Pd-Catalyzed Cross Coupling Strategy for Functional Porphyrin Arrays
Kaisheng Wang, Atsuhiro Osuka, and Jianxin Song*

ABSTRACT: Porphyrin arrays are an important class of compounds to study interporphyrin electronic interactions that are crucial in determining the rates of energy transfer and electron transfer reactions. When the electronic interactions become stronger, porphyrin arrays exhibit significantly altered optical and electronic properties owing to large oscillator strength and flexible electronic nature of porphyrins. In addition, porphyrins accept various metal cation in their cavities and the interporphyrin interactions depend upon the coordinated metal. With these in the background, porphyrin arrays have been extensively explored as sensors, multielectron catalysts, photodynamic therapy reagents, artificial photosynthetic antenna, nonlinear optical materials, and so on. Here, we review the synthesis of porphyrin arrays by palladium-catalyzed cross-coupling reactions, which are quite effective to construct carbon–carbon bonds and carbon–nitrogen bonds in porphyrin substrates. Palladium-catalyzed cross coupling reactions employed so far are Suzuki–Miyaura coupling reaction, Sonogashira coupling reaction, Buchwald–Hartwig amination, Mizoroki–Heck reaction, Migita–Kosugi–Stille coupling reaction, and so on. In each case, the representative examples and synthetic advantages are discussed.

INTRODUCTION

Porphyrins are a class of 18π aromatic macrocyclic compounds consisting of four pyrrole units and four methine bridges and has a square cavity suitable for metal-coordination. In porphyrin arrays, porphyrin subunits are connected by covalent, noncovalent, or metal coordination bonds.1–9 As early as the 1980s, many porphyrin arrays had been synthesized, which however had not attracted much widespread attention until 1984. In 1984, the X-ray crystal structure of the bacterial photosynthetic reaction center was first revealed,10 which imparted a big worldwide impact to the related fields. In 1995, the light-harvesting antenna complex LH2 in purple bacteria was revealed to consist of two different electronically interacting cyclic large arrays.11,12 Since these discoveries, many scientists have started to explore the synthesis of photosynthetic reaction center models to realize the same electron transfer events in the photosynthetic reaction center13–15 and cyclic porphyrin arrays to achieve the excitation energy transfer (EET) along with the porphyrin ring.16

In porphyrin chemistry, Suzuki–Miyaura cross-coupling reactions of borylated porphyrins with halogenated porphyrins to synthesize porphyrin arrays have been the most popular method. meso-Bromoporphyrins and meso-iodoporphyrins were usually prepared by electrophilic substitution of porphyrins at the meso-position with NBS or I2 and Ag salts.17,18 Miyaura et al. reported that palladium-catalyzed coupling reactions of bis(pinacolato)diboron or pinacolborane with aryl halide, which is an effective method to prepare arylboronic esters.19,20 As the first example, Therien et al. synthesized meso-borylporphyrins by Pd-catalyzed borylations of meso-bromoporphyrin with pinacolborane. Then meso-borylporphyrins were widely used to synthesize various meso-
Scheme 1. Synthesis of meso–meso Directly Linked Porphyrin Arrays

Suzuki–Miyaura cross-coupling reactions have been one of the most popular methods to construct porphyrin arrays.

Based on the previously reported method, β–β and β–meso directly linked linear porphyrin arrays 10 and 12 were synthesized in high yields by Senge and Bringmann et al. by a simple Suzuki–Miyaura cross-coupling reaction (Scheme 2).29–31 Porphyrin dimers 10 with $C_1$ symmetry were synthesized by coupling of 8 and 9. It is worthy to note that the coupling of 11 with 2 equiv of 9A gave β–meso directly linked trimer 12, which consisted of a 1:1.5 diastereoisomeric mixture of cis-12 and trans-12 due to the rotational restriction around the $C_{meso}$–$C_β$ bond.

meso–meso 2,5-Pyrrolylene bridged porphyrin arrays were synthesized by Song et al. in 2017 (Scheme 3).32 Dimer 16 and trimer 17 were synthesized by the one-pot Suzuki–Miyaura cross-coupling reaction of a mixture of 5,15-

