Porphyrinoids

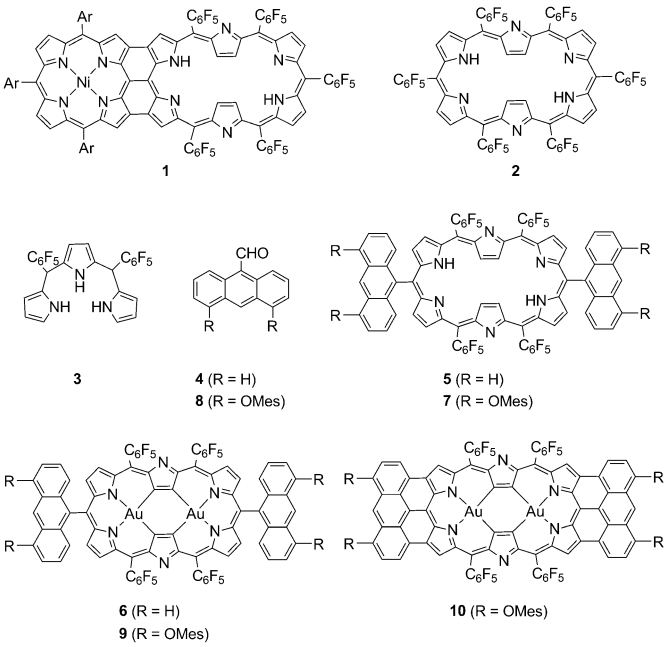
DOI: 10.1002/anie.201204446

Hexaphyrin Fused to Two Anthracenes**

Koji Naoda, Hirotaka Mori, Naoki Aratani, Byung Sun Lee, Dongho Kim, and Atsuhiro Osuka**

One of the current topics in porphyrin chemistry is the synthesis of highly conjugated porphyrins that exhibit absorption bands reaching into the near infrared (NIR) region and a large range of nonlinear optical properties; such molecules are promising in the fields of organic semiconductors and photovoltaics, two-photon excited photodynamic therapy, and all-optical processing.[1–3] Effective synthetic strategies are to bridge porphyrins with a conjugative linker,[2b,4] to directly fuse porphyrins,[5] and to fuse aromatic segments to the porphyrin periphery.[6–8] Conjugated porphyrins prepared by these strategies exhibit strongly perturbed optical and electronic properties, thus reflecting the flexible electronic nature of porphyrins. Anderson and co-workers have demonstrated that the fusion of anthracene is effective in the expansion of the conjugated network of porphyrins by exploring porphyrins fused to one, two, and four anthracenes, all of which display highly red-shifted Q bands ($\lambda_{max} = 855$, 973, and 1417 nm, respectively).[7]

In recent years, expanded porphyrins have emerged as new functional chromophores, which encompass larger conjugated networks and are electronically more flexible than porphyrins.[9] In this sense, these expanded porphyrins may be more promising as a component of highly conjugated chromophores, when fused with appropriate aromatic segments. Despite this potential, except for porphyrin-fused hexaphyrins **1** (Scheme 1), the peripheral fusion reactions of expanded porphyrins have been rarely studied,[10] largely because of synthetic difficulties. We envisioned that the fusion of anthracenes to rectangular hexaphyrins, such as **2**,[11] would be feasible, because their short sides are similar in length to the long side of anthracene, and the resultant anthracene-fused [26]hexaphyrins would show highly perturbed optical and electrochemical properties. Herein, we report the synthesis of **10**, a [26]hexaphyrin fused to two anthracenes, which exhibits an extensively red-shifted and sharp absorption band reaching into NIR region, and multiple reversible redox potentials. 5,20-Dianthryl-substituted [26]hexaphyrin **5** was prepared by the condensation of tripyrrane **3** and 9-formylanthracene (**4**) in the presence of methanesulfonic acid (MSA) at 0 °C for 2 hours followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[12] For easier separation, **5** was reduced with $NaBH_4$ to its [28]hexaphyrin congener, which after purification on a silica gel column was oxidized back to **5** with MnO_2. After recrystallization, hexaphyrin **5** was obtained in 26% yield as a brown solid. The spectroscopic data of **5** are fully consistent with the proposed structure, which was confirmed by X-ray diffraction analysis (see the Supporting Information).[13] One anthryl group was attached to each of the two short sides of the hexaphyrin;[14] this structure is favorable for our purpose. Oxidative fusion reactions of **5** were attempted with DDQ/$Sc(OTf)_3$,[7d] and $FeCl_3$,[15] but neither attempt was successful. We thought that the bis(Au^{III}) complex **6**, which is a more-conformationally rigid substrate, and might be more suitable for the oxidative fusion reaction. Our previous metalation procedure using $Na[AuCl_4]\cdot 2H_2O$[16] did not work well for **5**, but we found that stirring a solution of **5** in CH_2Cl_2/MeOH



