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The synthesis and characterization of novel metal-free and metallophthalocyanines bearing eight 16-membered macrocycles

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Abstract

Novel metal-free and metal-containing (Zn, Ni, Cu) derivatives bearing eight 16-membered tetrathiamonoaza macrocycles in peripheral positions were synthesized and characterized by a combination of elemental analysis, UV–vis, FT-IR, NMR and MS spectral data. The metal-free phthalocyanine was synthesized by two different routes namely from 4,5-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]thio}phthalonitrile and from 5,6-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]thio}-1*H*-isoindole-1,3(2*H*)-diimine.

Keywords: Phthalocyanine; Phthalonitrile; Metallophthalocyanines; Metal complex

1. Introduction

Phthalocyanines (Pcs) and their symmetrically substituted derivatives have been an important class of dyes and pigments since their first synthesis early last century [1]. They have also been used as catalysts for desulfurization processes in the oil industry. Recently, these macrocyclic compounds have been applied as photoconducting agents in photocopiers, laser printers, and optical read/write disks. They are expected to play a more versatile role in material chemistry due to their potential applications in molecular electronics and phototonics [2], electrochromic displays [3], nonlinear optics [4], electrocatalytic reagents [5], and medical applications [6]. All of these merit applications are connected by their high thermal and chemical stabilities, which, in turn, are closely related to the electrochemical properties of phthalocyanine macromolecules. It is well-known that the electrochemical and spectroscopic properties of phthalocyanines can be tuned by either varying the central metal atom, changing the size of the π-conjugated system of phthalocyanines, or altering the type, number, and positions of substituents on the macrocycle ligands.

Macrocyclic phthalocyanines that have been synthesized and studied are phthalocyanines with crown ether, azacrown, thiacrown, polyamines and other related macrocycle substituents which are capable of binding transition metal cations [7]. Furthermore, variations in the connection of the macrobicyclic rings to the phthalocyanine core have been introduced and polyalkaline earth metal as well as transition metal complexes have been prepared [8].

The exceptional chemical and physical properties of phthalocyanine compounds can be due to various substituents on the phenyl rings. Much research on this concept has been devoted to the synthesis of phthalocyanines that have been peripherally functionalized with appendages that can coordinate metal cations. Over 70 elements can be included into the phthalocyanine core, and its chemical versatility allows the introduction of many different substituents at peripheral positions [9,10]. These peripheral units are particularly noteworthy as they allow for cation selectivity and complex stability to be enhanced

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through changing the numbers and types of macrocycle donors [11,12]. The usual purification methods such as crystallization and chromatographic separation cannot be used in most phthalocyanines due to their extreme insolubility [13]. The solubility of phthalocyanines can be enhanced by adding various groups such as a crown ether [11,14–16], mixed donor macrocycle [17,18] or macropolycycle [8,19] to the benzene rings.

We lately outlined a concept for the synthesis of a new type of phthalocyanine with various functional groups. These phthalocycanines have N-, O- and S-containing functionalities such as diazadioxa [20], cylindrical and spherical macrotricycles [19,21,22], crown ether fused diloop [23,24], diazadithia macrocyclic with *tert*-butyl [25].

In this paper, we describe the synthesis of a novel phthalocyanine that contains a central Pc core and eight 16-membered monoazatetrathia macrocycles and its phthalocyaninato Zn(II), Ni(II), Cu(II) complexes (Schemes 1 and 2). There are two kinds of donor atoms in the peripheral substituent groups of synthesized products, the S-atom, which is a soft center, and the N-atom, which is considered as a hard center, enabling these ligands to coordinate to soft and hard metals. However, these compounds are expected to coordinate especially to soft transition metal cations. The new compounds were characterized by using elemental analysis, UV–vis, FT-IR, NMR, MS spectral data.

2. Experimental

Reactions were performed under an atmosphere of argon. 1,7,10,14-Tetrathia-4-azacyclohexadecane **2** [26] and 1,2-bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzene **1** [27] were prepared according to the literature procedures. *n*-Pentanol was distilled from sodium. All other reagents and solvents were of reagent grade quality from commercial suppliers and were dried before use as described in the literature [28]. Column chromatography was carried out on silica gel (70–230 mesh) and Merck 90 active neutral alumina columns with the indicated eluents.

