Angewandte Chemie

Expanded Porphyrins

DOI: 10.1002/anie.200906017

A Stable Organic Radical Delocalized on a Highly Twisted π System Formed Upon Palladium Metalation of a Möbius Aromatic Hexaphyrin**

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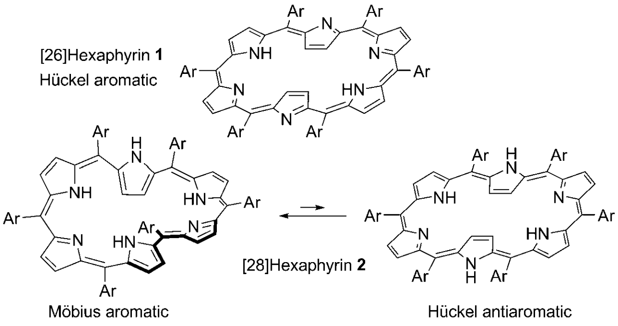
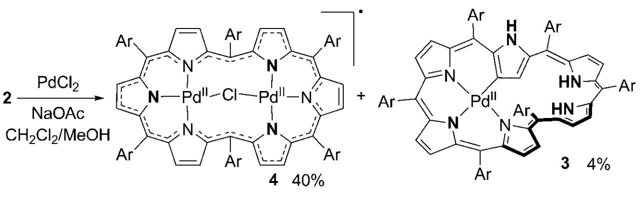
Stable organic radicals have received considerable attention recently, not only for purely scientific interest in their structures and properties, but also in applications, such as organic magnets, electronic devices, organic batteries, and optical materials.[1] To design stable organic radicals, kinetic stabilization by steric hindrance and delocalization of an unpaired electron by resonance through effective conjugation is essential to attain high stability. In most cases, the unpaired electron is delocalized on planar π-electronic systems, such as cyclopentadienyl and phenalenyl. Isolation of a stable organic radical on nonplanar π systems is quite rare.[2] However, such nonplanar stable organic radicals would have intriguing properties owing to unique features of their curved π-electronic systems.

Expanded porphyrins, which are porphyrin analogues with more than five pyrrolic subunits, have attracted much attention because of their fascinating optical, electrochemical, and coordination properties.[3] In particular, hexaphyrin(1.1.1.1.1.1) exhibits multi-redox behavior in which two stable oxidation states, namely [26]hexaphyrin **1** and [28]hexaphyrin **2**, are easily interconvertible through two-electron oxidation and reduction (Scheme 1).[4] [26]Hexaphyrin **1** exhibits distinct aromaticity in the rigid and flat structure; in contrast, [28]hexaphyrin **2** exists as a dynamic mixture of predominantly Möbius aromatic conformations along with a minor Hückel-antiaromatic planar structure.



Scheme 1. [26]Hexaphyrin and [28]hexaphyrin. Ar = C_6F_5.

Although the metalation of **1** has been extensively examined,[5] free-base **2** remains unexplored in coordination chemistry.[6] Palladium metalation of **1** provides a Möbius-aromatic [28]hexaphyrin monopalladium complex **3**.[5c] Consequently, we anticipated the formation of the same Möbius-aromatic complex **3** from **2** with palladium salts; however, this was not to be the case. Treatment of **2** with $PdCl_2$ in CH_2Cl_2/MeOH under a nitrogen atmosphere led to complex **4** in 40% yield as a major product, along with **3** in 4% yield (Scheme 2).[7] The new complex **4** was air- and moisture-stable, both in solid and solution states. High-resolution electrospray–ionization time-of-flight (HR-ESI-TOF) mass measurement of **4** has the parent-ion peak at $m/z = 1706.8417$ ($[M]^-$; calcd for $C_{66}H_{12}N_6F_{30}Pd_2Cl^-$: 1706.8421), thus revealing the product is a bis(palladium) complex. However, the complex **4** did not exhibit any clear ^{1}H NMR spectroscopy



Scheme 2. Palladium insertion to [28]hexaphyrin. Ar = C_6F_5.

