A Bottom-up Synthesis of Antiaromatic Expanded Phthalocyanines: Pentabenzotriazasmaragdyrins, i.e. Norcorroles of Superphthalocyanines

Taniyuki Furuyama, Takehito Sato, and Nagao Kobayashi*,[†]

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

S *Supporting Information*

ABSTRACT: The first example of an antiaromatic expanded phthalocyanine, classified as a norcorrole of a superphthalocyanine has been prepared and fully characterized. The newly developed phthalonitrile dimerization reaction was a crucial step, which allowed for the bottom-up synthesis of expanded phthalocyanines. Their structure was confirmed by single crystal X-ray diffraction analysis. The 20 π antiaromaticity of the macrocycles was suggested by optical and theoretical calculations.
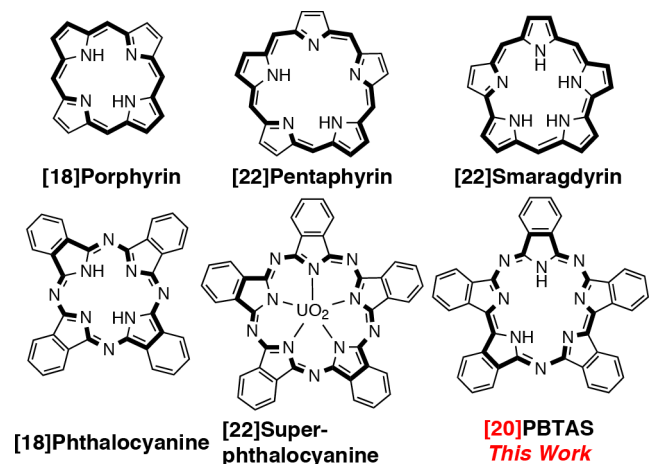
Typical porphyrin and azaporphyrins bearing four pyrrole units have an 18 π-electron conjugated system which possesses Hückel $(4n + 2)$ π aromatic character. Development of novel macrocyclic, fully π-conjugated systems is one of the most attractive research topics in porphyrinoid chemistry.[1] For example, the syntheses of expanded porphyrinoids, such as pentaphyrins (22 π aromatic molecules), with unique properties has been reported by some groups.[2] Azaporphyrinoids such as phthalocyanines (Pcs) and tetraazaporphyrins are the congeners of porphyrinoids. Here, the *meso*-positions are occupied by nitrogen moieties which make the optical properties of azaporphyrinoids quite different from those of porphyrins (Scheme 1). Expanded azaporphyrinoids, represented by expanded Pcs, are also important in various cutting-edge fields such as organic electronic devices and photodynamic therapy. In contrast to the expanded porphyrins, the chemistry of expanded Pcs is quite limited. A small number of expanded Pcs have been reported.[3] However, none of the reported expanded Pcs consist of pyrrole or isoindole units linked by nitrogen bridges, except in the case of superphthalocyanines.[4]

In this communication, we report the facile synthesis of a new type of antiaromatic expanded Pc with five isoindole units consisting of two direct pyrrole—pyrrole bonds, named pentabenzotriazasmaragdyrins (PBTASs). Parent smaragdyrins possess aromatic 22 π character, but are highly unstable, so that only a few stable core-modified smaragdyrins have been investigated to date.[5] The greatest drawback to the investigation of expanded Pcs is the limited synthetic possibilities available with the polypyrrole construction methods, in contrast to expanded porphyrins.[1] Recently, Cammidge et al. proposed a new building block for construction of a contracted phthalocyanine—porphyrin hybrid macrocycle.[6] Their results clearly indicate that the synthesis of novel expanded Pcs requires a novel synthetic procedure and/or building blocks. Antiaromatic porphyrinoids have recently attracted much interest in synthetic chemistry[7] and electrochemical energy storage systems,[8] although antiaromatic (aza)porphyrinoids are still very rare.[1,9] In this paper, the antiaromatic optical properties of PBTASs are interpreted using the perimeter model that was reported for expanded porphyrins.[10]

