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Synthesis of phthalocyaninatocobalt(II) and complex formation with imidazole

Jian Wang, Hui-Jun Xu *, Shu-Ying Shen

Laboratory of Photochemistry, Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, PR China

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Abstract

Two kinds of phthalocyaninatocobalt(II) with different substituents have been synthesized. Complexation of imidazole was observed to proceed in two steps to form a mono- and, subsequently, a di-imidazole complex in solution. It is thought that the steric effect of the substituents on the ring, control the number of coordinated imidazole molecules. The stoichiometry of the complexes was determined by Job's titration method and the formation constants were then evaluated. The absorption spectrum of phthalocyaninatocobalt(II) exhibits a very broad band in thin films due to molecular aggregation while its di-imidazole adduct showed a sharp and red-shifted absorption band which is critical for optical recording materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phthalocyaninatocobalt(II); Imidazole; Complex formation

1. Introduction

Phthalocyanines have been widely used as pigments and *p*-type organic photoconductors for electrophotography. They also have potential applications in gas-sensing devices, photovoltaic cells, electrochromic displays and in the photodynamic therapy of certain types of cancers [1,2]. They are useful for optical recording medium in optical disks since they effectively absorb GaAs semiconductor laser light [3]. Although many phthalocyanine dyes have been patented for use in optical recording medium [4–6], fundamental research on their spectral properties has been limited. For optical recording medium, high reflection at the wavelength of the semiconductor laser is required. For this particular application, a sharp and strong absorption band capable of matching the writing laser wavelength is necessary to obtain high reflectivity [7]. However, phthalocyanines have a high tendency to form molecular aggregates [8] both in solution and in thin films and these aggregates display a broad absorption band which is not suitable for optical recording materials. By choosing appropriate axial substituents, the aggregation of phthalocyanine dyes can be prevented and a sharp absorption with a narrow peak width can be obtained which is critical for optical recording medium. In this paper, we report the syntheses of phthalocyaninatocobalt(II) (CoPc) bearing different substituents. Spectral changes following axial legation of one or two imidazole molecules were investigated. It has been found

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* Corresponding author. Fax: +86-10-64879375.
E-mail address: g201@ipc.ac.cn (H.J. Xu).

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that the di-imidazole adducts possess a sharp Q-band which is suitable for optical recording materials using GaAs semiconductor laser.

2. Experimental

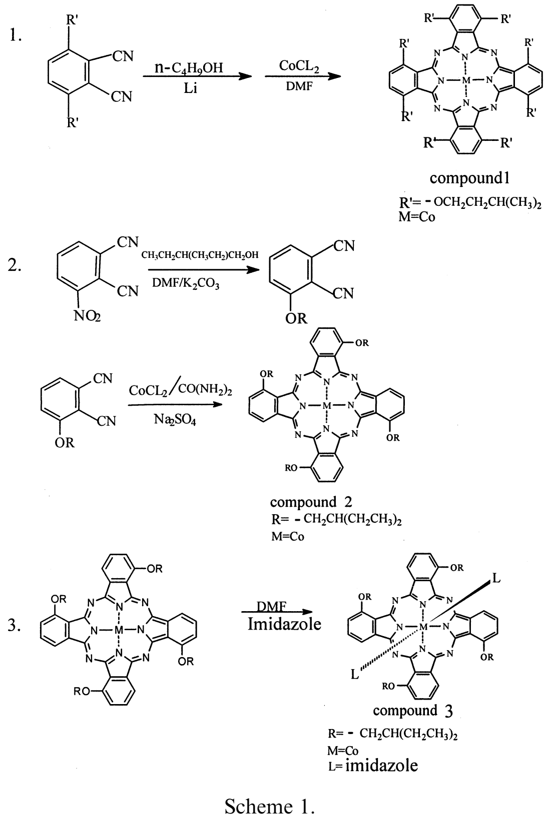
2.1. Synthesis

2.1.1. Compounds

1, **2** and **3** were synthesized by the route shown in Scheme 1.

2.1.2. Preparation of 3-(2-ethyl-butoxy)phthalonitrile

A solution of 3.28 g (25.6 mmol) of 3-nitrophthalonitrile in 200 cm^3 DMF was added to 5.6 cm^3 3-methylpentanol-1. The mixture was stirred at room temperature for 4–5 days under N_2 (99.94% pure) atmosphere. The mixture was then filtered and 2.9 g yellow solid material was obtained. The crude material was recrystallized from toluene to give 2.1 g (45% yield) of pure product, m.p: 163–164°C. MS($C_{14}H_{16}N_2O$): *m*/*z* 229 (M^+).