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[**] This work was supported by Grants-in-Aid for Scientific Research (Nos 19205006, 20108006 "pi-Space", and 21655013) from MEXT (Japan). We thank Dr. Mitsuo Shoji (Nagoya University) for his help on calculations. H.R. acknowledges the JSPS for a postdoctoral fellowship. The work at Yonsei University was supported by the Star Faculty and World Class University (2008–1955) programs from the Ministry of Education, Science and Technology, Korea.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906017.

signals. To our surprise, the single-crystal X-ray diffraction analysis of **4** revealed its doubly twisted structure (Figure 1).[8] Each palladium ion is coordinated by three nitrogen atoms and one μ-chloride ligand, and no counterion is found in the lattice.

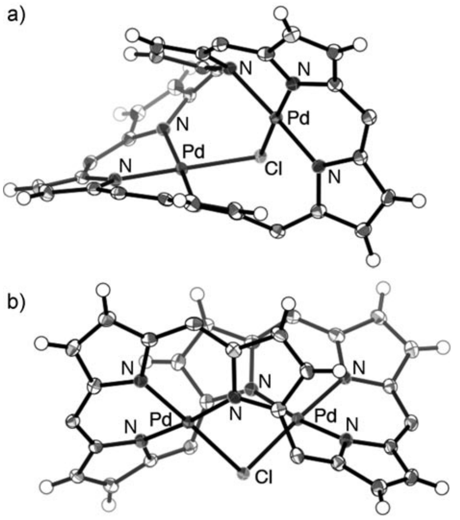

Figure 1. a,b) Two views of the X-ray crystal structure of **4** (ellipsoids set at 50% probability; *meso*-pentafluorophenyl substituents are omitted for clarity).

The lack of clear ^{1}H NMR spectroscopy signals can be explained by the presence of an unpaired electron. The ESR spectrum of a powder sample of **4** in at 6 K exhibited a distinct signal with $g = 2.0084$, 1.9966, and 1.9412 (Figure 2 a). The absence of any signals in the half-field region suggested its mono-radical nature. The radical character of **4** was further supported by temperature-dependent magnetic susceptibility measurement by SQUID magnetometry (Figure 2 b). The bis(palladium) complex **4** has a χT value of 0.345 emu K mol^{-1} at 300 K, thus clearly indicating its $S = 1/2$ state. The χT plot was reproduced by the Curie–Weiss model, with a Weiss temperature $\theta = -3.63$ K, which indicated an intermolecular antiferromagnetic interaction below 20 K. Theoretical calculations on **4** by the DFT method at the UB3LYP/631SDD[9]//UB3LYP/LANL2DZ level indicated marginal spin density on the palladium centers (0.004589, Mulliken spin density), thus strongly suggesting that **4** consists of two palladium(II) centers and a nonplanar neutral hexaphyin π radical, which is formally a 27π hexaphyrin.[10] The square-planar coordination around palladium atoms also supports the palladium(II) oxidation state. The calculated g values (2.0105, 1.9986, 1.9400) by the GIAO method are in good agreement with the experimental values, thus validating these theoretical calculations. Importantly, the spin density was delocalized over all of the highly twisted macrocyclic hexaphyrin ligand (Figure 2 c). The large anisotropic shift of the g value could be derived from small but non-negligible spin density on the palladium centers.

The absorption spectrum of **4** exhibits split Soret bands at about 650–700 nm (Figure 3). Interestingly, the absorption at