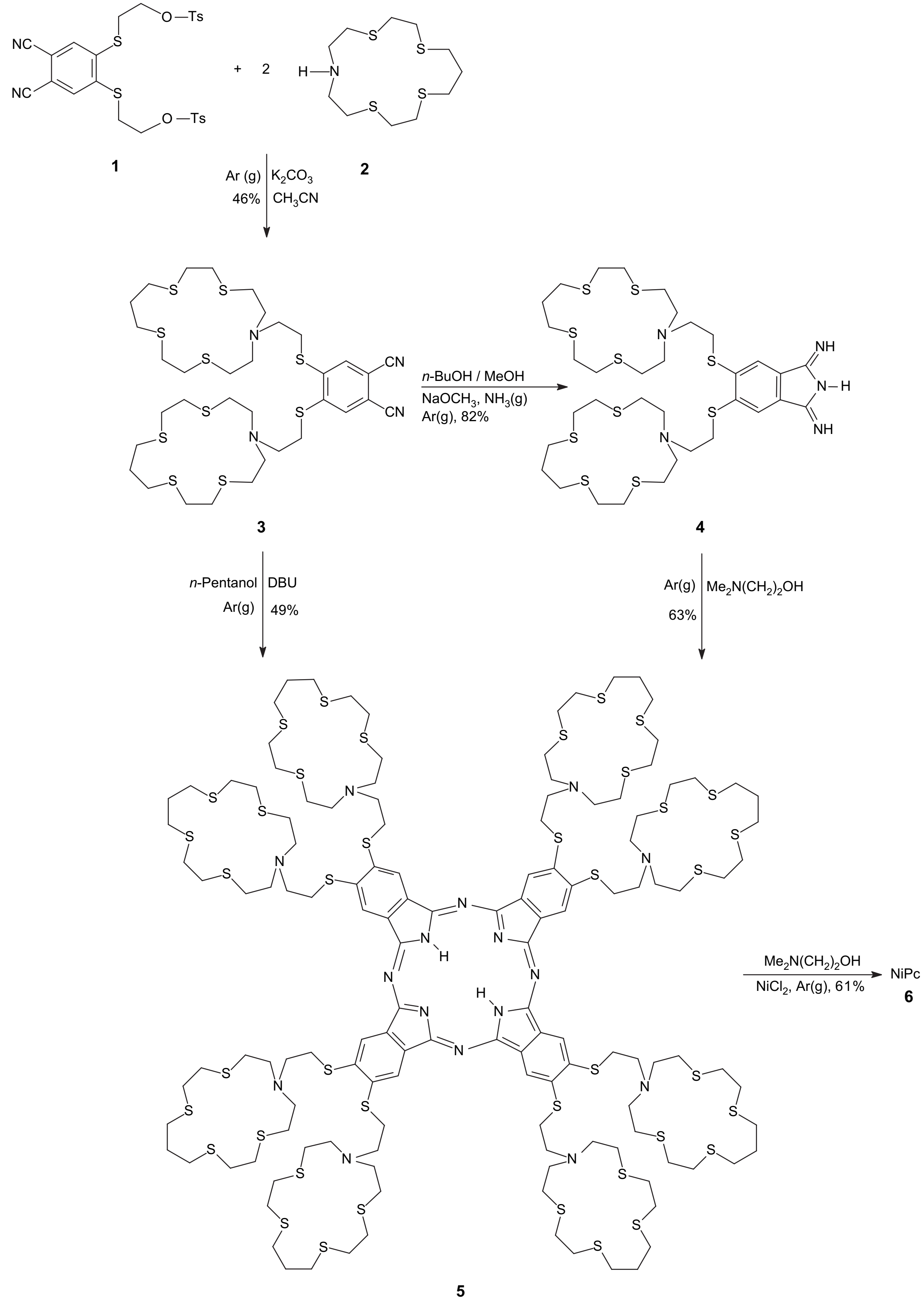
The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. The infrared spectra were recorded on a Perkin–Elmer spectrum one spectrometer with the samples in KBr pellets. Melting points were determined by an electrothermal apparatus and were uncorrected. Optical spectra in the UV–vis region were recorded with a model Shimadzu 1601 UV–vis spectrometer using a 1 cm pathlength cuvette at room temperature. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. The elemental analysis of the compounds was determined on a CHNS-932 LECO instrument.

