

A Core-Expanded Subphthalocyanine Analogue with a Significantly Distorted Conjugated Surface and Unprecedented Properties**

Soji Shimizu,* Shota Nakano, Ayaka Kojima, and Nagao Kobayashi*

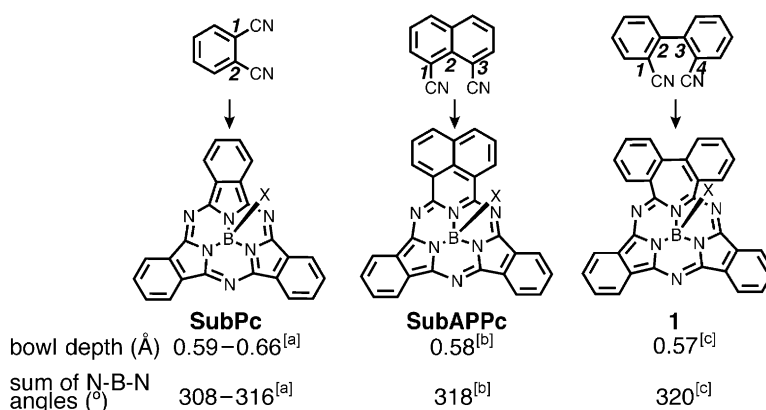
Abstract: The introduction of a seven-membered-ring unit in the place of a five-membered-ring unit in the structure of subphthalocyanine resulted in significant distortion of the bowl-shaped structure of the conjugated molecule as well as the following unprecedented properties: the preferential formation of the axially fluoro substituted species, the fluttering-dynamic-motion-induced rapid exchange of *P* and *M* enantiomers, markedly split *Q*-band absorption, and a clear difference in the ring-current effects arising from the convex and concave surfaces.

Conjugated molecules bearing a curved surface, as represented by fullerenes and carbon nanotubes, have attracted significant attention owing to their unique chemical and physical properties.^[1] With an aim to deepen insight into these properties arising from the convex and concave surfaces, conjugated molecules with curved surfaces, including fragments of these nanocarbons,^[2] such as corannulene,^[3] sumanene,^[4] and significantly distorted graphene,^[5] have been intensively investigated.

Among the conjugated molecules with curved surfaces, subphthalocyanine (SubPc),^[6] a ring-contracted analogue of phthalocyanine (Pc), represents a unique family. In addition to the optical and electrochemical properties characteristic of the Hückel-type $4n + 2\pi$ aromatic conjugated system, namely, intense *Q*-band absorption and fluorescence in the visible region, and a small HOMO–LUMO gap suitable for applications in optoelectronic and molecular electronic materials,^[7] SubPc exhibits a bowl-shaped molecular structure. This structural feature provides convex–concave surfaces for molecular recognition of fullerenes^[8,9] as well as unique chiral surfaces when fused ring units or substituents are

introduced onto SubPc in an unsymmetrical manner.^[10,11] Therefore, SubPc and its porphyrinoid counterpart, subporphyrin,^[12,13] can be regarded as suitable scaffolds not only for the creation of novel curved and/or distorted conjugated surfaces, but also for the study of differences in electronic properties between the convex and concave surfaces. However, research along this line has been limited to the pioneering studies by Torres and co-workers. They demonstrated differences in electron-transfer abilities and ring-current effects between the convex and concave surfaces.^[14,15] Herein, we present a novel approach to a highly distorted SubPc analogue. Not only does this analogue have unique properties, but we were also able to investigate its convex and concave conjugated surfaces.

Recently, we found that inner five-membered-ring units in Pc can be readily replaced with six- and seven-membered-ring



Scheme 1. Strategy towards core expansion in the SubPc structure. The numbers shown on the aromatic dicarbonitrile precursors indicate the number of carbon atoms between cyano groups. The bowl depth and sum of the N-B-N angles of the resultant SubPc structures are given: [a] from Ref. [7]; [b] from Ref. [17]; [c] for **1**, determined in this study.

units by using aromatic dicarbonitrile precursors with cyano groups at positions with a 1,3- or 1,4-relationship.^[16] This synthetic strategy also opened access to a SubPc analogue with a six-membered ring in the core; we referred to this analogue as subazaphthalenephthalocyanine (SubAPPC, Scheme 1).^[17] The course of our investigation on core expansion of the contracted SubPc structure further resulted in the synthesis of a novel seven-membered-ring-containing SubPc analogue, which exhibited a clear difference in the ring-current effects genuinely arising from the convex and concave surfaces. Furthermore, unique properties originating from the core expansion of the SubPc structures were also

