**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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**To cite this Article** Gök, Yaşar , Kantekn, Halt and Değrmencoğlu, İsmal(2003) 'Synthesis and Characterization of New Metal-free and Metallophthalocyanines Substituted with Tetrathiadiazamacrobicyclic Moieties', Supramolecular Chemistry, 15: 5, 335 — 343

**To link to this Article: DOI:** 10.1080/1061027031000088076
**URL:** http://dx.doi.org/10.1080/1061027031000088076

*Supramolecular Chemistry*, 2003 Vol. 15 (5), pp. 335–343

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# Synthesis and Characterization of New Metal-free and Metallophthalocyanines Substituted with Tetrathiadiazamacrobicyclic Moieties

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*Received (in Southampton, UK) 21 May 2001; Accepted 30 December 2002*

**New metal-free (5, 8) and metallophthalocyanines (6, 9) containing four diazatetrathiamacrobicycles or crosswise-disubstituted attached with two nitro and two macrobicyclic groups were synthesized by cyclotetramerization of 7,8-dicyano-4,11,22,23-tetrathia-1,14-diazapentacyclo[12.10.10.$0^{5,10}$.$0^{16,21}$.$0^{26,31}$]tetratriconta-5,7,12,19,20,21,28,30,32-nonane (3), 8,10-dihydro-8,11-diimino-4,14,24,34,-tetrathia-1,17-diazapentacyclo[15.13.13.$0^{5,13}$.$0^{19,23}$.$0^{28,33}$]tetratriconta-5,7,12,19,20,22,28,30,32-nonaisoiminoindoline (4) or 6-nitro-1,3,3-trichloroisoindolenine (7) in the presence of the corresponding metal salt or a strong organic base. The new compounds were characterized by a combination of elemental analysis and $^{1}$H NMR, $^{13}$C NMR, IR, UV–Vis and MS spectral data.**

*Keywords*: Phthalocyanine; Tetrathiadiazamacrobicycle; Template effect; Macrocyclization; Cryptand

## INTRODUCTION

Metal-free and metallophthalocyanines, which have been the subject of great interest for over 60 years, have a decisive disadvantage for very limited solubility in common organic solvents [1,2]. The first synthesis of soluble copper phthalocyanine with macrocyclic moieties was reported in 1986 [3–11] and its high tendency towards aggregation by solvents, cations and complexation properties was also investigated [12]. The peripheral substitution of aromatic rings by long alkyl or alkoxy chains [13], crown ethers or azacrown moieties enhances their solubility drastically [14–16].

A range of three-dimensional polycyclic ligand systems named cryptands have recently been investigated more intensively with respect to their strong selectivity towards individual alkali and alkaline earth metal cations [17–20]. The majority of this kind of ligands contain donor sets in which polyether donor functions predominate. However, compounds incorporating higher numbers of mixed donors such as diaza and/or dithia groups, have also been synthesized [21–23]. On the other hand, a generalized chelate effect, the cryptate effect, which causes high complexation stability, occurs in the formation of three-dimensional inclusion complexes than in the macrocyclic effect [24–26].

A part of the present paper reports the synthesis of the metal-free phthalocyanine containing four tetrathiadiazamacrobicyclic moieties in the molecule; a preliminary account of this study has been reported [27]. In addition, the synthesis of a novel crosswise-disubstituted metal-free phthalocyanines and their complexation ability are the major opportunities offered by these new compounds. In this way, soluble phthalocyanines peripherally substituted two amino and two macrobicyclic groups located crosswise can be synthesized and their reactivity has been exemplified through the formation of different compounds such as polymers [28].

In this study, the synthesis and characterization of metal-free and metallophthalocyanines are described, suggesting that the suitable combination of tetrathiadiazamacrobicycle and phthalocyanine may allow new functionalized materials to be prepared, which are of importance for analytical chemistry as novel heavy metal extraction agents. Polyazopolythia cryptands have strong coordination ability and special recognition function towards

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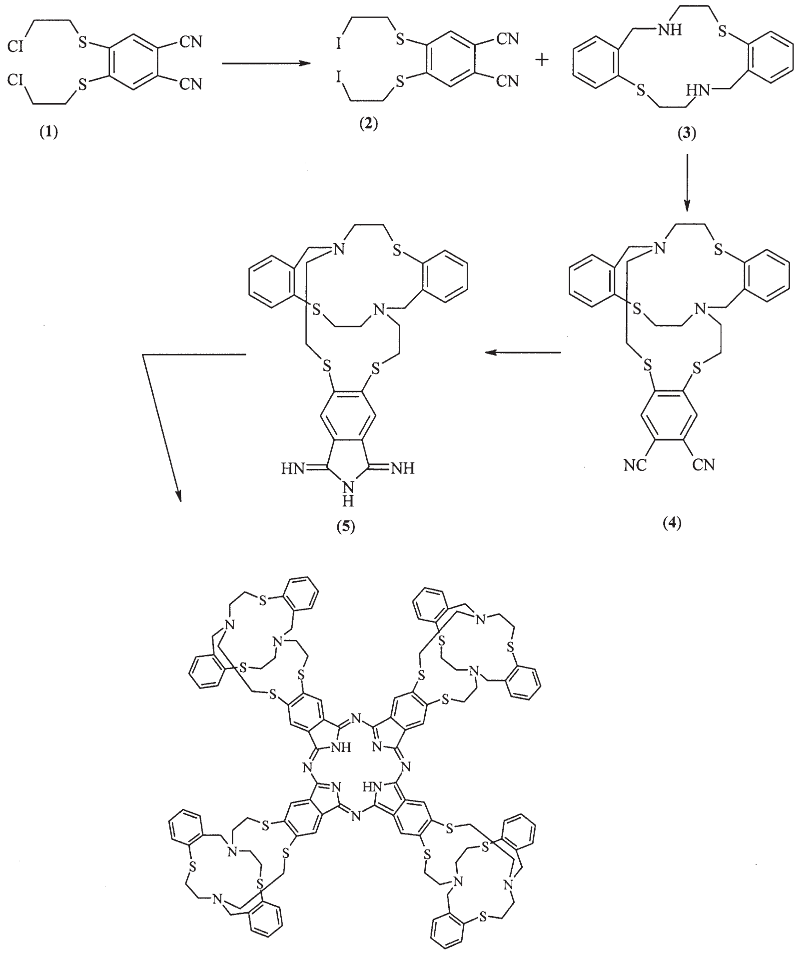
ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/1061027031000088076



