

## “N-Fused Porphyrin” from N-Confused Porphyrin

Hiroyuki Furuta,<sup>\*,†</sup> Tomoya Ishizuka,<sup>‡</sup> Atsuhiko Osuka,<sup>‡</sup> and Takuji Ogawa<sup>‡</sup>

Department of Chemistry, Graduate School of Science  
Kyoto University, Kyoto 606-8502, Japan  
Institute for Fundamental Research of  
Organic Chemistry (IFOC)  
Kyushu University, Fukuoka 812-8581, Japan

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In recent years, a variety of porphyrin analogues, whose basic framework differs largely from porphyrin, have been synthesized.<sup>1,2</sup> One of the interesting findings is a pyrrole inversion in a protonated sapphyrin, a 22  $\pi$  expanded porphyrin, which gave us an impression that the requirement of planarity for aromaticity is not severe and porphyrin with a large core size is flexible.<sup>3</sup> But still it is an open question whether such pyrrole-flipping could occur in more compact tetrapyrrolic porphyrin. “N-confused porphyrin (NCP, **1**)”, a porphyrin isomer, originally synthesized by us and, independently, by Latos-Grażyński et al., is unique in that one of the pyrrole rings is inverted.<sup>4</sup> Our earlier observation that the inverted pyrrole ring is tilted largely from porphyrin plane, e.g., 26.9° in **1**<sup>4a</sup> and 42.4° in **2**,<sup>5</sup> drove us to a further study on the core modification with the expectation of more tilting and/or flipping of the pyrrole ring. Interestingly, during the halogenation of NCP, we obtained a new type of porphyrinoid with a fused pyrrole tripentacyclic ring in the macrocyclic core, which was derived from the inversion of the inverted pyrrole. Moreover, this new compound was found to return to NCP by reinversion of the pyrrole ring. In this paper, we report the synthesis, structural characterization, and reversible inversion nature of this new porphyrin analogue, to which we have assigned the trivial name “N-fused porphyrin; NFP” (Chart 1).

The first N-fused porphyrin, NFP-Br (**5**), was spontaneously obtained from a pyridine solution of brominated NCP, NCP-Br (**3**).<sup>6</sup> When **3** was left in pyridine at room temperature for 8 h,

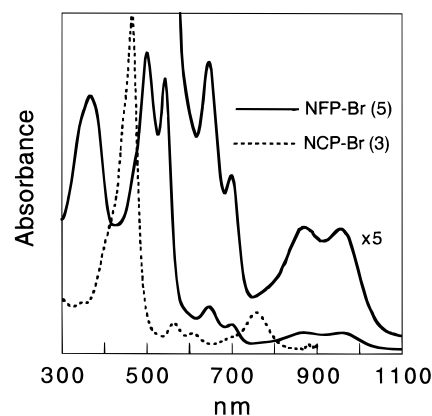
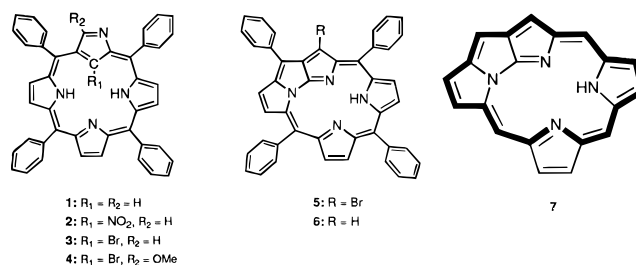


Figure 1. Absorption spectra for NCP-Br (**3**) (---) and NFP-Br (**5**) (—) in CH<sub>2</sub>Cl<sub>2</sub>.

Chart 1. N-Confused Porphyrins (**1–4**) and N-Fused Porphyrins (**5–7**)



the color of the solution changed gradually from green to red. After column chromatography, **5** was isolated in 91% yield. The optical spectra recorded in CH<sub>2</sub>Cl<sub>2</sub> showed Soret-like absorption maxima at 368, 500, and 542 nm, and Q-band at 646, 699, 868, and 957 nm. (Figure 1) Such optical transitions in the long-wavelength region are quite unusual and suggest the large modification of the porphyrin core.

