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The Synthesis and Properties of New Metal-free and Metallophthalocyanines Containing Four Diloop Macrocyclic Moieties

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The synthesis and characterization of new metal-free (9) and metal-containing (Zn, Ni or Cu 10, 11, 12) derivatives of a symmetrically octasubstituted phthalocyanine derived from 21,22-dicyano-2,3,5,6,8,9,11,12,15,17,18,25,26,28-tetradecahydro[1,4,7,12] benzodioxadithiacyclotetradeceno[6,7-b][1,4,7,10,13]benzopentaoxacyclopentadecene (7), which was synthesized in a multi-step reaction sequence, have been described. The novel compounds have been characterized by a combination of elemental analysis, ¹H and ¹³C NMR, IR, UV–vis and MS spectral data.

Keywords: Diloop macrocycle; Phthalocyanine derivatives; Isoiminoindoline; Nickel (II); Copper(II); Zinc(II)

INTRODUCTION

Metal-free and metallophthalocyanines, which have been the subject of a great interest topics for over 60 years, have a decisive disadvantage for very limited solubility in common organic solvents [1–3]. In order to improve the solubility of phthalocyanines, it is important to reduce its stacking propensity. The solubility of phthalocyanines can be enhanced by introducing different kinds of solubility-enhancing substituents at the peripheral or axial positions of the phthalocyanines core [4,5]. The peripheral substitution of aromatic rings by the introduction of lipophilic long alkyl, alkoxy, phenoxy groups, crown ethers or azacrown moieties makes it impossible for phthalocyanines to form dimers because of steric hindrance, which thus increase the solubility of them in common organic solvents [6–9]. These compounds have found wide applications in diverse area

as such as biomedical agents for diagnosis and therapy, dyes for ink jet printing, textile and paper, liquid crystals, Langmuir–Blodgett films, electronic devices, molecular metals, gas and chemical sensors, nonlinear optics, electrochromic devices, photosensitisers and ladder polymers [10–13].

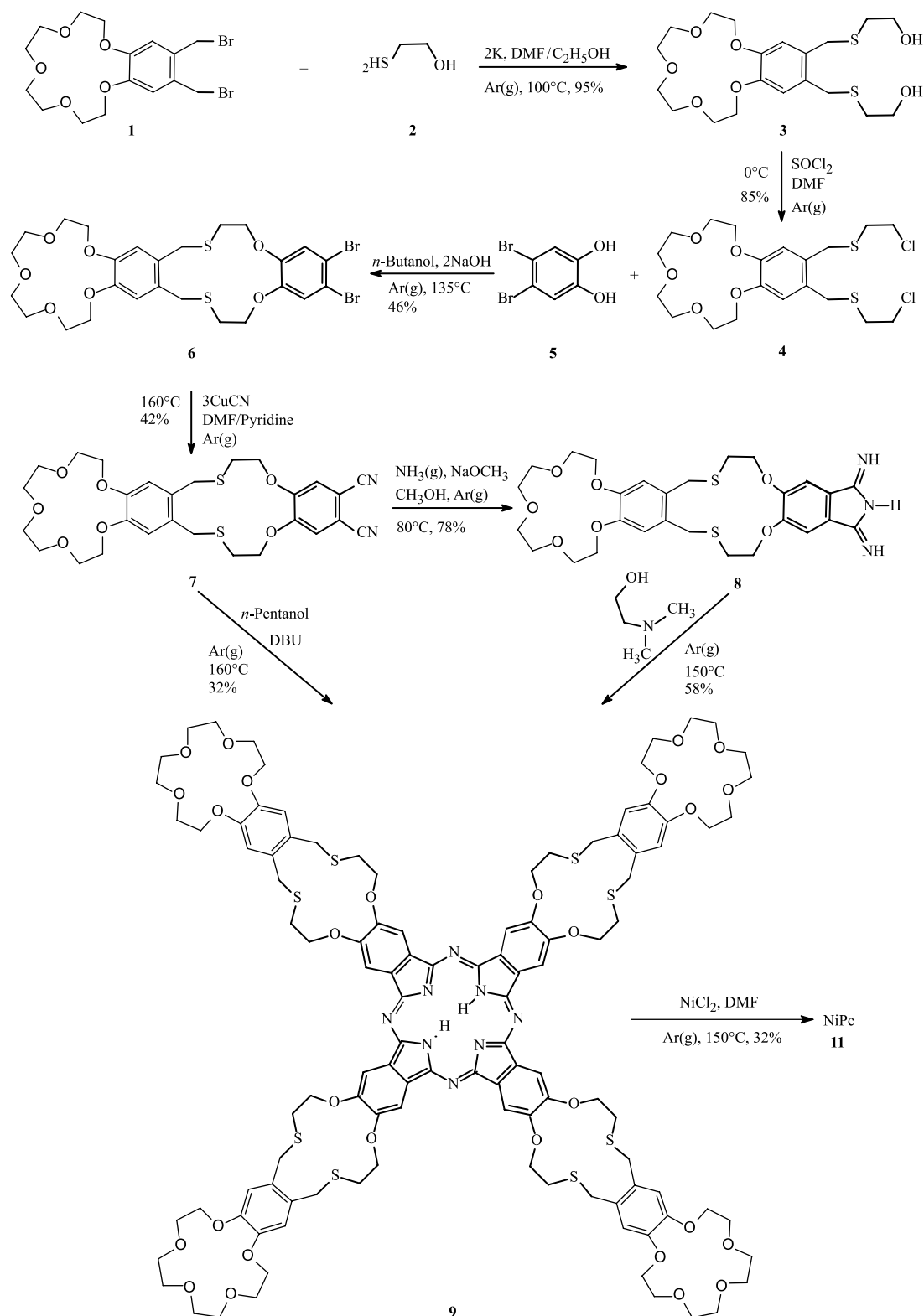
A part of the present paper reports the synthesis of metal-free phthalocyanine containing four diloop macrocycle moieties in the molecule; a preliminary account of this study has been reported [14]. In this way, we have designed a novel molecule carrying four 14-membered dioxadithiamacrocycles each of which is attached to a benzo-15-crown-5 unit as two-layered substituents. In addition, the complexation ability of this is the major opportunity offered by this new compound.

