Subphthalocyanines

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Subazaphenalenephthalocyanine: A Subphthalocyanine Analogue Bearing a Six-Membered Ring Unit**

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Subphthalocyanine (SubPc), a contracted congener of phthalocyanine (Pc) comprising three isoindole units bridged by imino-nitrogen atoms, has attracted much attention since its first synthesis by Meller and Ossko in 1972.[1] The interest lies in its unique properties, such as intense fluorescence and nonlinear optical properties stemming from its bowl-shaped structure and 14π-electron aromatic conjugation system.[2] Considerable effort has been devoted towards investigating not only SubPc and its analogues[3] but also their carbon congeners, subporphyrins, owing to their potential application in a variety of fields.[4] In 2006, Osuka and co-workers reported the first synthesis of the subporphyrin called tribenzosubporphine.[5] Subsequently, Kobayashi and co-workers reported a facile synthesis of *meso*-aryl-substituted subporphyrins using tri-*N*-pyrrolylborane as a synthetic precursor,[6] which was further developed by the Osuka research group.[7] With basic subfamily structures of both phthalocyanines and porphyrins and knowledge about the properties of these contracted analogues in hand,[5–9] research interest is now shifting to their modified analogues, as exemplified by subpyriporphyrin[10] and [14]triphyrin(2.1.1),[11] because of the expectation that such species will exhibit different absorption, emission, and coordination properties and lead to an in-depth understanding of contracted conjugation systems. This kind of information should be indispensable for tuning their properties in respective applications.

Subpyriporphyrin, which was reported by Latos-Grażyński and co-workers, is the first core-modified subporphyrin in which one pyrrole ring is replaced by a pyridine ring, and this molecule exhibits non-aromatic character when nonmetalated as a result of the localization of conjugation on the pyridine ring.[10] Core-modification with no loss of the 14π-electron macrocyclic conjugation has thus remained a challenge, and a core-modified analogue of SubPc has not yet been realized despite the expectation that absorption and emission properties in the visible and near IR region can be tailored by core-modification. Recently, our research group has found that core-modified Pc analogues bearing azaphenalene units in place of isoindole units can be synthesized using 1,8-naphthalenedicarbonitrile as a key precursor. These azaphenalenephthalocyanines (APPcs)[12] basically retained the 18π-electron aromatic characteristics of Pc, but the spectroscopic and electrochemical properties were significantly altered depending on the number and positions of the azaphenalene units. This motivated us to investigate a novel core-modified SubPc analogue with a macrocyclic 14π-electron aromatic conjugation system according to the same synthetic protocol.

Subazaphenalenephthalocyanine (SubAPPc) **2** was obtained in an overall yield of 1.6 % from a mixed-condensation reaction of 1,8-naphthalenedicarbonitrile[13] and 4,5-di-*p*-*tert*-butylphenyloxyphthalonitrile[14] in the presence of boron trichloride (1.0 M solution in *n*-heptane), followed by axial ligand replacement from chloride to phenoxide (Scheme 1). This replacement step was performed to prevent adsorption of axially chlorine- or hydroxy-substituted species formed during separation by column chromatography on silica gel.

