

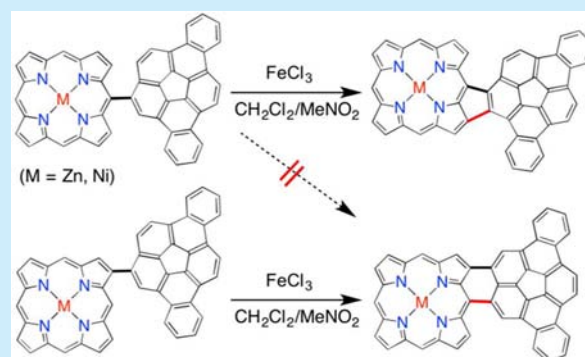
meso- β Dibenzo[*a,g*]corannulene-Fused Porphyrins

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S Supporting Information

ABSTRACT: FeCl₃-mediated oxidative fusion of *meso*-linked dibenzo[*a,g*]corannulene–porphyrin dyads **6M** afforded fused porphyrins **7M** bearing a five-membered ring connection, but similar oxidation of β -linked dyads **9M** provided fused porphyrins **10M** bearing a six-membered ring connection, both in a regiospecific manner. While fused dyads **10M** exhibit modestly red-shifted absorption and fluorescence profiles, fused dyads **7M** display characteristically red-shifted absorption bands reflecting antiaromatic dehydropurpurin electronic networks.



Fused porphyrins have attracted considerable attention in recent years owing to their attractive properties such as red-shifted absorption and emission profiles, intriguing nonlinear optical properties, high electron mobilities, and multicharge storage capabilities.¹ An increasing number of fused porphyrins have been continuously developed to date,² including naphthalene-fused,^{2a–c} anthracene-fused,^{2d–f} BODIPY-fused,^{2g} and planar polyaromatic hydrocarbon (PAH)-fused porphyrins.^{2h–j} In addition, directly fused porphyrin tapes have also been developed, which exhibit drastically red-shifted absorption bands.³ In all of these previous reports, the π -conjugated segment that was fused to the molecular scaffold of interest was planar. Just a handful of examples exist whereby curved π -conjugated segments have been successfully employed in fusion reactions of this type. As a rare and interesting example, Lash et al. reported a β – β corannulene-fused porphyrin **3** which was synthesized via a McDonald-type condensation using a corannulene-fused pyrrole as starting material (Figure 1).^{4,5} In this paper, we report the synthesis of *meso*, β -corannulene-fused porphyrin dyads which were successfully obtained via cross-coupling of the appropriate porphyrin and corannulene fragments followed by ferric chloride-mediated oxidative fusion. As a coupling partner, we chose 8-boryldibenzo[*a,g*]corannulene **5**

due to facile synthetic access from acenaphthenequinone (see the Supporting Information). In addition, the bowl depth of dibenzo[*a,g*]corannulene **2** (0.83 Å) is more shallow than that of the parent corannulene **1** (0.87 Å), an attribute that was envisaged to allow the intramolecular fusion reaction to proceed more favorably.^{6,7}

After extensive screening of catalysts and reaction conditions, we found that a Pd(II) precatalyst developed by Buchwald et al.⁸ was effective for the Suzuki–Miyaura coupling of brominated porphyrins **4Zn** and **4Ni** with 8-boryldibenzo[*a,g*]corannulene **5**. Under the mild conditions shown in Scheme 1, palladium-catalyzed cross-coupling reactions gave singly linked products **6Zn** and **6Ni** in 65% and 75% yields, respectively. The coupling reaction of *meso*-borylated porphyrins with 8-bromocorannulene

