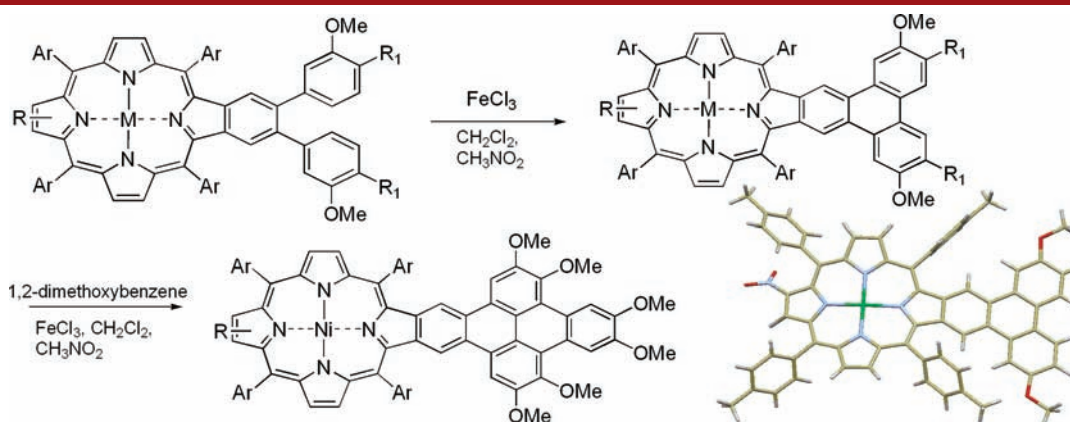# Triphenylene-Fused Porphyrins

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ABSTRACT

Triphenylene has been successfully fused to the porphyrin periphery through a convenient oxidative ring-closure reaction. Bistriphenylene-fused porphyrins and a dibenzo[*fg,op*]tetracene-fused porphyrin have also been obtained using a similar approach. These π-extended porphyrins exhibited broadened and bathochromic shifted UV−vis absorptions.

Porphyrins fused with external aromatic rings show promise in a broad range of applications in various areas, including near-infrared dyes,[1] molecular devices,[2] organic light-emitting diodes,[3] and biosensors.[4] In particular, porphyrins fused with polycyclic aromatic hydrocarbons (PAHs) hold great potential in the fast growing areas of molecular electronics and nanotechnology as heteroatom-containing molecular graphene mimics.[5] As such, the development of new methodologies to fuse aromatic rings to the porphyrin periphery has remained an intense area of interest.

The oxidative ring closure reaction has been proven to be an effective approach to construct polycyclic aromatic hydrocarbons.[6] Recently, this approach has also been utilized in porphyrins. Porphyrins fused with anthracene,[7] pyrene,[8]

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azulene,[9] and other porphyrins[5c,10] have been reported. In these π-expanded porphyrins, an aromatic fragment is designed to match the geometry of the porphyrin, such that the fusion occurs at the adjacent porphyrin *meso-* and *β*-positions. In this work, we use a different strategy. The polycyclic aromatic hydrocarbons are introduced at the porphyrin *β,β*-positions through a convenient oxidative coupling reaction. We report the synthesis and characterization of the first examples of triphenylene- and dibenzo[*fg,op*]tetracene-fused porphyrins.

Despite recent progress,[11] most of the syntheses of *β,β*-fused extended porphyrins require harsh conditions and/or are lengthy. Recently, we developed a concise method to prepare functionalized benzoporphyrins (Scheme 1).[12] In this method, an alkene reacts with a *β,β'*-dibromoporphyrin through a three-step cascade reaction involving a vicinal 2-fold Heck reaction, 6-π electrocyclization, and subsequent aromatization. This method made a new entry to access a number of functionalized benzoporphyrins. We envisioned that two vicinal aromatic rings could be introduced to the fused benzene ring(s) via this approach, and more benzene rings could then be fused to the porphyrin through the well-established oxidative ring-closure reaction.