In this study, describing the synthesis and characterization of metal-free and metallophthalocyanines suggesting the suitable combination of 14-membered mixed donor macrocycle, crown ether and phthalocyanine may allow new functionalized material to be prepared, while the combination of these two different donor rings is expected to result in the coordination of both alkali and transition metal ions in the same molecule.

RESULTS AND DISCUSSION

The synthetic route to 1–12 are summarized in Schemes 1–3. 15,16-Bis{[(2-hydroxyethyl)thio]-methyl}-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopenta-decene 3 was prepared by the

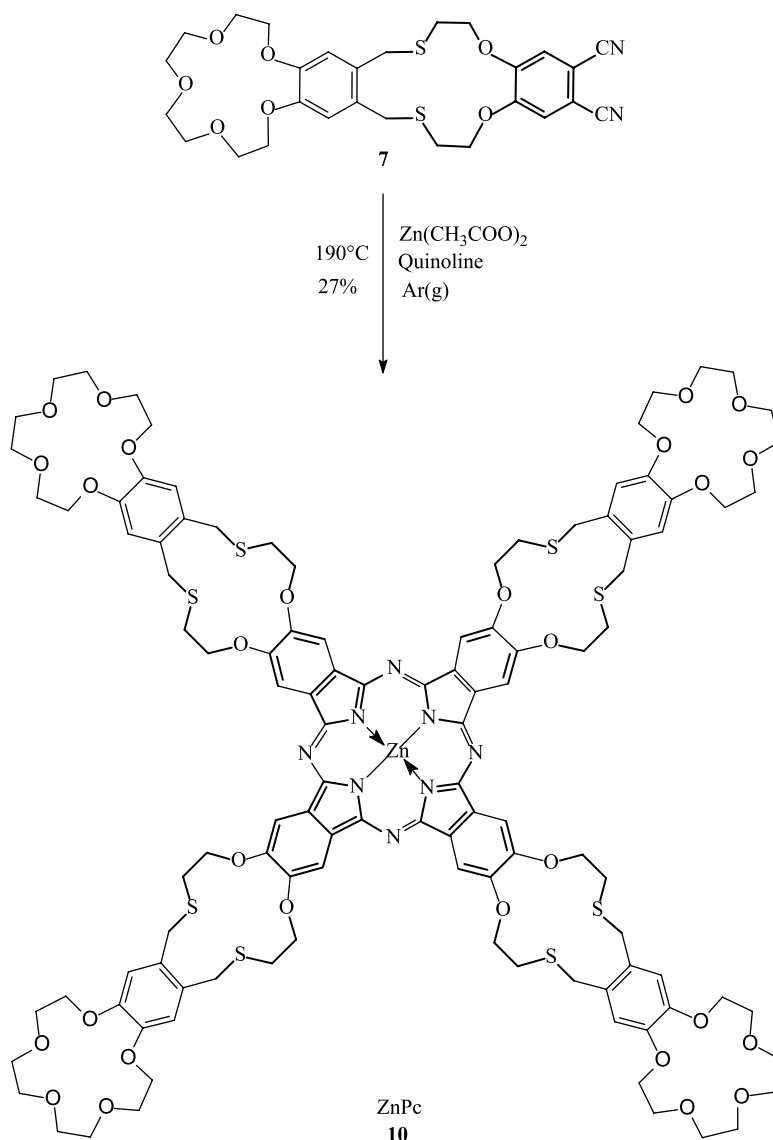
*Corresponding author. E-mail: yasar@ktu.edu.tr



SCHEME 1 Synthesis of metallo and metal-free phthalocyanines.

reaction of 2,3-bis(bromomethyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene **1** [15] with 2-mercapto ethanol **2** in the presence of potassium in dry DMF at reflux temperature under argon for 52 h afforded desired

compound (**3**) in quantitative yield. This new derivative was characterized by its spectroscopic and analytical data. ^1H NMR spectrum of **3** showed characteristic signals for SCH_2 and HOCH_2 protons at $\delta = 2.69$ and 3.67 ppm, respectively. The ^{13}C NMR



