Organic & Biomolecular Chemistry

COMMUNICATION

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Cite this: *Org. Biomol. Chem.*, 2014, **12**, 6990

Received 18th July 2014,
Accepted 23rd July 2014

DOI: 10.1039/c4ob01517g

www.rsc.org/obc

Switchable regioselectivity in the PIFA–BF_3·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·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 finding convenient synthetic methods 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 co-workers, 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] However, a conventional Suzuki coupling reaction is still needed to synthesize *meso*–β singly linked porphyrin dimers with prefunctionalized porphyrin monomers. Meanwhile, a method is generally wanted to achieve the switchable synthesis of different types of porphyrin dimers. Since the properties of such porphyrin dimers are closely related to the linking type and number, there remains a need to develop a convenient and efficient way to prepare various directly linked porphyrin dimers economically.

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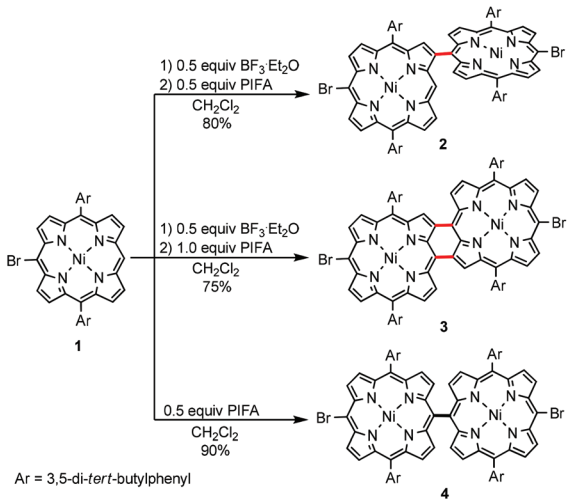
†Electronic supplementary information (ESI) available: Synthetic procedures, NMR data and CIF files for the single crystal X-ray structure of **2**. CCDC 978038. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01517g

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

Halogenated porphyrin is one of the most frequently used building blocks to achieve porphyrin-based functional molecules.[9] And though the *meso*-brominated porphyrin substrate is reported to be sensitive to oxidizing conditions, 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·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·Et_2O (Scheme 1). The molecular structure of **2** was identified using 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 the *meso*–β and *meso*–β doubly linked Ni(II) porphyrin dimer (8.61 Å).[1b,6b] The newly formed *meso*–β bond (C_{30}–C_{50}) length is evaluated to be 1.48 Å, and equal to the C–C single bond length (1.48 Å) of 1,3-butadiene. The mean distance of Ni–N is 1.93 Å, equal to that reported for Ni(II)–TPP.[6b]

Increasing the amount of PIFA from 0.5 to 0.75 equiv. resulted in a decreased yield 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). A slight decrease in yield was observed with a further increase in the



Scheme 1 Regioselective oxidative coupling of **1**.

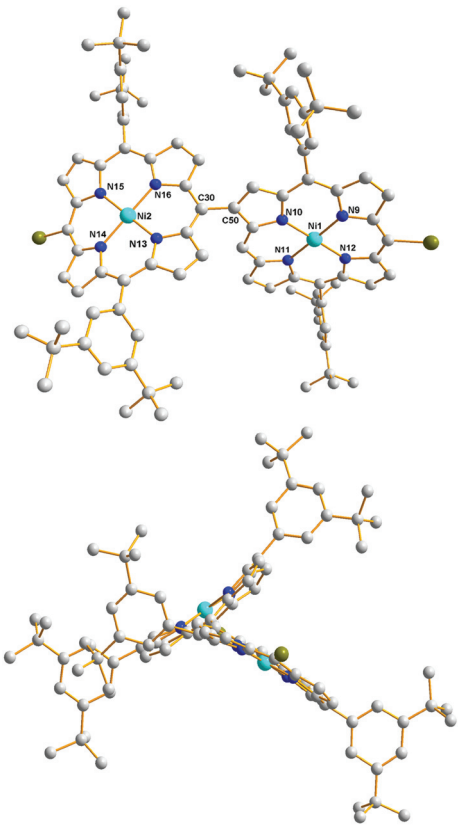
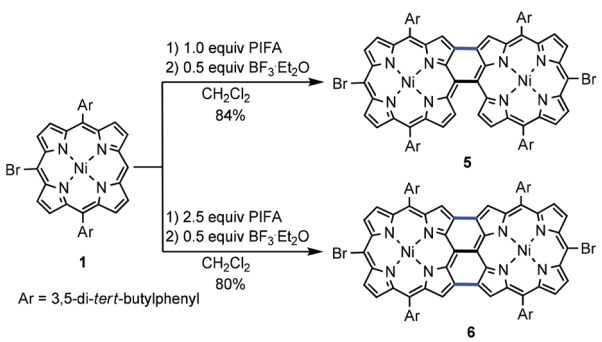


Fig. 1 X-ray crystal structure of **2** (CCDC 978038).

amount of PIFA (Table S1,† entry 6). As illustrated above, the oxidant PIFA and auxiliary reagent $BF_3·Et_2O$ both have a great influence on the regioselective oxidative coupling. The presence of $BF_3·Et_2O$ 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 the porphyrin substrate, as is required of the conventional transition metal catalyzed coupling reaction.[10] It also needs no tedious chromatographic separation, as reported with electrochemical oxidation. What's more, the existence of the bromine atom in the product will grant access to a variety of subsequent functionalizations.

