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A Convenient Synthetic Method for Pure Oxo(phthalocyaninato)titanium(IV) and Application to Other Metal Phthalocyanines

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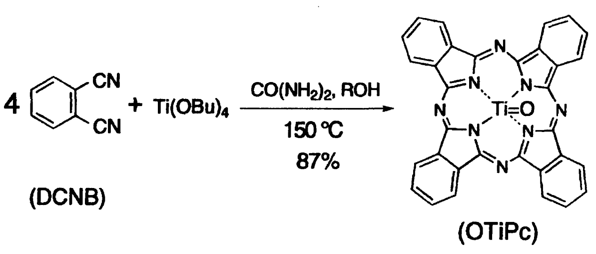
High-yield synthesis of pure oxo(phthalocyaninato)titanium(IV) was conveniently achieved by heating a mixture of 1,2-dicyanobenzene, titanium(IV) butoxide, urea, and 1-octanol at 150 °C. It is suggested that a key pathway of the efficient condensation reaction is the complex formation of titanium(IV) butoxide with ammonia generated by the nucleophilic attack of 1-octanol to urea. Applicabilities of this method were investigated for condensation reactions of 1,2-dicyanobenzene with other metal alkoxides.

Phthalocyanines (Pc's) are stable dyes of versatile functions, among which oxo(phthalocyaninato)-titanium(IV) (OTiPc) has been in commercial use as one of the most sensitive organic photoreceptors in electrophotographic printing.$^{1)}$ Industrial production of OTiPc has been carried out by a reaction of 1,2-dicyanobenzene (DCNB) and $TiCl_4$ at > 200 °C in aprotic solvents.$^{2)}$ Some other metal Pc's are also produced by similar condensation reactions of DCNB with the corresponding metal chlorides. In these reactions, however, ring-chlorinated Pc's are significantly formed as unavoidable by-products,$^{3)}$ which are generally inseparable from the major product by usual methods; most Pc's and their ring-chlorinated compounds are essentially insoluble in usual organic solvents and are sublimable only at high temperatures under high vacuum. This is clearly a crucial drawback for obtaining pure Pc's. Such by-products may exert undesired effects on photoconductive properties of relevant Pc photoreceptors.$^{4)}$ The purification of "impure" Pc materials requires tedious procedures (e.g., train sublimation$^{5)}$) which are only in laboratory use. It is therefore of practical significance to develop synthetic methods which do not yield any by-products inseparable from target Pc's. The reaction of 1,3-diiminoisoindoline (DIIN) with titanium(IV) butoxide ($Ti(OBu)_4$)$^{6)}$ yields OTiPc with no ring chlorination but requires high reaction temperatures (≥ 200 °C). From practical and economic viewpoints, however, other convenient methods should be developed for the direct production of "pure" OTiPc from DCNB under mild conditions. We wish to report a new, practical method for high-yield synthesis of "pure" OTiPc from DCNB and $Ti(OBu)_4$ at much lower temperatures than 200 °C and its application to synthesis of some other metal Pc's. In the reactions, the metal alkoxides are activated by complex formation with in-situ generated ammonia.

Results and Discussion

Synthesis of Pure OTiPc. A mixture of DCNB, $Ti(OBu)_4$, urea, and 1-octanol in a ca. 4 : 1 : 2 : 5 molar ratio was heated at 150 °C for 6 h to give analytically pure OTiPc in 87% yield after the crude product had been washed with hot methanol and then with toluene (Scheme 1). The structure of the product was firmly established by spectroscopic measurements.$^{7)}$ Ammonia was evolved during the reaction, and 1-octyl carbamate was isolated from the reaction mixture. The possible formation of metal-free phthalocyanine (H_2Pc) as a by-product would largely diminish the validity of the present reaction, since its separation from OTiPc can not be achieved by conventional methods. Therefore, we carefully analyzed the reaction products by FD mass and IR spectroscopic methods to see whether or not H_2Pc was contaminated in the products. However, we could detect no signal of H_2Pc at m/z 514 but an exclusive one of OTiPc at m/z 576 in FD mass spectra of the product. Since H_2Pc shows a strong IR absorption band at 1007 cm^{-1} separated from that of OTiPc at 965 cm^{-1}, possible contamination of H_2Pc in the product can be quantitatively estimated. IR analysis showed again no contamination of H_2Pc in the product within



