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Synthesis and characterization of metal-free and metallophthalocyanines containing N_2S_2-type macrocyclic moieties linked ferrocenyl groups

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Abstract

The new metal-free (**4**) and metallophthalocyanines (**5**) carrying macrocyclic moieties linked ferrocenyl groups have been synthesized by direct cyclotetramerization of the pre-cursor, 12,13-dicyano-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrocyclobenzo[*k*]-4,7-diaza-1,10-dithiacyclododecine (**3**) which has been prepared by the macrocyclization reaction of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**1**) with *N*,*N*′-ethylenebis-(ferroceneylmethyl)amine (**2**), in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong organic base. Nickel (II) phthalocyanine (**5**) was synthesized by the reaction of metal-free phthalocyanine with anhydrous $NiCl_2$ in dry quinoline. The target compound and its intermediates have been characterized by a combination of elemental analysis and ^1H, ^{13}C NMR, IR, UV–Vis and MS spectral data.

Keywords: Phthalocyanine; Mixed-donor macrocycle; Ferrocene; Macrocyclization; Template effect; Nickel (II)

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1. Introduction

Phthalocyanines are 18 π-electron aromatic planar macrocycles constituted by four isoindoline units linked together in the 1,3-positions by aza bridges [1]. These compounds and their macrocyclic analogues continue to attract considerable attention, due in part to their characteristic optical properties [2] and applications including medicinal therapeutic agents [3], field effect transistors [4], photosensitizers [5], photoconductors [6], organic light-emitting diodes [7], nonlinear optical devices [8], catalysts [9], dye industry and gas sensors [10] have been demonstrated. Owing to their rigid geometry as well as their unique electronic and photonic properties, phthalocyanines and their metal complexes are attractive and excellent building components. Many derivatives of these compounds can be prepared not only by changing the nature of the central metal atom, but also by formally fusing additional aromatic rings to the central core; or by forming planar or linear groups [11]. Phthalocyanine-based multicomponent systems have been explored, including porphyrins, ferrocenes, crown ethers [12], tetrathiafulvalenes, oligopridyl-metal complexes, dendrimers, and C_{60} [13]. Furthermore, Pcs have long been known to undergo electron transfer reactions, both to and from their excited states, and strong electron donors such as ferrocene are able to quench the Pc fluorescence by intermolecular electron transfer [14].

The fascinating structural properties of ferrocene and its derivatives have been the subject of increasing interest in all fields of organometallic chemistry, since the discovery of ferrocene in 1950 [15]. A sandwich structured compound ferrocene is suitable to functionalization by direct electrophilic substitution of the 6π-cyclopentadienide ring, like benzene. On the other hand ferrocene reacts 3×10^6 times faster than benzene [16]. Because of the high stability, ease

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of functionalization, and well defined electrochemistry, ferrocene has been widely used as a redox-active center which is linked together with a wide variety of structural units [17]. Furthermore, the combination of an electron donor unit such as ferrocene and an electron acceptor moiety such as phthalocyanine may give rise to inter-molecular charge transfer that may enhance the second order response. So far, only a few examples of Pcs covalently linked to one or more ferrocene units have been described, and also their NLO properties have not been studied adequately [18]. Therefore, to investigate phthalocyanine–ferrocene conjugates is worthwhile.

In the present paper we have synthesized a 12-membered N_2S_2-type macrocycle which connected two ferrocene units via methylene bridges and a metal-free and metallophthalocyanine compound.

2. Experimental

2.1. General and Instrumental

The reagents were used as supplied while the solvents were purified according to the standard procedure before use [19]. The IR spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS MS spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO elemental analyzer and Unicam 929 AA spectrophotometer, respectively. Electronic spectra were recorded at room temperature on a Unicam UV–Vis spectrophotometer. Melting points were determined in open capillaries on an Electrothermal apparatus and were uncorrected. 1,2-Bis(2-iodomercapto-ethyl)-4,5-dicyanobenzene (**1**) [20] and *N*,*N*′-ethylenebis(ferrocenylmethyl)amine (**2**) [21] were synthesized according to reported procedures.

