J|A|C|S
COMMUNICATIONS

A Facile One-Pot Synthesis of *meso*-Aryl-Substituted [14]Triphyrin(2.1.1)

Zhao-Li Xue,[†] Zhen Shen,*[,†] John Mack,[‡] Daiki Kuzuhara,[§] Hiroko Yamada,*[,§] Tetsuo Okujima,[§] Noboru Ono,[§] Xiao-Zeng You,*[,†] and Nagao Kobayashi*[,‡]

State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China, Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan, PRESTO, JST, Kawaguchi 332-0012, Japan, and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

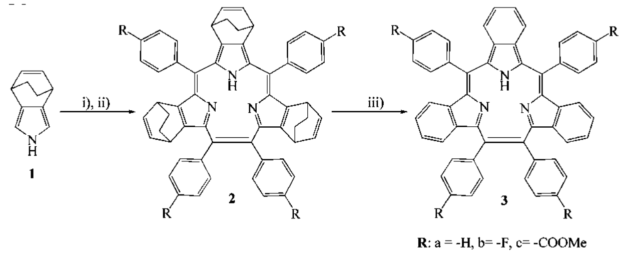
Received September 9, 2008; E-mail: zshen@nju.edu.cn; yamada@chem.sci.ehime-u.ac.jp; youxz@nju.edu.cn; nagaok@mail.tains.tohoku.ac.jp

There has been considerable interest in recent years in contracted porphyrinoids such as subphthalocyanines,[1] subporphyrazines,[2] and subporphyrins[3] due to potential applications in a variety of high technology fields.[1d,c,3e] In contrast with the porphyrins and phthalocyanines, the electronic structure of these molecules is based on a 14 π-electron system, since there are three, rather than four, pyrrole or isoindoline moieties. Although the subphthalocyanines have been the focus of considerable interest for over two decades, subporphyrins have only recently been characterized. In 2006, Osuka and co-workers reported the synthesis of tribenzosubporphyrins.[3a] Subsequently, Kobayashi and Osuka et al. independently developed synthetic protocols for meso-aryl substituted subporphyrins.[3b−g] With the exception of subpyriporphyrin,[4] [18]triphyrin(6.1.1),[5] [18]triphyrin(4.1.1),[6] [15]triphyrin(1.1.3),[7] [18]triphyrin(2.2.2), and [18]heterotriphyrin(2.2.2),[8] the subporphyrins reported to date have all been boron complexes with highly nonplanar cone-shaped conformations.[3] The development of new synthetic pathways for the structural modification of contracted porphyrinoids and the fine-tuning of their spectroscopic properties remains a considerable challenge.

In this Communication, we report the facile synthesis of a series of *meso*-aryl-substituted [14]triphyrin(2.1.1) and [14]benzotriphyrin(2.1.1) compounds. These compounds are unprecedented in porphyrinoid research since they represent the first examples of near planar metal -free contracted porphyrinoids with 14 π-electron aromatic systems containing only the standard pyrrole and isoindoline moieties of the porphyrins and tetrabenzoporphyrins. The insertion of a second sp^2-hybridized carbon atom between one of the three neighboring pairs of pyrroles eliminates the need for a central boron atom.

We initially prepared *meso*-aryl-substituted [14]triphyrin(2.1.1) serendipitously during a BF_3•Et_2O catalyzed Rothemund condensation of 4,7-dihydro-4,7-ethano-2*H*-isoindole (**1**) with aryl aldehyde in dichloromethane, Scheme 1, which was followed by an oxidation with *p*-chloranil. After silica gel column chromatography, **2a**−**c** (aryl = phenyl **2a**, 4-fluorophenyl **2b**, and 4-methylbenzoatephenyl **2c**) can be isolated in ca. 35% yield. The corresponding [14]benzotriphyrin(2.1.1) compounds **3a**−**c** can be formed quantitatively based on a retro Diels−Alder reaction of the bicyclo[2.2.2]octadiene (BCOD) rings by heating **2a**−**c** at 220 °C under vacuum (2 mmHg) for 20 min.