Scheme 1. Synthesis of *opp*-Dibenzoporphyrins via Pd⁰-Catalyzed Three-Step Cascade Reaction[12]
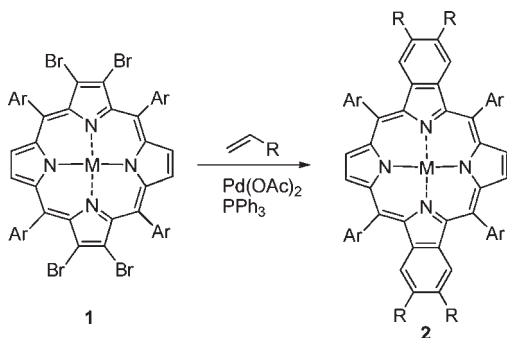
In order to investigate the viability of this approach, we prepared 2,3-dibromo-12-nitroporphyrins[13] **3a−d** (Scheme 2). Thus, **3a−d** were reacted with 3-methoxystyrene in the presence of a palladium catalyst to give aryl-substituted
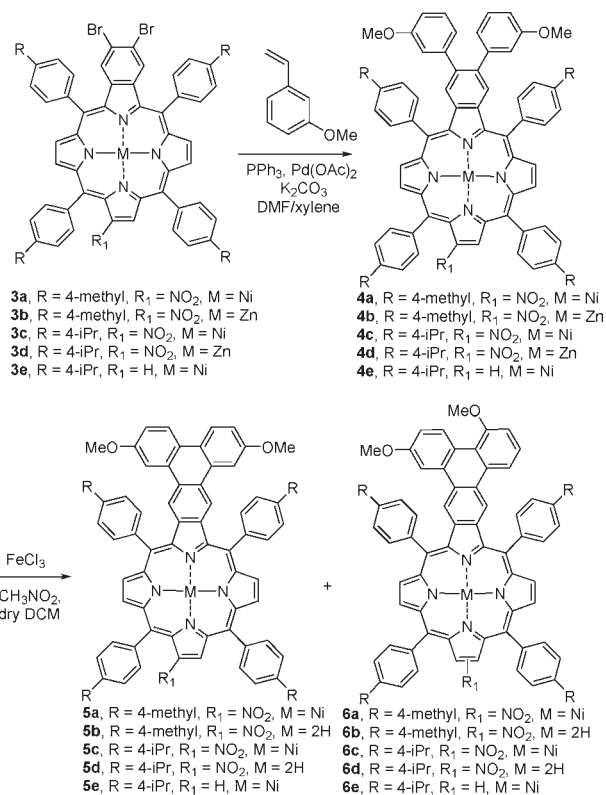
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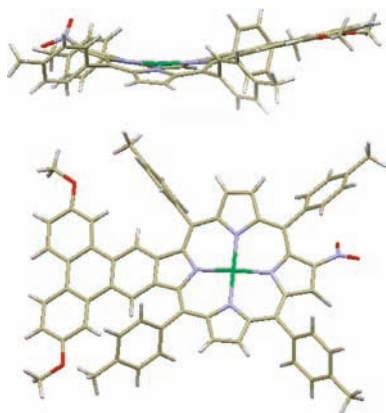
Scheme 2[a]

3a, R = 4-methyl, R₁ = NO₂, M = Ni
3b, R = 4-methyl, R₁ = NO₂, M = Zn
3c, R = 4-iPr, R₁ = NO₂, M = Ni
3d, R = 4-iPr, R₁ = NO₂, M = Zn
3e, R = 4-iPr, R₁ = H, M = Ni

4a, R = 4-methyl, R₁ = NO₂, M = Ni
4b, R = 4-methyl, R₁ = NO₂, M = Zn
4c, R = 4-iPr, R₁ = NO₂, M = Ni
4d, R = 4-iPr, R₁ = NO₂, M = Zn
4e, R = 4-iPr, R₁ = H, M = Ni

