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Cross-Bridging Reaction of 5,20-Diethynyl Substituted Hexaphyrins to Vinylene-Bridged Hexaphyrins

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In recent years, expanded porphyrins that are fully conjugated macrocycles consisting of more than four pyrrolic subunits have emerged as new annulene-variants.[1] An important structural feature is the presence of nitrogen atoms, which allows for formation of different neutral oxidation states through acceptance or release of two hydrogen atoms at the nitrogen atoms upon two-electron redox processes.[2] Even aromatic−antiaromatic switching is realized in a robust and reversible manner for a rigid system,[2b] hence encouraging exploitation of novel aromatic systems based on expanded porphyrins. Herein we report an unprecedented thermal cross-bridging reaction of 5,20-diethynyl substituted [26]hexaphayins(1.1.1.1.1.1) to *trans*-vinylene-bridged [26]hexaphyrins(1.1.1.1.1.1). Interestingly, a resonance contributor of the rearranged products can be regarded as [16]annuleno[16]annulene. [4*n*]Annuleno[4*n*]annulenes that consist of two annulated antiaromatic[4*n*]annulenes with a total of $(4n + 2)$ π-electrons have been extensively studied to examine a possibility that such conjugated molecular systems can possess overall aromaticity.[3]

We have recently shown that *meso*-aryl substituted [26]hexaphyrins(1.1.1.1.1.1) take two major different conformations, type-I and type-II (Scheme 1), depending on steric bulkiness of meso substituents. Most of hexaphyrins that bear all bulky 2,6-disubstituted aryl groups, including representative **1**, are forced to take type-II conformations,[4] while those bearing small substituents both at 5- and 20-positions tend to take type-I conformations, because of mitigated steric hindrance between two R* in the type-I conformation (Scheme 1).[5] 5,20-Bis(triisopropylsilylethynyl) (TIPS-ethynyl) substituted hexaphyrin **2** was prepared from 5,10-bis(pentafluorophenyl)tripyrrane **T** and TIPS-propynal in 12% yield, and its structure has been determined by X-ray crystallographic analysis to be a type-II conformation holding two TIPS-ethynyl groups at the short side (Supporting Information, SI). Refluxing a solution of **2** in ethyl acetate for 36 h caused almost quantitative conversion to **3** with vivid color change from indigo blue to magenta purple. The structure of **3** has been assigned on the basis of its spectroscopic data as well as following facts. Compound **3** was shown to be interconvertible with its reduced form **4** through reduction with $NaBH_4$ and oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and the structure of **4** has been characterized by X-ray crystallographic analysis to be a *trans*-vinylene-bridged [28]-hexaphyrin (Figure 1a).[6] The hexaphyrin outer frame (C30N6) is rather planar with the mean-plane-deviation of 0.58 Å, to which the central vinylene moiety is tilted almost perpendicular and thus the TIPS-ethynyl and TIPS groups are also perpendicular.

As indicated in Scheme 2, the overall conjugated electronic systems of **3** and **4** can be characterized as 26- and 28-π circuits (A and C), respectively, while a resonance form that contributes to **3** (B) can be regarded as [16]diazaannuleno[16]diazaannulene, but this contribution should be minor owing to the perpendicular arrangement of the central vinylene bridge. In the ^{1}H NMR spectra, the protons of the TIPS-ethynyl and the TIPS groups are observed in the range of −1.20 to approximately −2.63 ppm and the peripheral β-protons are observed in the range of 8.56$\sim$10.01 ppm for **3**, whereas the former are observed in the range of 3.26$\sim$3.46 ppm and the latter in the range of 4.34$\sim$5.33 ppm for **4**, hence indicating distinct diatropic and paratropic ring currents, respectively, for **3** and **4**. In addition, the absorption spectrum of **3** features a sharp Soret-like band at 556 nm and Q-bandlike bands at 695, 753, 852, and 974 nm, which is reminiscent of that of the aromatic hexaphyrin **1**, while the spectrum of **4** displays an ill-defined broad band at 506 nm without any distinct Q-bandlike absorption bands (SI).

