

Synthesis and characterization of new metal-free and metallophthalocyanines containing macrocyclic moieties

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Abstract

The synthesis and characterization of new metal-free **7** and metallophthalocyanines **8**, **9** carrying macrocyclic $N_2S_2O_4$ donor groups on peripheral positions have been investigated. Phthalonitrile derivative **6** was synthesized according to Rosenmund von Braun procedure from compound **5**. The novel compounds were characterized by elemental analysis, IR, 1H and ^{13}C NMR, UV–Vis and MS spectra data.

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1. Introduction

Phthalocyanines and structurally related compounds exhibit properties which are interesting for applications in various fields of material sciences [1]. For example, phthalocyanines are used in laser-beam printers and photocopiers [2], in nonlinear optics [3], as liquid crystals [4], as photosensitizers [5], in optical data storage [6], as gas sensors [7], as electrochromic substances [8] and as carrier generations materials in near infrared (NIR) [9]. Tetra- and symmetrically octasubstituted derivatives are useful compounds in nonlinear optics [10,11] as Langmuir–Blodgett (LB) films [12–16] as well as organic semiconductors. Specificity in the applications of phthalocyanines can be introduced by modification of the phthalocyanine ring or changes in the central metal. Remarkable progress has been made in recent years in the use of phthalocyanine derivatives as sensitizers for photodynamic therapy (PDT) of cancer [17,18]. As the second generation photosensitizers for photodynamic therapy (PDT) in the treatment of cancer, phthalocyanines, particularly the aluminum and zinc derivatives, are the most recently studied [19]. By controlling the kinds of central

metal ions or introducing appropriate substituents on the phthalocyanine ring, soluble complexes have been prepared, and some studies such as redox, photocatalytic, and oxidative catalytic reactions have been reported [20–24]. Macrocyclic ligands containing both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems. As might be anticipated, the macrocyclic polyamino polythioether ligands exhibit an interesting range of properties intermediate between those of macrocyclic polythioethers and macrocyclic polyamines [25,26].

We have previously described the synthesis of novel metal-free phthalocyanines and metallophthalocyanines bearing four 27-membered dioxadiazapentathia macrocyclic moieties on peripheral positions [27]. In the present paper, we have discussed the synthesis, characterization and structural investigation of these novel symmetrical phthalocyanine and its nickel(II) and cobalt(II) derivative.

2. Results and discussion

The amine groups of 2,2'-(propane-1,3-diylbis(sulfanediy))diethanamine (**1**) were then tosylated in pyridine

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at $-10\text{ }^{\circ}\text{C}$ with *p*-toluenesulfonylchloride (**2**) to protect amino groups and to make use of the high reactivity of tosylamides in cyclization reactions. In the IR spectra of **1** the intense absorption bands at $3365\text{--}3291\text{ cm}^{-1}$ for **1** corresponding to the --NH_2 groups, disappear after the conversion to the tosylamido compounds. In the IR spectrum of **3**, the intense absorption band at 3272 cm^{-1} corresponds to the N–H stretching vibration. Mass spectrum and elemental analysis also confirm the formation of **3** $m/z = 541\text{ [M+K]}^+$.

As in the case of most other phthalocyanines containing macrocyclic moieties, a convenient method for similar compounds is to start with the dibromo or dicyano derivatives of the corresponding macrocyclic units. For this aim, **3** was reacted with 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**4**) [29] in dry acetonitrile containing finely ground anhydrous Cs_2CO_3 as a template agent at reflux temperature in a Schlenk system under a nitrogen atmosphere to give the **5** in 62% yield. The relatively high yield of this macrocyclization reaction between two bifunctional reactants is clear indication of the template effect of the caesium ion. On the other hand, tosylation of aza groups, which are used as protective groups of aza functions in the cyclotetramerization, is also effective in the cyclization. Analytical and spectroscopic data of **5** clearly confirm the success of the cyclization reaction. In the ^1H NMR spectrum of **5** the chemical shifts of NH protons in precursor compound **3** disappear after the macrocyclization reaction. The other resonances in the ^1H and ^{13}C NMR spectra, concerning methyl, methylene and aromatic protons and carbons, are very similar to those of the precursor compounds **3**. The ^1H NMR spectrum of a CDCl_3 solution of **5** was well resolved and showed that the formation of this macrocycle was accomplished. The chemical shifts belonging to the deuterium exchangeable NH groups at $\delta = 5.36\text{ ppm}$ disappear after the condensation reaction between **3** and **4**. The differences between the infrared spectra of the precursor compounds and the macrocycle is clear from the presence of characteristic vibrations such as Ar–O–C (1089 cm^{-1}), and the absence of N–H (3272 cm^{-1}) stretching vibrations. The new macrocyclic **5** exhibited a molecular ion peak at $m/z = 823\text{ ([M+1]}^+)$, which supports the structure. The elemental analysis was confirm desired compound **5**.