Scheme 1. Synthesis of **6M** from **4M** and **5**

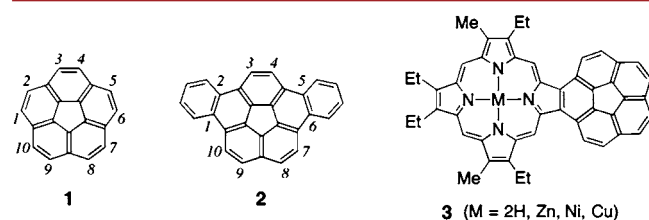
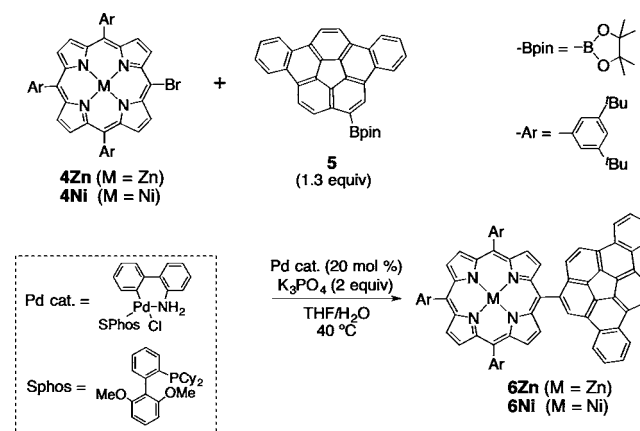


Figure 1. Corannulene **1**, dibenzocorannulene **2**, and Lash's β , β -corannulene-fused porphyrin **3**.

Received: April 17, 2014

Published: May 12, 2014

afforded the same product albeit with slightly lower efficiency (ca. 51% for **6Zn**). High-resolution atmospheric pressure–chemical ionization time-of-flight mass-spectroscopy (HR-APCI-TOF-MS) revealed the parent ion peaks at $m/z = 1284.5926$ (calcd for $C_{90}H_{84}N_4^{64}Zn$: 1284.5982, $[M]^+$) for **6Zn** and at $m/z = 1278.6000$ (calcd for $C_{90}H_{84}N_4^{58}Ni$: 1278.6044, $[M]^+$) for **6Ni**, respectively. Finally, single-crystal X-ray diffraction analysis revealed the structure of **6Zn** (Figure 2a). The bowl depth of the dibenzocorannulene unit in **6Zn** is

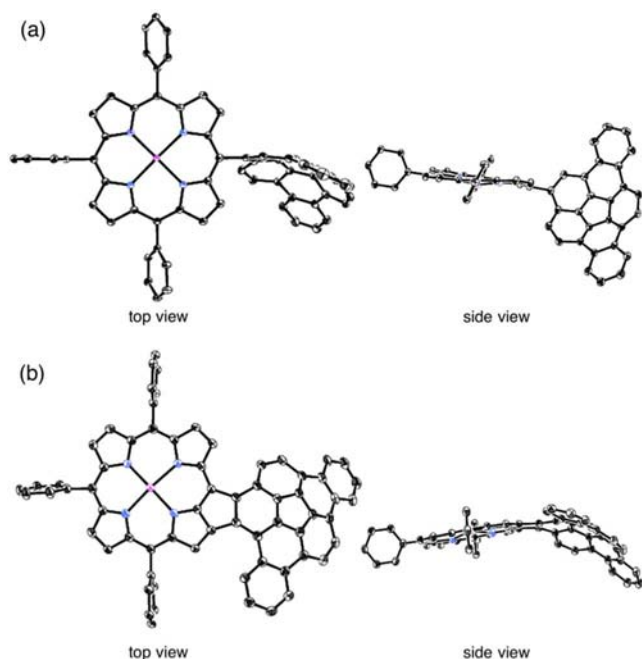
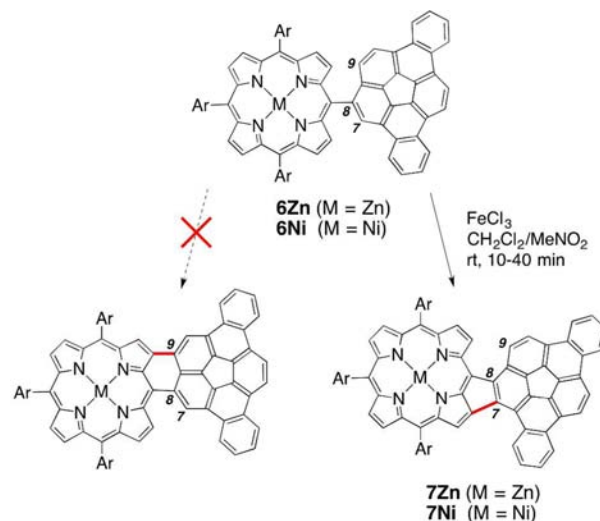


