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Oxidative Fusion Reactions of meso-(Diarylamino)porphyrins**

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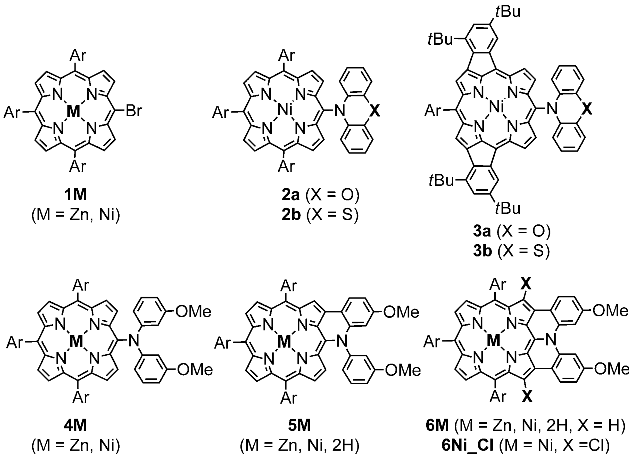
In recent years, meso-aminoporphyrins have received increasing attention owing to their potential for vastly improving the economic and environmental validity of dye-sensitized solar cells (DSSC).[1] As a prime example, Grätzel and co-workers have recently reported a co-sensitized DSSC device incorporating a meso-aminoporphyrin dye that is capable of a power conversion efficiency of 12.3% under simulated air mass 1.5 global sunlight conditions.[1d] Beside this, meso-aminoporphyrins have been explored as scaffolds for realizing novel nitrogen-connected dimers,[2] mixed-valent cation radicals,[3a] inter-valence charge-transfer absorption,[3b] photo-induced reductive meso–meso dimerization,[4] and light-harvesting supramolecular aggregates.[5] Although the amino groups of meso-(diarylamino)porphyrins raise the porphyrin HOMO level, electronic perturbation is only moderate because the diarylamino groups twist out of the bulky porphyrin plane, minimizing conjugation.[6,7] Our continued interest in conjugated porphyrinoids[8] led us to envision the fusion of a meso-diarylamino group onto the periphery of porphyrins as the expected fused porphyrin products would be interesting in their own right, because they would be structurally similar to azagraphene-type porphyrinoids. To the best of our knowledge, there are no reports of oxidative fusion of meso-aminoporphyrins, which would enable effective π-expansion by coplanarization of the peripheral nitrogen atom lone pair and porphyrin π-electronic system.[9]



Scheme 1. Formulas of porphyrins **1**–**6**. Ar = 3,5-di-*tert*-butylphenyl.

meso-Phenoxazinoporphyrin **2a** (Scheme 1)was prepared in 93% yield using a Buchwald–Hartwig amination[3b,10,11] of meso-bromo Ni^{II}-porphyrin **1Ni** with phenoxazine using Pd-PEPPSI-IPent[12] as the catalyst. By following previously reported procedures,[8b,d,13] oxidative fusion of **2a** was attempted by subjecting **2a** to 20 equivalents of $FeCl_3$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 1.5 hours in CH_2Cl_2/$MeNO_2$ at room temperature. This reaction afforded an unexpected fused porphyrin **3a** as a sole product in 48% yield, in which the two 3,5-di-*tert*-butylphenyl groups had fused to the porphyrin periphery and not the meso-phenoxazine moiety. Although we examined numerous fusion reactions of **2a** by changing the oxidants, solvents, and temperature, we could not find reaction conditions that gave us the desired phenoxazine-fused porphyrins. The ESI mass spectrum of **3a** showed a parent ion peak at m/z 1107.5374 (calcd for $C_{74}H_{75}N_5NiO$, m/z 1107.5320 $[M]^+$), supporting that four protons were removed as a result of oxidation. The ^1H NMR spectrum of **3a** in $CDCl_3$ shows a singlet signal owing to the β-protons adjacent to the fused positions at 7.78 ppm. The signals related to the phenoxazine moiety do not show particularly pronounced changes. X-ray crystallographic analysis unambiguously determined the structure of **3a** (Figure 1). Interestingly, the fusion reaction took place regioselectively at the β-positions, apart from the phenoxazine moiety. The UV/Vis absorption spectrum of **3a** displays broad, red-shifted bands reaching out to around 880 nm, which is similar to that of closely related fused porphyrins that are not functionalized with diarylamino moieties (Figure 2).[8,14] The electrochemical properties of **2a** and **3a** have been studied by cyclic voltammetry (see Supporting Information, Figures S40,S42). The fused porphyrin **3a** displays characteristic negative shifts of E_{ox2} and positive shifts of E_{red1}, while E_{ox1} is only slightly affected. As a result, the electrochemical HOMO–LUMO gap of **3a** (1.80 eV) is smaller than that of **2a** (2.14 eV).