19,20-Dicyano substituted macrocycle which synthesized by treating the dibromo compound **5** with three equivalents of CuCN according to Rosenmund von Braun reaction [30] in a moderately high-boiling solvent such as DMF at $150\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. After this reaction, the desired compound **6** was purified by column chromatography on silica gel using chloroform as eluent, was completed in 76% yield. In the IR spectrum of **6**, the intense absorption band at 2229 cm^{-1} corresponds to the C \equiv N stretching vibrations. The ^1H NMR spectrum of **6** closely resembles that of the precursor compound **5** as expected. The ^{13}C NMR spectrum of **6** shows the presence of nitrile carbon atoms at $\delta = 115.85\text{ ppm}$ which indicates the completion of conversion of **5**–**6**. FAB mass spectrum

and elemental analysis also confirm the formation of compound **6**.

Starting from the dicyano derivatives, many chemical routes may be used to form the corresponding metal-free phthalocyanine. The self-condensation of the dicyano compound **6** in the presence of a few drops of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as a strong base at $198\text{ }^{\circ}\text{C}$ under nitrogen atmosphere afforded the metal-free phthalocyanine **7** in 25% yield as a green solid after purification by column chromatography on silica gel [ethanol:chloroform (3:7)]. A diagnostic feature of the formation of **7** from **6** is the disappearance of the sharp C \equiv N vibration at 2229 cm^{-1} of the reactant. The stretching vibrations at 3335 cm^{-1} for **7** can be attributed to the N–H band of the inner core of the metal-free phthalocyanine. The ^1H NMR spectra of this compound the inner core protons of Pc-2H could not be observed due to strong aggregation of molecules [31]. The mass spectrum of this compound at $m/z = 2862\text{ [M+1]}^+$ support to the proposed formula for this structure. The elemental analysis were confirm desired compound **7**.

The synthesis of NiPc **8** was accomplished by reacting **6** and the anhydrous NiCl_2 salt in the presence of a few drops of DBU as a strong base at $198\text{ }^{\circ}\text{C}$ temperature under nitrogen. Column chromatography with [ethanol:chloroform (3:7)] as eluents removed the nickel phthalocyanine formed by self-condensation of **8** in 37% yield. The NMR characteristics of this compound were similar to those of the precursor dicyano compound **6** and the metal-free phthalocyanine **7**. The IR spectrum of **8** clearly indicates the disappearance of the C \equiv N groups stretching vibration at 2229 cm^{-1} of the precursor dicyano derivative after the conversion of **6** to nickel phthalocyanine **8**. The mass spectrum of **8** at $m/z = 2918\text{ [M]}^+$. The elemental analysis were confirm desired compound **8**.

The synthesis of CoPc **9** was accomplished by reacting **6** and the anhydrous CoCl_2 salt in 2-(dimethylamino)ethanol at $175\text{ }^{\circ}\text{C}$ temperature under microwaves (350 W power) for 10 min. Column chromatography with [ethanol:chloroform (3:7)] as eluents removed the cobalt phthalocyanine formed by self-condensation of **6** in 31% yield. The NMR characteristics of this compound were similar to those of the precursor dicyano compound **6** and the metal-free phthalocyanine **7**. The IR spectrum of **9** clearly indicates the disappearance of the C \equiv N groups stretching vibration at 2229 cm^{-1} of the precursor dicyano derivative after the conversion of **6** to cobalt phthalocyanine **9**. The mass spectrum of **9** at $m/z = 2955\text{ [M+2H}_2\text{O+1]}^+$.

