Antiaromaticity

DOI: 10.1002/ange.201006314

Metal-Mediated Synthesis of Antiaromatic Porphyrinoids from a BODIPY Precursor**

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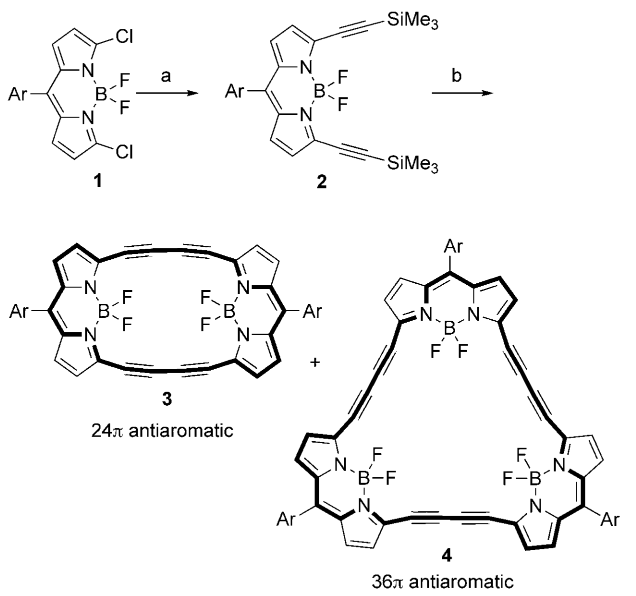
Porphyrinoids have been extensively investigated both in fundamental and applied chemistry. The synthesis of porphyrinoids largely relies on the acid-promoted condensation reaction of pyrroles.[1] Although metal-mediated reactions are a powerful tool in current synthetic chemistry, they have rarely been employed for the synthesis of porphyrinoid skeletons. Boron dipyrrin (BODIPY) dyes have also received much attention for materials such as labeling reagents, chemosensors, light-harvesting systems, and dye-sensitized solar cells.[2] These two important functional π-systems are structurally related, but the synthesis of porphyrinoids from a BODIPY precursor has largely remained unexplored.

Dehydroannulenes have received long-lasting attention in not only the basic aspect of aromaticity of large π-systems but also supramolecular chemistry and materials science.[3] For the synthesis of these π-conjugated macrocycles, facile synthetic methods have been established on the basis of transition-metal-catalyzed cross-coupling reactions. The ethynylene group in the macrocycles allows extension of π conjugation and offers rigidity for highly ordered structures. These properties promise the creation of macrocycles possessing unique structural and electronic features. Herein we report the incorporation of BODIPY units into dehydroannulenes to furnish stable antiaromatic porphyrinoids by transition-metal-mediated synthesis.[4]



Scheme 1. Synthesis of butadiyne-bridged BODIPY oligomers. Conditions: a) $Bu_3SnC{\equiv}CSiMe_3$ (2.4 equiv), [Pd(PPh$_3$)$_4$] (2.5 mol%), toluene, reflux, 4 h, 63% yield. b) CuCl (1.7 equiv), DMSO, under air, 60 °C, 24 h. Ar = 3,5-di-*tert*-butylphenyl.

The synthesis of novel porphyrinoid **3** was commenced with introduction of trimethylsilylethynyl groups to α,α'-dichloro BODIPY **1** via Stille coupling (Scheme 1).[5,6] Direct homocoupling by sila-Glaser coupling with CuCl in DMSO provided the target molecule **3** in 27% yield along with acyclic BODIPY oligomers (Scheme 1).[7] Normal Glaser coupling with terminal alkynes was hampered by the low solubility of diethynyl BODIPY after desilylation of **2**.

