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Metal-Dependent Regioselective Oxidative Coupling of 5,10,15-Triarylporphyrins with DDQ-Sc(OTf)$_3$ and Formation of an Oxo-quinoidal Porphyrin

**Makoto Kamo,[†] Akihiko Tsuda,[†] Yasuyuki Nakamura,[†] Naoki Aratani,[†]
Ko Furukawa,[‡] Tatsuhisa Kato,[‡] and Atsuhiro Osuka*,[†]**

*Department of Chemistry, Graduate School of Science, Kyoto University,
Sakyo-ku, Kyoto 606-8502, Japan, Institute for Molecular Science,
Myodaiji, Okazaki 444-8585, Japan*

osuka@kuchem.kyoto-u.ac.jp

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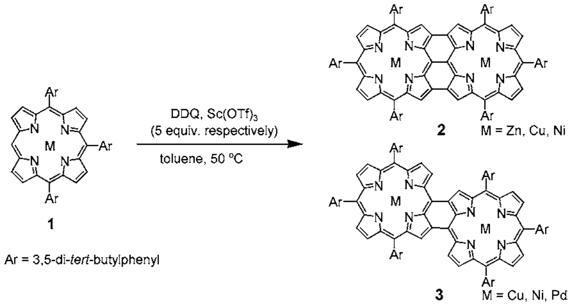
ABSTRACT



Regioselectivity of the oxidative coupling of 5,10,15-triarylporphyrin metal complexes with DDQ-Sc(OTf)$_3$ was dependent on the central metal and *meso*-aryl substituent. Oxo-quinoidal porphyrin was obtained from Ni(II) porphyrin under the same conditions.

In recent years, discrete π-conjugated porphyrin arrays with extensive delocalization have attracted considerable attention due to their wide applications for organic conducting materials, near-infrared dyes, nonlinear optical (NLO) materials, molecular devices, and molecular wires.[1−3] Along this line, a number of porphyrin arrays that have a large interporphyrin conjugation have been extensively exploited.[4−12] Since the remarkable properties of these arrays are attributed to the strong interaction between porphyrins, a promising

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[†] Kyoto University.

[‡] Institute for Molecular Science.

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approach may be to hold π-systems coplanar as a multiply covalently linked flat array.[7−12]

Recently, we reported the synthesis of *meso*−*meso*, β−β, β−β triply linked Zn(II) porphyrin tapes from corresponding *meso*−*meso* singly linked Zn(II) porphyrin arrays.[12a] The porphyrin tapes thus prepared exhibit unprecedented red-shifted absorption bands that reach into infrared and unique photophysical properties.[13] The fully *meso*-substituted triply linked Zn(II) diporphyrin can be obtained by oxidative coupling of 5,10,15-triarylporphyrins with DDQ-Sc(OTf)$_3$.[12a] Here we examined this coupling reaction for other metalloporphyrins and have found that the coupling regioselectivity depends heavily on the central metal as well as the *meso*-aryl substituents.

First we examined the reaction of 5,10,15-tris(3,5-di-*tert*-butylphenyl)metalloporphyrins **1** with DDQ-Sc(OTf)$_3$ (Scheme 1 and Table 1). Zinc complex **1**-Zn gave only *meso*−*meso*, β−β, β−β, triply linked diporphyrin **2**-Zn in 86% yield,[12a] while **1**-Pd gave only *meso*−β doubly linked diporphyrin **3**-Pd in 74% yield. The latter coupling regioselectivity has also been observed for the similar oxidative coupling of **1**-Pd with tris(4-bromophenyl)aminium hexachloroantimonate (BAHA).[10] Both fused diporphyrins, **2**-Cu and **3**-Cu and **2**-Ni and **3**-Ni, were isolated from the reactions of **1**-Cu and **1**-Ni, respectively. The observed coupling regioselectivites are analogous to those found for the oxidation with BAHA. The ratio of **2** and **3** may reflect the product ratio of the initially formed *meso*−β and *meso*−*meso* singly linked diporphyrins, and their different coupling regioselectivity may be accounted for in terms of the HOMO orbitals of the cation radical formed, presumably, a_{1u} for *meso*−β and a_{2u} for *meso*−*meso* coupling, since the a_{2u} orbital has a large spin density at the *meso*-carbons and the a_{1u} orbital has a node at the *meso*-carbons but a substantial spin density at the β-carbons. We thus examined the ESR detection of the cation radicals of **1**-Zn and **1**-Pd by using a simple two-electrode cell for ESR measurements.[14] At a potential of 1.6 V to the counter electrode, electrooxidation proceeded to give the ESR spectrum at $g = 2.0024$ assignable to the cation radical of **1**-Zn that was coupled with four equivalent nitrogens with $a_N = 1.7$ G. This indicated that one electron was removed from the a_{2u} orbital in **1**-Zn.[15] On the other hand, more potential (1.8 V) was needed for the one-electron oxidation of **1**-Pd, and decreasing the temperature to −50 °C was necessary to get the clear ESR spectrum. The resultant ESR spectrum at $g = 1.9966$ exhibited no splitting due to the coupling with the nitrogens, thus indicating that one electron was removed from the a_{1u} orbital in **1**-Pd. These results are consistent with the above mechanism involving the initial one-electron oxidation of metalloporphyrin followed by a nucleophilic attack of another neutral metalloporphyrin with its *meso*-position. In this mechanism, it is rather obvious that the the role of Sc(OTf)$_3$ is to interact with the DDQ anion radical, thus enhancing the oxidizing ability of DDQ.[16] In fact, the first one-electron reduction potential of DDQ observed at −0.50 V versus (Ag/AgClO$_4$) was shifted to −0.18 V in the presence of a 0.5 equiv of Sc(OTf)$_3$ and −0.09 V in the presence of 1 equiv of Sc(OTf)$_3$.