Scheme 1. Synthesis of *meso*-Aryl-Substituted [14]Triphyrins(2.1.1)[a]



[a] Reagents and conditions: (i) *p*-RC_6H_4CHO, $BF_3 \cdot Et_2O$, CH_2Cl_2, room temp, 12 h; (ii) *p*-chloranil, 2 h; (iii) 220 °C, 2 mmHg, 20 min.

The triphyrin structures were determined definitively by X-ray structural analysis of single-crystals of **2a** and **3a**, which were obtained by slow diffusion of hexane into the dichloromethane solution. The triphyrin macrocycle is near planar, Figure 1. The mean deviations of the ring atoms are 0.1077 Å for **2a** and 0.1309 Å for **3a**. In both **2a** and **3a**, the *meso*-phenyl rings are inclined 67.0°, 53.8°, 83.2°, and 86.5° with respect to the triphyrin mean plane. These values are larger than the phenyl dihedral angles that have been reported for the subporphyrins (ca. 50.3°),[3d] perhaps due to the greater steric hindrance caused by the presence of fused BCOD or benzene rings at the β-pyrrole positions. The average bond length between the *meso*-carbon atoms and the phenyl rings is 1.505 Å for **2a** and 1.498 Å for **3a**, Supporting Information, Table S1. The pyrrole rings are tilted relative to the triphyrin mean plane by 20.1°, 4.3°, and 6.7° in the case of **2a** and 16.6°, 7.5°, and 6.7° in the case of **3a**. The peripheral bond distances of **2a** and **3a** are very close to the values reported for subporphyrins with the exception of the pyrrole(β)−pyrrole(β) distance in **3a** (ca. 1.42 Å), which is significantly longer. The π-conjugation system is highly delocalized. For example, the C18−C19 bond between the two carbons bridging neighboring pyrroles (1.407 Å in **2a** and 1.423 Å in **3a**) is similar in length to the C19−C20 (1.424 Å in **2a** and 1.423 Å in **3a**) and C17−C18 bonds (1.438 Å in **2a** and 1.423 Å

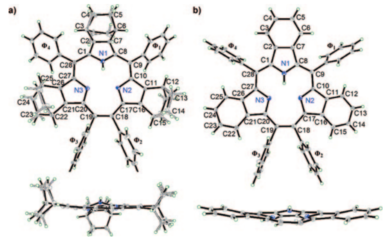


Figure 1. The crystal structures of **2a** (a) and **3a** (b) with 50% probability thermal ellipsoids (top, perspective view; below, side view with phenyl groups omitted). The solvent molecules are omitted for clarity.

[†] Nanjing University.
[‡] Tohoku University.
[§] Ehime University.

10.1021/ja8068769 CCC: $40.75

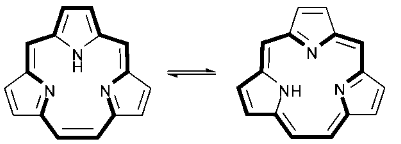


Figure 2. NH tautomers of [14]triphyrin(2.1.1).

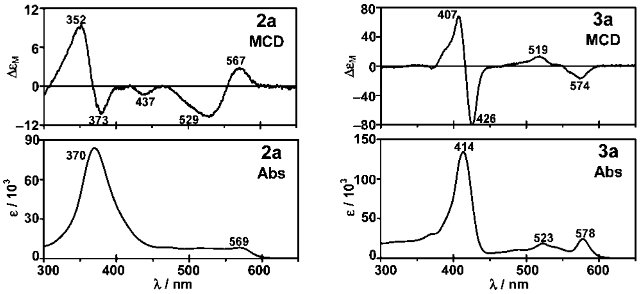


Figure 3. MCD (top) and UV−visible absorption spectra (bottom) of **2a** and **3a** in $CHCl_3$ at 298 K.