Scheme 1. Substrates and hexaphyrin derivatives. Ar = 3,5-di-*tert*-butylphenyl, Mes = mesityl.

[*] K. Naoda, H. Mori, Dr. N. Aratani, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University, Sakyo-ku, Kyoto 606-8502 (Japan)
E-mail: osuka@kuchem.kyoto-u.ac.jp
Dr. N. Aratani
PRESTO (Japan) Science and Technology Agency (Japan)
B. S. Lee, Prof. Dr. D. Kim
Spectroscopy Laboratory for Functional π-Electronic Systems and Department of Chemistry, Yonsei University
Seoul 120-749 (Korea)
E-mail: dongho@yonsei.ac.kr

[**] The work at Kyoto was supported by Grants-in-Aid (Nos. 22245006 (A) and 20108001 "pi-Space") for Scientific Research from MEXT of Japan. The work at Seoul was supported by the Midcareer Researcher Program (2010-0029668) and World Class University (R32-2010-000-10217-0) Programs of MEST of Korea.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204446.

(4:1) in the presence of $Na[AuCl_4]\cdot 2H_2O$, NaOAc, and Ag_2CO_3 resulted in a significant improvement in metalation, to give **6** in 47% yield. Disappointingly, however, the oxidative fusion reaction of **6** failed, merely giving a small amount of chlorinated products.

We thus tried a different substrate, [26]hexaphyrin **7**, bearing two 1,8-di(mesityloxy)anthracen-10-yl substituents, which are more electron-donating than the anthryl substituents and hence this substrate should be more appropriate for the oxidative fusion reaction.[7,8c] 1,8-Dimesityloxy-10-formylanthracene **8** was prepared by reported synthetic routes[7] to which we had added our own improvements (see the Supporting Information). Then, the MSA-catalyzed condensation of **3** and **8** produced [26]hexaphyrin **7** in 29% yield. The spectroscopic data of **7** are fully consistent with the proposed structure, which was confirmed by an X-ray crystallographic analysis performed on a single crystal of **7** (Figure 1a). This analysis revealed that the two anthryl groups are attached to the short sides of the hexaphyrin similarly to the case of **5**, and the hexaphyrin moiety is more planar than that of **5**.[13]

Next, we examined the oxidative fusion reaction of **7**; this reaction did not work well either with DDQ/$Sc(OTf)_3$ or $FeCl_3$. Thus, Au^{III} metalation of **7** was conducted under the same conditions to give bis(Au^{III}) complex **9** in 36% yield. The single-crystal X-ray analysis displays a considerably bent structure[13] of **9**, as a consequence of Au^{III} metalation (Figure 1b).[16] Gratifyingly, heating of a toluene solution of **9** to reflux in the presence of 10 equivalents of DDQ and 10 equivalents of $Sc(OTf)_3$ for 5 hours caused a drastic color change with formation of a discrete product that eluted slower than **9** on TLC. After the standard work up, compound **10**, a [26]hexaphyrin fused to two anthracenes was obtained in 24% yield as a dark blue solid, which showed a characteristic greenish blue color in CH_2Cl_2. High resolution electrospray ionization time-of-flight mass spectroscopy detected the parent ion peak of **10** at $m/z = 2398.3689$, which was smaller by 8 mass units than that of **9**. The ^1H NMR spectrum is simple, featuring a singlet at 9.94 ppm that corresponds to the outer β-protons of the hexaphyrin and a pair of doublets at 9.50 and 7.22 ppm ($J = 8.4$ Hz) that correspond to the 2,3- and 6,7-anthryl protons, thus indicating the formation of the doubly fused structure. The unambiguous structural determination of **10** was obtained by X-ray analysis.[13] Crystals of **10** were grown by allowing hexane vapor to diffuse into its CH_2Cl_2 solution. Compound **10** displays a remarkably elongated, rectangular (7.28 × 19.94 Å), almost planar structure; the dihedral angle of the two anthracene segments is 141.3° (Figure 2). In the crystal-packing structure of **10**, an infinite molecular network is observed, and features an alternate packing arrangement wherein two molecules are positioned in an offset manner with their concave sides facing each other so that half the molecule overlaps (see the Supporting Information, Figure S8-8). This arrangement is held by favorable C–H/π interactions between the mesityloxy substituents and hexaphyrin.

