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Synthesis and Characterization of Novel Metal-free and Metallophthalocyanines Containing 12-Membered Diazadioxamacrocycles

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New metal-free phthalocyanines fused in peripheral positions with eight N-monotosylated diaza-12-crown-4 macrocyclic moieties connected by diethylenethio groups have been synthesized by cyclotetramerization of a newly synthesized dicyano-substituted macrocycle. Metallophthalocyanines were also prepared by reaction of the dicyano-substituted macrocycle in the presence of corresponding metal salts and a strong organic base. The new compounds were characterized by a combination of elemental analysis, ^{1}H and ^{13}C NMR, IR, electronic and mass spectroscopies.

Keywords: Phthalocyanine; Diazadioxamacrocycle; Template effect; Macrocyclization; Tosylation

INTRODUCTION

The design and synthesis of metal-free and metallophthalocyanines has been an area of intense research activity for over 70 years [1–3]. In recent years, much effort has been dedicated to the synthesis and characterization of novel phthalocyanine derivatives having interesting electrical, optical, gas sensing and catalytic properties by making slight differences in peripheral substitution or in the central metal cation [4–8]. Remarkable progress has been made in the past decade in the use of phthalocyanine derivatives as sensitizers for photodynamic therapy of cancer [9–11]. The unsubstituted metallophthalocyanines are colored materials but they are not generally soluble in common organic solvents. However, bulky substituents on the periphery enhance the solubility and the donor atoms of these substituents are capable of complexation [12–14]. In the past decade, the preparation of various peripherally substituted derivatives has generated interesting novel physical and chemical properties for many different applications in material science.

Since crown ethers were first recognized by Pedersen as having selective metal-ion binding properties [15, 16], various crown ethers have been prepared and their complexation behavior studied extensively. The design of diazadioxa macrocyclic ligands featuring high selectivity for complexation of alkali metals, alkaline earth metals and primary alkyl ammonium cations has been of great interest since studies began on molecular recognition using artificial receptor compounds [17–19]. Lipophilic macrocyclic compounds are of particular interest because of their ability to dissolving inorganic salts in nonpolar organic solvents.

In the present paper, we describe the synthesis of metal-free and metallophthalocyanines in which eight 1,7-dioxa-4,10-diazamacrocyclic moieties are held together by eight diethylenthio groups. The synthesis of these compounds promotes cooperation between the macrocycle and the phthalocyanine core binding subunits, allowing formation of heteronuclear inclusion complexes.

RESULTS AND DISCUSSION

We report here the synthesis and structural properties of the dicyano compound 4,5-Bis-{2-[10-(toluene-4-sulfonyl)-1,7-dioxa-4,10-diaza-cyclododec-4-yl]-ethylsulfonyl}-phthalonitrile (**3**) prepared by

