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Enhancement of solubility via esterification: Synthesis and characterization of octakis (ester)-substituted phthalocyanines

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Abstract

Metal-free and metallophthalocyanines (M = Zn, Ni and ClFe) carrying eight hydroxyethylsulfanyl groups at peripheral positions were prepared from 4,5-bis(hydroxyethylsulfanyl)phthalonitrile. The reactivity of the hydroxyethyl groups was demonstrated by esterification of phthalocyanine derivatives with pyridine-4-carboxylic acid and also ferrocenecarboxylic acid in the presence of dicyclohexylcarbodiimide combined with *N*,*N*-dimethylaminopyridine or *p*-toluenesulfonic acid and acetic anhydride. Unlike the parent phthalocyanines, the symmetrically functionalized phthalocyanines with eight ester units were soluble in common organic solvents such as $CHCl_3$, THF, pyridine and DMF, sparingly soluble in ethanol and acetone and insoluble in water and hexane. The newly synthesized compounds were characterized by elemental analysis, IR, UV–vis, FAB-MS and ^1H NMR spectroscopy.

Keywords: Phthalocyanine; Esterification; Ferrocenecarboxylic acid; Pyridinecarboxylic acid; Zinc

1. Introduction

Among tetrapyrrole compounds, phthalocyanines which are full-aromatic planar molecules due to their 18-π electron structure are not only capable of undergoing classical displacement reactions, but they can also be substituted with a great deal of functional groups. In addition to their extensive use as dyes and pigments, this versatility provides many applications, such as liquid crystals, catalysts, electrochromic and photochromic substances, data storage systems, photodynamic cancer therapy agents, photoactive units, chemical sensors, and nonlinear optical devices [1–3].

Solubility is a key feature for phthalocyanines and most of their behaviors are best investigated in soluble form. Because parent unsubstituted metal-free and metallophthalocyanines and most of the metal polymeric phthalocyanines are insoluble in common organic solvents, the synthesis of new phthalocyanine systems should be essentially designed in such a way so that the final phthalocyanine derivatives are sufficiently soluble to perform the desired activities. A common means for preparing soluble phthalocyanines is to attach functional groups like tertiary butyl or hexyl groups, amide groups, carboxylic acid and sulfonic acid groups [1–16], bulky and crown ether groups [17–23], azo groups [24], *etc*. at the peripheral and axial positions of phthalocyanine ring. Compared to unsubstituted parent metal phthalocyanines, ester-containing porphyrazines and phthalocyanines are highly soluble in chlorinated hydrocarbons [25–28].

A further step for phthalocyanine esters is the possibility to form supramolecular structures with donor groups on the ester moiety. For instance, pyridyl-containing esters can coordinate metal ions with their nitrogen [29]. Another potential feature is to quaternize the terminal group, which is useful in providing an additional aqueous solubility [30].

The applications of ester-containing phthalocyanines are very variable. For example, some esters [31] showed gas-sensor response against NO_x gases, whereas some showed characteristics of liquid crystals with glassy transitions [23,32]. Furthermore, some patents and publications reported

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that ester-containing phthalocyanines could be used as electrophotographic photoconductors [33], photosensitizer in photodynamic therapy [34,35], optical storage agent [36], and tumor growth suppressor [37].

In our study, the reactivity of hydroxyethysulfanyl groups of some phthalocyanines, which are either novel (compound (**5**)) or synthesized before (compounds (**1–4**)) [38] has been demonstrated by the esterification with different carboxylate groups such as pyridinecarboxylic acid, ferrocenecarboxylic acid and acetic anhydride. Pyridine-containing ester (**6**) might be useful in a supramolecular arrangement through its pyridine nitrogens. The ferrocenecarboxylic acid esters (**7**,**8**) formed soluble multinuclear compounds with eight iron atoms at the periphery and metal ions (iron or zinc) at the core. They are highly soluble redox-active compounds; therefore, they might be used in catalytic applications. Acetyl ester (**9**) can be considered as an example of hydroxy group protection and solubilization via acetylation.