Scheme 1.

the detection limit ($\leq 3\%$). Other by-products were removed by washing with organic solvents or more completely by acid-pasting purification.[8] Thus, a standard pure sample of OTiPc was prepared by acid pasting of the analytically pure product followed by repeated vacuum sublimation. The absorption spectrum of the product in concentrated sulfuric acid was superimposable, within experimental errors ($\leq 5\%$), with that of the standard sample in the range of 400—1000 nm.

Table 1 summarizes some typical results of the reactions under various conditions. Of synthetic and mechanistic significance is that urea is esstential for the high-yield and selective formation of OTiPc. In the absence of urea, a remarkable decrease of OTiPc yield occurred and, more seriously, H_2Pc was significantly formed. When 2-octanol was used in place of 1-octanol, OTiPc yield was substantially decreased. With such primary alcohols as 1-pentanol and benzyl alcohol, on the other hand, the reaction proceeds as efficiently as the original reaction using 1-octanol. Moreover, it was found that a variety of aprotic solvents such as 1-chloronaphthalene, DMF, DMSO, quinoline, diethylene glycol dimethyl ether (diglyme), and mesitylene are commonly unfavorable for the OTiPc synthesis independently of solvent properties. Interestingly, either benzamide or acetamide can act as an effective substitute of urea, since the reactions using the amides under similar conditions gave pure OTiPc in 70—78% yields.

These observations can be interpreted by assuming that ammonia is generated from urea or the amides to play a key role in the efficient and selective formation of OTiPc. In fact, we confirmed the generation of ammonia during the reaction and isolated 1-octyl carbamate from the reaction mixture. Presumably, the nucleophilic attack of 1-octanol to urea should be facile enough for ammonia generation to occur at sufficient steady-state concentration (Eq. 1). This appears to be true in the cases of 1-pentanol and benzyl alcohol as well as in the reaction of 1-octanol with benzamide or acetamide. On the other hand, 2-octanol should be less reactive in the nucleophilic attack to urea because of steric hindrance. In aprotic solvents, ammonia generation can occur only by the thermal decomposition of urea which should be slow at 150 °C.

Table 1. Preparation of OTiPc under Various Conditions[a)]

Solvents	Yield/%	Purity/%[b)]
1-Octanol	87.6	>95
1-Octanol[c)]	ca. 52[d)]	20% H_2Pc[e)]
1-Octanol[f)]	78	93
1-Octanol[g)]	71	93
1-Octanol[h)]	75	>95
2-Octanol	63	>95
1-Pentanol	77	>95
Benzyl alcohol	77	>95
1-Chloronaphthalene	39	ca. 90
DMF	17	ca. 30
DMSO	27	ca. 44
Nitrobenzene	33	ca. 50
Quinoline	44	ca. 40
Diglyme	30	ca. 70
Mesitylene	18	ca. 65

a) For reaction of DCNB (15.6 mmol), $Ti(OBu)_4$ (4.29 mmol), and urea (7.8 or 15.6 mmol) in 6.0 cm^3 solvent at 140—150 °C. b) Determined by colorimetry for concentrated sulfuric acid solution; see text. c) In the absence of urea. d) Combined yield of OTiPc and H_2Pc. e) Determined by IR analysis. f) Benzamide was used in place of urea. g) Acetamide was used in place of urea. h) Under bubbling of NH_3 gas in the absence of urea.

$$XCONH_2 + ROH \rightarrow XCO_2R + NH_3 \tag{1}$$

$$(X = NH_2,\ CH_3,\ \text{and}\ C_6H_5;\quad R = 1\text{-}C_8H_{17},\ 1\text{-}C_5H_{11},\ \text{and}\ C_6H_5CH_2)$$

