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A Concise Approach to the Synthesis of *opp*-Dibenzoporphyrins through the Heck Reaction

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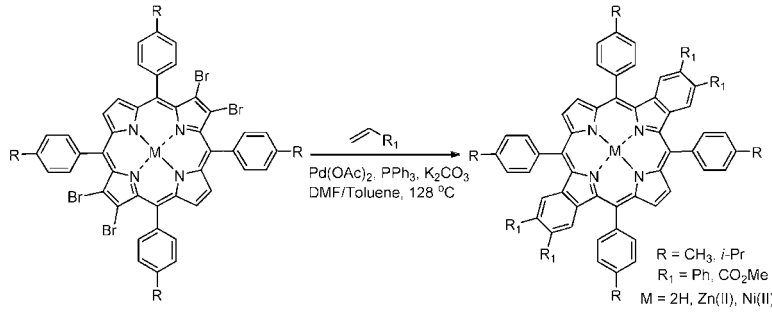
ABSTRACT



A concise approach to the synthesis of functionalized *opp*-dibenzoporphyrins is described. In this method, introduction of alkenyl groups to the porphyrin periphery through the vicinal 2-fold Heck reaction, 6-π electrocyclization, and subsequent aromatization occur in one pot.

Porphyrins with fused aromatic rings possess unique photophysical, optoelectronic, and physicochemical properties.[1] They were investigated in such areas of research as organic light-emitting diodes,[2] photodynamic therapy,[3] biomedical sensing and imaging,[4] and recently in dye-sensitized solar cells (DSSCs).[5] In our effort to develop dyes as light harvesters for DSSCs, we needed a concise methodology to prepare benzoporphyrins functionalized with carboxylic groups. Functionalization of the porphyrin periphery, as compared with total synthesis of porphyrin, was preferred to avoid the lengthy preparation of precursors and subsequent low-yielding assembly of the porphyrin. We decided to introduce vicinal alkenyl groups

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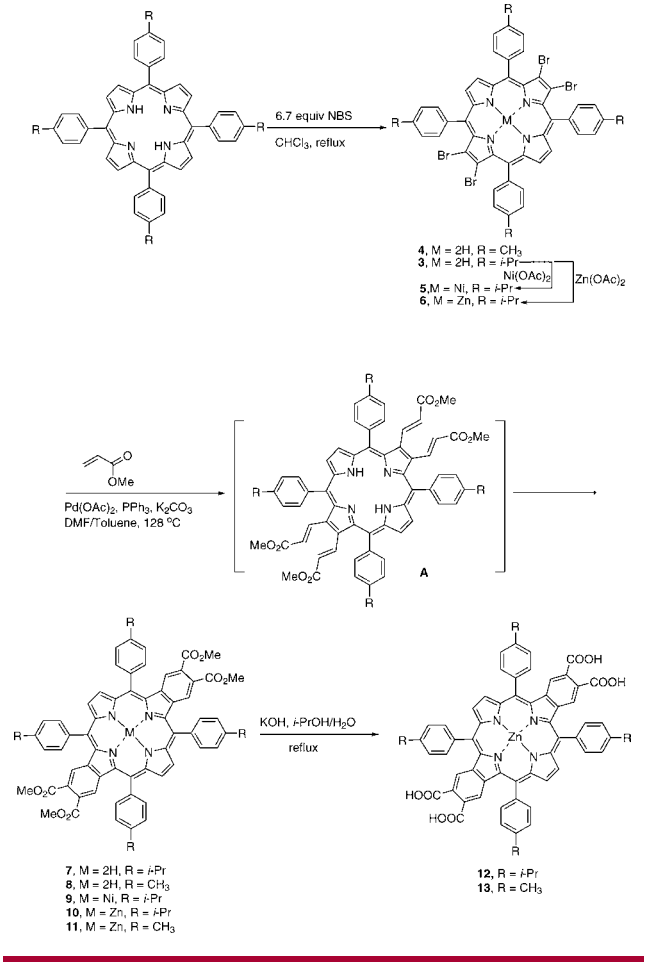
to the porphyrin β,β'-positions via the Heck reaction in order to subsequently attempt 6-π electrocyclization[6] and then aromatization as an entry to functionalized fused benzene rings.

Symmetrical tetrabenzoporphyrins were first synthesized by condensing highly reactive isoindoles[7] or by condensing phthalimides with CH-acid compounds at high temperature (300−400 °C). Fairly complex mixtures of benzoporphyrins were obtained and required laborious purifications.[8] More versatile approaches relied on traditional acid-catalyzed condensation of dihydroisoindoles and aldehydes followed by an aromatization step. Bicyclooctadiene-fused pyrrole or tetrahydroisoindole gave porphyrins that were aromatized to tetrabenzoporphyrins by a thermal retro-Diels−Alder reaction[9] or an oxidative dehydrogenation with DDQ, respectively.[10] Benzoporphyrins can also be obtained from β-functionalized porphyrins: via olefin ring-closure metathesis[11] or via Diels−Alder reactions on vinylporphyrins,[12] pyrrolo[3,4-*b*]-porphyrins,[13] or sulfolenoporphyrins.[14]

One drawback of most methods is the lack of functional groups introduced at the fused aromatic rings. Availability of regioselectively β-brominated porphyrins[15] and of a large variety of substituted alkenes led us to investigate the Heck reaction, which has been previously described with monobromoporphyrins.[16] As shown in Scheme 1, we

Scheme 1



attempted a tetra-fold Heck coupling of 2,3,12,13-tetrabromoporphyrin **3** and **4**[15a] with excess of methyl acrylate in the presence of in situ generated Pd^0 catalyst at 128 °C for 3 days under strict air-free conditions. *opp*-Dibenzoporphyrin **7** and **8** were obtained in 55% and 60% yield, respectively. The direct Heck products (**A**) were not isolated. When the Heck reaction was carried out at lower temperature, e.g., 110 °C, or for shorter reaction times (1 day), a complex mixture resulted with complete consumption of the starting porphyrins. ^{1}H NMR of the mixture showed olefinic doublets in the range of 4−6 ppm indicating that the Heck reaction occurred, but the ring closure was not complete.