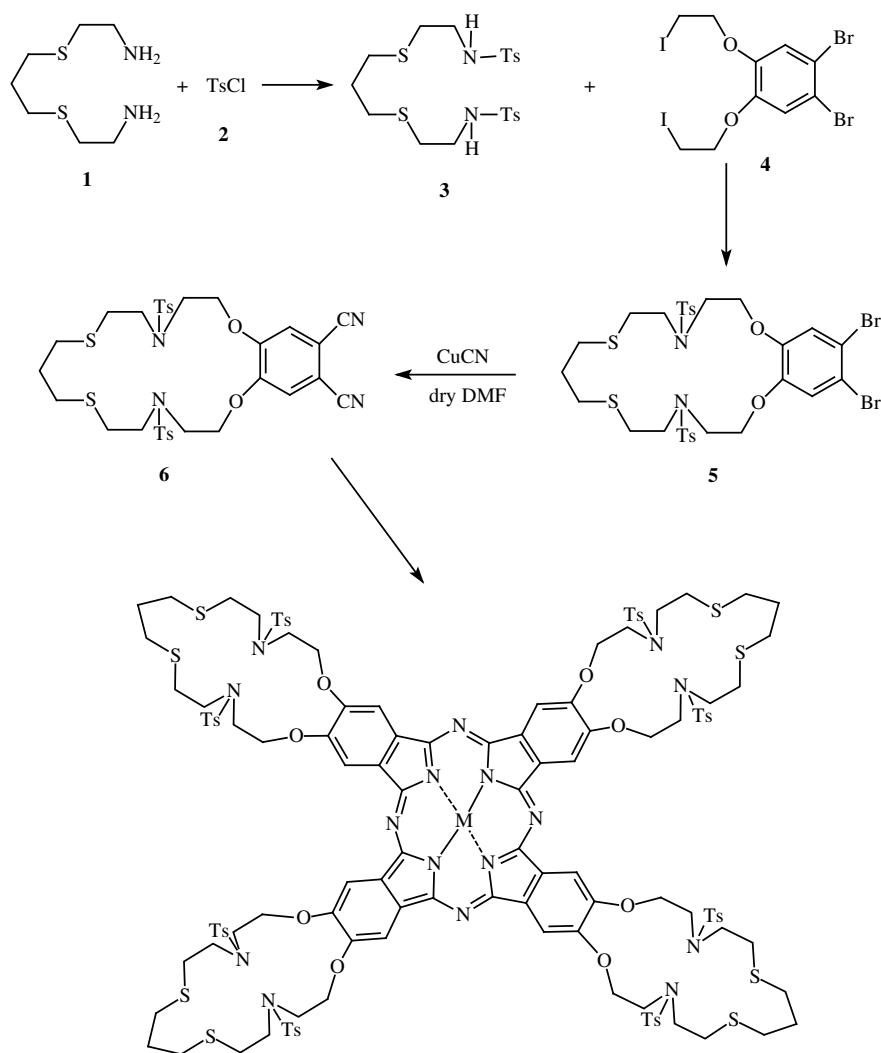
Phthalocyanines (**7**–**9**) show typical electronic spectra with two different strong absorption regions. The first, in the UV region at around 340 nm and called the Soret (or B) band [32], arising from the deeper π levels \rightarrow LUMO transition between an a_{2u} and the same eg orbitals and extending to the blue of the visible spectrum, is generally much less intense. The second, in the visible region at 600–700 nm and called the Q band, is attributed to the $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO of the

Pc^{2-} ring [33,34]. The purity and depth of colour of phthalocyanines arise from an isolated Q band at the far-red end of the visible spectrum [35]. The electronic absorption spectrum of the metal-free in chloroform at room temperature is shown in Fig. 1. The split Q bands in **7**, which are characteristic of metal-free phthalocyanines were observed at $\lambda_{\text{max}} = 705, 680$ and 632 nm. These Q band absorptions show the monomeric species with D_{2h} symmetry due to the phthalocyanine ring being related to the fully conjugated 18π electron system [36–38]. The metal-free phthalocyanine **7** showed B-band regions in chloroform appeared as an intense peak at 278 nm with a shoulder at around 338 nm.

plexes of substituted and unsubstituted phthalocyanine with D_{4h} symmetry [40] (see Tables 1 and 2).