in **3a**). This, in turn, suggests that there is rapid exchange between the two NH tautomers in the solid state, Figure 2 and that the inner NH proton forms part of a three-centered hydrogen bond. The average N−N distances (2.573 Å for **2a** and 2.578 Å for **3a**) lie in the range anticipated for a very strong hydrogen-bond interaction.[9]

The singlet NH resonance was determined to lie at 7.68 ppm in the ^{1}H NMR spectrum of **2c** in $CDCl_3$, since the peak disappears upon addition of a drop of D_2O, Figure S1b. With the exception of three broad singlet peaks at 3.63, 3.35, and 2.47 ppm, which are associated with the bridge head of three bicyclo[2.2.2]octadiene groups, the other signals of the peripheral protons lie in the 7−9 ppm range, reflecting the 14 π-electron aromatic pathway of the triphyrin macrocycle. In the ^{1}H NMR spectrum of **3c**, the peaks associated with the bicyclo[2.2.2]octadiene (bridge head, bridge, and olefin) groups are replaced by new peaks associated with the fused benzene rings, Figure S1c. The identification of the NH proton resonance is straightforward based on the COSY NMR spectrum, Figure S2, since it is not scalar coupled to any other proton resonance (δ = 8.16 ppm) (Figure S1c). The inner NH resonances lie at remarkably low field. Similar signals have been reported previously for N-fused porphyrins.[9] The strong hydrogen bonding probably compensates for the diamagnetic ring-current effect. The *meso*-phenyl and N−H proton signals of **2c** and **3a** are almost insensitive to temperature during variable-temperature ^{1}H NMR experiments, Figures S3 and S4. This indicates that the barriers to the rotation of the phenyl substituents are low even at low temperatures.

The UV−visible absorption spectra of **2a** and **3a**, Figure 3, contain intense bands at 370 and 414 nm, respectively, and weaker bands in the 500−600 nm region in a pattern similar to the B (or Soret) and Q bands of the porphyrins.[10] Similar absorption band data are reported for **2b**, **2c**, **3b**, and **3c**, Figure S5. The MCD spectra are dominated by coupled pairs of oppositely signed Gaussian-shaped Faraday $\mathbf{B_0}$ terms, similar to those observed for the Q and B bands of low symmetry porphyrins and phthalocyanines.[10] The relative intensification of the visible region bands of **2a** in the MCD spectrum is comparable to that observed for the Q bands of the porphyrins based on Gouterman's 4-orbital model.[11] Solutions of diprotonated $H_3(\mathbf{2a})^{2+}$ and $H_3(\mathbf{3a})^{2+}$ species were generated by adding a trace of TFA. Most of the spectral bands exhibit marked red shifts relative to the spectra of **2a** and **3a**. Similar trends have been observed previously in the spectra of porphyrin dications.[12]

In conclusion, we have successfully synthesized a series of *meso*-aryl substituted [14]triphyrins(2.1.1) in moderate yield from mild Rothemund porphyrin condensation reactions and the corresponding [14]benzotriphyrin(2.1.1) compounds based on retro Diels−Alder reactions. These compounds represent the first examples of free-base contracted porphyrinoids with 14 π-electron aromatic systems containing only the pyrrole and isoindoline moieties of the porphyrins and tetrabenzoporphyrins. Like other contracted porphyrinoids, they have potential applications in a variety of high technology fields.[1c,d,3e]

Acknowledgment. This work was supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 18550037 to H.Y. and 19655045 to N.K.), JGC-S Scholarship Foundation (T.O.), the National Basic Research Program of China (No. 2006CB806104 and 2007CB925103), and NSFC (Nos. 20875043 and 20721002. The authors thank Dr. Kimiko Hasegawa at Rigaku Corporation for the X-ray single crystal measurements and Prof. Yi-Zhi Li at Nanjing University for solving the X-ray structures.