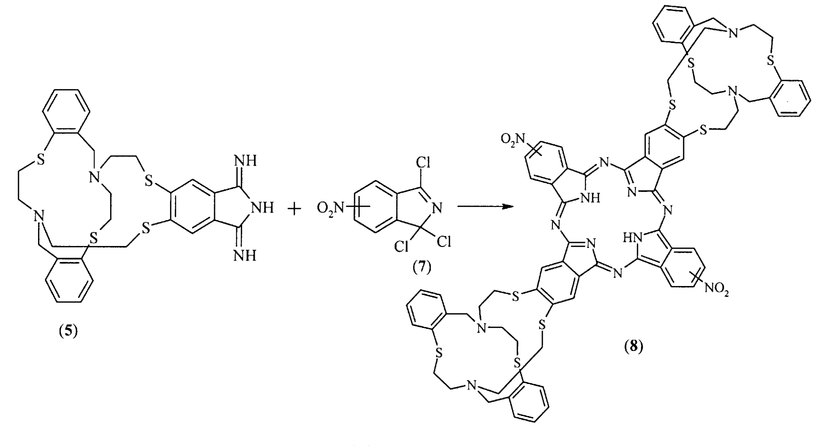
SCHEME 1

transition metal cations, with regard to biomimetic, catalytic, photo, electric and magnetic chemistry [29]. Relatively few reports of thia groups attached to benzene rings of phthalocyanine are known [30–32]. As donors in macrobicyclic units, thioether moieties can be used instead of oxa groups for their tendency to complex with transition metal ions [33]. On the other hand, the importance of these new types of compounds is that they enable the material to perform a dual function as a sensor material.

## RESULTS AND DISCUSSION

The preparation of the target metal-free (**5**, **8**) and metallophthalocyanines (**6**, **9**) is shown in Schemes 1 and 2. The structures of novel compounds were demonstrated by a combination of elemental analysis, $^1$H and $^{13}$C NMR, IR, UV–Vis and MS spectral data. Using the known procedure, 1,2-bis (2-chloroethylmercapto)-4,5-dicyanobenzene [34] was converted to 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**2**) in dry acetone containing finely ground anhydrous NaI under an argon atmosphere to give **2** in 49% yield [35,36]. The similarity of the IR spectra of these two compounds is very high except for the vibrations of the halogen-containing methylene groups. In the $^1$H and $^{13}$C NMR spectra (Fig. 1) of this compound, the characteristic signals of the aromatic protons and carbons are very similar to those of the starting material (**1**). The resonances of protons and carbons at $\delta = 3.47$ and 29.02 ppm, respectively, connected to halogens ($CH_2$–I) are different from those of the precursor compound (**1**), as expected. The IR spectrum of this compound exhibits characteristic frequencies at 1222 (Ar–O–$CH_2$), 2227 (C=N) and 535 (C–I) cm$^{-1}$. The mass spectrum (EI) and elemental analysis data of this compound also support the replacement of chlorine by iodine, with a peak at $m/z = 500$ indicating the formation of $[M]^+$.

Several methods can be applied to construct dissymetrical macrobicyclic compound **4** starting with dithiadiaza macrocycle **3** and coupling agent (**2**). In this 1:1 macrobicyclization processes, high dilution techniques or template synthesis are



SCHEME 2

necessary to prevent polycondensation, which causes a considerable decrease in the yield of the desired macrobicycle compound. We have previously reported [24–26] the synthesis of a dithiadiaza-based cryptand by using a 14-membered dithiadiaza macrocycle [37] as starting material and 4-nitro-1,2-bis(2-iodoethoxy)benzene [38] as cross-linker. The macrobicyclization procedure using $Cs_2CO_3$ as a base generated the caesium cations as promoters [39–42]. Treatment of **2** and **3** and $Cs_2CO_3$ using dry acetonitrile as solvent afforded macrobicycle **4** in high yield (73.17%). The $^1$H NMR spectrum of the reaction product **4** indicates the presence of new resonances for the methylene and aromatic protons $\delta = 3.36$ and 7.58 ppm, respectively, and the disappearance of the NH signals, which supports the formation of a bismacrocycle. In the proton-decoupled $^{13}$C NMR spectrum of this compound (Fig. 2), individual signals were observed for the new methylene, aromatic and cyano carbon atoms at $\delta = 33.07$, 142.58 and 115.14 ppm, respectively, clearly suggesting that macrobicyclic formation has occurred. The disappearance of N–H and appearance of intense C=N stretching vibrations at 2229 cm$^{-1}$ belonging to the starting material (**2**) and synthesized compound (**4**), respectively, also supports the formation of **4**. Compound **4** displays the expected molecular ion peak at $m/z = 574$ $[M]^+$ in its mass spectrum, as found using the FAB technique and *m*-nitrobenzyl alcohol as matrix.