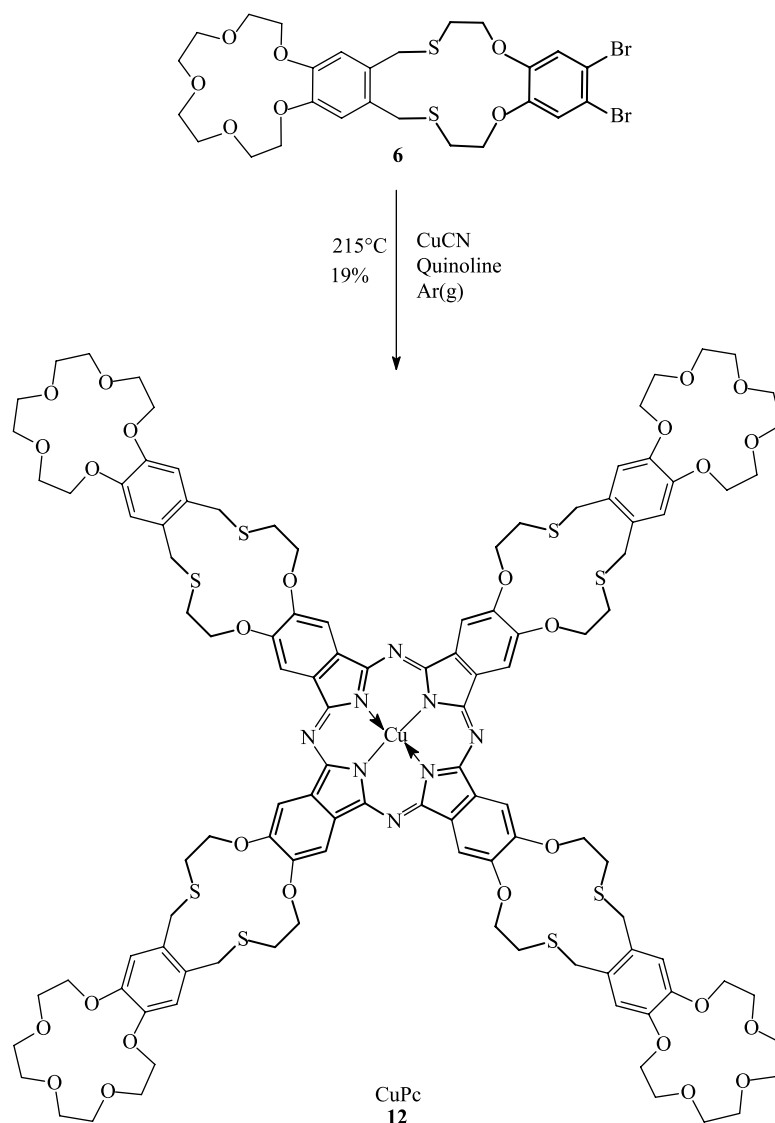
SCHEME 2 Synthesis of ZnPc.

spectrum of this compound also clearly indicates the presence of expected signals related to the above-mentioned groups at $\delta = 34.87$ and 60.71 ppm, respectively. The absence of S–H and the presence of O–H stretching vibrations in the IR spectrum confirmed the formation of **3**. The EI mass spectrum of this compound exhibited a molecular ion peak at $m/z = 448$ $[M]^+$, which also supports the same structure.

The conversion of **3** into the chloro derivative **4** was achieved in %86 overall yield when **3** was reacted with freshly distilled SOCl_2 in dry DMF at 0°C after the removal of the solvent and final purification by recrystallization from ethanol to afford **4**. The mass spectrum shows the parent ion at $m/z = 485$, which confirmed the $[M]^+$. The IR spectrum features a strong band at 655 cm^{-1} attributable to the $-\text{CH}_2\text{Cl}$ groups. The signals of protons and carbons in the ^1H or ^{13}C NMR

spectra of **4** are very similar to those of the precursor compound **3** except for the signals of carbons and protons connected to halogens at $\delta = 43.11$ and 3.57 ppm, respectively.

The diloop macrocycle 21,22-dibromo-2,3,5,6,8,9,11,12,15,17,18,25,26,28-tetradecahydro[1,4,7,12]benzodioxadithiacyclotetradeceno[6,7-b][1,4,7,10,13]benzopentaoxacyclopentadecene **6** was obtained by the cyclization reaction from **4** with 4,5-dibromocatechol **5** [16] in the presence of NaOH as a template agent and in dry DMF at reflux in a Schlenk tube under argon. The crude product was purified by column chromatography [silica gel, chloroform: ethyl acetate (7:2)] to give **6** in 46% yield. In the ^1H NMR spectrum of **6**, the signals concerning OH protons in the precursor compound (**5**) disappeared after the macrocyclization reaction. A singlet at $\delta = 4.32$ ppm corresponds to the new aromatic group connected to OCH_2 groups. The present of new



SCHEME 3 Synthesis of CuPc.

carbon resonances at $\delta = 148.42$, 117.46 and 114.73 ppm are also in good agreement with the proposed structure. In addition, comparison of the infrared data of **4** and **6** gives sufficient support for the desired formation. The difference between the IR spectra of the precursor compound (**4**) and diloop macrocyclic moiety is clear from the presence of characteristic vibrations belonging to **4** or **5** such as Ar-H, OCH₂, C-Br at 3044, 2910–2881 and 656 cm⁻¹, respectively, and the absence of CH₂Cl or O-H (**5**) stretching vibrations. The mass spectrum (FAB positive, matrix *m*-nitrobenzyl alcohol) of **6**, which shows a molecular ion peak at $m/z = 681$ [M + 1]⁺, confirms the proposed structure and rules out any polymeric or different macrocyclic forms.

The dibromo derivative of diloop macrocycle **6** with three equivalent of CuCN in dry DMF afforded **7** according to the Rosenmund von Braun reaction [17–19], which was converted into the corresponding

dicyano derivative after purification by column chromatography [silica gel, chloroform: petroleum ether: methanol (6:2:1)] in 42% yield. In the IR spectrum of this compound, the intense absorption band at 2229 cm⁻¹ corresponds to the C≡N groups. The rest of the spectrum is closely similar to that of the precursor dibromo derivative, including the characteristic vibrations of **6**. The ¹H NMR spectrum of **7** was recorded after dissolution in CDCl₃ at room temperature, gave the expected signals, indicating the integrity of **7** in that solvent and almost identical with **6** as expected. The proton-decoupled ¹³C NMR spectrum of this compound, the presence of signal at $\delta = 115.06$ ppm attributable to C≡N group indicates that the conversion has occurred. This compound (**7**) displayed the expected molecular ion peak in its FAB spectrum at $m/z = 572.2$ [M]⁺.

