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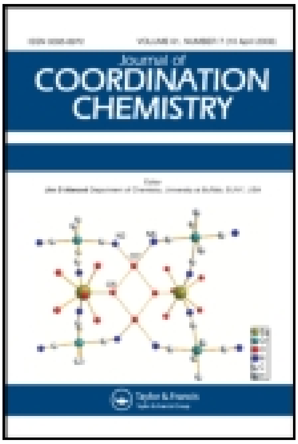

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Sıbel Eken Korkut [a] , Ulvı Avciata [a] & M. Kasim Şener [a]
[a] Department of Chemistry , Yildiz Technical University , 34210, Davutpaşa, İstanbul, Turkey

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Synthesis of non-peripherally substituted tetra(dihexylmalonate) alcohol soluble phthalocyanines

SİBEL EKEN KORKUT, ULVİ AVCIATA and M. KASIM ŞENER*

Department of Chemistry, Yildiz Technical University, 34210, Davutpaşa, İstanbul, Turkey

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Dimethyl-(2,3-dicyanophenyl)malonate was prepared by the reaction of dimethylmalonate and 3-nitrophthalonitrile. A cyclotetramerization reaction of dimethyl-(2,3-dicyanophenyl)malonate with the corresponding divalent metal salt was achieved in hexanol in the presence of DBU, affording the non-peripherally substituted tetra(dihexylmalonate) Cu(II), Pd(II), and Co(II) phthalocyanines. Transesterification occurred under these reaction conditions, so that methyls in the phthalonitrile derivative were converted into hexyl groups during phthalocyanine formation in hexanol. The new compounds were characterized by elemental analyses, FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and mass spectral data.

Keywords: Phthalocyanine; Phthalonitrile; Palladium; Transesterification; Copper

1. Introduction

Phthalocyanines (Pc) and their metal complexes (MPc) have been found to be highly promising candidates for dyes [1], liquid crystals [2], gas sensors [3], catalysts [4], photosensitizers [5], semiconductor materials [6], and dye-sensitized solar cells [7, 8]. Applications of unsubstituted phthalocyanines are limited due to their insolubility in common organic solvents and water. Phthalocyanines possess an extended π-conjugated electron system which permits π stacking (aggregation) between planar macrocycles, provided the distance between the macrocycles is small. Adding substituents to the periphery or non-periphery of the macrocycles increases their solubility since these substituents increase the distance between the stacked phthalocyanines and enable their solvation [9–11].

Peripheral substitution with long alkyl, alkoxy, or alkylthio chains [12] leads to phthalocyanine products soluble in apolar solvents; on the contrary, carboxy or quaternary ammonium groups enhance solubility in a wide pH range of aqueous solutions [13–16]. The size and the nature of the substituents is not the only criterion for the solubility of the substituted phthalocyanines; the change in symmetry caused by these moieties on periphery or non-periphery is also important. Generally, tetrasubstituted phthalocyanines are more soluble than symmetrically octasubstituted ones due to the formation of four positional isomers in the case of tetrasubstituted

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*Corresponding author. Email: mkasimsener@gmail.com

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analogs [17, 18]. Thus, a mixture of similar positional isomers may be preferred to a single less-soluble isomer [19].

