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Dyes and Pigments 72 (2007) 267–270

DYES and PIGMENTS

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Synthesis and electrochemistry of a substituted phthalocyaninatozinc

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Received 17 June 2005; accepted 25 August 2005
Available online 21 October 2005

Abstract

The synthesis of a zinc phthalocyanine (Pc) bearing four phenoxyl substituents was described and its molecular structure was fully characterized by ^{1}H NMR, MS, elemental analysis, UV−vis and IR, which were consistent with the proposed structure. This Pc possesses excellent solubility in polar organic solvents, such as dichloromethane and THF, and doesn't readily aggregate to the dimer. TOF-MS and elemental analysis prove its excellent purity. The compound's electrochemical redox reactions in THF occurred in the Pc ring and were quasi-reversible single-electron processes. The electrochemical reaction mechanism was proposed.

Keywords: Phthalocyanine; Dye; Synthesis; Phenoxyl; Electrochemistry; Cyclic voltammetry

1. Introduction

Since their accidental synthesis in Scotland, by Imperial Chemical Industries in 1928, phthalocyanines (Pcs) have enjoyed considerable industrial importance for use in dyestuffs, paints, colors for metal surfaces, fabrics and plastics. Meanwhile, chemical and physical studies of metal Pcs (MPcs) and their derivatives are also pursued by worldwide chemists for their potential applications in many areas. The functions of metal Pcs and their derivatives are almost based on a redox or electron transfer reaction. Electrochemical properties of MPcs have been intensively studied [1−3]. A variety of investigations are desirable in view of the potential utility of MPcs as the electrocatalysts [4,5]. An understanding of the nature of redox processes of metal Pcs in solution is essential in the design of more efficient catalysts.

Due to the intermolecular interactions between the macrocycles, peripherally unsubstituted metal Pcs are practically insoluble in common organic solvents, thereby minimizing their applications [6]. The solubility can be improved by introduction of substituents on the periphery that, to some extent, increases the distance between the 18-π electron conjugated systems of Pcs and makes their solution easier. A considerable effort has been made to generate novel Pc derivatives possessing enhanced properties, e.g. higher solubility in common organic solvents [7,8].

In the present work, we prepared the metallophthalocyanine, zinc 2,9(10),16(17),23,(24)-tetra(*p-tert*-butylphenoxy)-phthalocyanine (TTBPPcZn) (Fig. 1) and investigated its electrochemical properties. The purpose of this study is to gain an understanding of the redox process of TTBPPcZn in certain organic solvents, and to provide the possibility for the complex as an electrocatalyst.

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doi:10.1016/j.dyepig.2005.08.024

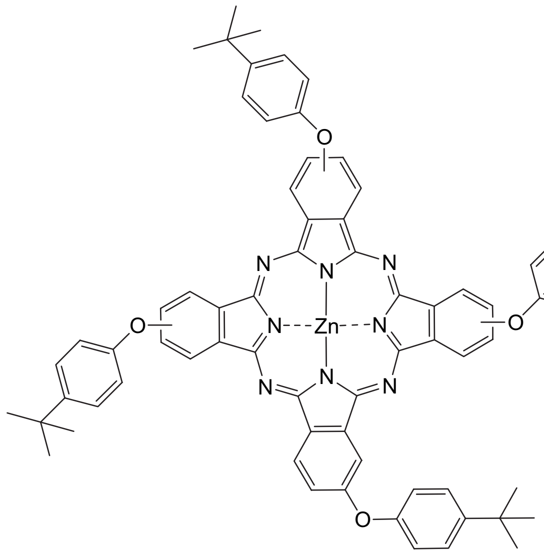

Fig. 1. Molecular structure of TTBPPcZn.

2. Experimental

2.1. Materials and methods

Dimethyl sulfoxide (DMSO) was predried over barium oxide and distilled under reduced pressure. All other reagents and solvents were commercially available and used without further purification.

Cyclic voltammetry: CHI610a Electrochemical Analyzer. Electrochemical data were recorded by a conventional three-electrode cell: a platinum disk (area 0.00502 cm^2) as the working electrode; a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. ^{1}H NMR: Varian Unity 500 spectrometer. UV–vis: Cary 500 UV–VIS–NIR spectrophotometer. MS: LDI-1700-TOF mass spectrometer. Elemental analyses: Flash EA1112 Elemental Analyzer.