Macrocycle **3** can be considered to possess a cyclic 24π-electron conjugation. In general, $4n\pi$ porphyrinoids take on highly distorted structures to avoid destabilization due to antiaromaticity.[8] Thus, elaboration to preserve the planarity of the macrocycle is often required to achieve distinct antiaromaticity.[9] In the case of **3**, the rigid butadiyne linker and the BF$_2$ unit should enforce the whole macrocycle into a flat structure. In fact, the single-crystal X-ray diffraction analysis unambiguously elucidated the planar and rectangular structure of **3**, for which the mean plane deviation is only 0.058 Å (Figure 1).[10] Accordingly, distinct antiaromaticity of **3** was confirmed by NMR spectroscopic analysis. In the ^{1}H NMR spectrum of **3**, a set of two peaks at $\delta = 5.01$ and 4.53 ppm was assigned as signals of the β-pyrrolic protons, which are significantly upfield-shifted in comparison to those of acyclic BODIPY **2** ($\delta = 6.82$ and 6.61 ppm), indicating the existence of paratropic ring current. The paratropic ring current effect also shifts the ^{19}F signal for the inner BF$_2$ moiety downfield ($\Delta\delta = 8.9$ ppm). In addition, the largely positive nucleus-independent chemical shift (NICS)[11] value ($\delta = +18.6$ ppm) supports strong antiaromaticity of **3**. Furthermore, antiaromaticity of **3** induced substantial bond length alternation around the *meso* position in **3** in comparison to BODIPY monomer **2′** (Ar = mesityl) and the

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[**] We are indebted to Prof. Kazuyuki Tatsumi and Prof. Yasuhiro Ohki (Nagoya University) for help with X-ray analysis and Prof. Atsuhiro Osuka and Prof. Naoki Aratani (Kyoto University) for help with NIR fluorescence measurements. This work was supported by MEXT (Japan) Grants-in-Aid for Scientific Research (Nos. 21685011 and 21108510 "pi-Space") and the Global COE Program in Chemistry of Nagoya University. H.S. also acknowledges the Asahi Glass Foundation for financial support. S.Y. appreciates the JSPS Research Fellowships for Young Scientists. BODIPY = boron dipyrrin.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006314.

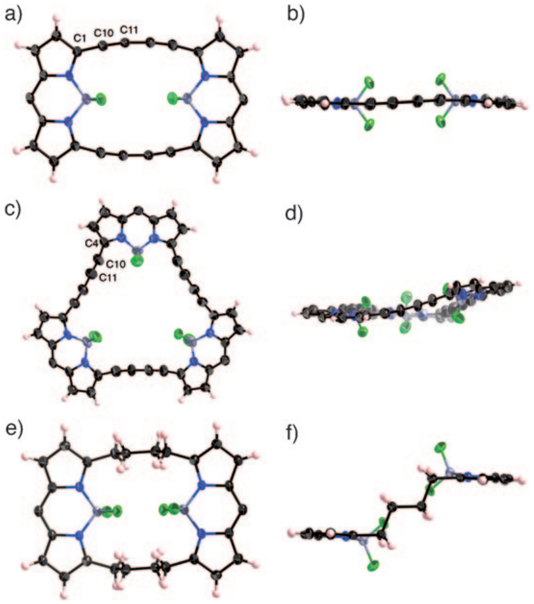


Figure 1. X-ray crystal structures showing a) top view and b) side view of **3**, c) top view and d) side view of **4′** (Ar = mesityl), and e) top view and f) side view of **5**. *meso*-Aryl substituents are omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

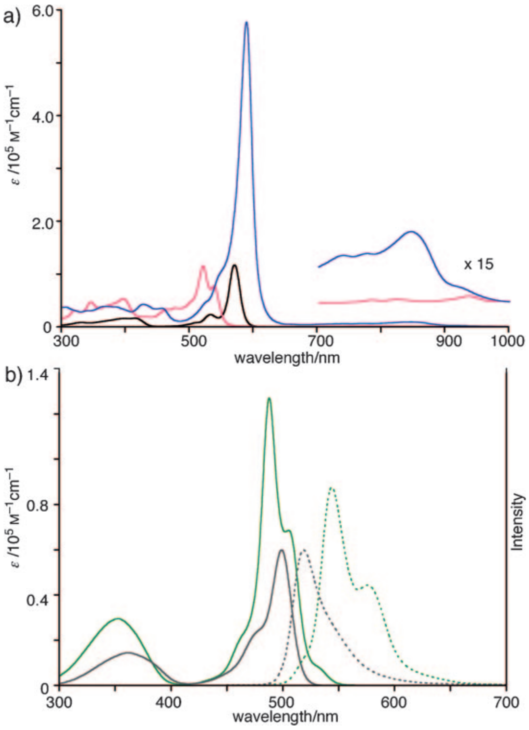


Figure 2. a) UV/Vis/NIR absorption spectra of **2** (black), **3** (red), and **4** (blue) in CH_2Cl_2. b) UV/Vis absorption (solid lines) and emission spectra (dashed lines) of **5** (green) and the parent *meso*–3,5-di-*tert*-butylphenyl BODIPY (gray) in CH_2Cl_2 with excitation at the longest absorption maxima.

