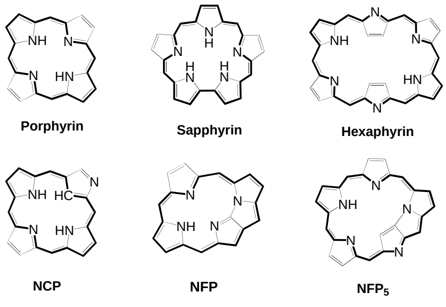
[8] For Pd^0-catalyzed reactions of alkadienols with aryl halides, see: K. Uemura, D. Shiraishi, M. Noziri, Y. Inoue, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1063.
[9] For the utility of cyclic carbonates, see: a) L. Hough, J. E. Priddle, R. S. Theobald, *Adv. Carbohydr. Chem.* **1960**, *15*, 91; b) V. Amarnath, A. D. Broom, *Chem. Rev.* **1977**, *77*, 183.
[10] For similar reactions to form dihydrofurans and epoxides via π-allylpalladium complexes, see: a) S. Ma, Z. Shi, *J. Org. Chem.* **1998**, *63*, 6387; b) S. Ma, S. Zhao, *J. Am. Chem. Soc.* **1999**, *121*, 7943.
[11] M. Yoshida, H. Nemoto, M. Ihara, *Tetrahedron Lett.* **1999**, *40*, 8583.

N-Fused Pentaphyrin

Ji-Young Shin, Hiroyuki Furuta,* and Atsuhiro Osuka*

Porphyrin analogues have been attracting considerable attention not only from the interest of annulenic chemistry but also from their use in a variety of applications.[1] Recently, reinvestigation of the Rothemund-type pyrrole–aryl aldehyde condensation[2] has revealed the concurrent formation of a porphyrin isomer, the *N*-confused porphyrin (**NCP**),[3] and expanded porphyrins such as sapphyrin[4] and hexaphyrin[5].



We have also reported a new analogue, the *N*-fused porphyrin (**NFP**), in which a unique fused tri-pentacyclic ring exists in the porphyrin core as the result of an inversion of the confused ring in **NCP**.[6] Herein we report the first example of a normal-type of fused expanded porphyrin, *N*-fused pentaphyrin (**NFP$_5$**), which contains a fused tri-pentacyclic ring in the core.

The title compound was synthesized under similar Rothemund-type conditions, namely, the acid-catalyzed condensation of pentafluorobenzaldehyde and unsubstituted pyrrole, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Along with the *meso*-pentafluorophenylporphyrin (12 %), *meso*-pentafluorophenylhexaphyrin[5] (20 %), and other higher homologues of *meso*-aryl type (around 13 %),[7] yellowish (**1-Y**) and reddish (**1-R**) products, both of which show parent mass peaks in the fast atom bombardment (FAB) mass spectra corresponding to the pentapyrrolic macrocycle, could be isolated in a total yield of approximately 15 %. The ratio of the two products **1-R** and **1-Y** changed greatly according to the amounts of oxidant used and converged to **1-R** when DDQ was used in excess (2.5 equiv). The similar products **2** and **3** were also obtained, in yields of 19 and 2 %, respectively, from the analogous reactions with 2,6-dichloro- and 2,4,6-trimethylbenzaldehyde.[8] Although the reaction is not optimized yet, the relatively high concentration of reactants (> 50 mM) seems effective for the formation of products.

The structure of the *N*-fused product **1-Y** was revealed by X-ray analysis on a single crystal (Figure 1).[9] A fused tri-pentacyclic ring with inward- and outward-pointing nitrogen atoms was found in a pentapyrrolic core. The inner nitrogen atom N(27) of the fused ring was connected to the β-carbon atom C(3) of the neighboring pyrrole ring. One of the pyrrole rings was canted significantly: the tilting angles of each ring, clockwise from the fused ring, were 24.96, 15.32, 22.46, and 99.18° to the mean plane of the 30 core atoms. Two of the