In consideration of the obvious assisting effect of $BF_3·Et_2O$ on the improvement of the oxidation potential of PIFA, we subsequently treated the *meso–meso* singly linked porphyrin **4** with PIFA–$BF_3·Et_2O$ to attempt to synthesize other types of fused porphyrin. Fortunately, treating compound **4** with 0.5 and 2.0 equiv. of PIFA in the presence of $BF_3·Et_2O$ gave doubly and triply linked porphyrin dimers (**5** and **6**) in 93% and 90% yields, 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 established to synthesize the fused dimers containing *meso–meso* linkages. As shown in Scheme 2, treating **1** with 1.0 equiv. of PIFA first and subsequently with 0.5 equiv. of $BF_3·Et_2O$ could give β–β and *meso–meso* doubly fused diporphyrin **5** in 84% yield. Adding $BF_3·Et_2O$ can activate the PIFA which remains unreacted and further form β–β bonds. 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% yield (Scheme 2).

As mentioned above, the PIFA–$BF_3·Et_2O$ 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 amount of PIFA and feeding order of PIFA *vs.* $BF_3·Et_2O$ is needed to synthesize different types of porphyrin dimers. The amount of PIFA corresponds to the number of bonds formed. And $BF_3·Et_2O$ is used to improve the oxidation potential of PIFA, whether added before or after PIFA feeding. When $BF_3·Et_2O$ is introduced into the reaction mixture prior to the real oxidant PIFA, a large excess environment of $BF_3·Et_2O$ could be maintained as the PIFA is dropped in. That will ensure the PIFA added is efficiently and quickly activated, and then oxidizes the porphyrin to form its radical cation at the β–carbon.[6d,11] Thereafter, attacking the neutral porphyrin at the *meso* position produces the *meso*–β linked porphyrin dimer. When PIFA is introduced first, it oxidizes the porphyrin monomer to form *meso–meso* singly linked diporphyrin and that state is retained,[7,8] then the

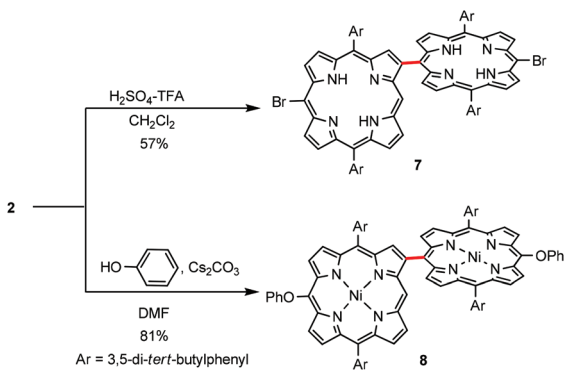


Scheme 2 PIFA–$BF_3·Et_2O$ mediated fusion reaction of **1**.

unreacted PIFA is activated by the $BF_3{\cdot}Et_2O$ added later to further oxidize the singly linked intermediate to a fused one.

The demetalation of metalloporphyrins was further investigated. *Meso–meso* singly linked Ni(II) porphyrin arrays were reported to be easily transformed into the corresponding freebases using concentrated sulfuric acid.[7d,12] The fused porphyrin dimers **3** and **6** were smoothly demetalated with the same method and the freebases were obtained in 76% and 81% yields, respectively (Scheme S1†). With regard to *meso*–β singly linked compound **2**, the mixture of TFA and H_2SO_4 could be used to give the freebase porphyrin dimer **7** (Scheme 3). The *meso*-brominated porphyrin dimers could 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, and the corresponding *meso*-derivatized **8** was obtained in 81% yield. This simple methodology will grant access to a variety of *meso*-functionalization possibilities for directly linked porphyrins.

The interesting absorption of the porphyrin derivatives 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 excitonic coupling. The Soret bands of the *meso*–β singly linked dimers **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 the freebase porphyrin monomer, the Q bands of compound **7** consist of four peaks, and the maximum absorption occurs at 522, 557, 597 and 653 nm, respectively. Owing to more extensive conjugation, the spectra of the fused dimers reach into the infrared region and include three broadened and red-shifted absorption zones (Fig. S1†).



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

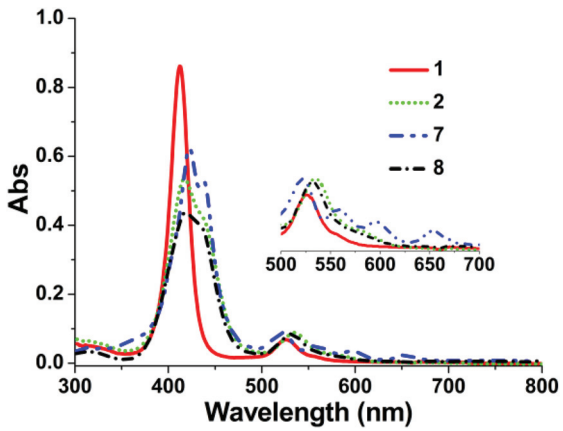


Fig. 2 Ultraviolet-visible absorption spectra of porphyrins **1** (red), **2** (green), **7** (blue), and **8** (black) in $CHCl_3$.

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 the amount of PIFA and the feeding order of PIFA *vs.* $BF_3{\cdot}Et_2O$, the respective syntheses of *meso–meso* singly, *meso*–β singly, *meso*–β and *meso*–β doubly, *meso–meso* and β–β doubly, and β–β, *meso–meso* and β′–β′ triply linked porphyrin arrays can be easily realized. The facile demetalation and S_NAr reaction of brominated porphyrin dimers make this method more valuable and general.

We thank the 973 Program (2011CB932502), NSFC (no. 21172126 and 21272123), and Asia Research Center in Nankai University (no. AS1217) for their generous financial support.

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