2.1. *4,5-Bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]thio}phthalonitrile (**3**)*

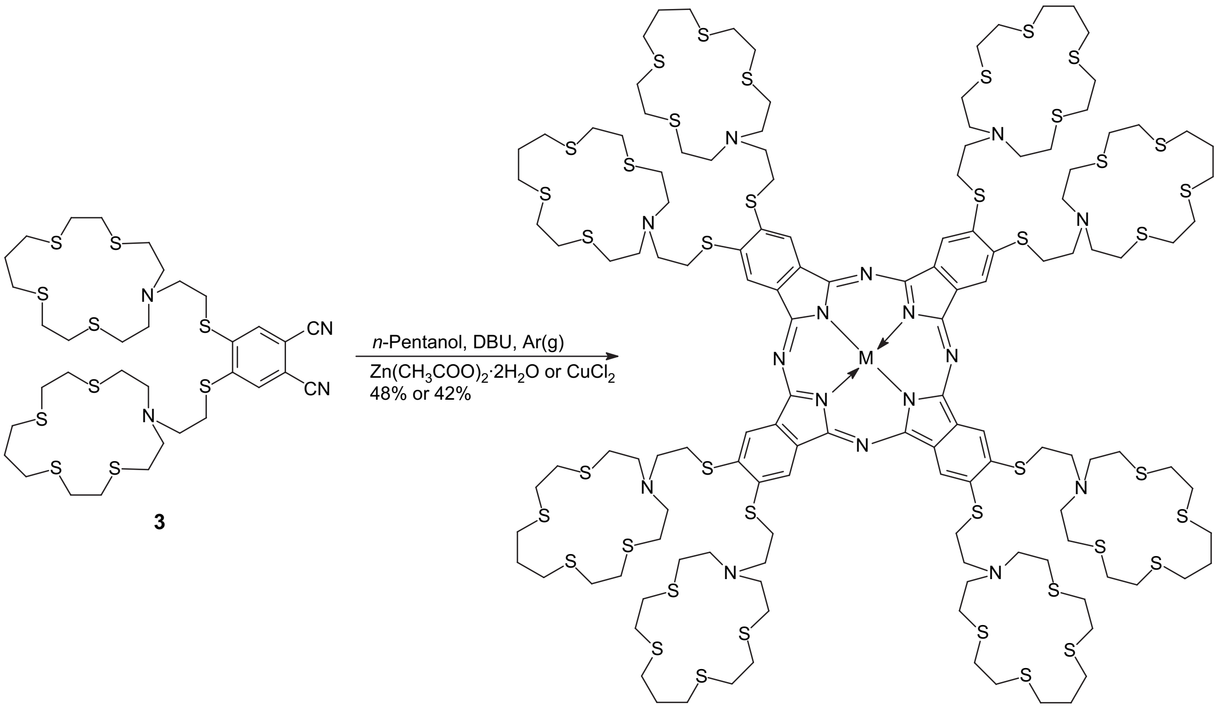
A 100-mL three necked round-bottomed flask containing 40 mL of dry acetonitrile and fitted with a condenser was evacuated, refilled three times with argon gas and connected to a vacuum line. Under argon gas, the flask was charged with 1,7,10,14-tetrathia-4-azacyclohexadecane **2** (1 g, 3.37 mmol), 1,2-bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzene **1** (0.99 g, 1.69 mmol) and finely ground anhydrous K_2CO_3 (2.33 g, 16.9 mmol). The reaction mixture was refluxed at 105 °C for 7 days under argon atmosphere. The reaction was monitored by thin layer chromatography [chloroform:petroleum ether:methanol (6:3:1)]. At the end of this period, the reaction mixture was cooled to room temperature and evaporated to dryness. The residue was added to 50 g ice and stirred for 1 h. Afterwards, 50 mL of chloroform was added and stirred at room temperature for 15 min and extracted with chloroform (4 × 75 mL). The organic phase was separated and dried with anhydrous $MgSO_4$ and filtered off. The pale brown solution was evaporated and semi-solid product was obtained. This crude product was dissolved in minimum amount of chloroform and 10 mL of ethanol was added and kept inside the refrigerator at −18 °C overnight. The precipitated light brown solid product was filtered off and dried *in vacuo*. The purification of phthalonitrile derivative **3** was carried out by column chromatography (3 × 20 cm column) on silica gel using chloroform:petroleum ether:methanol (6:3:1) as solvent mixture to give a light brown solid **3**. Yield: 0.65 g (46%); m.p. = 78–80 °C. $C_{34}H_{54}N_4S_{10}$ (839.5): calcd. C: 48.37; H: 6.16; N: 6.89; S: 38.58%; found C: 48.65; H: 6.48; N: 6.67; S: 38.20%. IR (KBr): ν_{max} (cm^{-1}) = 3078 (CH aromatic), 2958–2850 (CH_2 aliphatic), 2230 (C≡N), 1588 (aromatic C=C), 1262–1223 (*tert*-N), 704 (C–S). ^{1}H NMR (ppm, $CDCl_3$): $\delta = 7.54$ (s, 2H, ArH), 3.14 (t, 4H, ArSCH_2), 2.96–2.84 (m, 12H, NCH_2), 2.80–2.67 (m, 32H, CH_2SCH_2), 1.90–1.80 (m, 4H, CH_2–CH_2–CH_2). ^{13}C NMR (ppm, $CDCl_3$): $\delta = 144.2$ (ArCS), 130.5 (ArCH), 115.4 (Ar*C*N), 112.5 (ArC), 51.7 (CH_2NCH_2), 49.3 (NCH_2CH_2S–Ar), 32.8–32.7 (–N–CH_2–*C*H_2–S–*C*H_2–), 31.9 (*C*H_2SAr), 30.7–30.6 (–S–CH_2–*C*H_2–S–*C*H_2–), 29.8 (CH_2–*C*H_2–CH_2). MS (ES$^+$) *m/z*: 839.5 [M]$^+$.