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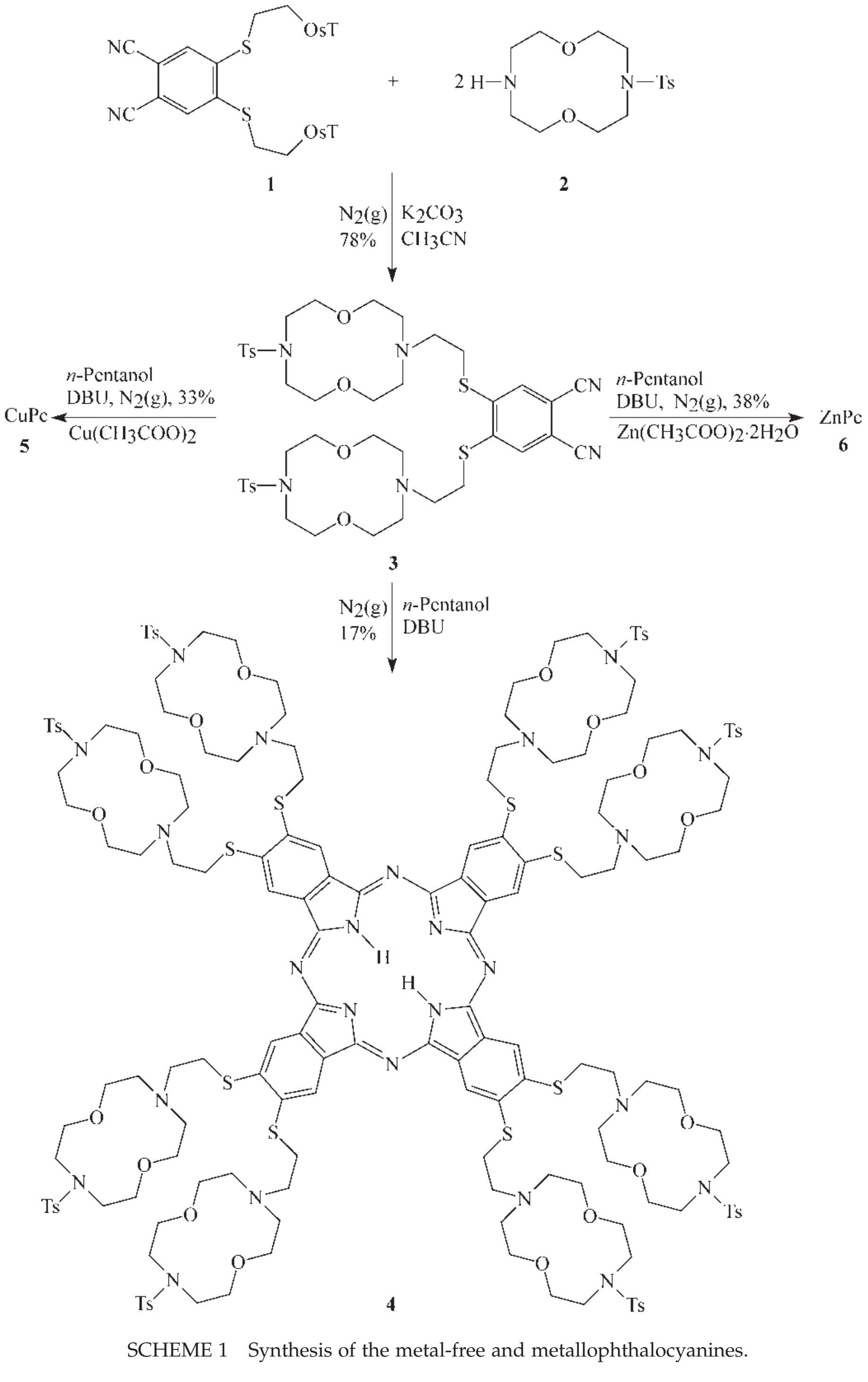
the 1:1 reaction of 1,2-bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzene **1** [20] and 4-[(4-methylphenyl)-sulfonyl]-1,7-dioxa-4,10-diazacyclododecane **2** [21] (Scheme 1). The addition reaction of **1** and **2** in refluxing acetonitrile containing finely ground anhydrous K_2CO_3 under a dry nitrogen atmosphere afforded the desired compound (**3**) in 78% yield after purification by column chromatography on silica gel (eluent chloroform:petroleum ether:methanol 7:2:1). 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 materials. In the ^1H NMR spectrum of **3**, the signal belonging to NH protons at 2.65 ppm in the precursor compound **2** disappear after the addition reaction. The singlet at 7.50 ppm and the multiplets at 7.32 and 7.70 ppm correspond to aromatic groups connected to $-SCH_2$ and $-SO_2-$, respectively. The signals concerning methylene protons neighboring nitrogen and sulfur show different values at 3.26 (NCH_2) and 2.91 ppm (SCH_2) as expected. Proton-decoupled ^{13}C NMR spectral data are in good agreement with



SCHEME 1 Synthesis of the metal-free and metallophthalocyanines.

the proposed structure. The characteristic signals concerning diazadioxa macrocycles and $C\equiv N$ groups at 68.76–70.33, 55.58, 51.15 and 111.14 ppm, respectively, also support the structure, as expected. The IR spectrum of **3** was easily verified with the disappearance of N–H and the presence of $C\equiv N$ stretching vibrations at 2228 cm^{-1}. This compound displayed the expected molecular ion peak at $m/z = 923$, indicating formation of $[M + Na]^+$.

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 **3** in a high-boiling solvent in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a dry nitrogen atmosphere afforded the metal-free phthalocyanine **4** in 17% yield as a green solid after purification by column chromatography on neutral alumina using chloroform:pyridine (8:2) as eluent. A diagnostic feature of the formation of **4** from **3** is the disappearance of the sharp $C\equiv N$ vibration at 2228 cm^{-1} of the reactant. The stretching vibrations at 3341 cm^{-1} for **4** can be attributed to the N—H band of the inner core of the metal-free phthalocyanine. ^{1}H NMR investigation of this compound provided the characteristic chemical shifts for the expected structure. A common feature of the ^{1}H NMR spectrum of **4** is the broad absorption caused probably by the aggregation of H_2Pc, which is frequently encountered at the concentration used for NMR measurements [22–24]. The inner core protons of this compound also could not be observed because of strong aggregation of the molecule [25, 26]. In the ^{13}C NMR spectrum of this compound, all signals are identical for the precursor dicyano derivative (**3**) except for the $C\equiv N$ carbons. The appearance of $C\equiv N$ signals at 154.15 ppm for **4** concerning the inner core instead of $C\equiv N$ absorptions in **3** is supported by the formation of phthalocyanine. The mass spectrum of this compound at $m/z = 3626.2$ $[M + Na + 1]^+$ lends support to the proposed formula for this structure.

