

Pyrene-Fused Porphyrins: Annulation Reactions of *meso*-Pyrenylporphyrins

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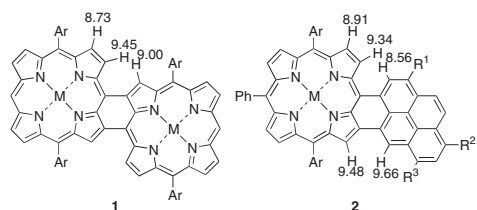
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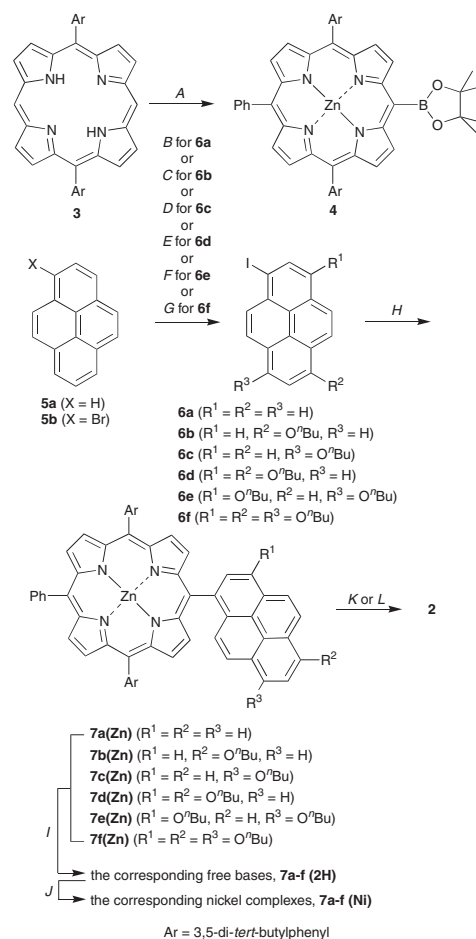
We prepared novel pyrene-fused porphyrins via the oxidative intramolecular ring closure reactions of *meso*-pyrenylporphyrin. The excitation energies and the oxidation potentials of the isolated dark-colored pyrene-fused porphyrins were significantly low compared with those of the corresponding precursors.

The expansion of the π -system is regarded as a challenge in organic synthesis.¹ π -Expanded porphyrins hold a unique position in this research field that aims at obtaining advanced materials having more elaborate functions, such as nonlinear optics and light-sensitive chemicals for photodynamic therapy, to name a few.² In the course of our synthetic study on porphyrin oligomers,³ we serendipitously found a novel highly conjugated porphyrin-fused porphyrin, i.e., [2]porphyracene **1**,⁴ which opened one of the new fields of π -expanded compounds leading to similar or identical compounds.⁵ To understand the details of this class of materials, replacement of one of the porphyrin moieties, i.e., the creation of fused compounds between porphyrin and other aromatic compound(s), is needed. Here we report novel pyrene-fused porphyrins **2**.



Formula 1. Molecular structures of **1** and **2** (Ar = 3,5-di-*tert*-butylphenyl, R¹-R³ = H or O^{*t*}Bu, M = 2H, Ni(II), and Zn(II)) along with ¹H NMR assignments (ppm) of bay-regions of **1** (M = Ni, from Ref. 4) and **2f**(Ni). Details of the substituents and the incorporated metals of **2** are consistent with those of **7** shown in Scheme 1.

We have isolated **1** via the cascade reaction of 5,15-diarylporphyrins, i.e., the electrophilic substitution of TeCl₄ at the *meso*-positions of two porphyrins, the bimolecular coupling reaction, and the subsequent elimination of telluride.⁴ By contrast, the synthesis of **2** involved the intramolecular ring closure reaction of *meso*-pyrenylporphyrin **7**, motivated by one of the well-known syntheses of polynuclear aromatic compounds, namely, the reaction of binaphthyl to afford perylene.⁶ The synthesis of **7** is shown in Scheme 1. The Suzuki-type porphyrin **4** was prepared according to previously reported reactions,⁷ i.e., introduction of a phenyl group to protect the reactive *meso*-position,⁸