The high-resolution ESI-FT-ICR mass spectrometry experiment revealed an intense peak at $m/z = 1187.4768$ (calcd for $C_{74}H_{66}BClN_6O_5Na$ [M^++Na]: 1187.4774), and is indicative of chlorination at one of the peripheral or non-peripheral positions, which is often induced during the formation of subphthalocyanines using BCl_3 as a template reagent.[15] The formation of this chlorinated species was also confirmed by ^1H NMR spectroscopy. Signals corresponding to the protons of the axial phenoxy ligand are observed at $\delta =$ 6.80, 6.66, and 5.74 ppm. The up-field shift of protons at *ortho* positions of the axial phenoxy ligand suggests the presence of a diatropic ring current effect arising from the 14π-electron aromatic conjugation system. The aromaticity of **2** is, however, rather less significant than that of **1**, which has a signal at $\delta = 5.30$ ppm that corresponds to the *ortho* protons of the axial phenoxy ligand. Signals corresponding to the naphthalene moiety are observed at $\delta = 8.77$ (1H), 8.63 (1H), 8.09 (1H), and 7.59 ppm (2H), the correlations of which suggest that the 4- or 5-position of the naphthalene moiety is chlorinated. To avoid chlorination, reaction parameters were varied including reaction temperature, amount of BCl_3, and solvents employed for the reaction. It was found that reactions performed at various temperature ranging from 160 °C to 230 °C did not afford the nonchlorinated species, and SubAPPc was not formed below 160 °C owing to the low reactivity of 1,8-naphthalenedicarbonitrile. The amount of BCl_3 influenced the yield of SubAPPc, but the nonchlorinated species was not obtained even though a minimal amount of BCl_3 was used for the reaction. It is well known that electron-

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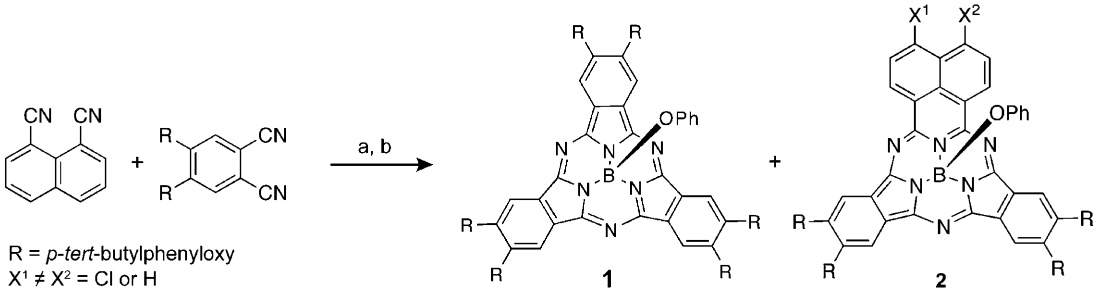

Scheme 1. Synthesis of subazaphenalenephthalocyanine **2**. Reaction conditions: a) BCl_3, 1-chloronaphthalene, 190 °C, 5 min; b) phenol, 120 °C, 2 h.

rich aromatic solvents such as *p*-xylene are efficient for preventing chlorination of SubPc during BCl_3-template syntheses,[16] but the use of a 1.0 M solution of BCl_3 in *p*-xylene did not provide the nonchlorinated species. These results can be attributed to the high reactivity of SubAPPc towards electrophilic aromatic substitution reaction.

Single crystals suitable for X-ray analysis were obtained by slow diffusion of 1-propanol into a solution of **2** in toluene.[17] Crystallographic analysis unambiguously revealed its bowl-shaped structure with a 0.58 Å deviation of the boron atom from the mean plane defined by three coordinating nitrogen atoms (Figure 1). This structural feature us comparable to those of general SubPcs. [2] A chloride substituent is placed at one of the peripheral positions of the naphthalene moiety as is expected by the mass spectrometry and ^{1}H NMR spectroscopy. Because the unsymmetrically substituted SubPc species is inherently chiral as previously reported by Claessens and Torres,[18] a pair of enantiomers, which possess the chloride substituent at the 4- or 5-position of the naphthalene moiety, respectively, are observed in the crystal structure of **2**. The position of the chloride atom, however, could not be resolved owing to its disorder at the 4- and 5-positions in one enantiomer or at the 5- and 4-positions in the other enantiomer with 7:3 occupancy. In the packing diagram, two molecules form a π–π stacking dimer using the naphthalene moieties (see the Supporting Information). The strain caused by incorporation of the six-memebered ring unit in the core is released by planar arrangement of the azaphenalene moiety from the mean plane defined by three *meso*-nitrogen atoms, whereas two isoindole units are tilted by about 23° from the mean plane. Slightly longer bond lengths of C1–C2 and C10–C12 of 1.467(8) and 1.475(8) Å, respectively, indicate small contribution of the outer naphthalene moiety to the macrocyclic 14π-electron conjugation system.

