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Skeletal Recombination Reaction of *N*-Fused Pentaphyrin(1.1.1.1.1) via Bromination

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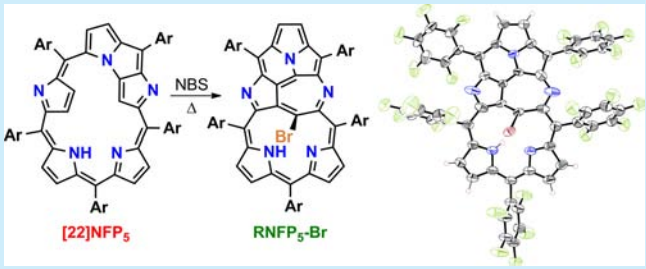
Supporting Information

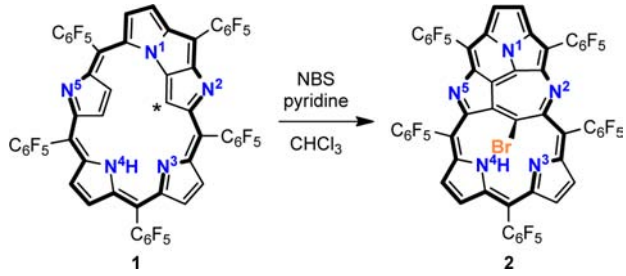
ABSTRACT: *N*-Fused [22]pentaphyrin(1.1.1.1.1) transformed into recombined *N*-fused pentaphyrin bromide after treatment with *N*-bromosuccinimide. This bromide was highly reactive to nucleophiles to give the corresponding substituted products including aminated, oxidized, and unsubstituted derivatives.



Bromination reaction is one of the most effective gambits to functionalize aromatic compounds. Porphyrinoids, a representative family of aromatic compounds, have attracted much attention in light of their optical and electrochemical properties, which are potentially applicable for artificial photosynthesis, organic solar cells, photodynamic therapy, and so on. Among them, expanded porphyrins that have larger macrocyclic rings than porphyrins[1] are a fascinating class of porphyrin higher analogues on the grounds that the mechanically flexible and chemically sensitive skeletons often cause unparalleled metamorphoses.[1g,2] In this regard, brominated expanded porphyrins can be promising scaffolds for applications mentioned above. However, the reported examples of bromination reactions of expanded porphyrins are still limited probably because the strongly electron-withdrawing *meso*-substituents make all the *β*-positions less reactive.[3] In the case of hexaphyrin, for example, extremely severe reaction conditions such as refluxing of bromine solution of a robust hexaphyrin−bisgold complex are required[3a] and they make it difficult to control regioselective and stoichiometric introduction. Herein, we report the bromination reaction of *N*-fused pentaphyrin (**NFP$_5$**) under the mild conditions and the resulting unprecedented skeletally recombined products including subsequent nucleophilic substitution reactions.

A solution of *meso*-pentakis(pentafluorophenyl)-substituted *N*-fused [22]pentaphyrin(1.1.1.1.1) ([**22**]**NFP$_5$**, **1**)[4] and *N*-bromosuccinimide (NBS, totally 4.0 equiv) in chloroform (8.2 mM) was refluxed for 4 h in the presence of pyridine (totally 16 equiv). After removal of the solvent, silica gel column chromatography gave a major product **2** as an olive-green fraction along with recovery of **1** (Scheme 1). [**24**]**NFP$_5$** (a reduced form of **1**)[4a] was quickly oxidized by NBS; thus, it resulted in obtainment of the same product. High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) displayed a parent molecular ion peak at m/z = 1293.9563 (calculated for $C_{55}H_8Br_1F_{25}N_5$, Figure S9, Supporting Information), which was 2H mass unit less than that of simply monobrominated [**24**]**NFP$_5$** ($C_{55}H_{10}Br_1F_{25}N_5$, $[M + H]^+$). The ^{1}H NMR spectrum exhibited six doublets around an aromatic region probably due to the outer *β*-protons along with a singlet assigned to the NH proton, which disappeared by addition of D_2O (Figure S1, Supporting Information). Unlike **1**, signals due to the inner *β*-protons around a high-field region were absent, indicating that some serious transformation occurred on the inward side of the macrocycle. The final structure determination was carried out by X-ray diffraction analysis for a single crystal of **2** provided by a vapor diffusion method of methanol into a $CHCl_3$ solution of **2**. Successive ring-opening and -closing recombination occurred to form multiply fused pentacyclic rings (Scheme 1, Figure 2). The bromine atom was positioned three bonds away from the pyrrolic nitrogen (N^2, Scheme 1); hence, the first bromination was probably took place at the inner position (marked with *) of fused tricyclic ring of **1**. The entire *π*-plane was slightly bent at the middle of the molecule and the mean-plane-deviation (MPD) values of the core 30 atoms, the upper 17 atoms (pentacyclic part, MPD*p*), and lower

