doi:10.1246/cl.2010.1108

# Subphthalocyanines Having Axial Substituent with Direct B–C Bond: General Preparation and Physical Properties

Yasuhiro Yamasaki* and Tomohiro Mori
*Department of New Business, Orient Chemical Industries Co., Ltd.,*
*8-1 Sanra-Higashi-Machi, Neyagawa, Osaka 572-8581*

(Received July 20, 2010; CL-100640; E-mail: y_yamasaki@orientchemical.com)

A novel synthetic methodology and the characterization of subphthalocyanines (SubPcs) having an axial substituent with a direct boron–carbon bond are reported. The SubPcs are found to be more light- and/or heat resistant than analogs with a heteroatom between boron and carbon, thereby making SubPcs suitable for application to functional dyestuff in display devices.

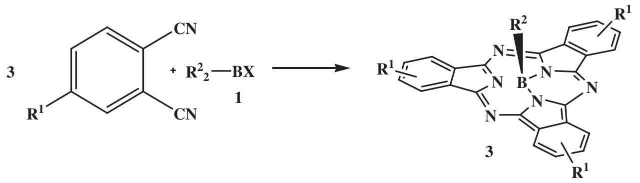
---

Subphthalocyanines (SubPcs) are homologs of tetraazaporphyrins as well as phthalocyanines, well-known warped 18$\pi$-electron aromatic systems consisting of three diiminoisoindole rings capable of coordinating with boron as the core.[1,2] Compared to those of phthalocyanines, the Q-band absorptions of SubPcs are in a relatively small region of around 500 to 600 nm; further, the solubility of SubPcs in some organic solvents is considerably better than that of phthalocyanines.[1,2] Because of these characteristics, SubPcs are attracting considerable attention for application as functional optical dyes for recording media and neon-cutting filters in plasma displays.[3] However, the stability of SubPcs against light and/or heat is considerably less than that of a conventional material because of the strain deformation caused by the size of the coordinated boron atom and the constrained electron distribution around the boron atom.

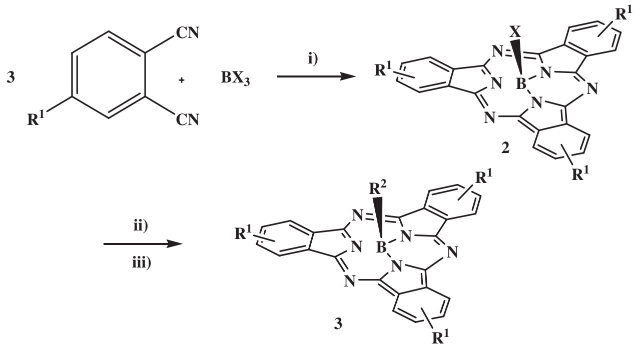
Many analogs of SubPcs with peripheral and/or axial substituents, including subazaporphyrins,[4] subnaphthalocyanines,[1,2] and $\mu$-oxo subphthalocyanine dimers[1,2,5] have been synthesized, and from the study of these derivatives, it has been found that the peripheral substituents affect the Q-band absorption, but the axial ones do not. Further, while both generally improve solubility, they are still insufficiently stable for practical thin-film applications.

SubPcB–OH is generally synthesized from phthalonitrile with boron trihalide and a subsequent hydrolysis reaction. In order to synthesize the derivatives with an axial substituent, because the central boron is ligated by an axial OH, this OH is usually modified to ether or ester as an axial substituent.[1a,6] This axial element, i.e., oxygen directly linking to boron, may cause the low stability of SubPcs.

We think that the direct bond between boron and carbon of the axial substituent should be sufficiently strong to improve the stability of the entire molecule. The only reported method to synthesize SubPcs with an axial substituent with a direct boron–carbon bond is the reaction of phthalonitrile with triphenyl- or tributylboron or dialkylboron bromide **1** in extremely low yields (R = Ph or Bu; the yields are below 1%).[7] The reported method is depicted in Scheme 1. However, this method requires a stoichiometric amount of a strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) together with expensive boron reagents **1** at a high temperature but result in extremely low yields. Further, it is difficult to make this type of boron reagent with various alkyl or aryl groups.