3. Experimental

All reactions were carried out under a dry nitrogen atmosphere using Standard Schlenk techniques. The IR spectra were recorded on a Perkin–Emler 1600 FTIR Spectrophotometer, using potassium bromide pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $\text{DMSO-}d_6$ or CDCl_3 , and chemical shifts are reported (δ) relative to Me_4Si as internal Standard. Mass spectra were measured on a Varian 711



The UV–Vis absorption spectra of the metallophthalocyanines **8** and **9** show intense Q band absorptions at λ_{max} 674 and 677 nm, with weaker absorptions at λ_{max} 629 and 614 nm, respectively. The single Q bands in metallo derivatives and the split form in their metal-free derivatives are characteristic [39]. The result is typical of metal com-

plexes of substituted and unsubstituted phthalocyanine with D_{4h} symmetry [40] (see Tables 1 and 2). The UV–Vis absorption spectra were measured by a Unicam UV–Vis spectrometer. Melting points were measured on an Electrothermal apparatus.

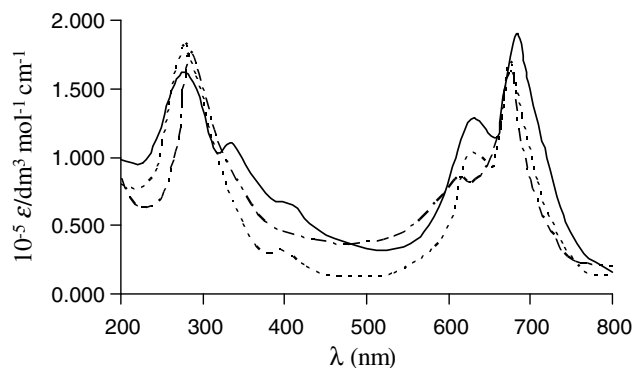


Fig. 1. UV-Vis spectra of H₂Pc (—), NiPc (.....) and CoPc (---) complexes.

Table 1
Electronic spectra of metal-free phthalocyanine and phthalocyanine complexes in chloroform

Compound	λ_{\max} (nm)	$10^{-4} \epsilon$ (dm ³ mol ⁻¹ cm ⁻¹)		
7	278 (5.21)	338 (5.03)	632 (5.10)	683 (4.28)
8	278 (5.26)	395 (4.50)	629 (5.01)	674 (5.23)
9	284 (5.24)	614 (4.92)	677 (5.21)	

3.1. Synthesis of *N,N'*-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (**3**)

Compound of 2,2'-(propane-1,3-diylbis(sulfanediyl))dithanamine (**1**) [28] (0.45 g, 2.31 mmol) was dissolved in pyridine (20 mL) under nitrogen and a solution *p*-toluenesulfonylchloride (**2**) (1.2 g, 5.79 mmol) in pyridine (5 mL) was added dropwise over a period of 1 h at -10 °C. Stirring and cooling of the reactions mixture was continued for 3 h at -10 °C, then the mixture was stirred at room temperature overnight. The solution was poured slowly on ice (100 g) and diluted with water (100 mL) and then extracted with chloroform (3 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered and the concentrated. The product was chromatographed on silica gel with chloroform as eluent. Yield: 0.91 g (78%). Anal. Calc. for C₂₁H₃₀N₂O₄S₄: C, 50.17; H, 6.01; N, 5.57; S, 25.51. Found: C, 50.73; H, 6.13; N, 5.19; S, 25.50%. IR(NaCl disk) ν_{\max} /cm⁻¹: 3272 (N–H), 3056 (Ar–H), 2922–2852 (Aliph. C–H), 1596, 1458, 1288, 1150, 1089, 812. ¹H NMR (CDCl₃), (δ : ppm): 7.76 (d, 4H, Ar–H), 7.31 (d, 4H, Ar–H), 5.36 (s, 2H, NH), 3.07 (t, 4H, N–CH₂), 2.59 (m, 4H, S–CH₂), 2.56 (m, 4H, S–CH₂), 2.41 (s, 6H, CH₃), 1.24 (m, 2H, CH₂). ¹³C NMR