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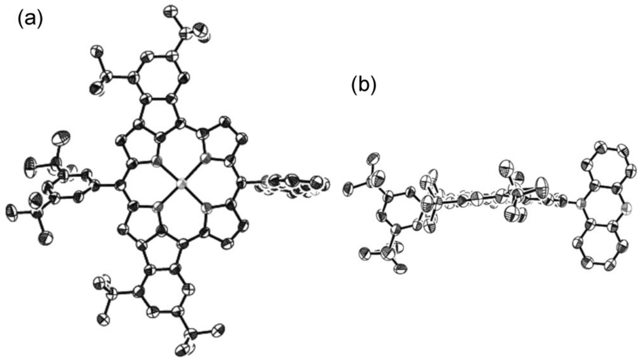

Figure 1. X-ray crystal structure of **3a**. a) Top view and b) side view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules and all hydrogen atoms are omitted for clarity.

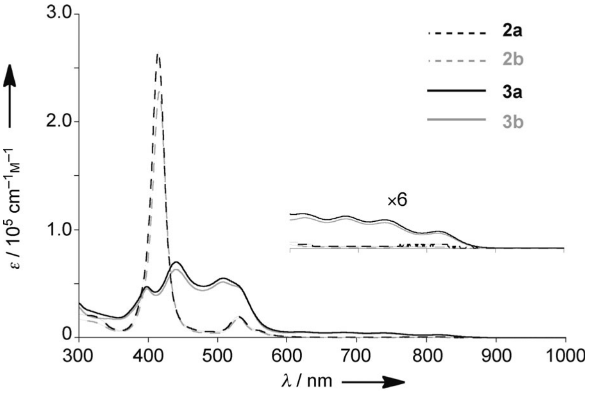

Figure 2. UV/Vis absorption spectra of **2a**, **2b**, **3a**, and **3b** in CH_2Cl_2. ε = molar extinction coefficient.

Phenothiazinoporphyrin **2b**, which was similarly prepared by the amination reaction of **1Ni** in 82% yield, was oxidized under analogous conditions to give fused porphyrin **3b** in 27% yield without forming sulfur-oxidized products. Product **3b** gives rise to ^{1}H NMR and UV/Vis absorption spectra that are closely related to those of **3a** (Figure 2; Figure S10).

Next, we attempted oxidative fusion of a meso-(diarylamino)porphyrin bearing a non-cyclic diarylamino substituent. meso-[Bis(3-methoxyphenyl)amino]porphyrin **4Ni** was prepared by Buchwald–Hartwig amination of **1Ni** with bis(3-methoxyphenyl)amine using Pd-PEPPSI-IPent as the catalyst in 76% yield. In contrast to **2**, the reaction of **4Ni** with ten equivalents of $FeCl_3$ and DDQ in $CH_2Cl_2/MeNO_2$ for 15 minutes gave the aminophenylene-fused porphyrin **5Ni** in 69% yield. The ESI mass spectrum of **5Ni** has a parent ion peak at m/z 1155.5934 (calcd for $C_{76}H_{83}N_5NiO_2$, m/z 1155.5895 $[M]^+$). The ^{1}H NMR spectrum of **5Ni** in $CDCl_3$ confirmed its low symmetric nature with a singlet being observed at 8.91 ppm owing to the β-proton next to the fused position. Under these conditions, formation of the doubly fused porphyrin **6Ni** was not detected. To try more forceful conditions, a 7 mM solution of **4Ni** in $CH_2Cl_2/MeNO_2$ was treated with 20 equivalents of $FeCl_3$ and DDQ for four hours. This reaction provided dichlorinated doubly fused porphyrin **6Ni_Cl** in 25% yield after separation using silica gel chromatography. The ESI mass spectrum of **6Ni_Cl** displays the parent ion peak at m/z 1221.4988 (calcd for $C_{76}H_{79}{}^{35}Cl_2N_5NiO_2$, m/z 1221.4959 $[M]^+$). The ^{1}H NMR spectrum of **6Ni_Cl** in $CDCl_3$ reveals a symmetric structure. The location of the chloro groups is suggested by the lack of a singlet signal related to the β-protons adjacent to the fused β-positions. The protons of the diphenylamino moiety are observed at significantly down-field positions owing to the ring current effect of the porphyrin core. Dechlorination of **6Ni_Cl** was achieved by palladium-catalyzed reduction with HCOOH and NEt_3 under our optimized $Pd(OAc)_2$/SPhos catalysis conditions in 81% yield.[15] The ^{1}H NMR spectrum of **6Ni** in $CDCl_3$ reveals a singlet signal corresponding to the newly introduced β-protons at 9.15 ppm. Treatment of **5Ni** and **6Ni** with H_2SO_4 and trifluoroacetic acid (TFA) gave free base porphyrins **5H** and **6H** in 44% and 21% yields, respectively. Furthermore, adding a zinc atom to **5H** and **6H** in the presence of an excess amount of $Zn(OAc)_2$ in CH_2Cl_2 yielded zinc complexes **5Zn** and **6Zn** in 77% and 86% yields, respectively. As a reference, **4Zn** was also synthesized in 78% yield by Buchwald–Hartwig amination of meso-bromo Zn^{II} porphyrin **1Zn** with bis(3-methoxyphenyl)amine, also using Pd-PEPPSI-IPr as the catalyst.[16]