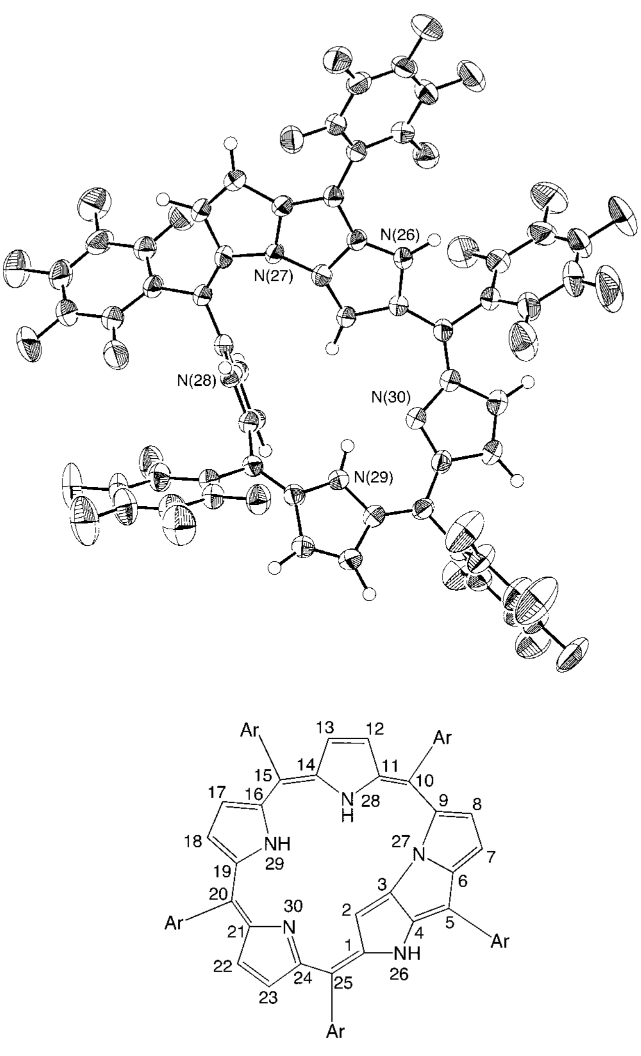


Figure 1. Top: X-ray crystal structure of *meso*-pentafluorophenyl *N*-fused pentaphyrin (**1-Y**). Bottom: Schematic representation of **NFP$_5$-Y** showing the numbering scheme.

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[*] Prof. H. Furuta,[+] Prof. A. Osuka, J.-Y. Shin
Department of Chemistry
Graduate School of Science
Kyoto University, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970

[+] PRESTO, Japan Science and Technology Corporation (JST)

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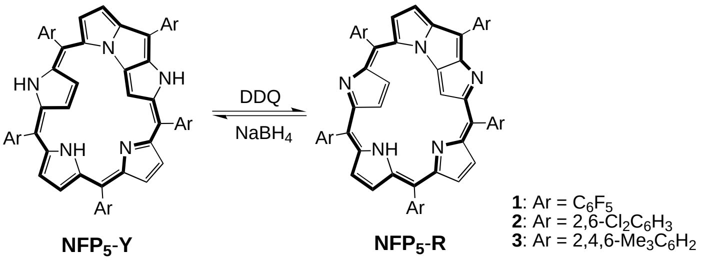
three pyrrole rings have protonated nitrogen atoms as judged from the interior angle: ∢C(11)N(28)C(14) 109.6° and ∢C(16)N(29)C(19) 110.6°, and the other is deprotonated ∢C(21)N(30)C(24) 106.0°.[10] Thus, the structure of **1-Y** can be drawn with a 24π anti-aromatic circuit (Scheme 1). In support of this, the ^{1}HNMR spectrum of **1-Y** (Table 1) shows three sets of β-H atoms in the range of $\delta = 8.2-5.5$ and three NH protons at $\delta = 6.69$, 6.59, and 13.73. The third extremely low-field-shifted signal could be attributed to N(29)–H···N(30), in which the distance of 2.728 Å between N(29) and N(30) is within the range for a hydrogen-bonding interaction. It is noteworthy that one of the nitrogen atoms of the fused ring in **NFP$_5$** is pointing outward, which is in contrast with the inward-pointing nitrogen atom in **NFP**. Therefore, the *N*-fused porphyrinoids can be classified as *normal*-type (**NFP$_5$**) and *confused*-type (**NFP**) based on the linkage (α-α and α-β) of the pyrrole rings. When a solution of **1-Y** in CH_2Cl_2 was treated with DDQ the yellow solution changed to red and afforded **1-R** quantitatively. In turn, the **1-R** obtained was reduced to **1-Y** by treatment with $NaBH_4$.[11, 12] The ^{1}HNMR spectrum of **1-R** (Table 1) showed the aromatic ring current effect: a set of β-C(12 and 13)H atoms of the inverted pyrrole ring, the inner N(29 or 30)H, and inner C(2)H signals of the fused ring appeared at $\delta = 2.19$, 1.70, 1.24, and −2.26, respectively, while the peripheral β-CH atoms resonated around $\delta = 9.2-8.3$. Consequently, the structure of **1-R** is inferred to have 22π aromaticity as shown in Scheme 1.