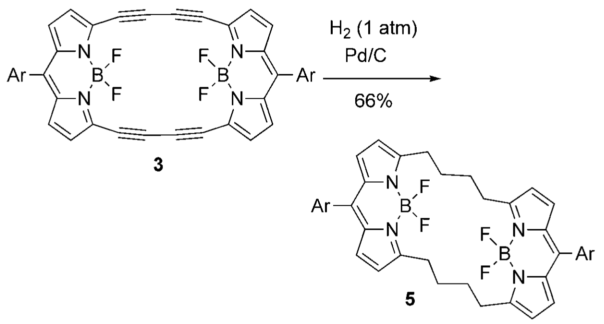
BODIPY unit in **5** (see below and Figure S24 in the Supporting Information,).

Another striking feature of an ethynylene linkage is tolerance to bending. In fact, the angle of C1-C10-C11 in BODIPY dimer **3** is rather large (165.3°). This feature also allowed the formation of larger macrocycle **4** with three BODIPY units in 10% yield (Scheme 1). Crystallographic analysis of **4** was difficult, but we obtained a nice crystal of **4′** (Ar = mesityl).[10] The structure of **4′** is slightly distorted planar with pseudo C_3 symmetry (mean plane deviation = 0.18 Å; Figure 1). This 36π porphyrinoid **4** also exhibits antiaromaticity in spite of its large π conjugation, as judged from its upfield-shifted signals for β protons and downfield-shifted signals for inner fluorine atoms in the ^1H and ^{19}F NMR spectra. A positive NICS value ($\delta = +4.0$ ppm) calculated on the solid-state structure also supports this assignment.[12]

The spectral features of the UV/Vis/NIR absorption of **3** are quite similar to those of known antiaromatic porphyrinoids: a broad Soret-like band at 522 nm and a weak absorption band in the near infrared region (936 nm) are observed (Figure 2a). BODIPY trimer **4** also exhibits a weak absorption band at 849 nm, and the longest absorption maxima of **3** and **4** are red-shifted by 365 and 278 nm relative to that of **2** as a result of cyclization. This result is an indication of small HOMO–LUMO gaps of **3** and **4**. Interestingly, trimer **4** has a large molar extinction coefficient, which is much larger than those of aromatic expanded porphyrins with six pyrrole units. This can be accounted for by the hyperchromic effect by alkynyl moieties at the α positions as well as attenuated antiaromaticity of **4**.[13] Porphyrinoids **3** and **4** are nonfluorescent.[14] This fact is rather remarkable in view of the highly emissive nature of BODIPY derivatives. This lack of fluorescence is probably due to the small HOMO–LUMO gap of antiaromatic porphyrinoids, which results in enhancement of the rate of nonradiative decay.[15]

Electrochemical properties of **3** and **4** were investigated by cyclic voltammetry, both of which exhibited two reversible reduction waves and one reversible oxidation wave. The HOMO–LUMO gaps of **3** and **4** are determined to be 1.44 and 1.45 eV, respectively (Figure S27 in the Supporting Information). These electrochemical HOMO–LUMO gaps are roughly matched with optical HOMO–LUMO gaps (1.32 and 1.46 eV for **3** and **4**) derived from the longest wavelength absorption maxima. It is also noteworthy that the splitting between the first and second reduction potentials of **3** (42 mV) is larger than that of **4** (25 mV), indicating more effective delocalization of the resultant radical anions of **3** on the macrocycles.