Direct evidence for the structural assignment of this new product came from a single-crystal X-ray diffraction analysis.<sup>7</sup> (Figure 2) The structure revealed the existence of two pyrrole rings and a fused tripentacyclic ring in the porphyrin skeleton. Despite its crowded multi-ring arrangement, the molecule is nearly planar. Three nitrogen atoms, N(2), N(3), and N(4), are closely located (2.48, 2.64, and 2.88 Å from each other), and one of the nitrogens, N(3), possesses hydrogen which forms hydrogen bonds with neighboring nitrogens and assists in the planarity of the molecule. Reflecting the strain of the structure, one of the pyrrole rings in the tripentacyclic moiety is largely deformed, for example, bond angles of N(1)–C(1)–C(2) 101.9°, C(1)–C(2)–C(3) 111.4°, and C(4)–N(1)–C(1) 112.3°. The bond distances between inner carbon and nitrogen in a tripentacyclic ring, C(1)–N(1), 1.404; N(1)–C(20), 1.391; C(20)–N(2), 1.273, and N(2)–C(8), 1.44 Å, are explicitly *single*, *single*, *double*, and *single* bonds, respectively, which indicates NFP is an 18-member 18  $\pi$  aromatic system (**7**).<sup>8</sup>

In CDCl<sub>3</sub> solution, the peripheral hydrogens of **5** showed up in the range 8.96–7.55 ppm in <sup>1</sup>HNMR. Interestingly, the inner

(7) The datum crystal was a violet prism obtained from a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH solution of **5**. Crystal data for **5**: C<sub>24</sub>H<sub>27</sub>N<sub>4</sub>Br, M<sub>w</sub> = 691.63, monoclinic, space group Cc (No. 9), with a = 21.119(3) Å, b = 12.021(4) Å, c = 12.901(3) Å,  $\beta$  = 94.12(2)°, V = 3267.2(9) Å<sup>3</sup>, Z = 4, D<sub>calcd</sub> = 1.406 g/cm<sup>3</sup>, F(000) = 1416,  $\lambda$ (Mo K $\alpha$ ) = 37.58 cm<sup>-1</sup>, crystal dimensions 0.40 × 0.30 × 0.20 mm. The data were collected at 300 K, and the structure was solved by direct methods. It refined to R = 0.065, R<sub>w</sub> = 0.040, GOF = 1.69 for 2611 reflections with I > 1.0 $\sigma$ (I).

(8) Average bond lengths for C–N and C=N are 1.47 and 1.36 Å, respectively. March, J. *Advanced Organic Chemistry (3rd edition)*; Wiley: New York, 1985; p 19.

<sup>†</sup> Kyoto University.

<sup>‡</sup> Kyushu University.

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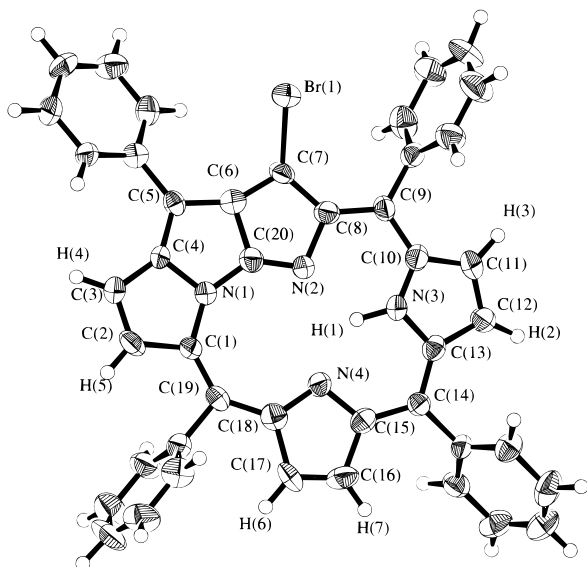
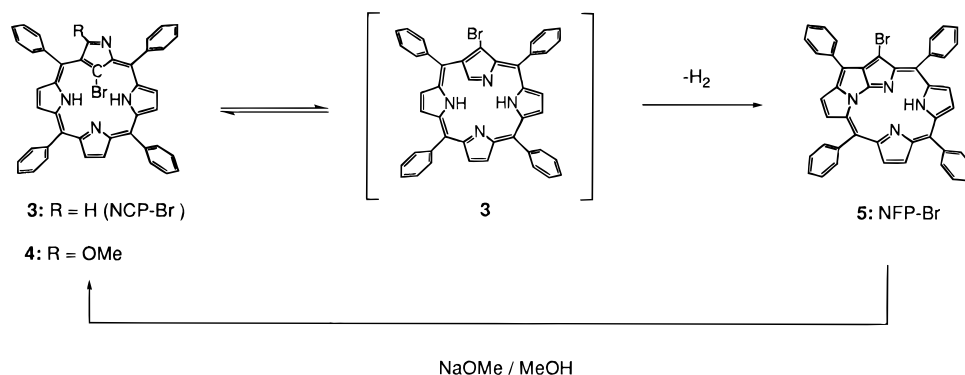
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(6) NCP-Br (**3**) was obtained by treating NCP (**1**) with *N*-bromosuccinimide (NBS) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 5 min in 80–90% yields; see Supporting Information.