The in-situ generated ammonia may activate $Ti(OBu)_4$ by adduct formation, since complexes are known to be formed between titanium alkoxides and aliphatic amines.[9] We obtained supporting evidence for the formation of an adduct between $Ti(OBu)_4$ and ammonia. An ammonia-saturated solution of $Ti(OBu)_4$ (0.2 mol dm^{-3}) in perdeuterated benzene showed the ^{1}H NMR signals at δ=0.99 (a triplet overlapped with a broad signal), 1.46, 1.64, and 4.17 in an integral ratio of 2.1 : 1 : 1 : 1 but none at δ=1.03, 1.52, 1.83, and 4.58 for uncomplexed $Ti(OBu)_4$ nor at δ=0.39 for free ammonia. Clearly, an adduct should be formed between $Ti(OBu)_4$ and ammonia (Eq. 2), probably in a 1 : 1 ratio as deduced from the ^{1}H NMR integral ratio. A mixture of $Ti(OBu)_4$ and liquid ammonia was warmed up to room temperature and then kept at 60 Torr (1 Torr=133.322 Pa) for 20 min to ensure the complete evaporation of free ammonia. The remaining oil still showed a strong, broad IR absorption band at 3310 cm^{-1} attributable to N–H stretching vibrations. Unfortunately, the full identification of this adduct was unsuccessful because of slow, but facile, decomposition at room temperature. To an oil obtained from $Ti(OBu)_4$ and liquid ammonia were added DCNB and 1-octanol, and then the mixture was heated at 155 °C to give OTiPc in 77% yield with no formation of H_2Pc (Eq. 3). A similar result was again obtained by a reaction of DCNB and $Ti(OBu)_4$ in 1-octanol at 150 °C under bubbling of ammonia.

$$Ti(OBu)_4 + NH_3 \rightarrow H_3N\cdot Ti(OBu)_4 \tag{2}$$

$$4DCNB + H_3N\cdot Ti(OBu)_4 \rightarrow OTiPc \tag{3}$$

Alternatively, the key role of the in-situ generated ammonia could be attributed to the prior formation of 1,3-diiminoisoindoline (DIIN) through which OTiPc would be produced, since DCNB and ammonia may yield DIIN. However, this DIIN pathway can be safely ruled out, since DIIN was very slowly formed only in

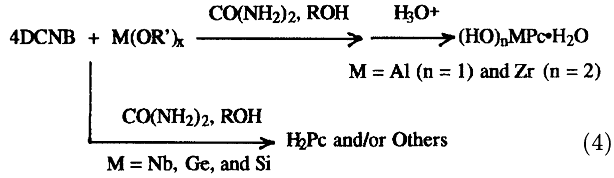
7% yield accompanied by 93% recovery of DCNB upon heating a mixture of CDNB and equimolar urea in 1-octanol at 155 °C for 6 h in the absence of $Ti(OBu)_4$. This is in sharp contrast to the efficient formation of OTiPc in the present synthetic reaction that was almost completed within 3 h. Another important observation is that the reaction of DIIN with $Ti(OBu)_4$ in 1-octanol at 160 °C gave both OTiPc and H_2Pc in a 83 : 17 ratio in the absence of urea and in a 93 : 7 ratio even in the presence of equimolar urea.

Application to Synthesis of Other Metal Phthalocyanines. In order to explore the scope and limitation of the present method in phthalocyanine synthesis, we investigated similar reactions using other metal alkoxides $M(OR')_x$ (M = Al, Zr, Nb, Ge, and Si); the reactions were carried out by heating a mixture of DCNB, $M(OR')_x$, urea, and a primary alcohol (ROH) in a ca. 4 : 1 : 2 : 5 ratio at 140—210 °C. Table 2 and Eq. 4 summarize the results. In the case of $Zr(OBu)_4$, acid hydrolysis of the product gave di(hydroxo)zirconium(IV), Pc, $(HO)_2ZrPc{\cdot}H_2O$, in 51% yield;$^{10)}$ thermal analysis (DTA and TG) showed that the hydrolysis product has water of crystallization in a 1 : 1 ratio. In the absence of urea, on the other hand, H_2Pc and methanol-soluble dark-brown materials were dominantly formed. Similarly, the reaction of DCNB with $Al(OBu)_3$ in the presence of urea gave pure $(HO)AlPc{\cdot}H_2O$ in 65% yield after acid hydrolysis,$^{10)}$ while the reaction in the absence of urea did not yield the metal Pc at all but black insoluble materials. In the other cases, however, intractable materials were formed, showing no clear indication for the formation of the corresponding metal Pc's; H_2Pc was formed mainly in the case of $Nb(OEt)_5$ and significantly in the case of $Ge(OEt)_4$.

