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Porphyrinoids

Doubly N-Fused Porphyrin**

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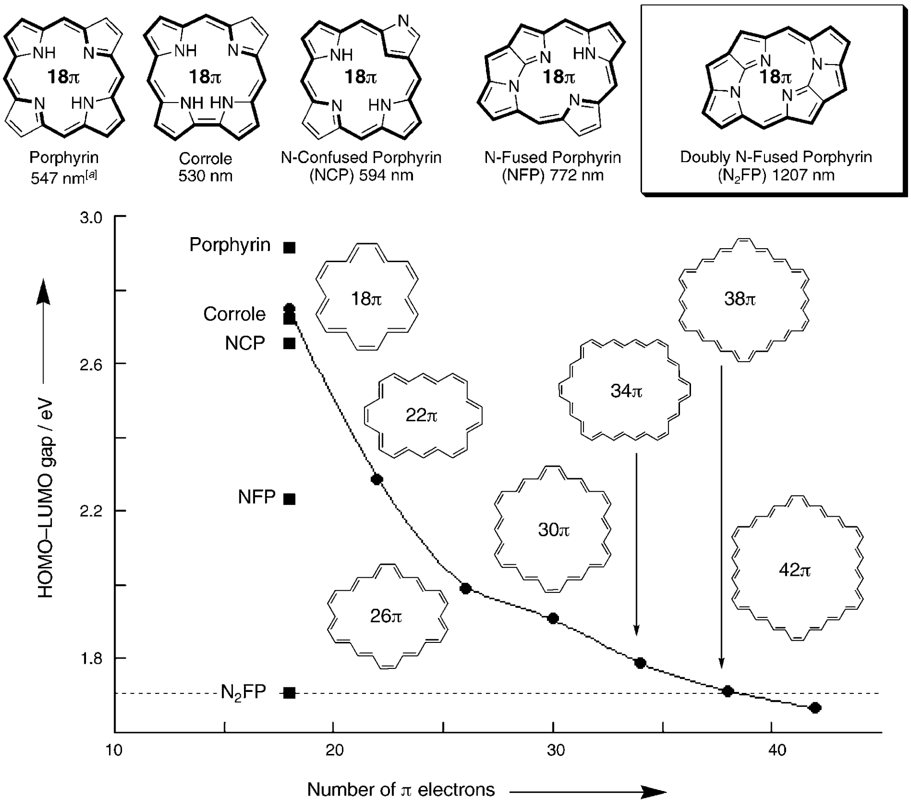

Figure 1. HOMO–LUMO gaps of unsubstituted tetrapyrrolic porphyrin mutants and [4*n*+2]annulenes at the B3LYP/6-31G** level. [a] Values in nm represent the longest wavelengths in TD-DFT calculations at the B3LYP/6-311++G**//B3LYP/6-31G** level.

Alteration of the porphyrin framework has generated an important class of compounds. One trend in such study is the synthesis of expanded porphyrins composed of five or more pyrrole rings, many of which possess [4*n*+2]annulenic substructures with distinct aromaticity as well as longer wavelength absorptions than those of porphyrins, resulting from the extended π-conjugated system.[1] Expanded porphyrins are, therefore, a potential component in the development of near-infrared dyes. The study of mutant tetrapyrrolic systems, such as corrole,[2,3] porphycene,[4,5] and N-confused porphyrin,[6,7] also continues to attract much attention. These tetrapyrrolic compounds commonly contain 18π aromatic ring systems and show HOMO–LUMO gaps similar to that of simple [18]annulene (Figure 1). We have reported an exceptional example of a tetrapyrrolic compound, N-fused porphyrin (NFP), which has a narrower HOMO–LUMO gap than simple [18]annulene.[8,9] The unusual bathochromic shift was attributed to the presence of an internally fused tripentacyclic ring within the [18]annulenic framework. Hence, the introduction of fused pyrrolic rings into the macrocyclic core would be an important strategy to develop near-infrared dyes with relatively small molecules. Using the so-called fusion approach, we synthesized doubly N-fused porphyrin **1**, which exhibits exceptionally long-wavelength absorption for an 18π aromatic system (in excess of 1600 nm) and has, to our knowledge, the narrowest HOMO–LUMO energy gap of all reported neutral [18]annulenic compounds.

