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Switchable regioselectivity in PIFA-$BF_3{\cdot}Et_2O$ mediated oxidative coupling of *meso*-brominated Ni(II) porphyrin

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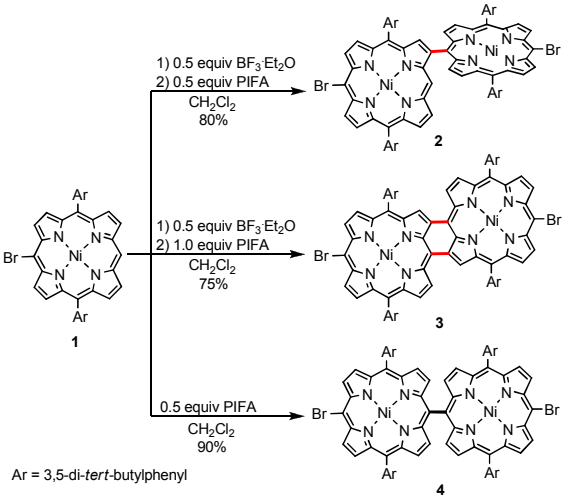
A simple and efficient method has been developed for the switchable synthesis of directly linked *meso*-brominated Ni(II) porphyrin dimers through PIFA-$BF_3{\cdot}Et_2O$ mediated oxidative coupling. The respective syntheses of *meso-meso* or *meso-β* singly, doubly, and triply linked porphyrin dimers can be easily realized with the same reagent system.

Directly linked porphyrin arrays have exhibited distinctive electrochemical, photochemical, and photophysical properties due to the strong electronic or excitonic interactions between two closely adjacent porphyrin moieties.[1] They have thus been used extensively in molecular wires,[2] photoelectric conversion devices,[3] functional supramolecular systems,[4] and nonlinear optical materials.[5]

Great efforts have been devoted to the convenient synthetic method for directly linked porphyrin arrays, and one-electron oxidative coupling was regarded as the most attractive one due to its high efficiency and simplicity.[6] With the pioneering and successful work by Osuka and coworkers, several reagent systems such as $AgPF_6$, BAHA, DDQ-$Sc(OTf)_3$, and $AuCl_3$-AgOTf have been successively developed and applied to synthesize different types of directly linked porphyrin dimers.[6a-f] But, a conventional Suzuki coupling is still needed, up to now, to synthesize *meso-β* singly linked porphyrin dimers with prefunctionalized porphyrin monomer. Meanwhile, a method switching was generally wanted to achieve the synthesis of different types of porphyrin dimers. Since the properties of such porphyrin dimers is closely related to the linking type and number, there remains a need to develop a convenient and efficient way to prepare various directly liked porphyrin dimers economically.

Iodine(III) reagents have been proved to be powerful in oxidative coupling, and successfully used to synthesize directly linked porphyrin dimers.[7] However, it was found to be inert to the substrate with high oxidation potential. In view of the effective improvement of the oxidation potential of phenyliodine(III) bis(trifluoroacetate) (PIFA) caused by $BF_3{\cdot}Et_2O$,[8] PIFA-$BF_3{\cdot}Et_2O$ was rationally expected to achieve a more powerful oxidative coupling of porphyrin monomers. Herein, we report a PIFA-$BF_3{\cdot}Et_2O$ mediated oxidative coupling for highly effective synthesis of five directly linked *meso*-brominated Ni(II) porphyrin dimers from the same brominated monomer. Switchable regioselectivity of this metal-free reaction is found to be strongly dependent on the equivalents of PIFA and the feeding order of PIFA vs $BF_3{\cdot}Et_2O$.



Scheme 1 Regioselective Oxidative Coupling of **1**.