We then reacted the dicyano compound containing the macrobicyclic moiety (**4**) with anhydrous ammonia in the presence of sodium methoxide in refluxing dry methanol [43–45] to give the corresponding isoiminoindoline derivative (**5**) as the first precursor in 63.4% yield. In the IR spectrum of **5**, the CN stretching vibrations disappeared after conversion of **4** to isoiminoindolinediimine (**5**), which shows absorptions at 3385 and 3177 cm$^{-1}$ for the N–H groups. The $^1$H NMR spectra of **4** and **5** are

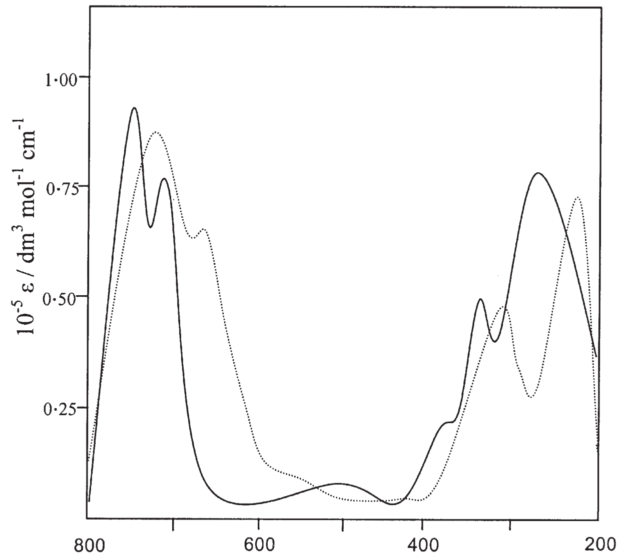


FIGURE 1 UV–Vis spectra of **6** (solid line) and **9** (dotted line) in pyridine.

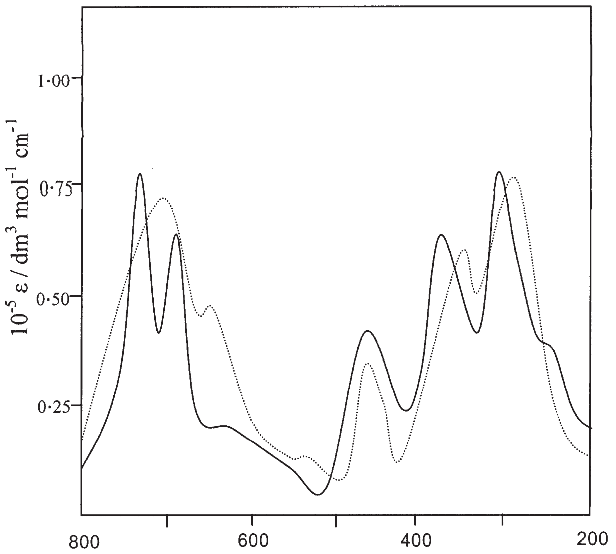


FIGURE 2 UV–Vis spectra of **8** (solid line) and **10** (dotted line) in pyridine.

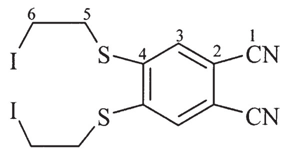


FIGURE 3

quite similar, but the spectrum of **5** indicates the presence of deuterium-exchangeable NH protons: imino groups observed as a broad signal at $\delta = 7.75$ ppm. When the proton-decoupled $^{13}$C NMR spectra of **4** was compared with that of **5** (Fig. 3), the characteristic feature of the carbon resonances of the isoiminoindoline derivative is the disappearance of nitrile carbon chemical shifts at $\delta = 115.14$ ppm. The mass spectrum (FAB) of this compound showed a peak at $m/z = 591$ $[M]^+$, which also supports the structure of the proposed formulation.

Condensation of four isoiminoindoline derivative into metal-free phthalocyanine **6** was carried out in 2-(dimethylamino)ethanol at reflux temperature for 30 h under argon to afford **6** in 21.7% yield as the green crystalline product after purification by crystallization using a pyridine:ethanol mixture (Scheme 1). This compound can be prepared directly by using dicyano compound (**4**). In the preparation of tetrasubstituted metal-free phthalocyanine (**6**), the isoiminoindoline procedure is more convenient than the phthalonitrile route since the reaction conditions employing isoiminoindolines are mild in comparison with those employing phthalonitriles. The yield of this reaction was rather low, as encountered for compound **6** with other bulky groups [27]. The formation of a phthalocyanine from four isoiminoindoline involves the formation of four new C–N bonds. Using the respective isoindolinediimine, which exhibits higher reactivity, may be an advantage. Even if each of these steps proceeds in high yield, the isolated yield of target compound is usually poor to moderate owing to loss of the product during purification of the product mixture. The $^1$H NMR spectrum of **6** in DMSO-d$_6$ exhibits the characteristic resonances of the macrobicycle and phthalocyanine moieties. Strong shielding of the cavity protons in the phthalocyanine core of this compound was manifested by a broad resonance at $\delta = -4.38$ ppm [46–48] at high concentration which could be attributed to the NH resonance and identified easily with deuterium exchange. The chemical shifts related to aromatic and aliphatic protons belonging to the macrobicyclic moieties and phthalocyanine skeleton gave significant absorbances characteristic of the proposed structure. This spectrum closely resembles that of the precursor compound (**5**). The IR spectrum of this compound also indicates the disappearance of the sharp C=N stretching vibration after the conversion of **5** to metal-free- phthalocyanine **6**, which shows a significant absorption at 3410 cm$^{-1}$ for the N–H groups [49]. The mass spectrum of **6** contained a strong peak at $m/z = 2298.3$ $[M]^+$ for the parent ion, which can be attributed to the formation of phthalocyanine **6**.