Scheme 1

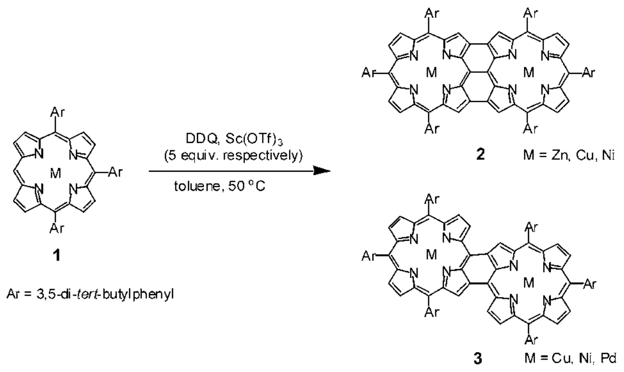

Table 1. Yields of the Oxidative Coupling Reaction of **1a**

entry	metal	time (h)	**2**	**3**
1	Zn	0.5	86	0
2	Cu	5	33	60
3	Ni	5	17	60
4	Pd	12	0	74

[a] Reaction conditions: DDQ (5 equiv), Sc(OTf)$_3$ (5 equiv), toluene, 50 °C.

Second, we have examined the similar reaction of Zn(II) porphyrin **4a** that bears a trimethylsilyl (TMS)-protected sterically hindered phenol. The porphyrin **4a** was designed in a view of possible transformation of fused diporphyrins **6** and **7** into the corresponding quinoidal structures. Such quinoidal porphyrins have been demonstrated to exhibit quite altered absorption spectral properties.[17,18] The porphyrin **4a**

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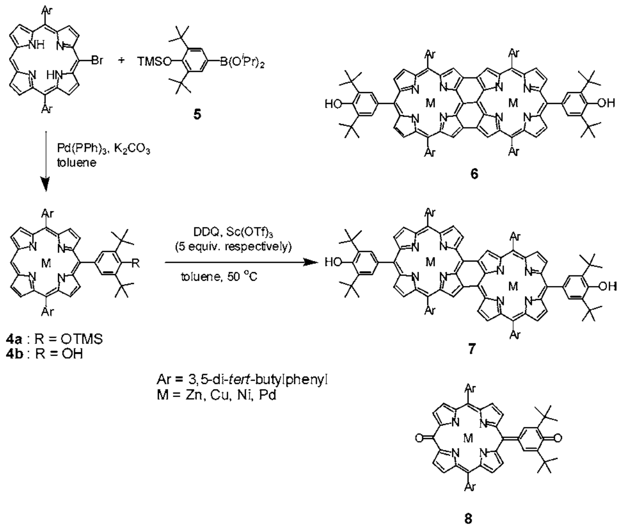
Scheme 2



