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Synthesis and Properties of Soluble Metal-free Phthalocyanines Containing Tetra- or Octa-alkyloxy Substituents

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ABSTRACT

Some polysubstituted metal-free phthalocyanines have been synthesized and their structures confirmed by elemental analysis, IR and UV–Vis. Their crystal patterns were investigated by X-ray powder diffraction. The introduction of alkyloxy substitutes greatly improved their solubility in many organic solvents, especially in ethanol. The absorbance wavelengths of their thin-films (760–850 nm) matched the wavelengths of commercial semiconductor lasers very well. The electrochemical properties of these compounds in solution were also studied. In addition, X-ray photoelectron spectroscopy(XPS) was applied to evaluate research into their properties.

Keywords: polysubstituted metal-free phthalocyanines, solubility, alkyloxy substituents.

INTRODUCTION

Phthalocyanines have continuously been the subject of research due to their wide application fields, such as in chemical sensors, electro-chromic display devices, photovoltaic cells, xerography, optical disk, catalysis and non-linear optics [1–5]. These versatile features have stimulated attempts on the

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synthesis of new phthalocyanine derivatives with the objective of developing new materials which may show improved or more functional characteristics. In recent years, special interest has been expressed with regard to the solubility of metal-free phthalocyanines in organic solvents.

With the current coating technology in the fabrication of optical disks, a good solubility of phthalocyanine in alcohols and other organic solvents is becoming more important. In order to match the requirement properties, we have now devised two series of phthalocyanines, viz, tetra- and octa-alkyloxy substituted metal-free phthalocyanines, which were synthesized and purified by two steps of silica-gel column chromatography. Their structures were confirmed by UV–Vis, IR and elemental analysis. X-ray powder diffraction data are reported in this paper. Furthermore, the absorption of their films was measured. The electrochemical properties of the compounds solutions were also studied. The core electrons in H_2Pc were investigated by the XPS method.

EXPERIMENTAL

Reagent grade solvents were dried over molecular sieve of 4A and further distilled before use. Other chemicals were of reagent grade and were used without further purification. The synthesis procedure is shown in Fig. 1.

4-Isopropoxyphthalonitrile (2a) [6, 7]

4-Nitrophthalonitrile (6.2 g, 36 mmol), iso-propanol (10.0 ml, 130 mmol) and anhydrous potassium carbonate (12 g, 84.5 mmol) were stirred at room temperature under an argon atmosphere in 46 ml dry DMF for 96 h. The crude reaction mixture was poured into 400 ml distilled water. The precipitate was collected by filtration, washed thoroughly with water and dried. The crude product was purified by silica gel column chromatography using ether–petroleum ether (2:3), and the recrystallized from a mixture of ether–hexane (1:1) to give 4.5 g slightly yellow crystals of 4-isopropoxyphthalonitrile (2a) in 63% yield mp 58–59°C. MS. *m/z*: 186(M^+, 11.66%).

4-Neopentoxyphthalonitrile (2b)

A solution of 13.6 g of potassium carbonate in 6.92 g (1), 9.20 g of neopentyl alcohol was stirred at 60°C as described for the preparation of (2a) above. Purification gave a 73% yield 4.8 g of 4-neopentoxyphthalonitrile (2b). mp. 50–51°C. IR (cm^{-1}): 2230(CN), 1590(C=C), 1562(C=C); ^1H-NMR ($CDCl_3$) δ: 7.88–7.12 (m, 3H, aromatic), 3.68 (s, 2H, CH_2O), 0.8–1.2 (s, 9H, CH_3C).