Table 2
The spectral IR data of new compounds

Compound	N–H	Ar–H	Aliph.–C–H	C≡N	C=N	C=C	C–O	C–Br
3	3272	3056	2922–2852					
5		3062	2924–2854			1493	1251–1198	651
6		3060	2925–2855	2229		1564	1287–1153	
7	3335	3072	2921–2851		1637	1484	1204–1156	
8		3072	2927–2856		1645	1454	1206–1159	
9		3075	2924–2858		1638	1462	1208–1156	

(CDCl₃), (δ : ppm): 145.55 (Ar–C), 143.59 (Ar–C), 138.96 (Ar–C), 129.80 (Ar–CH), 127.07 (Ar–CH), 42.04 (N–CH₂), 32.31 (S–CH₂), 30.16 (S–CH₂), 21.57 (CH₃). MS, (*m/z*): 541 [M+K]⁺.

3.2. Synthesis of 19,20-dibromo-4,14-ditosyl-3,4,5,6,8,9,10,12,13,14,15,16-dodecahydro-2H-benzo[*b*][1,4,10,14,7,17]dioxadithiadiazacyclononadecine (**5**)

Compound of **3** (0.86 g, 1.72 mmol) was dissolved in dry acetonitrile (50 mL) containing finely ground anhydrous Cs₂CO₃ (1.68 g, 5.16 mmol) and purged under nitrogen in a schlenk system. This solution was stirred at 50 °C and a solution 1,2-bis(2-iodo-ethoxy)-4,5-dibromobenzene (**4**) (0.99 g, 1.72 mmol) in dry acetonitrile (30 mL) was added dropwise over a period of 3 h at reflux temperature (90 °C). The reaction was monitored by TLC using acetone/chloroform/petroleum ether (2:3:5) and was complete in 6 days at the reflux temperature. At the end of this period the solvent was removed under reduced pressure, mixed with water (50 mL) and then extracted with chloroform (3 × 50). The combine extract was washed with water, dried over Na₂SO₄ and filtered and evaporated to dryness. Finally the oily product was obtained. The product was chromatographed on silica gel with chloroform as eluent. This compound was soluble in chloroform, dichloromethane, dimethyl formamid. Yield: 0.87 g (62%). Anal. Calc. for C₃₁H₃₈Br₂N₂O₆S₄: C, 45.26; H, 4.66; N, 3.41, S, 15.59. Found: C, 45.84; H, 3.98; N, 3.12; S, 15.76%. IR(NaCl disk) ν_{\max} /cm⁻¹: 3062 (Ar–H), 2924–2854 (Aliph. C–H), 1642, 1582, 1493, 1338, 1251, 1156, 814. ¹H NMR (CDCl₃), (δ : ppm): 7.66 (d, 4H, Ar–H), 7.25 (d, 4H, Ar–H), 7.04 (s, 2H, Ar–H), 4.13 (t, 4H, O–CH₂), 3.51 (t, 4H, N–CH₂), 3.39 (t, 4H, N–CH₂), 2.74 (m, 4H, S–CH₂), 2.56 (m, 4H, S–CH₂), 2.41 (s, 6H, CH₃), 1.82 (m, 2H, CH₂). ¹³C NMR (CDCl₃), (δ : ppm): 147.58 (Ar–C), 129.93 (Ar–CH), 127.10 (Ar–CH), 117.45 (Ar–CH), 68.20 (O–CH₂), 50.52 (N–CH₂), 48.39 (N–CH₂), 30.49 (S–CH₂), 29.71 (S–CH₂), 29.20 (CH₂), 21.58 (CH₃). MS, (*m/z*): 823 [M+1]⁺.