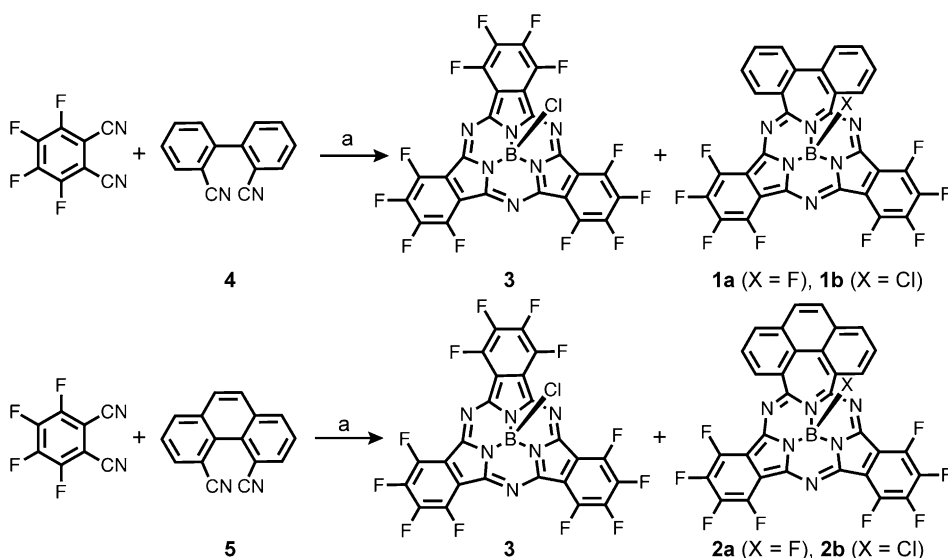
[*] Dr. S. Shimizu, S. Nakano, A. Kojima, Prof. N. Kobayashi
Department of Chemistry, Graduate School of Science
Tohoku University
Sendai 980-8578 (Japan)
E-mail: ssoji@m.tohoku.ac.jp
nagaok@m.tohoku.ac.jp

[**] This project was partly supported by Grants-in-Aid for Scientific Research (C; No. 23550040) and (B; No. 23350095) from the Japan Society for the Promotion of Science (JSPS) and a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No. 2401)” (25102503) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201310028>.

demonstrated, including markedly split Q-band absorption, unusual reactivity of the central boron atom, which caused preferential formation of the axially fluoro substituted species, and the exchange of *P* and *M* enantiomers as induced by fluttering dynamic molecular motion.

The seven-membered-ring-containing SubPc analogues **1** and **2** were obtained together with perfluorinated SubPc **3** from mixed-condensation reactions of tetrafluorophthalonitrile with 2,2'-biphenyldicarbonitrile (**4**) and 4,5-phenanthrenedicarbonitrile (**5**),^[18] respectively, in the presence of boron trichloride (BCl₃) in 1-chloronaphthalene (Scheme 2).



Scheme 2. Synthesis of seven-membered-ring-containing SubPc analogues **1** and **2**. Reaction conditions: a) BCl₃, 1-chloronaphthalene, 180 °C.

MALDI-TOF mass spectrometric analysis of the reaction mixtures demonstrated the presence of **1b** and **2b** with an axial chloride ligand. Such compounds are conventional products in the synthesis of SubPc analogues with BCl₃ as a template. However, to our surprise, more intense molecular-ion peaks of the axially fluorinated species **1a** and **2a** were observed as major ion peaks. Chromatographic separation provided only **1a** and **2a** in 9.1 and 9.8 % yield, respectively, whereas **1b** and **2b** could not be isolated owing to decomposition under chromatographic separation conditions with silica and alumina gels. A control experiment with *o*-phthalonitrile instead of tetrafluorophthalonitrile provided neither **1a** and **2a** nor **1b** and **2b** and thus let us assign the origin of the axial fluorine atom to tetrafluorophthalonitrile. This result also implies that the axial fluorine ligand stabilizes the seven-membered-ring-containing SubPc analogues. The characteristic B–F coupling in the ¹¹B and ¹⁹F NMR spectra (a quartet ¹⁹F signal at –149.6 ppm for **1a** and –149.4 ppm for **2a** and a doublet ¹¹B signal at –11.7 ppm for **1a** and –11.5 ppm for **2a** (see the Supporting Information)) further confirmed the presence of the axial fluorine ligand.