5a, R = 4-methyl, R₁ = NO₂, M = Ni
5b, R = 4-methyl, R₁ = NO₂, M = 2H
5c, R = 4-iPr, R₁ = NO₂, M = Ni
5d, R = 4-iPr, R₁ = NO₂, M = 2H
5e, R = 4-iPr, R₁ = H, M = Ni

6a, R = 4-methyl, R₁ = NO₂, M = Ni
6b, R = 4-methyl, R₁ = NO₂, M = 2H
6c, R = 4-iPr, R₁ = NO₂, M = Ni
6d, R = 4-iPr, R₁ = NO₂, M = 2H
6e, R = 4-iPr, R₁ = H, M = Ni

[a] When R₁ = NO₂, **6** might be a mixture of two isomers.

nitrobenzoporphyrin **4a−d** in 40−50% yields. Treatment of **4a−d** with excess of FeCl₃ in a mixture of nitromethane and dichloromethane (DCM) led to the formation of the triphenylene fused porphyrin **5a−d** in 35−40% yields. Other isomers (**6a−d**) were also isolated in 7−12% yield. When Zn(II) porphyrins (**4b** and **4d**) underwent oxidative coupling reactions, exclusive demetalation occurred, resulting in the formation of free base triphenylenoporphyrins (**5b**, **5d**, **6b**, and **6d**). The structures of **5a−d** were determined by ¹H and ¹³C NMR spectroscopy and MALDI-TOF MS and were further confirmed by an X-ray crystal structure of **5a** (Figure 1). The crystal structure of **5a** reveals that the *β,β*-pyrrole-fused triphenylene moiety retains its planarity, while the porphyrin core adopts a slight saddle conformation.

Initially, the identities of **6a−d** could not be determined because of their structural complexity. Compounds **5** and **6** are constitutional isomers, and their UV−vis absorptions are also similar. However, the ¹H NMR spectra of these two compounds are readily distinguished. We speculated that two types of oxidative couplings occurred to porphyrin **4a−d**. To further investigate the nature of this oxidative coupling reaction, we prepared a symmetrical benzoporphyrin **4e** from a simpler dibromoporphyrin **3e**.[13] The ¹H NMR spectrum of **6e**, which is much simpler than those of **6a−d**, suggests that **6e** resulted from an unsymmetrical ring closure of the two adjacent methoxyphenyl substituents

Figure 1. X-ray crystal structure of **5a**: top, edge view; bottom, top view.

(Scheme 2). A X-ray crystal structure of **6a** further confirmed our speculation (see the Supporting Information). This type of unsymmetrical oxidative ring closure is not favored due to the expected steric hindrance generated by the methoxy group in the bay region of the triphenylene and has never been reported previously to our knowledge. We believe that the observed unsymmetrical ring closure is caused by the competition that arises from additional steric hindrance introduced by the alkyl groups on the *meso*-phenyl rings and the methoxy group on the fused benzene ring.

Having established the feasibility of this approach of fusing one triphenylene to porphyrins, we prepared