2.2. *5,6-Bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]thio}-1H-isoindole-1,3(2H)-diimine (**4**)*

Compound **3** (1.678 g, 2.0 mmol) was dissolved in 120 mL dry methanol:dry *n*-butanol mixture (3:1, v/v) in 1000 mL three necked round-bottomed flask under argon atmosphere. Dry sodium methoxide (55 mg, 1 mmol) in 10 mL of dry methanol was added and the reaction mixture was evacuated, refilled two times with argon and connected to a vacuum line. Anhydrous ammonia was bubbled through the reaction mixture for 2 h at room temperature and then for 8 h at reflux temperature. The reaction was monitored by TLC using methanol:chloroform (8:2). At the end of this period, the ammonia inlet was closed and the reaction mixture was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography (2 × 25 cm column) on silica gel using methanol:chloroform (8:2) as solvent mixture. The second eluent was collected and evaporated to dryness. The residue was dissolved in 25 mL dry methanol and kept in the refrigerator at −18 °C overnight. The greenish yellow



Scheme 1. Synthesis of the metal-free phthalocyanine **5** and phthalocyaninato nickel(II) **6**.



3

M = Zn(II), Cu(II)
7 **8**

Scheme 2. Synthesis of the phthalocyaninato Zn(II) **7** and Cu(II) **8**.

solid product was filtered off and washed with petroleum ether and then recrystallized from methanol under argon atmosphere. Isoiminoindoline derivative **4** was dried *in vacuo* with P_2O_5. Yield: 1.40 g (82%); m.p. = 215–217 °C (dec.). $C_{34}H_{57}N_5S_{10}$ (856.5): calcd. C: 48.01, H: 6.99, N: 8.01, S: 36.99%; found C: 47.68, H: 6.72, N: 8.18, S: 37.42%. IR (KBr): ν_{max} (cm^{-1}) = 3434 (N–H), 3248 (N–H), 3072 (CH aromatic), 2942–2845 (CH_2), 1624 (N–H, bending), 1587–1543 (aromatic C=C), 1278 (*tert*-N), 680 (C–S). ^1H NMR (ppm, DMSO-d_6): $\delta = 8.24$ (br, 3H, N–H), 7.65 (s, 2H, ArH), 3.20 (t, 4H, $ArSCH_2$), 2.90–2.82 (m, 12H, NCH_2), 2.82–2.71 (m, 32H, CH_2SCH_2), 1.91–1.84 (m, 4H, CH_2–CH_2–CH_2). ^{13}C NMR (ppm, DMSO-d_6): $\delta = 168.2$ (C=N–H), 143.6 (ArCS), 137.3 (ArC), 130.1 (ArCH), 53.1 (CH_2NCH_2), 48.7 (NCH_2CH_2S–Ar), 32.9–32.7 (–N–CH_2–CH_2–S–CH_2–), 30.9 (CH_2SAr), 30.6–30.4 (–S–CH_2–CH_2–S–CH_2–), 29.3 (CH_2–CH_2–CH_2). MS (ES^+) *m/z*: 856.5 $[M]^+$.

2.3. Metal-free phthalocyanine (**5**)

Metal-free phthalocyanine **5** was synthesized from two different routes: one is from phthalonitrile derivative **3** and other one is from compound **4**.