2.2. Synthesis

2.2.1. 12,13-Dicyano-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrocyclobenzo[k]-4,7-diaza-1,10-dithiacyclododecine (3)

A three-necked flask containing dry acetonitrile (150 ml) and fitted with condenser was evacuated, refilled three times with argon, and connected to vacuum line. Under argon, the flask was charged with **1** (3.325 g, 5 mmol) and three-fold excess of finely ground anhydrous Na_2CO_3 (2.23 g, 21 mmol), anhydrous NaI (0.3 g, 2 mmol) and the mixture was stirred at 40 °C for 1 h. A solution of **2** (3.185 g, 7 mmol) in dry acetonitrile (120 ml) was added to this mixture under argon atmosphere and the reaction mixture was refluxed and stirred for 210 h. The reaction was monitored by thin layer chromatography [silica gel (chloroform:methanol) (95:5)]. At the end of this period, the mixture was cooled to room temperature and filtered using Celite as the filtering agent and washed with dry acetonitrile and then solvent was evaporated to dryness under reduced pressure. Brown oily crude product was purified by using column chromatography technique [silica gel (chloroform:methanol) (95:5)]. After combining the appropriate fractions, the solvent was removed under reduced pressure and the pale brown oily product was obtained. Yield: 1.68 g (34.3%).

Anal. Calc. for $C_{36}H_{36}N_4S_2Fe_2$: C, 61.71; H, 5.14; N, 8.00. Found: C, 61.47; H, 4.88; N, 8.36%. IR (NaCl disc, cm^{-1}): 3076 (Ar–H), 2919–2846 $(C–H)_{alip.}$, 2229 (C≡N), 1568, 1514 (C=C), 1459, 1415, 1333, 1265, 1117, 771. ^{1}H NMR ($CDCl_3$): δ 7.46 (m, 2 H, Ar–H), 4.05 (m, 18 H, C_5H_5), 3.37 (s, 8H, NCH_2), 2.68 (s, 4H, CH_2), 2.58 (s, 4H, SCH_2). ^{13}C NMR ($CDCl_3$): δ 115.10 (ArC), 117.50 (ArC≡N), 132.80 (ArCH), 138.10 (ArCS), 82.28 (C_5H_5), 68.87 (C_5H_5), 68.21 (C_5H_5), 68.11 (C_5H_5), 52.56 (NCH_2), 47.38 (CH_2), 28.67 (SCH_2). MS (*m*/*z*): 701 $[M+1]^+$.

2.2.2. Metal-free phthalocyanine (4)

Dinitrile derivative **3** (1.485 g, 1.08 mmol), 1.8 ml of dry *n*-pentanol, 0.33 ml of DBU and catalytic amount of pyridine was placed under argon atmosphere in a standard Schlenk tube and degassed several times. The reaction mixture was heated and stirred at 170 °C for 24 h under argon. After cooling to room temperature, the mixture was filtered and washed with dry methanol.The filtrate was evaporated to dryness under reduced pressure and chromatographed on a silica column [eluent chloroform:petroleum ether (60:40)] to give dark green solid product which dried in vacuo. Yield: 0.2 g (% 26.3), m.p. >300 °C.

Anal. Calc. for $C_{144}H_{146}N_{16}S_8Fe_8$: C, 61.70; H, 5.20; N, 7.99. Found: C, 61.63; H, 5.31; N, 7.58%. IR (KBr pellets, cm^{-1}): 3202(N–H), 3084(Ar–H), 2925–2854 $(C–H)_{alip.}$,1646 (C=N), 1585, 1511, 1444, 1367, 1322, 1261, 1204, 1105. ^{1}H NMR ($CDCl_3$): δ 7.64 (s, 4H, Ar–H), 7.47 (s, 4H, Ar–H), 4.21–4.01 (m, 72H, C_5H_5), 3.21 (m, 32H, CH_2N), 2.44 (m, 16H, CH_2S), 1.59 (s, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 163.04 (C=N), 135.55 (ArCS), 131.35 (ArCH), 129.23 (ArC), 82.05(C_5H_5), 68.93 (C_5H_5), 68.38 (C_5H_5), 68.17(C_5H_5), 53.39 (NCH_2), 48.61 (CH_2), 29.75 (SCH_2). UV–Vis [(in $CHCl_3 \lambda_{maks}$/nm $10^{-5}\varepsilon$ (mol^{-1} cm^{-1}))] : 696 (5.27), 676 (5.29), 630 (4.88), 355 (4.67), 270 (4.95), 243 (5.01). MS (m/z) = 2826 $[M+Na+1]^+$.