Figure 2. X-ray crystal structures of (a) **6Zn** and (b) **7Zn**. Solvent molecules, hydrogen atoms, and *tert*-butyl groups were omitted for clarity. Thermal ellipsoids were scaled to 30% probability level. One of the two molecules in the asymmetric unit of **7Zn** is shown.

0.77 Å, which is more shallow than that of **2** (0.83 Å).⁷ The dihedral angle between the mean plane of the Zn(II) porphyrin unit and the mean plane of the dibenzocorannulene unit (calculated with respect to C8 and the two neighboring carbon atoms of the dibenzocorannulene unit) is 77.0°.

Then, we attempted an oxidative fusion reaction of **6M** (Scheme 2). Oxidation of **6Zn** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $Sc(OTf)_3$, a combination known to be effective for the synthesis of directly fused porphyrin tapes,^{3c–e} yielded brown solids in 29% yield. The HR-APCI-TOF-MS of this product revealed the parent ion peaks at $m/z = 1282.5889$ (calcd for $C_{90}H_{82}N_4^{64}Zn$: 1282.5825, $[M]^+$), suggesting a loss of two hydrogen atoms from **6Zn**. The same product was obtained in a better yield (70%) by oxidation of **6Zn** with $FeCl_3$. Single-crystal X-ray diffraction analysis revealed that this product was **7Zn**, in which an additional bond has been formed between the 7-position of the dibenzocorannulene unit and the β -position of the Zn(II) porphyrin framework (Figure 2b). Interestingly, the formation of fused constitutional isomers was not observed, indicating the exclusive regioselectivity of the fusion reaction. Oxidative ring-closure reactions that give rise to fused structures containing a five-membered ring rather than a six-membered ring are quite rare in the literature.^{1k,8,9} In the present case, the observed high regioselectivity of the fusion reaction may be ascribed to a short distance between the fusing

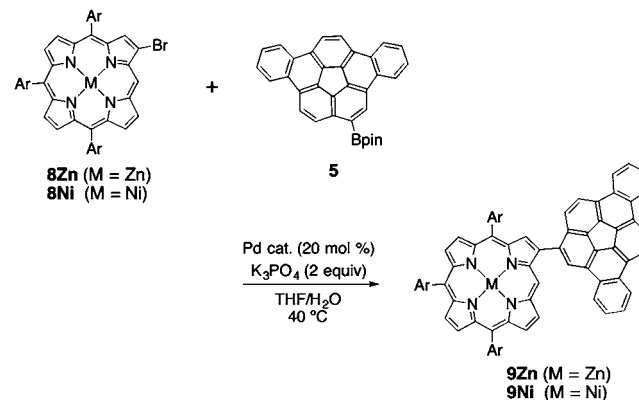
Scheme 2. Oxidative Fusion Reaction of **6M**



positions in **6Zn** (ca. 3.3 Å, Figure S11, Supporting Information), owing to the bent structure of the dibenzocorannulene segment. Similarly, the oxidation of **6Ni** with $FeCl_3$ gave **7Ni** in 88% yield. The structure of **7Ni** has been assigned on the basis of the similarity of its 1H NMR spectrum to that of **7Zn** (Figure S3, Supporting Information).