The lithium method is a well-known synthetic protocol for free-base Pcs.[11] The reaction is initiated by a nucleophilic attack of lithium alkoxide (oxyanion) on the cyano group of the phthalonitrile. The oxygen atom of the nucleophile is essential for the formation of Pcs. When carbanions are used as the nucleophile, tetrabenzotri-, di-, and monoazaporphyrins are obtained instead of Pcs.[12] These results motivated us to find alternative macrocyclic synthetic procedures using a different source of anion initiation. Thus, the thiolate anion, generated from dodecanethiol and sodium, was reacted with 4,5-disubstituted phthalonitrile (Scheme 2a). Although no macrocyclic compound was observed, an unexpected bright orange solid was obtained in moderate yields. Its structure, **2b**, was determined using single crystal X-ray diffraction analysis which
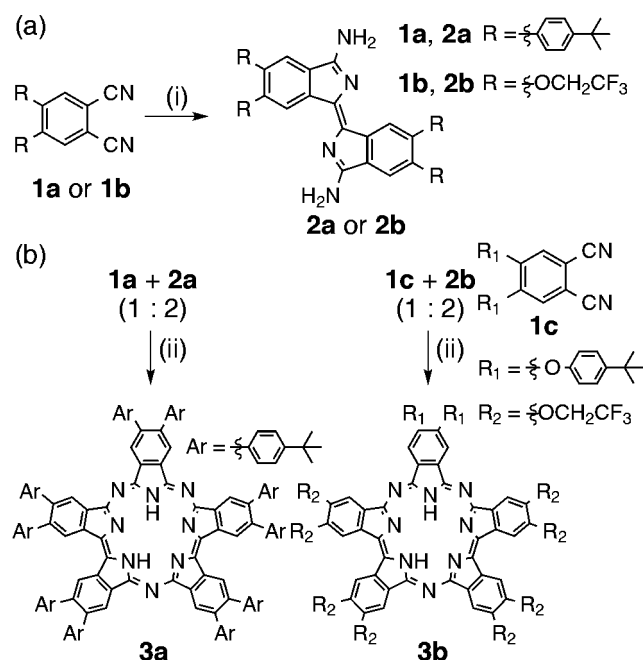
Scheme 1. Structures of Porpyrin, Pentaphyrin, Smaragdyrin, and Their Azaporphyrin Analogs[a]

[18]Porphyrin   [22]Pentaphyrin   [22]Smaragdyrin

[18]Phthalocyanine   [22]Super-phthalocyanine   [20]PBTAS *This Work*

[a]The bold lines indicate each conjugation circuit.

Scheme 2. Synthesis of (a) Diamino-β-isoindigos and (b) Pentabenzotriazasmaragdyrins[a]

(a)

1a, 2a R = <chemical structure>

1b, 2b R = OCH₂CF₃

1a or 1b → (i) → **2a or 2b**

(b)

1a + 2a (1 : 2) → (ii) → **3a**

1c + 2b (1 : 2) → (ii) → **3b**

Ar = <chemical structure>

R₁ = O <chemical structure>

R₁, R₁, R₂ = OCH₂CF₃

[a]Reagents and conditions: (i) Na, 1-dodecanethiol, 100°C, 1 h, then 180°C, 1 h, 50% (for **2a**), 39% (for **2b**); (ii) 1-chloronaphthalene, 200°C, 12 h, 18% (for **3a**), 14% (for **3b**).

revealed a diamino-β-isoindigo skeleton (Figure S1). Although the corresponding di*imino*-β-isoindigo skeleton has been reported by another group,[13] this one-step synthesis of di*amino*-β-isoindigo skeleton has been explored for the first time. **2b** has a highly planar structure with two isoindole units in a transoid configuration.

