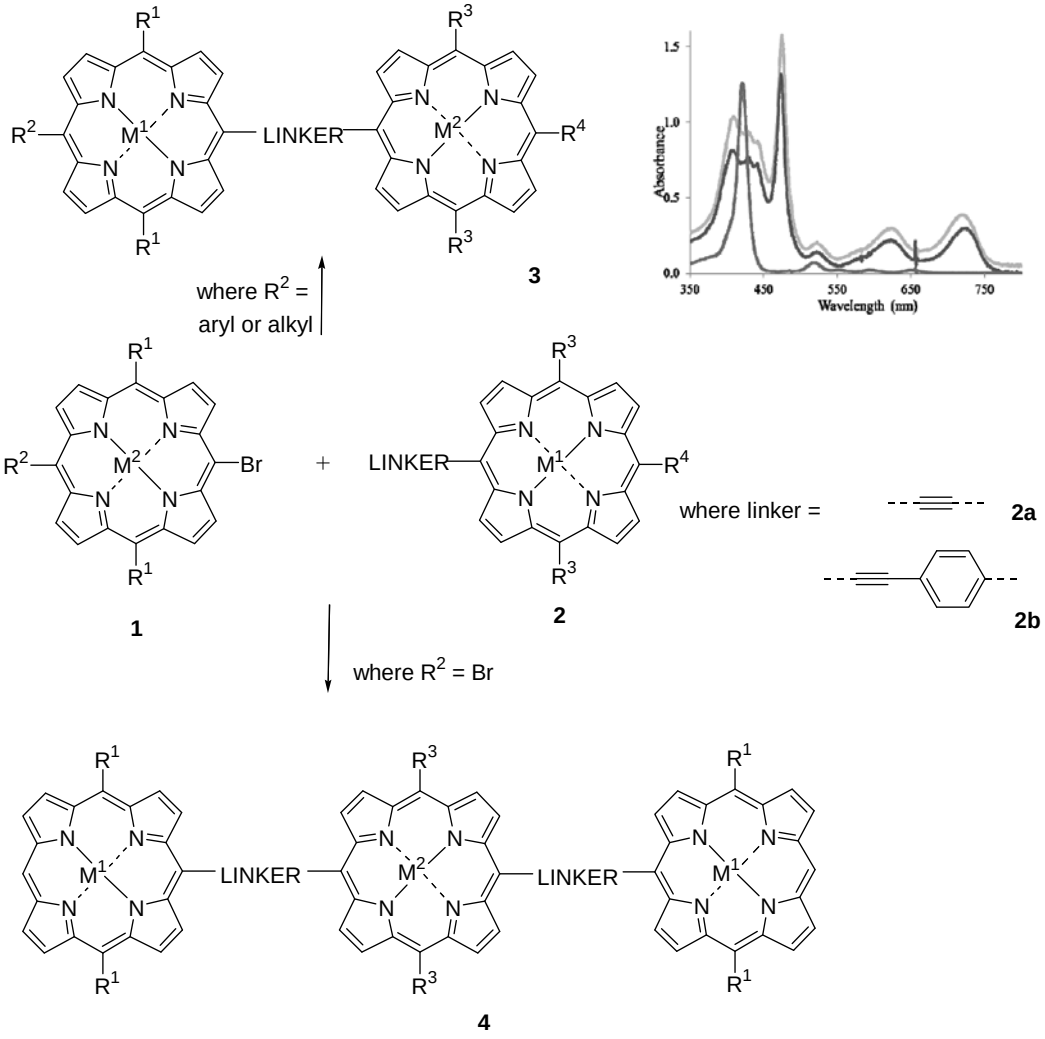
A convenient way to extend the absorption profile of porphyrins is via construction of alkynyl linked arrays, via palladium catalyzed reactions, whereby a λ_{max} of greater than 700 nm can be reached. To further extend the absorption into the near-IR region, oxidative fusing methods developed by Osuka and co-workers can be adopted for the generation of so-called triply fused porphyrin dimers. By doing so, a λ_{max} of 1050 nm and beyond may be achieved and these covalently linked multiporphyrin arrays can act as multichromophoric model systems for the study of electron transfer in light-harvesting systems. Although the Osuka group, amongst others (4), have extensively researched this area, their work primarily deals with symmetric arrays and photophysical studies of such

porphyrins (5). Only limited research has been carried out on so-called unsymmetrical fused dimers (6) and post-modifications of fused arrays (7).