Ester functionalities have often been added on the periphery of phthalocyanines to improve their solubility and to obtain phthalocyanines containing carboxylic acid moieties [20–26]. For example, Neilands and co-workers [27] showed for the first time that the acidic nature of the CH_2 group among two esters in dialkylmalonates can be used to displace nitro of 4-nitrophthalonitrile to obtain dialkyl-(3,4-dicyanophenyl)-malonates. Also, Koçak and co-workers [13] made use of the potential for exchanging the acidic –CH– protons of diethylmalonate with one of the chloro-groups in 4,5-dichlorophthalonitrile. These synthetic methods have been used by us and many other groups to obtain precursors of the functional phthalocyanines [7, 8, 28–40]; the most important was Nazeeruddin's [7] work which represented a breakthrough in the design and development of phthalocyanine-based sensitizers. Additionally, 1(4),8(11),15(18),22(25)-tetrasubstituted (non-peripheral position) phthalocyanines are obtained from 3-substituted phthalonitriles. For this purpose, 3-nitrophthalonitrile was recently used to prepare 3-monosubstituted phthalonitrile derivatives through base-catalyzed nucleophilic aromatic displacement [18]. In this work, we show for the first time that the reaction of acidic –CH– containing compounds with 3-nitrophthalonitrile can be used to prepare 3-monosubstituted phthalonitrile precursors. Also, we have described the synthesis of non-peripherally tetra(dihexylmalonate) substituted Cu(II), Pd(II), and Co(II) phthalocyanines. The most obvious feature of the newly synthesized metallophthalocyanines is their high solubility in common organic solvents, for example, ethanol, methanol, chloroform, dichloromethane, acetone, and tetrahydrofuran.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on an Agilent 8453 UV-Vis spectrophotometer. Elemental analyses were performed on a Thermo Flash EA 1112. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer using TMS as an internal reference. Mass spectra were measured on a Bruker Microflex LT MALDI-TOF MS and Micro TOF ESI-MS. Melting point was determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were of reagent grade obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2).

2.1. *Synthesis of dimethyl-(2,3-dicyanophenyl)malonate (1)*

About 1.5 g of 3-nitrophthalonitrile (7.5 mmol) was dissolved in 20 mL of dry DMF at 50°C under Ar and 0.2 g (0.86 mmol) of tetrabutyl ammonium tetrafluoroborate and 1.8 g finely ground anhydrous K_2CO_3 (13 mmol) were added. After stirring for 15 min, 1.25 mL of dimethlymalonate was added. The reaction mixture was stirred under Ar at 50°C for 25 h. Then the mixture was poured into 150 mL of ice-water. The resulting solid was collected by filtration and washed with water until the washings were neutral.

The crude product was crystallized from 70% solution of ethanol in water. The compound was soluble in chloroform, ethanol, tetrahydrofuran, and acetone. Yield: 0.66 g, 30%. m.p.: 120–123°C. FT-IR (ATR): ν_{max}, cm^{-1} 2958 (CH, aliphatic), 3085–3030 (CH, aromatic), 2233 (C≡N), 1758, 1743 (C=O), 1197–1145 (C–O–C). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ, ppm 8.05–8.03 (m, aromatic Hb), 7.86–7.78 (m, aromatic Ha, Hc), 5.21 (s, CH), 3.84 (s, CH_3). ^{13}C-NMR (400 MHz, $CDCl_3$, 298 K): δ, ppm 166.49 (C=O), 138.06 (aromatic C), 134.47 (aromatic C), 133.26 (aromatic C), 133.19 (aromatic C), 116.87 ($\underline{C}$–CN), 116.66 ($\underline{C}$–CN), 115.26 ($\underline{C}$N), 113.95 ($\underline{C}$N), 55.08 ($\underline{C}H_3$), 53.67 ($\underline{C}$H). MS (ESI+): m/z 281.03 $[M+Na]^+$. $C_{13}H_{10}N_2O_4$ (258.06): Calcd (%) C 60.47, H 3.90, N 10.85; Found (%) C 60.43, H 3.86, N 10.83.

2.2. *General procedure for metallophthalocyanines (2–4)*

A mixture of **1** (0.1 g, 0.38 mmol) and anhydrous metal salt (0.0097 mmol (0.013 g $CuCl_2$, 0.017 g $PdCl_2$, 0.013 g $CoCl_2$)) and a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in *n*-hexanol (2 mL) was fused in a glass tube. The mixture was heated to 160°C and stirred for 24 h in an oil bath. The reaction mixture was cooled to room temperature. After evaporation of solvent, **2** was chromatographed on silica gel and eluted first with dichloromethane and then with tetrahydrofuran : hexane (1 : 1). Compounds **3** and **4** were chromatographed on silica gel and eluted first with tetrahydrofuran and then with chloroform : tetrahydrofuran (10 : 1).