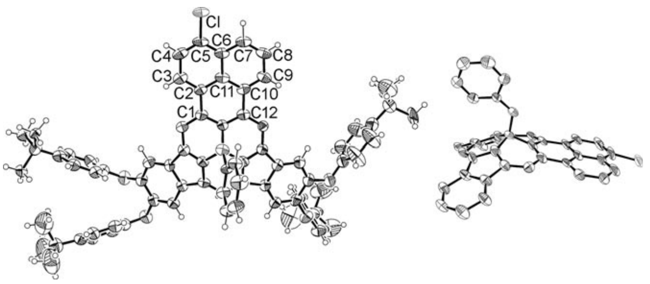

Figure 1. ORTEP plot of **2**, top view (left) and side view (right). The thermal ellipsoids are drawn at the 50% probability level. *para-tert*-Butylphenyloxy substituents and hydrogen atoms in the side view are omitted for clarity.

In the absorption spectrum, **1** exhibits one intense Q-band absorption at 573 nm, whereas **2** shows red-shifted and rather complex Q-band absorption at 708, 659, 616, and 600 nm, which is indicative of alteration of the electronic structure (Figure 2). The color of a solution of **2** is blue rather than pink which is the typical color of SubPc (see the Supporting Information). The tail of the lower-energy Q band extends to 750 nm, which is longer than that of subnaphthalocyanine.[3a,b] These results indicate that our synthetic protocol towards SubPc analogues bearing unique spectroscopic properties is effective. The magnetic circular dichroism (MCD) spectrum and band deconvolution analysis reveal the split Q_{00} bands at 708 and 659 nm, and the complex Q-band absorption is assigned tentatively based on the presence of overlapping pairs of Q_{00} and Q_{01} bands followed by a more complex set of vibrational bands at higher energy (see the Supporting Information). The MCD signals in this region can be regarded

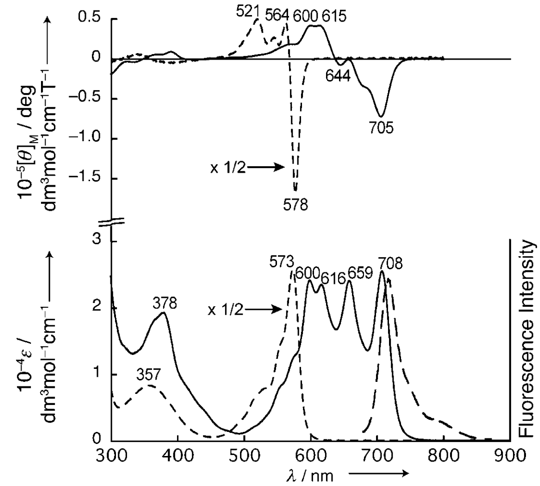

Figure 2. Absorption (bottom) and MCD (top) spectra of **1** (-----) and **2** (——) in $CHCl_3$, and fluorescence spectrum of **2** (– – –) in $CHCl_3$.

as Faraday *B* terms, which are indicative of the absence of a threefold or higher symmetry axis, and these kinds of SubPc molecules generally possess nondegenerated excited states.[19] Although the molar absorption coefficient of **2** is about half of that of **1**, it should be emphasized that the absorption spectrum of **2** covers a wide range in which neither general Pc nor SubPc have absorption. This observation is particularly favorable for photoenergy conversion processes because dyes which effectively absorb a wide range of light energy are strongly desired. Compound **2** also shows fluorescence at 718 nm with a Stokes shift of 197 cm^{-1}, and the fluorescence quantum yield (Φ_F) of 0.18[20] and fluorescence lifetime (τ_F) of 3.6 ns are comparable with those of the general SubPcs.[2]

