Porphyrinoids

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meso,β-Oligohaloporphyrins as Useful Synthetic Intermediates of Diphenylamine-Fused Porphyrin and meso-to-meso β-to-β Doubly Butadiyne-Bridged Diporphyrin**

Norihito Fukui, Hideki Yorimitsu, and Atsuhiro Osuka**

Abstract: *The chlorination of β-halo or β,β-dihaloporphyrins with 2-chloro-1,3-bis(methoxycarbonyl)guanidine (Palau' Chlor) proceeded selectively at the neighboring unsubstituted meso position to afford meso,β-dihalo or meso,β,β-trihaloporphyrins. Such oligohaloporphyrins are useful platforms for constructing more-elaborate porphyrin-based extended π systems. For example, meso-chloro-β,β-diiodoporphyrin participated in an efficient single-step synthesis of a diphenylamine-fused porphyrin. In addition, meso-chloro-β-iodoporphyrin was transformed in stepwise fashion into an efficiently conjugated meso-to-meso,β-to-β doubly butadiyne-linked porphyrin dimer, a system which was previously difficult to access without such haloporphyrin precursors.*

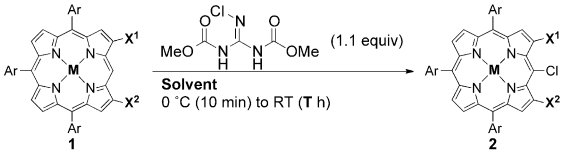
Porphyrins are an important class of arenes in light of the wide range of applications that arise from their intriguing electronic and optical properties.[1] Peripheral functionalizations of porphyrins have attracted considerable attention since they allow the creation of a variety of porphyrin-based functional materials.[2] In these recent studies, haloporphyrins play an important role as indispensable synthetic intermediates in reactions such as cross-coupling reactions,[3] aromatic nucleophilic substitution (S_NAr) reactions,[4] and peripheral metalations.[5] Therefore, development of a new class of haloporphyrin intermediates should lead to an increase in the number of usable synthetic strategies and hence easier access to desirable porphyrin derivatives.

The electrophilic halogenation of porphyrins usually occurs selectively at their electron-rich meso positions to afford meso-haloporphyrins.[6] As a complementary method, we recently reported the facile preparation of meso-free β-haloporphyrins and β,β-dihaloporphyrins by Cu-mediated halogenation of β-borylporphyrins.[7,8] These β-haloporphyrins allowed the synthesis of various functional porphyrins that were difficult to access without such precursors.[5d,8] Herein, we disclose an efficient synthetic route to oligohaloporphyrins that bear more than two halogen substituents at the meso and neighboring β positions. To the best of our knowledge, the efficient synthesis of such synthetic platforms has yet to be reported in the literature.[9]

We thought that meso-free β-haloporphyrins were attractive precursors of meso,β-oligohaloporphyrins because of the presence of the reactive meso position. Attempted halogenation reactions of β-chloro Ni^{II} porphyrin **1a** with various halogenating reagents were carried out (see Table S1 in the Supporting Information). Bromination with *N*-bromosuccinimide (NBS)[6a] or iodination with a combination of I_2 and [bis(trifluoroacetoxy)iodo]benzene[6b] afforded the corresponding β-halo-β-chloroporphyrins **3** as unwanted side products. On the other hand, we found that both $PhICl_2$[6c,10] and 2-chloro-1,3-bis(methoxycarbonyl)guanidine (Palau' Chlor)[11] were efficient chlorinating reagents to provide meso,β-dichloroporphyrin **2aCl**. Chen and co-workers reported that $PhICl_2$ was not suitable for the chlorination of electron-rich Zn^{II} porphyrins because of concomitant oxidative side reactions.[6c] This was also indeed the case for our reactions (see below). Therefore, we chose Palau'Chlor as a convenient and effective chlorinating reagent because of its commercial availability and moderate reactivity.

After further extensive optimization, we investigated the chlorination of β-haloporphyrins to reveal its wide scope in regard to central metal ions and β-halo substituents (Table 1). A solution of Palau'Chlor (1.1 equiv) in $CHCl_3$ was added dropwise to a solution of β-chloroporphyrin **1a** in $CHCl_3$ at 0 °C. The resulting mixture was then stirred at room temperature for 2.5 h to give **2aCl** in an excellent yield (entry 1). β,β-Dichloroporphyrin **1b** reacted smoothly to afford meso,β,β-

Table 1: Chlorination of β-haloporphyrins **1** with Palau'Chlor.