2.2.3. Nickel(II) Phthalocyanine (5)

A mixture of the metal-free phthalocyanine **4** (0.12 g, 0.043 mmol), anhydrous $NiCl_2$ (0.0055 g, 0.043 mmol) and 1 ml of dry quinoline was added into a sealed tube under argon atmosphere and then the reaction mixture was heated and stirred for 15 h at 210 °C After cooled to room temperature, the crude product was diluted with 5 ml of methanol and filtered off, washed with dry methanol and then dried *in vacuo*. The solid product was purified on a silicagel column using pyridine:methanol (100:1) as eluent to give dark green solid product **(5).** Yield 0.16 g (% 32.3), m.p. >300 °C.

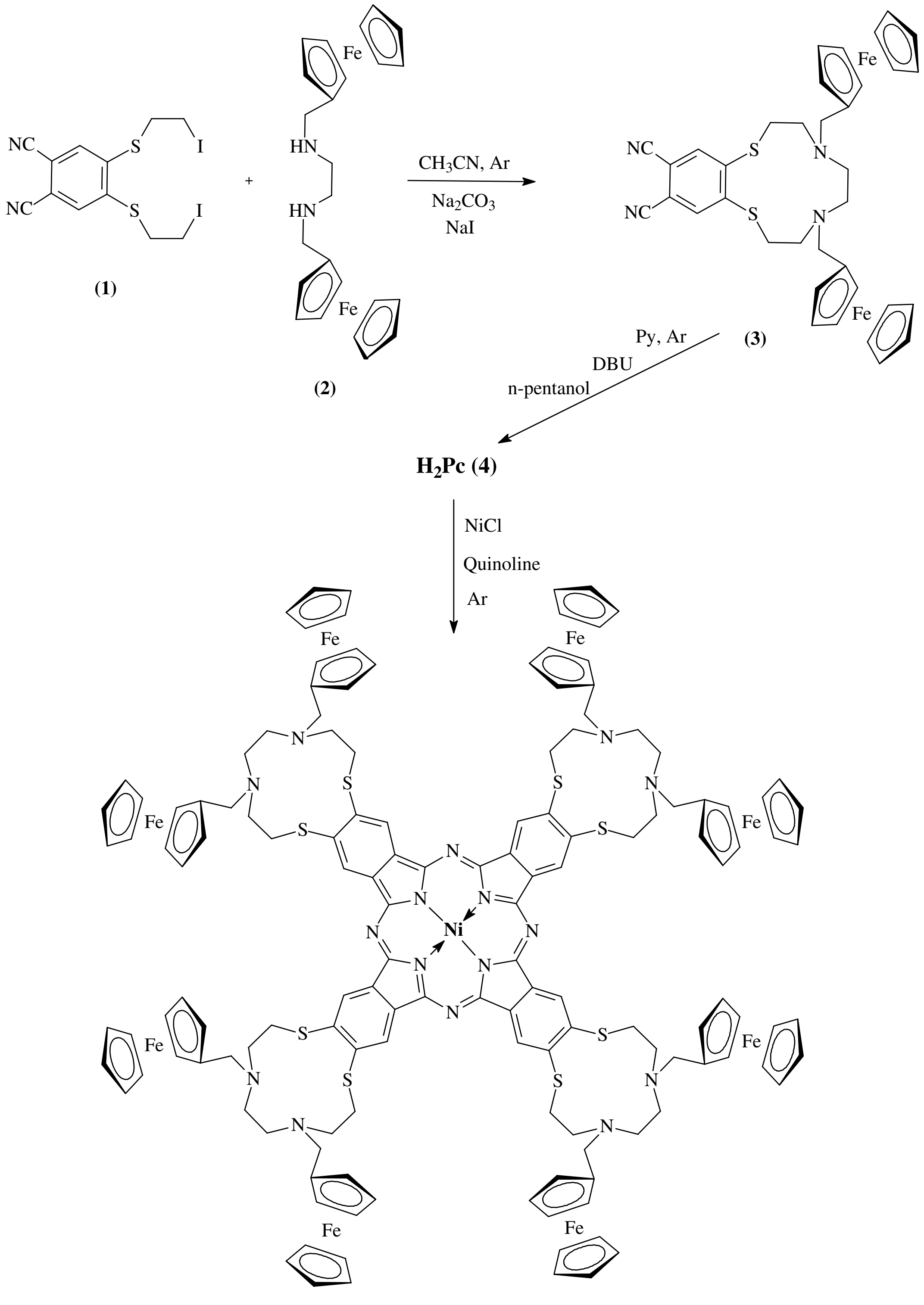
Anal. Calc. for $C_{144}H_{144}N_{16}S_8Fe_8Ni$: C, 60.47;H, 5.03; N, 7.83; Ni, 2.05. Found: C, 60.81;H, 4.77; N, 8.11; Ni, 1.81%. IR (KBr pellets, cm^{-1}) : 3072 (Ar–H), 3034 (Ar–H), 2929–2854 $(C–H)_{alip.}$, 1614 (C=N), 1594, 1501, 1466, 1376, 1322, 1263, 1207, 1107, 1033, 808. ^1H NMR ($CDCl_3$): δ 7.63 (m, 4H, ArH), 7.48 (m, 4H, ArH), 4.13–3.98 (m, 72H, C_5H_5), 3.29 (m, 32H, NCH_2), 2.21 (m, 16 H, SCH_2), 1.52 (s, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 150.14 (C=N), 142.08 (ArCS), 138.04 (ArCH), 135.46 (ArC), 83.18 (C_5H_5), 69.09 (C_5H_5), 68.67 (C_5H_5), 68.32 (C_5H_5),53.76 (NCH_2), 43.54 (CH_2), 30.37 (SCH_2). UV–Vis [in $CHCl_3\lambda_{max}$/nm $10^{-5}\varepsilon$ ($mol^{-1}cm^{-1}$)]: 693 (5.17), 627 (4.92), 357 (4.70), 268 (4.93), 240 (4.97). MS (m/z) = 2858 $[M]^+$, 2859 $[M+1]^+$.