The synthetic route to novel cross-wise disubstituted phthalocyanine **8** is outlined in Scheme 2. Whereas the isoiminoindoline derivative **5** was used as one of the precursor compounds, 6/7-nitro-1,3,3-trichloroisoindolenine [50,51] (**7**), which is a mixture of isomers with the nitro group at the 6- or 7-positions, was used as the second precursor. After the condensation of **5** and **7** in 2:2 ratio in the presence of triethylamine and sodium methoxide as the base and hydroquinone as the reductant [52,53], cyclotetramerization was accomplished in 34.9% yield. The solubility of **8** can be taken as an indication of the 2:2 combination of starting compounds (**5**, **7**). If compound **8** contains four nitro groups, the solubility would be extremely low and the solubility of another phthalocyanine with three nitro groups on the periphery cannot be sufficiently high, even when one macrobicyclic group is present [54]. The results of elemental analysis and the mass spectral data of phthalocyanine **8** confirmed that a 2:2 combination of reactants occurred. However, there are no spectroscopic data, with the exception of X-ray analysis, to verify that the *trans* assignment of the substitutions on phthalocyanine ring, but it can be said that the *trans* assignment seems very reasonable according to the literature [49]. On the other hand, the color of the crosswise-disubstituted metal-free phthalocyanine **8** tends more towards green than the tetrasubstituted metal-free phthalocyanine [38]. In the $^1$H NMR spectrum of this compound, a broad resonance observed at $\delta = -5.05$ ppm can be attributed to the typical strong shielding of the cavity NH protons. The band at 3389 cm$^{-1}$ belonging to N–H stretching vibrations also supports the proposed structure, which agrees well with the other reported IR spectra of phthalocyanine [55,56]. The mass spectrum of this compound was obtained by the FAB technique using a matrix in the region of the molecular ion peak at $m/z = 1497$ $[M + 1]^+$. These data are in good agreement with the proposed structure.

The synthesis of metallophthalocyanines **9** and **10** was accomplished with tetrasubstituted (**6**) and disubstituted (**8**) phthalocyanines and the corresponding dry metal acetate salt in dry pyridine and dry THF at reflux temperature, respectively. Column chromatography using silica gel with chloroform and THF/hexane (1:2) as eluents removed the nickel(II) and zinc(II) phthalocyanines in 78 and 49.7% yields, respectively. The structures proposed for these new compounds are consistent with the data obtained from their elemental analysis, IR, UV–Vis, $^1$H NMR spectra and mass spectra. The metal contents of the metallophthalocyanines **9** and **10** are in accord with their calculated analysis. This was also supported by the presence of the characteristic molecular ion peaks in the mass spectra of metallophthalocyanines **9** and **10** at $m/z = 2355$ $[M + 1]^+$ and 1559.1 $[M]^+$, respectively. The $^1$H NMR spectra of these compounds were almost identical with those of the metal-free phthalocyanines, the significant difference being the disappearance of the broad NH protons belonging to the cavity of phthalocyanine core. The other differences in the $^1$H NMR spectra of metal-free phthalocyanines and metallophthalocyanines were the broad signals encountered in the case of compounds **9** and **10**, owing to the aggregation of planar phthalocyanine molecules at the considerably high concentration used for NMR measurements [57]. The characteristic vibrations in the IR spectra of metallophthalocyanines are very similar to those of the precursor compounds (**6**, **8**) except for the disappearance of the N–H resonances of phthalocyanine core.

The UV–Vis absorption spectra of solutions of metal-free (**6**, **8**) and metallophthalocyanines (**9**, **10**) in pyridine at room temperature are shown in Table I. The spilt Q-bands, which are characteristic of the metal-free phthalocyanines **6** and **8**, are observed at $\lambda_{max}$ 734 and 704 nm and at $\lambda_{max}$ 711 and 682 nm, respectively. These intense Q-bands at 734 and 704 nm in compound **6** indicate the monomeric species because the monomeric species with $D_{2h}$ symmetry shows two intense absorptions around 700 nm [58,59]. The distributed metal-free phthalocyanine (**8**) shows the excepted splitting of the band at 711 and 682 nm, which can be attributed to the monomeric species of these compounds [60–62]. Such split Q-band absorptions in pyridine are due to the $\pi \rightarrow \pi^*$ transition of this fully conjugated 18π systems [27]. Upon dilution (*ca.* $1 \times 10^{-6}$ M), the absorption spectra of these compounds show significant changes such as in band positions and molar absorptivities [63,64]. The Ni(II) (**9**) and Zn(II) phthalocyanates (**10**) showed the expected absorptions at the main peaks of the Q- and B-bands appearing at 707, 687 and 332, 330 nm. This result is typical of metal complexes of substituted and unsubstituted $P_{cs}$ with $D_{4h}$ symmetry [65,66]. However, the presence of shoulders at 666 and 648 nm, corresponding to monomeric and aggregated species in pyridine in solvents of lower relative permittivity such as in $CCl_4$ showed that the spectra were completely different. Since four or two bulky macrobicyclic groups are bound to the periphery of the metallophthalocyanines **9** and **10**, respectively, the aggregations are not efficient as expected.