Table 2. Reactions of DCNB with Other Metal Alkoxides$^{a)}$

$M(OR')_x$	Solvent	Temp	Yields of metal Pc/%	
		°C	With urea	Without urea
$Al(OBu)_3$	1-Butanol	140	$65^{b)}$	c)
$Zr(OBu)_4$	1-Butanol	140	$51^{d)}$	e)
$Nb(OEt)_5$	1-Octanol	145	f)	g)
$Ge(OEt)_4$	1-Octanol	160	f)	g)
$Si(OEt)_4$	1-Octanol	210	h)	i)

a) For reactions of DCNB (7.8 mmol), $M(OR')_x$ (2.3 mmol), urea (7.8 or 3.9 mmol), and a solvent (1.8 cm^3) under N_2. b) $(HO)AlPc{\cdot}H_2O$. c) Formation of black insoluble solid. d) $(HO)_2ZrPc{\cdot}H_2O$. e) Formation of H_2Pc in 50% yield along with methanol-soluble dark brown materials. f) An intractable mixture containing a considerable amount of H_2Pc (indicated by MS and IR). g) Recovery of DCNB with formation of a small amount of black solid. h) Formation of black solid with recovery of a minor amount of DCNB. i) Recovery of most of DCNB used.



(4)

The different reactivities of the metal alkoxides might be attributable to their different capabilities in complex formation with ammonia. It can be predicted that $Zr(OBu)_4$ and $Al(OBu)_3$ are activated by the complex formation with ammonia, while the other metal alkoxides do not form complexes with ammonia. This was confirmed by ^1H NMR analysis of the metal alkoxides. In the cases of $Si(OEt)_4$ and $Ge(OEt)_4$, the signals in perdeuterated toluene appear at $\delta = 1.18$ (t) and 3.84 (q) for the former and at $\delta = 1.21$ (t) and 3.84 (q) for the latter, which are commonly unaffected at all by ammonia saturation of the solution. The ^1H NMR spectrum of $Nb(OEt)_5$ in perdeuterated toluene shows a broad triplet at $\delta = 1.29$ and a broad quartet at $\delta = 4.54$ due to rapid intramolecular ethoxide exchange of the ethoxide-bridged bi-octahedral dimer,$^{11)}$ which are again unchanged by ammonia saturation of the solution. Clearly, no significant interaction occurs between ammonia and the metal alkoxides (Eq. 5).

$$[M(OR')_x]_y + NH_3 \mathrel{-\!\!/\!\!\!\longrightarrow} H_3N{\cdot}M(OR')_x \tag{5}$$

$$M = Si\ (x = 4,\ y = 1),\ Ge\ (x = 4,\ y = 1),$$
$$\text{and } Nb\ (x = 5,\ y = 2)$$

The ^1H NMR spectra of $Zr(OBu)_4$ and $Al(OBu)_3$ in deuterated toluene commonly show very complex features at $\delta = 0.8$—2.2 and two signals at lower field, probably as the consequence of molecular association in equilibrium.$^{12)}$ In the case of $Zr(OBu)_4$, a very broad signal at $\delta = 4.0$—4.7 and a broad one at $\delta = 3.34$ appear in an integral ratio of 2.5 : 1, being assignable to $-OCH_2-$ of associated and monomeric species respectively. Ammonia saturation of the $Zr(OBu)_4$ solution caused a significant shift of the latter to $\delta = 3.42$ with a 1.7-fold increase of the relative intensity accompanied by considerable changes of the complex signals at $\delta = 0.8$—2.2, while the very broad signal still appears at $\delta = 4.0$—4.7 with a decrease of the integral ratio; the integral ratio of the two signals at $\delta = 4.0$—4.7 and 3.42 was changed to 1.5 : 1. Similarly, $Al(OBu)_3$ shows a very broad signal at $\delta = 3.8$—4.3 and a triplet at $\delta = 3.32$ in an integral ratio of 2.3 : 1. Upon ammonia saturation of the $Al(OBu)_3$ solution, the triplet is shifted to $\delta = 3.41$ with a 1.4-fold intensity increase accompanied by considerable changes of the complex signals at $\delta = 0.8$—2.2, whereas the lowest-field broad signal still appears at $\delta = 3.8$—4.3 with a decrease of the intensity. These observations clearly indicate that monomeric $M(OBu)_x$ forms an adduct with ammonia in equilibrium with its association (Eq. 6). In general, therefore, it is implied that the prior formation of $H_3N{\cdot}M(OR')_x$ is a requisite for the effective synthesis of the metal Pc's by the condensation reaction of DCNB with $M(OR')_x$ (Eq. 7).