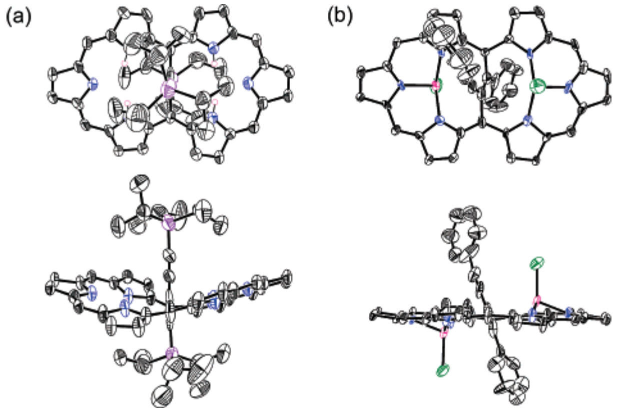
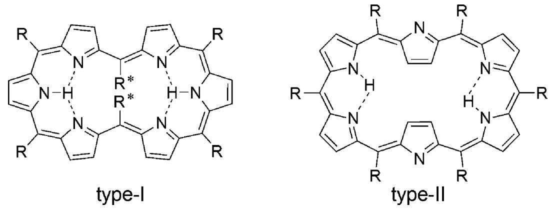
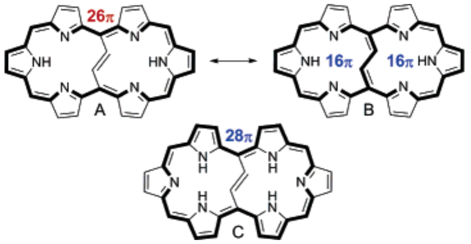


Figure 1. X-ray crystal structures of (a) **4** and (b) **8**: upper, top views; lower, side views. Pentafluorophenyl groups and hydrogen atoms except NH are omitted for clarity.

Scheme 1. Stable Conformations of [26]Hexaphyrins(1.1.1.1.1.1)



Scheme 2. Resonance Structures of *trans*-Vinylene-Bridged Hexaphyrins: **3**, **6** (A and B) and **4**, **7** (C)



Next, we attempted to prepare 5,20-bis(phenylethynyl) substituted hexaphyrin **5** by the reaction of **T** and phenylpropynal under the same conditions. The isolated major product was found, despite

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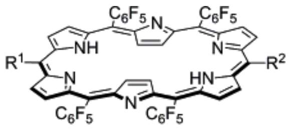
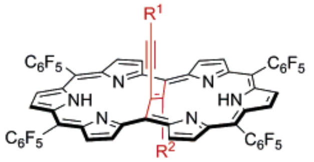
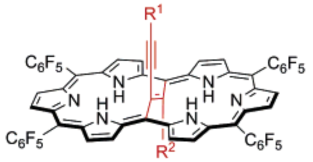


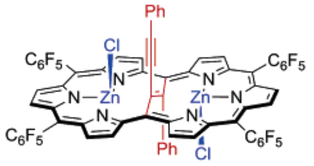
1: $R^1 = R^2 = C_6F_5$
2: $R^1 = R^2$ = TIPS-ethynyl
5: $R^1 = R^2$ = Ph-ethynyl
9: R^1 = TIPS-ethynyl, R^2 = Ph-ethynyl



3: $R^1 = R^2$ = TIPS
6: $R^1 = R^2$ = Ph
10: R^1 = TIPS, R^2 = Ph



4: $R^1 = R^2$ = TIPS
7: $R^1 = R^2$ = Ph
11: R^1 = TIPS, R^2 = Ph



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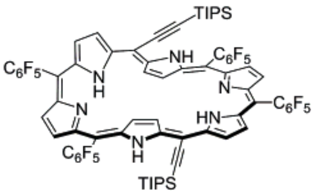

