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An Efficient PIFA-Mediated Synthesis of Fused Diporphyrin and Triply−Singly Interlacedly Linked Porphyrin Array

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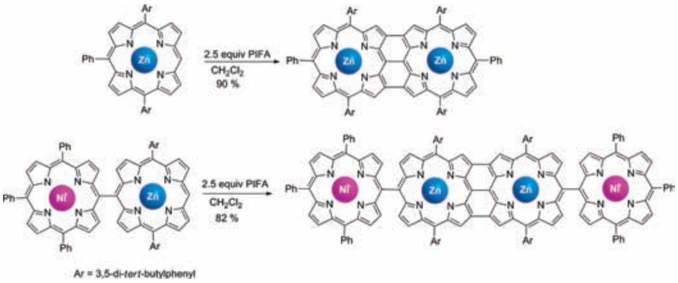
ABSTRACT



An efficient and metal-free oxidative method was reported for synthesis of triply linked diporphyrins with 2.5 equiv of phenyliodine bis(trifluoroacetate) (PIFA). This reaction showed high selectivity for Zn(II) porphyrins and had been successfully applied in the synthesis of a novel triply−singly interlacedly linked porphyrin array with lower energy gap.

In the past two decades, covalently linked multiporphyrin arrays have attracted interest for their numerous applications such as artificial photosynthetic systems, molecular wires, sensors, and nonlinear optical (NLO) devices.[1] Among these, $\beta-\beta$, *meso*−*meso*, $\beta-\beta$ triply fused multiporphyrins are of particular interest because of their remarkable properties including large electronic π-conjugation, extremely low HOMO−LUMO (highest occupied/lowest unoccupied molecular orbital) gaps, and the lowest energy absorption bands that reach the infrared region.[2] They have been used as conducting molecular wires,[2a] directed columnar liquid crystalline assembly,[3] functional conjugates with fullerenes,[4] and two-photon absorption materials.[5]

The synthesis of directly fused porphyrin arrays mostly relies on some powerful oxidants developed by Osuka's group including tris(4-bromophenyl)aminium hexachloroantimonate (BAHA), DDQ−Sc(OTf)$_3$, and AuCl$_3$−AgOTf.[2e,6] Recently, hypervalent iodine(III) reagents, such as phenyliodine diac-

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etate (PIDA) and phenyliodine bis(trifluoroacetate) (PIFA), have been widely recognized as safe and useful oxidants having reactivities similar to metal oxidizers.[7] Particularly, PIFA, with a highly electrophilic iodine center, can promote many coupling reactions,[8] including the synthesis of *meso*−*meso* directly linked diporphyrins with 0.6 equiv of PIFA.[9] We have also used this coupling reaction in the synthesis of singly linked chiral diporphyrins,[10] which should be terminated by addition of $NaBH_4$ and CH_3OH when excessive PIFA was added. Without termination, triply linked diporphyrins would be obtained as the main byproduct.

In this paper, a facile and potent method was described to prepare triply fused diporphyrins via the PIFA oxidative reaction in high yield, and this turned out to be more convenient and economical than previous methods. Since PIFA could selectively promote the oxidation reaction of Zn(II) porphyrin, triply−singly interlacedly linked tetraporphyrin, a novel covalently linked mode for molecular wire and functional material, was prepared from Zn(II)−Ni(II) hybrid diporphyrin.

A general procedure for PIFA oxidation has been optimized. To a solution of triaryl-Zn(II)-porphyrins in freshly distilled CH_2Cl_2 at −78 °C was added PIFA, and the resulting mixture was stirred at room temperature and then terminated by $NaBH_4$ and CH_3OH. With this procedure, the amount of PIFA added had great influence on the product distributions (Scheme 1 and Table 1). Treating **1a** or **1b** with 0.5 equiv of PIFA resulted in *meso*−*meso* singly linked dimer **2a** or **2b**. As the amount of PIFA added up to 1.5 equiv, a mixture was obtained with triply linked porphyrin dimer **3a** (55%) and singly linked porphyrin dimer **2a** (29%). Only triply linked porphyrins were produced with highest yields (90% of **3a** and 83% of **3b**) when 2.5 equiv was used. Increasing the amount of PIFA (up to 5 equiv) could depress the yield (67% of **3a**). Additionally, singly linked diporphyrin **2a** also could turn into triply linked diporphyrin **3a** with the same procedure in similar yield (84%).