Compounds **2a** and **2b** are isolable and bench-stable aminopyrrole derivatives, suggesting their candidacy as precursors for novel azaporphyrinoids. The condensation between phthalonitrile **1a** and aminoisoindigo **2a** at high temperatures produced the macrocyclic compound **3a** (PBTAS) in an acceptable yield (Scheme 2b). In the case of different substituents between phthalonitrile (**1c**) and amino-isoindigo (**2b**), the 1:2 condensed macrocycle **3b** was obtained as the sole product. The ¹H NMR spectrum of **3a** showed five sets of signals arising from the α protons of isoindoles, reflecting a highly symmetric structure (Figure S2). More importantly, two sets of broad signals for inner NH protons appeared in the far low field region (20−24 ppm) for both **3a** and **3b**, owing to a strong paratropic ring current effect,[7a,b] indicating an antiaromatic character of PBTASs. The ¹H NMR spectra of **3a** and **3b** remained unchanged even after storage as a solid in air under ambient light for over 6 months. The MS spectra after a metalation reaction of **3a** supported the formation of metalated PBTASs; however, their isolation was so far unsuccessful.

The structure of PBTAS was unambiguously elucidated by X-ray diffraction analysis of crystals obtained from the diffusion of pyridine into an ethyl acetate solution of **3b** (Figure 1). The macrocyclic skeleton of **3b** consists of five isoindole units with two direct pyrrole−pyrrole bonds. The whole structure is weakly twisted resulting from the steric interaction between the α protons of aminoisoindigo units. Selected bond lengths and angles are shown in Figure S3. Two amino pyrrole rings and
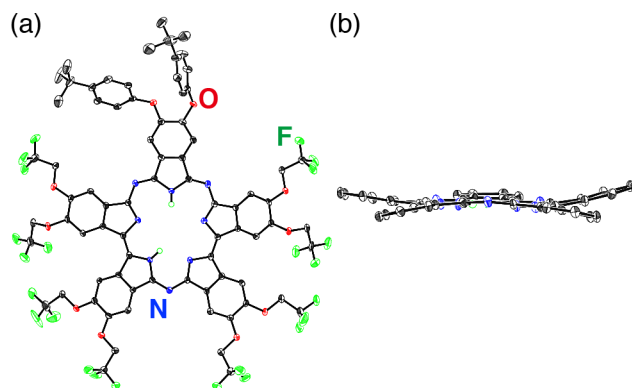

Figure 1. X-ray crystal structure of **3b**. The thermal ellipsoids were scaled to the 50% probability level. (a) Top view; (b) side view (peripheral substituents were omitted). In both views, hydrogen atoms and the solvent molecules have been omitted for clarity.

three imino pyrrole rings could be distiguished by the C−N−C angles of pyrrole.[14] In contrast to 22 π aromatic smaragdyrins, the structure of **3b** can be interpreted as a 20 π electron macrocyclic delocalization pathway. Reflecting its (4n π) antiaromaticity in the solid state, compound **3b** displays significant bond length alternation (the HOMA index is 0.587). The NICS(0) and NICS(1) values calculated at the center of the macrocycle of model structure **3c**, where the peripheral substituents were replaced with hydrogen atoms, are 16.2 and 14.3 ppm, respectively, supporting the antiaromaticity of the macrocycle (Figure S4).

Absorption and magnetic circular dichroism (MCD) spectra of **3a** and **3b** are shown in Figure 2. The absorption spectra
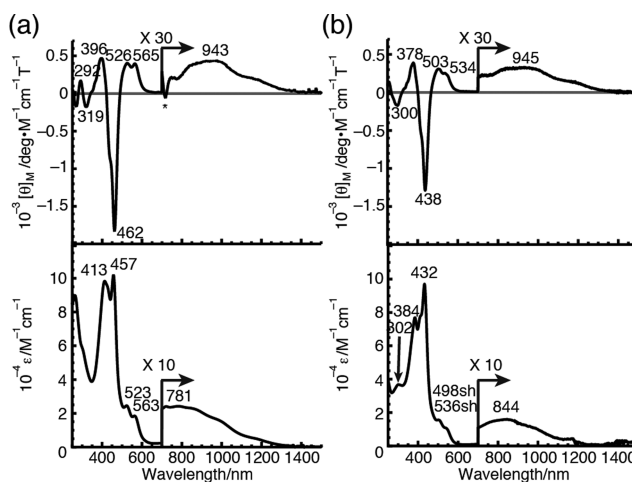

