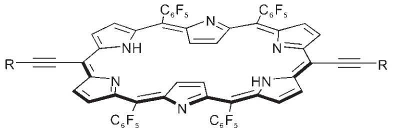
Porphyrinoids

DOI: 10.1002/anie.200700958

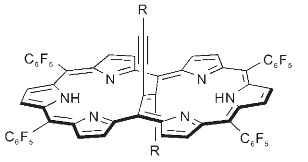
Intramolecular [3+2] Annulation of 5-Aryl-, 20-Ethynyl-Substituted [26]Hexaphyrin(1.1.1.1.1.1) Triggered by Molecular Compression through a Dynamic Conformational Change**

*Masaaki Suzuki and Atsuhiro Osuka**

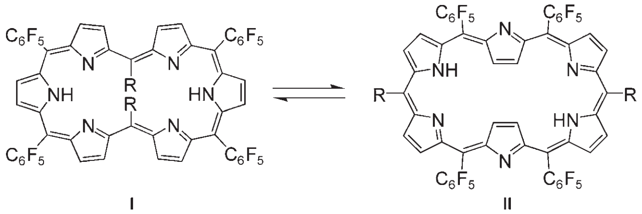
As a rare and interesting example of an intramolecular reaction of a bifunctional molecule in its folded conformation, we reported recently the cross-bridging reaction of 5,20-diethynyl-substituted hexaphyrins **1** to afford the vinylene-bridged hexaphyrins **2**.[1] The reaction is triggered by a dynamic conformational change from a rectangular conformation **II**, in which the two ethynyl groups are held apart on opposite sides of the macrocycle,[2a,b] to a spectacles-shaped conformation **I**, in which all pyrrole rings are oriented inward, and the ethynyl groups are forced into close proximity (Scheme 1).[2c] In this sense, the [26]hexaphyrins can be regarded as a convenient scaffold for forcing unsaturated meso groups located opposite one another into close contact through a dynamic conformational change. Herein, we report an intramolecular [3+2] annulation of 5-aryl 20-ethynyl [26]hexaphyrins(1.1.1.1.1.1). The meso aryl and ethynyl substituents undergo this unprecedented annulation reaction either upon thermal activation or spontaneously. In recent years, increasing attention has been focused on expanded porphyrins because of their attractive chemical, optical, and coordination properties.[2,3] However, there have been only scattered reports of transanular reactions of expanded porphyrins,[1,4] despite the great potential of such reactions for the creation of new skeletons.



1a: R = TIPS
1b: R = Ph



2a: R = TIPS
2b: R = Ph



Scheme 1. A dynamic conformational change (from conformation **II** to conformation **I**) in a hexaphyrin brings the substituents R in the 5- and 20-positions into close proximity.

The 5-triisopropylsilylethynyl-, 20-phenyl-substituted hexaphyrin **3a** was prepared by the cross-condensation of 5,10-bis(pentafluorophenyl)tripyrrane, benzaldehyde, and triisopropylsilylpropargyl aldehyde in 5% yield, along with the 5,20-bis(triisopropylsilylethynyl)-substituted and 5,20-diphenyl-substituted hexaphyrins. The conformation **II** was indicated for **3a** by the ^{1}H NMR and absorption spectra. When a solution of **3a** in toluene was heated at reflux for 12 h, the annulated product **4a** was formed quantitatively (Scheme 2). The structure of **4a** was determined by single-crystal X-ray diffraction analysis to be a 2-TIPS-1,3-indenylene-bridged hexapyrrolic macrocycle with a spiro sp^3 carbon center, which disrupts the cyclic electronic conjugation, at the meso position (Figure 1).[8] The conjugated hexapyrrolic moiety of **4a** is almost planar, with a mean plane deviation of 0.134 Å. The central indenylene segment is held nearly perpendicular to this plane, with a dihedral angle of 87°.