Doubly N-fused porphyrin **1** was synthesized as follows (Scheme 1): Firstly, N-confused N-fused porphyrin **3** was prepared in 13 % yield by acid-catalyzed [2+2] condensation of the N-confused dipyrromethane derivative **2**.[10] Secondly, **3** was treated with 1.5 equivalents of 1,3-dibromo-2,2-dimethylhydantoin, affording the tribrominated product **4** in 83 % yield. Bromination with *N*-bromosuccinimide was not effective in this case, possibly owing to the unexpected substitution reaction of N-confused N-fused porphyrin with succinimide, which was suggested by MS analysis of the reaction mixture. Finally, treatment of **4** with Hünig's base afforded **1** in 86 % yield; it was purified by column chromatography on silica gel and then recrystallized from CH_2Cl_2. Whereas **1** is stable in the solid state and in solution under an inert atmosphere, it gradually decomposes to a ring-opened N-confused N-fused porphyrin derivative on exposure to air in solution. In the ^{1}H NMR spectrum of **1** in $CDCl_3$, only one

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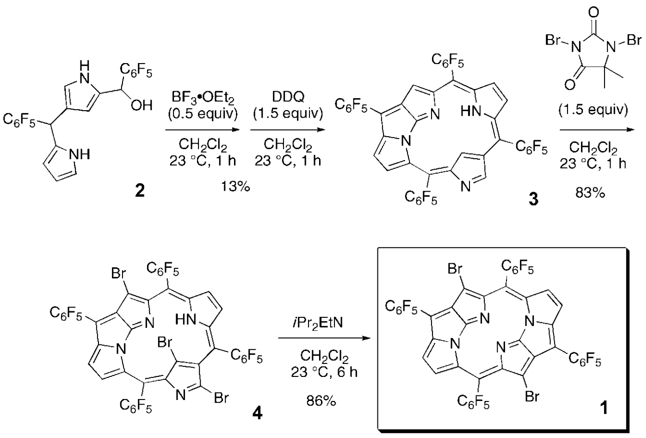

Scheme 1. Preparation of doubly N-fused porphyrin. DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone.

set of doublet peaks, corresponding to the pyrrole β protons, is observed at $\delta = 8.31$ ppm and $\delta = 8.36$ ppm ($^3J_{HH} = 4.9$ Hz). The shielding effect evident in the ^{1}H NMR spectrum indicates high aromaticity of **1**. The mass spectrum of **1** (*m*/*z* 1125.85) is also consistent with the assigned structure.

Explicit structural determination of **1** was carried out using X-ray crystallographic analysis (Figure 2).[11] The two tripentacyclic moieties are connected by two *meso* carbon atoms and the molecule has C_i symmetry. The tripentacyclic moieties are tilted at 12.1° from the porphyrin mean plane composed of 24 heavy (i.e. non-hydrogen) atoms. This distortion from planarity is possibly a result of repulsion between the lone-pair electrons of the interior nitrogen atoms (N–N interatomic distance = 2.368 Å). Nevertheless, no uncommon values are found for bond lengths and angles in **1**, indicating that the ring strain imposed on **1** by the two tripentacyclic moieties is not significant.

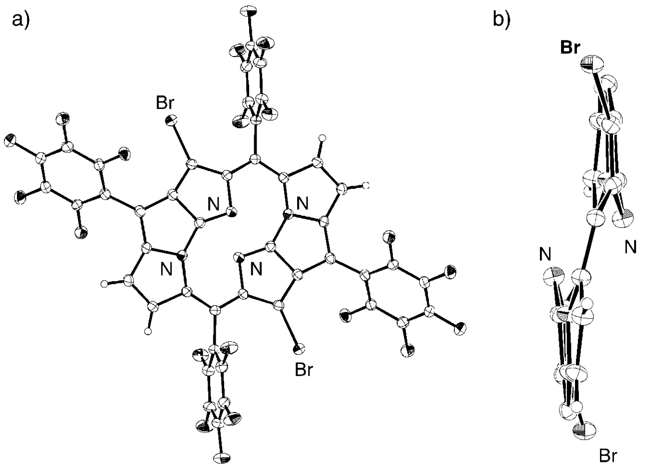

Figure 2. Molecular structure of **1** determined by X-ray crystallography; thermal ellipsoids are set at 30% probability. a) View of the doubly N-fused porphyrin ring; b) side view showing deviation from the porphyrin mean plane with C_6F_5 groups removed for clarity. One of the two independent molecules contained within the crystal structure is shown.