Finally, X-ray single-crystal analysis unambiguously established the structure of **1a** (Figure 1).^[19] Compound **1a** broadly adopts a similar bowl-shaped structure to that of

SubPc.^[7] The biphenyl moiety is tilted by 43° from the mean plane of the three coordinating nitrogen atoms (3N plane). In the molecular-packing diagram, *P* and *M* enantiomers of **1a** based on the helicity of the seven-membered unit, stack alternately to form one-dimensional columnar packing as a result of the π – π stacking interaction between the neighboring molecules, which is enhanced by the small fluorine atom at the axial position. Similar packing diagrams were observed for the axially fluoro substituted SubPc and subporphyrazine analogues.^[20] The shallower bowl depth of **1a** (0.57 Å), as defined by the deviation of the central boron atom from the

3N plane relative to that observed for SubPcs (0.59–0.66 Å)^[7] and SubAPPC (0.58 Å),^[17] implies a more planar coordination geometry around the boron atom in **1a** (sum of the N–B–N angles: SubPc, 308–316°; SubAPPC, 317.5°; **1a**, 319.9°; Scheme 1). Optimized structures of **1a** and **2a** based on DFT calculations at the B3LYP/6-31G(d) level exhibited similar structural features. This rather planarized coordination geometry may cause changes in the Lewis acidity of the central boron atom, hence resulting in the preferential formation of the axially fluoro substituted species, **1a** and **2a**, over the axially chloro substituted species, **1b** and **2b**.

Despite the asymmetric structure of **1a** in the solid state and the putative asymmetric structure of **2a**, symmetrical peak patterns observed for the ¹H NMR signals of the biphenyl and phenanthrene moieties at room temperature (**1a**: δ = 8.04, 7.74, 7.68, and 7.59 ppm; **2a**: δ = 8.60, 8.15, 7.92, and 7.87 ppm) are indicative of dynamic exchange of the *P*

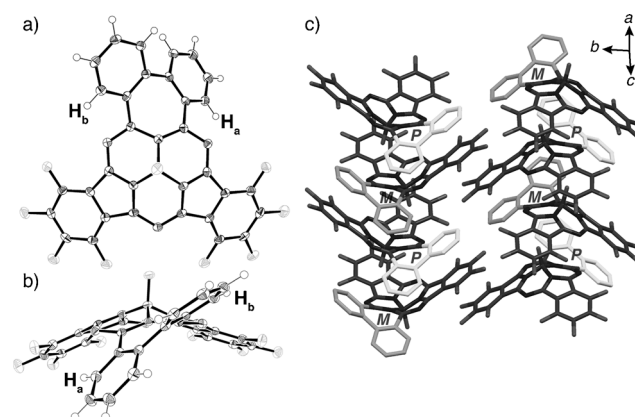


Figure 1. X-ray single-crystal structure of **1a**: a) top view, b) side view, and c) packing diagram. The thermal ellipsoids were scaled to the 50% probability level. In the packing diagram, the biphenyl units of the *P* and *M* enantiomers are highlighted.

and *M* enantiomers in solution. To demonstrate this dynamic motion, we performed variable-temperature ^1H NMR spectroscopy on **1a** (see the Supporting Information). Upon lowering of the temperature, all of the peaks became broad and then coalescent at -40°C . A further decrease in the temperature to -80°C resulted in the appearance of six peaks at $\delta = 8.07, 7.78, 7.73, 7.70, 7.64$, and 7.46 ppm, thus indicating that the fluttering motion of the biphenyl moiety of **1a** became thermally suppressed. On the basis of the coalescence temperature, the activation energy was estimated to be $10.7\text{ kcal mol}^{-1}$ at -40°C , which is similar to the rotation barrier of propyl-bridged biphenyl derivatives.^[21] The assignment of these proton signals on the basis of an H,H COSY experiment and DFT calculations at the B3LYP/6-311G(2d,p) level demonstrated the clear difference in the chemical shift of the biphenyl hydrogen atoms above and below the molecule, particularly for H_a at $\delta = 8.07$ ppm and H_b at $\delta = 7.78$ ppm (Figure 1; see also the Supporting Information). If the similar distances of H_a and H_b from either the center or the rim of **1a** are taken into consideration, the downfield shift of the H_a signal can be ascribed to the larger deshielding diatropic ring-current effect arising from the concave surface relative to the convex surface. In contrast to **1a**, variable-temperature ^1H NMR spectroscopic measurements on **2a** showed only an upfield shift of the single proton signal for the hydrogen atoms at the 3- and 6-positions of the phenanthrene moiety, but the dynamic fluttering motion was not suppressed even at low temperature owing to the smaller activation energy caused by the fused structure of the phenanthrene moiety (see the Supporting Information).