TABLE I Wavelength and absorption coefficients of the UV–Vis spectra of metal-free and metallophthalocyanines

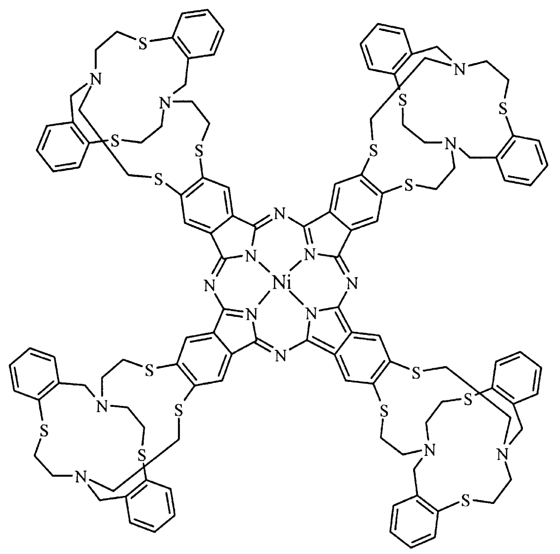
| Compounds | Solvent | λ (nm) [($10^{-5}$ ε (mol$^{-1}$cm$^{-1}$)] |
|---|---|---|
| **6** | Pyridine | 734 (11.44), 704 (10.15), 348 (6.70), 285 (10.74) |
| **8** | Pyridine | 711 (8.82), 682 (6.63), 434 (4.77), 342 (7.13), 291 (8.10) |
| **9** | Pyridine | 707 (10.65), 666 (8.21), 332 (6.53), 274 (9.50) |
| **10** | Pyridine | 687 (7.91), 648 (6.10), 430 (4.14), 330 (6.84), 278 (8.19) |

## CONCLUSIONS

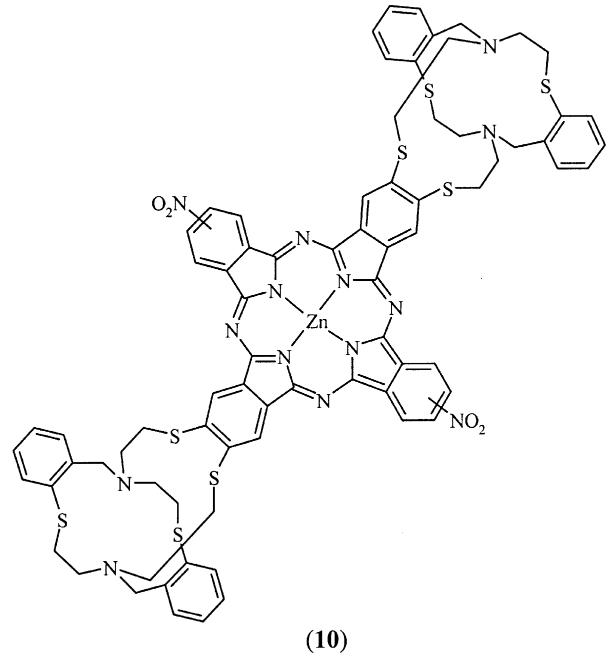
6,7,8,9,15,16,17,18-Octahydrodibenzo[*f*,*m*][1,4,8,11]-dithiadiazacyclotetradecine (**3**) reacted with 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**2**) in the presence of $Cs_2CO_3$ as a promoter and template agent in acetonitrile under an argon atmosphere to yield the precursor dicyano compound **4** containing a tetrathiadiaza macrobicycle moiety. Then, the derivative of isoiminoindolenine (**5**) was prepared by using the precursor compound in the standard conditions. Tetrasubstituted (**6**) and crosswise-disubstituted (**8**) metal-free phthalocyanines were synthesized by using isoiminoindolenine (**4**) in 2-(dimethylamino)ethanol or THF media containing 6-nitro-1,3,3-trichloroisoindolenine (**7**), respectively. With the desired anhydrous metal salts, it became possible to convert the metal-free phthalocyanines (**6**, **8**) into metallo derivatives (**9**, **10**). These acetates of Ni(II) or Zn(II) have been used in dry pyridine or THF to prepare metallophthalocyanines.

## EXPERIMENTAL

$^1$H, $^{13}$C NMR and IR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ or $d_6$-DMSO solutions and on a Perkin–Elmer 1600 FTIR spectrometer, respectively. Mass spectra were recorded on a Varian MAT 711 and VG Zapspec spectrometers by fast atom bombardment (FAB) using *m*-nitrobenzyl alcohol as the matrix. Electronic spectra were recorded on a Unicam UV2-100 spectrophotometer. The elemental analysis and metal contents of the compound were determined with a Hewlett-Packard and 185 CHN analyser and a Unicam 929 AA spectrometer, respectively. 1,2-Bis-(2-chloroethylmercapto)-4,5-dicyanobenzene, [34] 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,4,8,11]-dithiadiazacyclotetradecane [37] and 6/7-nitro-1,3,3-trichloroisoindolenine [38] were synthesized according to reported procedures. All solvents were purified according to the standard procedure before



(**9**)



(**10**)

use [67]. Melting points were determined by an electrothermal apparatus and are uncorrected.