Scheme 1. Skeletal Recombination Reaction[a]



[a]Bold lines indicate the conjugation circuit.

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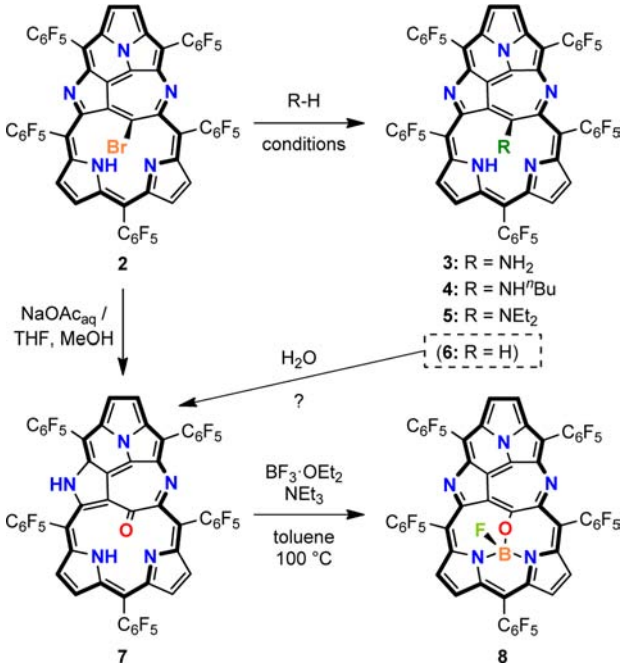
13 atoms (dipyrrin part, MPD*d*) were 0.350, 0.083, and 0.162 Å, respectively (Figure S8, Supporting Information), while the bromine substituent was tilted by 32.8° against the pentacyclic plane. The harmonic oscillator model of aromaticity (HOMA) value, a measure of bond-length alternation and therefore of aromaticity,[5] has been calculated to be 0.632, thus indicating that it possesses a well delocalized macrocycle. For the sake of convenience, we call this product **RNFP$_5$-Br** (*R*ecombined *N*-*F*used *P*entaphyrin-*Br*omide).

Since **2** was quite electron-deficient because of a well-conjugated π-network bearing several electron-withdrawing groups, we tried nucleophilic substitution reactions onto the brominated position.[6] When **2** was treated with primary or secondary amines, the corresponding mono- or dialkylamino groups, respectively, were smoothly introduced under ambient or moderate heating conditions (**3**−**5**, Scheme 2). Surprisingly,

Scheme 2. Nucleophilic Substitution Reactions and Coordination Reaction[a]



[a]Bold lines indicate the conjugation circuit.