We then turned our attention to attaching the dibenzocorannulene-8-yl unit at the β -position of the porphyrin scaffold. Under similar palladium-catalyzed cross-coupling conditions that worked for the *meso*-8-linked system, bromoporphyrin **8M**¹⁰ was coupled with **5** to afford corannulene-appended porphyrins in 69% yield for **9Zn** and 59% yield for **9Ni** (Scheme 3).

Scheme 3. Synthesis of **9M** from **8M** and **5**



Corannulene-appended porphyrins **9Zn** and **9Ni** were then subjected to oxidative fusion reaction conditions (Scheme 4). While the DDQ– $Sc(OTf)_3$ couple did not afford any desired fused products, $FeCl_3$ -mediated oxidation was effective to afford **10Zn** and **10Ni** in 45% and 29% yields, respectively. HR-APCI-TOF-MS revealed the parent ion peaks at $m/z = 1282.5869$ (calcd for $C_{90}H_{82}N_4^{64}Zn$: 1282.5825, $[M]^+$) for **10Zn**, and at $m/z = 1276.5866$ (calcd for $C_{90}H_{82}N_4^{58}Ni$: 1276.5887, $[M]^+$) for **10Ni**, respectively, again suggesting a loss of two hydrogen atoms from **9M** (Scheme 4). The structure of **10Zn** has been revealed by X-ray diffraction analysis to be a fused product, in which the 9-position of the dibenzocorannulene segment is directly linked to the *meso*-position of the porphyrin (Figure 3). In other words,

Scheme 4. Oxidative Fusion Reaction of 9M

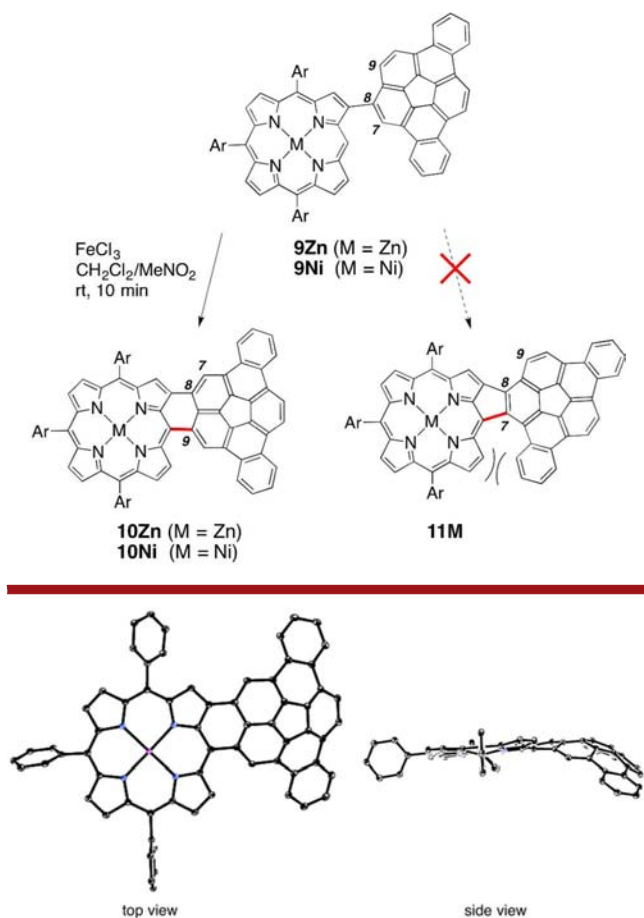


Figure 3. X-ray crystal structure of **10Zn**. Solvent molecules, hydrogen atoms, and *tert*-butyl groups were omitted for clarity. Thermal ellipsoids were scaled to 30% probability level.