3. Results and discussion

The synthesis of the dicyano compound 12,13-dicyano-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrocyclobenzo[*k*]-4,7-diaza-1,10-dithiacyclododecine (**3**) prepared by the 1:1 reaction of 1,2-bis(2-iodomercaptoethyl)-4,5-dicyanobenzene **1** [20] and *N*,*N*′-ethylenebis(ferrocenylmethyl)amine **2** [21] in acetonitrile containing finely ground anhydrous Na_2CO_3 and NaI under argon for 210 h. The solubility of Na_2CO_3 in CH_3CN media is quite low while NaI is considerable amount. In the initial stages of the reaction, the presence of a small amount of NaI aids in the cyclization reaction. Finally purification of the macrocycle by column chromatography afforded **3** in 34.3% yield for which elemental analysis and mass spectral data were satisfactory $m/z = 701$ $[M+1]^+$. In the ^1H and ^{13}C NMR spectra of this compound, the characteristic signals are very similar to those of the starting compounds. The chemical shift concerning NH protons in the precursor compound **2** disappeared after the macrocyclization reaction. The singlets at $\delta = 7.46$ and 2.58 ppm corresponds to aromatic group and connected to SCH_2 groups of it, respectively. Proton-decoupled ^{13}C NMR spectrum of this compound clearly indicates the presence of nitrile carbon atoms with peak at $\delta = 117.50$ ppm. This spectrum also reveals that the carbon atoms from the nonsubstituted cyclopentadienyl ring are equivalent at $\delta = 68.11$ ppm whereas the other carbon resonances concerning the substituted cyclopentadienyl ring comes out at $\delta = 68.21$ and 68.87 ppm as expected [21]. The carbon-13 NMR signal appearing at lower field at $\delta = 82.28$ ppm could be ascribed to the ipso carbon resonance. The IR spectrum of this compound was easily verified with the disappearance of N-H stretching motion and the presence of C≡N vibrations at 2229 cm^{-1}. The remaining resonances due to aromatic, cyclopentadienyl ring and aliphatic groups do not shift significantly on macrocyclization. This compound displayed the expected molecular ion peak at $m/z = 701$, indicating formation of $[M+1]^+$.