2.2. Synthesis of TTBPPcZn

4-(*p*-*tert*-Butylphenoxy)phthalonitrile [9] (4 mmol) and zinc acetate (1 mmol) were added to DMAE with stirring, which was heated at 135 °C under N_2 for 12 h. Then, DMAE was removed. The obtained solid was purified by chromatography (SiO_2, ether:petroleum ether = 1:3) to give TTBPPcZn 514 mg (44%). ^{1}H NMR ($CDCl_3$): $\delta = 7.359–7.469$ (m, 12H, ArH), 7.139–7.243 (m, 16H, ArH), 1.361–1.555 (m, 36H, 12CH_3). MS: $m/z = 1169.5$ [M^+H^+] (calcd. 1169.4). UV–vis ($CHCl_3$): λ_{max}(nm, $\log \varepsilon$) = 357(4.53), 615(4.42), 682(5.30). Elemental analysis: ($C_{72}H_{64}N_8O_4Zn$, FW 1168.4) C 73.98, H 5.52, N 9.59, Found: C 73.64, H 5.87, N 9.24.

3. Results and discussion

3.1. Synthesis

A well-established synthetic route to soluble tetrasubstituted Pcs involves the aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile or 3-nitrophthalonitrile and a suitable oxygen or sulfur nucleophile followed by cyclotetramerisation of the resultant phthalonitrile derivatives, e.g. 4-(cumylphenoxy)phthalonitrile [10] and 4-(neopentoxy)phthalonitrile [11]. In DMSO, using LiOH as the alkali, anion of *p*-*tert*-butylphenol displaced the nitro group of 4-nitrophthalonitrile to generate the corresponding phthalonitrile derivative in desirable yield. We fail to obtain 4-(*p*-*tert*-butylphenol)phthalonitrile in good yield by the use of K_2CO_3. The preparation of metal Pcs by cyclotetramerisation of phthalonitrile derivatives, catalysted by DBU, in 1-pentanol or DMAE is preferable due to its easier purification and higher yield.

3.2. Solubility of TTBPPcZn

The four *tert*-butyls of TTBPPcZn molecule will enhance its solubility in organic solvents. It presents excellent solubility in $CHCl_3$, CH_2Cl_2, THF and benzene, but the solubility in acetone, DMF and DMSO is not very good, which is probably determined by the solubility nature of *tert*-butyls in organic solvents. The good solubility of TTBPPcZn in certain organic solvents is also attributed to the steric hinderance of peripheral phenoxyl substituents, which make TTBPPcZn hard to form dimers.

3.3. Isomers of TTBPPcZn

Tetrasubstituted phthalocyanines are usually obtained as a mixture of four constitutional isomers (D_{2h}:C_s:C_{2v}:C_{4h}) (Fig. 2). According to reports of Prof M. Hanack [12,13],

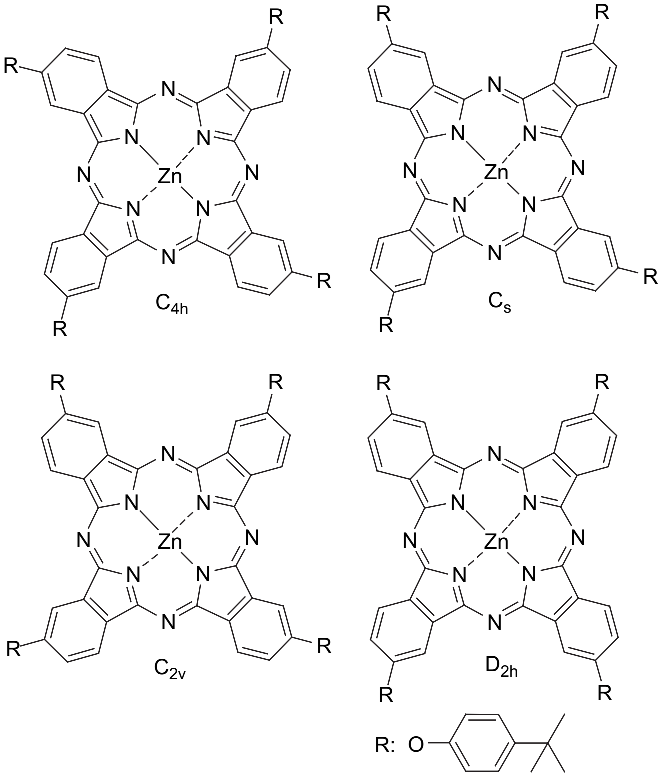

Fig. 2. Isomers of TTBPPcZn.