Figure 3 shows the absorption spectra of solutions of **9** and **10** in CH_2Cl_2. The bis(Au^{III}) hexaphyrin complex **9** exhibits a slightly split Soret-like band at 672 nm, which is red-shifted from that of **7** by 96 nm, and Q-band-like bands at 831 and

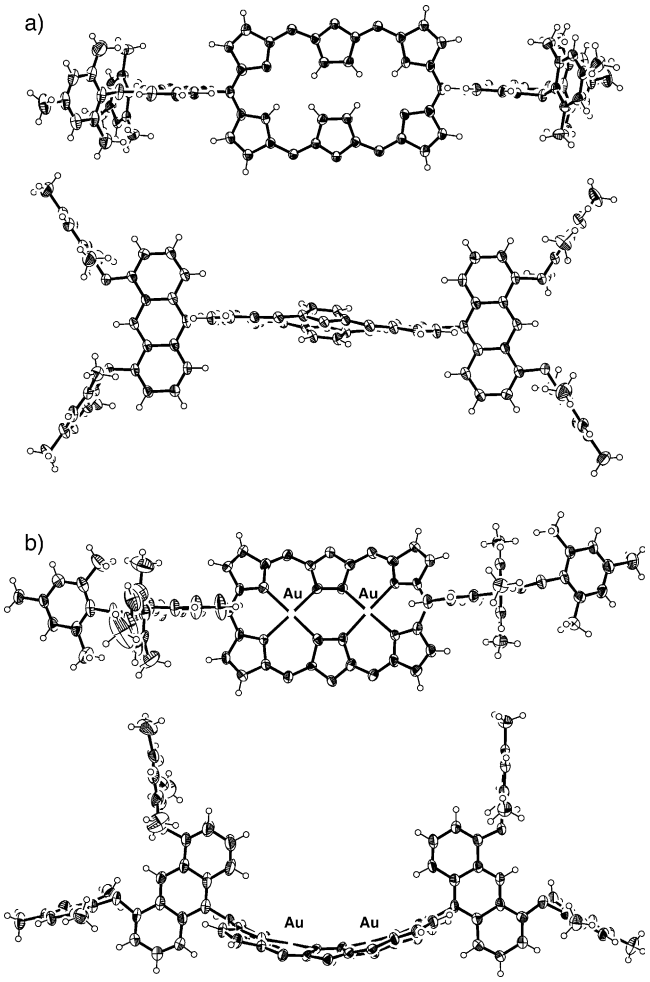


Figure 1. X-Ray crystal structures of a) **7** and b) **9**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to 50% probability. Solvent molecules and pentafluorophenyl groups are omitted for clarity.

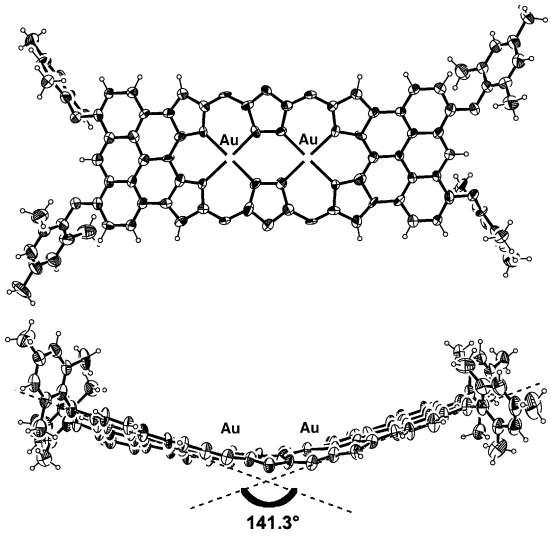


Figure 2. X-Ray crystal structure of **10**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to 30% probability. Solvent molecules and pentafluorophenyl groups are omitted for clarity.

