Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Dergisi/ Journal of The Institute of Natural & Applied Sciences 16 (2):40-44,2011

Araştırma Makalesi/Research Article

Synthesis of New Metallophthalocyanines Substituted with Dissimilar Groups

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Abstract: New metallophthalocyanines have been synthesized from 4-(2-dimethylaminoethylsulfanyl) phthalonitrile and diethyl 3, 4 dicyanophenylmalonate. Metallophthalocyanines (Co II, Ni II and Zn II) were prepared by cyclotetramerization of **i** and **ii** with metal salts. The phthalocyanines were separated and washed using different solvents. The newly synthesized compounds have been characterized by elemental analyses, UV-Visible and IR spectra.

Key words: Phthalocyanine; Characterization;Complex; Synthesis; Metal

Farklı Substitue Grouplu Yeni Metalli Ftalosiyaninlerin Sentezi

Özet: Yeni metalli ftalosiyaninler 4-(2-dimetilaminoetilsulfanil)ftalonitril ve dietil 3,4 disiyanofenilmalonat'dan sentezlendi. Metalli ftalosiyaninler (Co II,Ni II and Zn II) **i** ve **ii** nın metal tuzlar ile siklotetramerizasiyondan hazırlandı. Ftalosiyaninler farklı çözücüler ile yıkandı ve izole edildi. Yeni sentezlenen bileşikler elemental analiz, UV-Vis ve IR spektrumu ile karakterize edilmiştir.

Anahtar kelimeler: Ftalosiyanin; Karakterizasyon;Kompleks; Sentez; Metal.

Introduction

Phthalocyanines(Pcs) have found widespread industrial application as pigments and dyes, so that some derivatives have been extensively studied because of their interesting electrochromic, photovoltaic, catalytic, conductivity properties, non-linear optics (Leznoff and Lever,1989).The physical and chemical properties of soluble phthalocyanines have recently attracted the attention of materials chemists for their potential use in semiconducting materials, nonlinear optical devices(Ağırtaş and Bekaroğlu, 2001).

The growing use of phthalocyanines as advanced materials during the last decade has encouraged research on the synthesis of new derivative materials which differ in the peripheral substituents. Synthetic routes to symmetrical Pcs are relatively straightforward, starting from the appropriately substituted phthalonitrile. However, unsymmetrical phthalocyanines containing different substituent in the benzo ring are more difficult to obtain. Published routes for preparing unsymmetric phthalocyanines mostly involve in situ synthesis of the phthalocyanine macrocycle by condensation of two differently substituted phtalonitrile precursors in appropriate stoichiometric ratios to yield mono-trough tetrasubstituted Pcs (McKeown, 1998).Other more specific methods to prepare unsymmetrical phthalocyanines have also been reported including polymer support methods,stepwise synthetic procedures, the condensation of two different phthalyl precursors and the use of Meerwein reaction conditions(Kobayashi, 2002).

In previous studies, we described the synthesis of phthalocyanines with four N' (2-cyanoethyl) aminoethylsulfanyl groups on the periphery whose compounds might be considered as intermediates for dendrimeric phthalocyanines (Ağırtaş and Bekaroğlu, 2001).

Its is well known that the addition of bulky substituents on the periphery results in products soluble in apolar solvents, while sulphonium or quaternary ammonium groups are leading to water or polar sovent-soluble (Abdurahmanoğlu at all,2004). In this present paper, both asymmetric and dendrimeric Pcs soluble in water Pcs is proposed. For the first time we report the preparation and characterization of novel metal phthalocyanines with two 2-dimethylaminoethylsulfanyl and two dietoxycarbonylmethyl groups on the periphery. These compounds can be converted into quarterized product by reaction with methyl iodide. For this purpose, starting materials (Pcs) have been synthesized. As a result of this synthesis, these materials may be converted to a new structure by means CH_3I which may be soluble in water.