Scheme 1.

2.1.3. Preparation of 1,4,8,11,15,18,22,25-octa-(isopentyloxy)phthalocyaninatocobalt(II) (**1**)

Half a gram of lithium metal was added to a solution of 2 g (7.46 mmol) 3,6-bis-(isopentyloxy)penthalonitrile in 15 cm^3 *n*-butyl alcohol. The mixture was refluxed for 1 h. After cooling to room temperature, the mixture was filtered and the residue washed with water. The green solid obtained was dissolved in 15 cm^3 DMF and refluxed for 2 h and then cooled to room temperature. The crude product was recrystallized from ethyl acetate and 0.76 g of a green crystal was obtained. yield: 53%. Elemental analysis: $C_{72}N_8O_8H_{102}Co$. Found (calc) (%) C68.63 (68.46) N8.48 (8.87) H7.89 (8.08).

2.1.4. Preparation of 1,8,15,22-tetra-(2-ethyl-butoxy)phthalocyaninatocobalt(II) (**2**)

A mixture of 2.1 g (7.8 mmol) 3-(2-ethyl-butoxy)phthalonitrile, 0.254 g (2 mmol) $CoCl_2$, 0.01 g (0.07 mmol) Na_2SO_4, and a catalylic amount of $(NH_4)_6Mo_7O_{24}$ was heated at 150°C for 1 h, then the temperature was raised to 180°C and maintained at this temperature for 3 h. After cooling, to room temperature, the mixture was filtered and the residue washed with water until the washings became colorless. The green solid obtained was recrystallized from ethyl acetate and purified by flash chromatography on silica gel using $CHCl_3$/CH_3COCH_3 (1:1) as eluent, Evaporation of the solvent, 1.76 g of green crystals was obtained. yieid: 21%. MS: *m*/*z* 971 (M^+). Elemental analysis: found (calc) (%) $C_{56}H_{66}N_8O_4Co$ C69.23 (69.27) N11.26 (11.54) H6.68 (6.59).

2.1.5. Preparation of 1,8,15,22-tetra-(2-ethyl-butoxy)phthalocyaninatocobalt(II) imidazole complex (**3**)

A mixture of 100 mg (1.47 mmol) of imidazole and 50 mg (0.051 mmol) of 1,8,15,22-tetra-(2-ethyl-butoxy)phthalo cyaninatocobalt(II) were dissolved in 70 cm^3 DMF and stirred at room temperature for 4 h. After filtering, a green solid was obtained, which was purified by flash chromatography on silica gel using $CHCl_3/CH_3COCH_3$ as eluent. 28 mg (0.025 mmol) of green crystals was obtained. Yield: 49%. Elemental analysis: found (calc) (%) $C_{56}H_{66}N_8O_4Co.2C_3H_4N_2$ C66.97 (67.15) N 15.20 (15.16) H6.32 (6.49).

2.2. Instrument and methods

UV–vis absorption spectra were measured using a Hitachi-557 spectrometer using chloroform as blank solvent. Mass spectra were recorded by MALDI-TOF-MS on a Bruker Biflex III. Elemental analysis was determined by Carlo Zrba 1106 and ST-02-G.C methods.

For determining the stoichiometry and formation constant of the complex between phthalocyaninatocobalt(II) and imidazole, the absorbance of a series of imidazole and CoPc mixtures which were prepared from their 1×10^{-5} mol^{-1} chloroform solutions as $1+9$ mol^{-1}, $2+8$, $3+7$, $4+6$, $5+5$, $6+4$, $7+3$, $8+2$ and $9+1$ cm^3 were measured. The data were analyzed using Job's method [9,10].