Scheme 3
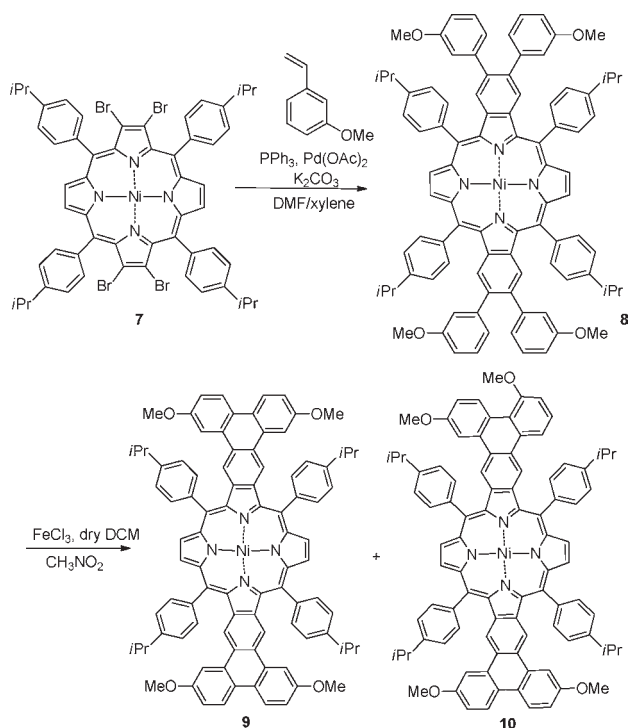
porphyrins fused with two triphenylenes to further extend the porphyrin π-system, starting from tetrabromoporphyrin **7**[13] (Scheme 3). Similar to the monofused systems, the unsymmetrical ring-closure product (**10**) was also isolated in 14% yield. The symmetrical **9** was obtained in 48% yield. The other two possible unsymmetrical ring-closure products may exist but were not isolated because of the extremely low yields.
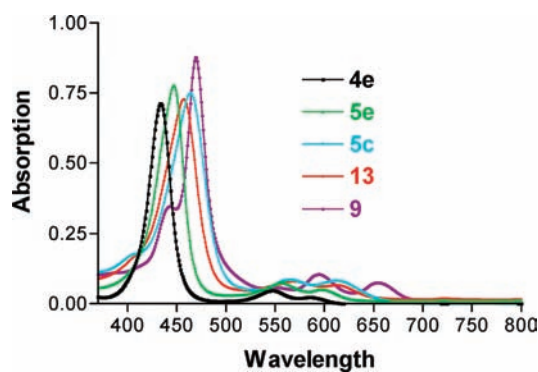
The geometry of triphenylene-fused porphyrins **5** provides an ideal template to conveniently fuse more aromatic rings, if the proper substituents are installed on the fused rings. Thus, we prepared monobenzoporphyrin **11** bearing two methoxy groups on the phenyl substituents (Scheme 4). Compound **11** was treated with 1,2-dimethoxybenzene in the presence of FeCl$_3$ as the oxidant, leading to the formation of the desired dibenzo[*fg*,*op*]tetracene-fused porphyrin **13** in 28% yield. Further investigation of this reaction suggests that, as expected, this one-pot reaction involves two steps: first, formation of the triphenylene-fused **12**; second, fusion of 1,2-dimethoxybenzene to the triphenylene moiety of **12**.

Scheme 4
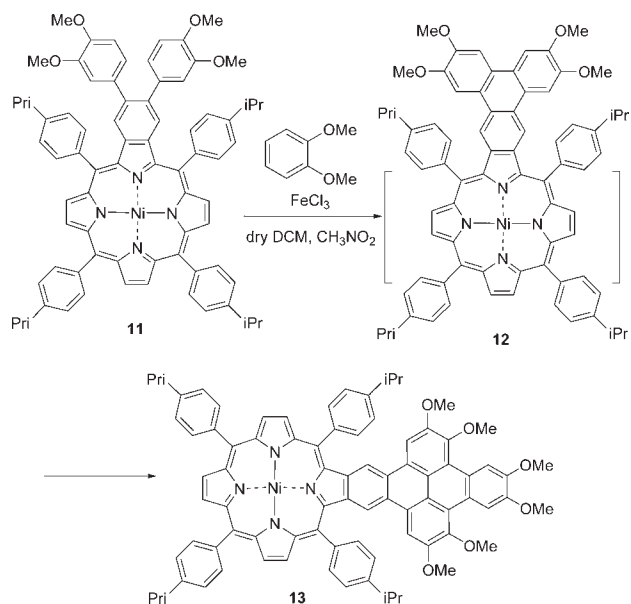
UV–vis absorption spectra of **4e**, **5e**, **5c**, **9**, and **13** are shown in Figure 2. The C_{2v} symmetrical monobenzoporphyrin **4e** showed an intense Soret band at 434 nm; upon fusion of the triphenylene moiety (**5e**), the Soret band was broadened and red-shifted to 447 nm; further extension of the π-system (**13**) pushed the Soret band to 457 nm. When two triphenylenes were fused (**9**), the UV–vis spectra displayed an interesting shouldered Soret band (with a peak maximum at 469 nm with a shoulder at 443 nm), a rare observation for Ni(II) porphyrins with D_{2h} symmetry. All the triphenylene-fused porphyrins exhibited broadened, red-shifted, and more intense Q bands, typical of π-extended porphyrins.
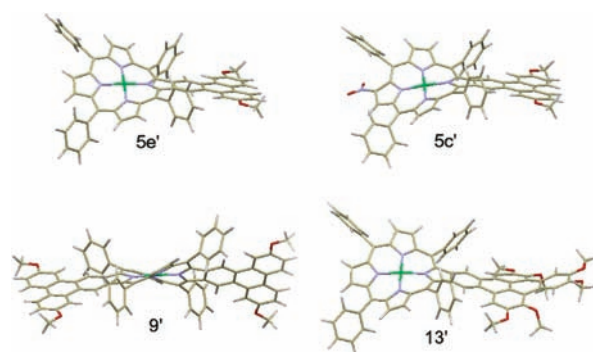
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Figure 2. UV−vis absorption spectra of **4e**, **5e**, **5c**, **9**, and **13** in CH₂Cl₂.

