Directly Linked and Fused Oligoporphyrin Arrays from Oxidation of Metalloporphyrins

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Abstract

The Ag^{I}-promoted oxidative *meso-meso* coupling reaction of 5,15-diaryl Zn^{II}-porphyrins is advantageous in light of its high regioselectivity as well as its easy extension to large porphyrin arrays. Linear *meso-meso* linked porphyrin 128-mer and three-dimensionally arranged grid porphyrin 48-mer were isolated in a discrete form by repetitive oxidation reaction and subsequent gel-permeation chromatography (GPC)-HPLC. 5,15-Diaryl Cu^{II}-, Ni^{II}-, and Pd^{II}-porphyrins were converted to *meso-β* doubly-linked diporphyrins by oxidation with (p-BrC$_6$H$_4$)$_3$NSbCl$_6$. End-aryl-capped *meso-meso* linked Cu^{II}-, Ni^{II}-, and Pd^{II}- diporphyrins were converted to completely fused *meso-meso β-β β-β* triply-linked diporphyrins through the oxidative ring closure (ODRC) reaction with (p-BrC$_6$H$_4$)$_3$NSbCl$_6$. Finally, we found that Sc^{III}-catalyzed oxidation with DDQ gave a very efficient ODRC reaction and hence allowed the synthesis of triply-linked oligoporphyrins up to 12-mer.

Introduction

The design and preparation of conjugated large molecules with precise length and constitution have attracted considerable interests in light of the potential applications of such molecules in the fields of material science and nanoscale molecular device [1]. Among these, porphyrins are intriguing building blocks from which to construct large π-conjugated molecules [2, 3]. In most cases, supramolecular architectures of porphyrins were made by assembling porphyrin subunits in a covalent or noncovalent manner. Recently, we have found that sterically uncongested metalloporphyrins such as 5,10-diaryl metalloporphyrins and 5,10,15-triaryl metalloporphyrins are made quite reactive for direct coupling upon subjecting to appropriate oxidation conditions. Here we summarize our recent efforts to prepare directly linked and fused porphyrin arrays.

Directly linked diporphyrins

One-electron oxidation of porphyrins bearing a sterically uncongested *meso*-position such as 5,15-diaryl-substituted metalloporphyrins and 5,10,15-triaryl-substituted metalloporphyrins is an effective route to prepare directly *meso-meso* and *meso-β* linked diporphyrins [4, 5]. Mg^{II}- and Zn^{II}-porphyrins **1a–c** gave *meso-meso* linked diporphyrins **2a–c** by Ag^{I} salt oxidation or electrochemical oxidation, while the Cu^{II}-, Ni^{II}- and Pd^{II}- porphyrins **1d–f** gave *meso-β* linked diporphyrin **3a–c** by electrochemical oxidation. The observed different regio-selectivity either giving **2** or **3** may

be explained in terms of different HOMO orbital characteristics; namely A$_{2u}$-HOMO for Mg^{II}- and Zn^{II}- porphyrins in which there is a large electron density at the *meso*-carbon and A$_{1u}$-HOMO for Cu^{II}-, Ni^{II}- and Pd^{II}-porphyrins in which there is a node at the *meso*-carbon and significant density at the β-position. The molecular structure of **2d** shows that the two porphyrin rings take a nearly orthogonal conformation (86.0°) and the bond connecting the two porphyrin units is 1.47 Å long, being similar to the C$_2$–C$_3$ bond length of 1,3-butadiene (1.48 Å) (Figure 1a). The structure of **3** was also confirmed by X-ray crystallography, and similar orthogonal conformation was observed (not shown). Therefore, both the singly-linked diporphyrins **2** and **3** take nearly orthogonal conformations, which minimize the electronic interaction between the neighboring porphyrin.

