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Cofacial Porphyrin–Ferrocene Dyads and a New Class of Conjugated Porphyrin

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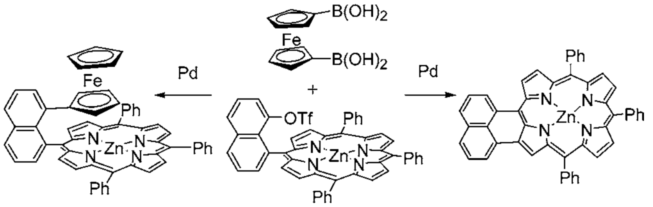
ABSTRACT



A porphyrin–ferrocene dyad has been synthesized in which there is close face-to-face contact between the two aromatic systems, providing a model for heterobimetallic polymers based on the same repeating unit. Attempts to synthesize the 2:1 adduct instead led to a remarkable intramolecular Heck-type cyclization which planarizes the system and extends the conjugation.

Porphyrins and metalloporphyrins[1] have been widely studied as building blocks for supramolecular and organic materials chemistry. Elaborate conjugated porphyrin assemblies have been prepared to give “molecular wires” for a variety of potential applications.[2] In most of the examples of porphyrins (and related macrocycles) as molecular wires, the conjugation arises through linear $\pi-\pi$ overlap (conventional conjugation pathways). Our ultimate aim is to prepare a unique class of heterobimetallic, π-overlapping polymers in which the communication between units arises through *face-to-face* π-overlap. Polymers of the general structure shown in Figure 1 are therefore being targeted.

The general molecular design can be analyzed in portions. The key porphyrin unit incorporates a *meso*-naphthalene unit attached via the 1-position. Such porphyrins are atropisomeric.[3] Close contact is ensured by attachment of the cyclopentadienyl/ferrocene unit through the naphthalene 8-position, either by a direct connection or through a rigid spacer. A particularly promising “spacer” is benzene itself (i.e. indenyl units), because a simple molecular model (Figure 1) indicates that introduction of indene through its 5-position places the cyclopentadienyl unit (and therefore metal M_2) above the center of the porphyrin (and therefore metal M_1). Polymers of the structure shown in Figure 1 will require synthesis of 5,15-α,β-bisnaphth-1-ylporphyrin building blocks as single atropisomers. Previous work in our laboratories[4] has studied the controlled syntheses of some related naphthyl porphyrins, and it is clear that, although not trivial, such derivatives can be prepared and isolated. Our initial targets for model compound synthesis were, however, based on mononaphthyl porphyrins and therefore are not complicated by the formation/isolation of atropisomers. The synthesis of the first model compounds is shown in Scheme 1.

The synthesis of such porphyrins could in principle be achieved from a suitably functionalized naphthaldehyde building block. However, we reasoned that a more versatile

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10.1021/ol050962g CCC: $30.25