3.3. Synthesis of 4,14-ditosyl-3,4,5,6,8,9,10,12,13,14,15,16-dodecahydro-2H-benzo[*b*][1,4,10,14,7,17]dioxadithiadiazacyclononadecine-19,20-dicarbonitrile (**6**)

A mixture of **5** (0.82 g, 0.99 mmol) and CuCN (0.27 g, 3 mmol) in dry DMF (10 mL) were refluxed under nitrogen

for 46 h. The mixture was cooled to room temperature and then poured into aqueous ammonia (20 mL, %25). After stirring for 4 h, the mixture was extracted with (2 × 50 mL) chloroform. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and filtered and the concentrated. After this reaction, the desired compound **6** was purified by column chromatography on silica gel using chloroform as eluent. Yield: 0.545 g (76%). Anal. Calc. for C₃₃H₃₈N₄O₆S₄: C, 55.44; H, 5.36; N, 7.84; S, 17.94. Found: C, 55.80; H, 5.41; N, 7.81; S, 17.92%. IR (NaCl disk) $\nu_{\max}/\text{cm}^{-1}$: 3060 (Ar–H), 2925–2855 (Aliph. C–H), 2229 (C≡N), 1591, 1564, 1514, 1456, 1287, 1153, 1088, 814. ¹H NMR (CDCl₃), (δ : ppm): 7.71 (d, 4H, Ar–H), 7.67 (d, 4H, Ar–H), 7.26 (s, 2H, Ar–H), 4.28 (t, 4H, O–CH₂), 3.57 (t, 4H, N–CH₂), 3.40 (t, 4H, N–CH₂), 2.74 (t, 4H, S–CH₂), 2.58 (t, 4H, S–CH₂), 2.42 (s, 6H, CH₃), 1.24 (m, 2H, CH₂). ¹³C NMR (CDCl₃), (δ : ppm): 151.29 (Ar–C), 144.11 (Ar–C), 130.91 (Ar–CH), 130.032 (Ar–CH), 129.54 (Ar–CH), 127.15 (Ar–CH), 122.78 (Ar–CH), 115.85 (C≡N), 68.53 (O–CH₂), 50.49 (N–CH₂), 48.21 (N–CH₂), 31.93 (S–CH₂), 30.16 (S–CH₂), 29.37 (CH₂), 22.71 (CH₃). MS, (m/z) = 714 [M]⁺.

3.4. Tetrakis [N,N'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide)-phthalocyanine] (7)

A mixture of dicyano compound **6** (0.2 g, 0.28 mmol) were placed in a Schlenk tube under nitrogen in the presence of DBU, gently heated, and subsequently heated at 198 °C for 5 h. After cooling to room temperature, the dark green solid product was precipitated by EtOH. The resulting dark green precipitate was washed with hot EtOH then MeOH. The green product was chromatographed on a silica gel with CHCl₃/EtOH (3:7, volume ratio) as eluent. Yield: 0.05 g (25%), m.p.: 210–213 °C. Anal. Calc. for C₁₃₂H₁₅₄N₁₆O₂₄S₁₆: C, 55.40; H, 5.42; N, 7.83; S, 17.93. Found: C, 55.22; H, 5.45; N, 7.58; S, 17.91%. IR (KBr pellets) $\nu_{\max}/\text{cm}^{-1}$: 3335 (N–H), 3072 (Ar–H), 2921–2851 (Aliph. C–H), 1597, 1458, 1377, 1284, 1156, 1089, 814. ¹H NMR (DMSO): (δ : ppm): 7.68 (m, 16H, Ar–H), 7.26 (s, 8H, Ar–H), 4.28 (t, 16H, O–CH₂), 3.40 (t, 16H, N–CH₂), 3.36 (t, 16H, N–CH₂), 2.86 (t, 16H, S–CH₂), 2.63 (t, 16H, S–CH₂), 2.41 (s, 24H, CH₃), 1.24 (m, 24H, CH₂). UV–Vis [(in chloroform) λ_{\max}/nm 10⁻⁵ ϵ (mol⁻¹ cm⁻¹): 683 (4.28), 632 (5.10), 338 (5.03), 278 (5.21). MS; m/z = 2862 [M+1]⁺.