Synthesis of Porphyrin Dimers in Solution

1) Unsymmetrically substituted dimers

First we targeted alkyne and phenylacetylene linked arrays and the further development of the synthetic chemistry for unsymmetrical array systems. As the π-delocalization extends into the alkyne spacer group, these arrays are linear and sterically non-demanding (8). Our approach incorporated two strands: the first was the synthesis of unsymmetric dimers, namely alkyne linked arrays. These unsymmetric dimers can contain both hydrophilic, hydrophobic and 'push-pull' entities at the various meso positions. The second approach was to synthesize symmetric conjugated porphyrin dimers and trimers with free meso positions (9).



Scheme 1: Synthesis of alkyne and phenylacetylene linked dimers/trimers. Sonogashira - $PdCl_2(PPh_3)_2$, CuI, TEA, THF, 40-60 °C, 16 h; copper-free Sonogashira - $Pd_2(dba)_3$, $AsPh_3$, THF, TEA, 60 °C, 16 h. Inset: UV-vis absorption spectra in CH_2Cl_2 of alkynyl dimers **3a** versus their monomeric alkyne of type **2a**.

Both strategies utilized Pd-catalyzed cross-coupling reactions and the free meso positions on the symmetric arrays allow subsequent chemical modifications to be carried out. They also utilize organolithium methods (10) to introduce the phenylacetylene linker and the substituents on the porphyrin core. Sonogashira coupling was used to introduce the alkyne linker and also for coupling reactions. The linear constructs can be generated in moderate to good yields adopting these methods. Additionally, non-linear, namely "L- and T-shaped" arrays can be synthesized via similar organometallic C-C coupling reactions, albeit in lower yields.

Introduction of alkyl substituents into the periphery greatly enhanced the solubility and hence the yields. Depending on the type of oligomer/linker desired, different palladium-catalyzed coupling methods were adopted for their synthesis (11). The most utilized method was copper-free Sonogashira coupling, Sonogashira coupling and also Pd-mediated Glaser-Hay type coupling for homocoupled dimers, the latter of which was used for the synthesis of more symmetric arrays. Porphyrin dimers **3** and trimers **4**, bearing various alkyl and aryl substituents, were synthesized in moderate to good yields of up to 67 % using Pd-mediated Glaser coupling reactions and copper-free Son with free meso positions allow for subsequent chemical modifications of the free meso positions. All dimers and trimers exhibited a bathochromic shift in their UV-vis absorption spectra compared to the monomers. In particular, the alkyne linked dimers showed strong absorption around 720 nm, making them good candidates for use in other optical applications (Inset Scheme 1). With unsymmetrical dimers and trimers, through the alteration of substitution patterns, they could allow for the fine-tuning of their optical properties for various applications.

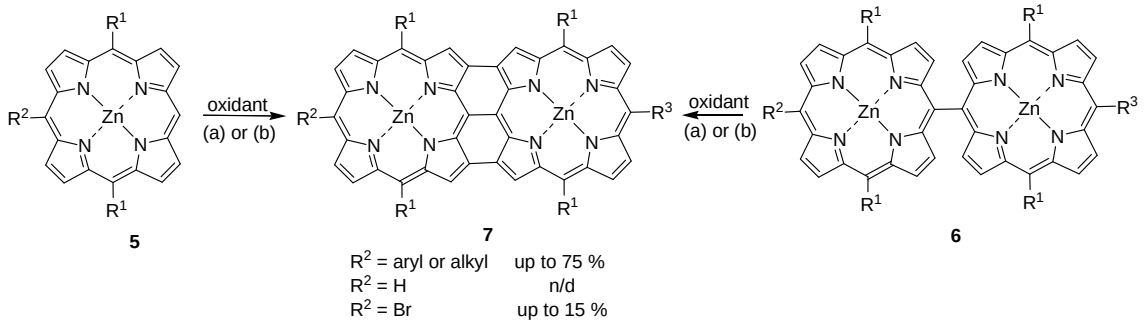
2) Fused Porphyrin Arrays

Following the synthesis of meso-meso directly linked porphyrins by Susumu *et al.* in 1996 via a condensation reaction (12), there has been extensive development of the synthesis of such arrays. These include total synthesis (13), Ulmann coupling (14), oxidative fusing of free meso porphyrins with oxidants such as hypervalent iodine (PIFA) (15), silver salts ($AgPF_6$) (16) and DDQ/$Sc(OTf)_3$, along with electrochemical oxidation (17), oxidative dimerization of porphyrin anions (10) and, additionally, a stepwise synthetic strategy involving the activation of the porphyrin and subsequent Suzuki coupling. These meso-meso directly linked porphyrin dimers are important precursors for triply fused bisporphyrins.