using NH_4OAc as an ammonia source allowed direct amination without any metal catalysts. Tertiary amine did not afford any substituted product probably owing to the steric hindrance. In addition, oxygen adduct **7** that gave the HR-ESI-MS: 1230.0401 (Figure S14, Supporting Information) was occasionally obtained during these reations. In the ^{1}H NMR spectrum of **7**, six doublets due to the outer β−protons appeared within slightly upfield region (7.17−7.63 ppm) compared to those of compound **2**-**5** along with the singlets assigned to the NH protons 9.61 and 10.87 ppm, which disappeared by addition of D_2O (Figure S6, Supporting Information). The crystal structure of **7** (Figure 1) revealed that the length of the C−O bond was 1.22 Å comparable to that of a carbonyl group (keto form). These results show loss of the aromatic nature of **7** (HOMA: 0.531) and agree with the structure in which the peripheral conjugation pathway is interrupted by the cross conjugation as illustrated in Scheme 2, while **7** has a similar planarity to that of **2** (MPD: 0.348 Å, MPD*p*: 0.057 Å, MPD*d*: 0.157 Å).

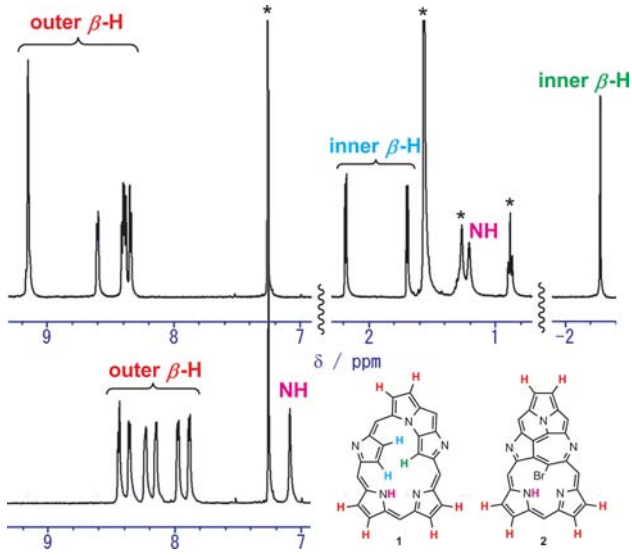


Figure 1. ^{1}H NMR spectra of **1** (upper) and **2** (lower) in $CDCl_3$ (* = solvent or impurity).

In the next step, metalation of the **RNFP$_5$** series was investigated. Unfortunately, most of our attempts did not work and led to recovery of the starting materials or formation of complicated mixtures even in the case of using $[RhCl(CO)_2]_2$ salt, which effectively form dipyrrin−$Rh(CO)_2$ complex with many common porphyrinoids.[4b,c,7] The narrow cavity and the stiff skeleton of **RNFP$_5$** framework accepted only boron atom to form complex **8** during the reaction of oxygen-adduct **7** with triethylamine and the subsequent treatment with BF_3·OEt_2. ^{1}H NMR spectrum of **8** displayed clear downfield-shifted signals due to the outer β-protons, suggesting the aromaticity of **8** (Figure S7, Supporting Information). According to the X-ray crystal structure shown in Figure 2, **8** adopted a slightly waving structure in contrast to the other derivatives and the length of the C−O bond was 1.37 Å that was comparable to a single bond, indicating