In 1996, Tanaka and Segawa first synthesized meso–meso directly linked linear porphyrin arrays in low yields by a condensation reaction between meso-formylporphyrin and meso-dipyrrylmethane.25 In 1997, Osuka et al. pioneered Ag(I)-promoted oxidative homocoupling of 5,15-diaryl Zn(II) porphyrins as an effective synthetic tool for the preparation of meso–meso directly linked multiporphyrin arrays.26 This method is extremely useful for homocoupling, providing various porphyrin arrays including linear 1024-mer and large porphyrin ring37 but is unsuitable for synthesis of hybrid meso–meso linked porphyrin arrays. To overcome this disadvantage, Osuka and Aratani explored the Suzuki–Miyaura cross-coupling reaction for the synthesis of meso–meso linked hybrid porphyrin arrays in 2001.28

β-Borylporphyrin was first prepared by Nocera et al. using a β-bromo-heptaalkylporphyrin substrate. This bromoporphyrin was employed to the synthesis of a β–β directly linked porphyrin dimer under the similar conditions.22 Selective β-bromination is difficult due to the inherent high reactivity of the meso-positions toward electrophilic substitution reactions. As an important milestone, Shinokubo and Osuka et al. found iridium-catalyzed selective C–H borylation of meso-free porphyrins by applying the Miyaura–Ishiyama borylation protocol.23 These β-borylporphyrins have been demonstrated to be particularly useful for construction of various novel architectures of porphyrin oligomers.24
dibromoporphyrin $14H$ and $S$-bromoporphyrin $15H$ with $2,5$-diborylpyrrole $13$. However, $meso$-monobrominations of $16$ and $17$ were difficult due to their instabilities under the bromination conditions. Thus, $N$-protected substrates $16Boc$-
{\textit{Br} \,(\textit{Boc} = \textit{tert}-butoxycarbonyl) and \textit{17Boc-Br} were used for the synthesis of higher oligomers in good yields. Yields of the higher oligomers were around 56\% after the cross coupling and deprotection.

In 2008, Osuka and co-workers reported the synthesis of a \textit{meso-\textit{meso}} directly linked cyclic porphyrin octamer square, 26, by the Suzuki–Miyaura cross-coupling reaction (Scheme 4).\textsuperscript{33} Synthesis of 26 was performed by cross-coupling-based cyclization of dibrominated porphyrin trimer 25Br and 23 in 8\% yield. This cyclic porphyrin array 26 has a large cavity that can capture a guest molecule 9,10-dipyridylanthracene inside.

In 2010, Song and Osuka et al. first proposed a concept of “Lego block” strategy for the synthesis of \textit{meso-\beta} linked cyclic porphyrin arrays 32 and 34 (Scheme 5).\textsuperscript{34} They prepared molecular building blocks 27H–31Ni. \beta,\beta-Diborylporphyrin 27H was coupled with 5,15-dibromoporphyrin 14H by the Suzuki–Miyaura reaction to provide \textit{meso-\beta} directly linked cyclic porphyrin tetramer 32AH in 21\% yield. Based on the same coupling strategy, a series of cyclic compounds such as 32BH, 32C, 32D, and 34H were synthesized and structurally well characterized.

Osuka and Song et al. synthesized the \textit{meso-\beta} directly linked cyclic porphyrin tetramer 32ANi and triangular porphyrin hexamer 36Ni by the one-pot Suzuki-Miyaura cross-coupling reaction of 27Ni and 14H in 16\% and 0.7\% yield, respectively (Scheme 6).\textsuperscript{35} In order to improve the yield of 36Ni, they also examined a stepwise rational synthetic route. First, \beta,\beta-diborylated porphyrin trimer 35 was obtained in 90\% yield by coupling of 7 equiv of 27Ni with 14H, then 35 coupled with an equivalent of 33NiBr provided 36Ni in 8\% yield. The structure of the hexamer 36Zn was confirmed by X-ray diffraction analysis.