^{1}H NMR of **7** (see Supporting Information) displays a singlet at 7.40 ppm assigned to the fused benzene protons. The one-pot formation of **7** was further confirmed by MALDI-TOF (*m*/*z*, 1114.45) and the resolution of an X-ray crystal structure (Figure 1). Due to the fusion of the two benzene rings to the porphyrin macrocycle through β,β'-positions and crowding on the porphyrin periphery, the porphyrin core is deviated from planarity and assumes a saddle-type conformation, similar to that found in other fused benzoporphyrins.[2]

opp-Dibenzoporphyrins were obtained in two steps starting from unfunctionalized free base tetraarylporphyrins. The

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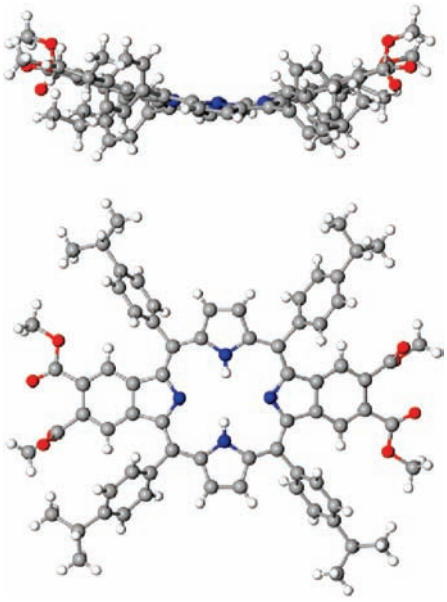


Figure 1. X-ray crystal structure of dibenzoporphyrin **7**: (top) edge view; (bottom) top view. Color code: N, blue; C, gray; O, red; H, white.

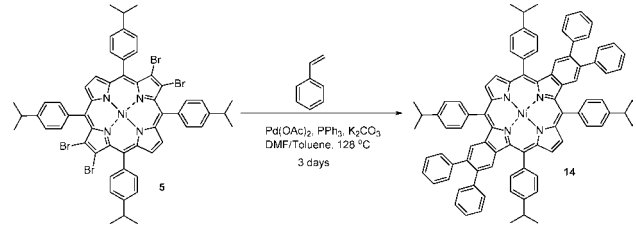
Heck reaction also took place smoothly on nickel(II)-2,3,7,8-tetrabromoporphyrin **5** with methyl acrylate, yielding dibenzoporphyrin **9** in 60% yield. When zinc(II)-tetrabromoporphyrin **6** was used, in situ demetalation during the Heck reaction gave free base dibenzoporphyrins **7** in 35−40% yield. Zinc insertion using $Zn(OAc)_2$ regenerated zinc(II)-dibenzoporphyrin **10**. Zinc(II)-dibenzoporphyrin **12** was obtained similarly.

Hydrolysis of zinc(II)-dibenzoporphyrin **10** and **11** with KOH in *i*-PrOH/H_2O produced DSSC-suitable porphyrin dyes **12** and **13** (Scheme 1).

The Heck reaction of tetrabromoporphyrin with electron-rich styrene took place on nickel(II)-tetrabromoporphyrins **5** affording the fused dibenzoporphyrin **14** in 48% yield (Scheme 2).

The UV−vis spectra of the dibenzoporphyrins **7** and **8** showed Soret bands bathochromically shifted by 20−30 nm relative to their parent porphyrin **1** and **2**, respectively, due to the π-extension. Similarly, nickel(II)-dibenzoporphyrins **9** and **14** also displayed bathochromical shift of Soret bands by 30−35 nm, as compared with simple nickel(II)-tetra(4-isopropylphenyl)porphyrin (Figure 2).

Scheme 2



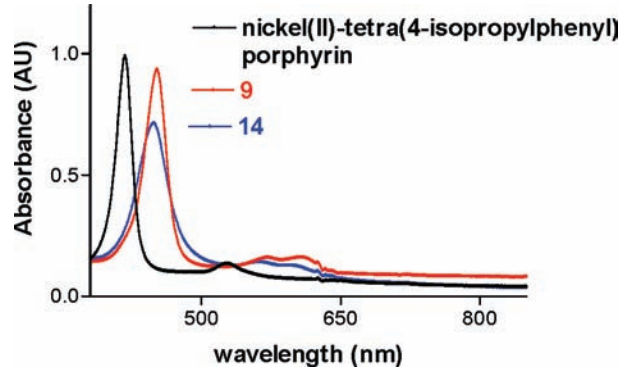


Figure 2. UV−vis absorption spectra of **9**, **14**, and nickel(II)-tetra(4-isopropylphenyl)porphyrin in CH_2Cl_2.

A two-step synthesis of *opp*-dibenzoporphyrins starting from free-base porphyrin was established. This methodology can be used to introduce a variety of functional groups to fused benzene rings. Application of this methodology to the synthesis of triphenylene and phenanthrene fused porphyrins is underway.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds and crystallographic data of **7** (CCDC 723537). This material is available free of charge via the Internet at http://pubs.acs.org.

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