The mass spectrum of **4a** contains a parent-ion peak at m/z 1385.2832 (m/z calcd for $C_{71}H_{41}F_{20}N_6Si$: 1385.2837), and its ^{1}H NMR spectrum is consistent with the X-ray structure (see the Supporting Information). Importantly, the two segments bisected by the indenylene bridge are not identical, as evident from the ^{1}H NMR spectrum, as one segment contains an NH,N,NH tripyrrolic sequence, and the other an N,NH,N tripyrrolic sequence. Whereas **3a** has an absorption spectrum that is characteristic of aromatic [26]hexaphyrins(1.1.1.1.1.1),[2] **4a** has an ill-defined absorption spectrum that is spread over 1000 nm, in accord with the disruption of cyclic conjugation (Figure 2).

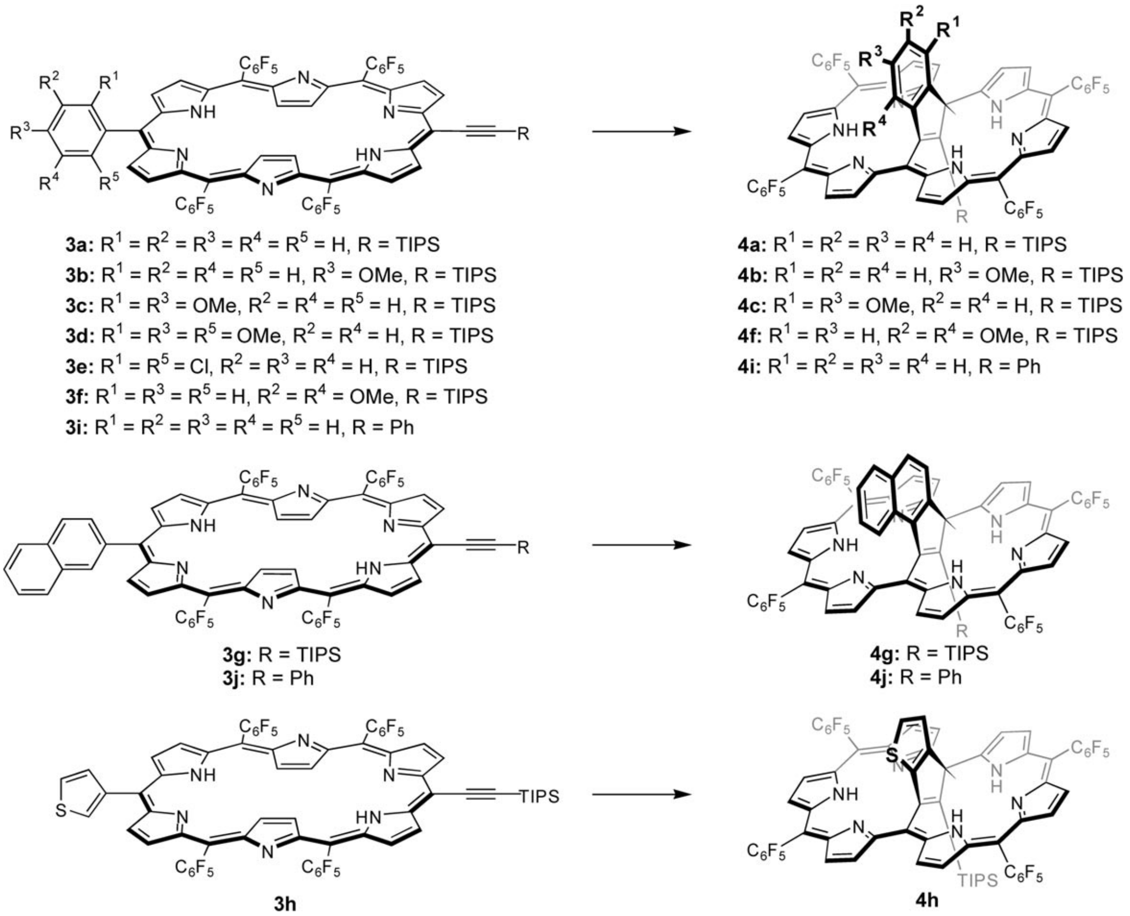
When heated at reflux in toluene, hexaphyrins **3b** and **3c** underwent the same intramolecular annulation reaction to

---

[*] Dr. M. Suzuki, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science, Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
Fax (+81) 75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp
Homepage: http://kuchem.kyoto-u.ac.jp/shuyu/index.html

[**] This research was partly supported by a Grant-in-Aid (B) (No. 17350017) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. M.S. thanks the JSPS for a Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 2. Intramolecular [3+2] annulation of 5-aryl-, 20-ethynyl-substituted [26]hexaphyrins **3** to give the 1,3-indenylene-bridged macrocycles **4**. TIPS: triisopropylsilyl.