Scheme 1. Conditions-A: (1) PhLi/THF, then H₂O, then DDQ, (2) Zn(OAc)₂·2H₂O/CHCl₃, (3) NBS/CH₂Cl₂, (4) HB(-OCMe₂CM₂O-), Pd(PPh₃)₄, NEt₃/(CH₂Cl)₂. **Conditions-B:** (from **5b**) KI, CuI/DMF. **Conditions-C and D[†]:** (from **5a**) (1) 2 equiv. Br₂/CHCl₃, (2) 1.5 equiv. *n*-BuONa/*n*-BuOH-toluene, (3) KI, CuI/DMF. **Conditions-E and F[†]:** (from **5a**) (1) 2 equiv. Br₂/CHCl₃, (2) 30 equiv. *n*-BuONa/*n*-BuOH-DMF, (3) NBS/CH₂Cl₂, (4) KI, CuI/DMF. **Conditions-G:** (from **5a**) (1) 3 equiv. Br₂/nitrobenzene, (2) 30 equiv. *n*-BuONa/*n*-BuOH-DMF, (3) NBS/CH₂Cl₂, (4) KI, CuI/DMF. **Conditions-I:** **4**, Pd(PPh₃)₄, Ba(OH)₂/DME-H₂O. **Conditions-J:** dil. HCl aq./CHCl₃. **Conditions-K:** Ni(acac)₂/toluene. **Conditions-L:** PhI(OTf)₂, BF₃·OEt₂/CH₂Cl₂. **Conditions-L:** Sc(OTf)₃, DDQ/toluene.[†] 1,6-Dibromo- and 1,8-dibromopyrenes were separated by fractional crystallization (See Ref. 9b).

metalation, bromination, and introduction of a dioxaborolan group. The synthesis of a series of pyrenes **6a–f** with or without alkoxy group(s), which enabled changing of the oxidation potentials of **7** systematically (vide infra), was carried out by a combination of bromination, substitution, and trans-halogenation reactions.⁹ Important intermediates **7a–f** (**Zn**) were prepared by the Suzuki–Miyaura coupling of **4** with **6a–f** in acceptable yields (ca. 70%). The corresponding free bases **7a–f** (**2H**) were prepared by treatments of **7a–f** (**Zn**) with mineral acid. Nickel(II) acetylacetonate processing of the free bases **7a–f** (**2H**) produced the nickel complexes.

There are two well-known representative reaction conditions for the intramolecular ring closure reactions that produce polyaromatic compounds: the reductive condition via an anion radical intermediate and the oxidative condition via a cation radical one.⁶ Treatment of **7a** with potassium–sodium alloy afforded a green solution suggesting the formation of an anion radical of **7a**; however, quenching of the reaction mixture led to the recovery of the starting material.

An oxidative ring closure reaction using combination of an oxidizing agent and a Lewis acid is known as the Scholl reaction and many revised methods have been reported. Employment of the widely used reaction condition, i.e., the combination of PhI(OTf)₂ and BF₃·OEt₂ developed by Kita et al.,¹⁰ afforded a brown product in 65% yield. Matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectroscopy detected the disappearance of two hydrogen atoms, M⁺ = 1234.3 (calcd. 1234.6 for C₈₂H₈₈N₄NiO₃), thereby supporting the formation of **2f** (**Ni**). Reliable evidence for the structure elucidation of **2f** (**Ni**) was provided by ¹H NMR analysis including rotation framework nuclear Overhauser effect measurements.¹¹ Characteristic resonance was observed in the low frequency region, namely, two singlet peaks and a set of doublet peaks attributable to protons of bay-region **2f** (**Ni**) (see Formula 1). These shifts were due to the ring current effect of the adjacent π-system and the compression effect from the sterically crowded protons.

Reflecting the expansion of the π-system, two notable features were found for **2f** (**Ni**): a negative shift of the oxidation potential and a bathochromic shift of the absorption spectrum. The electrochemical oxidation potential of **2f** (**Ni**) is negatively shifted compared with that of **7f** (**Ni**); it is 0.14 V for **2f** (**Ni**) and 0.33 V for **7f** (**Ni**) (vs AgNO₃ in PhCN). Reflecting the drastic change in color of **7f** (**Ni**), the absorption spectrum of **2f** (**Ni**) is extremely different from that of **7f** (**Ni**), which is a simple superimposition of porphyrin and pyrene absorptions.¹¹ The spectrum of **2f** (**Ni**) is composed of mainly three bands: Band I (13800 cm⁻¹, 724 nm), Q-band-like Band II (19300 cm⁻¹, 519 nm), and Soret-band-like split Band III (23300 cm⁻¹, 430 nm and 23800 cm⁻¹, 420 nm). Reflecting the highly conjugated structure, Band I appeared in the low energy region. This wavelength is similar to that of nickel(II) [2]porphyracene **1**, 13460 cm⁻¹ (743 nm).⁴ The decrease of the intensities of Band III (log ε = 4.38 for 23300 cm⁻¹ and 4.41 for 23800 cm⁻¹) is attributable to the lowering of the symmetry and the new π-electron system of pyrene-fused porphyrin.