The structures of **4Ni**, **5Ni**, and **6Ni_Cl** have been confirmed by X-ray crystallographic analysis (Figure 3). The dihedral angles between the porphyrin skeletons and the

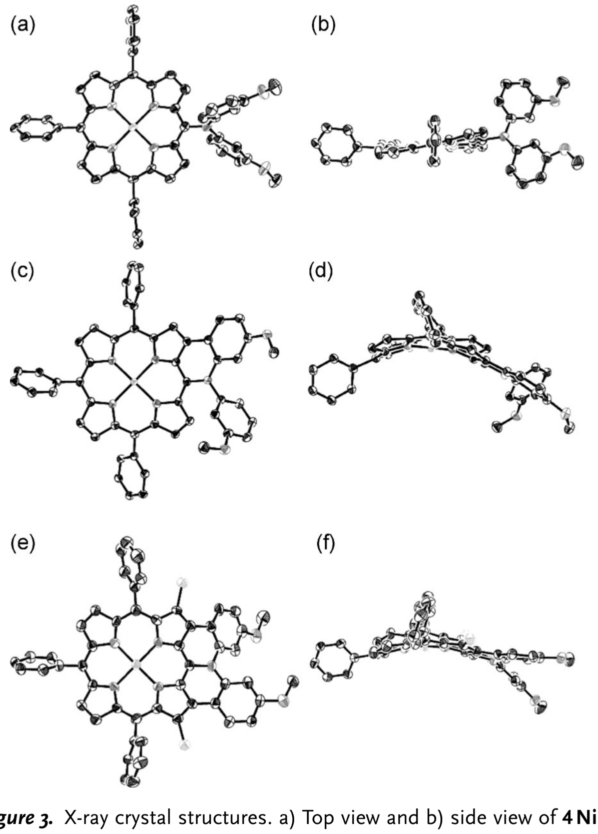

Figure 3. X-ray crystal structures. a) Top view and b) side view of **4Ni**, c) top view and d) side view of **5Ni**, e) top view and f) side view of **6Ni_Cl**. Thermal ellipsoids are shown at the 50% probability level for **4Ni** and **5Ni**, and at the 30% probability level for **6Ni_Cl**. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity.

diarylamino groups in **4Ni**, **5Ni**, and **6Ni_Cl** are 69.47°, 10.41°, and 19.16–22.30°, respectively (Supporting Information, Figures S49, S51, and S53), which indicates that the amino groups of **5Ni** and **6Ni_Cl** are almost coplanar while that of **4Ni** twists out of the porphyrin plane. To avoid repulsion, the two phenylene units of **6Ni_Cl** are fixed in a skewed conformation, which induces the dihedral angle of 19.16–22.30°. Compared with **6Ni_Cl**, singly fused **5Ni** can have flexibility in one aryl group to minimize steric repulsion, showing the smallest dihedral angle of 10.41°. The nitrogen atoms of **4Ni** and **5Ni** are linked to the porphyrin rings with C–N bond lengths of 1.443 Å and 1.411 Å, respectively. Because the crystal data of **6Ni_Cl** alone is not enough to draw conclusions about the bond lengths, the optimized structure of **6Ni_Cl** has been determined by density functional theory (DFT) calculations, which indicate the C–N distance of **6Ni_Cl** is 1.404 Å. The C–N distance became clearly shorter in the structures formed by the fusion reactions. These results reflect the more effective electronic interaction between porphyrin and the amino group of **5Ni** and **6Ni_Cl**. In addition, the structure of **6Ni** was obtained by preliminary X-ray diffraction analysis and DFT calculations, which is similar to the structure of **6Ni_Cl** (see Supporting Information, Figure S54 and Table S4).