It is noteworthy that feeding and postprocessing could affect the yields of triply linked diporphyrins. Feeding PIFA at −78 °C could reduce the polymeric residue. In contrast, the triply linked porphyrin **3a** was isolated in a lower yield (77%) when PIFA was added at room temperature. A refined workup procedure to reduce one electron oxidation product and remove excess PIFA was essential. After terminating the reaction mixture with $NaBH_4$ and CH_3OH, the pure product (90% of **3a**) was obtained by filtration with a short pad of silica gel. Aqueous $NaHCO_3$, aqueous $Na_2S_2O_3$, and triethylamine were also utilized in the reaction of **1a** but with lower yields (45%, 76%, and 80%, respectively).

Scheme 1. PIFA-Promoted Coupling Reactions

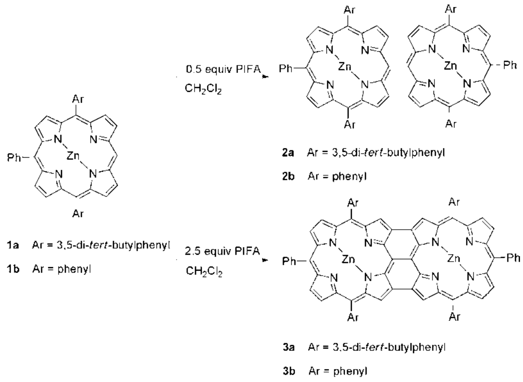

Table 1. Yields of Oxidative Coupling Reaction of **1a** and **1b** with PIFA

					yield[a]	
entry	reactant	solvent	equiv	time	**2**	**3**
1	**1a**	CH_2Cl_2	0.5	5 min	86	0
2	**1a**	CH_2Cl_2	1.5	2 h	29	55
3	**1a**	CH_2Cl_2	2.5	2 h	0	90
4	**1a**	CH_2Cl_2	5	2 h	0	67
5	**1b**	CH_2Cl_2	0.5	5 min	93	0
6	**1b**	CH_2Cl_2	1.5	2 h	23	53
7	**1b**	CH_2Cl_2	2.5	2 h	0	83
8	**1b**	$CHCl_3$	2.5	2 h	0	80
9	**1b**	$ClCH_2CH_2Cl$	2.5	2 h	0	78
10	**1b**	toluene	2.5	5 h	0	68
11	**1b**	THF	2.5	24 h	36[b]	0

[a] Isolated yield of **2a** or **2b** and **3a** or **3b**. [b] Together with the starting porphyrin and iodic porphyrin.

Similar results of the solvent effects in the PIFA coupling reactions were also reported by Chen and Guo.[9] The reaction of **1b** could be promoted in noncoordinating solvents with 68−83% yields of **3b**. However, in THF, a trace amount of triply linked diporphyrin was obtained. Moreover, when PIDA was used instead of PIFA, singly linked diporphyrin **2b** was obtained as the main product after 24 h reaction.

It is well-known that the center metal of porphyrin can affect the reactivity and reaction sites in some oxidative reactions.[6,11] The Cu(II), Ni(II), and Pd(II) porphyrins were also used instead of Zn(II) porphyrin in this reaction (Scheme 2). After stirring for 3 days, *meso*−*meso* singly linked

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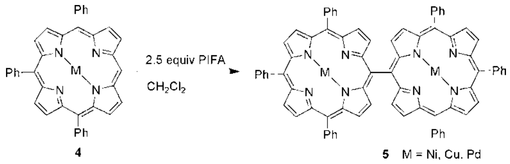
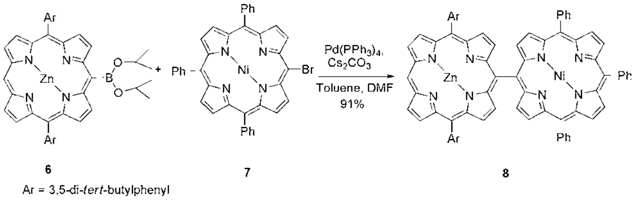
Scheme 2. Coupling Reactions of Cu(II), Ni(II), and Pd(II) Porphyrins