Entry	1	M	X^1	X^2	*t* [h]	2	Yield [%]
1[a]	**1a**	Ni	Cl	H	3	**2aCl**	88
2[a]	**1b**	Ni	Cl	Cl	6	**2b**	77
3[b]	**1c**	Ni	I	H	3	**2c**	84
4[b]	**1d**	Ni	I	I	10	**2d**	73
5[b]	**1e**	2H	Cl	H	2.5	**2e**	88
6[a,c]	**1f**	Zn	Cl	H	12	**2f**	69
7[a,d]	**1f**	Zn	Cl	H	1.5	**2f**	13

[a] Solvent: $CHCl_3$ (10 mM). [b] Solvent: CH_2Cl_2 containing 1% pyridine (5 mM). [c] Palau'Chlor (1.7 equiv). [d] $PhICl_2$ (1.1 equiv) instead of Palau'Chlor. Ar = 3,5-di-*tert*-butylphenyl.

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trichloroporphyrin **2b** in 77% yield (entry 2). Bulkier iodo groups did not retard the reaction (entries 3 and 4). Free-base porphyrin **1e** also underwent this halogenation efficiently (entry 5). Chlorination of Zn^{II} porphyrin **1f** proceeded with minimum oxidative decomposition, whereas the attempted chlorination of **1f** with $PhICl_2$ resulted in the formation of a messy mixture containing **2f** in 13% yield (entries 6 and 7). X-ray diffraction analysis unequivocally determined the structures of **2c** and **2d**, with both structures confirming the presence of a chlorine atom at the meso positions (Figure 1). The porphyrin core of **2d** adopted a ruffled structure to avoid steric repulsion between the meso chlorine atom and β-iodine atoms.

With meso,β-oligohaloporphyrins in hand, we next explored their potential as synthetic intermediates (Scheme 1). The Suzuki–Miyaura coupling reaction of **2aCl** with 2-thienylboronic acid took place smoothly under Pd/Sphos[12] catalysis to afford meso,β-di(2-thienyl)porphyrin **4** in 82% yield. The Migita–Kosugi–Stille coupling reaction of **2aCl** with tributyl(trimethylsilylethynyl)tin under Pd/Sphos catalysis followed by desilylation with tetrabutylammonium fluoride (TBAF) furnished meso,β-diethynylporphyrin **5** in 70% yield. The S_NAr reaction[4] of **2d** with 4-*tert*-butylphenol in the presence of Cs_2CO_3 as a base proceeded regioselectively at the meso position, despite the steric hindrance caused by the adjacent bulky iodine atoms.

Recently, Gryko's research group and our own have independently reported the synthesis of diarylamine-fused porphyrins by oxidative fusion reactions of meso-diarylaminoporphyrins.[13] The diarylamine-fused porphyrins showed interesting properties caused by coplanarization of the diarylamine unit with the porphyrin π system. However, they suffered from multistep syntheses and considerably low yields as a result of oxidative decomposition. To avoid oxidative fusion reactions, we planned to carry out an intramolecular arylation[2e,14] of meso-diphenylamino-β,β-diiodoporphyrin **8**. Surprisingly, the S_NAr reaction of **2d** with diphenylamine in the presence of NaO*t*Bu afforded diphenylamine-fused porphyrin **7** in one step in 81% yield. The substitution product **8** was not detected in the reaction. NaO*t*Bu is known to undergo single-electron transfer to aryl iodide (Ar-I) to generate its radical anion ($[Ar\text{-}I]^{\bullet-}$), and subsequent dissociation of I^- from $[Ar\text{-}I]^{\bullet-}$ affords a neutral radical intermediate ($Ar^{\bullet}$).[15] In our reaction, although the precise mechanism remains unclear, a similar electron-transfer process would produce a porphyrinyl radical, which would react with the phenyl group on the meso nitrogen atom to form **7**.[16] This non-oxidative synthetic strategy should be helpful for the efficient synthesis of nitrogen-embedded π-extended porphyrins.