We targeted a variety of A_3 and A_2B symmetric bisporphyrins with a range of substituents, some enabling follow-up chemistry or so-called post-fusing modifications to be carried out. The central metal ion is of great importance to the oxidative process and thus zinc porphyrins were employed for the synthesis, as they have a lower first oxidation potential and therefore are more easily oxidized than their Ni or Pd counterparts (18,19,20). Likewise, electron withdrawing substituents on the porphyrin periphery can affect yields for oxidative fusing (20). In spite of this, a series of symmetric dimers were synthesized as shown in Scheme 2. Comparable yields were obtained with both DDQ/$Sc(OTf)_3$ and PIFA oxidants, exhibiting the versatility of the oxidative fusing process and the reagents which can be employed. The novel triply fused bisporphyrins could thus be prepared from 5,10,15 trisubstituted zinc(II)porphyrin precursors, incorporating a variety of substituents, in moderate to excellent yields of 42-73 %,

following the Osuka oxidation method and this strategy can be applied for the synthesis of other fused arrays. In contrast, for the meso free dimers and bromo-substituted dimers, both the DDQ and PIFA method were employed. Unfortunately, due to the inherent extensive polymerizations of the monomers the corresponding fused dimers were not obtained. For the bromo-dimers, best results were acquired using PIFA as oxidant, although yields were much lower than for alkyl and aryl substituted dimers (up to 15 %). Previous syntheses of fused bromodimers using these oxidants also gave poor results, due to the electron-withdrawing nature of the bromo substituent which lowers the oxidation potential of the porphyrin and thereby reducing the yields of such arrays (21).

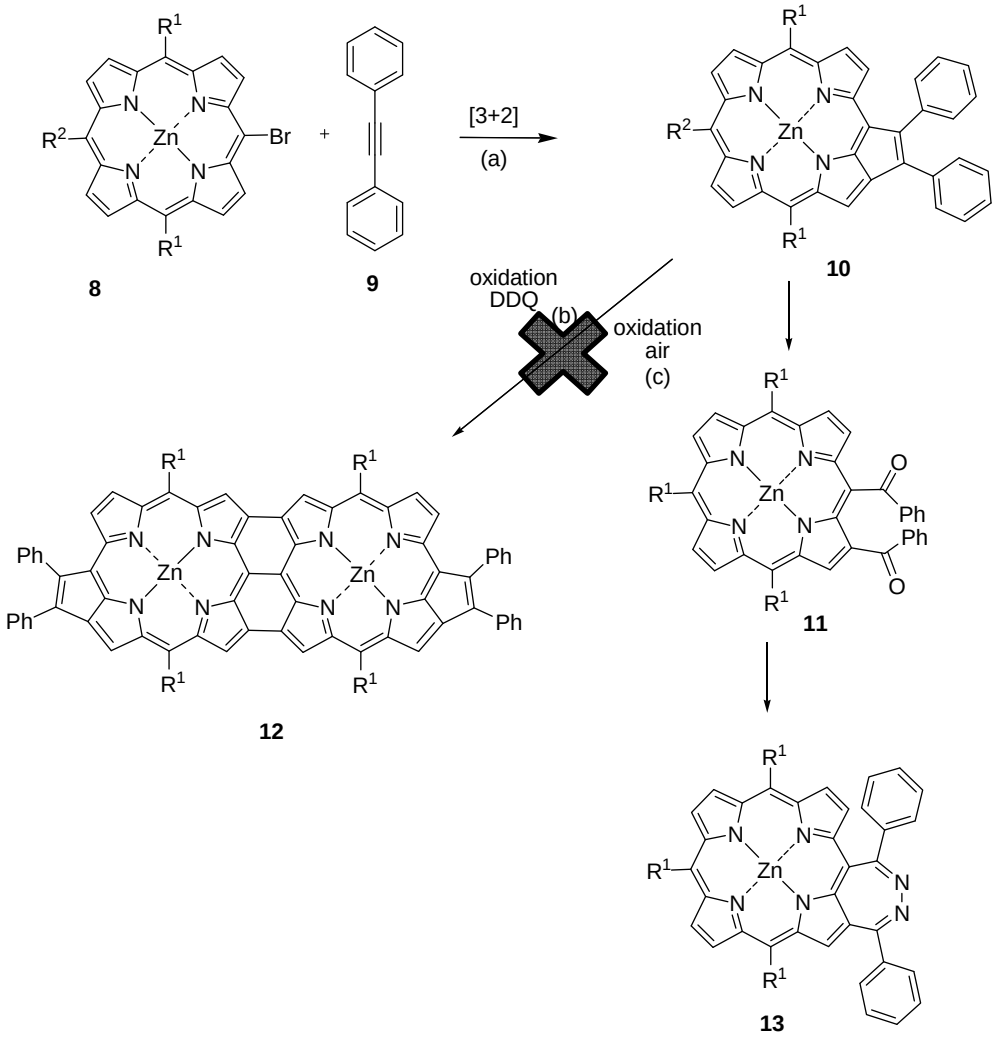
Adopting a synthetic strategy similar to that for the symmetric arrays, directly-linked unsymmetric bisporphyrins were fused oxidatively using DDQ/$Sc(OTf)_3$ or PIFA (Scheme 2). For the free meso arrays, the meso free bisporphyrins were not isolated due to polymerization, although trace quantities of these dimers were detected. Control over the oxidation for the generation of triply fused systems cannot be achieved in acceptable yields for free-meso dimers and therefore this strategy is not appropriate. For the unsymmetric hexasubstituted dimers this problem was not encountered and the triply-fused dimers can be obtained in good yields of up to 56 %. All triply fused bisporphyrins display absorption spectra with a λ_{max} of approximately 1100 nm.