2. Experimental

All reactions were carried out under nitrogen atmosphere in dried solvents. All chemicals used were of sufficient chemical purity. Ferrocenecarboxylic acid, pyridine-4-carboxylic acid, *N*,*N*-dicyclohexylcarbodiimide (dcc), 4-(*N*,*N*-dimethylamino)pyridine (dmap), *N*,*N*-dimethylformamide, and dichloromethane were purchased from Fluka, whereas pyridine, quinoline, *p*-toluenesulfonic acid, sodium sulfate, sodium carbonate, and iron(III)chloride were provided by Merck. Technical grade acetic anhydride was used after redistillation. Silica gel 60 (63–200 μm, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed using Merck 60 F_{254} silica gel (precoated sheets, 0.2 mm thick).

UV measurements were done with Unicam UV2–100 spectrophotometer. A Perkin–Elmer ATR Fourier transform infrared spectrometer was used for IR data collection. ^{1}H NMR spectra were recorded with a Bruker 200 MHz FT-NMR spectrometer. All mass spectra were obtained as ES^+ with FAB technique, and processed with a Hewlett-Packard HP-1100 LC/MS.

*2.1. Chloro-2,3,9,10,16,17,23,24-octakis (hydroxyethylsulfanyl)phthalocyaninatoiron(III) (**5**)*

This compound was prepared from the ligand (**1**) (0.200 g, 0.71 mmol), anhydrous iron(III)chloride (0.030 mg, 0.18 mmol) and quinoline (0.5 mL) by heating the reaction medium at 160 °C for 24 h. After cooling to room temperature, the solution was precipitated with ethanol. The precipitate was taken into 0.5 L of 20% hydrochloric acid solution to remove quinoline, filtered, washed with water until pH was neutral, and centrifuged to obtain the crude material. It was refluxed with ethanol until the supernatant is clear. The dark green product (Fig. 1) was washed several times successively with hot chloroform, hot methanol and then with diethyl ether. Yield: 0.330 g (38%); mp: >200 °C. Anal. Calcd. for $C_{48}H_{48}ClFeN_8O_8S_8$, C: 47.54, H: 3.99, N: 9.24. Found: C: 47.77, H: 4.01, N: 9.21.

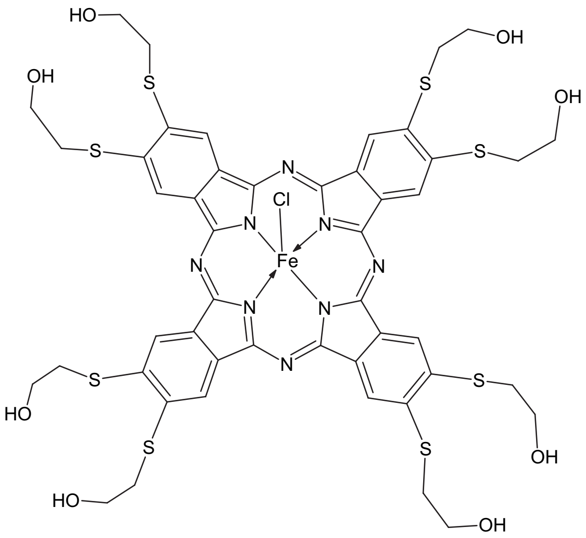

Fig. 1. Formula of (**5**).

*2.2. 2,3,9,10,16,17,23,24-Octakis [(4′-pyridylcarboxy)ethylsulfanyl]phthalocyanine (**6**)*

The compound was prepared from metal-free phthalocyanine (**2**) (0.250 g, 0.22 mmol), dicyclohexylcarbodiimide (1.102 g, 5.34 mmol), *p*-toluenesulfonic acid (0.038 g, 0.22 mmol), pyridine-4-carboxylic acid (0.657 g, 5.34 mmol) in dry pyridine (40 mL), by stirring in a flask at room temperature for 7 days. The contents were filtered and the filtrate was evaporated to dryness. The residue was treated with CH_2Cl_2 (50 mL) and the clear solution was extracted with 50 mL of 5% Na_2CO_3 solution. The extraction was repeated for several times with water until pH was neutral. The product (Fig. 2)