Scheme 1. Redox reaction between **NFP$_5$-Y** and **NFP$_5$-R**.

Table 1. Selected physical data for **1-Y** and **1-R**.

1-Y: m.p. >300 °C (decomp); ^{1}HNMR (500 MHz, $CDCl_3$): $\delta = 13.73$ (brs, 1H, N(29)H), 8.16 (d, $^2J = 4.0$ Hz, 1H), 8.09 (d, $^2J = 3.5$ Hz, 1H), 7.84 (s, 1H, C(2)H), 6.69 (brs, 1H, NH), 6.59 (brs, 1H, NH), 6.19 (d, $^2J = 5.5$ Hz, 1H), 6.16 (d, $^2J = 5.5$ Hz, 1H), 6.03 (d, $^2J = 5.5$ Hz, 1H), 6.00 (d, $^2J = 5.0$, 1H), 5.85 (d, $^2J = 4.5$ Hz, 1H), 5.58 (d, $^2J = 5.5$ Hz, 1H); ^{13}CNMR (125.65 MHz, $CDCl_3$): $\delta = 165.1$, 154.3, 150.8, 150.6, 150.2, 142.3, 136.9, 136.3, 133.7, 133.4, 133.3, 132.1, 129.5, 128.4, 126.9, 125.9, 125.0, 112.8, 110.6, 108.5, 106.9, 104.9 (C(2)), 102.0, 101.5, 93.9, 90.3 (pentafluorophenyl signals could not be assigned because of the multiple coupling of ^{13}C-^{19}F); UV/Vis (CH_2Cl_2): λ_{max} (ε [mol^{-1}dm^{3}cm^{-1}]) = 443.0 (51100), 499.0 (63100), 771.0 nm (7200); FAB-MS: *m*/*z* (% intensity): 1217.0 (100) [$M^+ + 2$]

1-R: m.p. >300 °C (decomp); ^{1}HNMR (500 MHz, $CDCl_3$): $\delta = 9.11$ (s, 2H), 8.56 (d, $^2J = 4.0$ Hz, 1H), 8.37 (d, $^2J = 5.0$ Hz, 1H), 8.35 (d, $^2J = 4.5$ Hz, 1H), 8.31 (d, $^2J = 4.5$ Hz, 1H), 2.19 (d, $^2J = 5.0$ Hz, 1H), 1.70 (d, $^2J = 4.0$ Hz, 1H), 1.24 (brs, 1H, NH), −2.26 (s, 1H, C(2)H); ^{13}CNMR (125.65 MHz, $CDCl_3$): $\delta = 161.0$, 160.9, 160.4, 159.7, 153.4, 152.2, 150.8, 148.0, 146.9, 136.6, 133.7, 133.3, 132.8, 132.4, 132.3, 131.5, 131.2, 129.3, 123.2, 122.4, 120.5, 112.7, 109.6, 100.7, 99.1(C(2)), 99.0; UV/Vis (CH_2Cl_2) λ_{max} (ε [mol^{-1}dm^{3}cm^{-1}]) = 349.5 (40600), 460.5 (59500), 553.5 (62600), 991.5 nm (2100); FAB-MS: *m*/*z* (% intensity): 1217.1 (100) [M^+]

The absorption spectra of both **1-Y** and **1-R** show broad bands relative to that of **NFP**, which presumably reflects the distortion from planarity and the extended π system (Figure 2). The long-wavelength absorption around 1000 nm observed in **NFP** is also observed for aromatic **1-R**. The quantitative interconversion between **1-Y** and **1-R** was confirmed by the observation of isosbestic points in the absorption spectra.