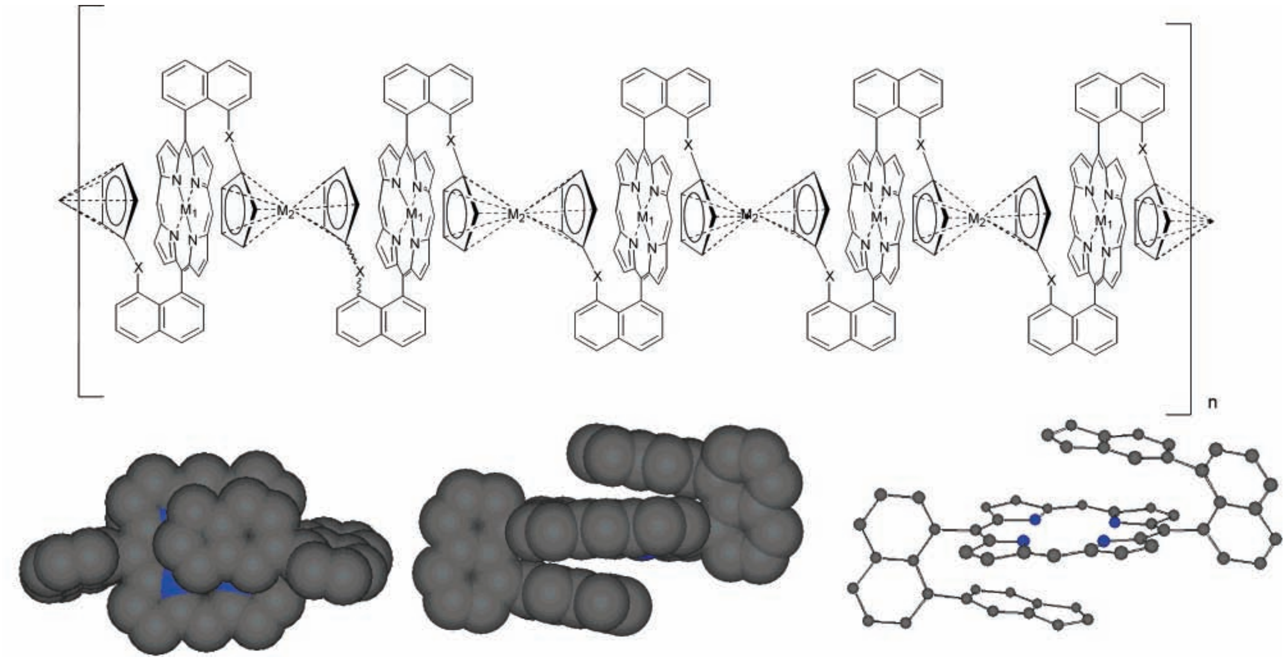

Figure 1. Heterobimetallic polymers with face-to-face π-overlap (top) and an example of a promising repeat unit with indenyl groups on the naphthalene 8-positions (bottom) (other atoms and groups omitted for clarity).

approach would involve synthesis of naphthyl porphyrins substituted with a triflate group at the 8-position, followed by subsequent cross-coupling to introduce a “cyclopentadienyl” fragment. The synthesis of the porphyrin monotriflate **2** was initially attempted using a statistical condensation between pyrrole, benzaldehyde, and naphthaldehyde triflate **1** using Setsune’s conditions.[5] However, only a trace of the desired product **2** was obtained and the product mixture was dominated by tetraphenylporphyrin (TPP). This remained the outcome even when the proportion of naphthaldehyde **1** was significantly increased. It is clear, therefore, that the reactivity of the naphthaldehyde is significantly lower than that of benzaldehyde. The problem was overcome by presynthesis of the dipyrromethane intermediate[6] **3** from naphthaldehyde **1** and pyrrole. Condensation of this dipyrromethane with benzaldehyde and pyrrole using Setsune’s conditions led to an acceptable yield (10%) of unsymmetrical porphyrin **2**, whereas Lindsey’s conditions[7] gave a slightly higher yield (16%).

The aryl triflate environment in derivatives such as **2** is highly hindered, and it was reasonable to expect that cross-coupling reactions to introduce further aryl residues would be challenging. The first model coupling reaction, therefore, aimed to introduce a simple phenyl group through Suzuki coupling[8] between **2** and excess benzene boronic acid **4**. Consequently, zinc porphyrin **2** was reacted with 3 equiv of benzene boronic acid in refluxing DME/water, using Pd(dppf) as catalyst, for 3 days. The crude product was separated by column chromatography to give the cross-coupled porphyrin **5** in 55% yield. As expected, ^{1}H NMR spectroscopy provided the most informative characterization data, with the signals for the new phenyl residue appearing in the strongly shielded region (3.06, 3.92, and 5.36 ppm, respectively), due to its location above the porphyrin ring. The same reaction was performed using indane-5-boronic acid (**6**), reasoning that, if successful, subsequent oxidation to indenes[9] in the later disubstituted 5,15-α,β-porphyrins would provide a route to heterobimetallic polymers through metallocene formation. Cross-coupling using the same conditions once again proceeded smoothly to give the indanyl porphyrin **7** in 78% yield. The protons associated with the indanyl five-membered ring are again dramatically shielded and appear as resolved signals between -2.25 and 0.9 ppm in the ^{1}H NMR spectrum. Crystals suitable for X-ray diffraction were also obtained from dichloromethane by slow evaporation. The crystal structure of **7** is also shown in Scheme 1. The molecular design strategy is validated by calculation of the ring−ring separation (ca. 3.6 Å) and location of the cyclopentane ring over the porphyrin center.