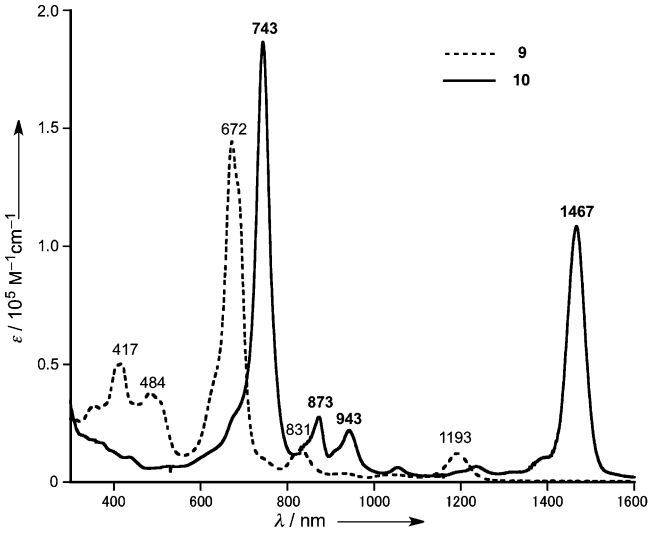


Figure 3. UV/Vis/NIR absorption spectra of **9** and **10** in CH_2Cl_2.

1193 nm. These spectral features are common for bis(Au^{III}) hexaphyrins, as reported previously.[16] The absorption spectrum of **10** exhibits a red-shifted and intensified Soret-like band at 743 nm and Q-band-like bands at 873, 943, and 1467 nm. Of these bands, the most red-shifted band is remarkably sharp and intensified (optical HOMO–LUMO gap; 0.84 eV, fwhm = 223 cm^{-1}). These absorption characteristics originate from the elongated conjugation along the long molecular axis of **10**.

Third-order nonlinear optical (NLO) responses of **9** and **10** are also of interest in view of their extended π-conjugation pathways through fused anthracene units. Two-photon absorption (TPA) measurements were conducted for **9** and **10** by using a wavelength-scanning open-aperture Z-scan method in the wavelength region ranging from 1400 to 2400 nm and from 1700 to 2400 nm, respectively, where one-photon absorption contribution is negligible (see the Supporting Information, Figure S11).[17] It was difficult to measure accurate TPA values by photoexcitations shorter than 1400 for **9,** and 1700 nm for **10**. Bis(Au^{III}) hexaphyrin complex **9** showed the maximum TPA cross section $\sigma^{(2)}$ value of 2500 GM by photoexcitation at 1700 nm, whereas anthracene-fused [26]hexaphyrin **10** exhibited the maximum $\sigma^{(2)}$ value of 7600 GM by photoexcitation at the same wavelength. The much higher $\sigma^{(2)}$ value for **10** compared to that for **9** can be explained by the extended π-conjugation in **10**. Furthermore, both **9** and **10** compounds showed larger TPA values than hexakis(pentafluorophenyl) substituted [26]hexaphyrin **2** (ca. 1000 GM). This result can be explained by the effect structural changes can have on donor(D)/acceptor(A)-type multichromophoric systems: the introduction of electron-rich anthryl substituents and electron-deficient pentafluorophenyl substituents perturbs the charge redistribution, and elongates the effective π-conjugation length. We can conclude that a combination of elongation of the π-conjugation, as well as D/A perturbation to hexaphyrin improves the overall TPA properties.

The electrochemical properties of **5**, **6**, **7**, **9**, and **10** were studied by cyclic voltammetry (Figure 4). Bis(Au^{III}) metal-