Song et al. reported the synthesis of a directly \beta-\beta linked cyclic porphyrin trimers 39Ni as the smallest directly linked porphyrin wheel known so far, and its twined pentamer 40Ni was also constructed smoothly via the Suzuki–Miyaura cross-
coupling of β-borylporphyrins and β-bromoporphyrins (Scheme 7). These porphyrin oligomers displayed small electrochemical HOMO−LUMO gaps, broad Soret bands, and red-shifted Q bands, suggesting large electronic interactions among the constitutional porphyrins units owing to less tilted structures.

2,5-Pyrrolylene- and α,α'-bithienylene-bridged cyclic porphyrin arrays 3-mer 42, 4-mer 43, and 5-mer 44 were synthesized via the one-pot Suzuki−Miyaura coupling reaction of 5,10-diaryl-15,20-dibromoporphyrin 29M with 13 or 41, respectively (Scheme 8). It is worthy to note that the UV−vis-NIR absorption spectra of 42AZn−44AZn exhibited sharp Soret bands, while those of 42BZn−44BZn displayed split Soret bands. These phenomena were interpreted in terms of much stronger interactions between the pyrrolylene and porphyrin units as compared with those between the bithienylene and porphyrin units.
There are more examples of $\beta-\beta$ bridged cyclic porphyrin arrays than $meso-meso$ bridged cyclic porphyrins. In 2008, Song and Osuka et al. synthesized doubly $\beta-\beta$ thienylene-bridged porphyrin dimer 46H and porphyrin trimer 47H (Scheme 9).39 Porphyrin dimer 46H were synthesized by one-step Suzuki-Miyaura coupling of diborylporphyrin 27H and 2,5-dibromothiophene in 29% yield. They also isolated thienylene-bridged porphyrin trimer 47H in 10% yield. In addition, the ladderlike trimer $49_{\text{Zn}}$ and tetramer $53_{\text{H}}$ were synthesized in 11% and 52%, respectively (Scheme 10).40 It was very interesting that $53_{\text{Ni}}$ could bind $C_{60}$ with a molar ratio of 1:2. Different from the $meso-meso$ 2,5-pyrrolylene bridged cyclic porphyrin oligomers 42B−44B, $\beta-\beta$ 2,5-pyrrolylene bridged cyclic porphyrin oligomers 50M and 51M were not synthesized under the same reaction conditions (Pd$_2$(dba)$_3$, PPh$_3$, CsF, Cs$_2$CO$_3$, DMF, toluene, reflux). Use of P($t$Bu)$_3$ instead of PPh$_3$ allowed for the formation of dimer 50Ni and trimer 51Ni in 30% and 15% yields, respectively (Scheme 9).41

In 2010, Song and Osuka et al. reported $\beta-\beta$ pyridylene-bridged cyclic dimer 63 and trimer 64, which were transformed to the corresponding Pd-complexes $63_{\text{Pd}}$ and $64_{\text{Pd}}$ via C−H activation (Scheme 12).43 Both compounds 63 and 64 were obtained by Suzuki–Miyaura cross-coupling of 54 with diborylporphyrin 27Ni and tetraborylporphyrin 28Ni, respectively, and subsequent metalation with Pd(OAc)$_2$ in CH$_2$Cl$_2$ provided $63_{\text{Pd}}$ and $64_{\text{Pd}}$ in 85% and 75% yields, respectively.

In addition, Song and Osuka et al. also synthesized porphyrin
nanobarrel 66. 64 Ni(II)porphyrin bearing four 2-bromopyridyls 65 prepared by Suzuki–Miyaura coupling of 28Ni with 2,6-dibromopyridine in 50% yield was subjected to intramolecular cyclization reaction with 28Ni under the similar but dilute conditions to afford porphyrin nanobarrel 66 in 10% yield (Scheme 13). This porphyrin nanobarrel could encapsulate C60 effectively. The structures of both 66 and C60@66 were confirmed by single-crystal X-ray diffraction analysis.