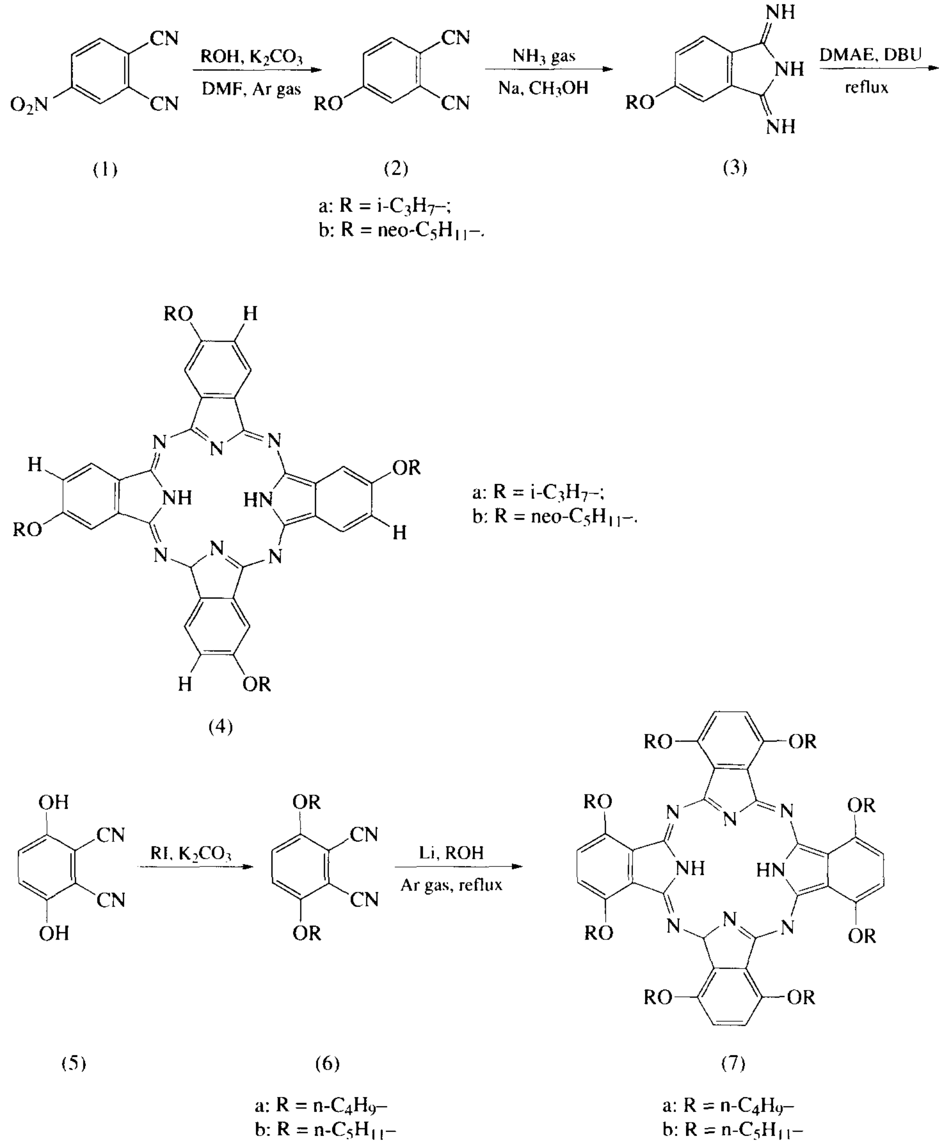

Fig. 1. The chemical structures of the phthalocyanines in the study.

4-Isopropoxy-diiminoisoindoline (3a) [8]

A rapid stream of gaseous ammonia was bubbled through 2a (4.0 g, 21.5 mmol) in absolute methanol (50 ml) with sodium methoxide (0.15 g, freshly prepared) at room temperature for 2 h. The greenish solution was heated at reflux for a further 6 h, whilst the addition of ammonia continued. The resulting precipitate was filtered after the liquor was left to stand overnight, and it was washed with a little cold methanol. Yield: 96%mp 197–198°C. IR: the –CN (2230 cm^{-1}) absorption was absent.

4-Neopentoxy-diiminoisoindoline(3b) was synthesized as described for the preparation of 3a above.