$$[M(OBu)_x]_y \rightleftarrows M(OBu)_x \underset{-NH_3}{\overset{NH_3}{\rightleftarrows}} H_3N{\cdot}M(OBu)_x \qquad (6)$$

(M = Al and Zr)

$$4DCNB + H_3N{\cdot}M(OR')_x \longrightarrow [(R'O)_nMPc] \longrightarrow$$

$$OTiPc/(HO)_nMPc{\cdot}H_2O$$

(M = Al, Ti, and Zr) (7)

Experimental

Melting points were measured on a Yanagimoto hot plate and are uncorrected. Spectroscopic data were obtained on a JEOL GSX-400 instrument for ^{1}H NMR spectra, on a Hitachi U-3500 spectrophotometer for visible-near IR absorption spectra, on a JASCO A-202 spectrometer for IR absorption spectra, and on a Shimadzu GC-MS 9100MK for FD mass spectra. HPLC analysis was performed on a Shimadzu LC-3A using a column of Lichrospher 100 RP-18 (4 mm×25 cm). Solvents were distilled before use. Commercially available reagents were used without further purification.

General Procedures for Reactions of 1,2-Dicyanobenzene and Metal Alkoxides. A flask containing DCNB (5.0 g, 39 mmol), a metal alkoxide (10.7 mmol), urea (1.17 g, 19.5 mmol), and a solvent (7.5 cm^3) was flushed with N_2 and then heated at 140—210 °C under stirring for 6—10 h. After cooling down to room temperature, methanol (30 cm^3) was added to the reaction mixture, refluxed for 0.5—1.0 h, and then filtered. The collected solid by filtration was successively washed with toluene (3×50 cm^3), methanol (3×30 cm^3), and water (100 cm^3) and then dried at 100 °C under reduced pressure for 3—5 h. The dried solid was subjected to FD mass and IR (KBr) measurements for the detection and quantitative estimation of H_2Pc involved in the solid product. The filtrate was subjected to HPLC analysis for detection of unreacted DCNB and other products. The results are summarized in Tables 1 and 2.

The phthalocyanine products were purified, if necessary, by acid pasting as follows. A crude product (3 g) was added, over a period of 10—20 min, to ice-cooled concentrated sulfuric acid (50 g) under stirring. The solution was further stirred for 0.5—1 h under ice cooling and then poured into 1 : 1 ice/water (600 g) under vigorous stirring. The suspension was stirred at 0 °C for 30 min and then filtered. The collected solid by filtration was washed with distilled water until the filtrate became neutral to litmus and then dried at 60 °C under 1 Torr for 2—4 h.

Synthesis of Pure OTiPc. (A) A mixture of DCNB (5.0 g, 39 mmol), $Ti(OBu)_4$ (3.65 g, 10.7 mmol), urea (1.17 g, 19.5 mmol), and 1-octanol (6.0 g, 46.1 mmol) was heated at 150 °C under N_2 for 6 h. After addition of methanol (30 cm^3) to the reaction mixture followed by refluxing for 30 min, fine blue crystals were collected by filtration, washed with toluene, methanol and water, and then dried at 100 °C under 1 Torr for 3 h to give 4.92 g of OTiPc (87.6%): ^{1}H NMR (1 : 4 CF_3CO_2D/CD_2Cl_2, −30 °C) $\delta = 8.31$ and 9.15; visible-near IR (H_2SO_4) λ_{max} 808 nm (ε 1.13×10^5 dm^3 mol^{-1} cm^{-1}); IR (KBr) ν_{max} 1335, 1120, 1075, 965, and 735 cm^{-1}; MS (FD) *m/z* 576 (M^+). Found: C, 66.47; H, 3.03; N, 19.09%. Calcd for $C_{32}H_{16}N_8OTi$: C, 66.68; H, 2.80; N, 19.44%.