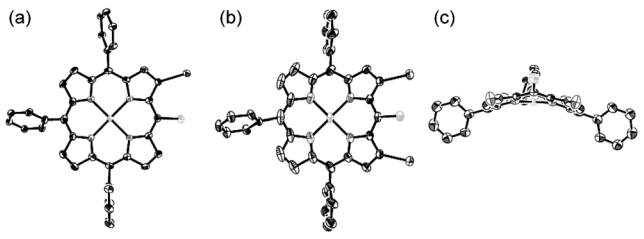
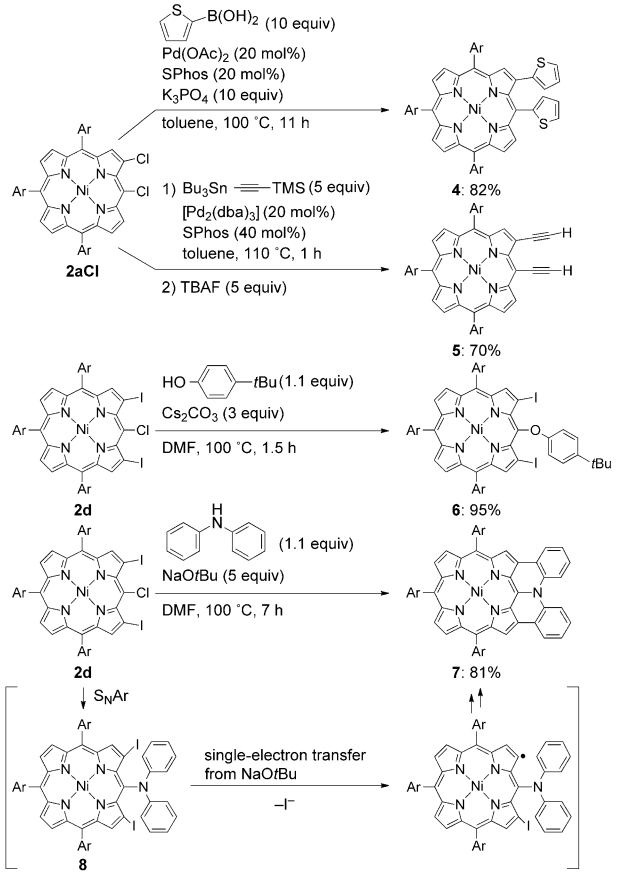


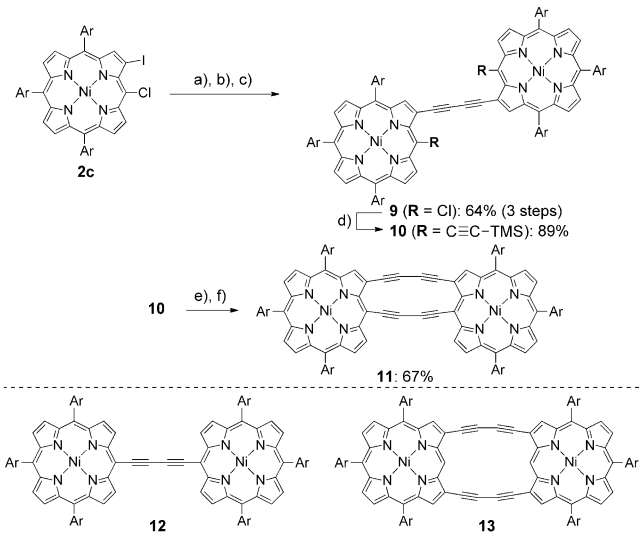
Figure 1. X-ray crystal structures. a) Top view of **2c**, b) top view of **2d**, and c) side view of **2d**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity.



Scheme 1. Conversions of meso,β-haloporphyrins **2aCl** and **2d**. Ar = 3,5-di-*tert*-butylphenyl, dba = dibenzylideneacetone, TMS = trimethylsilyl.