2,9,16,23-Tetraisopropoxyphthalocynine (4a)

A solution of 3a (1.80 g, 8.68 mmol) in *N*,*N*-dimethylaminoethanol (DMAE) (30 ml) underwent self-condensation as for the preparation of 4a to give 0.90 g of crude reaction product. At the beginning of the reaction, ten drops of DBU were added to the mixture as catalyst. The crude product was dissolved in CH_2Cl_2, filtered and the solvent was removed under reduced pressure. Flash chromatography of this product using dichloromethane-ether (1:1) as eluent gave 280 mg (0.375 mmol) of pure 2,9,16,23-tetraisopropoxyphthalocynine(4a) in 16.9% yield. mp 130–131°C. Elemental analysis: ($C_{44}N_8O_4H_{42}$, FW 746) Calc: C 70.78, H 5.63, N 15.01; Found: C 70.84, H 5.77, N 15.03. IR (cm^{-1}): 3300(NH), 1630(C=C), 1245, 1100, 1015(NH), 1385, 1370(–CH(CH$_3$)$_2$).

The preparation of 4b, was the same as that described for the preparation of 4a above. Elemental analysis: ($C_{52}N_8O_4H_{58}$, FW 858) Calc: C 72.73, H 6.76, N 13.05; Found: C 72.47, H 6.72, N 13.01.

3, 6-Dibutoxyphtalonitrile (6a) [9–11]

3,6-Dihydroxyphthalonitrile (5.0 g, 0.031 mmol), butyl iodide (20.0 g 0.108 mol) and anhydrous potassium carbonate (15.0 g) in freshly distilled acetone (250 ml) were stirred under reflux for 100 h and the liquor filtered. The residue was recrystallised from acetone to afford 3,6-dibutoxyphthalonitrile (6a); mp 193°C; IR (cm^{-1}): 2250(–CN).

The synthesis of 6b was carried out as for 6a; mp 169–171°C. ^{1}H-NMR(CDCl$_3$) δ: 7.70–7.50(2H, aromatic), 4.42–4.08 (4H, –OCH$_2$), 2.08(4H, –CH$_2$–), 1.86(4H, –CH$_2$–), 1.40(4H, –CH$_2$–), 0.94(6H, –CH$_3$).

1,4,8,11,15,18,22,25-Octabutoxyphthalocynine (7a)

Lithium metal (0.75 g) was added to a refluxing solution of 3,6-dibutoxyphthalonitrile (1.0 g, 3.6 mmol) in anhydrous butanol (10 ml) under an argon atmosphere. The reaction solution was maintained at reflux for 1 h. The crude product was washed with absolute methanol. The residue was column chromatographed (CHCl$_3$) and the dark green fraction was recrystallised from dichloromethane-methanol (5:95), and then the product was further column chromatographed using CH_2Cl_2 as eluent. 130 mg (0.119 mmol) 7a was obtained in 13.0% yield; mp 136–138°C. Elemental analysis. ($C_{64}N_8O_8H_{82}$, FW 1090) Calc: C 69.93, H 7.52, N 10.18; Found: C 69.46, H 7.47, N 9.71. IR (cm^{-1}): 3300(NH). 1630(C=C), 1100, 1015(NH), 1242(aromatic-O-),720($-(\text{CH2})-_4$).

The preparation of 1,4,8,11,15,18,22,25-octapentoxy phthalocyanine (7b) was similarly effected; mp 114–116°C. Elemental analysis ($C_{72}N_8O_8H_{98}$, FW 1202) Calc: C 71.88, H 8.15, N 9.32; Found: C 72.21, H 8.36, N 9.19.

MEASUREMENTS

Absorption spectra were measured on a Shimadzu UV260; thin-film absorption spectra was recorded on a Nanometrics SDP-2000(USA), fluorescence spectra on a Hitachi MPF-4 Fluorescence Spectrophotometer; and X-ray photoelectron spectroscopy (XPS) was carried out using an ES-300 (Kratos).