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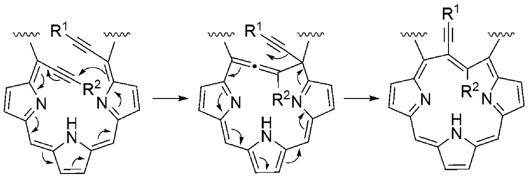
no heating during the reaction and work up procedures, to be already rearranged hexaphyrin **6** (4.5%). Interestingly, **6** was metalated with $ZnCl_2$ to provide biszinc(II) complex **8** in 74% yield. The structure of **8** has been confirmed to be a *trans*-vinylene-bridged planar hexaphyrin macrocycle with the mean-plane-deviation of 0.16 Å for the outer ligand, from which the zinc atoms are displaced by 0.94 Å and the central vinylene bridge is tilted by 74° (Figure 1b).[6,7] The symmetric two tripyrrodimethene segments serve as a monoanionic tridentate binding site for zinc(II) ion, and the resultant charges are balanced by chloride ions. The distances between the zinc atom and vinylene-bridge carbons are in the range of 2.86∼3.05 Å (SI), being shorter than the sum of van der Waals radii (3.17 Å).[8] This suggests favorable zinc(II)−alkene interactions in a η^2-fashion.[7,9] The aromatic character of **8** is evident from its ^{1}H NMR and absorption spectra but its reduction with $NaBH_4$ led to smooth demetallation with concomitant formation of **7**, indicating the lack of zinc(II) ion coordinating ability for **7**. The almost spontaneous cross-bridging reaction of the putative hexaphyrin **5** may be explained in terms of a smaller size of phenylethynyl group compared with TIPS-ethynyl group, which facilitates an approach of the two phenylethynyl groups into closer contact.

The detailed reaction mechanism is not clear but the reaction can be regarded as a formal insertion of a triple bond between the opposite *meso*-carbon and C1-ethynyl carbon. A possible mechanism is proposed in Scheme 3. It is also probable that the reaction occurs in the type-I conformation. In the case of **2**, thermal activation is required to cause such type-I conformation, whereas **6** and **10** are formed almost spontaneously through their type-I conformations. Thus, synthesis of hexaphyrin **9** was attempted by the cross condensation of **T** with TIPS-propynal and phenylpropynal to examine the fates of the two ethynyl groups. The result was clean, giving **10** as a sole rearranged hexaphyrin along with **2** and **6**. It was thus concluded that the smaller phenylethynyl group was connected at the opposite meso position and the larger TIPS-ethynyl group migrated from the meso position to the opposite C1 ethynyl carbon.

Scheme 3. A Possible Reaction Mechanism of the Cross-Bridging Reaction



Hexaphyrins **6** and **10** were also reversibly interconvertible with **7** and **11** through $NaBH_4$ reduction and DDQ oxidation. These interconversions were accompanied by distinct aromatic-to-antiaromatic switching as evident from their ^{1}H NMR data (SI). These results underscore the importance of the vinylene bridge that rigidifies the planar structure of hexaphyrins, hence allowing such switching. In contrast, the reduction of **2** with $NaBH_4$ gave nonplanar deformed reduced [28]hexaphyrin **12** without distinct antiaromatic characters (SI).

In summary, we found the intramolecular cross-coupling reaction of 5,20-diethynyl substituted [26]hexaphyrins to the vinylene-bridged [26]hexaphyrins, probably through folded type-I conformations.[10] The vinylene-bridged hexaphyrins are nice platforms for aromatic-to-antiaromatic switching, and their electronic systems are potentially attractive in view of their structural analogy to those of [4*n*]annuleno[4*n*]annulenes. Currently, we are exploring the extent to which the present cross-bridging procedure can be generalized while working to define the influence of [4*n*]annuleno[4*n*]annulene structures for their overall electronic systems. This would be more feasible, when the vinylene bridge is made planar to the outer hexaphyrin conjugated electronic system by removing the attached substituents. Exploration of such possibility is also underway.

Supporting Information Available: Experimental details and compound data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystal data for **4**: $C_{76}H_{58}F_{20}N_6Si_2 = 1491$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.432$ (4), $b = 17.460$ (5), $c = 31.649$ (9) Å, $\beta = 101.751$ (12)°, $V = 6726$ (3) Å^3, $Z = 4$, $D_{calcd} = 1.473$ g/cm^3, $T = -150$ °C, $R_1 = 0.076$ ($I > 2\sigma(I)$), $R_W = 0.225$ (all data), GOF = 0.862; CCDC, 622032. Crystal data for **8**: $C_{70}H_{22}F_{20}N_6Zn_2Cl_2{\cdot}(C_4H_8O){\cdot}(C_4O){\cdot}4O = 1729$, monoclinic, space group $P2_1$ (No. 4), $a = 17.0582(18)$, $b = 15.5874(17)$, $c = 14.5782(16)$ Å, $\beta = 98.290(2)$°, $V = 3835.7(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.497$ g/cm^3, $T = -183$ °C, $R_1 = 0.091$ ($I > 2\sigma(I)$), $R_W = 0.2920$ (all data), GOF = 1.060; CCDC, 622033.

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JA067102V