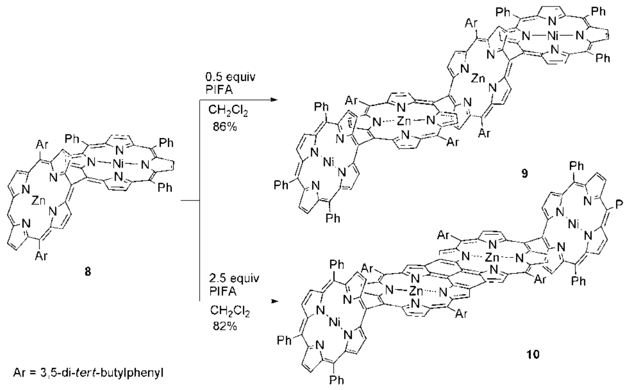


diporphyrins were isolated as major products in 68−80% yields with a trace amount of fused porphyrins. Increasing the temperature (up to refluxing) had little effect. The selectivity of metalloporphyrins may come from their different electronegativities, and thus different ability to form cation radical,[12] because Zn(II) porphyrin has lower first oxidation potential than Cu(II), Ni(II), and Pd(II) porphyrins.[13]

Scheme 3. Synthesis of Zn(II)−Ni(II) Hybrid Diporphyrin



Scheme 4. PIFA-Promoted Coupling Reactions of Hybrid Diporphyrin



Taking advantage of the described metal-dependent reactions, the triply−singly interlacedly linked multiporphyrin, as a new covalently linked mode, could be designed and synthesized from metal hybrid diporphyrin. This novel multiporphyrin system would combine the properties of singly linked porphyrins and fused porphyrins and should have applications in construction of molecular wire and functional material. *Meso*−*meso* Zn(II)−Ni(II) hybrid diporphyrin **8**, which was easily prepared in 91% yield (Scheme 3),[14] was selected as the precursor. When 0.5 equiv of PIFA was added, singly linked tetraporphyrin **9** was obtained in 86% yield. As the amount of PIFA added up to 2.5 equiv, porphyrin array **10**, containing one triple linkage between Zn(II) porphyrin monomers and two retaining single linkages, was selectively prepared with 82% yield (Scheme 4). Virtually, we had developed a highly selective method for *meso*−*meso* single linkage between Zn(II) porphyrin monomers in hybrid porphyrin arrays to turn into triple linkage, which offered a strategy in synthesis of interlacedly linked porphyrin arrays.

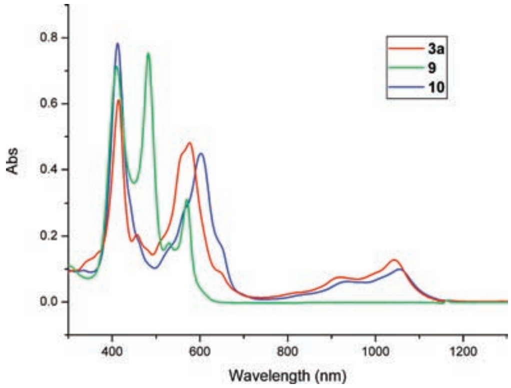


Figure 1. Ultraviolet−visible−infrared absorption spectra of porphyrins **3a** (4×10^{-6} mol/L, red line), **9** (2×10^{-6} mol/L, green line), and **10** (2×10^{-6} mol/L, blue line) in CH$_2$Cl$_2$.

The absorption spectra of fused diporphyrin **3a**, singly linked hybrid tetraporphyrin **9**, and interlacedly linked tetraporphyrin **10** were shown in Figure 1. As described,[2e,15] the absorption bands of the fused porphyrin are roughly categorized into three distinct well-separated bands, marked as **By**, **Bx**, and **Qx** bands in near UV, visible, and IR regions, respectively (also called I, II, and III bands). The tetraporphyrin **10** displayed remarkably red-shifted absorption spectra similar to fused porphyrin **3a**, especially for their absorption bands in the near UV region (**By** band) retaining nearly the

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same positions as those of the porphyrin **9**. In the visible and IR regions (**Bx** band and **Qx** band), interlacedly linked tetraporphyrin **10** showed a more obvious red-shift than fused diporphyrin **3a** by about 27 and 13 nm, respectively.