The second phase of this model study focused on the synthesis of simple face-to-face ferrocenyl porphyrins. Identical cross-coupling conditions were first applied to synthesize the model porphyrin ferrocene dyad **9** by reacting porphyrin triflate **2** with ferrocene bis(boronic acid) (**8**) (Scheme 2). In this case the reaction also proceeds relatively

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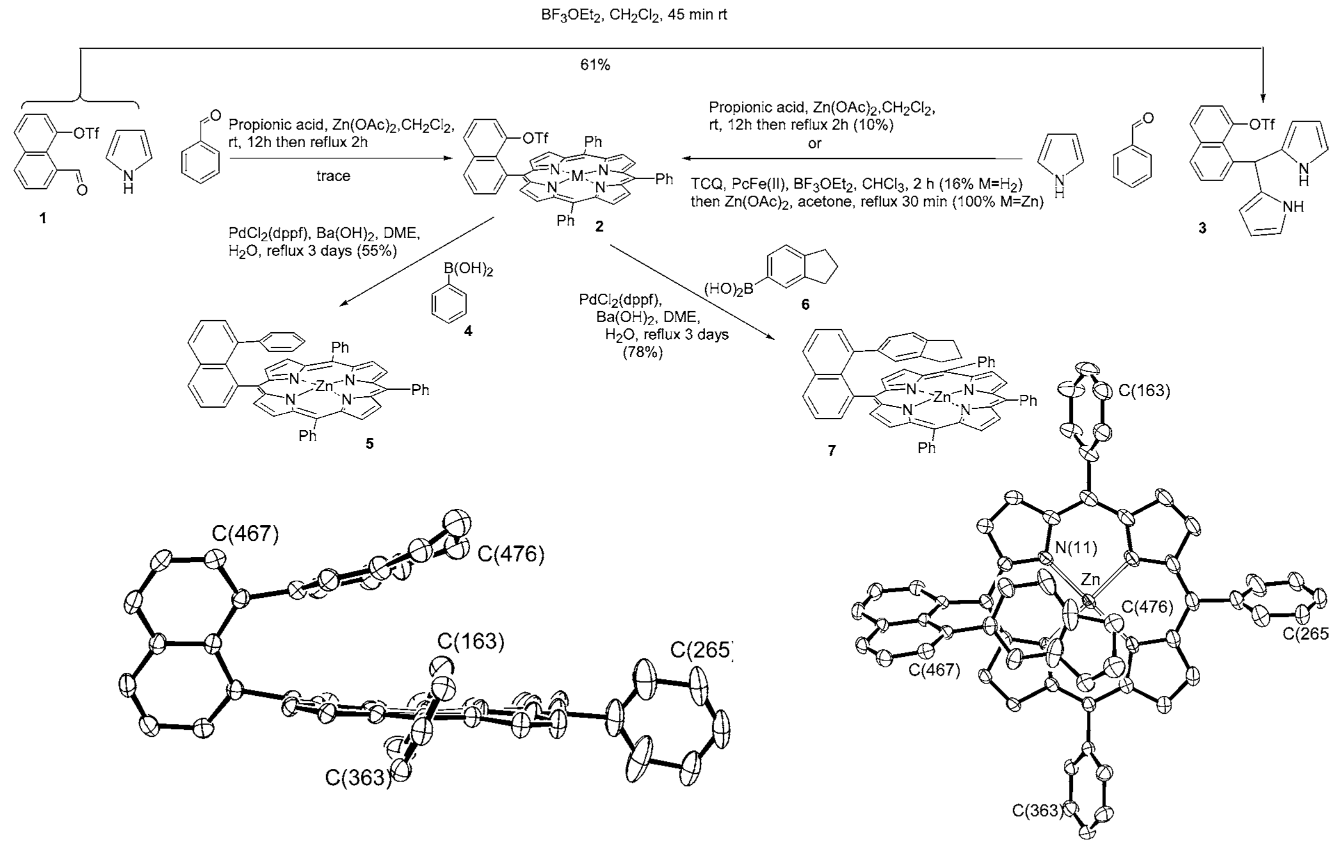
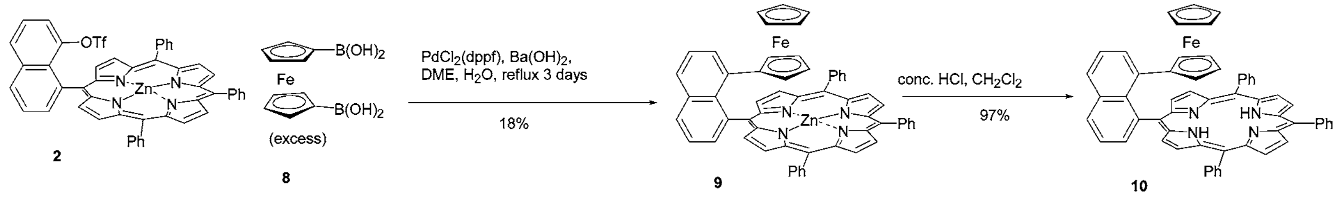
Scheme 1. Synthesis of Porphyrin Triflate **2**, Suzuki Cross-Coupling with Aryl Boronic Acids, and ORTEP Diagram of Indanyl Porphyrin **7**