In their absorption spectra, **1a** and **2a** both exhibited markedly split Q-band absorption in the shorter- and longer-wavelength regions as compared to that of regular SubPc at approximately 560 nm (**1a**: $\lambda_{\text{max}} = 682$ and 510 nm ; **2a**: $\lambda_{\text{max}} = 693$ and 513 nm ; Figure 2). In addition to the Q band, **2a** also showed distinctive absorption at 443 nm . In the magnetic circular dichroism (MCD) spectra, Faraday *B* terms corresponding to the split Q bands were observed for both compounds, thus indicating nondegenerate excited states of

1a and **2a**.^[22] Compounds **1a** and **2a** also exhibited fluorescence at 710 and 706 nm with fluorescence quantum yields of 0.08 and 0.006 , respectively. The smaller quantum yield of **2a** relative to that of **1a** is reasonable if the more flexible structure of **2a** indicated by the variable-temperature ^1H NMR spectroscopic measurements is taken into consideration.

To gain deeper insight into the electronic structures of these core-expanded SubPc analogues, we carried out DFT and time-dependent DFT (TDDFT) calculations at the B3LYP/6-31G(d) level. Calculations were also performed on the axially fluoro substituted SubPc **4** as a reference compound. The density-distribution patterns of the frontier orbitals (the HOMO, LUMO, and LUMO + 1) demonstrate that both **1a** and **2a** basically retain conjugated systems delineated by the similar 14π -electron 12-membered inner-perimeter model of SubPc (Figure 3).^[23] The delocalization of these molecular orbitals over the molecules also implies a contribution of the central seven-membered azepine moiety to the conjugated systems of **1a** and **2a** to some extent. Owing to the nondegeneracy of the LUMO and LUMO + 1 as a result of the presence of biphenyl and phenanthrene moieties, theoretical Q bands comprising transitions from the HOMO to the LUMO and from the HOMO to the LUMO + 1 become split (619 nm (oscillator strength: $f = 0.234$) and 484 nm ($f = 0.309$) for **1a** and 635 nm ($f = 0.191$) and 491 nm ($f = 0.218$) for **2a**; see the Supporting Information). These calculation results are in good agreement with the observed markedly split Q-band absorption. The TDDFT calculation also demonstrated an intramolecular-charge-transfer transition from the HOMO-1, which is localized on the biphenyl and phenanthrene moieties, to the LUMO (392 nm ($f = 0.124$) for **1a** and 447 nm ($f = 0.218$) for **2a**). The redshift of this band in the case of **2a** relative to the equivalent band of **1a** is caused by destabilization of the HOMO-1, which thus explains the observed absorption at 389 nm for **1a** and 443 nm for **2a**.

In summary, our core-expansion strategy on SubPc by the use of 2,2'-biphenyldicarbonylnitrile and 4,5-phenanthrenedicarbonylnitrile led to highly distorted SubPc analogues bearing a seven-membered-ring unit in the place of a five-membered-ring unit. This distorted structure resulted in a unique conjugated system, which enabled studies of the aromaticity of the convex and concave surfaces. The novel properties, such as markedly split Q-band absorption in wavelength regions in which neither regular SubPc nor Pc absorbs, the favorable formation of axially fluoro substituted species, and fluttering dynamic motion, which induced rapid exchange of the *P* and *M* enantiomers, were demonstrated. Porphyrins and phthalocyanines show potential for application in the fields of optoelectronics and molecular electronics.^[24] Fine-tuning of the molecular structures and concomitantly the aromaticity and optical properties by the introduction of perturbations (contraction, expansion, deformation, and so forth) is becoming indispensable in the design of functional molecules based on porphyrins and phthalocyanines. The core-expansion strategy can be regarded as one of the most useful strategies for introducing this kind of perturbation. This approach is being pursued further in our laboratory.