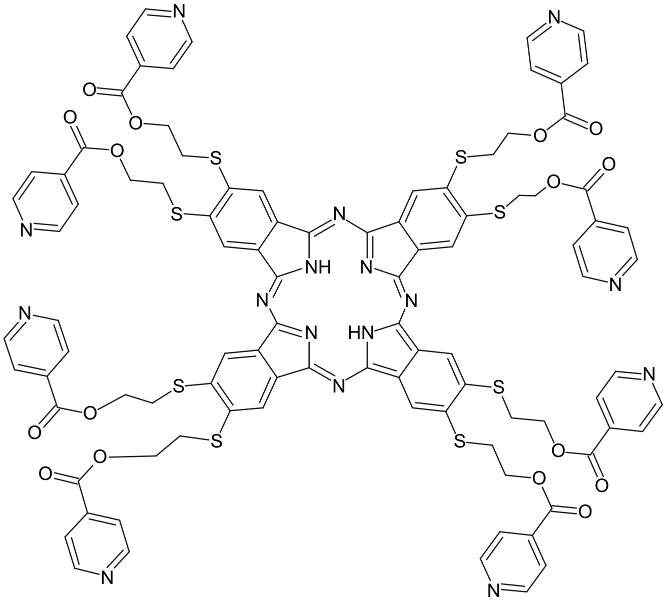

Fig. 2. Formula of (**6**).

was dried with anhydrous Na_2SO_4, filtered, and applied to column chromatography (SiO_2, CH_2Cl_2: THF, 10:1 v/v). Yield: 0.066 g (15%); mp: >200 °C. Anal. Calcd. for $C_{96}H_{74}N_{16}O_{16}S_8$, C: 58.70, H: 3.80, N: 11.41. Found: C: 59.00, H: 3.81, N: 11.36; FAB-MS (*m/z*), 1964.24. Found: 1966.57 $[M+2^+]$.

*2.3. 2,3,9,10,16,17,23,24-Octakis (ferrocenecarboxyethylsulfanyl)phthalocyaninatozinc (II) (**7**)*

Ferrocenecarboxylic acid (1.218 g, 5.29 mmol) and 0.250 g (0.21 mmol) of (**3**) were suspended in dry pyridine (40 mL). To the mixture were added 1.091 g of dicyclohexylcarbodiimide (5.29 mmol) and 0.036 g of *p*-toluenesulfonic acid (0.21 mmol), and the contents were stirred at room temperature for 7 days. The contents were filtered and the filtrate was evaporated to dryness. The residue was treated with CH_2Cl_2 (50 mL) and the clear solution was extracted with 50 mL of 5% Na_2CO_3 solution. The extraction was repeated for several times with water, until pH was neutral. The product (Fig. 3) was dried with anhydrous Na_2SO_4, filtered, and applied to column chromatography (SiO_2, CH_2Cl_2: THF, 10:1 v/v). Yield: 60 mg (10%); mp: >200 °C. Anal. Calcd. for $C_{136}H_{112}FeN_8O_{16}S_8Zn$, C: 56.66, H: 3.92, N: 3.89. Found: C: 56.95, H: 3.94, N: 3.70; FAB-MS (*m/z*), 2883.07. Found: 2883.20 $[M^+]$.

*2.4. Chloro-2,3,9,10,16,17,23,24-octakis (ferrocenecarboxyethylsulfanyl)phthalocyaninato iron(III) (**8**)*

Compound (**5**) (0.200 g, 0.16 mmol) was treated with dicyclohexylcarbodiimide (0.300 g, 1.44 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.180 g, 1.44 mmol), and ferrocenecarboxylic acid (0.340 g, 1.44 mmol) in dry DMF (5 mL). The mixture was stirred at room temperature for 48 h, and dissolved in CH_2Cl_2, centrifuged, and the solution (Fig. 3) was subjected to column chromatography (SiO_2, elution: MeOH, hexane, and THF, respectively). Yield: 0.120 g (25%); mp: >200 °C. Anal. Calcd. for $C_{136}H_{112}ClFe_9N_8O_{16}S_8$, C: 56.15, H: 3.88, N: 3.85. Found: C: 56.42, H: 3.90, N: 3.66.