10Zn is a fused product incorporating a six-membered ring as opposed to a 5-membered ring as seen for the previous fused dyads. Here again, other fused products were not detected, indicating high regioselectivity of the fusion reaction. This regioselectivity may also be explained in terms of the short distance between the two atoms involved in the fusing bond formation (Figure S12, Supporting Information). In addition, possible fused products such as **11M** may suffer from steric congestion between the β -hydrogen atom adjacent to the fused *meso*-position and the benzo-segment of the dibenzocorannulene unit (Figure S13, Supporting Information). The mean-plane deviations of Zn(II) porphyrin segments are 0.103, 0.075, and 0.085 Å for **6Zn**, **7Zn**, and **10Zn**, respectively, indicating increased planarity in **7Zn** and **10Zn** due to the fused structures. The bowl depths of the dibenzocorannulene unit in **7Zn** and **10Zn** are 0.71 and 0.83 Å, respectively.

The UV/vis absorption spectra of singly linked dyads **6Zn** and **9Zn** are very similar, being roughly a superposition of the individual absorption profiles of the Zn(II) porphyrin and dibenzocorannulene components (Figure 4). The fluorescence spectra of **6Zn** and **9Zn** are similar, with peak maxima at 596 and 651 nm and at 591 and 646 nm, respectively. The fluorescence quantum yields are 0.031 and 0.028 for **6Zn** and **9Zn**. These data indicate only weak electronic interactions between the Zn(II) porphyrin and dibenzocorannulene units in both **6Zn** and **9Zn**, probably due to the twisted conformations. On the other hand,

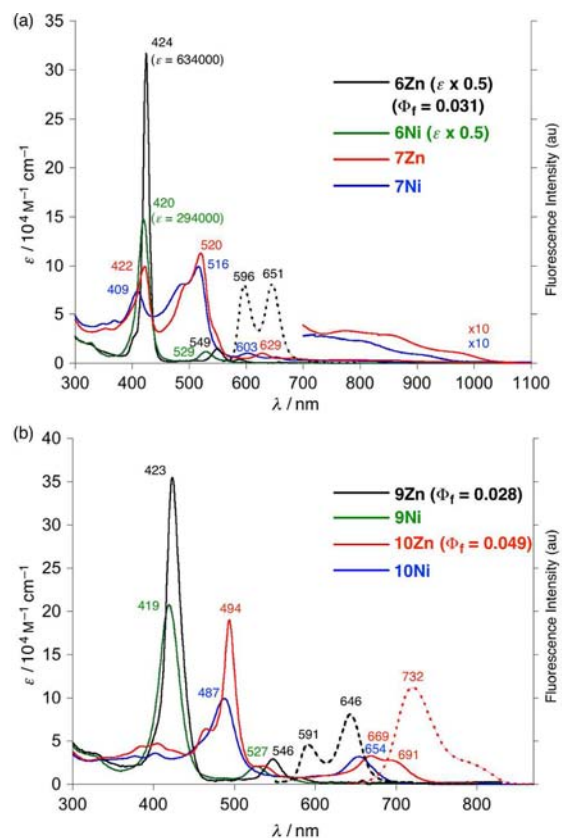


Figure 4. UV/vis absorption (solid line) and fluorescence (dashed line) spectra of (a) **6Zn**, **6Ni**, **7Zn**, and **7Ni** and (b) **9Zn**, **9Ni**, **10Zn**, and **10Ni** in CH_2Cl_2 .

the absorption and fluorescence properties of dyads **7Zn** and **10Zn** are drastically perturbed, but in different ways. Fused dyad **10Zn** displays a Soret band at 494 nm with a shoulder at 465 nm and Q-bands at 669 and 691 nm. This dyad emits fluorescence at 732 nm with an enhanced quantum yield ($\Phi_F = 0.049$) with respect to **9Zn**. Dyad **10Ni** exhibits an absorption spectrum that is similar to that of **10Zn**. These spectral features, which are similar to those of naphthalene-fused porphyrins reported by Imahori, Cammidge, and Gryko,^{2a-c} can be interpreted in terms of a simple extension of the π -conjugated network with preservation of the aromaticity of the segments. In contrast, the absorption spectrum of **7Zn** exhibits a split Soret band at 422 and 520 nm and low energy Q-like bands tailing into near-infrared (NIR) region around 1050 nm, and **7Zn** shows no fluorescence. The absorption spectrum of **7Ni** is similar to that of **7Zn**. The spectral features of **7M** are clearly different from those of **10M** and are characteristic of antiaromatic porphyrinoids. The optical properties of **7M** may be understood by considering that a dehydropurpurin-network present in **7M** possesses a pseudo 20π antiaromatic electronic circuit. Such antiaromatic contributions have been recently recognized in several dehydropurpurin-like molecules.¹¹