**Scheme 1.** Reported synthesis of SubPcB–R.



**Scheme 2.** Synthetic procedure for **3**: i) xylene, reflux; ii) $R^2$–MgX′/THF, −10–−15 °C; iii) mesitylene, rt.

We have succeeded in the syntheses of SubPcs with an axial substituent and a B–C direct bond (SubPcB–R **3**) in considerably better yields and report here the general synthetic technique together with the properties of the resulting derivatives.[8]

The synthetic procedure is illustrated in Scheme 2. The reaction of haloboron SubPcs **2**, prepared by a previously described method,[6] with an excess of the Grignard reagent in mesitylene afforded **3** in moderate yields of 10% to 40%. Other carbanions, such as alkyllithium reagents at a low temperature, did not provide the expected products but resulted in complex mixtures.

Either alkyl or aryl chloride/bromide could be employed as the Grignard reagent, and after completion of the reaction, the reaction mixture was subjected to a typical aqueous workup and condensation using a rotary evaporator. The obtained purple solid was purified by column chromatography eluting with a mixed solvent of ethyl acetate and toluene. By using this novel methodology, we can directly introduce various substituents on boron.

The results of the reaction are summarized in Table 1. It can be seen that the axial substituents do not affect the $\lambda_{max}$ value of the Q-band absorption, but the peripheral alkylsulfanyl groups resulted in approximately 20-nm-longer shifts.

**Table 1.** Reaction summary and characterization of **3**

| Entry | $R^1$ | X | X′ | $R^2$ | MW | Yield /% | $\lambda_{max}$ /nm | $\varepsilon \times 10^{-4}$ /L mol$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H | Br | Br | Et | 421.3 | 11.4 | 565.0 | 7.52 |
| 2 | H | Br | Br | Ph | 472.2 | 21.0 | 567.0 | 7.99 |
| 3 | H | Br | Br | *n*-Hexyl | 480.2 | 31.6 | 565.5 | 6.95 |
| 4 | H | Br | Br | *i*-Bu | 452.2 | 10.5 | 566.0 | 8.38 |
| 5 | Isopentyl–S | Br | Br | Ph | 778.3 | 9.4 | 587.5 | 8.92 |
| 6 | Isopentyl–S | Br | Br | *n*-Hexyl | 786.4 | 13.1 | 585.0 | 6.95 |
| 7 | Ph–S | Cl | Br | Ph | 796.2 | 26.5 | 587.5 | 7.03 |
| 8 | Ph–S | Br | Cl | Ph | 796.2 | 19.2 | 587.5 | 7.03 |
| 9 | Ph–S | Br | Br | Ph | 796.2 | 10.3 | 587.5 | 7.03 |
| 10 | Ph–S | Br | Br | *i*-Bu | 776.2 | 8.4 | 585.0 | 7.59 |

**Table 2.** Solubility in MEK, heat resistance, and light resistance in the solid and liquid states, compared with **2** and $R^1{}_3$SubPcB–O$R^2$

| Entry | $R^1$ | $R^2$ | Solubility in MEK /wt % | ΔAbs.[a] /% | ΔAbs.as liquid state[b] /% | ΔAbs.as solid state[c] /% |
|---|---|---|---|---|---|---|
| 1 | H | Ph | ≈1.0 | −53.2 | −14.9<br>(ETA) | −27.2 |
| 2 | H | *n*-Bu | >10 | —[d] | — | — |
| 3 | H | *n*-Hexyl | >10 | −71.2 | — | −89.1 |
| 4 | Isopentyl–S | Ph | >10 | −23.1 | — | −72.2 |
| 5 | Isopentyl–S | *n*-Hexyl | >10 | — | — | — |
| 6 | Ph–S | Ph | >10 | −26.5 | — | −35.3 |
| 7 | Ph–S | *i*-Bu | >10 | — | — | — |
| Ref. 1 | H | Cl | <0.01 | −68.2 | — | −22.5 |
| Ref. 2 | H | Ph–O | ≈0.3 | −83.6 | −87.4<br>(ETA) | −58.4 |
| Ref. 3 | H | *n*-Octyl–O | ≈0.6 | −13.8 | — | −72.2 |
| Ref. 4 | Isopentyl–S | Cl | <0.1 | −44.6 | — | −84.1 |
| Ref. 5[e] | N/A | N/A | <0.01 | — | −100<br>($CHCl_3$) | — |