The spectral changes of the tetraporphyrin array can be explained by Kasha's point−dipole exciton coupling theory[16] and the application in directly linked porphyrins developed by Osuka and Kim.[15,17] In the interlacedly linked system, the sideward Ni(II) porphyrins could be considered as special groups of the fused porphyrin core. It is appropriate to place two transition dipole moments of each porphyrin unit as shown in Figure 2. It is expected that the exciton coupling of **Bx** transition dipoles is possible, but the other interactions (**By** and **Bz**) should be zero for an averaged perpendicular conformation in porphyrin **10**. Thus, the **Bx** band (II band) was red-shifted, but the **By** band (I band) was the same.

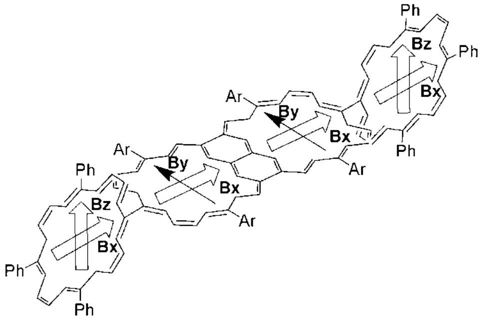

Figure 2. Schematic representations of transition moments in the interlacedly linked porphyrin tetramers.

The electrochemical properties were studied by cyclic voltammetry in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as supporting electrolyte. The cyclic voltammograms of the tetrapenyl Ni(II) porphyrin (NiTPP), **3a**, and **10** were shown in Figure 3. The tetraporphyrin **10** underwent reversible first and second oxidations at 0.07 and 0.26 V versus Fc/Fc^+, which were just similar with those of **3a** and assigned as oxidation waves for the fused core. However, the first and second reduction potentials of tetraporphyrin array **10** at −1.07 and −1.32 V were more positive than those of **3a** (−1.13 and −1.37 V), while the third reduction potential at −1.85 V was more negative than that of NiTPP (−1.79 V), indicating that Ni(II) porphyrin may play as electron-withdrawing groups to the fused porphyrin core in this interlacedly linked system. Moreover, it also suggests that the HOMO−LUMO gap of triply−singly interlacedly linked porphyrin **10** was 1.14 eV, lower than that of fused diporphyrin **3a** (1.19 eV).

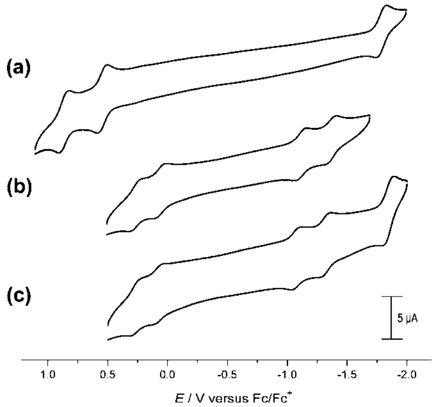

Figure 3. Cyclic voltammograms of (a) NiTPP in CH_2Cl_2, (b) **3a** in CH_2Cl_2, and (c) **10** in CH_2Cl_2 (containing 0.1 mol/L n-Bu_4NPF_6).

In summary, we have developed a practical and simple method for synthesis of triply linked diporphyrins through PIFA-mediated oxidation in high yields. We can facilely synthesize the triply or singly linked diporphyrins with triaryl Zn(II) porphyrin just by varying the added PIFA amount. The metal selectivity with Zn can also be used to faciliate the synthesis of the triply−singly interlacedly linked tetraporphyrin array. Further investigations to expand the reaction scope as well as to construct various molecular models by interlaced linked porphyrin arrays are ongoing and will be reported in due course.

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Supporting Information Available: Experimental procedures and compound data. This material is available free of charge via the Internet at http://pubs.acs.org.

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