Ar = 3,5-di-*tert*-butylphenyl
M = Zn, Cu, Ni, Pd

was prepared from Suzuki aryl coupling method of 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-porphyrin and boronate **5** in 64% yield. Results for their oxidative coupling reactions are summarized in Table 2. Zinc porphyrin **4a**-Zn gave triply linked diporphyrin **6**-Zn, and palladium porphyrin **4a**-Pd gave *meso*−β doubly linked diporphyrin **7**-Pd, both in highly regioselective manners that are essentially the same as those of **1**-Zn and **1**-Pd. In the both cases, the TMS protective group was cleaved during the reaction. On the other hand, Cu(II) porphyrin **4a**-Cu gave triply linked diporphyrin **6**-Cu exclusively. In the case of Ni(II) porphyrin **4a**-Ni, greenish product **8**-Ni was isolated as a major product (55%) along with diporphyrins **6**-Ni and **7**-Ni. We also examined the coupling reaction of TMS-removed substrate **4b**, which afforded practically the same products that were obtained from **4a** (entries 5−8, Table 2). It is thus likely that the one-electron oxidation of **4a** would lead to an instantaneous cleavage of TMS protecting group.

Table 2. Yields of the Oxidative Coupling Reaction of **4a** and **4b**[a]

entry	substrate (metal)	time (h)	**6**[b]	**7**[b]	**8**[b]
1	**4a**-Zn	3	78	0	trace
2	**4a**-Cu	12	85	0	trace
3	**4a**-Ni	12	17[c]	8[c]	55
4	**4a**-Pd	24	0	74	0
5	**4b**-Zn	3	65	0	trace
6	**4b**-Cu	12	80	0	trace
7	**4b**-Ni	12	23[c]	17[c]	33
8	**4b**-Pd	24	0	70	0

[a] Reaction conditions: DDQ (5 equiv), Sc(OTf)$_3$ (5 equiv), toluene, 50 °C. [b] Isolated yield. [c] Determined by ^{1}H NMR.

The greenish product **8**-Ni exhibited a parent ion peak at $m/z = 962.6$ ([M + H]$^+$, calcd for $C_{62}H_{71}N_4O_2Ni = 962.9$). The ^{1}H NMR spectrum indicated signals for the porphyrin β-protons at 6.36, 6.43, 6.65, and 6.81 ppm, in a relatively high-field region in comparison to those of porphyrins, indicating a lack of strong ring current of the porphyrin macrocycle in **8**-Ni.

A single crystal of **8**-Ni was obtained from $CHCl_3/CH_3CN$. The X-ray crystal structure of **8**-Ni (Figure 1)[19] exhibits a severely nonplanar, saddle-shaped conformation, the same as the previously reported quinodimethene-porphyrins[17,18] and oxoporphyrins,[20] in which two dipyrromethene units (B and C) and (D and A) are both rather planar and held with a dihedral angle of ca. 155°. The two aryl groups at 10- and 20-*meso*-positions are held rather perpendicular with respect to the planar dipyrromethene moieties, (B and C) and (D and A), with dihedral angles of ca. 125 and 80°. The quinodimethene moiety at the 15-*meso*-position is held symmetrically but tilted to the macrocycle at an angle of 130°, presumably due to the steric hindrance between the quinodimethene hydrogens and the adjacent β-hydrogens. The 5-*meso* C═O bond length is 1.26 Å. Bond lengths of C(15)═C(21), C(21)−C(22), C(22)═C(23), C(23)−C(24), C(24)═O(2) are 1.39, 1.46, 1.36, 1.45, and 1.23 Å, respectively, indicating a quinodimethene structure. **8**-Ni displays

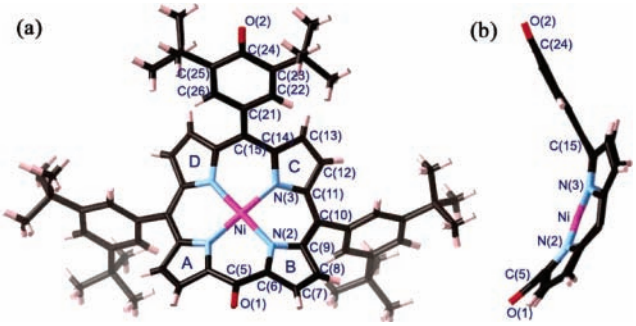


Figure 1. (a) Top view and (b) side view of X-ray crystallography of **8**-Ni.[19] *tert*-Butyl and aryl groups are omitted for clarity in b. Selected bond lengths [Å]: C(15)−C(21) 1.38(5), C(24)−O(2) 1.23(4), C(5)−O(1) 1.26(1), C(15)−C(14) 1.43(8), C(14)−C(13) 1.43(2), C(13)−C(12) 1.31(9), C(12)−C(11) 1.45(2), C(11)−C(10) 1.38(3), C(10)−C(9) 1.42(8), C(9)−C(8) 1.42(2), C(8)−C(7) 1.36(7), C(7)−C(6) 1.39(4), C(6)−C(5) 1.44(1), N(2)−C(9) 1.34(6), N(2)−C(6) 1.37(3), C(21)−C(22) 1.45(8), N(3)−C(14) 1.37(3), N(3)−C(11) 1.40(2), C(22)−C(23) 1.35(6), C(23)−C(24) 1.45(4), Ni−N(2) 1.89(4), Ni−N(3) 1.91(0).