### 1,2-Bis(2-iodoethylmercapto)-4,5-dicyanobenzene (2)

1,2-Bis(2-chloroethylmercapto)-4,5-dicyanobenzene (**1**) (5.2 g, 16.4 mmol) was dissolved in dry acetone (120 cm$^3$) containing anhydrous NaI (13.91 g, 93 mmol) under an argon atmosphere and refluxed for 80 h. At the end of this period, the reaction mixture was cooled to room temperature and the precipitate was filtered off and washed with dry acetone. The major liquor and the washing solvents were combined and evaporated to dryness under reduced pressure. The oily residue was extracted with chloroform (3 × 100 cm$^3$) and the organic phase was washed with water (2 × 100 cm$^3$) and dried over anhydrous $Na_2SO_4$. After filtration of the drying agent, the filtrate was evaporated to give an oily substance, which was dissolved in DMF (3 cm$^3$) and purified by silica gel column chromatography. The elution was carried out succesively with petroleum ether–ethyl acetate (4:1). Yield 4.0 g (49%); mp 156 158°C. IR (KBr pellets, cm$^{-1}$): 3027, 2918–2848, 2227, 1584, 1458, 1222, 1169, 1115, 930, 675, $^1$H NMR ($CDCl_3$): $\delta$ 7.53 (s, 2H, ArH, 3-H), 3.47 (t, 4H, $CH_2I$, 6-H), 3.34 (t, 4H, S-$CH_2I$, 5-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 143.98 ($C_4$), 131.57 ($C_3$), 115.94 ($C_1$), 113.96 ($C_2$), 36.44 ($C_5$), 29.02 ($C_6$). Found

(Calc. for $C_{12}H_{10}N_2S_2I_2$): C, 28.63 (28.80); H, 2.19 (2.0); N, 5.84 (5.60). MS (EI): $m/z$ 500 $[M]^+$.

### 7,8-Dicyano-4, 11,22,23-tetrathia-1,14-diazapentacyclo [12.10.10.$^{05,10}$.0$^{16,21}$.0$^{26,31}$]tetratriconta-5, 7,12,19,20,21,28,30,32-nonane (4)

A round bottom flask (300 cm$^3$) containing dry acetonitrile (120 cm$^3$) and fitted with a condenser was evacuated, refilled three times with argon and connected to a vaccum line. Under argon, the flask was charged with 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,4,8,11]dithiadiazacyclotetradecine (**3**) (2.475 g, 7.5 mmol) and finely ground anhydrous $Cs_2CO_3$ (4.9 g, 15 mmol) and the mixture at room temperature. A solution of **2** (3.75 g, 7.5 mmol) in dry acetonitrile (30 cm$^3$) was added to this mixture and the reaction mixture was heated and stirred at 60°C for 148 h. The reaction was monitored by thin layer chromatography [acetone–chloroform–petroleum ether (6:4:1)]. At the end of this period, the mixture was cooled to room temperature, filtered off, and washed with cold acetonitrile. The crude product was suspended and stirred in water (50 cm$^3$), filtered off and then dried *in vacuo*. The solid product was dissolved in chloroform (18 cm$^3$), then the solution was placed in a refrigerator at -18°C. The amorphous pale yellow solid was separated by filtration and dried *in vacuo* at room temperature. Yield 3.15 g (73.17%); mp 136°C (dec.). IR (KBr pellets, cm$^{-1}$): 3054, 2916–2818, 2229, 1588, 1463, 1260, 1109, 970, $^1$H NMR ($CDCl_3$): $\delta$ 7.58 (s, 2H, ArH, 6,9-H), 7.46–7.07 (m, 8H, ArH, 17,20-H), 5.89–5.79 (m, 4H, $ArCH_2$, 15,26-H), 3.36 (t, 4H, $ArSCH_2$, 3,12-H), 3.28–3.21(m, 8H, $NCH_2$, 2,24-H), 2.76(m, 4H, $SCH_2$, 23,33-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 142.58 ($C_5$), 138.47 ($C_{21}$), 132.36 ($C_6$), 131.31 ($C_{20}$), 129.32 ($C_{18}$), 128.31 ($C_{19}$), 127.70 ($C_{17}$), 125.98 ($C_{16}$), 115.14 (C N), 112.58 ($C_7$), 51.52 ($C_{15}$), 45.06 ($C_2$), 33.07 ($C_{23}$). Found (calc. for $C_{30}H_{30}N_4S_4$): C, 62.96 (62.71); H 5.04 (5.22); N, 9.94 (9.75). MS (FAB positive): $m/z$ 574 $[M]^+$.

### 8,11-Dihydro-8,11-diimino-4,14,24,34,-tetrathia-1,17-diazapentacyclo[15.13.13.0$^{5,13}$.0$^{19,23}$.0$^{28,33}$] tetratriconta-5,7,12,19,20,21,28,30,32-nonaisoiminoindolenine (5)