Experimental

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets, electronic spectra on a SHIMADZU UV/Vis spectrophotometer. Elemental analysis results were in good agreement with the calculated values (Table 1). 4-nitrophthalonitrile (Young and Onyebuagu, 1990), Diethyl 3, 4 dicyanophenylmalonate (Roze at all, 1992) and 4-(2-dimethylaminoethylsulfanyl) phthalonitrile (Dabak, 1996) were synthesized according to published procedures.

All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego and the solvents were stored over molecular sieves (4 Å)

Synthesis of metallophthalocyanine (1)

A mixture of compound **ii**(0.143 g, 0.5 mmol) and **i**(0.116, 0.5 mmol) and (0.016 g $CoCl_2$) was fused in a glass tube under N_2 by gentle heating ,cooled and sealed under vacuum. Then the mixture was heated at 160 ºC for 6 h. After it was cooled to room temperature, the tube was opened, and dark green powder was obtained. The resulting solid was washed several times with hot EtOH to dissolve any unreacted metal salt. Further, purification DMF was added in order to dissolve the crude product, which was then precipitated with ether. The dark green product was filtered, washed and dried in vacuum at 100 ºC. The product is soluble in DMF and DMSO. Yield: 0.099 g (36 %). IR(cm-1): 1733,1630,1476,900; UV-Vis(DMF) λmax nm (log ε): 672(5.15),608(4.67), Anal calculated for $C_{54}H_{54}N_{10}S_2O_8Co$: C% 59.28, H% 4.98, N% 12.80, found C%59.04 , H%4.94 , N%12.60.

Synthesis of metallophthalocyanine (2)

A mixture of compound **ii** (0.143 g, 0.5 mmol) and **i**(0.116, 0.5 mmol) and (0.016 g $NiCl_2$) was fused in a glass tube under N_2 by gentle heating ,cooled and sealed under vacuum. Then the mixture was heated at 160 ºC for 6 h. After it was cooled to room temperature, the tube was opened, and dark green powder was obtained. The resulting solid was washed several times with hot EtOH to dissolve any unreacted metal salt. Further, purification $CHCl_3$ was added in order to dissolve the crude product, which was then precipitated with ether. The dark green product was filtered, washed and dried in vacuum at 100 ºC. The product is soluble in $CHCl_3$, DMF and DMSO. Yield: 0.067 g (25 %). IR(cm^{-1}): 1733,1630,1477,958; UV-Vis($CHCl_3$) λmax nm (log ε): 673(5.06),608(4.67), Anal calculated for $C_{54}H_{54}N_{10}S_2O_8Ni$: C% 59.29, H% 4.98, N% 12.80, found C%59.11 , H%5.01 , N%12.69.

Synthesis of metallophthalocyanine (3)

A mixture of compound **ii**(0.143 g, 0.5 mmol) and **i**(0.116, 0.5 mmol) and (0.017 g $ZnCl_2$) was fused in a glass tube under N_2 by gentle heating ,cooled and sealed under vacuum. Then the mixture was heated at 160 ºC for 6 h. After it was cooled to room temperature, the tube was opened, and dark green powder was obtained. The resulting solid was washed several times with hot EtOH to dissolve any unreacted metal salt. Further, purification DMF was added in order to dissolve the crude product, which was then precipitated with ether. The dark green product was filtered, washed and dried in vacuum at 100 ºC. The product is soluble in

$CHCl_3$, DMF and DMSO. Yield: 0.148 g (54 %). IR(cm^{-1}): 1730,1630,1486,554; UV-Vis(DMF) λmax nm (log ε): 684(5.23),618(4.60),363(4.89) Anal calculated for $C_{54}H_{54}N_{10}S_2O_8Zn$: C% 58.93, H% 4.95, N% 12.73, found C%58.87 , H%4.96 , N%12.63