Figure 2. UV−vis−NIR absorption (bottom) and MCD (top) spectra of (a) **3a** in CH₂Cl₂ and (b) **3b** in THF. *: H₂Pc.

exhibit significantly different envelopes from those of typical Pcs and superphthalocyanines.[4] Both compounds have weak and broad absorption bands ranging from 600 to 1300 nm, which are characteristic bands for 4n π antiaromatic porphyrinoids. Moderate (around 500 nm) and intense (around 400 nm) bands appeared in the visible region. In the MCD spectra, very weak and moderate Faraday B terms appeared, corresponding to the weak near-IR band and moderately intense band at around 500 nm, respectively. Strongly coupled Faraday B terms with a − , + MCD sign in

ascending energy were observed, corresponding to the absorption bands at around 400 nm.

To investigate further optical properties and the antiaromaticity of PBTASs, MO coefficients for modeled compound **3c** have been calculated. Partial MO energy diagrams and the calculated absorption spectrum of **3c** are shown in Figure 3,
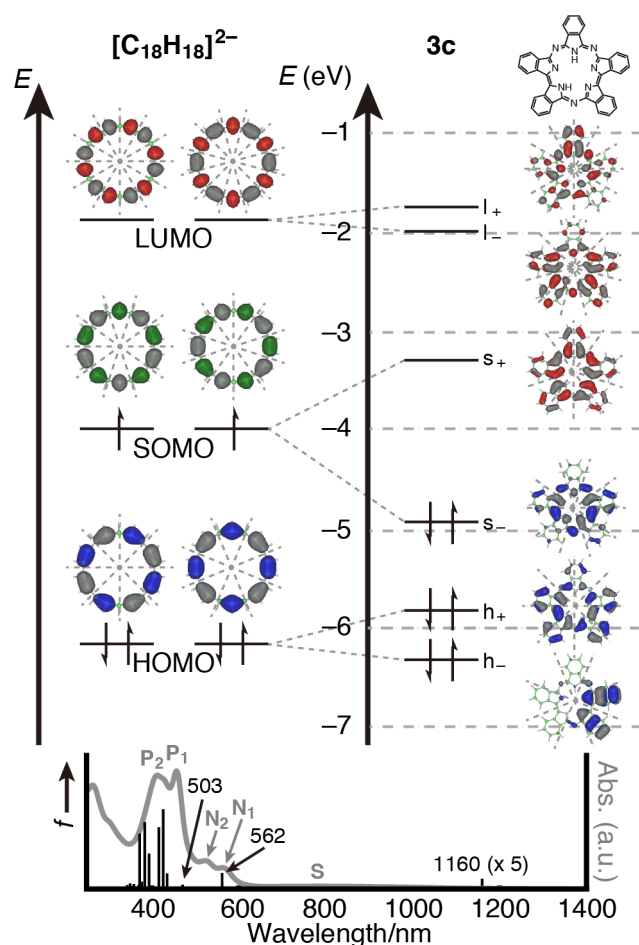

Figure 3. Partial molecular energy diagram, orbitals, and perimeter labels of **3c** (top, right), its calculated absorption spectra (black sticks) and the absorption spectrum of **3a** in CH_2Cl_2 (gray line) (bottom), and 20-electron [18]annulene perimeter ($[C_{18}H_{18}]^{2-}$) (top, left). Calculations were performed at the B3LYP/6-31G(d) level (for details, see the Supporting Information). Arbitrary nodal lines are drawn on the iso-surface plots.

