Subphthalocyanine Derivatives Having a Phosphorus Group as an Axial Substituent

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The synthesis and properties of novel subphthalocyanines having a phosphorus group as an axial substituent are reported. The excellent solubility of these materials may provide a good production method for optical films without impairing the excellent properties peculiar to the original subphthalocyanines.

Subphthalocyanines have been studied in an effort to apply them to various commercial products such as pigments, thin film chemical materials, information recording materials, and light-emitting materials, however subphthalocyanines generally have poor light resistance and poor solubility.^{1,2} Therefore, when thin films are required, it is necessary to prepare a pigment-dispersed liquid by dispersing the subphthalocyanines into a solvent and then apply the liquid to form a thin film. The thin film made from such pigment-dispersed liquid cannot achieve sufficient transparency unless the subphthalocyanines are pulverized into ultrafine particles smaller than $0.5\,\mu m$ with a very narrow particle size distribution.³ However, pulverization increases the surface area and negatively affects light resistance. Furthermore, it is difficult to prepare homogeneous thin films if a liquid that containing a nondispersible pigment is used.

In contrast, optical films such as functional optical thin films having light absorption in specific wavelength regions, antireflection films especially coated on marketable wide screen display panels, such as plasma display panels and liquid crystal display panels, color filters, optical recording media using light in the blue laser region, and photoreceptors are required to have small half width in the 530–580 nm wavelength range and sufficient light absorption properties.⁴

Because a hydroxy group replaces a halogen in the axial position on a centered-core boron and the subsequent reaction for making an ether linkage with an alkyl or aryl group takes place easily, there have been reports of several subphthalocyanine derivatives with an alkoxy or an aryloxy group as an axial substituent.⁵ In particular, we note the subphthalocyanines with a trialkylsilyloxy group as an axial substituent in the study of Torres on liquid crystalline properties.⁶ Peripheral substituents can generally improve the solubility of subphthalocyanines in various organic solvents but they always affect the Q-band absorption of the compound. On the other hand, although axial substituents do not affect the Q-band absorption, they are insufficiently stable to heat and/or light irradiation for practical thin-film applications. In order to solve the problems mentioned above, a large number of reports and patents, including our recent work,^{7,8} have dealt with modified derivatives of subphthalocyanines.

In this short article, we report the synthesis and properties of novel subphthalocyanines having a phosphorus group as an axial substituent and their excellent solubility; the axially substituted phosphorus group does not cause any significant changes in the peculiar properties, which is unique to the subphthalocyanines without any peripheral substituents. By using these subphthalocyanine derivatives with axial phosphorus group, we also tried to make functional optical films that are resistant to light and heat, and have light absorptivity in specific wavelength regions.⁹

Subphthalocyanine derivatives having the phosphorus group as an axial substituent were synthesized from axially chlorosubstituted subphthalocyanine with phosphate or phosphonic acid derivatives in fairly good yields and the synthetic procedure is illustrated in Scheme 1.

The results of the reaction are summarized in Table 1. The intensive synthetic procedure, ¹HNMR, ¹³CNMR, IR spectroscopy, and FD-MS data of each derivative (Entries 1–9) are available in the Supporting Information. The samples for the measurement of the UV–vis spectra were prepared as follows: 10.0 mg of the obtained compound (Entries 1–9 and Refs. 1–4) were completely dissolved in 100 mL of chloroform, and then 10 mL of the solution was diluted with chloroform to 100 mL total volume. Subsequently, the solution was analyzed with a spectrophotometer and the molar absorptivity was calculated according to the Lambert–Beer equation. The UV–vis spectra are depicted in Figure 1.

It can be seen that the axial substituent did not affect much the λ_{max} of the Q-band absorption, but peripheral substitution



Scheme 1. Synthetic route to the subphthalocyanine derivatives with an axially phosphorus substituent: (i) $BCl_3/xylene$, reflux/2 h; (ii) $HO-P(O)R^2_2/ODCB$, 180 °C/6 h.

Entry	\mathbb{R}^1	R ²	$[B(R^{1}_{3}subpc)\{OP(O)R^{2}_{2}\}]$ Yield/ $\%^{a}$	$\lambda_{ m max} / m nm$	$\varepsilon \times 10^{-4}$ /dm ³ mol ⁻¹ cm ⁻¹
1	H–	Ph	67.4	564.0	7.69
2	H–	O–Ph	64.4	564.5	6.96
3	H–	O– <i>n</i> -Bu	34.3	562.5	7.78
4	t-Bu-	Ph	23.3	570.5	8.74
5	t-Bu-	O– <i>n</i> -Bu	18.8	568.0	7.62
6	isopentyl-S-	Ph	57.6	586.0	7.12
7	isopentyl-S-	O–Ph	46.9	586.5	8.20
8	Ph-S-	Ph	56.0	584.5	7.24
9	Ph-S-	O– <i>n</i> -Bu	40.0	584.0	9.95
Ref. 1	H–	Cl	(34.0) ^{b)}	565.0	5.10
Ref. 2	t-Bu-	Cl	(27.9) ^{b)}	570.0	5.10
Ref. 3	isopentyl-S-	Cl	(44.0) ^{b)}	587.5	5.82
Ref. 4	Ph-S-	Cl	(34.2) ^{b)}	586.0	7.58

Table 1. The Reaction Yields of $[B(R^{1}_{3}subpc){OP(O)R^{2}_{2}}]$ with the λ_{max} and Molar Absorptivity (ε)

a) The yields are for the second step in Scheme 1. b) The yields in parentheses are for the first step in Scheme 1.