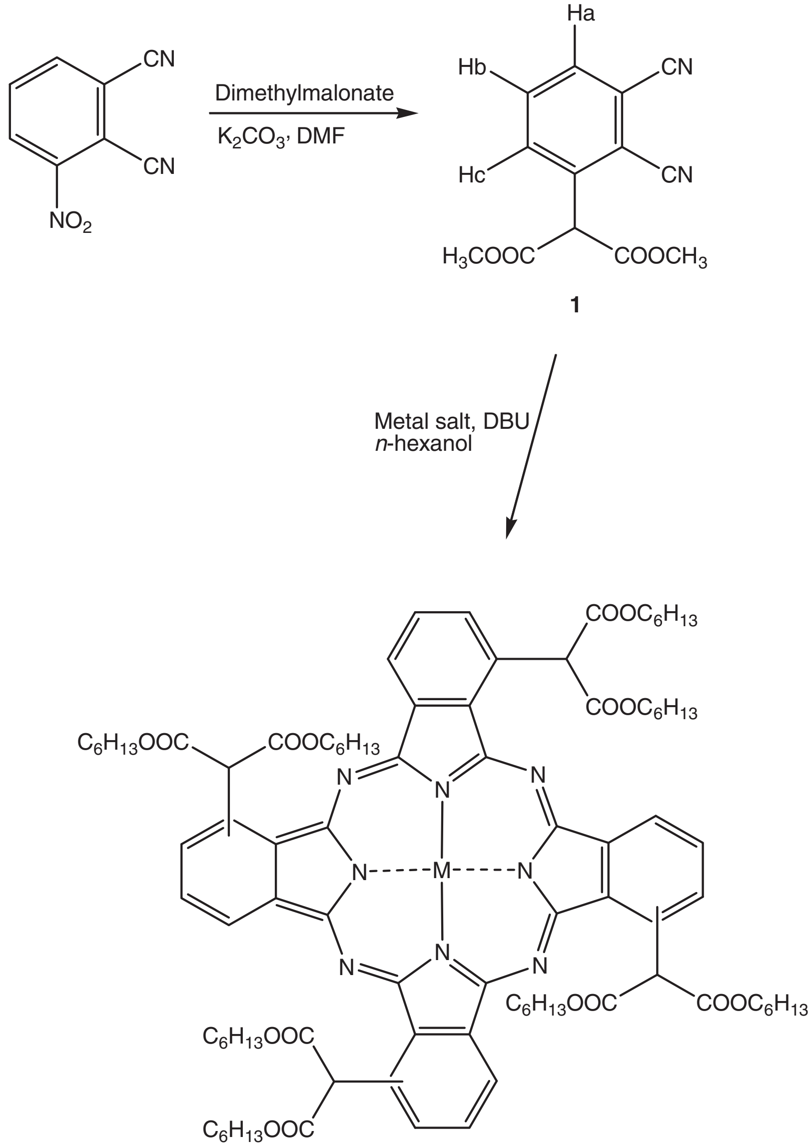
2.2.1. 1,(4)-Tetrakis[dihexoxymalonyl]-phthalocyaninatocopper(II) (2). Yield: 0.030 g, 25%. FT-IR (ATR): ν_{max}, cm^{-1} 2954–2853 (CH, aliphatic), 1731 (C=O), 1116–1094 (C–O–C). UV-Vis (chloroform): λ_{max}/nm (10^{-5} ε/l mol^{-1} cm^{-1}) 683 (4.96), 341 (4.54). MS (MALDI+, α-cyano-4-hydroxycinnamic acid): m/z 1719.21 $[M+Na+K]^+$. $C_{92}H_{120}N_8O_{16}Cu$ (1657.53): Calcd (%) C 66.66, H 7.30, N 6.76; Found (%) C 66.71, H 7.36, N 6.68.