(B) A mixture of DCNB (64.07 g, 0.50 mol), $Ti(OBu)_4$ (46.75 g, 0.138 mol), urea (15.15 g, 0.25 mol), and 1-octanol (76.8 g, 0.59 mol) was heated at 150 °C under stirring for 6 h. After addition of methanol (100 cm^3) followed by refluxing for 30 min, the suspension was filtered. The collected solid was washed with toluene (3×250 cm^3), methanol (3×100 cm^3), and water (500 cm^3), and dried at 100 °C under 1 Torr for 6 h to give 62.1 g of pure OTiPc (86.2%).

Reaction of 1,3-Diiminoisoindoline with Titanium(IV) Butoxide. A mixture of DIIN (1.45 g, 10 mmol), $Ti(OBu)_4$ (0.94 g, 2.76 mmol), urea (0.60 g, 10 mmol), and 1-octanol (3.5 cm^3) was heated at 140 °C under stirring for 6 h. To the reaction mixture was added methanol (15 cm^3), and the suspension was refluxed for 30 min and then filtered. The collected blue solid was washed with toluene, methanol, and water, and then dried to give 1.19 g of product. IR analysis showed that the product consists of 83% OTiPc and 17% H_2Pc.

Reaction of 1,2-Dicyanobenzene with Aluminum(III) Butoxide. A mixture of DCNB (1.0 g, 7.8 mmol), $Al(OBu)_3$ (0.58 g, 2.3 mmol), urea (0.47 g, 7.8 mmol), and 1-butanol (1.5 g, 20 mmol) was heated at 140 °C for 6 h. To the reaction mixture was added 25 cm^3 of dilute H_2SO_4 (3 mol dm^{-3}), and then the suspension was stirred at 100 °C for 2 h. The blue solid was collected by filtration, successively washed with water, 28% ammonia solution, water, and methanol, and then dried to give 0.73 g (65%) of pure (HO)-AlPc·H_2O: an endothermic peak at 100 °C in DTA with a 3.5% weight loss in TG; visible-near IR (H_2SO_4) λ_{max} 804 nm ($\varepsilon 2.27\times10^5$ dm^3 mol^{-1} cm^{-1}); IR (KBr) ν_{max} 3370br, 1490, 1325, 1115, 1060, 900, 760, and 725 cm^{-1}; MS (FD) *m/z* 556 (M^+ −H_2O). Found: C, 66.82; H, 3.58; N, 19.07%. Calcd for $C_{32}H_{19}N_8O_2Al$: C, 66.89; H, 3.33;, N, 19.50%.

Reaction of 1,2-Dicyanobenzene with Zirconium(IV) Alkoxide. A mixture of DCNB (1.0 g, 7.8 mmol), $Zr(OBu)_4$ (0.90 g, 2.3 mmol), urea (0.47 g, 7.8 mmol) and 1-butanol (1.5 g, 20 mmol) was heated at 140 °C for 6 h and then treated, as described above, to give 0.65 g (51%) of pure $(HO)_2$ZrPc·H_2O: an endothermic peak at 130 °C in DTA with a 3.3% weight loss in TG; visible-near IR (H_2SO_4) λ_{max} 807 nm ($\varepsilon 1.16\times10^5$ dm^3 mol^{-1} cm^{-1}); IR (KBr) ν_{max} 3370br, 1490, 1325, 1115, 1070, 885, 745, and 730 cm^{-1}. Found: C, 58.82; H, 3.31; N, 16.52%. Calcd for $C_{32}H_{20}N_8O_3Zr$: C, 58.61; H, 3.07; N, 17.09%.

References

1) K. Y. Law, *Chem. Rev.*, **93**, 449 (1993).