Directly *meso-meso* linked porphyrin arrays

The regio-selectivity of the Ag^{I}-promoted oxidative *meso-meso* coupling reaction of 5,15-diaryl Zn^{II}-porphyrins was quite high (Scheme 1). Linear polymeric porphyrin arrays were effectively obtained in the reaction with Ag^{I}-salt in CHCl$_3$ in the presence of 0.5% *N,N*-dimethylacetamide [6]. On the other hand, discrete oligoporphyrin arrays having precise length were obtained by repeating Ag^{I}-salt promoted coupling reactions and subsequent separation using GPC/HPLC (GPC = gel-preparation chromatography) up to 128-mer [7]. To the best of our knowledge, the 128-mer is the longest discrete rod-like organic molecule with ca. 108 nm molecular length.
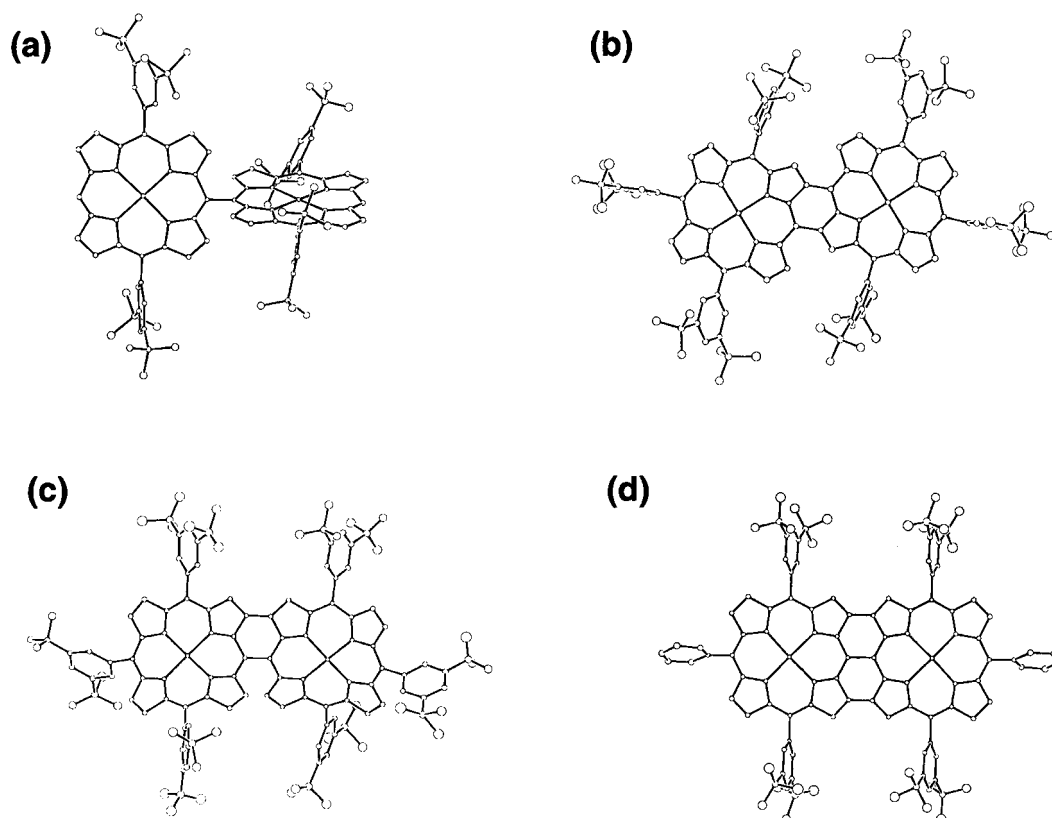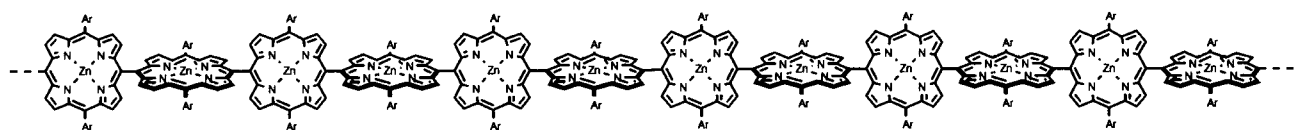
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Figure 1. X-ray crystal structures of directly linked and fused metallodiporphyrins (a) *meso-meso* linked Pd^{II}-diporphyrin **2d**, (b) *meso-β* doubly-linked Ni^{II}- diporphyrin **6b**, (c) *meso-meso β-β* doubly-linked Ni^{II}-diporphyrin **7** and (d) *meso-meso β-β β-β* triply-linked Cu^{II}-diporphyrin **8b**.

Scheme 1.