In 2015, Song et al. reported the synthesis of β–β azobenzene-bridged porphyrin dimer 70, trimer 71, and tetramer 72 in 40%, 40%, and 45% yield, respectively (Scheme
meso-meso Azobenzene-bridged porphyrin tetramer 75 was also synthesized in 15% yield by one-pot coupling of 73 with 74. They found that 71(ttt) was partially changed to 71(ttc) when exposed to light and 71(ttc) was returned to 71(ttt) completely when heated at 333 K. The fluorescence quantum yield of 75\(_{\text{Zn}}\) was higher than 70\(_{\text{Zn}}\)–72\(_{\text{Zn}}\) due to rigid cyclic structure of 75\(_{\text{Zn}}\). Excitation energy hopping rate of 75 was faster than that of 72, which may be attributed to the rigid coplanar structure of 75. In 2017, Song et al. also reported the synthesis of acyclic azobenzene-bridged porphyrin–dipyrrin 78\(_{\text{Ni}}\) and 78\(_{\text{H}}\) through Suzuki–Miyaura coupling of 76 with meso-borylated porphyrin 77\(_{\text{Ni}}\) or 77\(_{\text{H}}\) in 30% and 28% yields, respectively (Scheme 15). Porphyrin–Bodipy derivatives 79\(_{\text{M}}\) (M = Ni, 2H) were synthesized by boron complexation of 78\(_{\text{M}}\) with BF\(_3\)·OEt\(_2\) in decent yields. The UV–vis-NIR absorption spectra of 78\(_{\text{Zn}}\) and 79\(_{\text{Zn}}\) showed Soret bands at 424 and 421 nm and slightly extended Q bands ranging from 518 to 646 nm, respectively.

Sonogashira coupling has been also used as a very effective and useful method for synthesis of linear and cyclic acetylene-bridged porphyrin arrays. Arnold and co-workers first reported the synthesis of such porphyrin arrays.\(^{47,48}\) These authors synthesized diethynylphenylene-bridged dimers 81 and 82 in good yields by Sonogashira coupling (Scheme 16). Synthesis of 81 and 82 were effectively achieved by the coupling reaction of meso-ethynylloctaethyl Ni(II) porphyrin 80.

Therien and co-workers reported the synthesis of acetylene-bridged porphyrin dimer 85\(_{\text{A}}\) via lithium bis(trimethylsilylamide) mediated deprotonation of 5-ethynyl-10,20-diphenylporphinatozinc(II) 83\(_{\text{A}}\) and subsequent Pd-catalyzed coupling reaction with an equivalent of 5-bromo-10,20-diphenylporphinatozinc(II) 84\(_{\text{A}}\) (Scheme 17). Acetylene linked porphyrin trimer 87 was synthesized by the Sonogashira coupling reaction of 5,15-diethynyl-10,20-diphenylporphinatozinc(II) 86 with 84\(_{\text{A}}\). Anderson and co-
workers reported the syntheses of an acetylene linked porphyrin dimer 85B through Sonogashira coupling.50

Sonogashira coupling has been demonstrated to be also an effective strategy for synthesis of an acetylene-bridged diazaporphyrin dimer. Matano and co-workers reported the synthesis of acetylene-bridged 5,15-diazaporphyrin dimer 90 by Sonogashira coupling of Ni(II) 3-bromo-5,15-diazaporphyrin 89Ni with Ni(II) 3-ethynyl-5,15-diazaporphyrin 88 (Scheme 18).51
Lindsey and co-workers reported the synthesis of square porphyrin tetramer 93 by Sonogashira coupling of 91 and 92 under copper-free conditions in 7% yield (Scheme 19).\textsuperscript{52−55} They also reported the synthesis of free base and zinc porphyrin trimers with the same bridge.\textsuperscript{56} To prevent copper metalation of porphyrins, AsPh\textsubscript{3} was used instead of PPh\textsubscript{3}. Cyclic hexamer 97\textsubscript{a} was obtained in 5.5% by the similar one-step Sonogashira reaction of 94 and 95 in the presence of pyridine template 96.