2.2.2. 1,(4)-Tetrakis[dihexoxymalonyl]-phthalocyaninatopalladium(II) (3). Yield: 0.016 g, 13%. FT-IR (ATR): ν_{max}, cm^{-1} 2955–2856 (CH, aliphatic), 1733 (C=O), 1159 (C–O–C). UV-Vis (chloroform): λ_{max}/nm (10^{-5} ε/l mol^{-1} cm^{-1}) 663 (5.04), 332 (4.47). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ, ppm 8.30–6.98 (aromatic H), 5.29 (CH), 4.41–3.32 (CH_2), 2.31–0.60 (CH_2 and CH_3). MS (MALDI+, α-cyano-4-hydroxycinnamic acid): m/z 1699.85 $[M]^+$. $C_{92}H_{120}N_8O_{16}Pd$ (1700): Calcd (%) C 64.98, H 7.11, N 6.59; Found (%) C 65.01, H 7.12, N 6.56.

2.2.3. 1,(4)-Tetrakis[dihexoxymalonyl]-phthalocyaninatocobalt(II) (4). Yield: 0.046 g, 39%. FT-IR (ATR): ν_{max}, cm^{-1} 2954–2855 (CH, aliphatic), 1731 (C=O), 1122–1096 (C–O–C). UV-Vis (chloroform): λ_{max}/nm (10^{-5} ε/l mol^{-1} cm^{-1}) 671 (4.69), 331 (4.35). $C_{92}H_{120}N_8O_{16}Co$ (1652.91): Calcd (%) C 66.85, H 7.32, N 6.78; Found (%) C 66.88, H 7.34, N 6.81.

3. Results and discussion

The synthetic route followed is shown in scheme 1. We have made use of the potential for exchanging acidic –CH– protons of dimethyl malonate with the nitro group of 3-nitrophthalonitrile [13, 27]. For this purpose, 3-nitrophthalonitrile was treated with malonic acid dimethyl ester in the presence of K_2CO_3 in anhydrous DMF. In order to



M: Cu(II) (**2**), Pd(II) (**3**), Co(II) (**4**)

Scheme 1. Preparation of metallophthalocyanines **2**–**4**.

preserve dimethylester functionality after phthalocyanine formation, the reaction was done without using solvent. However, all efforts to accomplish this reaction failed. The conversion of phthalonitrile derivative (**1**) into metallophthalocyanines was accomplished in *n*-hexanol in the presence of DBU. The basicity of DBU was sufficient to carry out transesterification, so that methyl groups in the precursor (**1**) were converted into hexyl groups during phthalocyanine formation in hexanol [41]. The blue products were isolated by column chromatography on silica gel. As a natural consequence of the single substituent on each benzo group, the phthalocyanines are all a mixture of four constitutional isomers. In this study, mixture of isomers of the complexes may have been formed during synthesis, but no attempt was made to separate them. The new metallophthalocyanines are highly soluble in common organic solvents, for example, ethanol, methanol, chloroform, dichloromethane, acetone, and tetrahydrofuran.

The structures of the compounds were confirmed by elemental analysis together with FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and MS spectroscopic techniques. In **1**, stretching vibrations of C≡N (2233 cm^{-1}), C=O (1758 and 1743 cm^{-1}), and COC (1197–1145 cm^{-1}) appeared at expected frequencies; aliphatic CH stretching vibrations are observed at 2958 cm^{-1} and aromatic CH stretching vibrations at 3085–3030 cm^{-1}. After conversion of the dinitrile derivative (**1**) into the phthalocyanines (**2–4**), the sharp peak for the C≡N vibration around 2233 cm^{-1} disappeared. IR spectra of the metallophthalocyanines clearly prove the presence of the long alkyl chain by the intense absorption peak for aliphatic group at 2900 cm^{-1} (figure 1) [42].