The windmill-like porphyrin array **4a** was shown to serve as an effective substrate for further *meso-meso* coupling reactions, to give three-dimensionally arranged grid porphyrin arrays **5** ($\sim$48-mer) (Scheme 2) [8]. In the all Zn^{II}-metallated windmill porphyrin array **4b**, the energy level of the S1 state of the *meso-meso* linked diporphyrin core is lower than that of the peripheral porphyrins, thereby allowing an excitation energy flow from the peripheral porphyrins to the central diporphyrin core.
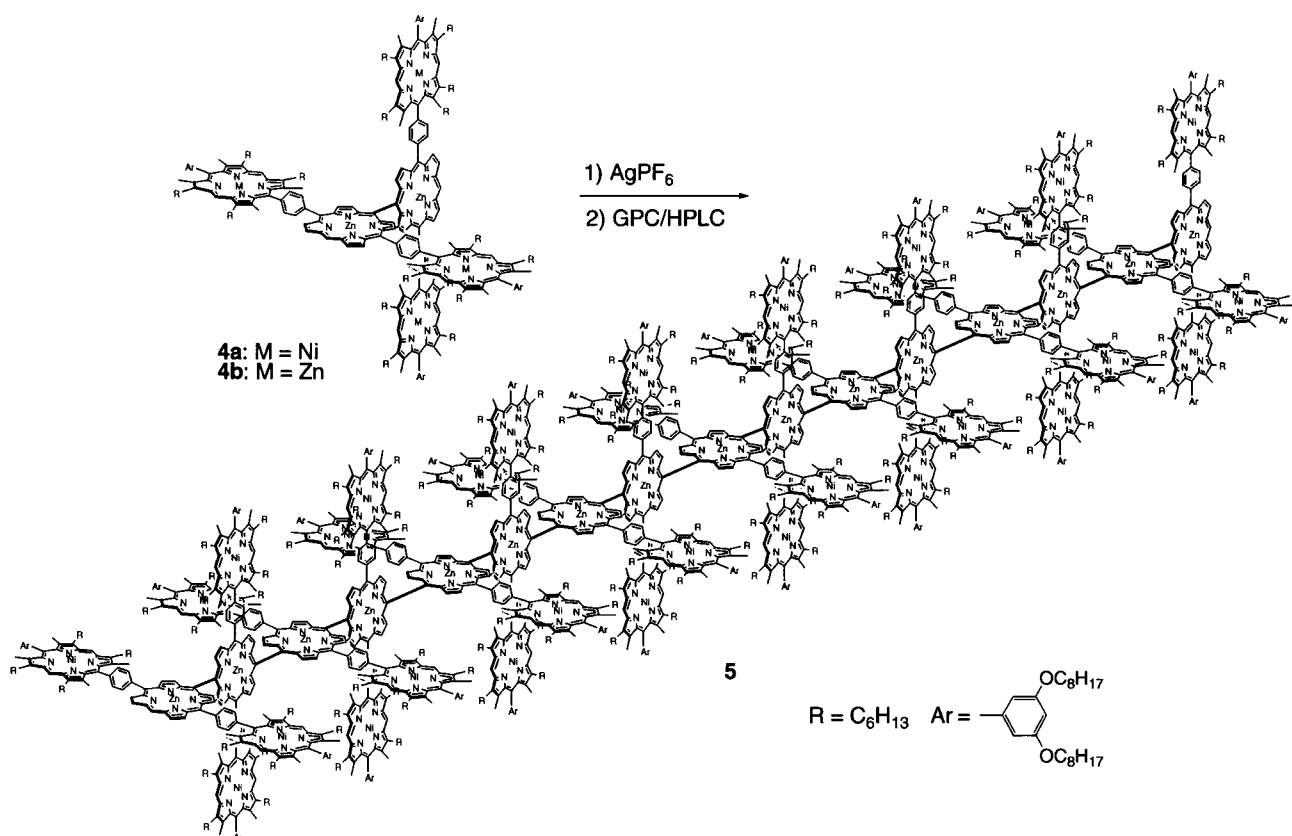
Directly fused diporphyrins