Figure 1. The UV-vis spectra of $[B(R^1_{3}subpc){OP(O)R^2_{2}}]$: the measurements were carried out in CHCl₃.

apparently resulted in red shift, the extent of which depends on the substituents. This may cause problems when a thin-filmed device requires its absorption at about 560 nm for Entries 1, 2, and 3.

In any case, the synthetic procedure for derivatives without peripheral substituents is advantageous from the viewpoint of industry, and it can be also seen that their molar absorptivity was enhanced by the axial substituents compared to those of the corresponding axially chloro-substituted subphthalocyanine. These facts reduce the required volume of the solution containing a functional dyestuff, i.e., the subphthalocyanines, for making a thin film and reduce the production cost.

We have also investigated the solubility of $[B(R^{1}_{3}subpc)-{OP(O)R^{2}_{2}}]$ in butan-2-one (MEK) as well as the Haze value, light resistance, and heat resistance for a thin film solid state. The results are summarized in Table 2. A thin film containing

the present subphthalocyanine derivative, which is a coloring dyestuff for a thin film obtained in its solid state, was produced as follows: 0.5 g of $[B(R^{1}_{3}\text{subpc})\{OP(O)R^{2}_{2}\}]$ and 1.0 g of polycarbonate were added into 68.5 g of cyclohexanone and 30 g of butan-2-one, stirred and dissolved to obtain a coating solution. The obtained coating solution was applied on 1 mm thick glass plate using an automatic film applicator.

It can be seen that both axial and peripheral substituents can indeed improve the solubility in MEK to make a thin film and even for the derivatives without peripheral substituents, the solubility of the derivative with $R^2 = O$ -Bu (Entry 3) was surprisingly enhanced more than 10 wt % and the solubility of the derivative with $R^2 = Ph$ or O-Ph (Entries 1 and 2) was more than 0.3 wt %. Their solubility should be enough to make a thin-filmed device from a coating solution compared to that of [B(subpc)Cl] (Ref. 1: 0.003 wt % means almost insoluble).

Table 2. The Solubility of $[B(R_{3}^{1}subpc)\{OP(O)R_{2}^{2}\}]$ in Butan-2-one (MEK), the Haze Value, the Light and Heat Resistance

Entry	Solubility in MFK /wt %	Haze value	Heat	Light resistance/%
	WILK/ WU //	value	Teststatiee/ //	Teststance/ //
1	0.44	0.52	-14.1	-32.1
2	0.34	0.38	-8.3	-25.8
3	>10.0	0.43	-9.7	-29.0
4	>10.0	0.33	-11.8	-32.9
5	>10.0	0.34	-9.5	-38.6
6	>10.0	0.31	-17.4	-38.5
7	>10.0	0.37	-14.9	-33.3
8	>10.0	0.32	-7.8	-17.3
9	>10.0	0.48	-9.4	-15.6
Ref. 1	0.003	9.89	-52.8	a)
Ref. 2	>10.0	0.35	-27.1	-37.1
Ref. 3	>10.0	0.34	-21.2	-33.6
Ref. 4	>10.0	0.25	-17.8	-9.4

 a) Measurement could not be carried out because only inhomogeneous solution was obtained and accordingly nonuniform thin films were obtained.

In the case of [B(subpc)Cl] (Ref. 1), the measurement of light resistance could not be carried out because only an inhomogeneous solution was obtained and accordingly nonuniform thin films were produced (the Haze value for the film that contained [B(subpc)Cl] (Ref. 1) was 9.89.). In contrast, the Haze values were 0.52 and 0.38 for thin-films that contained [B(subpc){OP(O)Ph₂}] or [B(subpc){OP(O)(OPh₂}] (Entries 1 and 2) respectively. Taking this into consideration, it might be feasible to produce thin films that contain [B(R¹₃subpc)-{OP(O)R²₂}] to afford good Haze values in industrial coating processes. Additionally, both heat and light resistance of thin films containing [B(subpc){OP(O)R²₂}] were improved to some extend as shown in Table 2. This improvement might be due to the molecular stability based on the energy and/or structural difference between B–CI and B–OP bond.⁷

Furthermore, we also confirmed by the UV-vis spectra that the shift of the wavelength and broadening of the Q-band absorption due to molecular association in the state of a thin film could be remarkably suppressed when the present subphthalocyanine bearing the phosphorus group as an axial substituent was used. The UV–vis spectra of the thin film containing each derivatives (Entries 1–9) are available in the Supporting Information.

In summary, we report the synthesis and properties of novel subphthalocyanines having a phosphorus group as an axial substituent, and propose that their excellent solubility may provide a good production method for optical thin-filmed devices without impairing the properties peculiar to the original subphthalocyanines. In a subsequent paper, we will describe this and other recent work^{7,8} regarding subphthalocyanine derivatives.

Supporting Information

Experimental details including synthetic procedures, ¹H NMR, ¹³C NMR, IR spectroscopy, and FD-MS data of the novel subphthalocyanines having a phosphorus group as an axial substituent ($[B(R_{3}^{1}subpc){OP(O)R_{2}^{2}}]$; Entries 1–9), are available electronically on the CSJ-Journal Web site. This material is available free of charge on the web at http://www. csj.jp/journals/bcsj/.

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