A similar reaction of the corresponding zinc complex **7f** (**Zn**) induced the demetalation to afford the free base, **7f** (**2H**). The employment of a reaction condition using a weak Lewis acid, i.e., the combination of 2,3-dichloro-4,5-dicyano-*p*-benzoquinone (DDQ) and Sc(OTf)₃,⁵ solved the problem and afforded

the corresponding pyrene-fused porphyrin, **2f** (**Zn**).

The oxidative intramolecular coupling reaction via a cation biradical is the most plausible reaction mechanism, i.e., the formation of a biradical located on both porphyrin and pyrene moieties and the subsequent ring closure reaction.¹⁰ To obtain basic information regarding this reaction mechanism, systematic studies were carried out, changing the oxidation potential of the pyrene moiety. Not only trialkoxy derivatives (**7f** (**Zn**)) but also di- and mono-alkoxy derivatives **7b–e** (**Zn**) afforded the corresponding pyrene-fused porphyrins. However, the precursor having no alkoxy group (**7a** (**Zn**)) did not promote the ring closure reaction.

In conclusion, novel and highly conjugated pyrene-fused porphyrins were prepared and spectroscopically characterized. The reactions discussed above enable the opening of a new field of π-expanded porphyrin chemistry that has been hitherto restricted to porphyrin-fused porphyrins. We are currently investigating the detailed properties of the molecules, the reaction mechanism and other ring closure reactions of *meso*-arylporphyrins (aryl = polyaromatics such as perylene, coronene, and so on).

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References and Notes

- M. D. Watson, A. Fechtenkotter, and K. Müllen, *Chem. Rev.*, **101**, 1267 (2001).
- J. L. Sessler, A. Gebauer, and S. J. Weghorn, in "The Porphyrin Handbook Vol. 2," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2000), Vol. 1.
- K.-i. Sugiura, H. Tanaka, T. Matsumoto, T. Kawai, and Y. Sakata, *Chem. Lett.*, **1999**, 1193.
- K.-i. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda, and Y. Sakata, *Chem. Commun.*, **1999**, 1957.
- a) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, and A. Osuka, *Angew. Chem., Int. Ed. Engl.*, **39**, 558 (2000). b) A. Tsuda and A. Osuka, *Science*, **293**, 79 (2001). c) A. Tsuda, H. Furuta, and A. Osuka, *J. Am. Chem. Soc.*, **123**, 10304 (2001).
- P. Michel and A. Moradpour, *Synthesis*, **1988**, 894, and references cited therein.
- A. G. Hyslop, M. A. Kellett, P. M. Iovine, and M. J. Therien, *J. Am. Chem. Soc.*, **120**, 12676 (1998).
- X. Feng, I. Bischoff, and M. O. Senge, *J. Org. Chem.*, **66**, 8693 (2001).
- a) H. Vollmann, H. Becker, M. Corell, H. Streeck, and G. Langbein, *Ber. Dtsch. Chem. Ges.*, **531**, 1 (1937). b) J. Grimshaw and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1622. c) T. Yamato, M. Fujimoto, A. Miyazawa, and K. Matsuo, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 1201.
- Y. Kita, M. Gyoten, M. Ohtsubo, H. Tohma, and T. Takada, *Chem. Commun.*, **1996**, 1481.
- Selected spectroscopic data of **7f** (**Ni**): ¹H NMR (CDCl₃) δ = 9.66 (s, 1H), 9.48 (s, 1H), 9.34 (d, *J* = 4.9 Hz, 1H), 8.91 (d, *J* = 4.9 Hz, 1H), 8.63 (d, *J* = 4.9 Hz, 1H), 8.58–8.54 (m, 5H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.03–7.95 (m, 4H), 7.87 (br t, 2H), 7.78 (br d, 1H), 7.70 (br d, 1H), 7.66–7.62 (m, 3H), 7.19 (s, 1H), 4.58 (t, *J* = 7.0 Hz, 2H), 4.47 (t, *J* = 7.0 Hz, 2H), 4.42 (t, *J* = 7.0 Hz, 2H), 2.20–2.05 (m, 6H), 1.80–1.70 (m, 6H), 1.55 (s, 9H), 1.49 (s, 9H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H), and 1.11 (t, *J* = 7.0 Hz, 3H) ppm. UV–vis. (CHCl₃) λ = 13800 (724 nm, log ε = 4.57), 14970 (sh., 668 nm, log ε = 4.16), 19300 (519 nm, log ε = 4.52), 23300 (430 nm, log ε = 4.38), 23800 (420 nm, log ε = 4.41), 26400 (379 nm, log ε = 4.29) cm⁻¹.