The unprecedentedly narrow HOMO–LUMO energy gap of **1** is demonstrated by the absorption spectrum (Figure 3) and electrochemical measurements. It has a long-wavelength absorption at $\lambda_{max} \approx 1300$ nm (7700 cm^{-1}) in toluene,[12] which is exceptionally large among 18π aromatic compounds. Electrochemical measurements of **1** (0.1 M Bu_4NPF_6 in CH_2Cl_2) detected a first reversible oxidation potential at $E_{ox} = 0.48$ V (vs. Fc/Fc$^+$) and a first reversible reduction potential at $E_{red} = -0.76$ V. The estimated HOMO–LUMO energy gap of **1** is thus calculated to be 1.24 eV. The calculated electronic structure of **1** at the B3LYP/6-311++G**//B3LYP/6-31G** level is in good agreement with the experimental results. Time-dependent density functional theory (TD-DFT) calculations gave the expected wavelengths and oscillator strengths (Figure 3). The theoretical HOMO–LUMO energy gap is 1.43 eV, which is similar to the experimental value. The nucleus-independent chemical shift (NICS) value (−13.90 ppm) indicates that **1** is strongly aromatic, which is consistent with the ^{1}H NMR spectrum.

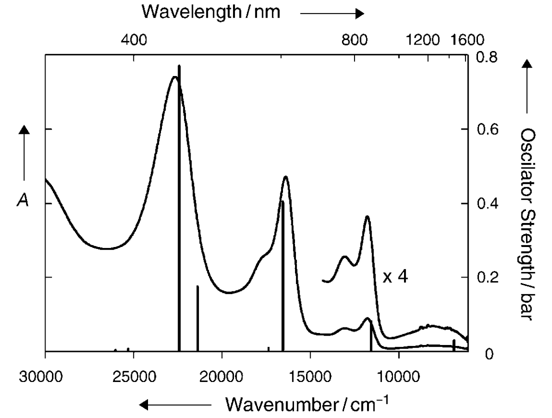

Figure 3. Electronic absorption spectrum of **1** in toluene and TD-DFT calculation results of **1**.

In comparison to the relationship between the HOMO–LUMO energy gaps and the numbers of π electrons in [4*n*+2]annulenes (Figure 1),[13] the HOMO–LUMO energy gap of **1** is exceptionally small. The similarity in the HOMO–LUMO energy gaps of tetrapyrrolic porphyrinoids such as corrole and N-confused porphyrin with that of simple [18]annulene indicates that pyrrolic NH moieties, as well as C=C or C=N bonds, have little effect on the HOMO–LUMO energy gaps. C=C and C=N bonds which do not participate in the main conjugation are placed outside the [18]annulenic substructures (indicated in bold in Figure 1). However, the HOMO–LUMO energy gap of **1**, which is also an [18]annulene, is equal in magnitude to that of [38]annulene. In this case, the two C=N bonds are placed inside the [18]annulenic substructure. Double bonds within annulenic structures facilitate an increase in HOMO energy levels.[14]

Molecular orbital analysis on model compounds gives further insight into the origin of the unusually narrow HOMO–LUMO energy gap in doubly N-fused porphyrin **1**.

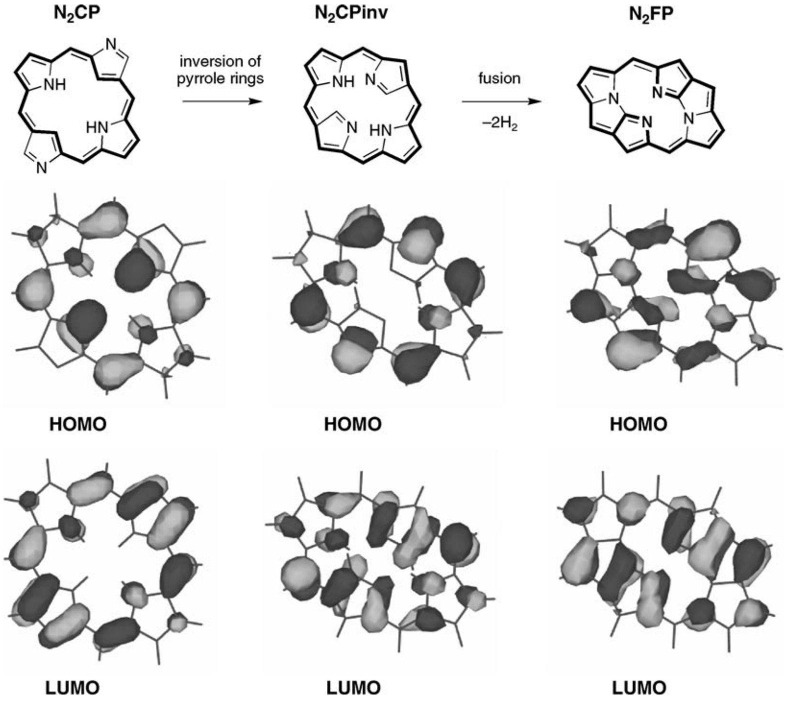

Figure 4. Kohn–Sham orbitals of HOMO and LUMO for doubly N-confused porphyrin (N_2CP), its inverted conformer (N_2CPinv), and doubly N-fused porphyrin (N_2FP).