2.3.1. Route 1

Compound **4** (1.4 g, 1.64 mmol) and 1.5 mL of dry 2-(dimethylamino)ethanol were placed in a Schlenk tube connected to a vacuum line under argon atmosphere. The mixture was heated and stirred at 100 °C for 1 h. Then it was refluxed under argon for 52 h. After cooling to room temperature, the mixture was filtered off and washed with 50 mL of hot dry ethyl acetate. The green crude product was purified on silica gel using chloroform:petroleum ether (6:4) as eluent. The combined eluent was evaporated to 10 mL. The dark green product was filtered off, washed with ethyl acetate, ethanol, and diethyl ether and dried in open air. Yield: 0.87 g (63%); m.p. >300 °C. $C_{136}H_{218}N_{16}S_{40}$ (3359.9): calcd. C: 48.31, H: 6.89, N: 6.39, S: 38.41%; found C: 48.62, H: 6.54, N: 6.67, S: 38.17%. IR (KBr): ν_{max} (cm^{-1}) = 3268 (N–H), 3066 (CH aromatic), 2917–2849 (CH_2), 1627 (aromatic C=N), 1595–1569 (aromatic C=C), 1268 (*tert*-N), 1123, 1040 (N–H), 752, 685 (C–S). ^1H NMR (ppm, DMSO-d_6): $\delta = 7.92$ (s, 8H, ArH), 3.12 (t, 16H, $ArSCH_2$), 2.91–2.79 (m, 48H, NCH_2), 2.75–2.69 (m, 128H, CH_2SCH_2), 1.93–1.81 (m, 16H, CH_2–CH_2–CH_2), −4.20 (br, 2H, N–H). ^{13}C NMR (ppm, DMSO-d_6): $\delta = 153.2$ (C=N), 140.6 (ArCS), 133.8 (ArC), 129.5 (ArCH), 52.7 (CH_2NCH_2), 48.9 (NCH_2CH_2S–Ar), 33.2–32.9 (–N–CH_2–CH_2–S–CH_2–), 31.2 (CH_2SAr), 29.8–29.5 (–S–CH_2–CH_2–S–CH_2–), 28.6 (CH_2–CH_2–CH_2). UV–vis (pyridine) λ_{max} (log ε) = 716 (4.72), 688 (4.71), 652 (4.34), 621 (4.15), 432 (4.40), 346 (4.85), 330 (4.83). MS (ES^+) *m/z*: 3359.9 $[M]^+$.

2.3.2. Route 2

A standard Schlenk tube under a dry argon atmosphere was charged with phthalonitrile derivative **3** (0.3 g, 0.358 mmol), 1.5 mL dry *n*-pentanol and 3–5 drops of 1, 8-diazabicyclo[5.4.0]undec-7-ene (DBU) and degassed for several times. The reaction mixture was refluxed at 150 °C for 24 h. The reaction was controlled by TLC technique using chloroform:methanol (9:1) and then cooled to room temperature. Solvent was decanted and 10 mL methanol:diethyl ether (1:1, v/v) was added and stirred for 45 min. The precipitated light green solid was filtered off and washed with diethyl ether. This product was eluted by column chromatography on silica gel using chloroform:methanol (9:1) as solvent mixture. The combined solvents were evaporated to dryness and a little amount of ethyl acetate was added to the residue and stirred for 30 min. The dark green product was filtered off, washed with diethyl ether for several times and dried in open air. Yield: 147 mg (49%). Physical and spectral data were nearly the same as given in route 1.

2.4. Phthalocyaninato nickel(II) (**6**)

Compound **5** (0.51 g, 0.152 mmol), anhydrous $NiCl_2$ (21 mg, 0.162 mmol) and 2.5 mL of dry 2-(dimethylamino) ethanol were placed in a standard Schlenk tube under argon atmosphere and held at reflux temperature for 48 h. After cooling to room temperature, 10 mL of diethyl ether was added in order to maintain the precipitation. The dark green solid was filtered off, washed with ethanol, water and diethyl ether and dried *in vacuo*. Yield: 0.317 g (61%); m.p. >300 °C. $C_{136}H_{216}N_{16}S_{40}Ni$ (3416.7): calcd. C: 47.49; H: 6.68; N: 6.22; S: 38.12; Ni: 1.49%; found C: 47.81; H: 6.37; N: 6.56; S: 37.54; Ni: 1.72%. IR (KBr): ν_{max} (cm^{-1}) = 3045 (C–H aromatic), 2922–2848 (CH_2), 1616 (C=N aromatic), 1589–1506 (C=C aromatic), 1420 (C–H), 1297 (*tert*-N), 1120, 947, 750–675 (C–S). ^1H NMR (ppm, DMSO-d_6): $\delta = 7.81$ (s, 8H, ArH), 3.02 (t, 16H, $ArSCH_2$), 2.85–2.77 (m, 48H, NCH_2), 2.70–2.66 (m, 128H, CH_2SCH_2), 1.91–1.83 (m, 16H, $CH_2–CH_2–CH_2$). UV–vis (pyridine) λ_{max} (log ε) = 685 (5.44), 640 (5.42), 611 (5.33), 386 (5.39), 354 (5.52), 322 (5.51). MS (ES^+) *m/z*: 3417.7 $[M + 1]^+$.