3.5. Tetrakis [N,N'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide)-phthalocyaninato] nickel(II) (8)

A mixture of dicyano compound **6** (0.15 g, 0.21 mmol) and anhydrous NiCl₂ (0.0067 g, 0.052 mmol), was placed in a Schlenk tube under nitrogen in the presence of

DBU, gently heated, and subsequently heated at 198 °C for 5 h. After cooling to room temperature, the dark green solid product was precipitated by EtOH. The resulting dark green precipitate was washed with hot EtOH then MeOH. The green product was chromatographed on a silica gel with CHCl₃/EtOH (3:7, volume ratio) as eluent. Yield: 0.057 g (37%). Anal. Calc. for C₁₃₂H₁₅₂N₁₆NiO₂₄S₁₆: C, 54.32; H, 5.25; N, 7.68; S, 17.58. Found: C, 54.35; H, 5.29; N, 7.70; S, 17.56%. IR (NaCl disk) $\nu_{\max}/\text{cm}^{-1}$: 3072 (Ar–H), 2927–2856 (Aliph. C–H), 1592, 1454, 1323, 1206, 1159, 1107, 984, 898. ¹H NMR (CDCl₃): (δ : ppm): 7.68 (m, 16H, Ar–H), 7.45 (s, 8H, Ar–H), 4.16 (t, 16H, O–CH₂), 3.43 (t, 16H, N–CH₂), 3.21 (t, 16H, N–CH₂), 2.74 (t, 16H, S–CH₂), 2.49 (t, 16H, S–CH₂), 2.12 (s, 24H, CH₃), 1.21 (m, 24H, CH₂). UV–Vis [(in chloroform) [(10⁻⁵ ϵ dm³ mol⁻¹ cm⁻¹): 674 (5.23), 629 (5.01), 395 (4.5), 278 (5.26). MS; m/z : 2918 [M]⁺.

3.6. Tetrakis [N,N'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide)-phthalocyaninato] cobalt(II) (9)

A mixture of dicyano compound **6** (0.15 g, 0.21 mmol) and anhydrous CoCl₂ (0.0067 g, 0.053 mmol), was placed in a tube. The solid was then irradiated under microwaves (350 W power) for five to fifteen minutes. The dark green product was obtained. After cooling to room temperature, the dark green solid product was precipitated by EtOH. The resulting dark green precipitate was washed several times with hot EtOH–MeOH. The green product was chromatographed on a silica gel with CHCl₃/EtOH (3:7, volume ratio) as eluent. Yield: 0.047 g (31%), m.p.: 274–276 °C. Anal. Calc. for C₁₃₂H₁₅₂CoN₁₆O₂₄S₁₆: C, 54.32; H, 5.25; N, 7.68; S, 17.58. Found: C, 54.40; H, 5.27; N, 7.70; S, 17.54%. IR (KBr pellets): $\nu_{\max}/\text{cm}^{-1}$: 3075 (Ar–H), 2924–2858 (Aliph. C–H), 1594, 1462, 1339, 1156, 1075, 948, 897, 782. UV–Vis [(in chloroform) [(10⁻⁵ ϵ dm³ mol⁻¹ cm⁻¹): 677 (5.21), 614 (4.92), 284 (5.24). MS; m/z : 2955 [M+2H₂O+1]⁺.

4. Conclusion

We have presented new dicyano starting materials (ligands) and their conversion to metallophthalocyanines that are soluble in a number of solvents. For this, N,N'-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (**3**) was reacted with 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**4**) in dry acetonitrile containing finely ground anhydrous Cs₂CO₃ as a template agent to give the Synthesis of 19,20-dibromo-4,14-ditosyl-3,4,5,6,8,9,10,12,13,14,15,16-dodecahydro-2H-benzo[*b*][1,4,10,14,7,17]dioxadithiadi azacyclononadecine (**5**). The dicyano compound (**6**) is obtained from the dibromo derivative by refluxing in DMF with three equivalents of CuCN. Starting from **6**, metal-free **7**, nickel(II) phthalocyanines **8** and cobalt(II) phthalocyanines were prepared.

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