Figure 4 shows the UV/Vis absorption and fluorescence spectra of **4Zn**–**6Zn** measured in CH_2Cl_2. Compared to **4Zn**, fused porphyrins **5Zn** and **6Zn** show sharper, split, and red-shifted Soret bands. The observed split Soret bands of **5Zn** and **6Zn** may reflect the broken degeneracy of molecular orbitals owing to the fused structures. The Q bands of **5Zn** and **6Zn** are also red-shifted with the longest wavelength absorption maxima at 640 nm and 629 nm, respectively, indicating decreased HOMO–LUMO gaps. The fluorescence spectra of **5Zn** and **6Zn** show peak maxima (λ_{max}) at 653 nm and 637 nm, respectively, which are also red-shifted compared with **4Zn** (λ_{max} = 627 nm). The fluorescence quantum yields and fluorescence lifetimes were determined to be 0.036 and 1.5 ns for **4Zn**, 0.127 and 2.9 ns for **5Zn**, and 0.079 and 1.6 ns for **6Zn**, respectively. On the basis of this data, radiative and nonradiative decay rates were calculated to be $k_r = 2.3\times10^7\,s^{-1}$ and $k_{nr} = 6.4\times10^8\,s^{-1}$ for **4Zn**, $k_r = 2.9\times10^7\,s^{-1}$ and $k_{nr} = 3.2\times10^8\,s^{-1}$ for **5Zn**, and $k_r = 4.2\times10^7\,s^{-1}$ and $k_{nr} = 5.8\times10^8\,s^{-1}$ for **6Zn**, respectively. The fused structures lead to increased radiative rate constants probably owing to the expanded conjugated network. The decrease in nonradiative decay constants is likely due to less conformational freedom. The relatively large k_{nr} of **6Zn** may be ascribed to the steric crowding between the aromatic hydrogen atoms adjacent to the nitrogen atoms. Two-photon absorption (TPA) cross-section values of porphyrinoids are useful measures, often reflecting conjugated chromophore size.[17] TPA values determined by open-aperture Z-scan measurements at 1200 nm are 260 GM and 290 GM for **2a** and **3a**, and 170 GM, 250 GM, and 430 GM for **4Ni**, **5Ni**, and **6Ni**, respectively. This data indicates expanded π-conjugation by fusion of meso-diarylamino group on the porphyrin periphery.

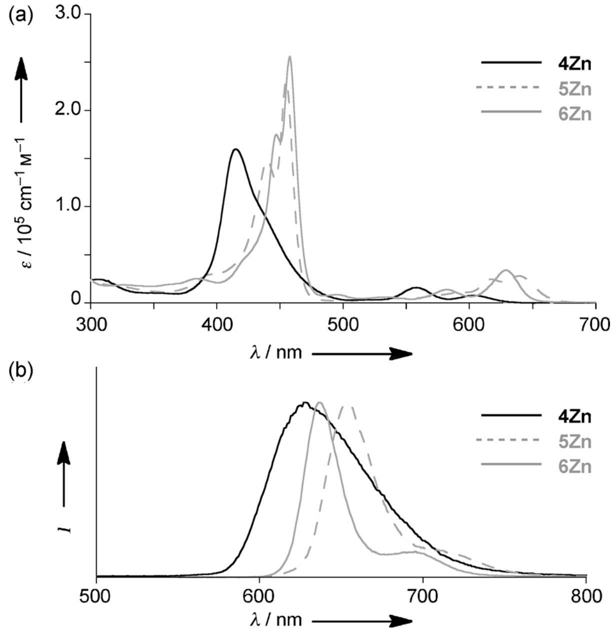

Figure 4. a) UV/Vis absorption spectra and b) fluorescence spectra of **4Zn**, **5Zn**, and **6Zn** in CH_2Cl_2. ε = molar extinction coefficient.