2.5. Phthalocyaninato zinc(II) (**7**)

A well-stopped Schlenk tube was charged with **3** (0.839 g, 1 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (55 mg, 0.25 mmol), 2 mL of dry *n*-pentanol and 3–5 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under argon atmosphere. The reaction mixture was heated gently to 90 °C for 1 h and then held at 150 °C for 24 h. The reaction was monitored by TLC using chloroform:methanol (100:1). After cooling to room temperature, the dark green reaction mixture was diluted and precipitated with a mixture of 25 mL of methanol:water (1:1) and stirred for 45 min. The resulting green precipitate was filtered off, washed with methanol, water and diethyl ether and then it was dissolved in minimum amount of DMF and eluted on neutral alumina using chloroform:methanol (100:1) as eluent. The extract was evaporated to dryness under vacuum and a mixture of 5 mL of methanol:diethyl ether (1:1) was added to this solid and placed inside the refrigerator at −18 °C overnight. The light green crystallized solid was filtered off and then dried *in vacuo* with P_2O_5. Yield: 0.410 g (48%); m.p. >300 °C. $C_{136}H_{216}N_{16}S_{40}Zn$ (3423.4): calcd. C: 47.38; H: 6.78; N: 6.81; S: 37.30; Zn: 1.73%; found C: 47.72; H: 6.36; N: 6.55; S: 37.46; Zn: 1.91%. IR (KBr): ν_{max} (cm^{-1}) = 3069 (Ar–H), 2923–2853 (CH_2), 1616 (C=N), 1587–1558 (C=C), 1270 (*tert*-N), 1100, 956, 760, 680 (C–S). ^1H NMR (ppm, DMSO-d_6): $\delta = 7.83$ (s, 8H, ArH), 3.06 (t, 16H, ArSCH_2), 2.87–2.79 (m, 48H, NCH_2), 2.72–2.67 (m, 128H, CH_2SCH_2), 1.94–1.85 (m, 16H, $CH_2–CH_2–CH_2$). UV–vis (pyridine) λ_{max} (log ε) = 695 (5.43), 664 (5.38), 617 (5.22), 382 (5.42), 354 (5.57), 324 (5.60). MS (ES^+) *m/z*: 3424.4 $[M + 1]^+$.

2.6. Phthalocyaninato copper(II) (**8**)

A standard Schlenk tube under argon atmosphere was charged with compound **3** (0.838 g, 1 mmol), $CuCl_2$ (26 mg, 0.26 mmol), 5 mL of dry *n*-pentanol and 3–4 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and heated at 160 °C with stirring for 12 h. At the end of this period, the mixture was cooled to room temperature, filtered and washed with methanol, water and acetone to remove any unreacted organic residue. The crude product was dissolved in minimum amount of DMF and launched into a column and eluted on neutral alumina using chloroform:methanol (1:1) as eluent. The extract was evaporated to dryness and 5 mL of ethyl acetate was added and stirred for 30 min. The dark green product was filtered and dried *in vacuo* in the presence of P_2O_5. Yield: 0.36 g (42%); m.p. >300 °C. $C_{136}H_{216}N_{16}S_{40}Cu$ (3421.5): calcd. C: 47.85; H: 6.37; N: 6.64; S: 37.33; Cu: 1.81%; found C: 47.52; H: 6.63; N: 6.28; S: 37.50; Cu: 2.07%. IR (KBr): ν_{max} (cm^{-1}) = 3058 (Ar–H), 2928–2857 (CH_2), 1616 (C=N), 1585–1557 (C=C), 1270 (*tert*-N), 1093, 962, 682 (C–S). UV–vis (pyridine) λ_{max} (log ε) = 703 (4.87), 646 (4.26), 631 (4.20), 470 (4.11), 351 (4.82), 327 (4.80). MS (ES^+) *m/z*: 3422.5 $[M + 1]^+$.