Supporting Information Available: Experimental procedures and spectral data for **2a**−**c** and **3a**−**c**; bond lengths and angles for **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Meller, A.; Ossko, A. *Monatsh. Chem.* **1972**, *103*, 150. (b) Claessens, C. G.; Gonzáles-Rodriguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835. (c) Torres, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2834. (d) de la Torre, G.; Vázquez, P.; Agulló-López, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723.

(2) (a) Rodríguez−Morgade, M. S.; Esperanza, S.; Torres, T.; Barberá, J. *Chem.—Eur. J.* **2005**, *11*, 354. (b) Stork, J. R.; Brewer, J. J.; Fukuda, T.; Fitzgerald, J. P.; Yee, G. T.; Nazarenko, A. Y.; Kobayashi, N.; Durfee, W. S. *Inorg. Chem.* **2006**, *45*, 6148. (c) Rodríguez−Morgade, M. S.; Claessens, C. G.; Medina, A.; Gonzáles−Rodriguez, D.; Gutiérrez-Puebla, E.; Monge, A.; Alkorta, I.; Elguero, J.; Torres, T. *Chem.—Eur. J.* **2008**, *14*, 1342.

(3) (a) Inokuma, Y.; Kwon, J. H.; Ahn, T. K.; Yoo, M.-C.; Kim, D.; Osuka, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 961. (b) Kobayashi, N.; Takeuchi, Y.; Matsuda, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 758. (c) Inokuma, Y.; Seok Yoon, Z.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 4747. (d) Takeuchi, Y.; Matsuda, A.; Kobayashi, N. *J. Am. Chem. Soc.* **2007**, *129*, 8271. (e) Inokuma, Y.; Osuka, A. *Dalton Trans.* **2008**, 2517. (f) Saito, S.; Kim, K. S.; Yoon, Z. S.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5591. (g) Yasuhide, I.; Osuka, A. *Chem. Commun.* **2007**, 2938. (h) Makarova, E. A.; Shimizu, S.; Matsuda, A.; Luk'yanets, E. A.; Kobayashi, N. *Chem. Commun.* **2008**, 2109.

(4) Myĺiborski, R.; Latos-Grażyński, L.; Szterenberg, L.; Lis, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3670.

(5) Pacholska, E.; Latos-Grażyński, L.; Ciunik, Z. *Chem.—Eur. J.* **2002**, *8*, 5403.

(6) Berlicka, A.; Latos-Grażyński, L.; Lis, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5288.

(7) Krivokapic, A.; Cowley, A. R.; Anderson, H. L. *J. Org. Chem.* **2003**, *68*, 1089.

(8) (a) Badger, G. M.; Elix, J. A.; Lewis, G. E. *Proc. Chem. Soc.* **1964**, 82. (b) Badger, G. M.; Elix, J. A.; Lewis, G. E. *Aust. J. Chem.* **1965**, *18*, 70. (c) Hu, Z.; Atwood, J. L.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 8071.

(9) (a) Furuta, H.; Ishizuka, T.; Osuka, A.; Ogawa, T. *J. Am. Chem. Soc.* **1999**, *121*, 2945. (b) Furuta, H.; Ishizuka, T.; Osuka, A.; Ogawa, T. *J. Am. Chem. Soc.* **2000**, *122*, 5748.

(10) (a) Mack, J.; Stillman, M. J. in *Handbook of Porphyrins and Related Macrocycles*; Kadish, K.; Smith, K.; Guilard, R., Eds.; Academic Press: New York, 2003; Vol. 16,Chapter 103, pp 43−116. (b) Kobayashi, N.; Fukuda, T. *J. Am. Chem. Soc.* **2002**, *124*, 8007. (c) Kobayashi, N.; Miwa, H.; Nemykin, V. N. *J. Am. Chem. Soc.* **2002**, *124*, 8021. (d) Kobayashi, N.; Nakai, K. *Chem. Commun.* **2007**, *40*, 4077.

(11) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, pp 1−165.

(12) Mack, J.; Asano, Y.; Kobayashi, N.; Stillman, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 17697.

JA8068769