Paper in Celebration for the 2010 Nobel Prize in Chemistry

doi:10.1246/cl.2011.902
Published on the web September 5, 2011

A Hexameric Porphyrin Triangle Constructed by Suzuki–Miyaura Cross-coupling Reaction

Jianxin Song,[1] Shoma Anabuki,[1] Naoki Aratani,*[1,2] Hiroshi Shinokubo,*[3] and Atsuhiro Osuka*[1]
[1]*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502*
[2]*PRESTO, Japan Science and Technology Agency*
[3]*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,*
Chikusa-ku, Nagoya, Aichi 464-8603

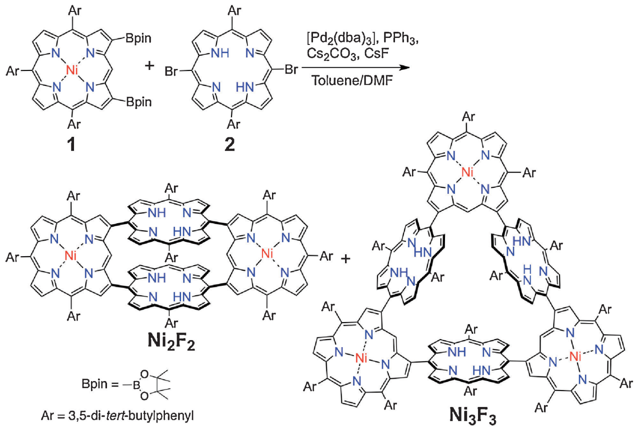
(Received February 14, 2011; CL-110122; E-mail: osuka@kuchem.kyoto-u.ac.jp)

A *meso*-to-β directly linked hexameric porphyrin triangle was synthesized by the Suzuki–Miyaura cross-coupling reaction via either one-pot or a stepwise route. Hexakis-zinc(II) complex of the porphyrin triangle exhibits a split Soret band in the absorption spectrum, reflecting the effective exciton coupling over the whole molecule.

Electronically interactive multiporphyrinic systems have received much attention in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, and nonlinear optical (NLO) materials.[1] To achieve desirable electronic and photophysical properties, manipulation of interporphyrinic interaction is often essential.[2] Along this line, we reported Ag(I)-promoted *meso–meso* coupling reactions of 5,15-diaryl-substituted Zn(II) porphyrins and subsequent DDQ/Sc(OTf)$_3$-induced oxidative fusion reaction into porphyrin tapes,[3] which yielded extremely long molecules,[3b] extensively π-conjugated molecules,[3c] directly linked porphyrin rings,[3e] and an antiaromatic porphyrin sheet.[3f] These examples showed that the directly linked porphyrin arrays have a strong advantage of precise control in the large electronic interactions.

The Suzuki–Miyaura coupling[4] is another effective synthetic protocol for directly linked porphyrin arrays.[5,6] Along this line, we have explored Ir-catalyzed β-borylation reaction of *meso*-free *meso*′-aryl-type porphyrins.[7] These borylated porphyrins have been used for the construction of various functional oligomeric porphyrinoids including doubly β-to-β bridged diporphyrins that have butadiyne-,[8a] 2,5-thiophene-,[8b] and 2,6-pyridine-spacers.[8c–8e] This double bridging strategy secures a rigid conformation and substantial electronic interaction, which induce significant enhancements of two-photon absorption (TPA) properties.[8a–8d]

Recently we have reported a porphyrin LEGO block strategy, which provides directly and multiply *meso*–β linked porphyrin rings efficiently.[8f] The Suzuki–Miyaura cross-coupling of diborylated Ni(II) porphyrin **1** and dibromoporphyrin **2** gave directly linked cyclic porphyrin tetramer **Ni_2F_2** in 16% yield.[8f] Careful examination of the reaction products led to an isolation of hexamer **Ni_3F_3** in 0.7% yield[13] (Scheme 1). The ^{1}H NMR spectrum of **Ni_3F_3** exhibits a singlet signal for the *meso*-protons and one singlet and four doublet peaks for β-protons, suggesting the high symmetry of **Ni_3F_3**. The parent ion peak of **Ni_3F_3** was observed at m/z 4843.87 (calcd for $C_{330}H_{366}N_{24}Ni_3$, 4843.75 $[M]^+$) in its MALDI-TOF mass spectrum. Free-base hexamer **F_3F_3** was quantitatively obtained by demetallation of **Ni_3F_3** with H_2SO_4, which was quantitatively converted to zinc(II) complex **Zn_3Zn_3** upon treatment with Zn(OAc)$_2$.



Scheme 1. One-pot synthesis of *meso*-to-β directly linked cyclic porphyrin arrays.