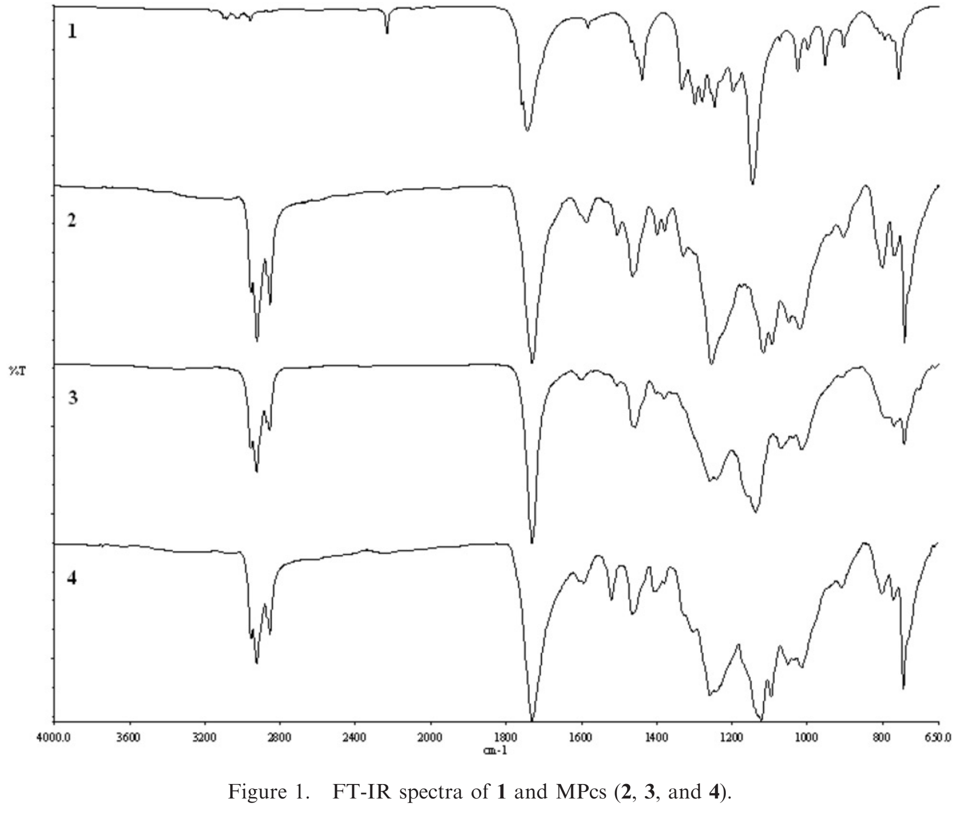


Figure 1. FT-IR spectra of **1** and MPcs (**2**, **3**, and **4**).