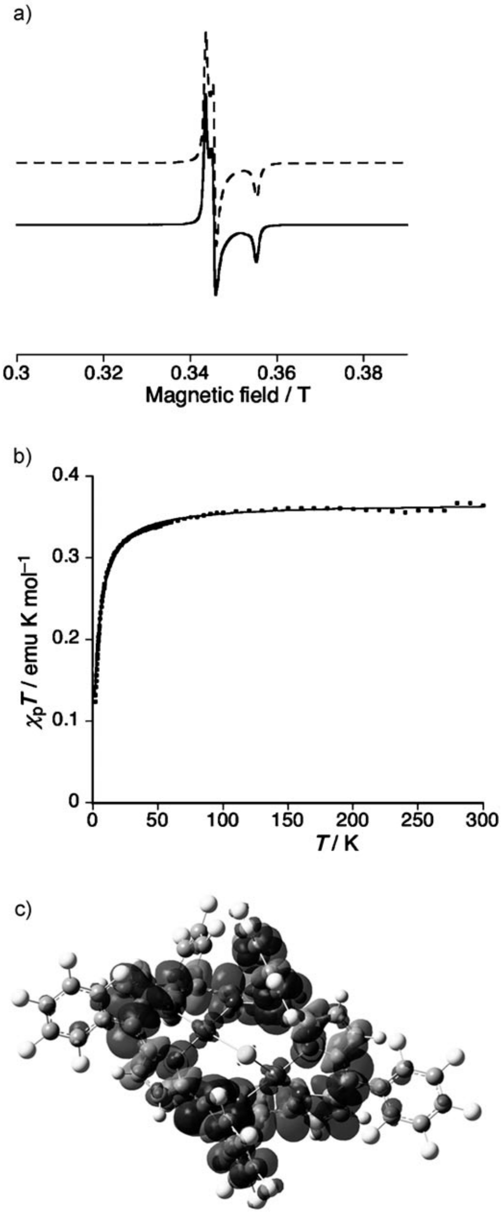

Figure 2. a) ESR spectrum at 6 K (—— observed, ••••• simulated). b) Temperature-dependent magnetic susceptibility of **4** in the solid state (••••• observed, —— calculated). c) Calculated spin density at the B3 LPY/631SDD level.

circa 1500 nm reaches deep into the near infrared region, and is substantially red-shifted relative to **1**, **2**, and metal complexes of hexaphyrins. These unique features probably resulted from the radical character of **4**. In fact, the TD-DFT calculation indicates the absorption band around 1500 nm is originated from the transition of β spin in the highest doubly occupied orbital to the SOMO (Supporting Information). These results demonstrate the prospective property of stable π radicals for NIR materials.

Development of organic molecules with large two-photon absorption (TPA) cross-section values $\sigma^{(2)}$ is desirable because of their potential applications in diverse fields.[11] However, understanding of factors that lead to large TPA materials still

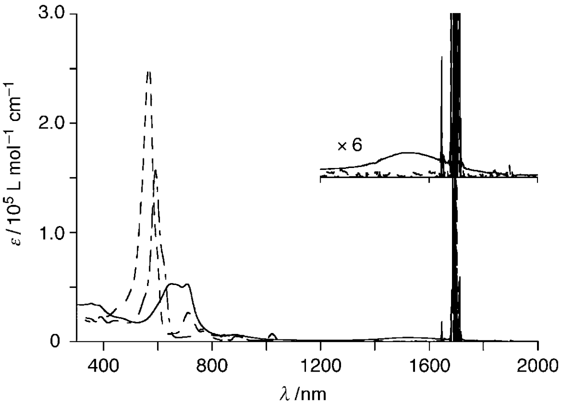

Figure 3. UV/Vis/NIR absorption spectra of **1** (-----), **2** (–---), and **4** (——) in CH_2Cl_2.

remains insufficient. Recently, a delocalized radical species is suggested to have a large TPA cross-section value.[12] In particular, the electron delocalization in neutral open-shell π-conjugated systems can contribute to the large second hyperpolarizability, leading to the generation of the efficient TPA materials. The $\sigma^{(2)}$ value of **4** was measured to be 4300 GM at 2100 nm by an open-aperture *Z*-scan method.[13] The measurements were carefully performed in the near-infrared region to avoid contribution from one-photon absorptions. This TPA cross-section value is comparable to those of metalated aromatic hexaphyrins (ca. 5000 GM) having Möbius conformation.[5g] Moreover, this value is substantially larger than those of non-aromatic expanded porphyrins (< 1000 GM). On the basis of harmonic oscillator model of aromaticity (HOMA, 0.534)[14] value, **4** can be considered to be non-aromatic (Supporting Information).[15] The relatively large TPA cross-section value of **4** might be attributed to the delocalized π-radical nature of **4**.[12c,d]

In conclusion, we have isolated a delocalized π-radical on a doubly twisted hexaphyrin π system, which is stable toward air and moisture. The high stability can be accounted for by effective delocalization of the unpaired electron and steric and electronic effects of pentafluorophenyl substituents. Furthermore, the formation of **4** probably reflects the flexible and dynamic behavior of [28]hexaphyrins. Further investigation on the metalation behavior of Möbius aromatic expanded porphyrins is currently under way in our laboratory.