Cyclic voltammetry (CV) measurements revealed reversible oxidation and reduction waves at 0.34 and -1.82 V for **6Zn** and 0.36 and -1.81 V for **9Zn** versus ferrocene/ferrocenium ion couple, indicating that the directly linked dibenzocorannulene unit has negligible influence on the electronic properties of the Zn(II) porphyrin (Table 1). On the other hand, the fused porphyrins **7Zn** and **10Zn** exhibited the first oxidation and reduction potentials at 0.12 and -1.38 V and at 0.23 and -1.46

Table 1. Electrochemical Properties of 6M, 7M, 9M, and 10M^a

compd	$E^{1/2}_{ox,2}$	$E^{1/2}_{ox,1}$	$E^{1/2}_{red,1}$	$E^{1/2}_{red,2}$	ΔE^b
6Zn		0.34	−1.82		2.16
6Ni		0.62	−1.73		2.35
7Zn	0.51	0.12	−1.38		1.50
7Ni	0.58	0.34	−1.34	−1.69	1.68
9Zn	0.69	0.36	−1.81		2.17
9Ni	0.84	0.62	−1.73		2.35
10Zn	0.60	0.23	−1.46	−1.76	1.69
10Ni	0.65	0.48	−1.40	−1.72	1.88

^aConditions: Bu₄NPF₆ electrolyte 0.1 M in PhCN, Ag/AgClO₄ reference electrode, Pt working electrode, Pt wire counter electrode, scan rate 0.05 V s^{−1}. All values given in V. ^b ΔE = electrochemical HOMO–LUMO gap (= $E^{1/2}_{ox,1} - E^{1/2}_{red,1}$ [eV]).

V, respectively, indicating stronger electronic perturbation. The electrochemical HOMO–LUMO gaps are 1.50 eV for 7Zn and 1.69 eV for 10Zn, respectively. The smaller HOMO–LUMO gap of 7Zn is consistent with the partial antiaromatic character.

In summary, *meso*- β dibenzocorannulene-fused porphyrins have been obtained by FeCl₃-mediated intramolecular oxidative ring-closure reactions of dibenzocorannulene-8-yl-porphyrins. Upon oxidation, *meso*-8-linked dyads 6M gave fused porphyrins 7M bearing a five-membered ring, and β -8-linked dyads 9M gave fused porphyrins 10M bearing a six-membered ring both in a regiospecific manner. Fused porphyrins 10M display red-shifted absorption spectra and 10Zn shows red-shifted fluorescence owing to the π -extended conjugation, whereas fused porphyrins 7M show absorption features characteristic of antiaromatic porphyrinoids and 7Zn is nonfluorescent, reflecting the contribution of the pseudo 20 π electronic circuit of the dehydropurpurin. Further investigations on the fused porphyrinoids with bowl-shaped PAHs are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedure, complete characterizations (NMR, UV/vis, fluorescence), DFT calculations, cyclic voltammetry, and X-ray crystallographic data for 6Zn, 7Zn, and 10Zn. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grant-in-Aid from JSPS (No. 25220802 (Scientific Research (S))).

■ DEDICATION

Dedicated to Prof. Lawrence T. Scott (Department of Chemistry, Boston College) on the occasion of his 70th birthday.

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