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First observation of the circular dichroism spectra of chiral subphthalocyanines with C_3 symmetry

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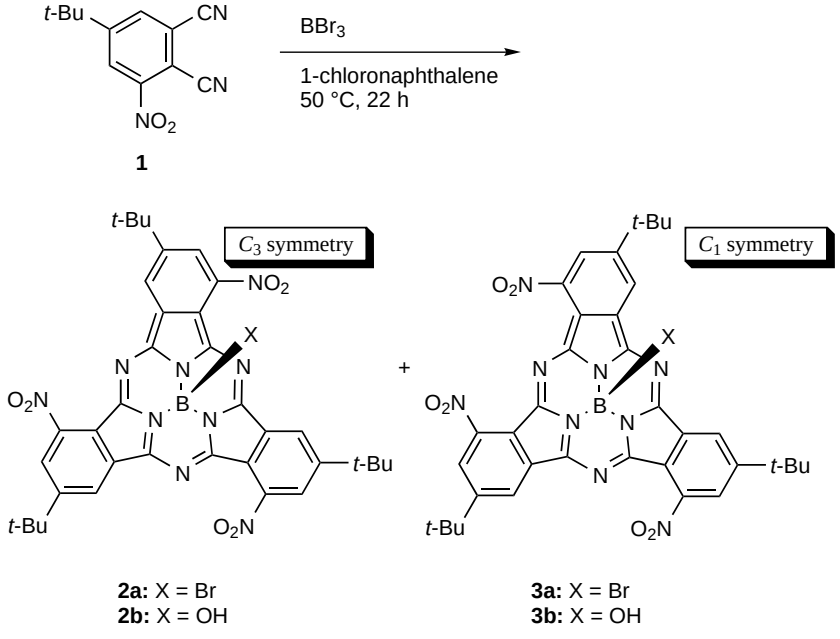
Abstract—Subphthalocyanines (SubPc) with C_3 symmetry due to peripheral tri-nitro and *tert*-butyl groups have been resolved using an optically active HPLC column, and their circular dichroism (CD) spectra, which show a mirror-image relationship with respect to the line of $[\theta]=0$, recorded as the first example of the CD spectra of SubPcs.

Subphthalocyanines (SubPcs) are phthalocyanine derivatives composed of three isoindoline units and one boron atom as a central metal, with cone-shaped (non-planar) delocalized π-electron systems,[1] and have received considerable attention in relation to non-linear optics.[2] SubPcs prepared by condensation reactions of mono-substituted phthalonitriles are generally mixtures of two substitutional isomers; C_1 and C_3 regioisomers. Originating from their non-planar geometry, each regioisomer is intrinsically chiral. A few attempts have been made on the resolution of these regioisomers.[3] However, no circular dichroism (CD) spectrum, which is the most direct identification of complete separation of these isomers, has been reported to date. In one respect, this is due to the low solubility of the pure isomers, and in another respect, it is due to the weak-



Scheme 1.

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ness of the CD intensity of the resultant enantiomers (the CD intensity of compounds having only alkyl, alkoxy, or alkylthio groups is generally very weak).[4] In addition, we cannot use alkoxy groups since they are cleaved by BBr_3 or BCl_3 which is used as a template of SubPc formation reactions. In this paper, we have succeeded in overcoming these obstacles inherent in SubPcs, and report the optical resolution and clear circular dichroism spectra of C_3-symmetrical subphthalocyanines (Scheme 1).

In order to confirm complete separation/resolution by multiple spectroscopic methods, i.e. mainly HPLC, NMR and CD, we had to carefully choose the substituents on the starting phthalonitrile. As shown in Scheme 1, we chose nitro and *tert*-butyl groups. The strongly electron-withdrawing nitro group should help to generate a large dipole moment, which is expected to be advantageous for strengthening the circular dichroism signals.[4] In addition, the presence of the nitro group will prevent halogenation in the cyclization step (BBr_3 or BCl_3 is often used as a template, and the liberated Br or Cl often halogenates the SubPc periphery.[5]) However, on the other hand, the nitro group concomitantly lessens the solubility of the compounds, particularly in non-polar organic solvents suitable for resolution by chiral column chromatography and measurements of circular dichroism spectra, which is a negative factor in resolving enantiomers using columns. Accordingly, *tert*-butyl groups were introduced to increase the solubility of the resultant compounds.

The synthesis of **2** and **3** was started from 3-nitro-5-*tert*-butyl-phthalonitrile (**1**) (Scheme 1).[6] The trimerization reaction was carried out by heating **1** in the presence of boron tribromide in 1-chloronaphthalene at 50°C for 22 h (Scheme 1).[5] Although B-Br products (**2a** and **3a**) were initially formed, the bromium on the boron atom was rapidly hydrolyzed to form B-OH products (**2b** and **3b**) during the purification processes. The C_1 and C_3 symmetry regioisomers (**3b** and **2b**, respectively) were easily separated by silica gel column chromatography, detected by ^{1}H NMR analyses, and their ratio, determined from integration of the signals, was C_1:C_3=9:1.[7] These compounds have good solubility, as expected, in non-polar solvents, even in hexane containing a small amount of chloroform.