[a]Polystyrene film (toluene solution of dye/PS = 1/2 was coated on a glass plate with a bar coater (#16)); the decay ratio of absorbance after sunlight irradiation for 1 day. [b]Solution (10 wt % of dye); decay ratio of absorbance after sunlight irradiation for 1 week. [c]Polystyrene film (same as a); decay ratio of absorbance after heating for 2 h at 180 °C. [d]Not carried out. [e]3,3′-Diethyl thiacarbocyanine; Ref. 2 and Ref. 3 were prepared according to the reference.[3a]

We have also investigated the light- and heat resistance in the liquid and solid states, together with the solubility in MEK (methyl ethyl ketone). The results are summarized in Table 2, and the UV–vis spectra, the elemental analyses, and the $^1$H NMR, $^{13}$C NMR, and IR spectroscopic data are in Supporting Information.[9]

Both axial and peripheral substituents can improve the solubility in various organic solvents to make a practical thin film, compared to SubPcB–Cl,[1] and both light- and heat resistance of SubPcB–Ph (Entry 1) apparently improved more than 50%, as compared to those of SubPcB–O–Ph.[2] In the case of the alkyl group (SubPcB–*n*-Hexyl: Entry 3), the decay ratio was worse than that of SubPcB–O–Octyl.[3] It was found that in the case of $R^2$ = Ph, $R^1{}_3$SubPcB–$R^2$ **3** improved both the light- and the heat resistance to a greater extent than the analogous $R^1{}_3$SubPcB–O–$R^2$; however, no substituent could significantly improve both the properties simultaneous, and this improvement depended on the axial substituent. In particular, SubPcB–Ph (Entry 1) is more applicable as a functional purple dyestuff film composite than the common cyanine dye[5] from the point of solubility and resistance as shown in Table 2.

We reported here a general method to synthesize SubPcs with an axial substituent with a direct boron and carbon bond and thus obtained analogs with possibly improved the light- and/or heat resistance. Further investigation will be described elsewhere as a full paper.

## References and Notes

1 a) M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, T. Torres, *Synthesis* **1996**, 1139. b) N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096.
2 C. G. Claessens, D. González-Rodríguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835.
3 a) M. Tsuchiya, M. Shinkai, J. Tanabe, Appl. JP 252448, **2005**. b) T. Kodama, A. Takeda, Appl. JP 120252, **2005**. c) S. Masuda, M. Kitao, Appl. JP 317437, **2004**.
4 Y. Inokuma, J. H. Kwon, T. K. Ahn, M.-C. Yoo, D. Kim, A. Osuka, *Angew. Chem., Int. Ed.* **2006**, *45*, 961.
5 a) B. del Rey, M. V. Martínez-Díaz, J. Barbera, T. Torres, *J. Porphyrins Phthalocyanines* **2000**, *4*, 569. b) T. Mori, Y. Yamasaki, Appl. JP 053,265, **2007**. c) T. Mori, Y. Yamasaki, Appl. JP 206,016, **2008**.
6 T. Masaoka, K. Horiuchi, B. Sawano, Y. Kumatani, T. Nishimoto, T. Misawa, K. Goma, Appl. JP 138510, **1997**.
7 J. Rauschnabel, M. Hanack, *Tetrahedron Lett.* **1995**, *36*, 1629.
8 Y. Yamasaki, T. Mori, Appl. JP 282,039, **2009**.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.