Finally, the chemical reactivity of **3** was briefly investigated. Hydrogenation of **3** in the presence of Pd/C occurred selectively at butadiyne units without touching the pyrrole moiety to furnish butylene bridged BODIPY dimer **5** in good yield (Scheme 2). X-ray crystallographic analysis of BODIPY dimer **5** revealed its steplike structure, which is fabricated by two parallel BODIPY units (Figure 1e,f).[10] The breaking of π-conjugation retrieves bright green fluorescence as a BODIPY dye at 543 nm (Figure 2b). The absorption spectrum of **5** consists of a blue-shifted strong absorption band at 488 nm and a red-shifted weak one at 534 nm as a shoulder, in comparison to the parent *meso*-mesityl BODIPY mono-



Scheme 2. Hydrogenation of BODIPY dimer **3**.

mer.[16] The excitation spectra of **5** monitored at 543 and 577 nm exhibited identical spectra including the shoulder absorption, indicating that this minor peak is also the absorption band of **5** (Figure S26). This spectral feature may be interpreted as follows by exciton coupling theory:[17] the exciton coupling between the two almost parallel transition dipoles along the long axis of the BODIPY units generates one high-energy transition and one low-energy forbidden transition, which could be assigned to the absorption bands at 488 and 534 nm, respectively.[18]

In conclusion, we have demonstrated the usefulness of transition-metal-mediated reactions to synthesize novel stable antiaromatic porphyrinoids. Incorporation of the BODIPY unit into porphyrin-like cyclic π-conjugation greatly alters its photophysical properties. The prospective properties of antiaromatic porphyrinoids for NIR materials have been also demonstrated. Crossover between porphyrin and BODIPY research will offer chances to create novel porphyrinoids as well as cyclic BODIPY arrays with fascinating characteristics. Further exploration of synthesis of novel porphyrinoids by transition-metal-mediated reactions is currently underway in our group.

Received: October 8, 2010
Revised: November 26, 2010
Published online: February 2, 2011

Keywords: annulenes · aromaticity · cross-coupling · dyes/pigments · porphyrinoids

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[10] Crystal data for **3**: $C_{56}H_{52}B_2Cl_6F_4N_4$, $M_w = 1091.34$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.421(4)$, $b = 10.307(5)$, $c = 15.049(7)$ Å, $\alpha = 83.34(2)$, $\beta = 75.43(2)$, $\gamma = 72.636(16)$°, $V = 1348.6(11)$ Å^3, $Z = 1$, $D_{calcd} = 1.344$ g cm^{-3}, $T = 173(2)$ K, $R = 0.0921$ ($I > 2.0\sigma(I)$), $R_w = 0.3209$ (all data), GOF = 1.142 ($I > 2.0\sigma(I)$). Crystal data for **4′**: $C_{136}H_{94}B_6Cl_{12}F_{12}N_{12}O_2$, $M_w = 485.21$, triclinic, space group $P\bar{1}$ (No. 2), $a = 18.358(14)$, $b = 18.505(15)$, $c = 20.125(14)$, $\alpha = 95.249(19)$, $\beta = 91.390(19)$, $\gamma = 94.952(14)$°, $V = 6779(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.297$ g cm^{-3}, $T = 173(2)$ K, $R = 0.1053$ ($I > 2.0\sigma(I)$), $R_w = 0.3499$ (all data), GOF = 0.957 ($I > 2.0\sigma(I)$). Crystal data for **5**: $C_{27.5}H_{33}BCl_{1.26}F_2N_2$, $M_w = 485.21$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.745(5)$, $b = 10.728(5)$, $c = 13.170(5)$ Å, $\alpha = 87.222(5)$, $\beta = 78.102(5)$, $\gamma = 81.505(5)$°, $V = 1332.3(11)$ Å^3, $Z = 2$, $D_{calcd} = 1.210$ g cm^{-3}, $T = 153(2)$ K, $R = 0.0780$ ($I > 2.0\sigma(I)$), $R_w = 0.2251$ (all data), GOF = 1.032 ($I > 2.0\sigma(I)$). CCDC-795975 (**2′**), 795976 (**3**), 795977 (**4′**), and 795978 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] The optimized structure of **4** takes a completely flat conformation with an NICS value of +8.1 ppm. These results imply a somewhat more flexible nature of **4** in comparison to the rigid dimer **3**.

[13] Alkynyl substituents at the α positions of BODIPYs enhance molecular absorption coefficients. The molar absorption coef-

ficient of bis(trimethylsilylethynyl) BODIPY **2** is $1.2\times10^5\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, while that of the parent *meso*-3,5-di-*tert*-butylphenyl BODIPY is only $6.0\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$.

[14] No emission peak was detected in the range 1000–1500 nm.

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[18] DFT calculations for **5** at the B3LYP/6-31G(d) level suggested the involvement of through-bond interactions between molecular orbitals of two BODIPY units (Figure S33).