Anderson and co-workers developed this template-directed Sonogashira coupling reaction for the synthesis of acetylene-bridged cyclic porphyrin nanorings 101 and 103 (Scheme 20).\textsuperscript{57} The cyclic hexamer 100 was synthesized by the Sonogashira coupling reaction of 98 with template T6 in
Scheme 14. Synthesis of \( \beta-\beta \) and \( \textit{meso}-\textit{meso} \) Azobenzene-Bridged Cyclic Porphyrin Arrays

Scheme 15. Synthesis of Azobenzene-Bridged Porphyrin–Dipyrrin Dimers
Scheme 16. Synthesis of Diethynylphenylene-Bridged Porphyrin Dimers

Scheme 17. Synthesis of meso−meso Acetylene-Bridged Porphyrin Oligomers

Scheme 18. Synthesis of β−β Acetylene-Bridged 5,15-Diazaporphyrin Dimer
15% yield, and addition of pyridine liberated the template T6 to provide the free nanoring 101. Sonogashira coupling of linear precursor 99 afforded 102 in 32% yield in the presence of template T4, and liberation of the template was also done by the addition of pyridine to obtain 103.

Buchwald–Hartwig amination is a powerful technique for the synthesis of nitrogen-atom-bridged porphyrin arrays. In 2006, Arnold and co-workers pioneered the synthesis of diporphyrinylamine 106 by the Buchwald–Hartwig coupling reaction of meso-aminoporphyrin 104 and meso-bromoporphyrin 105 in 25% (Scheme 21). The UV–vis-NIR absorption spectrum of 106 exhibited a broad Soret band and red-shifted Q bands, indicating the strong electronic interaction between the two porphyrins via the nitrogen atom bridge.
Ruppert and co-workers used this Buchwald–Hartwig coupling for the synthesis three types of (meso–meso, β–meso, and β–β) nitrogen-bridged diporphyrinylamines with some synthetic modifications from Arnold’s paper (Scheme 22). They used meso-iodo Ni(II) porphyrin 108 as a better substrate than meso-bromo Ni(II)porphyrin 105 and changed...
Scheme 22. Synthesis of β–meso and β–β Nitrogen-Bridged Diporphyrinylamine

Scheme 23. Synthesis of 1,3,5-tris(Zn(II)-porphyrinylamino)benzene and Triaminyl Radical
the molecular ratio of BINAP/Pd molarity from 2.8 to 1 and t-BuOK as a base. These modifications resulted in an accelerated reaction between 104 and 108, giving 106 in a shorter reaction time (1.5 h) with a better yield of 56% as compared with Arnold’s result (for 3 d with 25% yield.) Using this modified protocol, Ruppert et al. synthesized β-meso linked Ni(II) diporphyrinylamine 110 and β-β linked Ni(II) diporphyrinylamine 111 in 43% and 18% by the Buchwald–Hartwig reaction of 2-aminoporphyrin 107 with 108 and 2-bromoporphyrin 109 in dioxane and toluene, respectively.

Recently, Osaka and co-workers reported the synthesis of 1,3,5-tris(Zn(II)-porphyrinylamino)benzene 114 by a stepwise Buchwald–Hartwig reaction sequence (Scheme 23).60 Porphyrin trimer 114 was employed for the synthesis of triaminyl radical 116. It is remarkable that triradical 116 was exceptionally stable despite its high-spin nature. The UV−vis-NIR spectrum of 116 showed a split Soret state to be a quartet (S = 3/2). In 2019, they synthesized nitrogen-atom-bridged 5,10,15-tris(pentafluorophenyl)porphyrin dimer by similar Buchwald–Hartwig coupling under similar conditions.61 This dimer was used to demonstrate a coordination-induced spin crossover from doublet to sextet.

Some methods may be better to prepare some porphyrin functional molecules, which are determined by building blocks and the market.

The Mizoroki–Hartwig reaction is a good and useful method for synthesis of alkenylated porphyrin monomers and alkenyl-bridged porphyrin dimers. Arnold and co-workers synthesized various meso-alkenylated porphyrins by using Mizoroki–Hartwig reactions.62 While this coupling reaction was not applicable to for synthesis of meso−meso vinylene-bridged Ni(II) porphyrin dimer 118 from meso-bromoporphyrin 105 with Ni(II) meso-vinylporphyrin 117 due to serious steric hindrance. Instead, meso−β vinylene-bridged Ni(II) porphyrin dimer 119 was isolated in a moderate yield of 33%, indicating the occurrence of a migration (Scheme 24).