Scheme 2: Synthesis of fused symmetric dimers. a) DDQ, $Sc(OTf)_3$, toluene, 50 °C, 3 h. b) i) PIFA, CH_2Cl_2, -78 °C – rt, 3 h. ii) $NaBH_4$, MeOH, 0.5 h.

Cycloaddition reactions on monomeric porphyrins are widely known, generating perturbed macrocycles with enhanced photophysical properties (22). To investigate the reactivity of the triply fused brominated dimers, a [3+2] annulation strategy developed by Osuka and co-workers (23), was adopted. This involves a palladium catalyzed C-C bond forming reaction via carbopalladation of a bromo-porphyrin with internal alkynes (24). The resulting product is a 7,8-dehydropurpurin incorporating a fused cyclopentadiene ring which causes a significant distortion of the porphyrin macrocycle. Tetrapyrroles with exocyclic 5-membered rings have biological significance but in spite of this synthetic derivatives of such are not that common (25). Resulting from the perturbation of the macrocycle, these species have interesting photophysical properties and exhibit a bathochromic shift in their absorption profile (26). We sought to apply this chemistry to dimeric porphyrins and develop a novel ‘fused on fused’ system which we hoped would further enhance the properties of the triply-fused array. The initial strategy involved the synthesis of a dehydropurpurin macrocycle with a free meso position and subsequent fusing with standard oxidative conditions which we anticipated would yield the desired triply-fused dimeric dehydropurpurin. To test reaction conditions, the [3+2] annulation was carried out on zinc(II) bromoporphyrins of type **8** and diphenylacetylene **9** (Scheme

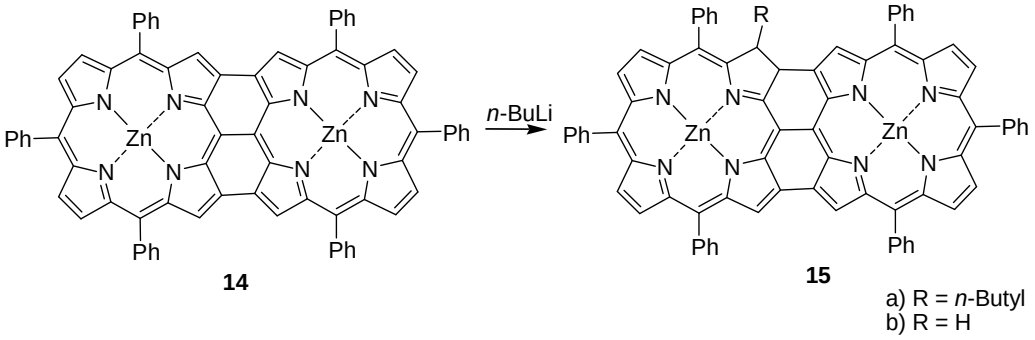
3) in yields of up to 82 %. Unfortunately, as discovered by Osuka and co-workers, the zinc-dehydropurpurins are unstable in dilute solution and on exposure to air and light. The cyclopentadiene ring-opens, most likely following a singlet oxygen oxidation mechanism, to give the 1,5-diketones **11** in almost quantitative yields. This is not seen with nickel(II) or palladium(II) porphyrins and it is thus presumed to occur from singlet oxygen generation. Attempts to triply-fuse meso cycloadduct **10** bearing a free meso position using DDQ/$Sc(OTf)_3$ for the generation of dimer **12** were ineffective, with the main product isolated being the ring-opened adduct **11** (Scheme 3).



Scheme 3: Synthesis of dehydropurpurin porphyrins and ring-opening products. a) $Pd_2(dba)_3$, (*o*-Tol)$_3$P, toluene, *N,N*-dicyclohexylamine, 120 °C, 24 h. b) DDQ, $Sc(OTf)_3$, toluene, rt. c) $CHCl_3$, air, light, 24 h. d) hydrazine hydrate, toluene, AcOH, MW, 7 min.