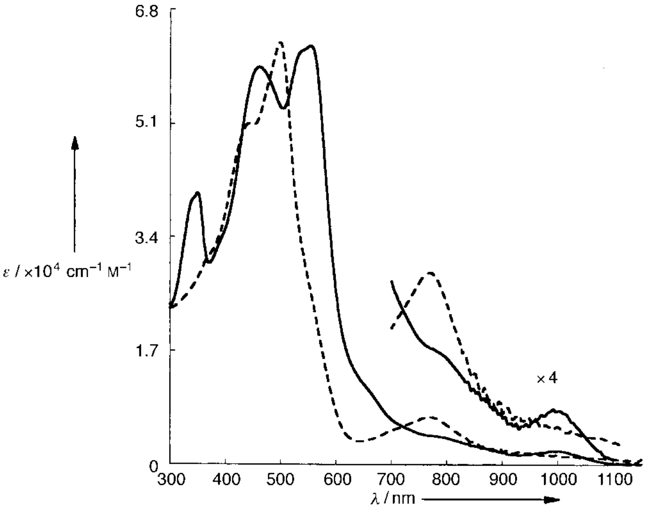
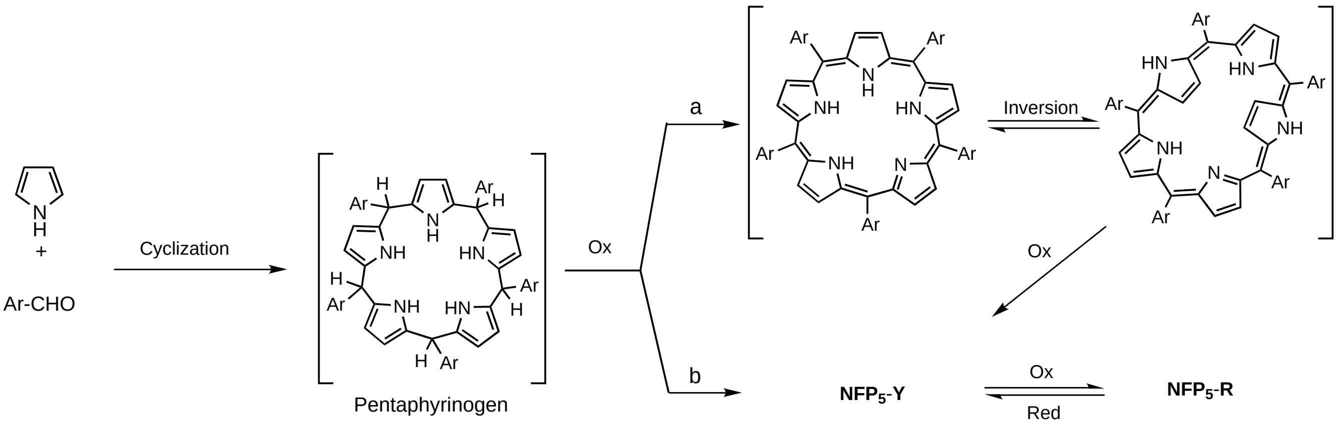


Figure 2. Absorption spectra of **1-Y** (----) and **1-R** (——).

In the porphyrin synthesis, the porphyrinogen is presumed to be oxidized to a corresponding porphyrin.[13] Mechanistically, therefore, **NFP$_5$-Y** and **NFP$_5$-R** might be derived from the putative precursor pentaphyrinogen during the oxidation process (Scheme 2). If the oxidation proceeds by route a, *meso*-pentaarylpentaphyrin, which has not been synthesized so far, could be formed. To release the strain of the molecule, one or two pyrrole rings could be inverted, then oxidized to **NFP$_5$-Y**. Such a pyrrole inversion was observed in *meso*-arylsapphyrin[4a] and *meso*-arylhexaphyrin.[5] On the other hand, route b presumes that a direct oxidation of the pentaphyrinogen occurs. In either way, the proposed mechanism would explain why *meso*-arylpentaphyrin has not been obtained from the standard acid-catalyzed pyrrole–aryl aldehyde condensation reaction. As the total amount of **NFP$_5$** obtained is comparable to that of porphyrin and hexaphyrin, we believe the absence of *meso*-arylpentaphyrin in the reaction mixture is because of the formation of **NFP$_5$**. The isolation of *meso*-arylsapphyrin from similar reaction conditions would be also relevant to the intrinsic instability of *meso*-arylpentaphyrin.[4] Further mechanistic study as well as the investigation of the metal coordination chemistry are currently underway.

Experimental Section

1-R: A solution of 2.5 M $BF_3 \cdot OEt_2$ in CH_2Cl_2 (100 μL) was added to a solution of pentafluorobenzaldehyde (494 μL, 4 mmol) and pyrrole (278 μL, 4 mmol) in CH_2Cl_2 (60 mL), and the resulting solution was stirred



Scheme 2. A possible reaction mechanism for the formation of **NFP$_5$**.

for 2 h under nitrogen. After adding DDQ (2.27 g, 10 mmol), the solution was stirred for 10 h, then passed through a short alumina column to remove the tar. The reaction mixture was then separated by column chromatography on silica gel with CH_2Cl_2:*n*-hexane (1:4). The red solution of **1-R** was eluted after the purple fraction of *meso*-pentafluorophenylhexaphyrin. The solution of **1-R** was evaporated, and the residue recrystallized from *n*-hexane to give pure **1-R** (146 mg, 15%).