Yu and co-workers reported that the porphyrin-based polymer 122M was produced by the Mizoroki–Heck coupling reaction of bis(vinylbenzene)-porphyrin 120M and 1,4-diiodobenzene 121 with palladium acetate as a catalyst (Scheme 25).63 Through GPC analysis with polystyrene standards, the authors found that the molecular weight of the resulting polymer was 8 300 to 46 000 Da. The porphyrin polymer exhibited interesting photoconductivity and photo-refractive effect. Similar reactions can also be used in the synthesis of various porphyrin-based polymers that can be used as photosensitizers.64,65

Introduction of substituents at the β-position of porphyrin through Mizoroki–Hartwig coupling of β-bromoporphyrin has been extensively studied. In 1997, Risch et al. successfully prepared a β−β bridged linear porphyrin arrays in the Heck cross-coupling (Scheme 26).66 trans-Isomer 125 was obtained by the coupling reaction of 1,4-divinylbenzene 124 with two equivalent amounts of 123 in a yield of 76% (Scheme 26). Trimer 127 was obtained by coupling of 1,3,5-trivinylbenzene 126 with three equivalent amounts of 123. The UV−vis-NIR spectra of 125 and 127 indicated stronger electronic interaction in 125 than 127.

As discussed above, meso−meso ethenylene-linked dimer 118 could not be synthesized by the Heck reaction. However, Anderson et al. developed an efficient synthetic method for the synthesis of meso−meso vinylene-bridged porphyrin dimer 128 by Migita−Kosugi−Stille cross-coupling of bromoporphyrin 112 with bis(triethylstannyl)ethene in 2005 (Scheme 27).67 In this case, a combined use of CuI and CsF provided product 128 in 58%. Absence of CsF decreased the product yield, and no product was obtained in the absence of CuI. Compared with the acetylene-bridged porphyrin dimer, the vinylene-linked dimer exhibited larger reverse-saturable absorption in the 700−900 nm range.

Migita−Kosugi−Stille coupling was also an efficient strategy for synthesis of pyrrole-bridged and thiophene-bridged diazaporphyrin dimers 129M and 130M. In 2014, Matano et al. reported the synthesis of 129M and 130M by reactions of 89M with N-Boc-2,5-bis(triethylstannyl)pyrrole and 2,5-bis-

![Scheme 24. Synthesis of meso−β Ethenylene-Bridged Dimer](image-url)
Scheme 25. Synthesis of Di(vinylphenyl)porphyrin Polymers

Scheme 26. Synthesis of $\beta-\beta$-Vinylbenzene-Bridged Porphyrin Oligomers

Scheme 27. Synthesis of meso–meso (E)-Vinylene-Bridged Porphyrin Dimer
In 2009, Senge et al. reported the synthesis of p-terphenyl-bridged porphyrin dimer 132 by the Migita−Kosugi−Stille coupling reaction of 131 and 1,4-bis(tri-n-butylstannyl)-benzene in 21% yield (Scheme 29).69 In addition, they also prepared p-phenylene-bridged and m-phenylene-bridged porphyrin dimers in moderate yields.

**SUMMARY**

As discussed, various palladium-catalyzed cross coupling reactions have been used for the synthesis of porphyrin arrays. So far, the Suzuki−Miyaura reaction, Sonogashira reaction, Buchwald−Hartwig amination, Mizoroki−Heck reaction, and Migita−Kosugi−Stille reaction have been successfully used. This means that porphyrins are simple stable aromatic hydrocarbons from the viewpoint of Pd-catalyzed cross coupling. However, porphyrins possess attractive electronic and photophysical properties, making porphyrin arrays quite important and attractive. Some of them are actually used in many fields. β-Selective borylations provided various β-borylated porphyrins and subsequent halogenations provided various β-halogenated porphyrins. These products have been widely used in Suzuki−Miyaura reactions to provide novel porphyrin arrays. New and fascinating porphyrin functional molecules are expected to be prepared through suitable precursors and Pd-catalyzed cross coupling conditions in the near future.

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**Notes**

The authors declare no competing financial interest.

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