2) a) Reactions of DCNB with $TiCl_3$ or $TiCl_4$ gave OTiPc in 60—70% yields after hydrolysis of the initial product, Cl_2TiPc. b) F. H. Moser and A. L. Thomas, "The Phthalocyanines," CRC Press, Florida (1983) Vol. II; c) V. L. Goedken, G. Dessy, C. Ercolani, V. Fares, and L. Gastaldi, *Inorg. Chem.*, **24**, 991 (1985); d) T. Enokida, R. Hirohashi, and Y. Nakamura, *J. Imaging Sci.*, **34**, 234 (1990); e) J. Silver, P. Lukes, P. Hey, and M. T. Ahmet, *J. Mater. Chem.*, **1**, 881 (1991); f) T. Harazono and I. Takagishi, *Bull. Chem. Soc. Jpn.*, **66**, 1016 (1993).

3) a) It was reported that OTiPc products from the re-

actions of DCNB with $TiCl_4$ contain 0.2—4.5% Cl.[3b,7] In our investigation on a reaction of DCNB with $TiCl_4$ in 1-chloronaphthalene at 200—220 °C, elemental analysis of the OTiPc product showed 1.8% Cl contamination. b) L. P. Shklover, V. E. Plyushchev, I. A. Rozdin, and N. A. Novikova, *Zh. Neorg. Khim.*, **9**, 478 (1964); c) Ph. Ghosez, R. Cote, L. Gastronguay, G. Veilleux, G. Denes, and J. P. Dodetet, *Chem. Mater.*, **5**, 1581 (1993). Also see Ref. 7.

4) a) Y. Sadaoka and Y. Sasaki, *J. Chem. Soc., Faraday Trans. 2*, **72**, 379 (1976); b) R. O. Loutfy and Y. C. Cheng, *J. Chem. Phys.*, **73**, 2902 (1980); c) T. Kitamura, S. Imamura, and M. Kawamata, *J. Imaging Technol.*, **14**, 136 (1988).

5) a) J. Mizuguchi, *J. Cryst. Res. Technol.*, **16**, 695 (1981); b) H. J. Wagner, R. O. Loutfy, and C.-K. Hsia, *J. Mater. Sci.*, **17**, 2781 (1982).

6) Y. Fujimaki, H. Tadokoro, Y. Oda, H. Yoshioka, T. Homma, H. Moriguchi, K. Watanabe, A. Konishita, N. Hirose, A. Itami, and S. Ikeuchi, *J. Imaging Technol.*, **17**, 202 (1991).

7) a) XPS analysis of the OTiPc product using a Shimadzu ESCA-850 showed peaks for Ti(IV) at 458.2 eV (Ti $2p_{3/2}$) and 463.2 eV (Ti $2p_{1/2}$)[7b,7c] but none for Ti(III).[7c] Moreover, the signals at 530.3 and 532.6 eV for O 1s[7b,7d] also appeared, demonstrating the Ti=O bond in OTiPc. b) T. Enokida and A. Hirohashi, *Nippon Kagaku Kaishi*, **1990**, 211; c) C. J. Groenenboom, G. Sawatzky, H. J. D. Meijer, and F. Jellinek, *J. Organomet. Chem.*, **76**, C4 (1974); d) T. J. Klofta, J. Danziger, P. Lee, J. Pankow, K. W. Nebesny, and N. R. Armstrong, *J. Phys. Chem.*, **91**, 5646 (1987).

8) S. Takano, Y. Mimura, N. Matsui, K. Utsugi, T. Gotoh, C. Tani, K. Tateishi, and N. Ohde, *J. Imaging Technol.*, **17**, 46 (1991).

9) C. M. Cook, *J. Am. Chem. Soc.*, **81**, 3828 (1959).

10) Before acid hydrolysis, the formation of $(R'O)_nMPc$'s was indicated by ^1H NMR and MS, but attempts to purify the initial products failed because of facile hydrolysis during the isolation procedures.

11) D. C. Bradley and C. E. Holloway, *J. Chem. Soc.*, **1968**, 219.

12) D. C. Bradley, *Chem. Rev.*, **89**, 1313 (1989).