Table 1. Analytical data (found) and calculated for metal-phthalocyanines

Compound	Formula	C (%)	H (%)	N (%)
1	$C_{54}H_{54}N_{10}S_2O_8Co$	59.28 (59.04)	4.98 (4.94)	12.80 (12.60)
2	$C_{54}H_{54}N_{10}S_2O_8Ni$	59.29 (59.11)	4.98 (5.02)	12.80 (12.69)
3	$C_{54}H_{54}N_{10}S_2O_8Zn$	58.93 (58.87)	4.95 (4.96)	12.73 (12.63)

Results and Discussion

For the preparation of unsymmetrical Pcs, a mixed condensation of two different groups, appropriately substituted phthalonitrile in the presence of a metal salt was applied. For this purpose, phthalonitriles were synthesized. It is known that the nitro group in compound is easily substituted by O and N-nucleophiles. In this present study, we have made use of the potential for exchanging the acidic- CH –protons of the diethyl malonate first with the nitro group of 4- nitrophthalonitrile and subsequent nucleophilic displacement of the nitro group with diethyl malonates. The reaction was conducted in solution in anhydrous N, N-dimethylformamide in the presence of potassium carbonate and tetrabutylammoniumtetrafluoroborat as phase transfer catalyst.

On the other hand 4-(2 dimethylaminoethylsulfanyl) phthalonitrile was synthesized according to published procedure (Dabak,1996). After the desired **i** and **ii** had been obtained phthalonitrle derivatives, cyclotetramerization of **i** and **ii** to the phthalocyanines structure was accomplished by reaction with anhydrous salts in fused state.**1-3** compounds were prepared under the same conditions(Fig.1). Spectral data on the newly synthesized intermediates and phthalocyanines are consistent with proposed structures. For example, in compound **i** we observed C≡N at 2238 cm^{-1}, C=O at 1730-1733, 1630 cm^{-1},C-O aster at 1294 cm^{-1}, C aromatic O-C at (1243-1217)cm^{-1},C-O-C at (1190-1115)cm^{-1} and in compound **ii** 4-(2-dimethylaminoethylsulfanyl) phthalonitrile CH_3,CH_2 at (2880-2800)cm^{-1}, C≡N at 2240cm^{-1}. In the case of Mpc, IR spectroscopy can be used only to identify the substituents on the periphery of each PC core; here the characteristic stretching vibrations attributable to C=O, C=C and C-H groups are observed at 1730, 1630 and 1476-1486 cm^{-1} respectively. The IR spectra of MPc (M=Co, Ni, Zn) were similar, and the C≡N at 2238 cm -1 had disappeared in each case.

The new metallo phthalocyanines show typical electronic spectra, with strong absorption regions, at 300-350 nm (B band) and the second at 650-700 nm (Q band). The absorption spectra of **3** in DMF are shown in Fig.2. The spectra showed typical of metallated phthalocyanine with absorption bands at 363, 618and 684 nm. Other phthalocyanines **1-2** have also electronic spectra similar to **3** with absorption bands at 672 and 673 nm respectively. These results agree with the familiar characteristics of electronic spectra of soluble substituted metal phthalocyanines. These new compounds were synthesized by a good yield. The reactions were carried out without using solvent. In this way, purification of product has become easy