The diloop macrocycle **7** was reacted with anhydrous ammonia in the presence of sodium

methoxide in refluxing dry methanol to give the corresponding isoiminoindoline **8**. The purification of this compound required column chromatographic separation on silica gel using chloroform:petroleum ether:methanol (7:2:1) as eluent and gave an oil product in 78% yield. The structure of **8** was inferred through the appearance of a broad signal in ^1H NMR spectrum at $\delta = 8.22$ ppm assignable for the imino groups which provided evidence for the formation of an isoiminoindoline. The disappearance of the $\text{C}\equiv\text{N}$ signals, in the ^{13}C NMR spectrum of **8**, along with the appearance of new signals at $\delta = 163.48$ ppm corresponding to $\text{C}=\text{NH}$ groups was in agreement with the proposed structure. The appearance of new stretching vibrations at 3353 cm^{-1} concerning with $\text{C}=\text{NH}$ groups and disappearance of the CN vibrations at 2229 cm^{-1} in the IR spectrum of **8** also suggested the formation of desired compound (**8**). The FAB mass spectral result confirms the isoiminoindoline containing diloop macrocyclic moiety nature of **8**, the most intense peak at $m/z = 590.3$ corresponding to $[\text{M} + 1]^+$.

Metal-free phthalocyanine (**9**) was synthesized by two different methods. In the first route, condensation of four isoiminoindoline derivatives (**8**) into metal-free phthalocyanine **9** was carried out in 2-(dimethylamino)ethanol at reflux temperature for 48 h in a Schlenk tube under argon to afford **9** in 58% yield as a dark green product after purification by column chromatography on silica gel [chloroform:methanol (9:1)]. In the second route, this compound was prepared directly by using dicyano derivative of diloop macrocycle (**7**). In the preparation of octasubstituted metal-free phthalocyanine (**9**), 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 [14,20]. The formation of a phthalocyanine from four isoiminoindoline involves the formation of four new C–N bonds. Using the respective isoiminoindoline, which exhibits higher reactivity, may be an advantage [21]. The structure of the metal-free phthalocyanine was established through spectroscopic and elemental analyses data. The IR spectrum of **9** reveals the presence of a N–H stretching vibration band at 3413 cm^{-1} and lack any bands assignable to the $\text{C}=\text{NH}$ function. The ^1H NMR spectrum of **9** displayed broad signals, and the inner core protons of the H_2Pc (**9**) could not be observed due to strong aggregation of the molecules [16]. The chemical shifts related to aromatic and aliphatic protons belonging to the diloop macrocyclic moieties and phthalocyanine skeleton gave significant absorptions characteristic of the proposed structure. This spectrum closely resembles that of the precursor compound (**8**). The mass spectrum (FAB positive) of **9** contained a strong peak at $m/z = 2291.3$ $[\text{M} + 1]^+$

for the parent ion, which can be attributed to the formation of H_2Pc (**9**).

To prepare the metallophthalocyanines ($\text{M} = \text{Zn}, \text{Ni}$), different routes have been employed in Schemes 1 and 2. The conversion into zinc(II) phthalocyanine (**10**) was carried out by treatment with equivalent amounts of $\text{Zn}(\text{CH}_3\text{COO})_2$ and corresponding dicyano compound (**7**) in high boiling solvent such as quinoline gave monomeric $ZnPc$ (**10**). The yield of the product (**10**) (27%) was fairly low as countered for phthalocyanine with other macrocyclic groups which can be attributed to the attachment of the bulky moieties such as diloop macrocycles [22–24]. Another efficient route based on this approach was used to prepare nickel(II) phthalocyanine (**11**). This method involves the equivalent amounts of anhydrous NiCl_2 and metal-free phthalocyanine (**9**) in dry DMF under argon atmosphere. Purification of the $NiPc$ (**11**), the solid product was passed through on alumina column. The final yield (32%) was lower than those obtained for phthalocyanines having other macrocyclic groups due to above-mentioned sterical hindrances. The elemental analysis and mass spectral data of **10** (m/z : 2354.5 $[\text{M} + 1]^+$) and **11** (m/z : 2346.4 $[\text{M}]^+$) are in accord with their calculated values. The NMR spectra of these compounds were almost identical with that of the metal-free phthalocyanine. The differences in the NMR spectra of H_2Pc , $NiPc$ and $ZnPc$ were the broad signals encountered in the case of compound **10** and **11** owing to the aggregation of planar phthalocyanine molecule at the considerable high concentration used for NMR measurement [25]. The other characteristics of these compounds were quite similar to those of the precursor dicyano compound and metal-free phthalocyanine. Cyclotetramerization of the dicyano compound (**7**) was confirmed by the disappearance of the sharp $\text{C}\equiv\text{N}$ stretching vibration at 2229 cm^{-1} . The IR spectrum of $NiPc$ is also very similar to that of the precursor H_2Pc except for the disappearance of the N–H vibration of phthalocyanine core.

Copper(II) phthalocyanine (**12**) has been synthesized directly from the dibromo derivative (**6**) and CuCN in a high boiling solvent such as quinoline. The crude product was washed several times with ethanol to remove the unreacted starting material and was subsequently treated with a solution of NaCN to separate the excess of CuCN . Although the yield of the crude product was a moderate yield, the purification steps were tedious and required a final chromatography with neutral alumina so the final yield (19%) was lower than that synthesized for phthalocyanine having similar two-fold macrocyclic units [26–28]. Comparison of the IR spectra obtained on **6** and **12** confirmed the conversion of bromo groups to characteristic skeleton moiety of phthalocyanine. In this case, the C–Br band at 656 cm^{-1} disappeared and $\text{C}=\text{N}$

stretching vibrations at 1645 cm^{-1} appeared. The mass spectrum of **12** was measured by LS-MS MS technique. In positive scan mode the complex showed a peak corresponding to $[M]^+$ at m/z : 2351.2 for **12**.

The UV-Vis absorption spectra of solution of metal-free (**9**) and metallophthalocyanines (**10–12**) The metal-free phthalocyanine (**9**) displayed a typical electronic spectrum with two significant absorption bands, one of them in the visible region at about 640–710 nm corresponding to the Q band, and the other in the UV, approximately at 300 nm. The Q band absorptions in chloroform: pyridine mixture (2:3) at $\lambda_{\text{max}} = 718, 682, 658$ and 641 nm and the other absorption at 303 nm are consistent with the results obtained previously for similar phthalocyanines [29]. The Q band absorption in present **9** can be attributed that the symmetry of the metal-free phthalocyanine is D_{2h} [30,31]. The bands between 300–500 nm show superimposed bands of phthalocyanine due to the existence of Soret band of phthalocyanine (*Pc*). The lower absorptions than the the typical Q bands at around 640 nm is due to the dimmeric association and up to 615 nm for higher aggregation [32–34].