*2.5. 2,3,9,10,16,17,23,24-Octakis [(acetoxy)ethylsulfanyl]phthalocyaninato nickel (II) (**9**)*

Compound (**4**) (0.250 g, 0.21 mmol) was refluxed in acetic anhydride (5 mL) at 150 °C for 48 h. A clear green solution was obtained, and it was poured onto 0.5 L of water–ice mixture, filtered and washed with water to reach a neutral pH value. The dark green precipitate (Fig. 4) was dissolved in dichloromethane, dried over anhydrous sodium sulfate and the clear solution was applied to column chromatography (SiO_2, CH_2Cl_2: DMF, 20:1, v/v). Yield: 0.113 g (35%); mp: >200 °C. Anal. Calcd. for $C_{64}H_{64}N_8NiO_{16}S_8$, C: 50.69, H: 4.25, N: 7.39. Found: C: 50.95, H: 4.27, N: 7.03; FAB-MS (*m/z*), 1516.45. Found: 1515.99 $[M^+]$.

3. Results and discussion

A common route for obtaining octasubstituted alkoxy/alkylsulfanyl phthalonitriles is to react 4,5-dichlorophthalonitrile with corresponding hydroxy/thiol compound in the presence of Na_2CO_3 or K_2CO_3 as the base, with DMF or DMSO as the solvent [35,38,39]. In this reaction, a base-catalyzed displacement of chloro group with deprotonated nucleophile occurs with moderate to high yields. It is generally observed that a temperature of 50 °C is sufficient in the conversion.

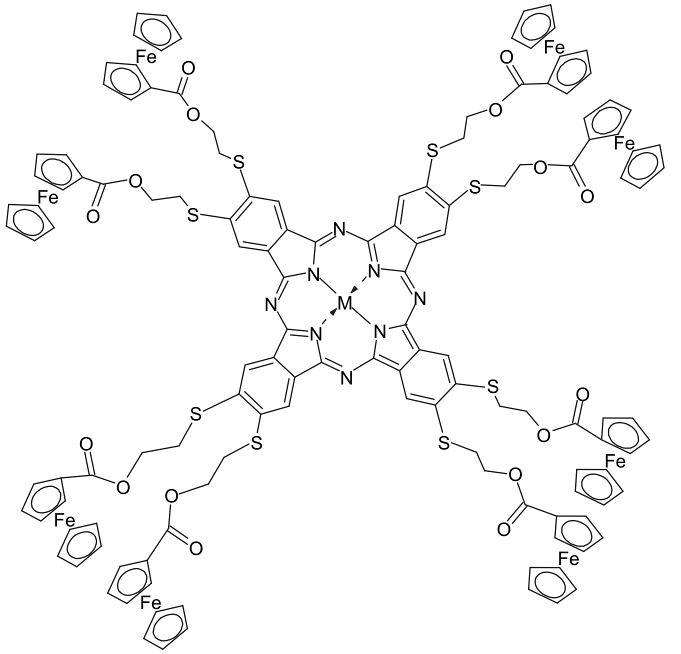

Fig. 3. Formula of (**7**) and (**8**) (M = Zn for (**7**) and ClFe for (**8**)).

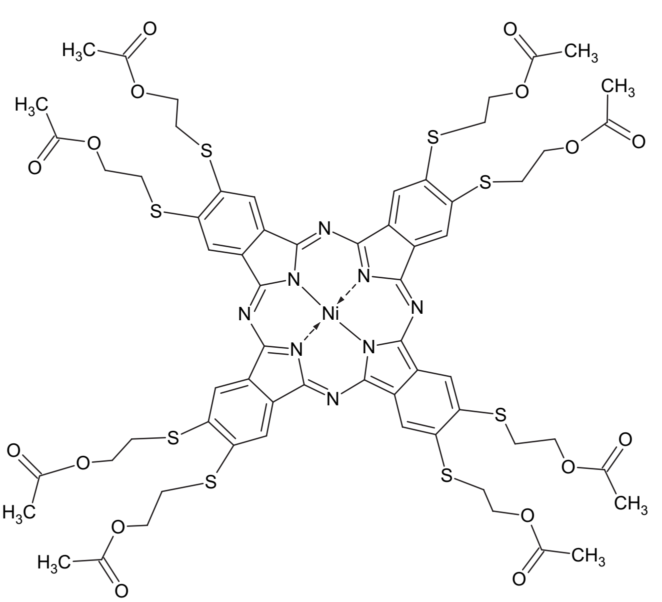

Fig. 4. Formula of (**9**).

The hydroxyethyl substituents on the phthalocyanine core bring out a vast number of possibilities for binding with carboxylic acids, anhydrides or acid chlorides. In our study, we have managed to obtain pyridine- (Fig. 2), ferrocene- (Fig. 3) and acetyl-terminated (Fig. 4) phthalocyanine esters.

