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Porphyrinoids

Palladium-Catalyzed β-Selective Direct Arylation of Porphyrins**

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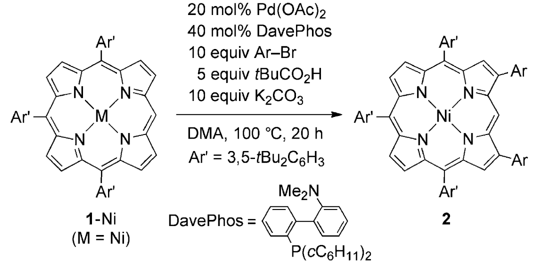
Porphyrins are an important class of aromatic compounds that exhibit interesting optical and electrochemical properties and have attracted much attention as key components of functional materials and supramolecular architectures.[1] Creation of new porphyrins that feature intriguing properties is hence essential in developing the chemistry and applications of functional π-rich molecules. Peripheral functionalization of porphyrins can effectively modify the electronic and steric nature of the parent porphyrins, and is thus useful when investigating new porphyrins.[2] Among the possible functionalizations, arylation is promising since the introduced aryl groups can induce electronic perturbation through extension of π conjugation. Nucleophilic addition of aryllithium reagents to meso-unsubstituted porphyrins followed by oxidation can be employed for peripheral arylation reactions.[2c,d,3] The nucleophilic arylation reaction inherently lacks functional-group compatibility because of the high reactivity of aryllithium reagents. Presently, the most reliable and chemoselective functionalization is based on palladium-catalyzed cross-coupling reactions.[4,5] However, the cross-coupling strategy always requires preparation of halogenated[5,6] or metalated[7,8] porphyrins prior to arylation. More straightforward and efficient methods for peripheral arylation of porphyrins are thus needed.

Transition-metal-catalyzed direct C–H arylation of arenes with aryl halides has been rapidly emerging as a promising alternative to traditional cross-coupling arylations because preparations of aryl metal reagents can be omitted.[9–11] We envisaged that the direct arylation would be applicable to porphyrins. After extensive screening of porphyrin substrates and reaction conditions, we found that the pivalate-assisted conditions developed by Fagnou and co-workers, with some modifications, are effective for the synthesis of meso-free Ni^{II} porphyrins.[9f,10a] Treatment of the Ni^{II} complex of 5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin (**1**-Ni) with aryl halides in the presence of pivalic acid,[12] potassium carbonate, and catalytic amounts of palladium acetate and DavePhos in *N,N*-dimethylacetamide (DMA) at 100 °C resulted in diarylation with satisfactory efficiency (Table 1). To our surprise, the reaction proceeded exclusively at the β positions adjacent to the free meso position with excellent selectivity, and no meso-arylated products were detected. Although the sequential iridium-catalyzed borylation/palladium-catalyzed Suzuki–Miyaura coupling had been the only efficient and practical method for β-selective arylation,[8] this sequence often suffers from the gradual protodeborylation of borylated porphyrins in protic media during purification and cross-coupling processes. Naturally, the present direct method is much more efficient and does not suffer from such demetalation. Moreover, this method is the first palladium-catalyzed reaction that selectively functionalizes the β positions of porphyrins.

The yields of the diarylated products **2** are generally satisfactory, and the scope of aryl bromides is wide (Table 1). The reactions with aryl bromides that bear no heteroatom-containing substituents proceeded smoothly (Table 1, entries 1–6), and the steric hindrance of 2-bromotoluene did not retard the reaction (entry 2). Although the reaction with 4-bromoanisole was sluggish under the standard reaction conditions, the use of potassium pivalate instead of pivalic acid dramatically improved the yield of **2h** (Table 1, entry 8). The reactions with other functionalized aryl bromides were slow and did not proceed to completion within 20 h (Table 1,

Table 1: Scope of diarylation reactions.



1-Ni
(M = Ni)

2

Entry	Ar	2	Yield[a] [%]
1	C_6H_5	**2a**	76
2	2-MeC_6H_4	**2b**	71
3	3-MeC_6H_4	**2c**	81
4	4-MeC_6H_4	**2d**	79
5	$3,5\text{-Me}_2C_6H_3$	**2e**	80
6	2-naphthyl	**2f**	84
7	3-MeOC_6H_4	**2g**	72
8	4-MeOC_6H_4	**2h**	8 (62[b])
9	$4\text{-Me}_2NC_6H_4$	**2i**	32 (63[c])
10	$4\text{-EtO}_2CC_6H_4$	**2j**	28 (62[c])
11	$4\text{-O}_2NC_6H_4$	**2k**	3 (43[d])

[a] Yield of isolated product after recrystallization. [b] $tBuCO_2K$ (5 equiv) was used instead of $tBuCO_2H$. [c] 40 h reaction time; a solution of $Pd(OAc)_2$ (20 mol%) and DavePhos (40 mol%) in DMA was added again after 20 h. [d] 60 h reaction time; a solution of $Pd(OAc)_2$ (20 mol%) and DavePhos (40 mol%) in DMA was added every 20 h.