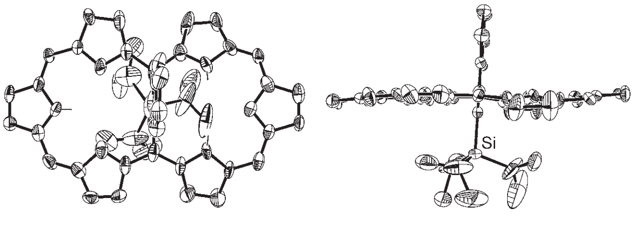


Figure 1. X-ray crystal structure of **4a**. The meso aryl groups and hydrogen atoms other than the nitrogen-bonded ones are omitted for clarity. Thermal ellipsoids are scaled to the 50% probability level.

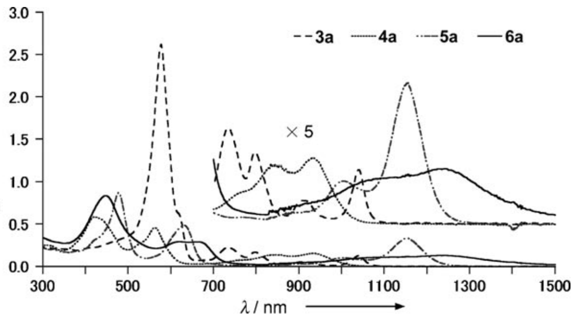
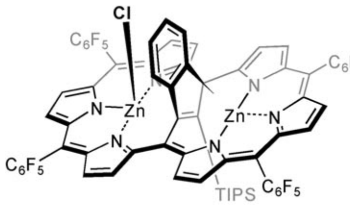


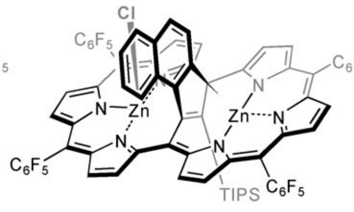
Figure 2. UV/Vis absorption spectra of **3a**, **4a**, **5a**, and **6a** in CH_2Cl_2.

give **4b** and **4c** quantitatively, whereas hexaphyrins **3d** and **3e**, which have an aryl group that is substituted in the 2- and 6-positions, are chemically robust under these conditions. In contrast, the annulated products **4f**, **4g**, and **4h** formed spontaneously during the synthesis of the corresponding hexaphyrins without particular thermal activation. The failure to isolate the putative hexaphyrins **3f**, **3g**, and **3h** is an indication of their high reactivity. These results suggest that the annulation reaction may proceed through a nucleophilic attack of the meso aryl group at the β carbon atom of the TIPS-substituted ethynyl group, as the *ortho* positions of the meso aryl substituents of **3g** and **3h** that are involved in the annulation are more nucleophilic than the equivalent positions in the other hexaphyrins. However, the spontaneous formation of the annulated products **4i** and **4j** during the synthesis of **3i** and **3j** also indicated that a nonpolarizable triple bond can participate in the reaction. The observed higher reactivity of the putative hexaphyrins **3i** and **3j** may be ascribed to the lower steric hindrance of the phenylethynyl group relative to that of the TIPS-substituted ethynyl group. Thus, we believe that the steric compression effect is more crucial for the present annulation reaction than the electro- or nucleophilicity of the participating groups.

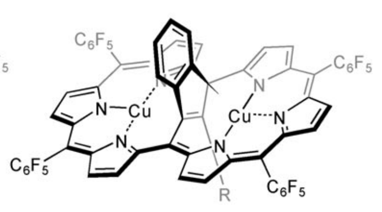
The annulated products contain two different tripyrrolic cavities, which may be used for the coordination of two metal



5a



5g



6a

ions. This idea prompted us to subject **4a** and **4g** to zincation by treatment with $ZnCl_2$ in a methanol/CH_2Cl_2 mixture. The biszinc(II) complexes **5a** and **5g** were isolated quantitatively. The mass spectra of these complexes show peaks due to the $[M-Cl]^+$ ion at m/z 1513.1084 (m/z calcd for $C_{71}H_{37}F_{20}N_6SiZn_2$: 1513.1083) and m/z 1563.1242 (m/z calcd for $C_{75}H_{39}F_{20}N_6SiZn_2$: 1563.1241), respectively, and the ^1H NMR spectra are fully consistent with the assigned structures (see the Supporting Information).