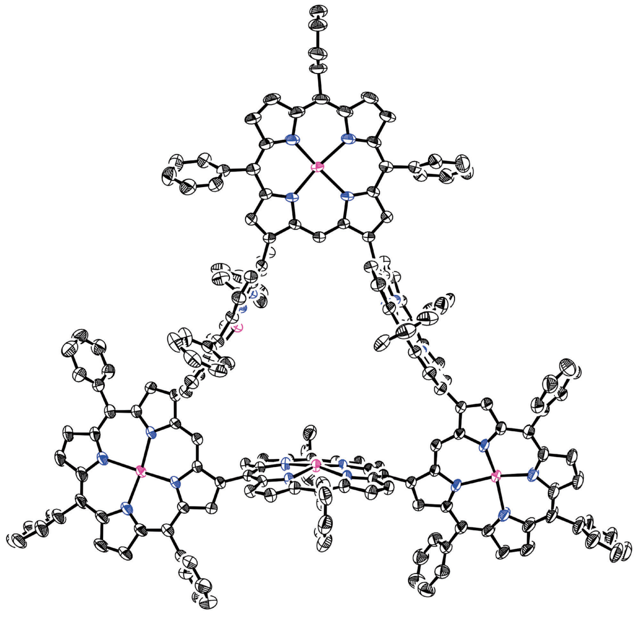
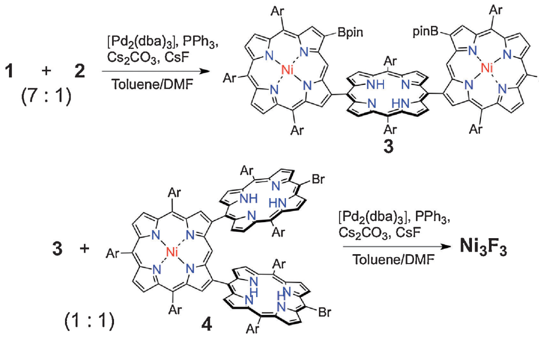


Figure 1. X-ray crystal structure of **Zn_3Zn_3**. *tert*-Butyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The ellipsoids are scaled to 50% probability.

Definitive structural assignment has been accomplished through single-crystal X-ray diffraction analysis of **Zn_3Zn_3**,[9] which unveiled a triangle conformation as a rare case (Figure 1). The porphyrin rings are relatively planar, suggesting less



Scheme 2. A stepwise synthesis of **Ni$_3$F$_3$**.

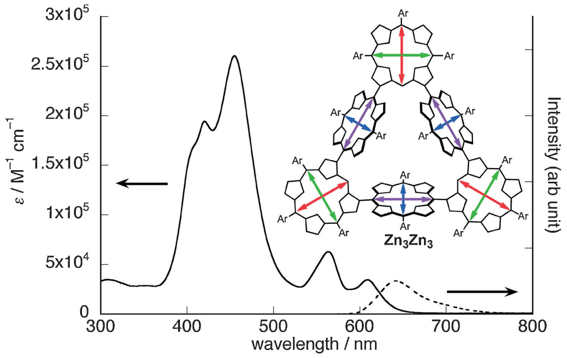


Figure 2. UV–vis absorption (—) and fluorescence (- - -) spectra of **Zn$_3$Zn$_3$** in CH$_2$Cl$_2$.

structural strain than **Ni$_2$F$_2$**.[8f] The central 5,15-linked porphyrin moiety is tilted by 74.4° to the adjacent 2,18-linked porphyrin moiety.[10] Zn–Zn distance between the 5,15-linked porphyrin moieties is 8.19 Å.

We then examined a stepwise rational synthetic route to **Ni$_3$F$_3$** (Scheme 2). Coupling of 7 equiv of **1** with **2** provided diborylated porphyrin trimer **3** in ca. 90% yield, which was then coupled with an equivalent of brominated porphyrin trimer **4**[8f] in the presence of a palladium catalyst to afford **Ni$_3$F$_3$** in 8% yield.

The UV–vis absorption spectrum of **Zn$_3$Zn$_3$** showed Soret bands at 455 and 422 nm with a shoulder at 410 nm and Q-bands at 609 and 564 nm (Figure 2). These split Soret bands can be understood in terms of exciton coupling theory[11] in the same manner as performed for the *meso–meso*-linked Zn(II) porphyrin oligomers.[3b] It is appropriate to place two transition dipole moments of each porphyrin unit as shown in inset of Figure 2. Given the roughly orthogonal conformations for the neighboring porphyrins, the exciton coupling of parallel transition dipoles (red and purple arrows) is effective but other interactions (blue arrows) should be zero. The interacting component leads to a red-shifted Soret band (455 nm), while the noninteracting component leaves a Soret band at the same position as the porphyrin monomer (around 410 nm). Small interaction between purple and green arrows results in the slightly red-shifted Soret band (422 nm). The fluorescence spectrum of **Zn$_3$Zn$_3$** exhibits a broad structure with a relatively high fluorescence quantum yield ($\Phi_F = 0.085$, Figure 2).