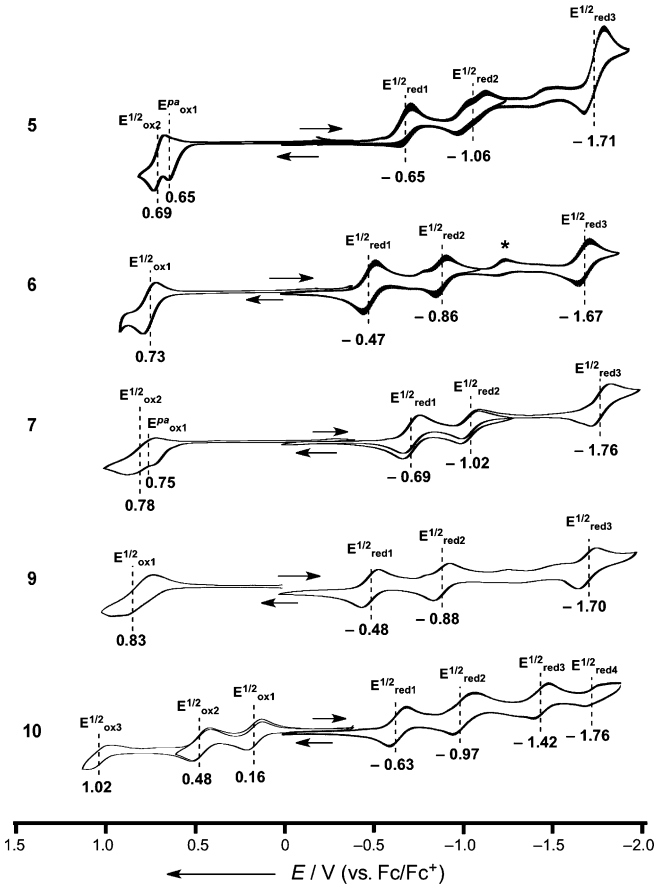


Figure 4. Cyclic Voltammograms of **5**, **6**, **7**, **9**, and **10** in anhydrous CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte, and $Ag/AgClO_4$ as reference electrode. Fc/Fc^+ was used as external reference.

ation of the hexaphyrins **5** and **7** led to positive shifts of the waves as a result of the electron-withdrawing property of Au^{III} ion. Also, the replacement of the unsubstituted anthryl groups by electron-rich ones (**5**→**7** and **6**→**9**) caused negative shifts of the waves. The cyclic voltammogram of **10** in CH_2Cl_2 is remarkable, displaying seven redox potentials at 1.02, 0.48, 0.16, −0.63, −0.97, −1.42, and −1.76 V all as fully reversible waves, thus implying multicharge storage ability of **10**. The fused structure causes low oxidation potentials. The electrochemical HOMO–LUMO gap is thus 0.79 eV. DFT calculations at the B3LYP/6-31G(d) level using the Gaussian package revealed that **10** has a more delocalized HOMO and LUMO than **7** and **9** (see the Supporting Information). In accord with the electrochemical studies, the HOMO of **10** is higher in energy than those of **7** and **9** and HOMO–LUMO gap of **10** has been calculated to be 1.12 eV.

In summary, bis(Au^{III}) complex **10**, containing a hexaphyrin fused to two anthracenes, was prepared and characterized. Owing to the flat and elongated rectangular conjugated network, **10** displays a remarkably red-shifted and sharp Q-band-like band at 1467 nm, higher reversible oxidation potentials, multicharge storage ability, and a large TPA cross-section value. Hence, this work demonstrates the utility of [26]hexaphyrin as an electronically more-flexible unit to create extensively π-conjugated networks.

Received: June 8, 2012
Published online: August 2, 2012

Keywords: anthracene · conjugation · hexaphyrin · porphyrinoids · two-photon absorption

[1] a) M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771; b) H. L. Anderson, *Chem. Commun.* **1999**, 2323; c) D. P. Arnold, *Synlett* **2000**, 296; d) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57; e) M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, E. M. N. Mhuircheartaigh, *Adv. Mater.* **2007**, *19*, 2737; f) M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem.* **2009**, *121*, 3292; *Angew. Chem. Int. Ed.* **2009**, *48*, 3244.

[2] a) D. P. Arnold, G. A. Heath, *J. Am. Chem. Soc.* **1993**, *115*, 12197; b) V. S.-Y. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105; c) L. Jaquinod, O. Siri, R. G. Khoury, K. M. Smith, *Chem. Commun.* **1998**, 1261; d) M. Hoffmann, C. J. Wilson, B. Odell, H. L. Anderson, *Angew. Chem.* **2007**, *119*, 3183; *Angew. Chem. Int. Ed.* **2007**, *46*, 3122.