Optical resolution of the C_3 regioisomer **2b** was carried out using a chiral HPLC technique.[8,9] Fig. 1 shows the chromatogram. Well-separated comparable peaks (fr. 1 and fr. 2) are observed. Fig. 2 shows the electronic absorption (bottom) and CD spectra (top) of optically resolved **2b** with C_3 symmetry (an almost indistinguishable electronic spectrum was obtained for the C_1 enantiomer **3b** (spectrum not shown)). As has been seen for SubPcs reported to date,[1,2,5] the Q_{00}– and Soret bands appear at ca. 560–570 and ca. 280–300 nm, respectively. It is known that, in the absence of aggregation, the shapes of the CD spectra of allowed transitions are similar to those of the electronic absorption spectrum, apart from the sign.[10] In accordance with this, the first- and second eluted enantiomers (fr. 1 and fr.2, respectively) show mostly negative and positive CD signals, respectively, throughout all the regions. In order to obtain the correlation between the structure and ICD sign, we attempted to obtain single crystals of the regioisomers of **2b**. In the course of time, however, the color of the solutions changed, which suggested decomposition of compounds. Another way to correlate the isomeric structure with the ICD sign is through calculations. However, we could not have confidence in the accuracy of calculation, since the SubPc π system bends continuously,[1] and the ICD intensity changes very sensitively depending on the fine difference of structures.[11] Unfortunately, optical resolution of the C_1 isomer **3b** ended in failure, although various conditions were attempted.

In summary, we have succeeded in resolving well-designed chiral SubPcs with C_3 symmetry and recording the CD spectra having a mirror symmetry with respect to the $[\theta]=0$ line. To our knowledge, this is the first example of the CD spectra of SubPcs.

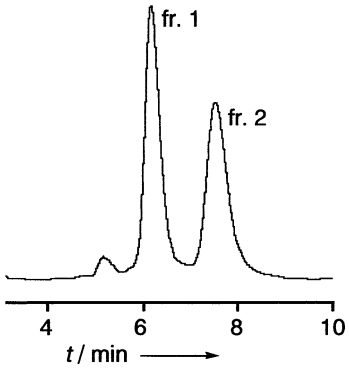

Figure 1. Chromatogram of **2b** at 570 nm.

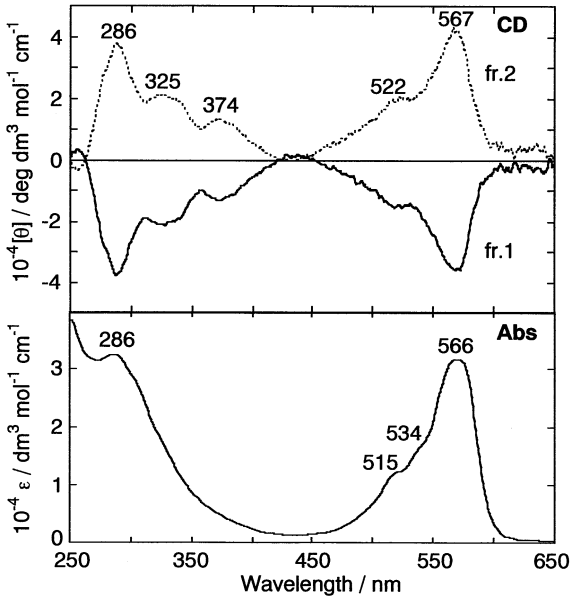

Figure 2. Electronic (bottom) and circular dichroism (top) spectra of **2b** in chloroform.

Acknowledgements

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7. Selected data for **2b** and **3b**: **2b** (C_3 isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, $J=1.6$ Hz, 3H), 8.62 (d, $J=1.6$ Hz, 3H), 1.55 (s, 27H). HR-FABMS (*m*-NBA) *m*/*z*, calcd for $C_{36}H_{35}BN_9O_7$ [M+H$^+$] 715.2789; found 715.2788. **3b** (C_1 isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, $J=1.6$ Hz, 1H), 9.12 (d, $J=1.6$ Hz, 1H), 9.01 (d, $J=1.6$ Hz, 1H), 8.64 (d, $J=1.6$ Hz, 1H), 8.61 (d, $J=1.6$ Hz, 1H), 8.58 (d, $J=1.6$ Hz, 1H), 1.59 (s, 9H), 1.57 (s, 9H), 1.53 (s, 9H). HR-FABMS (*m*-NBA) *m*/*z*, calcd for $C_{36}H_{35}BN_9O_7$ [M+H$^+$] 715.2789; found 715.2788.
8. Optical resolution of the C_3 isomer was performed under the following conditions; chiral LC column: silica gel modified by cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate),[9] 4.6×125 mm, DAICEL), eluent: chloroform:hexane = 0.5:0.5 mL min^{-1}.
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