3. Results and discussion

Complex formation between CoPc and imidazole is thought to proceed in two steps :

$$\mathrm{CoPc} + \mathrm{L} \rightleftharpoons \mathrm{CoPcL}$$
$$K_1 = (\mathrm{CoPcL})/(\mathrm{CoPc})(\mathrm{L}) \qquad (1)$$

$$\mathrm{CoPcL} + \mathrm{L} \rightleftharpoons \mathrm{CoPcL_2}$$
$$K_2 = (\mathrm{CoPcL_2})/(\mathrm{CoPcL})(\mathrm{L}) \qquad (2)$$

the overall reaction $\mathrm{CoPc} + 2\mathrm{L} \rightleftharpoons \mathrm{CoPcL_2}$
$$K = (\mathrm{CoPcL_2})/(\mathrm{CoPc})(\mathrm{L})^2 \qquad (3)$$

It is most conveniently studied by Job's method of continuous variations. The Job's diagram of complexation of compound **1** with imidazole is obtained by plotting the absorbance A at 780 nm; where $A = A_c - (A_{Pc+}A_L)$ vs f_L [mol fraction of imidazole , $f_L = C_L / (C_{Pc} + C_L)$] (Fig. 1). A_C is the absorbance of the complex, A_{Pc} is the absorbance of Pc, A_L is the absorbance of imidazole which is negligible at 780 nm, C_L is the molar concentration of imidazole and C_{Pc} the molar concentration of Pc. The plot consists of two straight lines intersecting at $f_L = 0.5$, as is typically the case when only a 1:1 complex is formed [11]. In contrast, the diagram obtained for complexation of compound **2** with imidazole (Fig. 2). presents three regions: for f_L smaller than 0.5, the value A varies linearly with f_L as in the preceeding case, for f_L greater than 0.5, the evolution comprizes two distinct linear stages with an intersection at $f_L = 0.67$. In this case, therefore, two different species are formed in

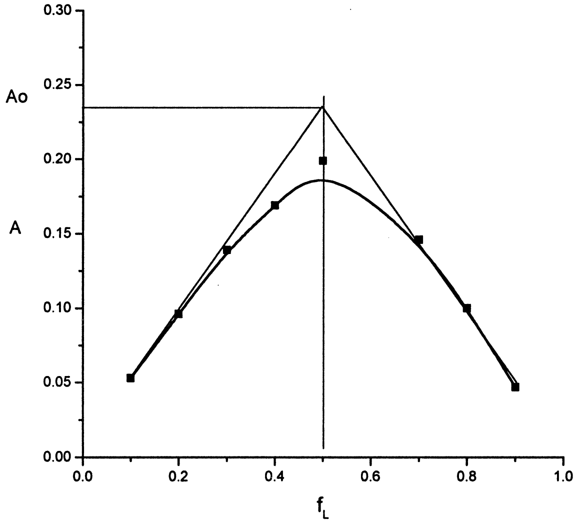


Fig. 1. Job's diagram for compound **1** — imidazole system in chloroform $\lambda = 780$ nm.

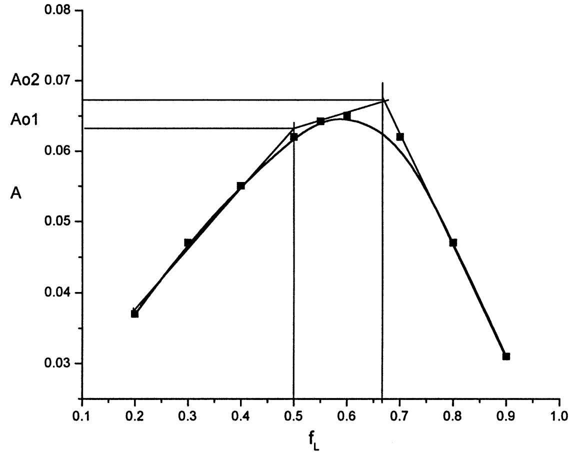


Fig. 2. Job's diagram for compound **2** — imidazole system in chloroform $\lambda = 730$ nm.

solution, namely one with a 1:1 stoichiometry and another one with 1:2 stoichiometry.

The complex formation constant K can be graphically assessed from the Job's diagram. If the complex is very stable, the absorbance value should be A_o; deviation from A_o is due to dissociation of the complex. At equilibrium:

$$\begin{aligned}&\mathrm{CoPc} + n\mathrm{L} \rightleftharpoons \mathrm{CoPcL}n\\ &\text{and } C_{\mathrm{pL}} = (1-\alpha)C \quad C_{\mathrm{Pc}} = \alpha C \quad C_{\mathrm{L}} = n\alpha C\end{aligned} \tag{4}$$

where C_{pL} is the concentraton of the complex at equilibrium, C is concentration of the complex without dissociation and α denotes the fraction of dissociation of the complex which can be deduced from the figures.