The single-crystal X-ray structure of **5g** (Figure 3)[8] revealed that one Zn^{II} ion (Zn(2)) is bound at the monoanionic tridentate (N,NH,N) segment of the molecule with Zn–N distances of 2.03, 1.99, and 2.04 Å, and that a chloride ion is attached as a charge-balancing anion. The other Zn^{II} ion (Zn(1)) is coordinated to the dianionic tridentate (NH,N,NH) segment with Zn–N distances of 1.97, 1.99, and 1.98 Å, and a molecule of pyridine, which was used in the recrystallization, is coordinated to this zinc ion on the same side of the molecule as the chloride ligand, probably to avoid the steric bulk of the TIPS group. The complex is roughly planar with a mean plane deviation of the hexapyrrolic conjugated network of 0.182 Å. The zinc atoms are displaced from the plane by 0.955 (Zn(2)) and 0.724 Å (Zn(1)). In analogy with the bis(Zn^{II}) complex of **2b**,[1] the distances between the Zn atoms and the 3*H*-benz[*g*]indenylene carbon atoms are in the range 2.79–3.13 Å. These distances are shorter than the sum of the van der Waals radii (3.17 Å)[5] and suggest the existence of favorable Zn^{II}–alkene interactions of an η^2 nature.[6,7] A relatively strong absorption band was observed for complex **5a** at 1156 nm (Figure 2).

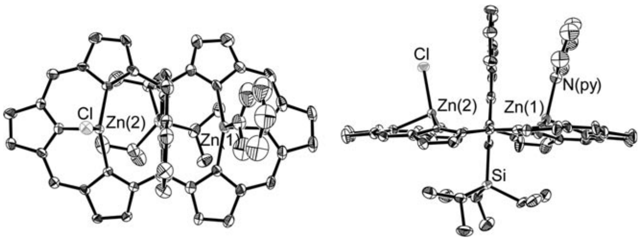


Figure 3. X-ray crystal structure of **5g**. The meso aryl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids are scaled to the 50% probability level.

Finally, we explored the formation of a mixed-valence complex from **4**. The treatment of **4a** with CuCl in a methanol/CH_2Cl_2 mixture provided the Cu^I/Cu^{II} mixed-valence complex **6a** in 84% yield. The solid-state X-ray crystal structure of **6a** revealed a planar skeleton with a mean planar deviation of 0.130 Å.[8] The Cu^I and Cu^{II} atoms are displaced by 0.072 and 0.153 Å, respectively, from the plane (Figure 4). The Cu–N distances are in the range 1.90–2.00 Å, and the distances between the Cu atoms and the indenylene carbon atoms are in the range 2.26–2.87 Å. These distances again suggest favorable Cu^I/Cu^{II}–olefin interactions. Curiously, the absorption spectrum of **6a** spans around 1500 nm (Figure 2). Overall, the structure of **6a** is similar to that of **5g**, but it accommodates the Cu^I and Cu^{II} ions in a neutral state without a charge-balancing extra ligand. In agreement with the mixed-valence state, **6a** exhibits a virtually temperature independent magnetic-susceptibility value ($\chi_p T$) of approximately 0.4 $emu\,K\,mol^{-1}$ (see the Supporting Information), which corresponds to an $S = 1/2$ state. These results indicate that the annulated product can serve as a ligand for the effective formation of a mixed-valence complex.

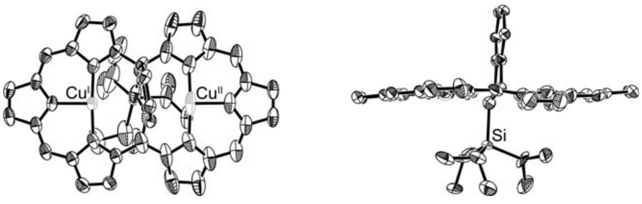


Figure 4. X-ray crystal structure of **6a**. The meso aryl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids are scaled to the 50% probability level.