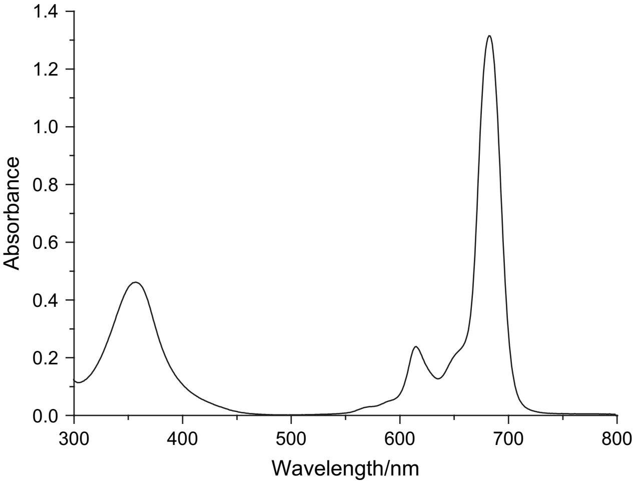

Fig. 3. UV–vis spectrum of TTBPPcZn.

the bulky phenoxyl substituents in TTBPPcZn don't affect the distribution of its isomers, so its isomers should be in the expected statistical proportion (D_{2h}:C_s:C_{2v}:C_{4h} = 1:4:2:1). To the best of our knowledge, there is no literature presently available that reports the successful separation of these four isomers with ordinary column chromatography. Our attempts to separate these isomers by column chromatography are not successful. However, Prof M. Hanack and his co-workers separated all four isomers of two different tetrasubstituted Pcs by HPLC [14–16]. The conclusions of this paper do not depend on having a pure isomer.

3.4. UV–vis and MS analysis

The Pc characteristic absorption band, *Q* band and *B* band, were found in UV–vis spectrum of TTBPPcZn at 682 nm and 357 nm (Fig. 3), respectively, which means that the Pc ring formed. A small band appeared at 615 nm cannot be attributed to dimer because it didn't cause a broadening of the *Q* band [17] with the concentration increasing as high as 10^{-4} mol/L, so the small band should be vibronic. The UV–vis spectrum indicates the weakly aggregative nature of TTBPPcZn, which may arise from the steric hinderance of bulky phenoxyl groups, hindering the π–π interaction among TTBPPcZn molecules, in its peripheral moiety. From its TOF-MS (Fig. 4), we could found the excellent purity of TTBPPcZn. Dimer peak wasn't observed, probably suggesting that TTBPPcZn didn't aggregate readily in solid state.

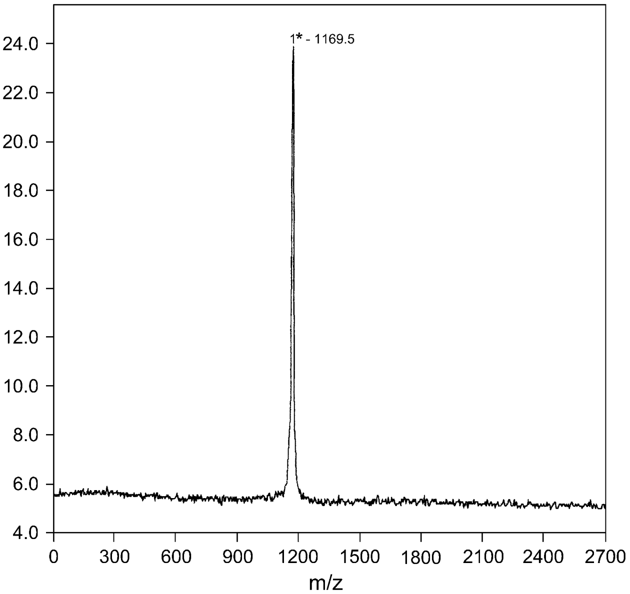

Fig. 4. Scanned picture of MS spectrum of TTBPPcZn.