Received: October 26, 2009

Keywords: aromaticity · palladium · porphyrinoids · radicals · two-photon absorption

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[1] R. G. Hicks, *Org. Biomol. Chem.* **2007**, *5*, 1321.

[2] a) Y. Morita, A. Ueda, S. Nishida, K. Fukui, T. Ise, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Angew. Chem.* **2008**, *120*, 2065; *Angew. Chem. Int. Ed.* **2008**, *47*, 2035; b) P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton, K. F. Preston, *Science* **1991**, *254*, 1183.

[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) S. Shimizu, A. Osuka, *Eur. J. Inorg. Chem.* **2006**, 1319.

[4] J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J. Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

[5] a) S. Shimizu, V. G. Anand, R. Taniguchi, K. Furukawa, T. Kato, T. Yokoyama, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 12280; b) M. Suzuki, M. C. Yoon, D. Y. Kim, J. H. Kwon, H. Furuta, D. Kim, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1754; c) S. Mori, S. Shimizu, R. Taniguchi, A. Osuka, *Inorg. Chem.* **2005**, *44*, 4127; d) S. Mori, A. Osuka, *Inorg. Chem.* **2008**, *47*, 3937; e) S. Mori, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 8030; f) S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 11344; g) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 693; *Angew. Chem. Int. Ed.* **2008**, *47*, 681.

[6] H. Rath, N. Aratani, J. M. Lim, J. S. Lee, D. Kim, H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 3762.

[7] Decomposition of **2** was observed by TLC analysis, and none of **2** was recovered.

[8] Crystal data for **4**: $C_{69}H_{15}Cl_{10}F_{30}N_6Pd_2$, $M_r = 2065.17$, monoclinic, space group $P2_1/n$ (No. 14), $a = 16.3245(18)$, $b = 23.420(3)$, $c = 19.862(2)$ Å, $\beta = 109.575(2)°$, $V = 7154.8(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.917$ g cm^{-3}, $T = 90(2)$ K, $R = 0.0353$ ($I > 2.0\sigma(I)$), $R_w = 0.1028$ (all data), GOF = 1.064 ($I > 2.0\sigma(I)$). CCDC 752335 (**4**) contains 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.

[9] 631SDD denotes a basis set consisting of SDD for Pd and 6-31G(d) for other atoms.

[10] Insertion of palladium ions is associated with one-electron oxidation of [26]hexaphyrin. A possible oxidating species could be palladium chloride.

[11] M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem.* **2009**, *121*, 3292; *Angew. Chem. Int. Ed.* **2009**, *48*, 3244.

[12] a) K. Kamada, K. Ohta, T. Kubo, A. Shimizu, Y. Morita, K. Nakasuji, R. Kishi, S. Ohta, S. Furukawa, H. Takahashi, M. Nakano, *Angew. Chem.* **2007**, *119*, 3614; *Angew. Chem. Int. Ed.* **2007**, *46*, 3544; b) S. Cho, J. M. Lim, S. Hiroto, P. Kim, H. Shinokubo, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 6412; c) M. Nakano, T. Nitta, K. Yamaguchi, B. Champagne, E. Botek, *J. Phys. Chem. A* **2004**, *108*, 4105; d) P. C. Jha, Z. Rinkevicius, H. Ågren, *J. Chem. Phys.* **2009**, *130*, 014103.

[13] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. G. Hagan, E. W. van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760.

[14] a) T. M. Krygowski, M. K. Cyranski, *Chem. Rev.* **2001**, *101*, 1385; b) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70; c) M. K. Cyrañski, T. M. Krygowski, M. Wisiorowski, N. J. R. v. E. Hommes, P. von R. Schleyer, *Angew. Chem.* **1998**, *110*, 187; *Angew. Chem. Int. Ed.* **1998**, *37*, 177.

[15] The nucleus-independent chemical shift (NICS) value was calculated to be $\delta = +3.3$ ppm for **4**, which also indicates its non-aromaticity: a) Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842; b) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.