The UV-Vis absorption spectra of metallophthalocyanines (**10–12**) in chloroform, pyridine–chloroform (3:1) mixture or pyridine, respectively, at room temperature are given in Fig. 1. These compounds showed the expected absorptions at the main peaks of the Q- and B bands appearing 693, 695, 678 and 290, 282, 285 nm. This result is typical of metal complexes of substituted and unsubstituted *Pc* with D_{4h} symmetry [35,36]. Although the *ZnPc* (**10**), *NiPc* (**11**) and *CuPc* (**12**) have a typical spectral pattern in the UV-Vis region for metallophthalocyanines, the *NiPc* and *CuPc* showed the new absorption bands at around 400 nm in addition of the B band [37,38]. These new bands are some-times observed which can be ascribed to metal-to-ligand charge transfer or ligand-to-metal charge transfer transitions due to metals having partially filled d orbitals.

EXPERIMENTAL

Unless otherwise stated, all operations were carried out under argon in a vacuum line or using standard Schlenk techniques 2,3-bis(bromomethyl)-6,7,9,10,12,13,15,16-octa-hydro-5,8,11,14,17-pentaoxabenzocyclopentadecene (**1**) and 4,5-dibromocatechol (**5**) were prepared according to the methods described in the literature [15,16]. Other reagents were commercially available and were used without further purification unless otherwise noted. All solvents were purified according to the standard procedure before use [39]. ^1H , ^{13}C NMR and IR spectra were recorded on a Varian XL-200 spectrometer in CDCl_3 or DMSO-d_6 and on a Perkin-Elmer Spectrum one spectrometer, respectively. The metal contents of the metallophthalocyanines were determined with a Unicam 929 AA spectrophotometer. Electronic spectra were recorded on a Unicam UV2-100 spectrophotometer. Mass spectra were measured on a Varian MAT 711 and on a Micromass Quatro LC/ULTIMA LC-MS MS spectrometers.

15,16-Bis[(2-hydroxyethyl)thio]methyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecene (**3**)

A solution of **1** (8.22 g, 15 mmol) in a mixture of DMF and ethanol [200 cm^3 (1:1)] was added dropwise to a solution of 2-mercapto ethanol potassium salt, prepared by the reaction of 2-mercapto ethanol (2.34 g, 30 mmol) with potassium (0.117 g, 30 mmol) in absolute ethanol (300 cm^3) under argon atmosphere at room temperature over a period of 3 h and the mixture was heated and stirred to 100°C for 52 h. At the end of this period, the reaction mixture was filtered, washed with dry ethanol and then evaporated to dryness under reduced pressure. The crude product was dissolved with chloroform (150 cm^3) and filtered off. The filtrate was evaporated to dryness and 100 ml of

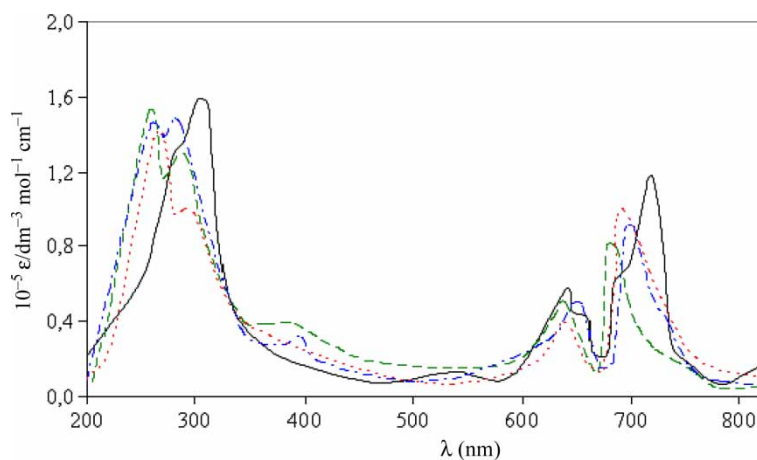


FIGURE 1 UV-Vis spectra of **9** (—), **10** (.....), **11** (- · - ·) and **12** (- - -).

water was added to this oily product and extracted with chloroform ($4 \times 75 \text{ cm}^3$). After drying over MgSO_4 , the solvent was evaporated to dryness under reduced pressure. The oily product was dissolved in a minimum amount of ethyl acetate (25 cm^3) and cooled to -18°C in a refrigerator for overnight to give a solid product. The crystalline solid which precipitated was isolated by filtration, dried *in vacuo* and then recrystallized from ethyl acetate yielding white needles and gave 6.42 g (95.6%) of the product: mp 105°C . IR (KBr, cm^{-1}): 3330, 3051, 2925–2871, 1594, 1517, 1455, 1349, 1277, 1216, 1120, 1046. ^1H NMR (CDCl_3): δ 6.81 (s, 2H, ArH), 4.85 (s, 2H, OH), 4.14 (t, $J = 4.48 \text{ Hz}$, 4H, ArOCH_2), 3.90 (m, 8H, OCH_2), 3.82 (t, $J = 5.32 \text{ Hz}$, 4H, OCH_2), 3.67 (t, $J = 4.33 \text{ Hz}$, 4H, HOCH_2), 2.92 (m, 4H, ArCH_2), 2.69 (t, $J = 4.35 \text{ Hz}$, 4H, SCH_2). ^{13}C NMR (CDCl_3): δ 148.13 (ArC), 130.91 (ArCO), 116.24 (ArCH), 70.95–68.13 (OCH_2), 60.71 (HOCH_2), 34.87 (SCH_2), 33.18 (ArCH_2). Found (calc. for $\text{C}_{20}\text{H}_{32}\text{O}_7\text{S}_2$): C, 53.42 (53.57); H, 7.32 (7.14). MS (EI) m/z : 448 $[\text{M}]^+$.