with the results of TDDFT calculations summarized in Table S3. In our previous work, Michl's $4n$-electron perimeter model[15] could be applied to the interpretation of absorption properties belonging to antiaromatic porphyrinoids.[7c,10] According to the model, six frontier π-orbitals of a 20-electron[18] annulene perimeter ($[C_{18}H_{18}]^{2-}$) are of particular importance for the 20 π antiaromatic PBTASs and, thus, are also shown in Figure 3. As can clearly be seen in Figure 3, the number of nodal planes (4, 5, and 6) of the six frontier orbitals belonging to **3c** are the same as those for $[C_{18}H_{18}]^{2-}$. The calculated lowest-energy band (1160 nm) is composed of transitions from the HOMO to the LUMO ($s_- \rightarrow s_+$). Since this transition is of an intrashell nature, the absorption and MCD intensities of the band are very weak[15c] and the observed weak near-IR band (781 nm for **3a**) could be assigned as the S band. Two weak (N_1, N_2) and two strong (P_1, P_2) transitions

are also predicted on the basis of the perimeter model. The other four electronic transitions are intershell transitions derived from the (h_- or h_+) $\rightarrow$ s_+ or $s_- \rightarrow$ (l_- or l_+) transition. Since the TD-DFT calculations of **3c** agree well with the antiaromatic perimeter model, the experimental absorption and MCD spectra could be assigned.

Finally, electrochemical properties of **3a** and **3b** were examined. Cyclic voltammograms of **3a** and **3b** (Figure S5) indicate two reversible reduction couples while clear oxidation couples could not be obtained due to the low stabilities of the oxidized species. For assignment of the reduced species, spectroelectrochemical measurements were performed with the results of **3a** in Figure S6. When the potential that was sufficiently negative for the first reduction was applied to the solution of **3a**, a new mid-intense band appeared (1010 nm) in the near-IR region beyond 1000 nm. When a negative potential high enough for the second reduction reaction to occur was applied, the near-IR band almost disappeared and new sharp and intense bands appeared in the mid-near-IR (848 nm) and visible (567 and 550 nm) regions. The series of spectral changes for **3a** was similar to that of $4n - 4n + 1 - 4n + 2$ π spectral changes for expanded porphyrinoids.[16] Therefore, the final reduced species could be assigned to a two-electron reduced 22 π aromatic compound. Further, to enhance the interpretation, MO calculations of the two-electron reduced form of **3c** ($[3c]^{2-}$) were carried out. As depicted in Figure S7 and Table S4, the frontier orbitals and transition components were consistent with Michl's $(4n + 2)$-electron perimeter model[17] (22-electron[18]annulene perimeter, $[C_{18}H_{18}]^{4-}$), supporting an electrochemical antiaromatic/aromatic switching of **3a**. Unfortunately, the 22 π species could not be isolated as a stable molecule. The reasons for low stability may be similar to the case of aromatic smaragdyrins.[5]

In summary, the first 20 π expanded antiaromatic azaporphyrinoid PBTASs have been prepared and characterized. The sulfur-mediated phthalonitrile dimerization reaction was explored, allowing for the facile synthesis of diamino-β-isoindigos. Mixed condensation with aminoisoindigos and phthalonitriles produced new macrocyclic compounds consisting of five isoindole units. The crystal structure, ^{1}H NMR, absorption, and MCD spectra of PBTASs revealed clear 20 π electronic conjugations both in solution and in the solid state. Moreover, Michl's $4n$-electron perimeter model, in conjunction with TD-DFT calculations, could be applied to explain the optical properties results. The new azaporphyrinoids were constructed using only phthalonitriles so that the expanded Pcs synthesis in this report is a true bottom-up synthesis that is led by new synthetic methodology. Further work is currently underway to synthesize metal complexes of PBTASs and other azaporphyrinoids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09853.

> Additional spectroscopic and calculation results, full details of experimental and calculation procedures (PDF)
> X-ray crystallographic data for **2b** (CIF)
> X-ray crystallographic data **3b** (CIF)

AUTHOR INFORMATION

Corresponding Author
*nagaok@m.tohoku.ac.jp

Present Address
†Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda, 386-8567, Japan.

Notes
The authors declare no competing financial interest.

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