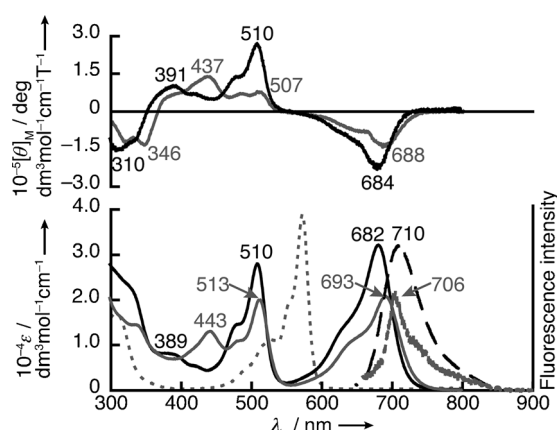


Figure 2. UV/Vis absorption (bottom, solid lines), MCD (top), and fluorescence spectra (bottom, dashed lines) of **1a** (black) and **2a** (gray) in CHCl_3 . The normalized UV/Vis absorption spectrum of SubPc (**3**) in CHCl_3 is shown as a reference (the intensity is shown in arbitrary units; bottom, gray dotted line).

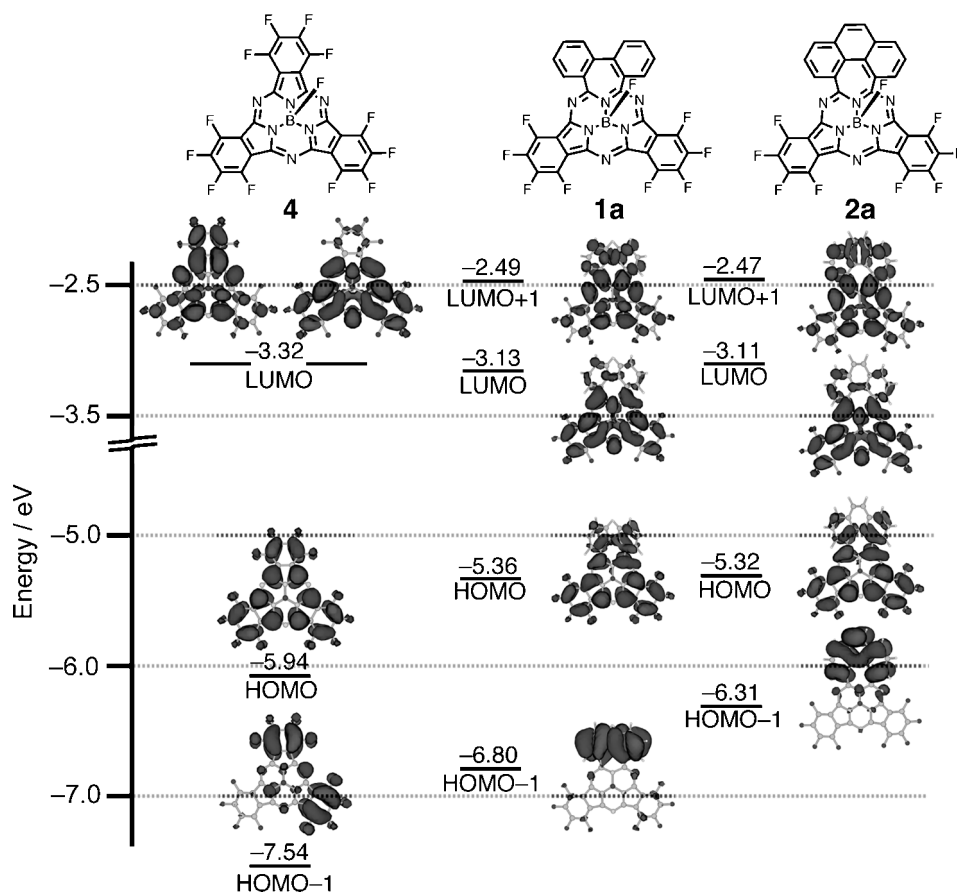


Figure 3. Partial MO diagrams of 1a (middle), 2a (right), and 4 (left).

Received: November 19, 2013
Published online: January 29, 2014

Keywords: aromaticity · conjugation · convex–concave surfaces · ring contraction · ring expansion

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