The macrocyclization of phthalonitrile **3** to the corresponding metal-free phthalocyanine **4** was carried out in a high-boiling solvent in the presence a few drops of DBU as a strong organic base and catalytic amount of pyridine at reflux temperature under argon atmosphere for 24 h (Scheme 1). Several reaction conditions [1,2] can be applied to construct H_2Pc starting with dicyano compounds (**3**). Above mentioned route was chosen to obtain metal-free phthalocyanine in this reaction due to it is easily to perform and the condition is relatively mild, together with a relatively high yield of H_2Pc. The yield of metal-free phthalocyanine (**4**), after purification column chromatography, is rather low which can be attributed to the other bulky groups [20]. A diagnostic feature of the formation of **4** from **3** is the disappearance of the sharp C≡N and the presence of C=N and N–H stretching vibrations at 1646 and 3202 cm^{-1}, in the IR spectrum of this compound, respectively, confirms the formation of H_2Pc. The rest of the IR spectrum of **4** closely resembles that of **3**, including the characteristic vibrations of aromatic and aliphatic groups. The aggregation of H_2Pc which is frequently encountered at the concentration used for NMR measurements caused the broad absorptions in the NMR signals of this compound [22]. The inner core protons of this compound also could not be observed because of strong aggregation of the molecule [23]. The signals related to aromatic, cyclopentadienyl groups and aliphatic protons in the macrocyclic connected ferrocenylmethyl moieties and phthalocyanine skeleton gave significant absorbance characteristic of the proposed structure. ^{13}C NMR spectrum of this compound, all signals are identical for the precursor dicyano derivative (**3**) except for the C≡N carbons as expected. The chemical shift appeared at $\delta = 163.04$ ppm of this compound should be related to inner core C=N absorptions [24]. The elemental analyses of 4 are in accord with its calculated results. This is also supported by the presence of the main peak in the mass spectrum of **4** at $m/z = 2826$ $[M+Na+1]^+$.

The synthesis of metallophthalocyanine (**5**) was accomplished with metal-free phthalocyanine (**4**) and dry $NiCl_2$ in dry quinoline at 210 °C for 15 h into a sealed tube under argon atmosphere. Column chromatography using silica gel with pyridine:methanol (100:1) as eluents removed the nickel(II) phthalocyanine (**5**) in 32.3% yield. According to the experimental result, including elemental analysis, metal content, ^1H NMR, ^{13}C NMR, IR, UV–Vis, and MS it was believed that the formation of **5** was in good agreement with the proposed structure. This results is also in accord with the presence of the molecular ion peak in the mass spectral data of nickel(II) phthalocyanine (**5**) at $m/z =$ 2858 $[M]^+$. The IR spectrum of the nickel(II) complex **5** was very similar to those of **4**. A characteristic band belonging to the N–H stretching vibrations at 3202 cm^{-1}in precursor compound disappeared after complexation of **4** which can be attributed the formation of nickel–nitrogen bonds. The ^1H NMR spectrum of nickel phthalocyanine and metal-free species are almost identical as expected. Also, the peaks of spectrum for **5** are the broad absorptions probably caused by aggregation of the planar



(1)

(2)

(3)

H_2Pc (4)

NiPc (5)

Scheme 1.

phthalocyanine. On the other hand, the ^{13}C NMR spectrum of this compound was fully consistent with the proposed structure.