3.5. Electrochemistry of TTBPPcZn

The cyclic voltammogram data of TTBPPcZn are summarized in Table 1. Its cyclic voltammetric curves at different scanning rates are presented in Fig. 5. The reduction and oxidation of MPc derivatives are due to the interaction between the Pc ring and the central metal. The redox properties of MPc derivatives have been studied by many authors [1–3]. According to these studies, the first oxidation and first reduction processes occur on the metal center in the metal Pcs for Mn, Fe, and Co derivatives. According to Lever et al. [18,19], for Ni, Cu and Zn Pcs, redox processes take place on the Pc ring. Thus, three redox couples of TTBPPcZn should be attributed to the Pc ring. Therefore, a couple of redox peaks at around 0.78 V are attributed to oxidation of TTBPPcZn ring and those at about −0.82 V and −1.30 V should be assigned to reduction of TTBPPcZn ring. No splitting of the redox couples of TTBPPcZn was observed, the redox processes occurred via multi-electron transfers, at the same potential, so its electrochemical reactions are single-electron processes. ΔE_p and $|i_{p,a}/i_{p,c}|$ of TTBPPcZn indicates that its redox reactions should be quasi-reversible processes although the oxidation couples

Table 1
Cyclic voltammogram data of TTBPPcZn

Scanning rate (mV/s)	Pc **1**								
	$E_{1/2}$(Ox)	ΔE_p	$\lvert i_{p,a}/i_{p,c}\rvert$	$E_{1/2}$(Red 1)	ΔE_p	$\lvert i_{p,a}/i_{p,c}\rvert$	$E_{1/2}$(Red 2)	ΔE_p	$\lvert i_{p,a}/i_{p,c}\rvert$
50	0.786	0.202	0.98	−0.832	0.095	0.96	−1.310	0.100	0.98
100	0.785	0.213	0.89	−0.827	0.107	0.95	−1.303	0.103	0.98
200	0.778	0.241	0.80	−0.822	0.135	0.96	−1.301	0.132	0.99

$E_{1/2} = (E_{p,c} + E_{p,a})/2$, $\Delta E = |E_{p,c} - E_{p,a}|$.

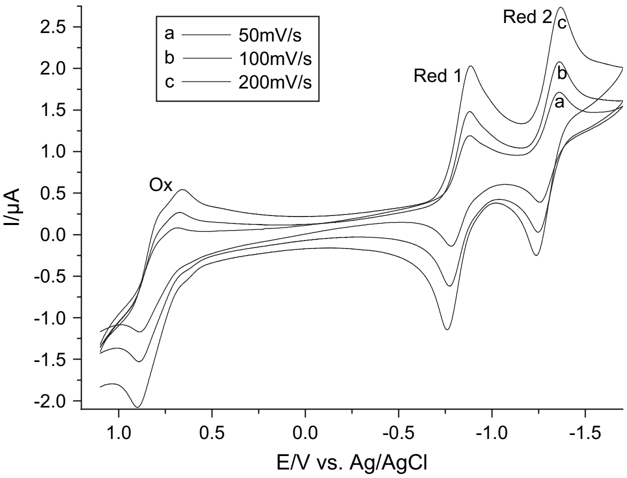

Fig. 5. Cyclic voltammetric curves of TTBPPcZn.

of Pc ring are less quasi-reversible. Based on discussion above, we can give the electrochemical reaction mechanism of TTBPPcZn shown as follows:

$$\mathrm{Pc(-2)Zn(II)} \rightleftharpoons \mathrm{Pc(-1)Zn(II)} + e^- \quad \mathrm{(Ox)}$$

$$\mathrm{Pc(-2)Zn(II)} + e^- \rightleftharpoons \mathrm{Pc(-3)Zn(II)} \quad \mathrm{(Red\ 1)}$$

$$\mathrm{Pc(-3)Zn(II)} + e^- \rightleftharpoons \mathrm{Pc(-4)Zn(II)} \quad \mathrm{(Red\ 2)}$$

4. Conclusion

In summary, a metal Pc derivative was newly prepared and its solubility is greatly improved due to the introduction of phenoxyl substituents in the peripheral moiety. The compound's electrochemical redox reactions in THF are one-electron quasi-reversible processes.

Acknowledgements

This work was financially supported by National Science Foundation of China (No. 60307002) and Innovation Foundation of Jilin University.

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