Molecular orbital calculations were performed using DFT methods at the B3LYP/6-31G(d) level on model compounds of **1** and **2** in which the peripheral substituents and axial ligand were replaced with hydrogen atoms and a hydroxy group for simplicity (Figure 3). The frontier orbitals of **2** show similar density distribution patterns to those of **1**, and coefficients are found at the naphthalene moiety in the case of highest occupied molecular orbital (HOMO) and LUMO + 1 (LUMO = lowest occupied molecular orbital). This results in significant destabilization of the HOMO and an energy difference between the LUMO and LUMO + 1 by 0.08 eV. Furthermore, TDDFT calculations reveal two bands in the Q-band region which mainly consist of transitions from the HOMO to LUMO and LUMO + 1. The smaller HOMO–LUMO energy gap of **2**, therefore, explains the red shift of the lower-energy Q band, and the substantial energy difference between the LUMO and LUMO + 1 explains the splitting of the Q bands. These calculation results are in good agreement with the observed Faraday *B* terms in the MCD spectrum of **2**.

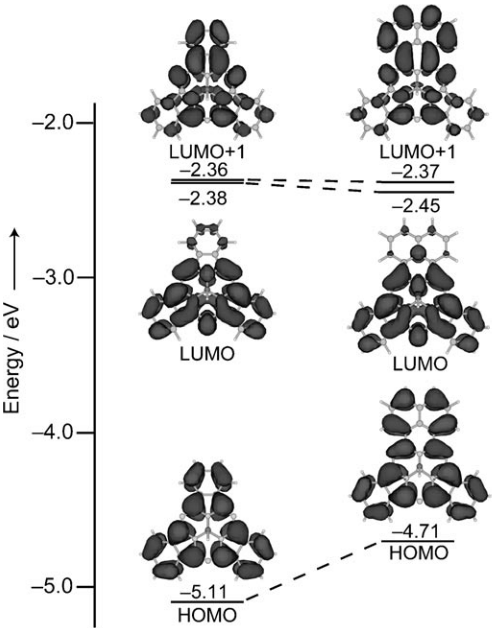

Figure 3. Frontier molecular orbital diagrams of **1** (left) and **2** (right).

To further support the absorption spectra and MO calculations, electrochemical measurements were performed on these compounds. A quasireversible one-electron oxidation process and a reversible one-electron reduction process are observed at 0.53 and −1.54 V (vs. Fc^+/Fc), respectively, for **1** (see the Supporting Information). The first reduction potential of **2** at −1.61 V is comparable with that of **1**, whereas the first oxidation potential at 0.15 V is shifted negatively, and is indicative of a high-lying HOMO as predicted by DFT calculations. This results in a decrease of the potential energy difference (1.76 V for **2** and 2.06 V for **1**), which is in agreement with the large red shift of the Q band.

In summary, a novel subphthalocyanine analogue comprising an azaphenalene moiety was prepared according to the same synthetic protocol employed for the synthesis of APPcs.[12] This new species retained a 14π-electron aromatic conjugation system despite the presence of a six-membered ring unit in its conjugated system, and the electronic structure was significantly altered as a result of the incorporation of the azaphenanlene moiety. SubAPPc can absorb a wide range of light energy, which is a useful property for functional dyes employed in various fields. The introduction of azaphenalene units is a promising method for modifying electronic structures and properties of Pc, SubPc, and their related compounds. Further investigation using this approach is currently underway.