Finally, we attempted the synthesis of meso-to-meso, β-to-β doubly butadiyne-linked porphyrin dimer **11**. 1,3-Butadiyne-bridged cyclic porphyrin oligomers have attracted much attention as catalytic artificial hosts, light-harvesting antennas, and nonlinear optical materials.[17] The β-to-β, β-to-β double butadiyne bridges in **13** secure a rather coplanar conformation, thereby conferring moderate π conjugation between the two porphyrin units.[17j] However, larger electronic interaction would be expected for dimer **11** because through-bond interaction between the meso positions might be larger than that of the β-to-β linkage.[17e,f]

Unfortunately, attempted oxidative coupling of meso,β-diethynylporphyrin **5** with $Cu(OAc)_2$[17i,k] provided an inseparable mixture of **11** and the meso-to-β, meso-to-β doubly butadiyne-bridged porphyrin dimer. Therefore, we planned the stepwise synthesis of **11** from meso-chloro-β-iodoporphyrin **2c** (Scheme 2). The Sonogashira coupling reaction of **2c** with trimethylsilylacethylene proceeded selectively at the iodo substituent, and subsequent desilylation with TBAF followed by Cu-mediated oxidative coupling afforded β-to-β butadiyne-linked meso-chloroporphyrin dimer **9** in 64% yield. The Migita–Kosugi–Stille coupling reaction of **9** with tributyl(trimethylsilylethynyl)tin introduced trimethylsilyle-



Scheme 2. Synthesis and structure of meso-to-meso,β-to-β doubly butadiyne-linked dimer **11**, and structures of meso-to-meso butadiyne-linked dimer **12** and β-to-β,β-to-β doubly butadiyne-linked dimer **13**. Reaction conditions: a) trimethylsilylacetylene (5 equiv), $[PdCl_2(PPh_3)_2]$ (20 mol%), CuI (50 mol%), THF/NEt_3, 50°C, 1 h; b) TBAF (3 equiv), 0°C, 10 min; c) $Cu(OAc)_2$ (5 equiv), THF/pyridine, 50°C, 3.5 h; d) tributyl(trimethylsilylethynyl)tin (10 equiv), $[Pd_2(dba)_3]$ (25 mol%), SPhos (50 mol%), toluene, 110°C, 1 h; e) TBAF (2.1 equiv), THF, 0°C, 10 min; f) $Cu(OAc)_2$ (2 equiv), THF/pyridine, RT, 2 h. Ar = 3,5-di-*tert*-butylphenyl.

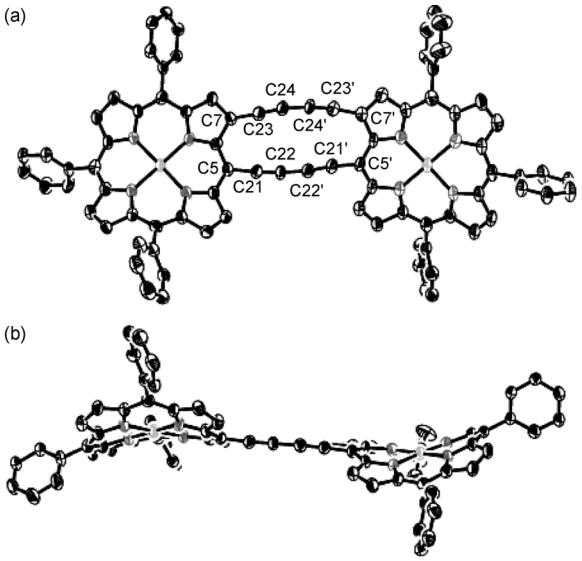


Figure 2. X-ray crystal structure of **11**. a) Top view and b) side view. Thermal ellipsoids are drawn at the 30% probability level. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity. Selected bond lengths and transannular distances [Å]: C5-C21 1.447(7), C21-C22 1.191(6), C22-C22′ 1.361(7), C22′-C21′ 1.226(7), C21′-C5′ 1.414(7), C7-C23 1.418(7), C23-C24 1.202(7), C24-C24′ 1.354(7), C24′-C23′ 1.182(6), C23′-C7′ 1.435(7), C5-C7 2.535(8), C21-C23 2.897(8), C22-C24 3.197(8), C22′-C24′ 3.195(8), C21′-C23′ 2.866(8), C5′-C7′ 2.509(8).