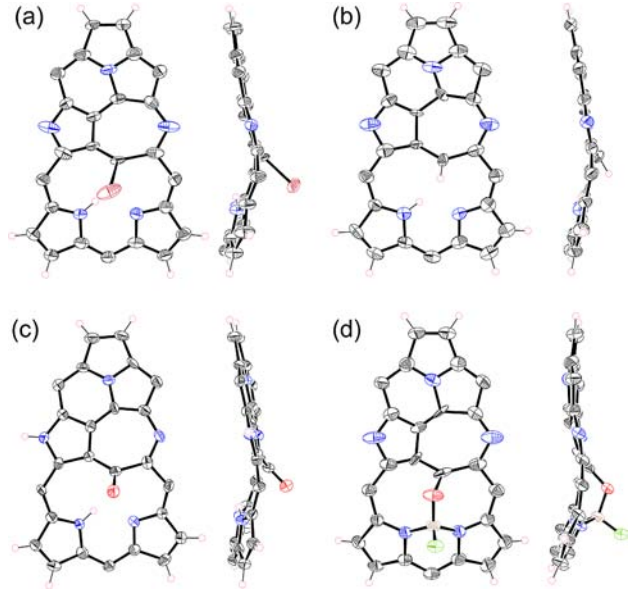


Figure 2. Crystal structure of (a) **2**, (b) **6**, (c) **7**, and (d) **8**. Right: top view. Left: side view. Thermal ellipsoids are set at the 50% probability level. *meso*-Substituents are omitted for clarity.

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that **8** employed the aromatic tautomer (enol form) as illustrated in Scheme 2. The boron atom was coordinated by NNO core together with the axial fluorine atom in a tetrahedral fashion, but could not stay in the inner cavity and was displaced from the entire mean plane by 1.218 Å. In order to obtain a planar coordination, removal of the inner substituent (bromine for **2**, oxygen for **7**, and so on) seems to be necessary. Luckily, we accidentally obtained an inner unsubstituted derivative **6** as a byproduct of **7**. Since **6** was gradually changed into **7** in a hydrophilic solvent such as methanol, the oxygen source of **7** was likely to be water. In the ^{1}H NMR of **6** (Figure S5, Supporting Information), a signal due to the inner C−H proton appeared at 0.70 ppm, revealing the influence of a clear aromatic ring current effect (HOMA: 0.640). The absence of the bromine atom moderated the steric strain of the framework, therefore **6** approximated the flatter structure than that of **2** (MPD: 0.279 Å). However, the reproducibility of this reaction was quite poor, so we have too little amount of **6** in hand to explore in detail.

UV/visible/near-IR absorption spectra are shown in Figure 3. Most compounds exhibit ill-defined Soret-band-like bands and

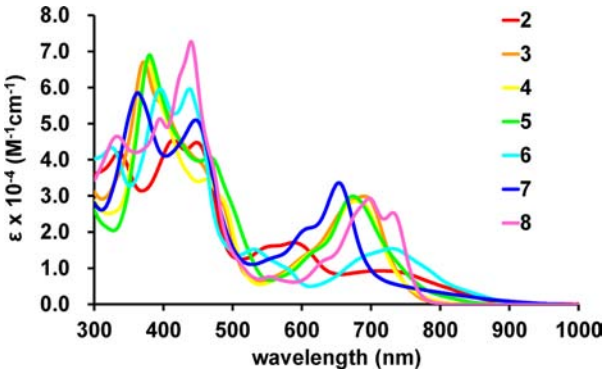

Figure 3. UV−vis absorption spectra in CH_2Cl_2.

Q-band-like bands around 300−500 nm and 600−800 nm, respectively. The overall wave shapes and the λ_{max} were significantly differed by the functionalities, suggesting smooth electronic interaction between the macrocyclic plane and the substituents. In the cases of reported nucleophilic substitution reactions of hexaphyrins,[5] no remarkable spectral changes were recognized through the introduction of substituents because the perpendicular geometry of *meso*-aryl linkers to the macrocyclic plane suppressed the electronic communication between them. In this work, the absorption property of each compound was distinctive depending on the substituent. In addition, the conditions of the reactions were relatively milder and no tedious separation processes were required.

In summary, we developed a regioselective monobromination of **NFP$_5$** followed by a skeletal recombination reaction giving an **RNFP$_5$** framework under mild and common conditions. **RNFP$_5$-Br** showed an aromatic nature derived from the 22π conjugation network and was quite reactive to several fuctionalizations. The derivatives exhibit distinctive absorption spectra depending on the substituents so that they can potentially attain various electronic interactions between the core and side chains. Although the detail reaction mechanism is still unclear, further investigation is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, spectral data for compounds, and ^{1}H NMR and ESI-mass spectra. X-ray data for **2**, **6**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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