[3] a) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735; b) N. Aratani, D. Kim, A. Osuka, *Chem. Asian J.* **2009**, *4*, 1172.

[4] a) H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 972.

[5] a) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, A. Osuka, *Angew. Chem.* **2000**, *112*, 572; *Angew. Chem. Int. Ed.* **2000**, *39*, 558; b) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549; c) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304; d) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79; e) Y. Nakamura, S. Y. Young, T. Tanaka, N. Aratani, J. M. Kim, K. S. Kim, D. Kim, A. Osuka, *Chem. Eur. J.* **2008**, *14*, 8289.

[6] a) M. J. Crossley, P. L. Burn, *J. Chem. Soc. Chem. Commun.* **1991**, 1569; b) H. J. Callot, E. Schaetfer, R. Cromer, F. Metz, *Tetrahedron* **1990**, *46*, 5253; c) L. Barloy, D. Dolphin, D. Dupre, T. Wijesekera, *J. Org. Chem.* **1994**, *59*, 7976; d) S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert, H. J. Callot, *J. Am. Chem. Soc.* **2002**, *124*, 6168; e) H. S. Gill, M. Harmjanz, J. Santamaria, I. Finger, M. J. Scott, *Angew. Chem.* **2004**, *116*, 491; *Angew. Chem. Int. Ed.* **2004**, *43*, 485; f) O. Yamane, K. Sugiura, H. Miyasaka, K. Nakamura, T. Fujimoto, K. Nakamura, T. Kaneda, Y. Sakata, M. Yamashita, *Chem. Lett.* **2004**, *33*, 40; g) S. Fox, R. W. Boyle, *Chem. Commun.* **2004**, 1322; h) M. Pawlicki, M. Morisue, N. K. S. Davis, D. G. McLean, J. E. Haley, E. Beuerman, M. Drobizhev, A. Rebane, A. L. Thompson, S. I. Pascu, G. Accorsi, N. Armaroli, H. L. Anderson, *Chem. Sci.* **2012**, *3*, 1541.

[7] a) N. K. Davis, M. Pawlicki, H. L. Anderson, *Org. Lett.* **2008**, *10*, 3945; b) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *Org. Lett.* **2010**, *12*, 2124; c) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *J. Am. Chem. Soc.* **2011**, *133*, 30.

[8] a) C. Jiao, L. Zhu, J. Wu, *Chem. Eur. J.* **2011**, *17*, 6610; b) C. Jiao, K.-W. Huang, C. Chi, J. Wu, *J. Org. Chem.* **2011**, *76*, 661; c) C. Jiao, N. Zu, K.-W. Huang, P. Wang, J. Wu, *Org. Lett.* **2011**, *13*, 3652.

[9] a) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; b) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795; c) T. K. Chandrashekar, A. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676; d) Z. S. Yoon, A. Osuka, D. Kim, *Nat. Chem.* **2009**, *1*, 113; e) M. Stępień, N. Spritta, L. Latos-Grażyński, *Angew. Chem.* **2011**, *123*, 4376; *Angew. Chem. Int. Ed.* **2011**, *50*, 4288; f) S. Saito, A. Osuka, *Angew. Chem.* **2011**, *123*, 4432; *Angew. Chem. Int. Ed.* **2011**, *50*, 4342.

[10] a) T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Chem. Sci.* **2011**, *2*, 1414; b) T. Tanaka, N. Aratani, A. Osuka, *Chem. Asian J.* **2012**, *7*, 889.

[11] 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.

[12] R. Taniguchi, S. Shimizu, M. Suzuki, J.-Y. Shin, H. Furuta, A. Osuka, *Tetrahedron Lett.* **2003**, *44*, 2505.

[13] CCDC 884114 (**5**), 884115 (**7**), 884116 (**9**), and 884113 (**10**) 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.

[14] Another conformer bearing two anthryl substituents on the longer side of the hexaphyrin was detected in ^{1}H NMR spectrum in $CDCl_3$ but upon heating this conformer was converted into **5**.

[15] M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267.

[16] a) S. Mori, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 8030; b) S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 11344.

[17] M. Ishida, J.-Y. Shin, J. M. Lim, B. S. Lee, M.-C. Yoon, T. Koide, J. L. Sessler, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2011**, *133*, 15533.