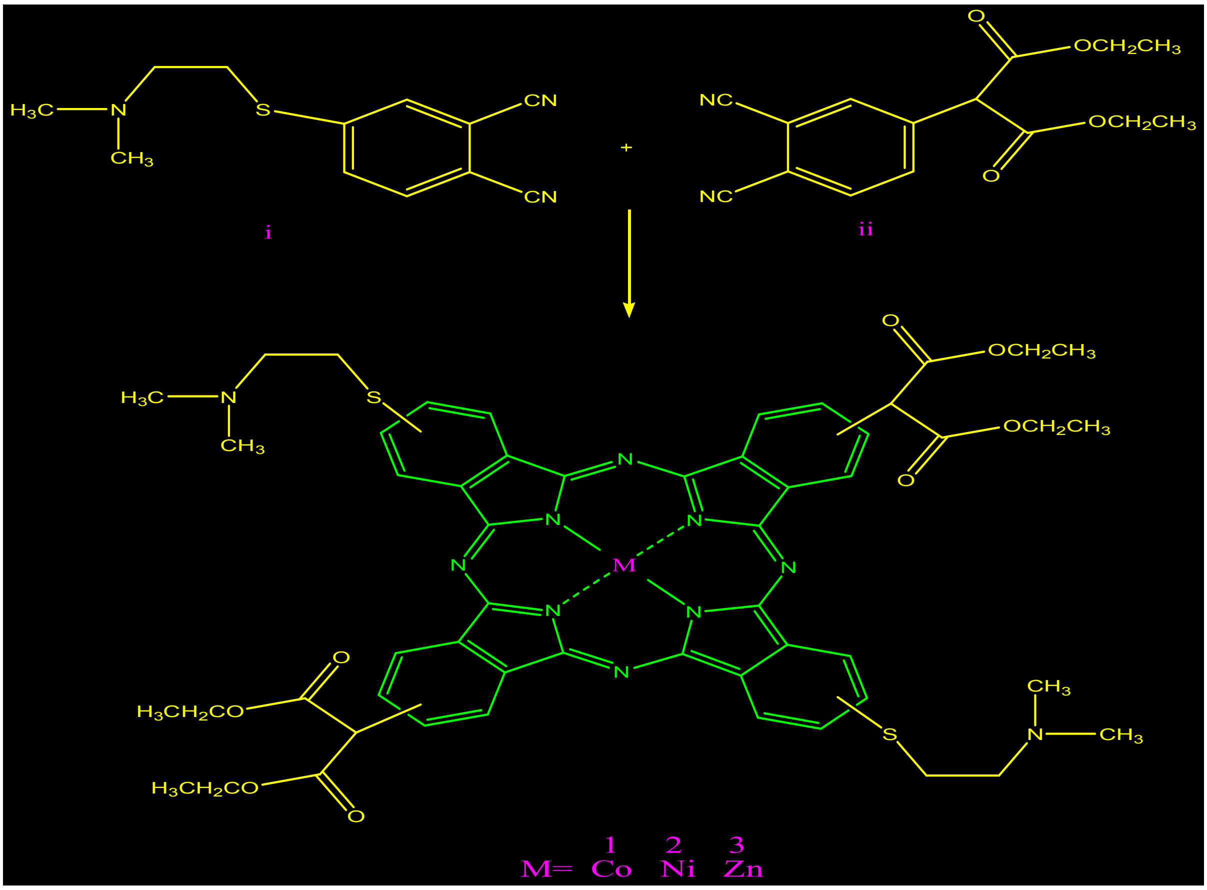

Fig.1. Synthesis of metallophthalocyanines

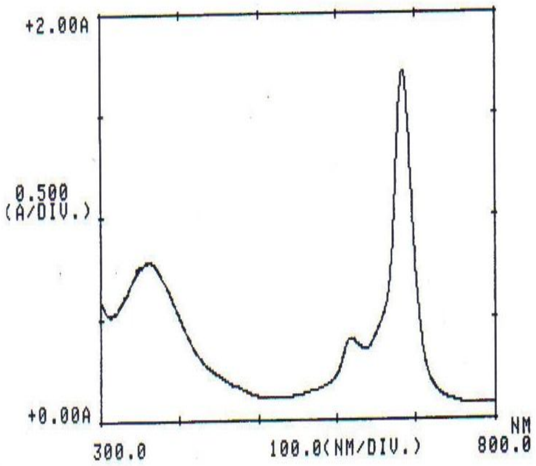

Fig.2. UV/Vis spectra of **3** in DMF

Conclusion

These synthesized compounds have got active groups such as –CH in the dietoxycarbonylmethyl and dimethylaminoethylsulf anyl which can turn into ionic structure. The design of a Pc derivative with optimal, pharmacokinetic and photodynamic properties largely depends on understanding the structure activity relationships of this class of compounds. This study indicates that these compounds may be important for studying the effect of structural modifications on biological activities of this class of photosentensitiezers.

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