The electrochemical properties of **4Ni**, **5Ni**, and **6Ni** were studied by cyclic voltammetry (Table 1). The first oxidation potentials of **5Ni** and **6Ni** are lower than that of **4Ni** as a result of the enhanced electron donation from the fixed amino groups. The energy gaps between $E^{1/2}_{ox1}$ and $E^{1/2}_{ox2}$ of **5Ni** and **6Ni** are 0.47 V and 0.56 V, respectively, which are significantly larger than that of **4Ni** (0.22 V). The radical cations of **5Ni** and **6Ni** are hence stabilized by their π-expanded structures. In accordance with UV/Vis absorption spectroscopic studies, the electrochemical HOMO–LUMO gaps of **5Ni** and **6Ni** are 1.98 eV and 1.93 eV, respectively, which are slightly smaller than for **4Ni** (2.17 V). The slightly higher $E^{1/2}_{ox1}$ and $E^{1/2}_{red1}$ of **6Ni** than those of **5Ni** may result from the steric distortion caused by the presence of the two aromatic hydrogen atoms.

Table 1: Redox potentials for compounds **4Ni**, **5Ni** and **6Ni**.[a]

	oxidation [V]		reduction [V]	$E^{1/2}_{ox1}-E^{1/2}_{red1}$
	$E^{1/2}_{ox1}$	$E^{1/2}_{ox2}$	$E^{1/2}_{red1}$	[eV]
4Ni	0.36	0.58	−1.80	2.17
5Ni	0.04	0.51	−1.93	1.98
6Ni	0.15	0.71	−1.78	1.93

[a] The redox potentials were measured by cyclic voltammetry in anhydrous CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte and Ag/$AgClO_4$ as reference electrode. Fc/Fc$^+$ was used as external reference.

As demonstrated above, this is an unusual example of oxidative fusion reactions of meso-(diarylamino)porphyrins being heavily dependent on the structures of the diarylamino groups. To understand the marked reactivity difference of **2a,b** and **4Ni**, DFT calculations were performed at the B3LYP/6-31G*(C,H,N,O) + LANL2DZ(Ni) level using the Gaussian package.[18] In the usual oxidative fusion reactions of porphyrins, a porphyrin π-system is initially oxidized to form its cation radical, which is attacked by a neutral electron-rich meso-aryl group.[8,13] Because the HOMOs of **2a** and **2b** are predominantly localized on the electron-rich phenoxazine and phenothiazine moieties (Figure 5a; Figure S55), the oxidation of **2a,b** should take place preferentially at the phenoxazine or phenothiazine moiety. This situation may be unfavorable for fusion of a cyclic diarylamino moiety upon one-electron oxidation. Therefore, the formation of **3a,b** may be accounted for in terms of the occurrence of further oxidation that generates a porphyrin cation radical, which may be attacked by the meso-(3,5-di-*tert*-butyl)phenyl groups. On the other hand, the HOMO of **4Ni** is well distributed over both the porphyrin core and the diarylamino group (Figure 5b), which allows the meso-diarylamino group to fuse oxidatively by the nucleophilic attack of the meso-diarylamino group at the porphyrin cation radical.

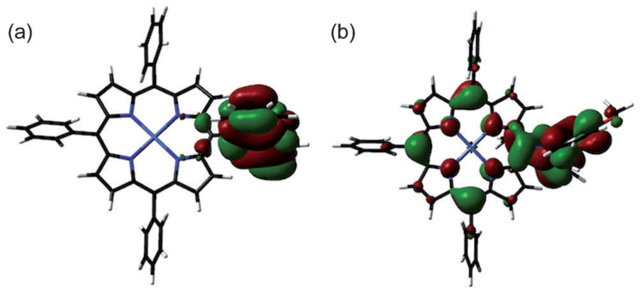

Figure 5. Kohn–Sham orbital representations obtained by DFT calculations at the B3LYP/6-31G*(C,H,N,O) + LANL2DZ(Ni) level. a) HOMO of **2a** and b) HOMO of **4Ni**. *tert*-Butyl groups were replaced with hydrogen atoms to simplify the calculations.

In summary, the oxidative fusion reactions of meso-(diarylamino)porphyrins depend upon the structure of the meso-diarylamino groups (cyclic versus noncyclic). meso-Phenoxazinoporphyrin **2a** and meso-phenothiazinoporphyrin **2b** gave the doubly 3,5-di-*tert*-butylphenyl-fused products **3a** and **3b**, respectively, whereas meso-[bis(3-methoxyphenyl)-amino]porphyrin **4Ni** gave singly and doubly diarylamino-fused products **5Ni** and **6Ni_Cl**, depending on the reaction conditions. Because of the enforced conjugation and rigid structures, fused porphyrins **5** and **6** display red-shifted and sharper absorption bands, red-shifted and enhanced fluorescence profiles, lower first oxidation potentials, and slightly larger TPA values. These fundamental studies should be helpful for the rational design of aminoporphyrins for use in dye-sensitized solar cells.

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