In summary, *meso*-to-β directly linked porphyrin hexamer with a trigonal structure was constructed by the Suzuki–Miyaura cross-coupling reaction. Recognition of guest molecules by this hexameric porphyrin triangle and detailed photophysical studies are currently being explored in our laboratories.

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

References and Notes

1 a) M. J. Crossley, P. L. Burn, *J. Chem. Soc., Chem. Commun.* **1991**, 1569. b) V. S. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105. c) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57. d) N. Aratani, A. Osuka, H. S. Cho, D. Kim, *J. Photochem. Photobiol., C* **2002**, *3*, 25. 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.

2 a) M. J. Crossley, T. W. Hambley, L. G. Mackay, A. C. Try, R. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 1077. b) M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771. c) H. L. Anderson, *Chem. Commun.* **1999**, 2323. d) K. Susumu, T. V. Duncan, M. J. Therien, *J. Am. Chem. Soc.* **2005**, *127*, 5186. e) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735. f) M. Hoffmann, C. J. Wilson, B. Odell, H. L. Anderson, *Angew. Chem., Int. Ed.* **2007**, *46*, 3122. g) Y. Nakamura, N. Aratani, A. Osuka, *Chem. Soc. Rev.* **2007**, *36*, 831. h) N. Aratani, D. Kim, A. Osuka, *Chem. Asian J.* **2009**, *4*, 1172. i) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* **2009**, *42*, 1922.

3 a) A. Osuka, H. Shimidzu, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135. b) N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong, D. Kim, *Angew. Chem., Int. Ed.* **2000**, *39*, 1458. c) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79. d) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304. e) Y. Nakamura, I.-W. Hwang, N. Aratani, T. K. Ahn, D. M. Ko, A. Takagi, T. Kawai, T. Matsumoto, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 236. f) Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 4119.

4 a) N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513. b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

5 N. Aratani, A. Osuka, *Org. Lett.* **2001**, *3*, 4213.

6 a) Y. Deng, C. K. Chang, D. G. Nocera, *Angew. Chem., Int. Ed.* **2000**, *39*, 1066. b) G. Bringmann, S. Rüdenauer, D. C. G. Götz, T. A. M. Gulder, M. Reichert, *Org. Lett.* **2006**, *8*, 4743.

7 H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1011.

8 a) I. Hisaki, S. Hiroto, K. S. Kim, S. B. Noh, D. Kim, H. Shinokubo, A. Osuka, *Angew. Chem., Int. Ed.* **2007**, *46*, 5125. b) J. Song, S. Y. Jang, S. Yamaguchi, J. Sankar, S. Hiroto, N. Aratani, J.-Y. Shin, S. Easwaramoorthi, K. S. Kim, D. Kim, H. Shinokubo, A. Osuka, *Angew. Chem., Int. Ed.* **2008**, *47*, 6004. c) J. Song, P. Kim, N. Aratani, D. Kim, H. Shinokubo, A. Osuka, *Chem.—Eur. J.* **2010**, *16*, 3009. d) J. Song, N. Aratani, J. H. Heo, D. Kim, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 11868. e) J. Song, N. Aratani, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 16356. f) J. Song, N. Aratani, P. Kim, D. Kim, H. Shinokubo, A. Osuka, *Angew. Chem., Int. Ed.* **2010**, *49*, 3617.

9 **Zn$_3$Zn$_3$**: $C_{330}H_{360}N_{24}Zn_6 \cdot 6H_2O$, $M_r = 5150.64$, *Rhombohedral*, space group $R\bar{3}c$ (#167), $a = 31.2547(17)$ Å, $\alpha = 59.10°$, $V = 21144(2)$ Å^3, $T = 90(2)$ K, $Z = 2$, reflections measured 98586, 12254 unique. The final R_1 was 0.0888 ($>2\sigma(I)$), and the final $_wR$ on F^2 was 0.2494 (all data), GOF = 0.920. CCDC 808444. The contributions to the scattering arising from the presence of the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.[12]

10 a) M. O. Senge, B. Rößler, J. von Gersdorff, A. Schäfer, H. Kurreck, *Tetrahedron Lett.* **2004**, *45*, 3363. b) S. Tokuji, T. Yurino, N. Aratani, H. Shinokubo, A. Osuka, *Chem.—Eur. J.* **2009**, *15*, 12208.

11 M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371.

12 Squeeze-Platon: a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht, The Netherlands, **2005**. b) P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.