15,16-Bis[(2-chloroethylthio)methyl]-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecene (4)

Freshly distilled SOCl_2 (3.2 cm^3 , 43.5 mmol) was added dropwise to a solution of **3** (5.9 g, 13.2 mmol) in dry DMF (20 cm^3) at 0°C for 30 min. Then the stirring was continued at room temperature under argon atmosphere for 24 h. At the end of this period, 100 g of ice was added to this solution and stirred to room temperature. The reaction mixture was filtered, washed with a concentrate solution of NaHCO_3 and water and then dried *in vacuo*. The aqueous solution was extracted with chloroform ($3 \times 50 \text{ cm}^3$) and dried over MgSO_4 and then filtered and evaporated to dryness. The solid product and the residue of extraction was combined and crystallized from ethanol yielding grey crystals and gave 5.5 g (86%) of the product: 100°C . IR (KBr, cm^{-1}): 3037, 2919–2870, 1597, 1515, 1454, 1349, 1277, 1211, 1127, 1048. ^1H NMR (CDCl_3): δ 6.80 (s, 2H, ArH), 4.12 (t, $J = 4.54 \text{ Hz}$, 4H, ArOCH_2), 3.93 (m, 8H, OCH_2), 3.76 (m, 4H, OCH_2), 3.57 (t, $J = 7.72 \text{ Hz}$, 4H, ClCH_2), 2.90 (m, 4H, Ar-CH_2), 2.78 (t, $J = 7.72 \text{ Hz}$, 4H, SCH_2). ^{13}C NMR (CDCl_3): δ 148.10 (ArC), 128.56 (ArC), 116.34 (ArCH), 71.04–69.42 (OCH_2), 43.11 (ClCH_2), 35.56 (SCH_2), 33.88 (ArCH_2). Found (calc. for $\text{C}_{20}\text{H}_{30}\text{O}_5\text{Cl}_2\text{S}_2$): C, 49.67 (49.48); H, 6.13 (6.18). MS (EI) m/z : 485 $[\text{M}]^+$.

21,22-dibromo-2,3,5,6,8,9,11,12,15,17,18,25,26,28-tetradecahydro[1,4,7,12]benzodioxadithiacyclo-tetradeceno[6,7-b][1,4,7,10,13]benzopentaoxacyclopentadecene (6)

A round-bottom flask which contained finely ground NaOH (0.8 g, 20 mmol) and a suspension of **5** (2.68 g,

10 mmol) in dry *n*-butanol (100 cm^3) and which was fitted with a condenser was evacuated, refilled three times with argon and connected to the vacuum line. The reaction mixture was heated to stirred until dissolving was totally completed completely. A solution of **4** (4.85 g, 10 mmol) in dry *n*-butanol (200 cm^3) was added to this solution dropwise for over 3 h and then refluxed for 44 h under argon atmosphere. At the end of this period, the mixture was cooled to 0°C and acidified with conc. HCl (5 cm^3) and filtered off, washed with methanol. The solution was evaporated to dryness under reduced pressure and the solid residue was mixed with crushed ice (250 g) and mixed to room temperature. The mixture was extracted with chloroform ($4 \times 100 \text{ cm}^3$) and the combined extracts were dried over MgSO_4 and filtered off, washed with dry chloroform and then evaporated to dryness under reduced pressure. The solid residue was crystallized from ethyl acetate yielding brown crystals and gave 3.13 g (46%) of the product: mp 218°C . IR (KBr, cm^{-1}): 3044, 2910–2881, 1598, 1590, 1510, 1496, 1450, 1355, 1280, 1215, 1121, 1091. ^1H NMR (CDCl_3): δ 7.13 (s, 2H, ArH), 6.73 (s, 2H, ArH), 4.32 (t, $J = 4.42 \text{ Hz}$, ArOCH_2), 4.08 (t, $J = 5.18 \text{ Hz}$, 4H, ArOCH_2), 3.89 (m, 8H, OCH_2), 3.79 (m, 4H, OCH_2), 3.51 (m, 4H, ArCH_2), 3.18 (t, $J = 5.2 \text{ Hz}$, 4H, SCH_2). ^{13}C NMR (CDCl_3): δ 148.42 (ArC), 148.06 (ArC), 129.92 (ArCH₂), 117.46 (ArBr), 116.11 (ArCH), 114.73 (ArCH), 71.42–68.88 (OCH_2), 67.12 (ArOCH_2), 35.12 (ArCH₂), 30.37 (SCH_2). Found (calc. for $\text{C}_{26}\text{H}_{32}\text{O}_7\text{Br}_2\text{S}_2$): C, 45.78 (45.89); H, 4.94 (4.70). MS (FAB) m/z : 681 $[\text{M} + 1]^+$.