Phthalocyanines are obtained by cyclotetramerization of the corresponding phthalonitriles in a high-boiling solvent like quinoline or *n*-hexanol at high temperatures [1–3]. In normal conditions, phthalocyanine core has −2 charge, so divalent metal ions give neutral phthalocyanine complexes. A trivalent metal ion like iron(III) will also give neutral products with involvement of its counter anion, as in the examples of iodoiron(III) phthalocyanine and chloroiron(III) phthalocyanine [1–3,40,41].

The aim of esterification, as explained above, is to enhance the overall solubility in common organic solvents. The parent hydroxy-terminated phthalocyanines [38] are not practically soluble in solvents like chloroform or tetrahydrofuran; therefore, in order to be used more efficiently in some organic transformations or in some technological applications, these compounds must be converted into a more soluble form. Ester groups are known to provide good solubility, and they were selected because of the ease of their synthesis [25–28]. In esterification reactions mediated by dicyclohexylcarbodiimide (dcc), conversion of all alcohol functionalities to ester form has been accomplished; here dimethylaminopyridine (dmap) or *p*-toluenesulfonic acid helps isolation from the acylurea formed. By referring to mass spectrometric data, the usage of dcc-mediated esterification system for octakis(hydroxyethylsulfanyl) phthalocyanines ensured that all of the available OH groups reacted in the process. The choice of reaction time was based on routine TLC tests and changed with different conditions. Another aim of this study was to see different esterification conditions on the reaction yield. Our results show that the best condition was to utilize dcc:dmap:OH group in 9:9:1 molar ratio. Other procedures involved the usage of dcc with *p*-toluenesulfonic acid or dmap and OH group in molar ratios like 32:1:1 and 9:1:1 [22,25,27,29].

Characterization of the products involved a combination of methods including melting point, elemental analysis, ^{1}H NMR, IR, UV–vis and mass spectroscopy. Spectral investigations for all new products were consistent with the assigned structures. Comparison of the IR spectra (Table 1) at each step gave some insights on the nature of the compounds. IR spectra of the parent phthalocyanines prove valuable information, as the CN vibration at *ca.* 2220 cm^{-1} disappears with cyclotetramerization. This peak can be used to monitor the conversion, and to detect any ligand impurities in the macrocycle. Another utility of IR spectra is to see the NH vibrations at around 3290 cm^{-1} in metal-free phthalocyanines. IR spectra are also more important in ester derivatives, because ester C=O vibration at *ca.* 1730 cm^{-1} is a sharp outcome of esterification. Moreover, the presence of excess dcc could be readily detected with IR spectroscopy, by the presence of a peak at 2130–2140 cm^{-1} which is characteristic for R–N=C=N–R groups. The reaction product of dcc is dicyclohexylurea (dcu), which appears as sharp C–H vibrations at 2950 and 2840 cm^{-1} and C=O vibrations at about 1700 cm^{-1}, thus indicating a contamination. It must be noted that phthalocyanines and their esters give very similar IR spectra regardless of the central metal atom, unless they have a special vibrational mode (like Mo=O or V=O) in 400–4000 cm^{-1} range. Esterification of the phthalocyanines was confirmed by the disappearance of the OH vibration. In addition, the characteristic vibrations of C=O and C–O–C belonging to the new ester group were observed.

Table 1
IR data of the compounds (cm^{-1})

Compound	ν(OH/NH)	ν(aryl CH)	ν(alkyl ch)	ν(C=O$_{ester}$)	ν(C–O$_{ester}$)
(**5**)	3277	2920	2880	–	–
(**6**)	3290	2930	2880	1725	1273
(**7**)	–	2930	2860	1693	1226
(**8**)	–	2930	2860	1670	1235
(**9**)	–	2921	2850	1731	1218

Table 2
UV–vis data of the compounds

Compound	Solvent	λ_{max} (nm)	log ε (dm^3 mol^{-1} cm^{-1})
(**5**)	DMF	330	4.89
		657	5.32
(**6**)	CHCl$_3$	271	4.54
		354	3.97
		696	4.86
		726	4.88
(**7**)	CHCl$_3$	309	2.96
		365	3.02
		705	3.85
(**8**)	THF	380	4.13
		690	5.10
(**9**)	CHCl$_3$	317	4.86
		697	4.91