To a solution of **4** (1.6 g, 2.8 mmol) in dry methanol (200 cm$^3$) under an argon atmosphere, dry sodium methoxide (0.296 g, 5.6 mmol) was added. Anhydrous ammonia was bubbled through the reaction mixture for 6.5 h at reflux temperature. The reaction was monitored by TLC using chloroform–methanol (8:2). At the end of this period, the ammonia inlet was closed and the volume of the solution reduced to 60 cm$^3$ under reduced pressure and filtered. The filtrate was evaporated to dryness and the mixture was stirred with water at room temperature for 6 h. The mixture was filtered off, washed with water and dried *in vacuo*. The pale green crude product was crystallized from chloroform–ethanol (1:1). Yield 1.3 g (63.4%); mp 284°C (dec.). IR (KBr pellets, cm$^{-1}$): 3385, 3177, 3048, 2921–2816, 1636, 1609, 1585, 1541, 1459, 1376, 1287, 1107, 872, 750. $^1$H NMR ($CDCl_3$): $\delta$ 7.75 (br, 3H, NH, 8,10-H), 7.54 (s, 2H, ArH, 6,12-H), 7.33–6.71 (m, 8H, ArH, 20,23-H), 5.67–5.58 (m, 4H, $ArCH_2$, 18,28-H), 3.44 (m, 4H, $ArSCH_2$, 3,15-H), 3.34–3.22 (m, 8H, $NCH_2$, 2,27-H), 2.73 (m, 4H, $SCH_2$, 26,36-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 162.26 ($C_8$), 138.49 ($C_{24}$), 135.52 ($C_5$), 133.49 ($C_6$), 132.28 ($C_{23}$), 130.90 ($C_{21}$), 128.82 ($C_{22}$), 128.08 ($C_{20}$), 127.85 ($C_{19}$), 125.46 ($C_7$), 51.93 ($C_{18}$), 45.25 ($C_2$), 33.29 ($C_{26}$). Found (calc. for $C_{30}H_{33}N_5S_4$): C, 61.16 (60.91); H, 5.40 (5.58); N, 11.67 (11.84). MS (FAB positive); $m/z$ 591 $[M + 1]^+$.

### Metal-free Phthalocyanine (6)

A solution of **5** (1.04 g, 1.76 mmol) in dry 2-(dimethylamino)ethanol (5 cm$^3$) was refluxed and stirred under argon atmosphere on a vacuum line for 24 h. After cooling to room temperature, dry ethyl acetate (100 cm$^3$) was added and stirred into the green reaction mixture was filtered off, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. The green crude product was crystallized from pyridine–ethanol mixture (1:3). Yield 0.22 g (21.7%); mp 260°C IR (KBr pellets, cm$^{-1}$): 3410, 3060, 2934-2847, 1633, 1620, 1590, 1560, 1476, 1420, 1346, 1296, 1121, 1080, 895. $^1$H NMR ($d_6$-DMSO): $\delta$ $-4.38$ (s, 2H, NH, 9-H), 7.84 (m, 8H, ArH, 6,12-H), 7.62–7.47 (m, 16H, ArH, 20,22-H), 7.40–6.71 (m, 16H, ArH, 21,23-H), 5.62 (m, 16H, $ArCH_2$, 18,28-H), 3.58 (m, 16H, $ArSCH_2$, 3,15-H), 3.42–3.29 (m, 32H, $NCH_2$, 2,27-H), 2.81 (m, 16H, $SCH_2$, 26,36-H). Found (calc. for $C_{120}H_{122}N_{16}S_{16}$): C, 62.40 (62.66); H, 5.47 (5.40); N, 9.62 (9.74). MS (FAB positive): $m/z = 2298.3$ $[M]^+$.

### Crosswise-substituted Metal-free Phthalocyanine (8)

A solution of **7** (0.25 g, 0.92 mmol) in dry THF (30 cm$^3$) was added dropwise over 30 min to a cooled solution (approximately 0°C) of 5 (0.54 g, 0.92 mmol) containing triethylamine (0.28 g, 2.76 mmol) in freshly distilled dry THF (60 cm$^3$) under an argon atmosphere in a cryostat. The reaction mixture was stirred for over 1 h at this temperature and then allowed to warm up to room temperature slowly with stirring for 16 h. During this time the reaction mixture turned from yellow to green. At the end of this period, the reaction mixture was filtered off, washed with dry THF and the filtrate was returned to a three-necked round-bottom flask connected to

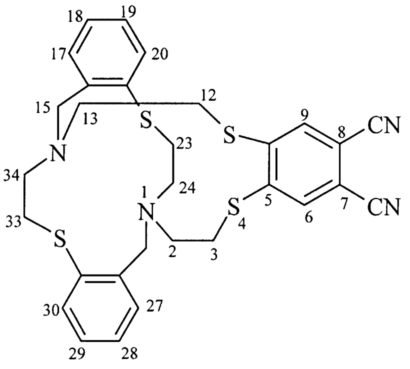


FIGURE 4

a vacuum line. Hydroquinone (0.18 g, 0.92 mmol) and sodium methoxide (0.145, 2.7 mmol) were added to the filtrate under argon and refluxed for 6 h. After refluxing, the reaction mixture was cooled to room temperature and filtered off, washed with THF and boiling water and ethanol until the filtrate was clear. The crude dark green product was recrystallized from a pyridine–ethanol mixture (1:3). Yield 0.24 g (34.9%); mp 298°C (dec.). IR (KBr pellets, cm$^{-1}$): 3389, 3052, 2950–2840, 1627, 1610, 1594, 1568, 1487, 1432, 1390, 1303, 1139, 1093, 901, 763. $^1$H NMR ($d_6$-DMSO): $\delta - 5.05$ (s, 2H, NH, 9-H), 7.94 (m, 6H, ArH, 41, 44-H), 7.68–6.82 (m, 20H, ArH, 20, 22-H), 5.71 (m, 8H, ArCH$_2$, 18, 28-H), 3.64 (m, 8H, ArSCH$_2$, 3, 15-H), 3.51 (m, 16H, NCH$_2$, 2,27-H), 2.92 (m, 8H, SCH$_2$, 26,36-H). Found (calc.for C$_{76}$H$_{68}$N$_{14}$S$_8$O$_4$): C, 60.68 (60.86); H, 4.71 (4.54); N, 12.88 (13.10). MS (FAB positive): $m/z$ 1497 [M]$^+$.