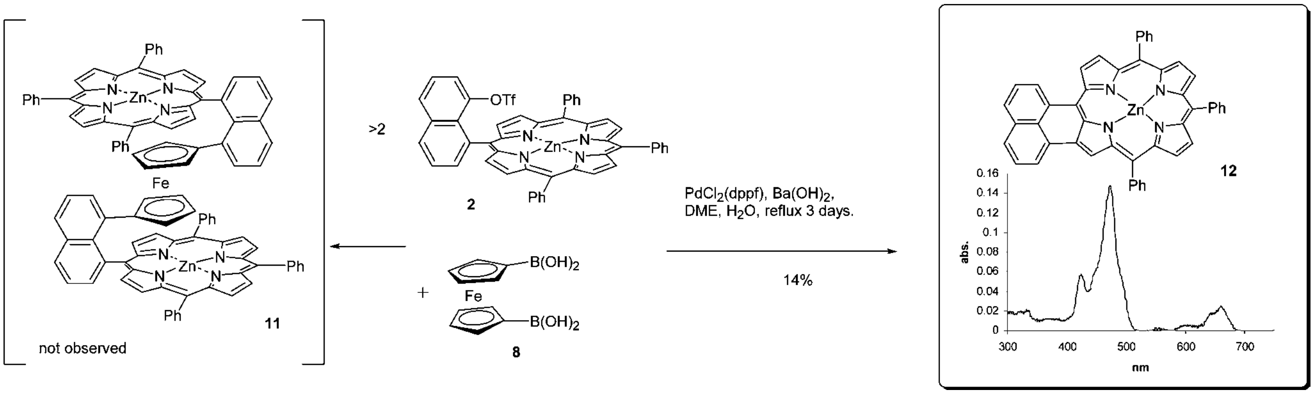
smoothly. However, the coupling is somewhat more challenging and is accompanied by partial hydrolysis of the triflate starting material, lowering the overall yield. The second boronic acid group is lost under the reaction conditions through protodeboronation. Once again ^{1}H NMR proves to be a powerful characterization tool. Ferrocene protons appear at 0.07 and 2.35 ppm (bottom ring) and 3.32 ppm (unsubstituted top ring). Demetalation (removal of the central zinc ion) was easily achieved by treating **9** with HCl in dichloromethane.

The second model system (**11**) required reaction of 2 equiv of porphyrin triflate **2** with ferrocene bis(boronic acid) (**8**) (Scheme 3). The coupling reaction was therefore performed using a 4:1 ratio of **2** to **8** under the reaction conditions described above. Unfortunately under all conditions investigated the desired product **11** was never observed. TLC analysis of the reaction mixtures typically indicated the presence of unreacted starting material and hydrolyzed porphyrin. The dominant new product, however, was green. This new material was isolated by column chromatography and characterized as **12** (14% yield), the product of a formal intramolecular Heck-type reaction.[10] This intramolecular cyclization significantly extends the conjugation of the π system and breaks the symmetry of the porphyrin core. Consequently, this cyclization results in a dramatic change to the UV−visible absorption spectrum (Scheme 3), which shows absorbances across most of the visible spectral region. The red-shifted, broad spectrum also arises, in part, because the porphyrin itself is likely to be deformed from a fully planar conformation[11] due to steric interactions between pyrrole β-H and naphthyl 2-H (Scheme 3). Comparable spectral changes are observed for related fused porphyrin systems.[12] It is interesting to note that only trace quantities

Scheme 2. Synthesis of the First Face-to-Face Porphyrin−Ferrocene Dyads



Scheme 3. Intramolecular Heck-Type Cyclization of **2**



of **12** are obtained when the reaction is performed under identical, unoptimized conditions in the absence of **8**.

In conclusion, we have demonstrated that cross-coupling can, under specific conditions, be used to introduce aryl residues on to sterically demanding porphyrin platforms. These reactions force the new residues into close (ca. 3.6 Å) contact with the porphyrin, allowing face-to-face π overlap and therefore communication between units. The first such bimetallic dyad has been prepared through introduction of ferrocene. This chemistry will inform synthetic strategy to deliver unique heterobimetallic oligomers and polymers. Subtle changes to the cross-coupling conditions lead to a remarkable intramolecular (Heck-type) cyclization, giving a new class of conjugated porphyrin with a distinctive electronic absorption spectrum. These observations themselves demonstrate potential for both synthetic and materials development and exploitation, which will be the subject of further investigation.

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Supporting Information Available: Synthetic details and characterization data for all new compounds and X-ray data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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