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(19) Crystal data for **8**-Ni: $C_{64}H_{72}N_4O_4NiCl_6$, $M = 1228.34$, monoclinic, space goup $P2_1/c$, $a = 18.52(1)$, $b = 16.78(1)$, $c = 21.51(1)$ Å, $\beta = 113.07(4)°$; $V = 6150.5(6)$ Å^3, $Z = 4$, $\mu = 6.257$ cm^{-1}, $R = 0.061$, $R_w = 0.070$, $I_o = 22\,115$ observed, reflection out of $N = 11\,700$ unique, GOF = 0.752. This crystallography was performed on a Rigaku-Raxis imaging plate system.

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a reversible reduction wave ($E_1^{Red} = -0.7$ V versus Ag/$AgClO_4$) in CH_2Cl_2 with 0.1 M Et_4NBF_4 (Pt working electrode). The absorption spectrum of **8**-Ni is altered markedly from those of porphyrins (Figure 2). The oxo-quinoidal porphyrin **8**-Ni was reduced with $NaBH_4$ to *meso*-hydroxy porphyrin **9**-Ni, which was accompanied by the recovery of the usual absorption features of Ni(II)porphyrin, a sharp and strong Soret band and two weak Q-bands.

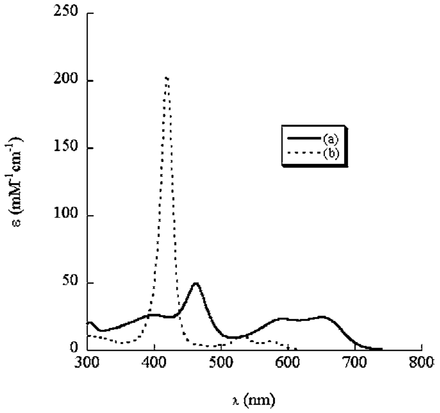
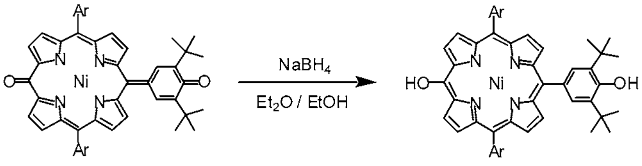


Figure 2. Absorption spectra of (a) **8**-Ni and (b) **9**-Ni.

The formation of **8**-Ni may be accounted for in terms of nucleophilic attack of water at the 5-*meso*-position in the cation radical of **4a**-Ni or **4b**-Ni. Similar attack by another neutral **4a**-Ni or **4b**-Ni would lead to **6**-Ni or **7**-Ni. To the best of our knowledge, the formation of the oxo-quinoidal porphyrin structure is rare. Dolphin *et al.* reported a *meso*-oxoporphyrin derivative from the reaction of 5,15-diarylporphyrin with tetracyanoethylene oxide without the X-ray structure.[21] Similar greenish products were detected just after the reaction of Zn(II) and Cu(II) substrates (Table 1) but disappeared immediately probably due to their thermal instability. Similar products have never been detected in the reaction of **1**. Therefore, it is likely that the (3,5-di-tert-butyl)-4-hydroxylphenyl group at the 15-*meso*-position is playing an important role in the production of **8**-Ni.[18] In summary, *meso*−*meso*, $\beta-\beta$, $\beta-\beta$ triply linked diporphyrins and *meso*−β doubly linked diporphyrins were prepared by the oxidative coupling reaction of 5,10,15-triaryl-substituted metalloporphyrins with DDQ and $Sc(OTf)_3$. The coupling regioselectivities have been shown to depend on the central metal in the porphyrin core and *meso*-aryl substituents. Oxo-quinoidal porphyrin was isolated from the oxidation reaction of the porphyrins **4a**-Ni and **4b**-Ni.

Scheme 3



8-Ni

9-Ni

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Supporting Information Available: Experimental procedure and characterization data for new compounds and ESR spectra of the cation radicals of **1**-Zn and **1**-Pd. This material is available free of charge via the Internet at http://pubs.acs.org.

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