As an extension of the above oxidative coupling reactions, we found a novel synthetic route to fused porphyrins through the oxidation of metallopoprhyins with tris(4-bromophenyl)aminium hexachloroantimonate (BAHA). The oxidation of Cu^{II}-, Ni^{II}- and Pd^{II}- porphyrins **1g–i** gave rise to formation of *meso-β* doubly-linked diporphyrins **6a–c** (25, 53, and 59% yields, respectively) (Chart 1) [9], while the oxidation of *meso-meso* linked diporphyrins **2e–g** with A$_{1u}$-HOMO led to formation of *meso-meso β-β β-β* triply-linked diporphyrins **8a–c** (74, 76, and 30% yields,
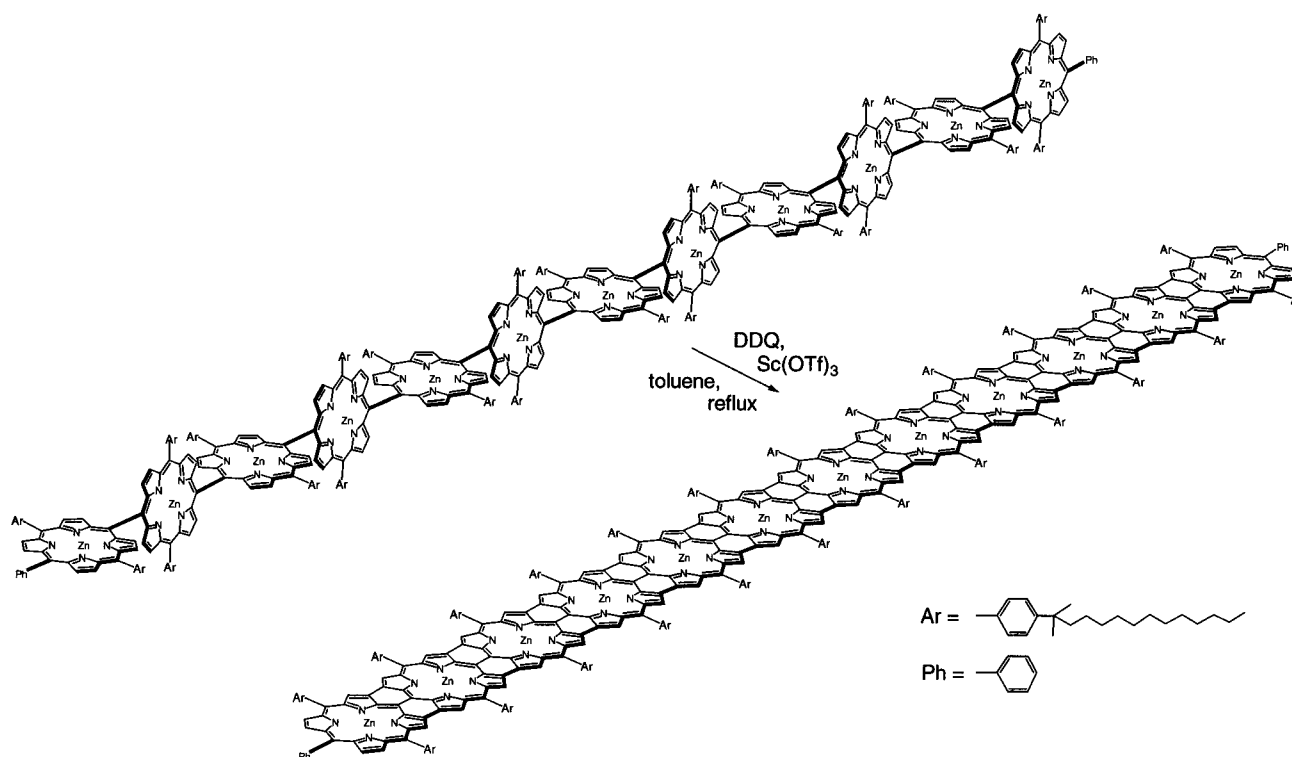
respectively) probably through the *meso-meso β-β* doubly-linked diporphyrin as an intermediate compound [10]. The *meso-meso β-β* doubly-linked diporphyrin **7** was isolated only in the reaction of **2g** with BAHA (10% yield).

Zn^{II}- and Cu^{II}-complexes of directly linked and fused diporphyrins can be easily converted to the free-base forms upon treatment with acids such as HCl and H$_2$SO$_4$, and subsequent metal insertion led to the desired metal complexes. The X-ray crystal structures of the some complexes, *meso-meso* linked Pd^{II}-diporphyrin **2d**, *meso-β* doubly-linked Ni^{II}-diporphyrin **6b**, *meso-meso β-β* doubly-linked Ni^{II}-diporphyrin **7**, and *meso-meso β-β β-β* triply-linked Cu^{II}-diporphyrins **8b**, are shown in Figure 1 [11]. Although *meso-meso* linked diporphyrin **2d** adopts nearly perpendicular conformation, the fused diporphyrins **6b**, **7**, and **8b** take nearly flat structures, being favorable for the extensive π-conjugation over the array.