## Nickel(II) Phthalocyanine (9)

Anhydrous nickel(II) acetate (0.127 g, 0.072 mmol) was mixed with a vigorously stirred solution of **6** (0.166 g, 0.072 mmol) in dry pyridine (60 cm$^3$) under an argon atmosphere. The reaction mixture was held at reflux temperature for 42 h, then it was cooled to room temperature, filtered off using Celite as filtering agent, and washed with pyridine. The filtrate was evaporated to dryness under reduced pressure and chromatographed on a silica column (eluent chloroform) to give a green solid. Yield 0.132 g (78%); mp > 300°C. IR (KBr pellets, cm$^{-1}$): 3044, 2920–2836, 1618, 1590, 1503, 1445, 1336, 1288, 1119, 1062, 982. $^1$H NMR ($d_6$-DMSO): $\delta$ 7.90 (m, 8H, ArH, 6,12-H), 7.71–7.54 (m, 16H, ArH, 20,22-H), 7.47–6.66 (m, 16H, ArH, 21,23-H), 5.70 (m, 16H, ArCH$_2$, 18,28-H), 3.71 (m, 16H, ArSCH$_2$, 3,15-H), 3.52 (m, 32H, NCH$_2$, 2,27-H), 2.95 (m, 16H, SCH$_2$, 26,36-H). Found (calc. for C$_{120}$H$_{120}$N$_{16}$S$_{16}$Ni): C, 61.34 (61.15); H, 5.27 (5.09); N, 9.29 (9.51); 2.30 (2.49). MS (FAB positive): $m/z$ 2355 [M + 1]$^+$.

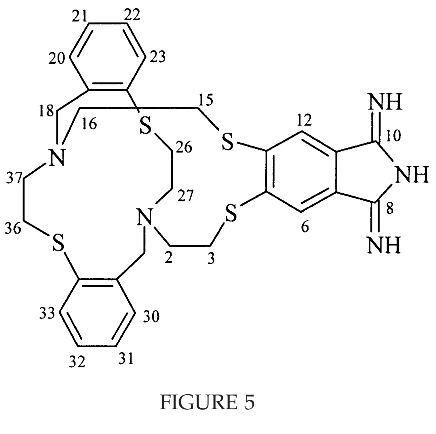


FIGURE 5

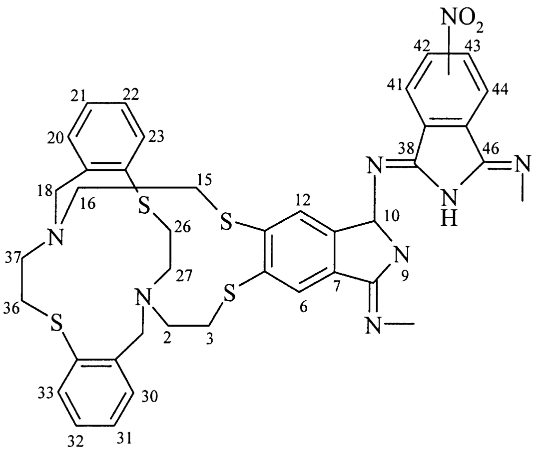


FIGURE 6

## Zinc(II) Phthalocyanine (10)

Anhydrous zinc(II) acetate (0.14 g, 0.74 mmol) was added and stirred to a solution of **8** (0.2 g, 0.124 mmol) in dry THF (70 cm$^3$), which was connected to a vacuum line, under argon. The reaction mixture was refluxed for 40 h, then cooled to room temperature, filtered through Celite, and washed with dry THF. The filtrate was evaporated to dryness under reduced pressure and chromatographed on a silica column [eluent THF: *n*-hezane (1:2)] to give a dark green solid. Yield 0.124 g (49.7); mp 275–277°C. IR (KBr pellets, cm$^{-1}$): 3053, 2952–2848, 1612, 1597, 1505, 1457, 1376, 1311, 1130, 1088, 907. $^1$H NMR ($d_6$-DMSO): $\delta$ 8.09 (m, 6H, ArH, 41,44-H), 7.78–6.90 (m, 20H ArH, 20,22-H), 5.63 (m, 8H, ArCH$_2$, 18,28-H), 3.67 (m, 8H, ArSCH$_2$, 3,15-H), 3.54 (m, 16H, NCH$_2$, 2,27-H), 2.88 (m, 8H, SCH$_2$, 26,36-H). Found (calc. for C$_{76}$H$_{66}$N$_{14}$S$_8$O$_4$Zn): C, 58.71 (58.48); H, 4.04 (4.23); N, 12.37 (12.56); Zn, 3.97 (4.19). MS (FAB positive): $m/z$ 1559.1 [M]$^+$ Figs. 4–6.

## *Acknowledgements*

This study was supported by the Research Fund of Karadeniz Technical University (Trabzon, Turkey). We are also indepted to Professor M. Hanack (Tübingen University, Germany) for his assistance with MS spectral data. Y.G. thanks the Deutscher Akademischer Austauschdienst (DAAD) for an invitation to Germany for two months at Tübingen University.

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