The best indications for phthalocyanine systems are given by their UV–Vis spectra in solution (Fig. 1). The electronic spectra of phthalocyanines **4** and **5** show the same typical B and Q bands of symmetrical substitute Pcs. In the UV–Vis spectrum of metal-free pthalocyanine in chloroform, the characteristic split Q band was observed with absorptions at 696 and 676 nm. These intense Q bands

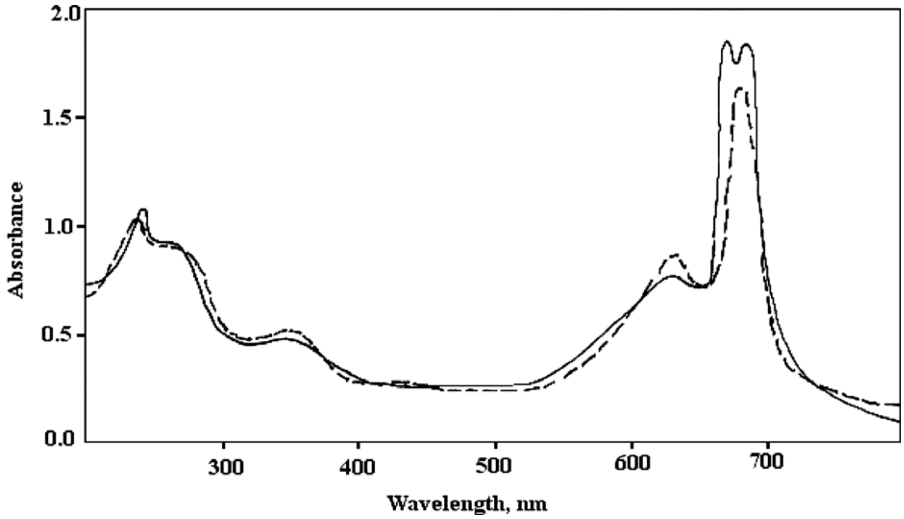


Fig. 1. Electronic spectra of **H_2Pc** (—) and **NiPc** (- - -) in chloroform.

indicate monomeric species as species with D_{2h} symmetry show two intense absorptions around 700 nm [25]. The lower absorption than the typical split Q band at 630 nm is due to the dimmeric association and up to 615 nm for higher aggregates [26]. The low-energy band has been attributed to unaggregated Pc and the high-energy absorptions to aggregate species [1]. Such split Q band absorptions are due to the $\pi \Rightarrow \pi*$ transition from the HOMO to the LUMO of the phthalocyanine ring related to fully conjugated 18π electron system. The presence of strong absorption bands in **(4)** in the UV region at $\lambda_{\max}$ 400–300 nm shows superimposed bands of the phthalocyanine due to the existence of Soret band of Pc which has been ascribed to the deeper $\pi \Rightarrow \pi*$ levels of LUMO transition [27]. However, in the state of Ni(II) derivate of phthalocyanine the average Q-bands are slightly shifted to the blue with respect to the parent metal-free compound [28]. The position of Q band of metallophthalocyanine (**5**) changed due to the central Ni(II) which Q band absorption without splitting and centered at around 693 nm. The characteristic Q band transitions of metal phthalocyanines were observed as a single band of high intensity region [29]. Observed peaks as mentioned above indicate that the symmetry of the molecule has been changed. This result is typical of metal complexes of substituted and unsubstituted Pcs with D_{4h} symmetry [30].

4. Conclusion

In summary, the metal-free **(4)** and metallo-phthalocyanines **(5)** bearing ferrocenyl moieties in the peripheral positions were newly prepared by direct cyclotetramerization of precursor phthalonitrile **(3)**. The phthalonitrile derivative **(3)** which has been prepared by the macrocyclization reaction of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**1**) with N,N′-ethylenebis-(ferroceneylmethyl)amine (**2**), in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a strong organic base.

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