1-Y: $NaBH_4$ (22.7 mg, 0.6 mmol, 15 equiv) was added to a solution of **1-R** (50 mg, 0.04 mmol) in CH_3OH (10 mL) and the solution was stirred for 10 min under nitrogen. After removing the solvent, the residues were dissolved in CH_2Cl_2, and filtered through a short alumina column. After evaporation, the residue was recrystallized from *n*-hexane to give **1-Y** (50 mg, 100%).

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[1] a) E. Vogel, *J. Heterocycl. Chem.* **1996**, *33*, 1461–1487; b) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267–2340; c) J. L. Sessler, A. Gebauer, E. Vogel, *The Porphyrin Handbook*, *Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **1999**, Chap. 8; d) D. Lash, *Angew. Chem.* **2000**, *112*, 1833–1837; *Angew. Chem. Int. Ed.* **2000**, *39*, 1763–1767.

[2] P. Rothemund, *J. Am. Chem. Soc.* **1939**, *61*, 2912–2915.

[3] a) H. Furuta, T. Asano, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 767–768; b) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, T. Głowiak, *Angew. Chem.* **1994**, *106*, 805–808; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779–781.

[4] a) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, *Chem. Eur. J.* **1995**, *1*, 68–72; b) G. R. Geier III, J. S. Lindsey, *J. Org. Chem.* **1999**, *64*, 1596–1603.

[5] M. G. P. M. S. Neves, R. M. M. Martins, A. C. Tome, A. J. D. Silvestre, A. M. S. Silva, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* **1999**, 385–386.

[6] H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc.* **1999**, *121*, 2945–2946; H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc.* **2000**, *122*, 5748–5757.

[7] A variety of higher homologues, such as octaphyrins, nonaphyrins, decaphyrins, undecaphyrins, and dodecaphyrins, are isolated from the reaction mixture: J.-Y. Shin, H. Furuta, A. Osuka, unpublished results.

[8] Spectral data and the X-ray structure of **2-Y** are shown in the Supporting Information.

[9] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147880. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] *The Porphyrin Handbook*, *Vol. 10* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **1999**, pp. 1–254.

[11] The absorption spectral changes of the redox reaction between **1-Y** and **1-R** are shown in the Supporting Information.

[12] Supporting this facile interconversion, the two-electron redox processes between **1-Y** and **1-R** were recorded at low potential, -0.447 V and $+0.067$ V (versus the ferrocene/ferrocenium couple (F_c/F_c^+)) by cyclic voltammetry.

[13] D. Dolphin, *J. Heterocycl. Chem.* **1971**, *7*, 275–283.

Iron-Catalyzed Regio- and Stereoselective Carbolithiation of Alkynes[**]

Makoto Hojo, Yoshio Murakami, Hidenori Aihara,
Rie Sakuragi, Yu Baba, and Akira Hosomi[*]

Organolithium compounds are one of the most popular organometallics and have been used for organic synthesis as nucleophiles in carbon–carbon bond formation, and as transmetalation agents onto other metals.[1] Carbometalation of alkynes is recognized to be useful in the preparation of stereochemically defined tri- and tetrasubstituted alkenes, while in reactions of alkynes without a conjugated electron-withdrawing group, the regioselectivity becomes the principal problem.[2] The carbolithiation of alkynes has limited synthetic use because only particular kinds of alkynes can be used, and as for the stereochemistry, the vinyllithium intermediates produced tend to isomerize with ease.[3] We report herein a preliminary result on the regio- and stereoselective carbolithiation of alkynes by a simple procedure that uses cheap iron salts as a catalyst.

We found that 3-pentynyl 3-phenylpropyl ether (**1a**), upon addition of a catalytic amount of $FeCl_3$, reacted with

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[*] Prof. Dr. A. Hosomi, Dr. M. Hojo, Y. Murakami, Dr. H. Aihara,
R. Sakuragi, Y. Baba
Department of Chemistry
Graduate School of Pure and Applied Sciences
University of Tsukuba, Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81)298-53-6503

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