The absorption spectra of diporphyrins were red-shifted in the order of **1** < **3** < **2** < **6** ~ **7** < **8**. In addition, the ^{1}H NMR chemical shifts indicated that the porphyrin ring current seems to be weakened in the order of **2** < **6** < **8**. These red-shifted-absorption spectra and reduced ring current may be ascribed to the increased conjugation over the
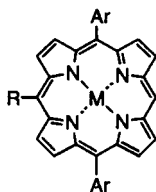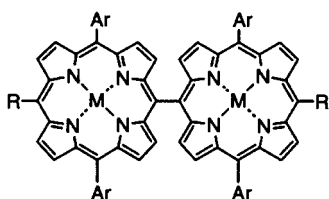
4a: M = Ni
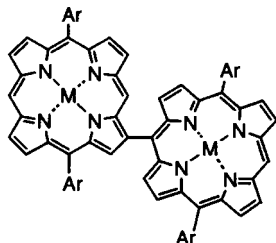**4b**: M = Zn

1) AgPF$_6$
2) GPC/HPLC

5

R = C$_6$H$_{13}$ Ar =

Scheme 2.

DDQ,
Sc(OTf)$_3$
toluene,
reflux

Ar =

Ph =

Scheme 3.

1a ; M=Mg R=H
1b ; M=Zn R=H
1c ; M=Zn R=Ar
1d ; M=Cu R= H
1e ; M=Ni R= H
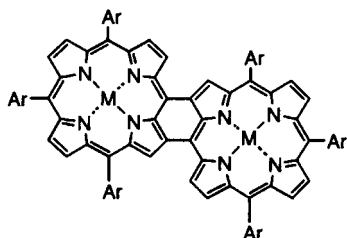1f ; M=Pd R= H
1g ; M=Cu R=Ar
1h ; M=Ni R=Ar
1i ; M=Pd R=Ar

2a ; M=Mg R=H
2b ; M=Zn R=H
2c ; M=Zn R=Ar
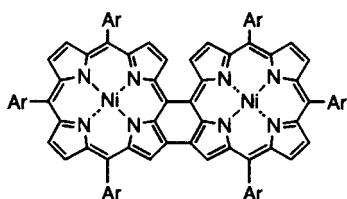2d ; M=Pd R=H
2e ; M=Cu R=Ar
2f ; M=Cu R=Ph
2g ; M=Ni R=Ar

3a ; M=Cu
3b ; M=Ni
3c ; M=Pd

6a ; M=Cu
6b ; M=Ni
6c ; M=Pd

7

8a ; M=Cu R=Ar
8b ; M=Cu R=Ph
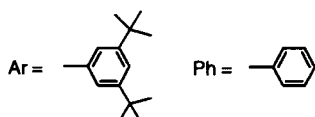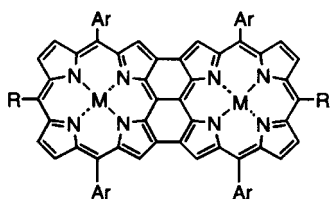8c ; M=Ni R=Ar

Ar =   Ph =

Chart 1.

π-network of the diporphyrins upon increasing connection between the two units. However, the X-ray crystallography structural parameters such as bond lengths and angles of the porphyrin cores are quite similar to those of the corresponding metallated porphyrin monomers. Therefore, it may be concluded that the fused connection scarcely alters the basic skeletons of each porphyrin ring but serves to provide the coplanar π-network over the array in which the electron is extensively delocalized.

Fully conjugated porphyrin tapes

Recently, we found that Sc[III]- catalyzed oxidation of *meso-meso* linked Zn[II]-diporphyrin with DDQ led to efficient formation of *meso-meso β-β β-β* triply-linked Zn[II]-diporphyrin through multiple ODRC reactions with complete suppression of undesirable peripheral halogenation [12]. This synthetic method was applicable to higher *meso-meso* linked Zn[II]-porphyrin arrays (up to 12-mer) to give the corresponding fused tape-shaped porphyrin arrays in $62 \sim 91\%$ yields (Scheme 3). The completely fused oligoporphyrin arrays produced display extremely red-shifted absorption bands, reflecting the extensively π-conjugated electronic systems over the array. The lowest energy electronic absorption bands become more red-shifted and intensified upon increase of the number of the porphyrins, and eventually reach into infrared frequency. Up to the stage of 12mer, the directly fused oligoporphyrins do not show effective conjugation length (ECL) effects. The extremely small HOMO-LUMO gaps, the exceedingly low oxidation potentials, and the linearly long rigid molecular shapes of the higher triply-linked fused porphyrin arrays encourage their potential use as a molecular wire.

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