As the outer C-C double bond in the cyclopentadiene ring is prone to oxidation in zinc porphyrins, it does not survive these strong oxidative conditions. To provide a utility for the ring-opened products, further chemistry was investigated. 1,5-diketones are widely known to undergo various cyclization reactions to give 5, 6 and 7-membered ring products, depending on reagent and conditions used (27). The reaction of 1,5-diketones with various amino derivatives can result in the generation of nitrogen containing heterocycles (28). We decided to use hydrazine as a substrate to develop a novel diazepine-fused porphyrin. Taking 1,5-diketone **11** and employing microwave conditions,

(29) the desired azepine-porphyrin product **13** can be obtained in a good yield of 80 % (Scheme 3).

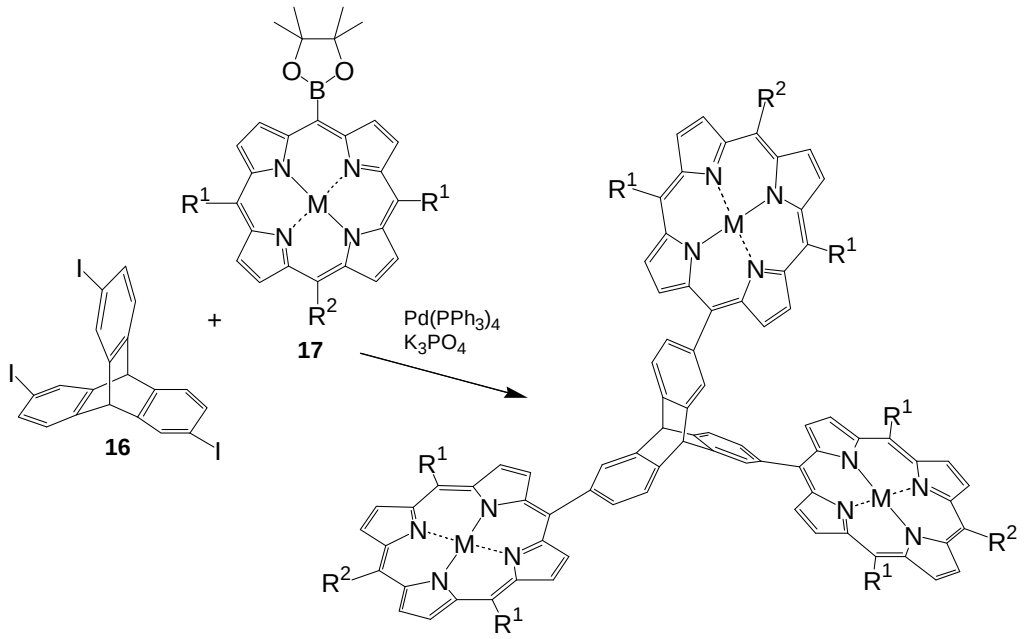


Scheme 4. a) Synthesis of *β*-butylated dimer 258 via RLi:a) i) n-BuLi, -78 °C, THF, 1 h ii) H_2O, 0.5 h iii) DDQ, 1 h. b) Diimide reduction: Tosyl hydrazine, *β*-picoline, K_2CO_3, 120 °C, 20 h.

In further attempts to functionalize the *β* positions of dimers, a chlorin formation, using organolithium reagents was investigated. Although high yielding for the introduction of meso substituents, the introduction of *β* substituents via organolithium methods can be quite challenging and low yielding and can result in the formation of chlorins, bacteriochlorins and porphodimethenes, depending on reaction conditions and substrates (30). Adopting a method developed by Senge *et al.*, whereby TPP was monobutylated at the *β*-position in 17 % yield, the fused dimer **14** was butylated under standard organolithium conditions. Dimer **15a** was isolated in a yield of 15 %, with trace quantities of the dibutylated dimer detected. The classic reduction of the porphyrin periphery to generate a chlorin species was also attempted. The diimide reduction of monomeric porphyrins, developed by Whitlock *et al.*, to their respective chlorins and bacteriochlorins, is widely known (31). Under these reductive conditions, the porphyrin pyrrolic double bond is reduced via diimide, which is generated *in situ*. The diimide species hydrogenates the double bond to generate the chlorin or bacteriochlorin, depending on the quantity of diimide generated. It was envisaged that similar principles could be applied to dimeric porphyrins to generate a novel fused porphyrin-chlorin dimer **15b** but results were inconclusive and further investigations are required.