Cyclic voltammetric measurements were performed with a EG&G PARC model 175 universal programmer, model 174A polarographic analyser and model RE0074 X-Y recorder at room temperature using DMF (dimethylformamide) solutions containing the polyalkyloxy H_2Pc (2 mM) and a supporting electrolyte of $TEABF_4$ (0.1 M). A Pt disc (3 mm in diameter) was used as working electrode. The counter electrode was a Pt plate and a satured calomel electrode (SCE) was used as reference electrode. The solution was deaerated by bubbling with nitrogen gas before measurements. Scan rate was 20 mV s^{-1} and its range was from -1.5 V to $+1.5$ V.

TABLE 1
Solubility of Compounds in Various Solvents

Solvents	*4a*	*4b*	*7a*	*7b*
CH_2Cl_2	+ +	+ +	+ +	+ +
Toluene	+ +	+ +	+ +	+ +
Ethyl acetate	+	+	+	+
Iso-propanol	+	+	+	+
Acetone	+	+	–	–
Methanol	–	–	–	–

+ + solubility in the range of 0.701–1.20 mol $litre^{-1}$ at 20°C; + solubility in the range of 0.05–0.20 mol $litre^{-1}$ at 20°C; – insoluble at 20°C.

RESULTS AND DISCUSSION

A: Solubility in organic solvents

With the introduction of alkyloxy groups into the peripherical positions of phthalocyanine, the solubility in organic solvents increased. From the data shown above, it can be concluded that the solubility is better in solvents of weak polarity than in the solvents of strong polarity. This can be related to the symmetric structure of phthalocyanine molecule; high symmetry decreases the polarity of the ground-state molecule.

Polycarbonate (PC) is widely applied in industry as a material for CD's substrate plate. As shown above, the objective phthalocyanines dissolved in CH_2Cl_2, but at the same time, the resin is also dissolved by CH_2Cl_2. Because alcohol is relatively non-toxic, has no effect on the resin and evaporates easily, solubility of the recording medium in alcohol is becoming more important. The metal-free phthalocyanine is synthesized above is soluble in iso-propanol and this characteristic makes it possible to manufacture CDs by spin-coating technology using the phthalocyanine compounds as optical recording medium.

B: Crystal structure analysis

Polymorphism is a common phenomenon in phthalocyanines, since the intermolecular forces between phthalocyanine molecules are relatively weak and a variety of molecular stacking arrangements of similar energies are possible. As seen in Table 2, 4a and 4b have no satisfactory forms within the 16 isomers; they are probably mixtures of many different arrangements. But for compound 7b, stronger lines occur at 2-θ values of approximately 8.3 and 9.7°, having interplanar spacings 10.6 Å and 9.11 Å, respectively. Both the X-ray diffraction spectra of 7a and 7b are similar to β-H_2Pc [12, 13]. Their absorption spectra in the visible region accord with β-H_2Pc. X-ray diffraction data shows that 7a and 7b have excellent patterns and are thus suitable for application as optical recording materials.

C: Absorption and fluorescence emission spectrum

Metal-free phthalocyanine (H_2Pc) belongs to the D_{2h} matrix group, has 186 valence electrons, and an anti-magnetic ground-state electronic structure. The absorbance spectra of 4a and 4b are similar, both having the characteristic absorption peak of phthalocyanine in the visible region. Splitting of the absorbtion peak of 7a and 7b in visible region is not obvious, but their λ_{max} values are red-shifted about 50–70 nm, since the alkyloxy groups take

TABLE 2
X-ray Powder Diffraction Data

$2\text{-}\theta(°)$	4a Relative intensity	d (Å)	$2\text{-}\theta$ (°)	4b Relative intensity	d (Å)
5.5	100	16.01	5.16	100	17.11
17.86	26	4.96	16.7	35	5.3
26.38	30	3.38	26.46	28	3.36

$2\text{-}\theta(°)$	7a Relative intensity	d (Å)	$2\text{-}\theta$ (°)	7b Relative intensity	d (Å)
7.34	90	12.02	8.36	90	10.57
8.08	95	10.93	9.7	77	9.11
17.82	64	4.97	16	38	5.53
21.08	70	4.21	19.38	39	4.58
22.1	77	4.02	20.0	76	4.43
22.78	58	3.90	23.12	40	3.84
24.06	100	3.70	24.5	100	3.63

Samples were chromatographed; CH_2Cl_2 was evaporated and the products washed with methanol.