Halogenated porphyrin is one of the most frequently used building blocks to achieve porphyrin-based functional molecules.[9] And the *meso*-brominated porphyrin substrate is reported to be sensitive to oxidizing condition, a reliable and effective method for achieving the oxidative coupling of *meso*-brominated porphyrin is still lacking. As shown in Table S1, in the absence of $BF_3{\cdot}Et_2O$, treating **1** with 0.5 equiv of PIFA resulted in *meso-meso* singly linked porphyrin dimer **4** in 90% yield (Scheme 1). While *meso-β* singly linked porphyrin dimer **2** was obtained by using 0.5 equiv of PIFA in the presence of $BF_3{\cdot}Et_2O$ (Scheme 1). The molecular structure of **2** was identified by NMR and MS data, and further confirmed by X-ray crystal structure analysis (Fig. 1). The Ni_1-Ni_2 distance is 8.70 Å which is longer than that of *meso-β,meso-β* doubly linked Ni(II) porphyrin dimer (8.61 Å).[1b,6b] The newly formed *meso-β* bond (C_{30}-C_{50}) is evaluated to be 1.48 Å, and equal to the C-C single bond (1.48 Å) of 1,3-butadiene. The mean distance of Ni-N is 1.93 Å, equal to the reported one for the Ni(II)-TPP.[6b]

Increasing the amount of PIFA from 0.5 to 0.75 equiv resulted in the decrease of **2**, and the occurrence of fused porphyrin dimer **3**

(Table S1, entry 4). When the feeding amount of PIFA was increased up to 1 equiv, the yield of compound **3** reached the maximum 75% (Scheme 1). Slight decrease in yield was observed with further increase of the amount of PIFA (Table S1, entry 6). As illustrated above, the oxidant PIFA and auxiliary reagent $BF_3{\cdot}Et_2O$ both has great influence on the regioselective oxidative coupling. The presence of $BF_3{\cdot}Et_2O$ undoubtedly improves the oxidation potential of PIFA, and finally leads to a practical route to synthesize *meso*-*β* linked porphyrin dimers. This method needs no further derivatization of porphyrin substrate to accord with the requirement of the conventional transition metal catalyzed coupling reaction.[10] It also needs no tedious chromatographic separation of the reported electrochemical oxidation. What's more, the existence of bromine atom in product will grant access to a variety of subsequent functionalization.

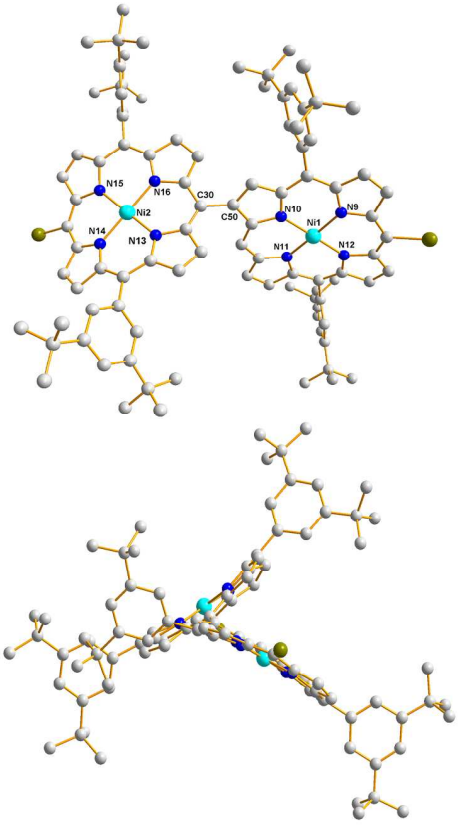
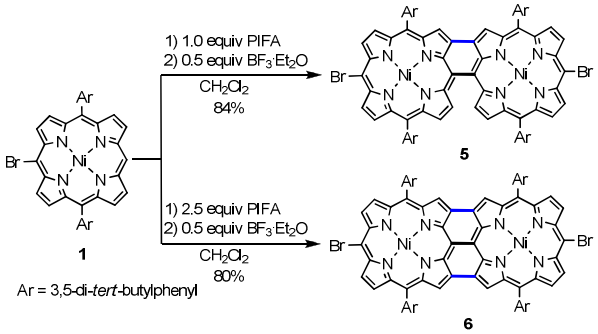