## Scheme 1



**Figure 2.** Molecular structure of NFP-Br (**5**). Thermal ellipsoids have been drawn at the 50% probability level. Selected bond lengths and interatom distances (Å): C(1)–C(2), 1.439(11); C(2)–C(3), 1.363(11); C(3)–C(4), 1.39(1); C(4)–C(5), 1.364(13); C(5)–C(6), 1.424(11); C(6)–C(7), 1.38(1); C(6)–C(20), 1.475(10); C(7)–C(8), 1.453(12); N(1)–C(1), 1.404(12); N(1)–C(4), 1.401(11); N(1)–C(20), 1.391(13); N(2)–C(20), 1.273(10); N(2)–C(8), 1.44(1); N(2)···N(3), 2.476; N(3)···N(4), 2.642; N(4)···N(2), 2.879. Selected angles (deg): C(1)–N(1)–C(4), 112.3(7); N(1)–C(1)–C(2), 101.9(8); C(1)–C(2)–C(3), 111.4(9); C(2)–C(3)–C(4), 108.5(9); N(1)–C(4)–C(3), 105.9(7); C(10)–N(3)–C(13), 112.2(7); C(15)–N(4)–C(18), 105.5(7).

NH signal which might be susceptible to the shielding effect of a ring current, appeared at 8.38 ppm. The low field shift is due to the strong hydrogen bonding which overcomes the ring current effect.<sup>9</sup> **5** is stable in acid and exhibited the stepwise absorption band shifts (5–10 nm) upon protonation.<sup>10</sup> The existence of the diprotonated form was confirmed from the appearance of three NH's signals around 11.50, 4.50, and 3.05 ppm at  $-40$  °C in 20% TFA–CDCl<sub>3</sub>.

On the other hand, the compound was unstable in basic media. For example, after the treatment of **5** in CH<sub>2</sub>Cl<sub>2</sub> with NaOMe/MeOH for 30 min, the red color solution of **5** gradually changed to green, and surprisingly, methoxy-substituted NCP-Br (**4**) was formed in 72% yield. Although the reaction mechanism is not

(9) NH stretching of **5** was not clearly observed in FTIR, probably because of the overlap with the CH stretching near 3000 cm<sup>-1</sup>.

(10) Three phase pH transitions were observed around pH 4 and 9 for **5** in aqueous 2.5% sodium dodecyl sulfate solution, where diprotonated, mono-protonated, and free base NFP (**5**) could exist.

clear at this moment, disappearance of hydrogen bonding due to the deprotonation by the added base and successive nucleophilic attack at bridged C(20) position of **5** by MeO<sup>-</sup> might be a trigger of the ring opening and rebirth of the inverted pyrrole ring. Furthermore, when pyridine solution of **5** was refluxed for 2 days, debromination took place to afford a basic frame of NFP (**6**).<sup>11</sup>

To the best of our knowledge, this type of porphyrinoid with a fused pyrrole tripentacyclic ring is the first one, and it might be formed by the reinversion of an inverted pyrrole ring, followed by the nucleophilic attack of adjacent pyrrole (Scheme 1). As the reaction was deterred significantly under the argon condition, dioxygen might be a plausible oxidant in this transformation.<sup>12</sup> In preliminary experiments using other NCPs such as chlorinated and nitro-substituted NCP (**2**), the formation of the same type of NFPs has been observed, which suggests that this type of reaction is general for NCP systems.<sup>13</sup>

The reason for unusual long-wavelength absorption is not known at this time. One possibility is intramolecular charge-transfer transition in NFP, and the support for this comes from the observed bathochromic shifts with the solvent polarity. Although the changes of absorption maxima for long-wavelength bands are not large (~10 nm), a good correlation between  $\lambda_{\text{max}}$  and Kosower's *Z* parameters was obtained.<sup>14</sup> (cf. Supporting Information)

In conclusion, the synthesis and characterization of a new type of porphyrin analogue, N-fused porphyrin (NFP) has been described. The unusual long-wavelength absorption and reversibility between NFP and NCP, associated with color change might be potentially useful for the optical application. Easy access to NCP and its facile transformation to NFP shown here would make both porphyrinoids very attractive for many applications compared to the known porphyrin families.<sup>15</sup>

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**Supporting Information Available:** Synthetic procedures and spectral data for **3–6** and solvent effects for **5**; experimental procedures, table of positional and isotropic thermal parameters, bond lengths and angles, a listing of observed and calculated structure factors for **5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) Satisfactory spectroscopic and analytical data were obtained for **4** and **6**; see Supporting Information.

(12) The reaction showed the first-order kinetics and a half-life time was found 80 min at 27 °C from NMR experiments in pyridine-*d*<sub>5</sub>.

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