Experimental Section

Preparation of **1** and **2**: A suspension of 1,8-naphthalenedicarbonitrile (90 mg, 0.5 mmol) and 4,5-di-*p*-*tert*-butylphenyloxyphthalonitrile (1 equiv, 212 mg, 0.5 mmol) in 1-chloronaphthalene (2 mL) was heated at 190 °C for approximately 10 seconds. Then, a solution of boron trichloride in *n*-heptane (1.0 M, 1 mL, 1 mmol) was added by a syringe under a nitrogen atmosphere and the mixture was heated at 190 °C for another 5 min to give a blue/purple solution. Preparative thin-layer chromatography (silica gel, F_{254}, 60, eluent: $CHCl_3$) was employed to remove impurity and the purple and the blue fractions were collected. These fractions were further purified by GPC-HPLC. The first fraction (purple) to elute from the GPC was characterized as a mixture of axially chloro- or hydroxy-substituted subphthalocyanines, and the second fraction (blue) was identified as a similar mixture of subazaphenalenephthalocyanines. Finally the first and the second fractions were treated with phenol at 120 °C for 2 h in the dark, respectively, and the products were further purified by column chromatography on silica gel to provide axially phenoxy-substituted subphthalocyanine (**1**) and axially phenoxy-substituted subazaphenalenephthalocyanine (**2**) in 5.6 % and 1.6 % yields, respectively.

Characterization of subphthalocyanine (SubPc; **1**): ESI-FT-ICR-MS: *m*/*z* calcd for $C_{90}H_{89}BN_6NaO_7$ [M^++Na]: 1399.6783; found: 1399.6778; ^{1}H NMR ($CDCl_3$, 400 MHZ, 298 K): $\delta = 8.25$ (s, 6 H; α-benzo), 7.42 (d, 12 H, $J = 8.83$ Hz; phenyl), 7.08 (d, 12 H, $J = 8.81$ Hz; phenyl), 6.74 (dd, 2 H, $J_1 = 7.36$ Hz, $J_2 = 8.35$ Hz; axial *meta*-phenyl), 6.60 (t, 1 H, $J = 7.34$ Hz; axial *para*-phenyl), 5.31 (d, 2 H, $J = 8.66$ Hz; axial *ortho*-phenyl), 1.37 ppm (s, 54 H; *tert*-butyl); UV/Vis ($CHCl_3$): λ_{max} (nm); $\varepsilon = 357$ (16900), 528 (sh, 15600), 553 (sh, 28500), 573 (51400).

Characterization of subazaphenalenephthalocyanine (SubAPPc; **2**): ESI-FT-ICR-MS: *m*/*z* calcd for $C_{74}H_{66}BClN_6O_5Na$ [M^++Na]: 1187.4774; found: 1187.4768; ^{1}H NMR ($CDCl_3$, 600 MHZ, 298 K): $\delta =$ 8.77 (d, 1 H, $J = 7.37$ Hz; naphthalene), 8.63 (d, 1 H, $J = 8.04$ Hz; naphthalene), 8.09 (m, 3 H; naphthalene (1 H) and α-benzo (2 H)), 8.01 (s, 2 H; α-benzo), 7.59 (m, 2 H; naphthalene), 7.41 (m, 8 H;

phenyl), 7.07 (m, 8H; phenyl), 6.80 (dd, 2H, $J_1 = 7.41$ Hz, $J_2 = 8.37$ Hz; axial *meta*-phenyl), 6.66 (t, 1H, $J = 7.32$ Hz; axial *para*-phenyl), 5.74 (d, 2H, $J = 8.62$ Hz; axial *ortho*-phenyl), 1.36 ppm (s, 36H; *tert*-butyl); UV/Vis ($CHCl_3$): λ_{max} (nm); $\varepsilon = 378$ (17400), 600 (24100), 616 (23500), 659 (24100), 708 (25400).

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[17] Crystallographic data for **2**: $C_{81}H_{74}N_6O_5BCl$, $M_w = 1257.72$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.215(8)$, $b = 18.627(14)$, $c = 19.764(15)$ Å, $\alpha = 72.428(10)$, $\beta = 86.386(10)$, $\gamma = 76.354(10)°$, $V = 3484(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.199\ g\,cm^{-3}$, $T = -173\,°C$, 16079 measured reflections, 11920 unique reflections ($R_{int} = 0.0588$), $R = 0.0859$, $R_w = 0.2363$ (all data), GOF = 0.835. CCDC 782513 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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