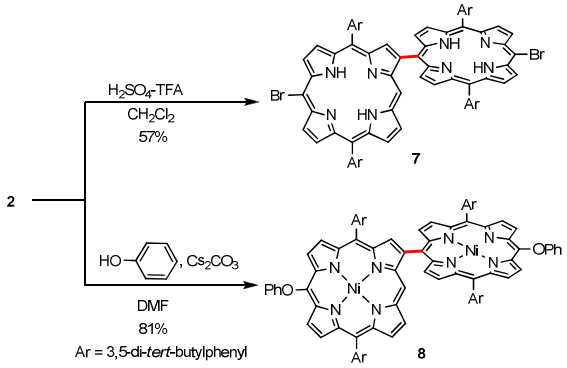
Fig. 1 X-ray crystal structure of **2** (CCDC 978038).



Scheme 2. PIFA-$BF_3{\cdot}Et_2O$ Mediated Fusion Reaction of **1**.

In consideration of the obvious assistant effect of $BF_3{\cdot}Et_2O$ on the improvement of the oxidation potential of PIFA, we subsequently treated the *meso*-*meso* singly linked porphyrin **4** with PIFA-$BF_3{\cdot}Et_2O$ for attempting to synthesize other types of fused porphyrin. Fortunately, treating compound **4** with 0.5 and 2.0 equiv of PIFA in the presence of $BF_3{\cdot}Et_2O$ gave doubly and triply linked porphyrin dimer (**5** and **6**) in 93% and 90% yield respectively (Table S2). Since the *meso*-*meso* singly linked porphyrin **4** can be prepared only with PIFA (Scheme 1), a one-pot two-step method was then accomplished to synthesize the fused dimers containing *meso*-*meso* linkage. As shown in Scheme 2, treating **1** with 1.0 equiv of PIFA first and subsequently with 0.5 equiv of $BF_3{\cdot}Et_2O$ could give *β*-*β*, *meso*-*meso* doubly fused diporphyrin **5** in 84%. Adding $BF_3{\cdot}Et_2O$ can activate the PIFA which remains unreacted and further perform the formation of *β*-*β* bond. Increasing the amount of PIFA will benefit the formation of triply fused porphyrin dimers. When 2.5 equiv of PIFA was added, porphyrin dimer **6** was finally obtained in 80% (Scheme 2).

As mentioned above, the PIFA-$BF_3{\cdot}Et_2O$ mediated oxidative coupling reaction is of great advantage in the synthesis of directly linked porphyrin dimers from easily accessible porphyrin monomers. No transition-metal reagent is needed for the transformation. Only adjustment of the equivalent of PIFA and feeding order of PIFA vs $BF_3{\cdot}Et_2O$ is needed for synthesizing different types of porphyrin dimers. The equivalent of PIFA corresponds to the number of bonds forming. And $BF_3{\cdot}Et_2O$ is used to improve the oxidation potential of PIFA whatever it was added prior to or after PIFA feeding. When $BF_3{\cdot}Et_2O$ is introduced into the reaction mixture prior to the real oxidant PIFA, a large excess environment of $BF_3{\cdot}Et_2O$ could be maintained as the PIFA is dropped in. That will ensure the PIFA added is efficiently and fast activated, and then oxidize the porphyrin to form its radical cation at *β*-carbon.[6d,11] Thereafter, attacking the neutral porphyrin at *meso* position produces *meso*-*β* linked porphyrin dimer. When PIFA is introduced first, it oxidizes the porphyrin monomer to form *meso*-*meso* singly linked diporphyrin and retain that state,[7,8] then the unreacted PIFA is activated by the later added $BF_3{\cdot}Et_2O$ to further oxidize the singly linked intermediate to a fused one.



Scheme 3. Demetalation and S_NAr reaction of **2**.