The Kohn–Sham orbitals of doubly N-confused porphyrin (N_2CP), its inverted conformer (N_2CPinv), and doubly N-fused porphyrin (N_2FP) are summarized in Figure 4. The HOMO and LUMO of N_2CP have basically same shapes as those of standard porphyrin. Introduction of confusion to the porphyrin macrocycles does not affect the shape of molecular orbitals. In N_2CPinv, the HOMO and LUMO can be described simply by the inversion of those of N_2CP. Mere inversion of the pyrrole rings is not sufficient to drastically alter the electronic structure. The situation is changed in N_2FP. Whereas the LUMO of N_2FP is almost equal to that of N_2CPinv, a distinct difference is found between the HOMO of N_2FP and that of N_2CPinv. The contribution of the C=N bonds in confused pyrrole is clearly detected in only the HOMO of N_2FP. The calculated HOMO–LUMO energy gap of N_2FP (1.71 eV) is much smaller than that of N_2CP (2.43 eV) and N_2CPinv (2.32 eV), indicating that the contribution of the C=N π orbitals, which are placed inside the [18]annulenic substructure, is an important factor important in the unusually narrow HOMO–LUMO gap of **1**.

In summary, we have synthesized doubly N-fused porphyrin **1** and revealed its unprecedentedly narrow HOMO–LUMO gap. The unique electronic structure of **1** is a result of the contribution from C=N π orbitals to the HOMO, an ingenious example of endocyclic extension of the porphyrin π system.[14] The strategy developed here can be applied to other macrocycles,[15] in the development of outstanding electronic structures and novel near-infrared dyes.

Experimental Section

Synthesis of **4**: To a solution of **3** (10.0 mg, 0.010 mmol, 1.0 equiv)[10] in 20 mL of CH_2Cl_2, 1,3-dibromo-5,5-dimethylhydantoin (4.4 mg, 0.015 mmol, 1.5 equiv) was added. After it had been stirred for 1 h at 23 °C, the reaction mixture was poured onto a silica gel column and eluted with CH_2Cl_2/hexane (1:1). The first red fraction afforded **4** in 83 % yield (10.3 mg, 0.0083 mmol). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.51$ (br s, 1 H), 7.74 (br s, 1 H), 8.31 (d, $J = 4.3$ Hz, 1 H), 8.41 (d, $J = 4.3$ Hz, 1 H), 8.69 ppm (br s, 1 H); MALDI-TOF MS: m/z: 1207.446 $[M+H]^+$.

Synthesis of **1**: To a solution of **4** (20.0 mg, 0.017 mmol, 1.0 equiv) in 5 mL of CH_2Cl_2, *N,N*-diisopropylethylamine (3.5 µL, 0.020 mmol, 1.2 equiv) was added and the resulting mixture was stirred for 6 h at 23 °C. Then the reaction mixture was poured onto a silica gel column and eluted with CH_2Cl_2/hexane (4:6). The first green fraction afforded **1** in 87 % yield (16.2 mg, 0.014 mmol). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.31$ (d, $J = 4.9$ Hz, 2 H), 8.36 ppm (d, $J = 4.9$ Hz, 1 H); HRMS (ESI): m/z calcd for $C_{44}H_4Br_2F_{20}N_4$: 1125.84834; found: 1125.84528; UV/Vis (toluene) $\lambda_{max} = 441, 610, 766, 849$ nm.

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[11] Crystal structure data for **1**: $2(C_{44}H_4Br_2F_{20}N_4)\cdot 1.6\,(C_2H_4Cl_2)$, $C_{91.2}H_{14.4}Br_4Cl_{3.2}F_{40}N_8$, $M_r = 2414.95$, triclinic, space group $P\bar{1}$ (2), $a = 12.204(3)$, $b = 12.477(4)$, $c = 14.990(4)$ Å, $\alpha = 83.310(11)$, $\beta = 67.400(8)$, $\gamma = 82.310(10)°$, $V = 2083.1(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.925$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.182$ mm^{-1}, $T = 150(2)$ K; Rigaku Mercury 8; $55° > 2\theta > 6°$, 27810 measured reflections, 9563 unique reflections, 7045 with $I > 2\sigma(I)$ used in F^2 refinement, 704 parameters, $R = 0.0639$, $wR = 0.1969$ (all data), GOF = 1.053. CCDC 689220 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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