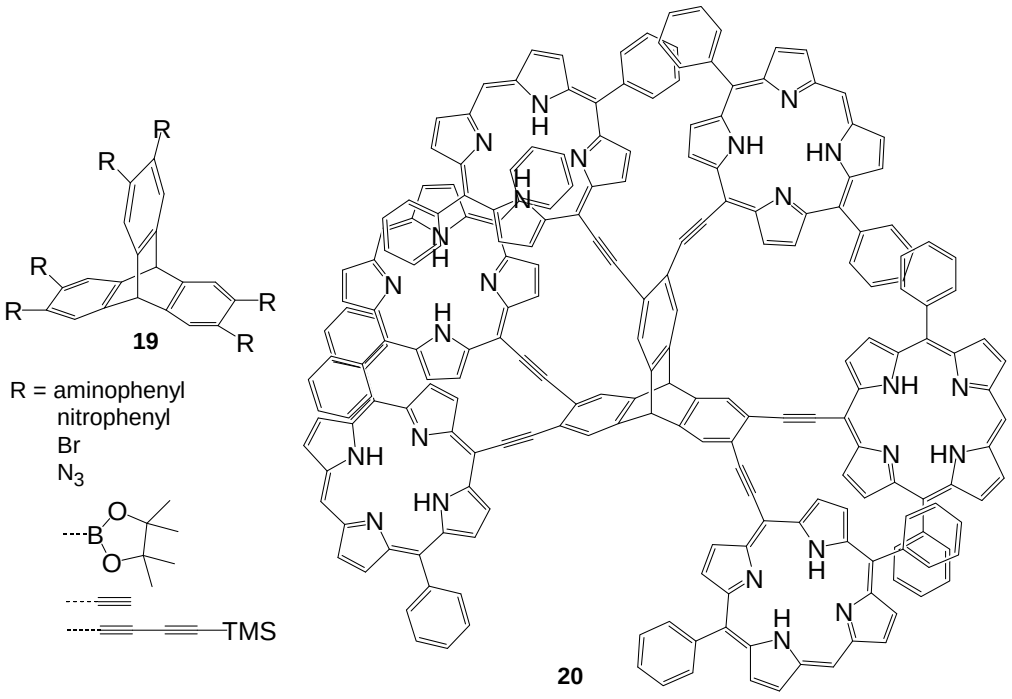
Presenting Scaffolds for Porphyrin Arrays

While linearly conjugated porphyrin arrays are required for novel optical applications such a structural arrangement is not desirable for all uses. For example, modeling of the photosynthetic light harvesting complexes or the preparation of artificial antenna systems for use in electron transfer studies or solar energy conversion requires the preparation of structurally divers systems with a larger number of porphyrin units. Next to supramolecular systems only two other approaches are possible. These are the preparation of dendritic multiporphyrins or the use of presenting scaffolds (32).



Scheme 5: Synthesis of triporphyrin triptycenes.

The latter are necessary for the design and construction of porphyrin arrays with well-defined geometries. They can provide rigid molecular machinery frameworks via relatively straightforward synthetic pathways. We have focused on the use of the triptycene unit (33) a convenient molecular scaffold to construct rotationally oriented light harvesting devices. Initially we focused on the use of triiodotriptycene **16** which can be used in Sonogashira or Suzuki coupling reactions to yield arrays with three porphyrin units **18** (Scheme 5) (34).



In order to increase the number of porphyrin units we have recently developed a set of triptycene synthons **19** that will allow the introduction of six residues at all outer aryl positions. Indeed, use of appropriate porphyrin precursors together with these synthons allowed the preparation of hexaporphyin triptycene derivatives with a rotational arrangement of the dyes (e.g., **20** in 33 % yield).

Towards Organometallic Porphyrin Chemistry on Surfaces

Next to the three-dimensional porphyrin arrays described above two-dimensional surface structures are becoming increasingly of interest. Most of the initial work in this area relied on concepts derived from supramolecular chemistry, *i.e.* the hope to create self-organized ordered structures on appropriate surfaces (35). This has been aided greatly by advances in STM technology and electron microscopy for the identification of the molecular arrangement on the surfaces. Due to the large delocalized π-system and their potential application in photovoltaic devices and as smart electrooptical materials porphyrins are especially suited for studies in this area.

1) Monomeric Porphyrins

Porphyrins in solution tend to form H- or J-type aggregate structures. Thus, one of the aims of surface deposition studies was the creation of ordered monolayer structures (36). Initial studies in this area used easily available standard porphyrins such as octaethyl-, proto- or tetraphenylporphyrin (35). In order to investigate the influence of macrocycle structure, conformation and regiochemical arrangement of substituents we have embarked on a systematic study of more appropriate porphyrin "2D synthons".

The simplest porphyrin is the unsubstituted (porphine) parent compound. The nickel(II) complex **21** can form a highly ordered closely packed 2D lattice (Figure 4) 37a). However, even a simple variation of the surface material, *e.g.*, a shift from a Ag/Si(111)-(√3×√3)R30° to a Ag(111) surface results in a completely different 2D arrangement. Here, separated, dimeric rows of porphyrin lines are formed (37b). Likewise, an extreme dependency of the self-assembled structures and lattice parameters on the reactivity of the substrate was found for (5,15-diphenylporphyrinato)nickel(II) (37c).