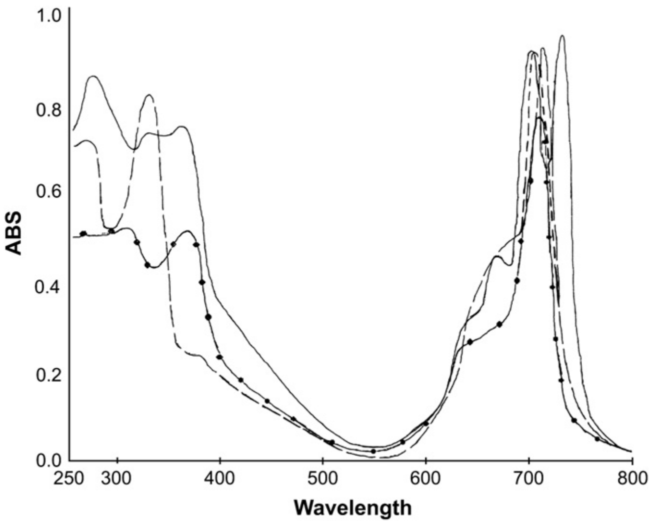

Fig. 5. UV–vis spectra for selected compounds in chloroform (—) (**6**), (-●-) (**7**), (---) (**9**).

Table 3
^{1}H NMR data of the compounds (δ, ppm)

Compound[a]	Substituent CH[b]	Aryl CH (s, 8H)	O–CH$_2$ (t, 16H)	S–CH$_2$ (t, 16H)	Ring NH (s, 2H)
(**6**)	8.61, m, 32H	7.82	4.79	3.71	−5.56
(**7**)	4.82, s, 16H	7.24	4.58	3.77	–
(**9**)	2.07, s, 24H	7.55	4.48	3.45	–

[a] The solvents used were CDCl$_3$ for (**6**) and (**9**) and DMSO-d_6 for (**7**).

[b] The substituents present in the groups were 4-pyridyl (**6**), ferrocenyl (**7**) and acetyl (**9**).

UV spectra of phthalocyanines (Table 2, Fig. 5) show two sharp bands as a result of π–π* transitions of the macrocycle. The one around 300 nm is called the ‘‘B’’ or Soret band, while the one at 600–700 nm is called the ‘‘Q’’ band. These two bands are present in all kinds of phthalocyanines. The Q band splits in metal-free phthalocyanine due to a D_{2h} symmetry [1–3]. However, nickel phthalocyanines show a similar splitting due to their d^8 configuration and their square planar nature [38]. A similar splitting was also seen in our nickel phthalocyanine derivative (**9**). Due to the presence of ferrocenyl groups, a weak broad band around 400–450 nm is present, but often obscured by the phthalocyanine-based transitions and appear as a shoulder [25]. Pyridyl groups increased the intensity of the B band due to their additional π–π* transitions at *ca.* 350 nm [29].

^{1}H NMR spectra of the compounds (Table 3) gave chemical shifts belonging to S–CH$_2$ (triplet), O–CH$_2$ (triplet), phthalocyanine ring protons (singlet) at *ca.* δ 3.7, 4.8 and 7.8 ppm, respectively. Ferrocenyl side groups yielded doublets at δ 4.1–4.4 and δ 4.8 ppm integrating nine protons per moiety. Pyridyl side groups appeared as a multiplet at δ 8.6–8.7 ppm. Protons belonging to the acetyl groups were present as a singlet at around δ 2.1 ppm.

The fast atom bombardment mass spectrometry (FAB-MS) results of pyridyl-substituted metal-free phthalocyanine (**6**), ferrocene-substituted zinc phthalocyanine (**7**) and acetoxyethylsulfanyl-substituted nickel phthalocyanine (**9**) confirmed the complete esterification of OH groups by the presence of molecular ion peaks, at *m*/*z* 1966 [M + 2$^+$], 2883.20 [M$^+$] and 1515.99 [M$^+$], respectively.

As a result, this study shows that a poorly soluble phthalocyanine derivative containing reactive groups can be used as a framework for subsequent reactions such as esterification. We believe that some of the synthesized compounds might be utilized as catalysts, soluble dyes, and optical recording agents.

Acknowledgments

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