In summary, we found that a novel [3+2] annulation between a simple aryl group and an ethynyl group proceeds efficiently on the hexaphyrin scaffold as a result of dynamic conformational changes. The resulting indenylene-bridged macrocycles provide preorganized twin tripyrrolic ligands that can serve as efficient ligands for mixed-valence complexes. Further exploration of different modes of reaction on the hexaphyrin scaffold on the basis of molecular compression is under way.

Received: March 5, 2007
Published online: June 5, 2007

Keywords: annulation · conformational dynamics · macrocyclic ligands · porphyrinoids · zinc

---

[1] M. Suzuki, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 464.

[2] a) M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* **1999**, 385; b) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190; c) M. Suzuki, A. Osuka, *Chem. Eur. J.* **2007**, *13*, 196.

[3] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267; b) T. D. Lash, *Angew. Chem.* **2000**, *112*, 1833; *Angew. Chem. Int. Ed.* **2000**, *39*, 1763; c) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; d) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; e) T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676; f) A. Ghosh, *Angew. Chem.* **2004**, *116*, 1952; *Angew. Chem. Int. Ed.* **2004**, *43*, 1918.

[4] a) E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzym, K. N. Houk, *Angew. Chem.* **2003**, *115*, 2964; *Angew. Chem. Int. Ed.* **2003**, *42*, 2857; b) Y. Tanaka, W. Hoshino, S. Shimizu, K. Youfu, N. Aratani, N. Maruyama, S. Fujita, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 3046–3047.

[5] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[6] a) R. Benn, H. Grondey, H. Lehmkuhl, H. Nehl, K. Angermund, C. Krüger, *Angew. Chem.* **1987**, *99*, 1303; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1279; b) A. Krivokapic, A. R. Cowley, H. L. Anderson, *J. Org. Chem.* **2003**, *68*, 1089.

[7] Similar interactions of an η^2 nature were reported for $\mathrm{Cd^{II}}$–tetraphenyl-*p*-benziporphyrin: M. Stepien, L. Latos-Grazynski, *J. Am. Chem. Soc.* **2002**, *124*, 3838.

[8] Crystal data for **4a**: $C_{71}H_{40}F_{20}N_6Si\cdot 2\,(CH_2Cl_2)$ ($M_r = 1555$), orthorhombic, space group $Pna2_1$ (No. 33), $a = 9.8643(9)$, $b = 23.667(2)$, $c = 28.153(3)$ Å, $V = 6572.5(10)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.572\ \mathrm{g\,cm^{-3}}$, $T = -183\,°\mathrm{C}$, $R_1 = 0.100$ ($I > 2\sigma(I)$), $R_W = 0.306$ (all data), GOF = 1.029. Crystal data for **5g**: $2(C_{75}H_{39}F_{20}N_6SiZn_2Cl)\cdot 2(C_5H_5N)\cdot 5\text{-}(CH_3CN)\cdot H_3CCN$ (hydrogen atoms not defined in acetonitrile) ($M_r = 3614$), orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 18.9871(18)$, $b = 27.174(3)$, $c = 30.942(3)$ Å, $V = 15\,965(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.572\ \mathrm{g\,cm^{-3}}$, $T = -183\,°\mathrm{C}$, $R_1 = 0.078$ ($I > 2\sigma(I)$), $R_W = 0.213$ (all data), GOF = 1.033. Crystal data for **6a**: $C_{71}H_{37}F_{20}N_6SiCu_2\cdot 4\,H_2O$ (hydrogen atoms not defined in water) ($M_r = 1573$), monoclinic, space group $P2_1/a$ (No. 14), $a = 9.9094(14)$, $b = 23.468(3)$, $c = 28.280(4)$ Å, $V = 6576.7(16)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.589\ \mathrm{g\,cm^{-3}}$, $T = -183\,°\mathrm{C}$, $R_1 = 0.0998$ ($I > 2\sigma(I)$), $R_W = 0.297$ (all data), GOF = 1.026. The original space group of **6a** was orthorhombic $Pna2_1$ (No. 33). CCDC-638473 for **4a**, CCDC-638474 for **5g**, and CCDC-638475 for **6a** 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.