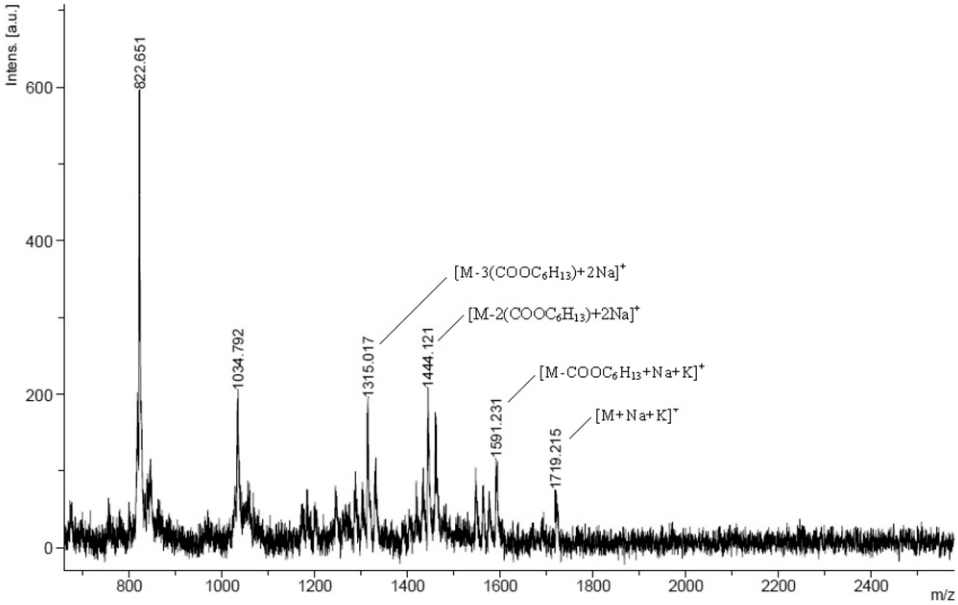


Figure 2. MALDI-MS spectrum of **2** in α-cyano-4-hydroxycinnamic acid MALDI matrix.

The ^{1}H-NMR spectrum of **1** exhibited aromatic protons, integrating for a total of three, at 8.05–8.03 and 7.86–7.78 ppm. Also, CH and CH_3 protons of **1** were observed as singlets at 5.21 and 3.84 ppm which integrated for seven protons. ^{13}C-NMR data of **1** confirm the result of the ^{1}H-NMR spectrum. In the ESI-MS spectrum of **1**, we observed the $[M + Na]^+$ peak at m/z 281.03 amu. ^{1}H-NMR investigation of **3** provided the characteristic chemical shifts for the structure expected. The ^{1}H-NMR spectrum of **3** is somewhat broader than the corresponding signals in the dinitrile derivative **1**. Tetrasubstituted phthalocyanines obtained from 4-substituted phthalonitriles are a mixture of isomers, which is a primary reason for the broadness of the peaks. The mass spectra of **2** and **3** were obtained by MALDI technique. MALDI TOF mass spectrum of **2**, in addition to the $[M + Na + K]^+$ peak at 1719.21, fragment ions such as $[M\text{-}COOC_6H_{13} + Na + K]^+$ at 1591.23, $[M\text{-}2(COOC_6H_{13}) + 2Na]^+$ at 1444.12, $[M\text{-}3(COOC_6H_{13}) + 2Na]^+$ at 1315.01, were easily identified. In the case of **3**, we observed an $[M]^+$ peak at 1699.85 and the other ions such as $[M\text{-}COOC_6H_{13}\text{+}3H]^+$ at 1573.44, $[M\text{-}2(COOC_6H_{13}) + 2H]^+$ at 1443.12, $[M\text{-}3(COOC_6H_{13}) + 4H]^+$ at 1316.96 (figures 2 and 3) [38, 43, 44].

Electronic spectra are especially useful to establish the structure of the phthalocyanines **2**–**4**. The UV-Vis spectrum of phthalocyanine core is dominated by two intense bands, the Q band around 680 nm and the B band in the near UV region around 330 nm, both correlated with π–π* transitions. UV-Vis spectra of all metallophthalocyanines **2**–**4** in chloroform exhibit intense Q bands around 663–683 nm and the B bands in the near UV region, around 331–341 nm, both correlated with π–π* transitions (figure 4).