21,22-dicyano-2,3,5,6,8,9,11,12,15,17,18,25,26,28-tetradecahydro[1,4,7,12]benzodi-oxadithiacyclo-tetradeceno[6,7-b][1,4,7,10,13]benzopentaoxacyclopentadecene (7)

A Schlenk tube was charged with the dibromo compound **6** (2.72 g, 4 mmol), CuCN (1.07 g, 12 mmol), 8 drops of dry pyridine and dry DMF (25 cm^3) under argon atmosphere at room temperature. The reaction mixture was heated and stirred at 150°C for 36 h in an oil bath. During this time, the reaction mixture became dark brown. At the end of this period, the reaction mixture was cooled to room temperature, opened to air and diluted with aqueous NH_4OH (130 cm^3) and air was passed through the solution for 48 h. During this period, the solution became dark blue and a brown precipitate was formed. The mixture was filtered through a filter agent (Celite) and washed with dilute aqueous NH_4OH (10%) and with water until the filtrate was neutral and then dried *in vacuo*. The crude product was purified by column chromatography [silica gel, chloroform:petroleum ether:methanol (6:2:1)]. Yield: 0.96 g (42%), mp $136\text{--}138^\circ\text{C}$. IR (KBr, cm^{-1}): 3044, 2924–2854, 2229, 1598, 1513, 1457, 1358, 1269, 1215,

1127, 1106, 1057, 947. ^1H NMR (CDCl_3): δ 7.30 (s, 2H, ArH), 6.87 (s, 2H, ArH), 4.37 (t, $J = 4.67$ Hz, 4H, ArOCH_2), 4.22 (t, $J = 5.7$ Hz, 4H, OCH_2), 3.92 (m, 8H, OCH_2), 3.84 (m, 4H, OCH_2), 3.51 (m, 4H, ArCH_2), 3.34 (t, $J = 5.35$ Hz, 4H, SCH_2). ^{13}C NMR (CDCl_3): δ 151.88 (ArC), 148.42 (ArC), 129.93 (ArCH₂), 121.17 (ArCH), 115.06 (CN), 114.92 (ArC), 114.04 (ArCH), 72.16–68.79 (OCH_2), 35.14 (ArCH₂), 31.94 (SCH_2). Found (calc. for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_7\text{S}_2$): C, 58.90 (58.74); H, 5.80 (5.59); N, 4.71 (4.89). MS (FAB) m/z : 572.2 $[\text{M}]^+$.

22,24-Dihydro-22,24-diimino-2,3,5,6,8,9,11,12,15,17,18,28,29,31-tetradecahydro[1,4,7,12] Benzodioxadithiacyclotetradeceno [6,7-b][1,4,7,10,13] Benzopentaoxa-cyclopentadecene (8)

A suspension of dry sodium methoxide (0.11 g, 2 mmol) in dry methanol (20 cm³) was added to a solution of **7** (0.57 g, 1 mmol) in dry methanol (200 cm³) under argon atmosphere. Anhydrous ammonia was bubbled through the reaction mixture for 8 h at re-flux temperature. The reaction was monitored by TLC using chloroform:petroleum ether:methanol (7:2:1). At the end of this period, the ammonia inlet was stopped and the volume of the mixture reduced to 50 cm³ under reduced pressure and filtered. The filtrate was evaporated to dryness and purified by column chromatography [silica gel, chloroform:petroleum ether:methanol (7:2:1)] as eluent and gave oily product. Yield: 0.45 g (78%). IR (NaCl disc, cm⁻¹): 3353, 3052, 2952–2882, 1667, 1613, 1591, 1451, 1411, 1349, 1304, 1275, 1177, 1124, 1056, 936. ^1H NMR (CDCl_3): δ 8.22 (br, 3H, NH), 7.41 (s, 2H, ArH), 6.82 (s, 2H, ArH), 4.35 (s, 4H, ArOCH_2), 4.13 (t, $J = 4.55$ Hz, 4H, ArOCH_2), 4.03 (m, 8H, OCH_2), 3.90 (m, 4H, OCH_2), 3.49 (m, 4H, ArCH_2), 3.30 (t, $J = 4.58$ Hz, 4 H, SCH_2). ^{13}C NMR (CDCl_3): 163.48 (C=NH), 151.74 (ArC), 150.85 (ArC), 131.96 (ArCH₂), 126.86 (ArC), 118.45 (ArCH), 114.21 (ArCH), 71.67–69.11 (OCH_2), 66.94 (ArOCH_2), 36.45 (ArCH₂), 31.87 (SCH_2). Found (calc. for $\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_7\text{S}_2$): C, 56.88 (57.04); H, 6.17 (5.94); N, 7.34 (7.13). MS (FAB) m/z : 590.3 $[\text{M} + 1]^+$.

Metal-free Phthalocyanine (1. Route) (9)

A Schlenk tube was charged with precursor isoiminoindoline compound (**8**) (0.236 g, 0.4 mmol) and dry 2-(dimethylamino)ethanol (2.5 cm³) under argon atmosphere connected to a vacuum line at room temperature. The reaction mixture was heated and stirred at 150°C for 48 h in an oil bath. During this time, the reaction mixture became dark green. After cooling to room temperature, dry ethyl acetate was added and stirred into the green reaction mixture for 3 h to precipitate completely. The mixture was filtered off, washed with ethyl acetate, ethanol and diethyl ether and then dried *in vacuo*. The green

product was purified on silica gel using chloroform:methanol (9:1) as eluent. Yield: 0.14 g (58%), mp > 300°C. IR (KBr, cm⁻¹): 3413, 3057, 2919–2846, 1621, 1603, 1594, 1487, 1448, 1398, 1322, 1157, 1119, 1086. ^1H NMR (CDCl_3): 7.45 (m, 8H, ArH), 6.71 (m, 8H, ArH), 4.28 (m, 16H, ArOCH_2), 4.09 (m, 16 H, ArOCH_2), 3.98 (m, 32 H, OCH_2), 3.83 (m, 16H, OCH_2), 3.41 (m, 16H, ArCH_2), 3.17 (m, 16H, SCH_2). UV–Vis [(in chloroform:pyridine (1:1) $\lambda_{\text{max}}/\text{nm}$ 10⁻⁵ ϵ (mol⁻¹cm⁻¹)]: 718 (4.92), 682 (4.58), 658 (4.21), 641 (4.48), 303 (5.08), 272 (5.12). Found (calc. for $\text{C}_{112}\text{H}_{130}\text{N}_8\text{O}_{28}\text{S}_8$): C, 58.84 (58.68); H, 5.45 (5.67); N, 5.16 (4.89). MS (FAB) m/z : 2291.3 $[\text{M} + 1]^+$.