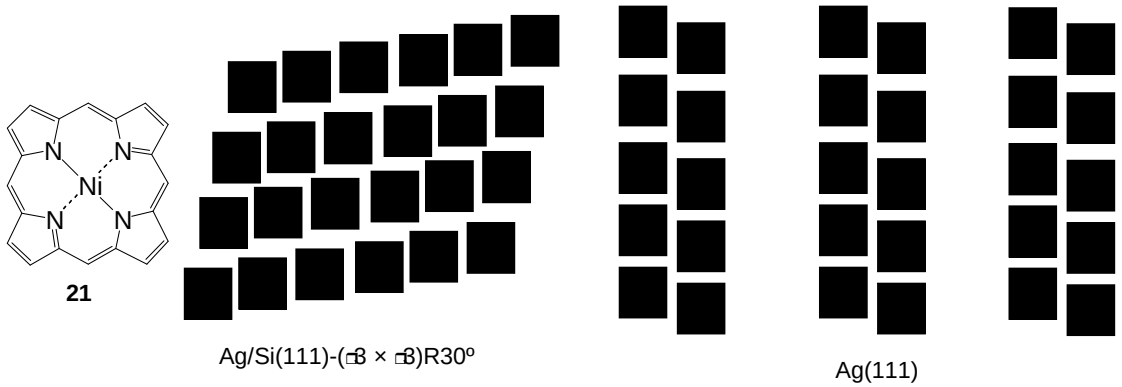


Figure 4: Surface structures of (porphyrinato)nickel(II).

2) Dimeric Porphyrins

Similarly, bisporphyrins can form closely packed arrays on the surface upon vacuum deposition. For example, a scanning tunneling microscopy/spectroscopy (STM/STS) and low-energy electron diffraction (LEED) study of the meso-meso directly-linked dimer **22** showed that at one monolayer coverage it forms a well-ordered close-packed molecular layer on a Ag(111) surface in which the porphyrin molecules have a flat orientation with the molecular plane lying parallel to the substrate. Three domains could be identified on the Ag(111) surface which grow along the main crystallographic directions of the substrate. Overall, the dimers packed sideways into long chains with close contacts between the phenyl residues (Figure 5) (38).

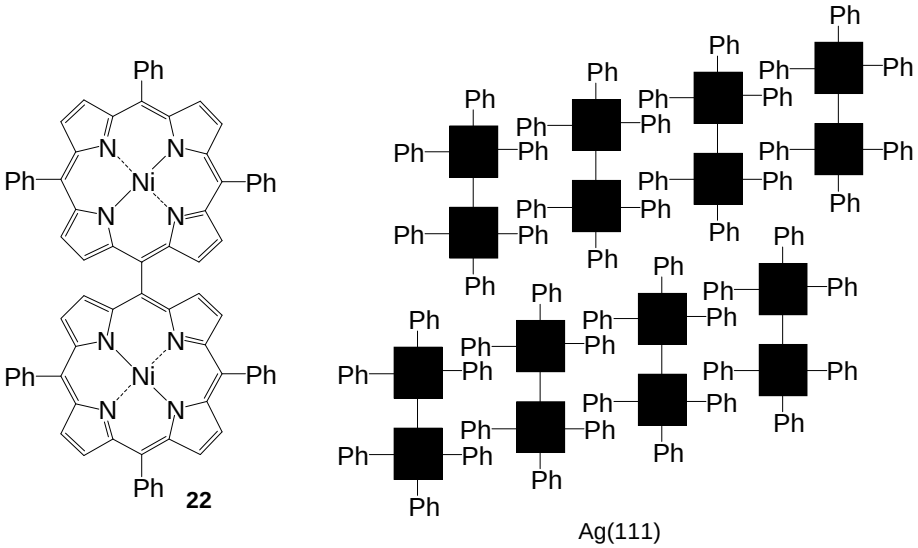
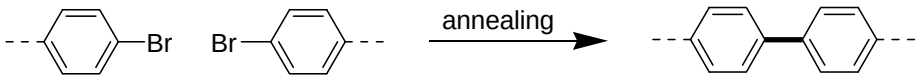


Figure 5: Surface structure of a meso-meso linked bisporphyrin on Ag(111).

3) Covalently-linked Systems

Ultimately the goal of all surface deposition studies is the creation of highly ordered layers. Similar to solution or solid phase supramolecular chemistry the use of hydrogen bond donor-acceptor units or of crystal engineering synthons is possible (39). However, emerging studies indicate the possibility to pursue logically constructed covalently linked arrays on surfaces whereby the covalent bond is formed *after* deposition on the surface. Such work was pioneered for porphyrins by Grill *et al.* in 2007 (40). As shown in Scheme 6 they were able to show that bromoaryl species can undergo C–C bond formation under elimination of the bromine atoms upon thermal annealing (Scheme 6).