TABLE 3
Absorption and Fluorescence Spectral Data

	λ_{max}^{ab} (CH_2Cl_2)	λ_{max}^{ab} ($i\text{-}C_3H_7OH$)	λ_{max}^{ab} (film)**	λ_{max}^{em} (CH_2Cl_2)
4a	708;670;640(1.08)*	703;665(4.13)	793;710;670	732
4b	710;670;642(0.51)	704;667(1.86)	793;710;670	732
7a	772(0.88)	761(4.86)	840;790;760	No detection signal
7b	776;748(0.69)	762;740(10.67)	852;800;760	No detection signal

*represents ε–10^4 l mol^{-1} cm^{-1}; ** film was prepared by spin-coating.

TABLE 4
Redox Potential Data of the Compounds

	4a	4b	7a	7b	X
Eox	—	—	0.56 V,0.9 V	0.55 V,0.88 V	0.55 V,1.15 V
Ered	—	—	−0.05 V,−0.4 V	−0.45 V	−0.35 V

— represents no detected signal; X is 1,4,8,11,15,18,22,25-octatertbutoxy Nickel(II) phthalocyanine (Aldrich).

part in the macro π conjugation system of the phthalocyanine moiety. Increase in the numbers of alkyloxy groups leads to a decrease of the energy of the π^* orbital; and the absorbance therefore shifts to longer wavelength. The Stokes shift is 20–30 nm for 4a and 4b, but the emission phenomena was not detected for 7a and 7b.

TABLE 5
XPS Data

Binding energy	*C(1s)*	*N(1s)*	*O(1s)*	*$Ni(2p_{3/2})$*
4a	286.02;284.60	399.32;397.69	532.47	No nickel atom
7a	286.42;284.80	398.79	533.23	No nickel atom
X	286.7;284.77	398.86	532.98	856.14

D: Electrochemical property

Table 4 shows the cyclic voltammograms (CV) of the four compounds. From the CV curves, two facts are ascertained [14]: (i) tetra-alkyloxy H_2Pc has no oxidation and reduction peaks, demonstrating that the electrochemical reactions do not occur under this condition, (ii) the octa-alkyloxy H_2Pc has two oxidation peaks (0.56 V, 0.90 V) and a high reduction peak potential (−0.4 V), indicating that these reactions are reversible.

Two aspects of the phthalocyanine structure are of importance in determining the influence of akyloxy substitutes and their number. H_2Pc is the 18-electron aromatic core of the phthalocyanine ring and interaction of this core occurs with sustitutuents on the ring [15]. The effect of the alkyloxy group is to increase the electron density on the phthalocyanine ring, which leads to a more facile oxidation of the phthalocyanine ring. With increasing number of alkyloxy groups, the electrochemical reaction becomes easier.

The second oxidation potential of compound *X* (1.15 V) is higher than that of 7a and 7b, which results from the complexation of the central metal atom (nickel). The nickel atom draws the electrons away from the phthalocyanine ring, so that the electron density of the conjugated system is decreased. As a result, the electrochemical properties of *X* decline.

E: XPS analysis

X-ray photoelectron spectroscopy (XPS), which measures the binding energy (B.E.) of the core electrons in atoms and molecules, has been successfully applied to the study of some copper(II) tetraaza complexes [16]. There are no reports on phthalocyanines concerning XPS, especially on metal-free phthalocyanines. All ‘ls’ orbitals of the carbon atom are split, which shows that there are un-paired electrons in the carbon atoms ground state. The sequence of the binding energy is: 7a > *X* > 4a, which indicates that 7a oxidises more readily than *X* and 4a. The result is consistent with the cyclic voltammetric measurements.

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