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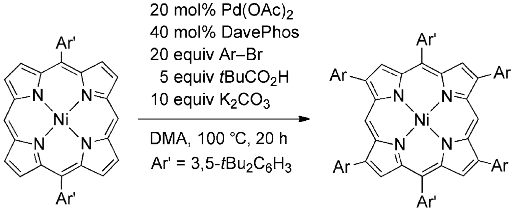
entries 9–11). We observed that the catalyst was deactivated after 20 h, thus we simply added the catalyst repeatedly until substrate **1**-Ni disappeared, in order to considerably improve the yields of **2i**–**k**.

Nickel(II) proved to be the best central metal in the substrate. The reaction of Zn^{II} porphyrin **1**-Zn (M = Zn) with 3,5-dimethylbromobenzene afforded none of the diarylated product and the corresponding monoarylated porphyrin in 33 % yield. The lower reactivity of **1**-Zn, which is less electron-deficient than **1**-Ni, may indicate that the concerted metalation/deprotonation (CMD) process[10a] would be rate-determining (see below). No conversion was observed in the reaction of free-base porphyrin **1**-H_2 (M = 2H) because a palladium cation was captured by the substrate. Demetalation of nickel porphyrins **4** requires highly acidic conditions, thus reaction conditions for the direct arylation of **1**-Zn and **1**-H_2 are now being explored to obtain the free-base porphyrin of **4**. The high efficiency of the arylation reaction culminated in direct tetraarylation of the nickel complex of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (**3**; Table 2), where four carbon–carbon bonds were formed simultaneously with complete β selectivity without any prefunctionalization of the porphyrin.[13,14]

According to Fagnou and co-workers,[9f,10a,15] the most plausible mechanism for the arylation reaction consists of the following elementary steps (Scheme 1 a): 1) oxidative addition of an aryl bromide to Pd^0 to produce an arylpalladium bromide, 2) bromide–pivalate exchange to provide an arylpalladium pivalate, 3) CMD of the porphyrin with the arylpalladium pivalate to form an aryl(porphyrinyl)palladium, and 4) reductive elimination to result in arylation of the porphyrin and liberation of the initial Pd^0 complex. The more electron-rich **1**-Zn was less reactive because its β protons are less acidic than those of **1**-Ni. The low reactivity of **1**-Zn also strongly supports the hypothesis that the β palladation of the porphyrins does not proceed by an electrophilic aromatic substitution (S_EAr)[9a,e,i] pathway but by the CMD process. The perfect regioselectivity of the di- and tetraarylation would be controlled by steric factors. The substituted β protons are the most readily accessible among the peripheral protons, including the meso protons and the β protons next to the meso-aryl groups (Scheme 1 b). Large-scale computational studies will be required for detailed rationalization of the regioselectivity.

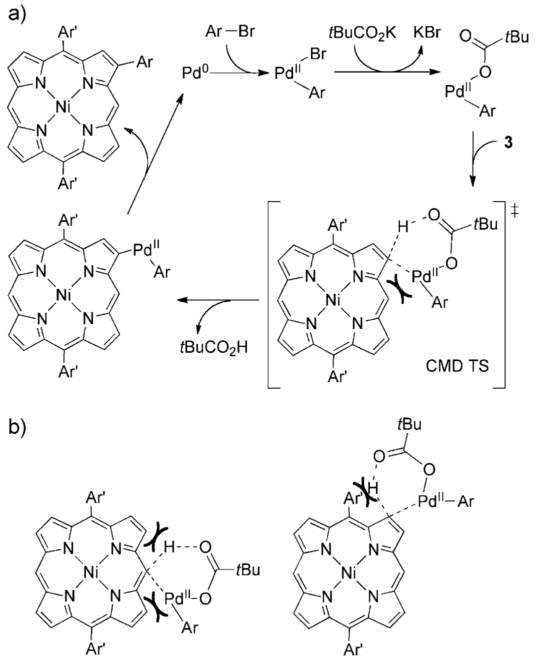
Table 2: Attempted tetraarylation reactions.