$$\alpha = \frac{A_o - A}{A} \tag{5}$$

The formation constant K of the complex is then calculated from the following equation:

$$K = \frac{1-\alpha}{n^n \alpha^{n+1} c^n} \tag{6}$$

where n denotes the number of axial ligands. The results are listed in Table 1 from which it is clear that the number of substituents and, hence the steric effect, determine the formation of either 1:1 and 1:2 complex. In the case of compound **2** with four substituents, ligation of one or two imidazole molecules are possible to form 1:1 and 1:2 complexes. For compound **1**, the introduction of eight substituents on the ring at non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) positions exerts significant steric hindrance to prevent an additional imidazole molecule coordinating in an axial position to form a 1:2 complex. It is also known that ligation of a nitrogenous base with a metal phthalocyanine is generally observed in thermodynamic studies. The failure to detect a 1:1 complex was taken as an indication that $K_1 \ll K_2$ [Eqs. (1) and (2)]. It is interesting to note the inverse behavior ($K_1 \gg K_2$) observed in the reaction between imidazole and compound **2**, so that the stepwise formation of 1:1 and 1:2 complexes can be detected.

Table 1
Formation constants of the complex of CoPc with imidazole in chloroform

Compound	Complex	K_1	K_2
1	1:1	1.03×10^6	
2	1:1 and 1:2	2.03×10^8	2.80×10^5

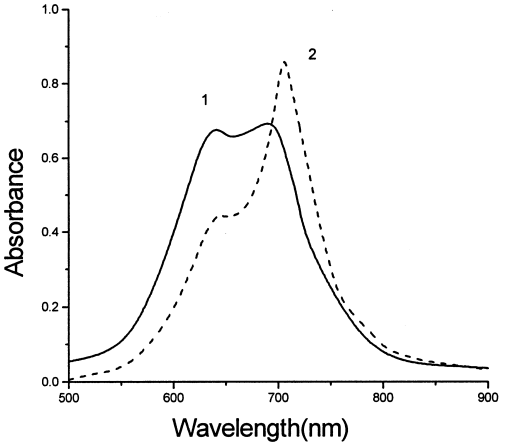


Fig. 3. Absorption spectra of compound **2** (—) and its di-imidazole adduct (- - -) thin films.

Thin films of phthalocyaninatocobalt(II) compound **2** and its di-imidazole adduct compound **3** were prepared by spin-coating of their chloroform solution on glass. Fig. 3 shows the absorption spectra of thin films of compound **2** and compound **3**. The spectrum of compound **2** gives a broad band with two peaks at 630 and 690 nm, respectively, as a result of molecular aggregation in the film. In contrast, the spectrum of compound **3** has a sharp and red-shifted absorption band with a steep absorption edge on the 705 nm side which is critical for high reflectivity. This indicates that compound **3** is suitable for optical recording materials using GaAs laser.

Acknowledgements

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References

[1] Leznoff CC, Lever ABP, editors. Phthalocyanines properties and applications, vols. I and III. New York: VCH Publishers, 1889–1993.

[2] Simon J, Andre JJ. Molecular semiconductors. Berlin: Apring Verlag, 1985.

[3] Kobayashi S, Iwasaki K, Sasaki H, Oh-Hare S, Nishizawa M, Katayose M. Jap J Appl Phys 1991;30:L114.

[4] Umehara H, Sugimoto K, Nishimoto T, Misawa T, Ito N. (Mitsui Toatsu Chemicals; Yamamoto Chemicals Inc. Japan). Jpn. Kokai Tokkyo Koho Jp 07 207, 172 [95 207, 172].

[5] Sato T, Tomura T, Sasa N. (Ricoh Kk, Japan). Jpn. Kokai Tokkyo Koho Jp 08 115, 533 [96 115, 533].

[6] Uematsu T, Imamura S. (Mitsubishi Chemical Industries Ltd., Japan). Jpn. Kokai Tokkyo Koho Jp 10 222,884 [98 222,884].

[7] Suzuki Y, Horie M, Okamoto Y, Kurose Y, Maeda S. Jpn J Appl Phys Part 1 1998;37(4B):2084.

[8] Tai S, Hayashi N. J Chem Soc Perkin Trans 1991;2: 1275.

[9] Hill ZD, Jmaccorthy P. J Chem Edu 1986;63:162.

[10] Rossotti FJC, Rossotti H. The determination of stability constants. New York: McGraw-Hill Book Co, 1961.

[11] Lipskier JF, Trans-Thi TH. Inorg Chem 1993;32:722.