3. Results and discussion

The synthetic routes to **3**–**6** and **7**, **8** are demonstrated in Schemes 1 and 2, respectively. Herein, we reported the synthesis and structural properties of the dicyano compound **3** by the 2:1 addition reaction of 1,7,10,14-tetrathia-4-azacyclohexadecane **2** with 1,2-bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzene **1** in the presence of finely ground anhydrous K_2CO_3 and dry acetonitrile with the yield of 46% after purification by column chromatography on silica gel [chloroform:petroleum ether:methanol (6:3:1)]. This compound was characterized by its spectroscopic and analytical data. In the ^1H and ^{13}C NMR spectra of this compound, the signals of the aromatic protons and carbons are very similar to those of the starting material **1**. In the ^1H NMR spectrum of **3**, the signal belonging to N–H proton at $\delta = 2.44$ ppm in the precursor compound **2** disappeared after the addition reaction, the singlet at 7.54 ppm corresponds to aromatic protons connected to $–S–CH_2$. Also some other characteristic signals were observed for $Ar–S–CH_2–S$, $N–CH_2$, $CH_2–S–CH_2$ and $CH_2–CH_2–CH_2$ protons at $\delta = 3.14$, 2.96–2.84, 2.80–2.67 and 1.90–1.80 ppm, respectively. Proton-decoupled ^{13}C NMR spectral data were in good agreement with the proposed structure. The characteristic signals related to aromatic carbon atoms and dicyano carbon atoms at $\delta = 130.5$ and 115.4 ppm, respectively, supported the structure. The IR spectrum of **3** was easily verified with the disappearance of N–H and the presence of benzene ring (3078 cm^{-1}) and C≡N (2230 cm^{-1}) stretching vibrations. This compound displayed the expected molecular ion peak at $m/z = 839.5$ indicating formation of $[M]^+$.

The transformation of dicyano derivative **3** into isoiminoindoline derivative **4** was performed by bubbling dry ammonia through a solution of **3** in dry methanol:dry *n*-butanol mixture (3:1, v/v) in the presence of catalytic amounts of CH_3ONa for a period of 10 h. In the ^1H NMR spectra of **4**, there is a broad signal at $\delta = 8.24$ ppm due to the imino groups, which can be identified easily owing to deuterium exchangeable characteristics of these N–H protons. In the ^{13}C NMR spectra of **4**, the disappearance of the C≡N signals, along with the appearance of new peaks at $\delta = 168.2$ ppm concerning C=NH groups, is in agreement with the proposed structure. In the IR spectra of the compound, the C≡N stretching vibrations disappeared after conversion of **3** to isoiminoindoline derivative **4** which shows absorptions at 3434 and 3248 cm^{-1} for the N–H groups. In the mass spectra of the compound, the presence of the characteristic molecular ion peak at $m/z = 856.5$ $[M]^+$ confirmed the proposed structure.

Metal-free phthalocyanine **5** was synthesized by two different methods. In the first route, condensation of four isoiminoindoline derivatives **4** into metal-free phthalocyanine **5** was carried out in 2-(dimethylamino)ethanol at reflux temperature for 52 h in a Schlenk tube under argon to afford **5** in 63% yield as a dark green product after purification by column chromatography on silica gel [chloroform:petroleum ether (6:4)]. In the second route, this compound was prepared directly by using dicyano derivative **3**. Transformation of compound **3** into **5** was carried out in a Schlenk tube in dry *n*-pentanol and 3–5 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 150 °C for 24 h to afford 49% yield after purifying the compound on silica gel using chloroform:methanol (9:1) as solvent mixture. In the preparation of metal-free phthalocyanine **5**, the isoiminoindoline procedure is more convenient than the dicyano derivative route since the reaction condition employing isoiminoindoline is mild in comparison with that employing dicyano compound [26,29]. The formation of a phthalocyanine from four isoiminoindoline units involve the formation of four new C–N bonds. Using the respective isoiminoindoline, which exhibits higher reactivity, may be an advantage. The structure of the metal-free phthalocyanine was established through spectroscopic and elemental analyses data. In the ^1H NMR spectrum of **5**, the typical shielding of inner core protons was seen as a broad signal at around $\delta = -4.20$ ppm which could be attributed to the N–H resonances as confirmed by deuterium exchange. This spectrum closely resembles that of the precursor compound **3** as expected. The IR spectrum of **5** is very similar to that of **3** and contains the characteristic stretching peaks of aromatic and macrocyclic groups. The resonances at 3268 and 1040 cm^{-1}, belonging to N–H stretching and bending vibrations of metal-free phthalocyanine **5**, also support the proposed structure. In addition to the results of elemental analysis, the mass spectra were determined and the molecular ion peak at $m/z = 3359.9$ $[M]^+$ was found by the MS (ES^+) technique for the metal-free phthalocyanine **5**. All spectral data regarding the metal-free phthalocyanine **5**, that were obtained from isoiminoindoline derivatives **4**, closely resemble the compound **5**, as expected.