Metal-Free Phthalocyanine (2. Route) (9)

A standard Schlenk tube was charged with (0.570 g, 1 mmol) of compound **7**, 5 mL of dry *n*-pentanol and 0.155 g (0.15 mL, 1 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under argon atmosphere and degassed several times. The temperature was gradually increased up to 90°C and degassed again by argon gas. Then the reaction mixture was stirred at 160°C for 5 h. After the reaction mixture was cooled and decanted, the remaining dark green solid was stirred with 25 mL of methanol:petroleum ether mixture (1/1; v/v). The dark green product **9** was filtered off, washed with hot methanol and diethyl ether and then dried *in vacuo* at 50°C. Yield: 0.18 g (32%), mp > 300°C.

The spectral analyses of **9** were the same to that of metal-free phthalocyanine which was synthesized by route 1.

Zinc (II) Phthalocyanine (10)

A well-stopped Schlenk tube was charged with **7** (0.36 g, 0.6 mmol), $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.028 g, 0.156 mmol), dry quinoline (2 cm³) under argon atmosphere and then the mixture was heated and stirred at 80°C for 1 h. At the end of this period, the reaction mixture was heated and stirred at 190°C for 6 h. After cooling to room temperature, a mixture of methanol:water (20 cm³) (1:1) was added to the this mixture and stirred for 30 min at room temperature. The mixture was filtered off and evaporated and the residue was passed through a short neutral alumina column using chloroform as eluent. Yield: 0.099 g (27%), mp > 300°C. IR (KBr, cm⁻¹): 3051, 2924–2854, 1651, 1587, 1458, 1432, 1344, 1185, 1159, 1080, 1039. ^1H NMR (d_6 -DMSO): δ 7.52 (m, 8H, ArH), 6.83 (m, 8H, ArH), 4.29 (m, 16H, ArOCH_2), 4.18 (m, 16H, ArOCH_2), 4.01 (m, 32H, OCH_2), 3.78 (m, 16H, ArCH_2), 3.18 (m, 16H, SCH_2). UV–Vis [(in chloroform) $\lambda_{\text{max}}/\text{nm}$ 10⁻⁵ ϵ (mol⁻¹cm⁻¹)]: 693 (4.80), 638 (4.28), 290 (4.88), 252 (5.01). Found (calc. for $\text{C}_{112}\text{H}_{128}\text{N}_8\text{O}_{28}\text{S}_8\text{Zn}$): C, 56.91 (57.10); H, 5.68 (5.43); N, 5.07 (4.75); Zn, 2.56 (2.77). MS m/z : 2354.5 $[\text{M} + 1]^+$.

Nickel(II) Phthalocyanine (11)

Metal-free phthalocyanine (9) (0.23 g, 0.1 mmol), anhydrous NiCl₂ (0.023 g, 0.1 mmol) and 3 cm³ of dry DMF was placed in a standard Schlenk tube under argon atmosphere and refluxed at 150°C for 24 h. After cooling to room temperature, diethyl ether was added to the reaction mixture until the precipitation was completed. The mixture was filtered off and evaporated and then the residue was passed through a short neutral alumina column using chloroform as eluent. Yield: 0.08 g (32%), mp > 300°C. IR (KBr, cm⁻¹): 3048, 2924–2851, 1630, 1596, 1495, 1443, 1335, 1159, 1105, 1083. ¹H NMR (*d*₆-DMSO): δ 7.56 (m, 8H, ArH), 6.80 (m, 8H, ArH), 4.33 (m, 16H, ArOCH₂), 4.21 (m, 16H, ArOCH₂), 4.05 (m, 32H, OCH₂), 3.85 (m, 16H, OCH₂), 3.50 (m, 16H, ArCH₂), 3.15 (m, 16H, SCH₂). UV–Vis [(in chloroform:pyridine) (1:3) λ_{max}/nm 10⁻⁵ ε (mol⁻¹cm⁻¹)] 695 (4.68), 648 (4.17), 397 (4.05), 282 (5.05), 260 (5.01). Found (calc. for C₁₁₂H₁₂₈N₈O₂₈S₈Ni): C, 57.06 (57.27); H, 5.21 (5.45); N, 5.03 (4.77); Ni, 2.79 (2.50). MS *m/z*: 2346.4 [M]⁺.

Copper(II) Phthalocyanine (12)

Dibromo compound (6) (0.40 g, 0.59 mmol), dry CuCN (0.16 g, 1.78 mmol) and 2.5 cm³ of dry quino-line was placed in a standard Schlenk tube under argon atmosphere and heated at 215°C for 24 h. After cooling to room temperature, 20 cm³ of ethanol was added to this mixture and stirred for 45 min at the same temperature. This step was repeated several times. The reaction mixture was filtered off, washed with water, ethanol and diethyl ether to remove unreacted starting materials and then dried *in vacuo*. The crude product was heated and stirred three times in 50 cm³ of aqueous NaCN solution (3 M) to remove unreacted CuCN in product. The mixture was filtered and evaporated and then the residue was passed through a short alumina column using chloroform as eluent. Yield: 0.066 g (19%), mp > 300°C. IR (KBr, cm⁻¹): 3054, 2922–2857, 1645, 1593, 1454, 1347, 1262, 1121, 1072. UV–Vis [(in pyridine) λ_{max}/nm 10⁻⁵ ε (mol⁻¹cm⁻¹)] 678 (4.52), 640 (4.33), 405 (4.16), 285 (4.94), 255 (5.08). Found (calc. for C₁₁₂H₁₂₈N₈O₂₈S₈Cu): C, 57.37 (57.15); H, 5.29 (5.44); N, 4.99 (4.76); Cu, 2.51 (2.70). MS *m/z*: 2351.2 [M]⁺.

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