Scheme 6: Grill's groundbreaking concept for the generation of covalent C–C bonds on surfaces.

This strategy opens the way for a more logical means to construct 2D-ordered structures. By using the right precursor compounds it should be possible to now introduce specific design principles into surface structures. This would allow the use of synthon-like building blocks for – in the end – multifunctional surface molecules. Indeed, similar

to the free base (40) the nickel(II) complex **25** was shown to undergo self-assembly on a metal surface and upon thermal annealing formed an extended 2D network of covalently linked porphyrins (Figure 6) (41a).

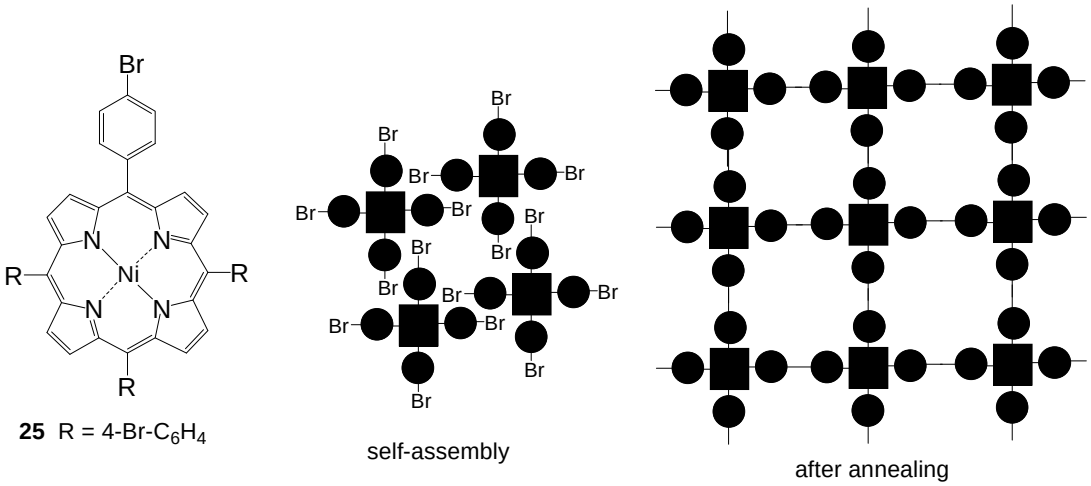


Figure 6: Self-assembled structure and formation of a covalently-linked lattice after annealing of (5,10,15,20-tetra(4-bromophenyl)porphyrinato)nickel(II) on Ag(111).

It is also possible to directly study one of the most fundamental processes in porphyrin chemistry. Use of the free base 5,10,15,20-tetra(4-bromophenyl)porphyrin on a Cu(111) surface allowed us to directly follow the metal insertion form the surface and to identify an intermediate form wherein the metal is coordinated to two imine nitrogen atoms while the pyrrole nitrogen atoms remained protonated (41b). This is the result of conformational distortion of the molecule resulting in a nonplanar porphyrin structure. These structures are known to undergo metallation quite easily (42). In a related study chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III) was found to self-assemble on a Ag(111) surface at room temperature. The axial chloride ligand is orientated away from the surface. However, upon adsorption the molecules become thermally labile. At ~423 K the chloro ligand dissociates but leaves the porphyrin macrocycle intact, giving rise to a coordinatively unsaturated Mn(III) derivative. (41c).

Conclusions

The last two decades have seen significant advances in the development of organometallic reactions for the functionalization of porphyrins. Initially applied for the derivatization of monomeric porphyrins or simple bisporphyrins these methods can now routinely be applied for the preparation of unsymmetrically substituted porphyrin arrays. Depending on the choice of precursors, catalysts and sometimes reaction conditions porphyrin dimers, trimers and oligomers of defined shape and peripheral substitution are now accessible. Likewise, functionalized materials based on scaffold materials which present peripheral porphyrins in a geometrically defined fashion allow the logical construction of structurally designed molecules.

From an organic chemists viewpoint the use of a rational synthon approach in solution chemistry and similarly in crystal engineering or supramolecular chemistry must be transferred to respective "2D" or "3D" surface chemistry. Recent advances in the characterization of porphyrin monolayers reveal a breadth of possible self assembled

structures on metal and semiconductor surfaces in dependence of the deposited porphyrin, the surface material, and the deposition conditions. Indeed, judicious choice of the porphyrin monomers, the metal and the annealing conditions allows the development of a synthon approach on surfaces.

Acknowledgments

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