3 **4**

Entry	Ar	**4**	Yield[a] [%]
1	3,5-$Me_2C_6H_3$	**4a**	91
2	4-$C_8H_{17}OC_6H_4$	**4b**	38 (69[b])
3	4-[$Bu_2NC(=O)$]C_6H_4	**4c**	(60[c])
4	3,5-$(MeO)_2C_6H_3$	**4d**	13 (60[c])

[a] Yield of isolated product after recrystallization. [b] *t*BuCO$_2$K (5 equiv) was used instead of *t*BuCO$_2$H; 40 h reaction time. [c] 60 h reaction time; a solution of Pd(OAc)$_2$ (20 mol%) and DavePhos (40 mol%) in DMA was added every 20 h.



Scheme 1. a) Plausible mechanism and b) less favorable transition states (TS) for CMD. Ar' = 3,5-*t*Bu$_2$C$_6$H$_3$.

The structures of β-arylated porphyrins **2i** and **4a** were unambiguously determined by X-ray crystallographic analysis (Figure 1)[16] as well as ^1H and ^{13}C NMR spectroscopy and NOESY analysis (see the Supporting Information). The introduction of the aryl groups at the β positions did not significantly distort the structures of the parent porphyrins. The dihedral angles between the β-aryl groups and the porphyrin plane are 46–53°, which are distinctly smaller than those of the meso-aryl groups (64–89°). In addition, the distances between the substituted β-carbon atoms and the adjacent benzene carbon atoms are 1.46–1.49 Å, which are shorter than those between the substituted meso-carbon atoms and the directly connected benzene carbon atoms (1.50–1.53 Å). These structural features indicate that the β-aryl groups are more effectively conjugated with the porphyrin than the meso-aryl groups.

The UV/Vis absorption spectra of the diarylated porphyrins **2h** and **2j** showed that the Soret and Q bands were slightly but distinctly red-shifted compared to that of β-unsubstituted **1**-Ni, probably because of the extension of the π-electronic network (Figure 2). The electronic nature of the aryl groups likely have no significant influence on the absorption band. On the other hand, the shifts of the first oxidation potentials of **2** depend on the electronic nature of the introduced β-aryl substituents. When plotted against the $2\sigma_p$ value (σ_p: Hammett substituent constant) of the substituents, the first oxidation potentials of **2** lie on a linear slope with $\rho = 0.099$ (Figure 3; see the Supporting Information for cyclic voltammograms). The ρ value is somewhat larger than that of the nickel complexes of *para*-substituted tetraphenyl-

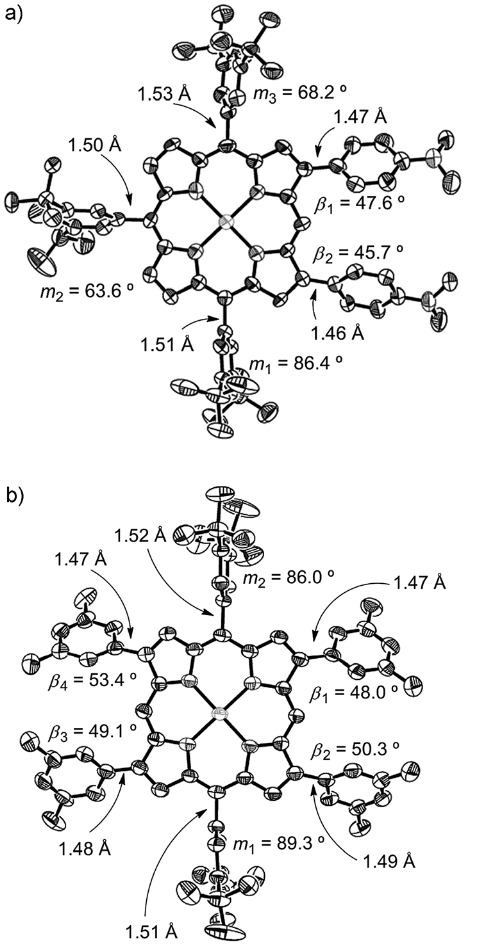


Figure 1. X-ray crystal structures of a) diarylated porphyrin **2i** and b) tetraarylated porphyrin **4a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Dihedral angles at the meso and β positions are denoted as m_i and β_i, respectively.