Figure 3. Optimized molecular structures of **5e**, **5c**, **9**, and **13** (B3LYP/6-31G(d,p)).

Density functional calculations (B3LYP/6-31G(d,p)) were conducted for **5e′**, **5c′**, **13′** and **9′**, simplified versions of **5e**, **5c**, **13**, and **9** with the isopropyl groups removed (Figure 3). Similar to the crystal structure (**5a**), the β,β-pyrrole-fused triphenylene moiety in **5c′** is essentially planar in the calculated structure; the porphyrin core is, however, a little more distorted from planarity, adopting a conformation somewhere between a saddled and a ruffled distortion. This exaggerated distortion of the porphyrin core in the DFT-minimized geometries is a well-known consequence of the shallow potential energy surfaces of Ni(II) porphyrins.[14] In the absence of a nitro group at the porphyrin β- position, **5e′** shows a less distorted structure with a ruffled conformation. In the more π-extended **13′**, the fused polycyclic aromatic hydrocarbon slightly deviates from planarity, likely due to the full occupation of the methoxy groups at the bay positions. It should be noted that, while both of the triphenylene moieties in the bis-triphenylene-fused porphyrin **9** retain their planarity, the porphyrin core displays a ruffled conformation with significant distortion from planarity. As a result, the two planar triphenylene moieties do not lie in the same plane. This distortion causes the loss of its D_{2h} symmetry.

In summary, we have synthesized the first examples of triphenylene-fused porphyrins through a Pd⁰-catalyzed cascade reaction followed by oxidative ring closure. Further extension of the porphyrin π-system to fuse one dibenzo[*fg,op*]tetracene has also been achieved using a similar approach. Unusual unsymmetrical ring-closure products were obtained, likely resulting from two competing steric effects. These π-extended porphyrins displayed much broadened and bathochromic-shifted UV−vis absorptions, as compared with their unfused precursors. Structural optimization suggests that the two planar triphenylene moieties of the bis-triphenylene-fused porphyrin (**9**) do not lie in the same plane due to significant distortion of the porphyrin core, breaking the expected D_{2h} symmetry. Currently, we are engaged in generalizing this method to fuse nonalkoxy-substituted triphenylene(s). The development of methodologies to fuse more aromatic polyhydrocarbons is also underway.

Supporting Information Available. Experimental procedures and characterization data for all new compounds, including ¹H and ¹³C NMR spectroscopy and UV−vis absorption data. X-ray crystallography data for compounds **5a** and **6a** (CIF).This material is available free of charge via the Internet at http://pubs.acs.org.