Demetalation of metalloporphyrin was further investigated. *Meso*-*meso* singly linked Ni(II) porphyrin arrays were reported to be easily transformed into corresponding freebase using concentrated sulfuric acid.[7d,12] The fused porphyrin dimers **3** and **6** were smoothly demetalated with the same method and the free base were got in 76% and 81%, respectively (Scheme S1). With regard to *meso*-*β* singly linked compound **2**, the mixture of TFA and H_2SO_4 should be used to give the freebase porphyrin dimer **7** (Scheme 3). The *meso*-brominated porphyrin dimers would be useful precursors for further functionalization using the simple S_NAr reaction we recently reported.[9a] A typical experiment was carried out in DMF with compound **2** and phenol in the presence of Cs_2CO_3 at 100°C, corresponding *meso*-derivatized **8** was obtained in 81% yield. This simple methodology will grant access to a variety of *meso*-functionalization of directly linked porphyrins.

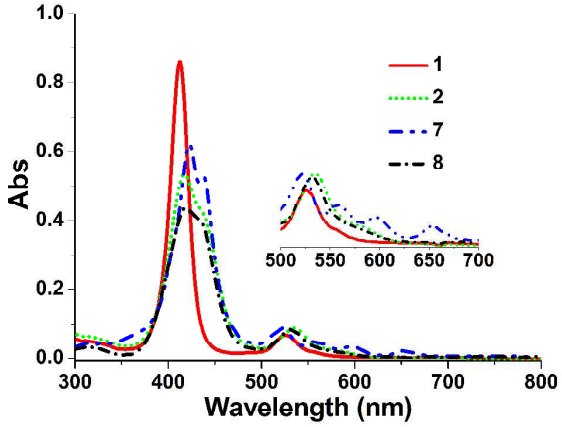


Fig. 2 Ultraviolet-visible absorption spectra of porphyrins **1** (red), **2** (green), **7** (blue), and **8** (black) in $CHCl_3$.

The interesting absorption of the porphyrin derivative is of great significance to the development of photoelectric conversion materials and sensors.[3,13] UV/vis absorption spectra of *meso-β* singly linked dimers **2**, **7**, **8**, and the monomer **1** are shown in Fig. 2 (see Fig. S1 for spectra of other directly linked porphyrin dimers). In contrast to the sharp Soret band of **1**, the singly linked dimers **2**, **7** and **8** exhibit perturbed Soret bands because of the excitonic coupling. The Soret bands of the *meso-β* singly dimer **2** and **8** are observed as broad bands at 417 and 419 nm with shoulders at 431 and 432 nm, respectively. That of freebase **7** is obviously split and appears at 423 and 438 nm. The Q bands at 534 and 530 nm are observed for both compounds **2** and **8**. Similar to freebase porphyrin monomer, the Q bands of compound **7** are consisting of four peaks, and the maximum absorption occurred at 522, 557, 597 and 653 nm respectively. Owing to more extensive conjugation, the spectra of fused dimers reach into the infrared region and include three broadened and red-shifted absorption zones (Fig. S1).

In conclusion, We have developed a simple and efficient method to synthesize various *meso*-brominated Ni(II) porphyrin dimers. This PIFA-$BF_3{\cdot}Et_2O$ mediated oxidative coupling reaction shows excellent regioselectivity. By simply changing that equivalent of PIFA and feeding order of PIFA vs $BF_3{\cdot}Et_2O$, the respective synthese of *meso-meso* singly, *meso-β* singly, *meso-β* and *meso-β* doubly, *meso-meso* and *β-β* doubly, and *β-β*, *meso-meso*, *β'-β'* triply linked porphyrin arrays can be easily realized. Facile demetalation and S_NAr reaction of brominated porphyrin dimers make this method more valuable and general.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, NMR data and cif files for the single crystal X-ray structure of **2** (CCDC 978038) are avaliable. See DOI: 10.1039/b000000x/

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