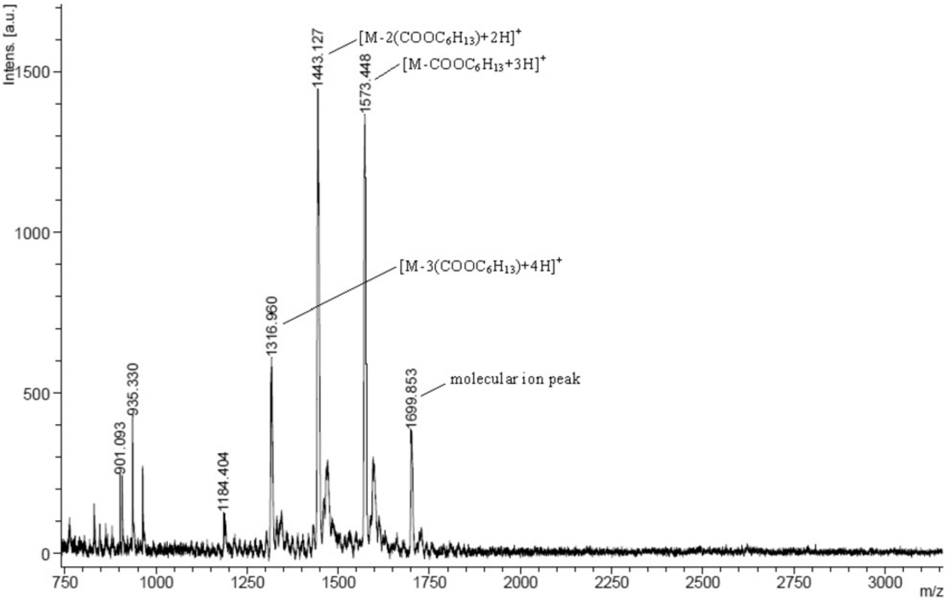


Figure 3. MALDI-MS spectrum of **3** in α-cyano-4-hydroxycinnamic acid MALDI matrix.

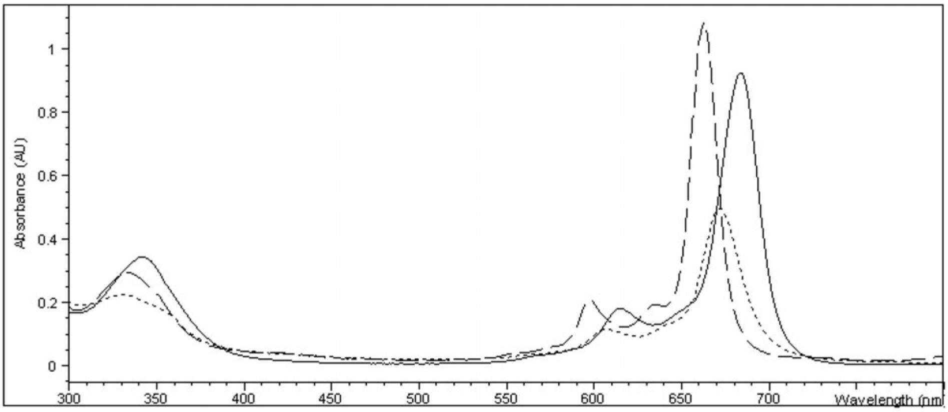


Figure 4. UV-Vis spectra of metallophthalocyanines **2** (—), **3** (- - -), and **4** (· · ·).

4. Conclusion

We have shown that the reaction of acidic –CH– containing compound with 3-nitrophthalonitrile can be used to prepare 3-monosubstituted phthalonitrile precursors and described the synthesis and the spectral characterization of non-peripherally substituted tetra(dihexylmalonate) Cu(II), Pd(II), and Co(II) phthalocyanines. Transesterification is inevitable when the cyclotetramerization reaction is carried out in high-boiling alcohol (e.g., pentanol or hexanol), so that methyl in the phthalonitrile derivative **1** convert into hexyl groups during phthalocyanine formation in hexanol. The most obvious feature of the newly synthesized metallophthalocyanines is their high solubility in common organic solvents, for example, ethanol, methanol, chloroform, dichloromethane, acetone, and tetrahydrofuran. Further studies on the synthesis of potassium salt of dimethyl-(2,3-dicyanophenyl)malonate and hydrolyzed phthalocyanine derivative of **2–4** are currently in progress.

Acknowledgments

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