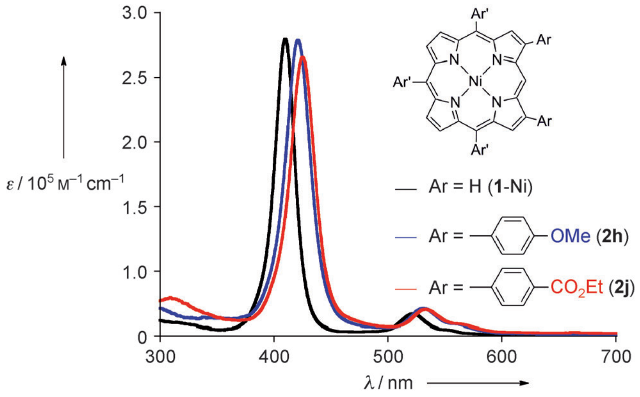


Figure 2. UV/Vis absorption spectra of **1**-Ni (Ar = H, black), **2h** (Ar = 4-MeOC$_6$H$_4$, blue), and **2j** (Ar = 4-EtO$_2$CC$_6$H$_4$, red) in CH$_2$Cl$_2$ (Ar' = 3,5-tBu$_2$C$_6$H$_3$).

porphyrins ($\rho = 0.089$).[17] These observations clearly reflect the existence of small yet effective conjugation between the porphyrin core and the peripheral β-aryl groups.

In summary, we have developed a palladium-catalyzed direct arylation of porphyrins with aryl bromides as a rare example of β-selective functionalization. The reaction allows the rapid synthesis of a series of new β-arylated porphyrins. The simultaneous tetraarylation of the nickel complex of 5,15-diarylporphyrin underscores the high efficiency and utility of our strategy for porphyrin functionalization. The electrochemical characters of newly created β-arylated porphyrins could be modulated by the substituents on the introduced aryl groups through conjugation between the porphyrin core and the moderately tilted β-aryl groups. Further investigations are underway to achieve much higher catalytic activity and to efficiently synthesize new and/or elusive porphyrin-based functional molecules.

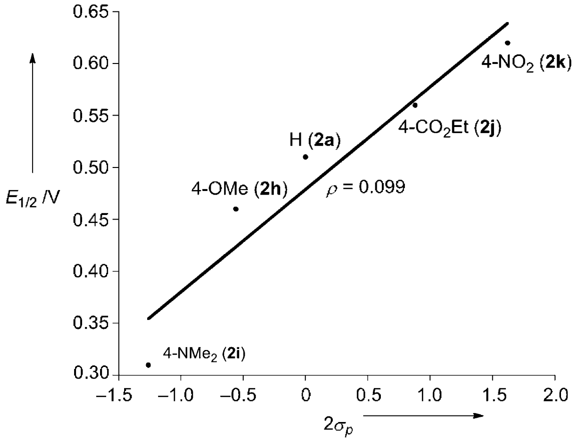


Figure 3. Plot of first oxidation potentials ($E_{1/2}$) of **2** against 2σ_p values of the substituents ($E_{1/2} = 2\sigma_p\rho$).

Experimental Section

Typical procedure for the direct arylation of Ni^{II} complexes of 5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin (**1**-Ni): Porphyrin **1**-Ni (23.3 mg, 0.025 mmol), Pd(OAc)$_2$ (1.1 mg, 0.005 mmol), DavePhos (3.9 mg, 0.010 mmol), K$_2$CO$_3$ (34.5 mg, 0.25 mmol), tBuCO$_2$H (12.8 mg, 0.125 mmol), and 2-bromonaphthalene (51.7 mg, 0.25 mmol) were placed in a Schlenk tube. The reaction vessel was purged with argon, and DMA (1.0 mL) was added. The resulting mixture was then stirred at 100 °C for 20 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (2.0 mL) and passed through a short silica gel column. After evaporation of the solvent, the product was separated by column chromatography on silica gel (CH$_2$Cl$_2$/hexane 2:1). Further purification by recrystallization from CH$_2$Cl$_2$/MeOH afforded **2f** (24.7 mg, 0.0215 mmol, 84 %).

Typical procedure for the direct arylation of Ni^{II} complex of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (**3**): Porphyrin **3** (22.2 mg, 0.03 mmol), Pd(OAc)$_2$ (1.3 mg, 0.006 mmol), DavePhos (4.7 mg, 0.012 mmol), K$_2$CO$_3$ (41.4 mg, 0.30 mmol), and tBuCO$_2$H (15.3 mg, 0.15 mmol) were placed in a Schlenk tube. The reaction vessel was purged with argon, and DMA (1.0 mL) was added. 3,5-Dimethylbromobenzene (81.5 μL, 0.60 mmol) was added by microsyringe. The mixture was then heated at 100 °C for 20 h. The resulting mixture was diluted with CH$_2$Cl$_2$or CHCl$_3$ (2.0 mL), passed through a pad of silica gel, and concentrated in vacuo. The product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/hexane 1:5) followed by recrystallization from CH$_2$Cl$_2$/MeOH to afford **4a** (31.3 mg, 0.0271 mmol, 84 %).

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