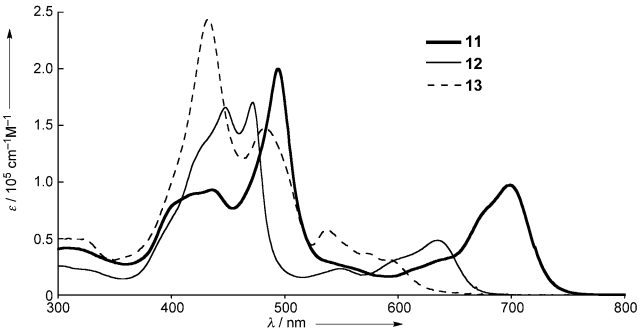


Figure 3. UV/Vis absorption spectra of **11**, **12**, and **13** in CH_2Cl_2.

thynyl groups at the meso positions in 89% yield. After removal of the trimethylsilyl groups of **10**, Cu-mediated intramolecular oxidative coupling gave the desired porphyrin dimer **11** in 67% yield.

The structure of **11** was confirmed by X-ray crystallographic analysis (Figure 2). Both the porphyrin units adopted ruffled structures and were bent alternately upwards and downwards. The double butadiyne bridges forced a rather coplanar arrangement with a small dihedral angle (29.67°) between the two porphyrin units. The two butadiyne units were not linear and were distorted to take an elliptic conformation, in which the transannular distances between the central carbon atoms (C22-C24 and C22′-C24′) were elongated by 0.67–0.69 Å relative to those of the edge (C5-C7 and C5′-C7′). The central stretch was larger than that of the acenaphthylene derivative **15** (0.63 Å),[18] thus indicating the large structural distortion in **11**. On the other hand, the C22-C24 (C22′-C24′) distance of **11** (3.20 Å) was comparable to those in naphthalene derivative **14** (ca. 3.18 Å), acenaphthylene derivative **15** (3.23 Å from X-ray diffraction analysis), and fluoranthene derivative **16** (ca. 3.25 Å).[18] It is noteworthy that **11** was remarkably stable under ambient conditions and showed no reactivity towards the intramolecular cyclization of the two butadiyne units, unlike **14**.[19] Anthony and co-workers also observed similar stabilities for **15** and **16**.[18] Our results likely support their hypothesis that the distance between the two butadiyne units is less important to the stability than the degree of conjugation along the macrocyclic π circuit.

The UV/Vis absorption spectra of **11**, **12**,[17j] and **13**[17j] in CH_2Cl_2 are shown in Figure 3. β-to-β,β-to-β Doubly butadiyne-bridged porphyrin dimer **13** displayed split Soret bands at 432 and 482 nm, and Q bands at 537, 568, and 573 nm, while meso-to-meso singly butadiyne-bridged porphyrin dimer **12** showed split Soret bands at 448 and 472 nm, and Q bands at 548, 597, and 636 nm. Despite the single bridge, the more red-shifted and intensified Q band at 636 nm for **12** suggests comparable or greater electronic interactions relative to those in **13**. The large electronic interactions in **12** could be ascribed to the meso-to-meso connection.[17e,f] The absorption spectrum of **11** showed a strongly perturbed Soret band with bands at 436 and 494 nm, and Q bands at 638 and 699 nm. Both the Soret and Q bands of **11** were considerably red-shifted relative to those of **12** and **13**. The effective conjugation between the two porphyrin moieties of **11** can be attributed to the forced coplanar conformation and large through-bond electronic interaction through the meso-to-meso connection.

The intensified Q band at 699 nm probably indicates an enhanced transition dipole moment along the longer molecular axis. Density functional theory (DFT) calculations on **11** were performed at the B3LYP/6-31G*(C,H,N) + LANL2DZ(Ni) level using the Gaussian 09 package (see Figure S64 Supporting Information).[20] Characteristically, the HOMO and LUMO were delocalized over the two porphyrin π systems as well as the meso-to-meso butadiyne bridge, but with only small distributions on the β-to-β butadiyne bridge.

In summary, we have developed facile access to a series of new meso,β-oligohaloporphyrins by the chlorination reaction of β-haloporphyrins with Palau'Chlor. This procedure offered effective and convenient routes to meso,β-functionalized porphyrins such as the diphenylamine-fused porphyrin and meso-to-meso,β-to-β doubly butadiyne-linked porphyrin dimer. Further investigations are underway to create porphyrin-based functional materials from meso,β-oligohaloporphyrins.

Keywords: butadiyne bridge · fusion reaction · halogenation · π extension · porphyrinoids

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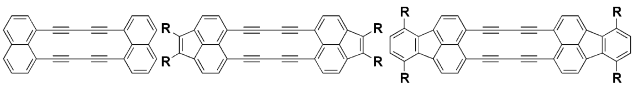

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