The formation of nickel phthalocyanine derivative **6**, anhydrous $NiCl_2$ and metal-free phthalocyanine **5** were reacted in dry 2-(dimethylamino)ethanol at reflux temperature under dry argon atmosphere in a standard Schlenk tube to afford 61% yield. The syntheses of metallophthalocyanines **7** and **8** were achieved by reacting **3** and the corresponding metal salts: $Zn(CH_3COO)_2 \cdot 2H_2O$ and $CuCl_2$ separately in dry *n*-pentanol in the presence of a few drops of DBU as a strong base at reflux temperature under dry argon. Column chromatography was applied to purify compound **8** on neutral alumina using chloroform:methanol (1:1, v/v) as eluent to afford 42% yield. Copper phthalocyaninate complex **7** was eluated on neutral alumina using chloroform:methanol (100:1) as eluent and obtained with the yield of 48%. The ^1H NMR spectrum of **10** was very similar to that of the metal-free phthalocyanine **5** except for the disappearance of the N–H protons. The N–H band in IR spectrum of **5** at 3268 cm^{-1} also vanished in the case of compound **6**. The ^1H NMR spectra of **7** and **8** were similar to those of the precursor dicyano compound **3**. ^1H NMR measurements are precluded because of the paramagnetic nature of the copper(II) phthalocyanine **8**. The peak at $\delta = 115.4$ ppm related to the C≡N groups in the ^{13}C NMR spectrum of **3** vanished in the case of complexes **7** and **8**. The ^{13}C NMR spectrum of **6** was almost identical with that of the metal-free phthalocyanine **5**. Cyclotetramerization of the dinitrile compound **3** into **7** and **8** was confirmed by the disappearance of the sharp C≡N stretching vibration in the IR spectra at 2230 cm^{-1} of the precursor dicyano derivative **3**. The rest of the IR spectra of **7** and **8** closely resemble that of **3**, including the characteristic vibrations of aliphatic and aromatic groups. The mass spectra of **6**, **7** and **8** were obtained by the MS (ES^+) technique. In positive scan mode the metallophthalocyanines showed a peak corresponding to $[M+1]^+$ at $m/z = 3417.7$ for **6**, a peak corresponding to $[M+1]^+$ at $m/z = 3424.4$ for **7** and a peak corresponding to $[M+1]^+$ at $m/z = 3422.5$ for **8**. The results of elemental analysis and the mass spectral data for the metallophthalocyanines **6**, **7** and **8** confirmed that the ratio of reactants was 1:1 metal:ligand [30–32].

The electronic absorption spectrum of the metal-free phthalocyanine **5** in pyridine at room temperature is shown in Fig. 1. It displayed the split Q-band as expected and there are two strong bands in the Soret region [33]. The split Q-band, characteristic of metal-free phthalocyanines, is observed at $\lambda_{max} = 716$ and 688 nm with a shoulder at 652 nm, indicating the monomeric species; the monomeric species with D_{2h} symmetry shows two intense absorptions at around 700 nm [34–38].

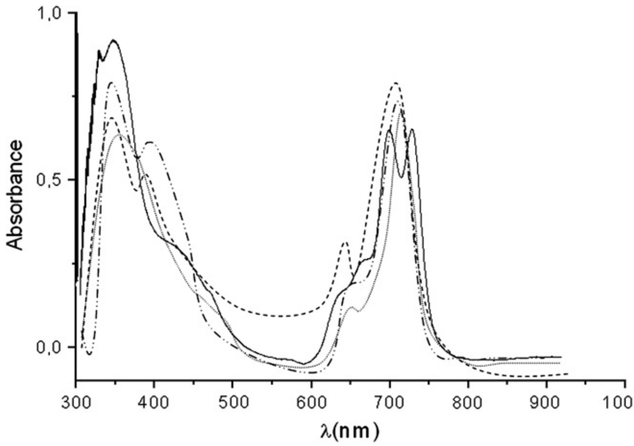


Fig. 1. UV–vis spectra. Metal-free (——), CuPc (·········), ZnPc (- - - -) and NiPc (— · · — · ·).

On the other hand, such split Q-band absorptions in pyridine are due to $\pi \rightarrow \pi^*$ transition of these fully conjugated 18π electron systems [8]. The nickel(II) **6**, zinc(II) **7** and copper(II) **8** phthalocyanine complexes showed the expected absorptions (Fig. 1) at the main peaks of the Q- and B-band appearing at $\lambda_{\max} = 685$, 695, 703 nm and 386, 382, 351 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [39,40], which is observed as a single band of high intensity in the visible region. Upon dilution (*ca.* 1×10^{-6} M), the absorption spectra of these compounds displayed significant changes in band positions and molar absorptivities [41]. Increasing the concentration (from 1×10^{-4} to 1×10^{-5} M) led to aggregation, which is easily monitored by the position of the Q-band, which shifted to shorter wavelengths and showed a decrease in molar absorption coefficient.

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