The synthesis of metallophthalocyanines **5** and **6** was accomplished by reacting **3** and the corresponding metal acetate salts in *n*-pentanol in the presence of a few drops of DBU as a strong base at reflux temperature under dry nitrogen. Column chromato graphy with chloroform:methanol (9:1) and chloroform:ethanol (100:1) as eluents removed the copper and zinc phthalocyanines formed by self-condensation of **3** in 33% and 38% yields, respectively. The ^{1}H NMR spectrum of **6** was very similar to that of the metal-free phthalocyanine Pc except for the disappearance of the NH protons. The other NMR characteristics of this compound were similar to those of the precursor dicyano compound **3** and the metal-free phthalocyanine **4**. ^{1}H NMR measurements are precluded because of the paramagnetic nature of the copper(II) phthalocyanine (**5**). Cyclotetramerization of the dinitrile compound **3** was confirmed by the disappearance of the sharp $C\equiv N$ stretching vibration at 2228 cm^{-1} of the precursor dicyano derivative. The rest of the IR spectra of **5** and **6** closely resemble those of **3** and **4**, including the characteristic vibrations of tosyl, aliphatic and aromatic groups. The mass spectra of **5** and **6** were obtained by the fast atom bombardment (FAB) technique with *m*-nitrobenzyl alcohol as matrix. In positive scan mode the metallophthalocyanines showed a peak corresponding to $[M + Na]^+$ at m/z 3686.3 for **5** and a peak corresponding to $[M + Na + 1]^+$ at m/z 3689.2 for **6**. The 12-$[N_2O_2]$ macrocycles bind to Cu^{2+}, Zn^{2+} and Ag^+, but in this work the results of elemental analysis and the mass spectral data for the metallophthalocyanines **5** and **6** confirmed that the ratio of reactants was 1:1 metal:ligand [27–29].

The electronic absorption spectrum of the metal-free phthalocyanine **4** in chloroform 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 [30]. The split Q-band, characteristic of metal-free phthalocyanines, is observed at λ_{max} 727 and 706 nm with a shoulder at 635 nm, indicating the monomeric species; the monomeric species with D_{2h} symmetry shows two intense absorptions at around 700 nm [31–35]. On the other hand, such split-Q band absorptions in chloroform are due to $\pi \rightarrow \pi^*$ transition of this fully conjugated 18π electron systems [36, 37].

The copper(II) (**5**) and zinc(II) (**6**) phthalocyanates showed the expected absorptions (Fig. 1) at the main peaks of the Q- and B-bands appearing at 717, 715 and 365, 375 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted

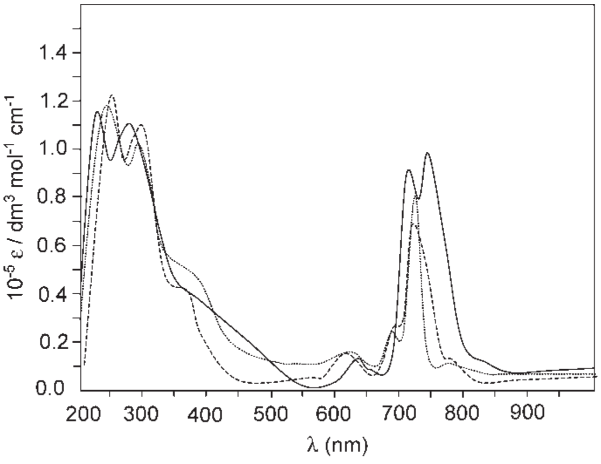


FIGURE 1 UV-Vis spectra of **4** (solid line), **6** (dotted line) in chloroform (1×10^{-5} M) and **5** (broken line) in pyridine (1×10^{-5} M).

MPc with D_{4h} symmetry [38–39], 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 showed significant changes in band positions and molar absorptivities [40]. Increasing the concentration (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.

EXPERIMENTAL

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to standard procedures [27–29]. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ or d_6-DMSO solution. Mass spectra were recorded on a Kratos MS-50 triple analyzer and VG Zap-Spec mass spectrometer by FAB using *m*-nitrobenzyl alcohol as matrix in concentrated DMF or DMSO solution. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1 spectrometer (KBr pellets). Electronic spectra were obtained on a Unicam UV2-100 spectrophotometer. Elemental analysis and metal contents of the compound were determined with a Hewlett-Packard 185 CHN analyzer and a Unicam 929 AA spectrometer, respectively. Melting points were determined by an electrothermal apparatus and are uncorrected. 1,2-Bis(2-tosyloxyethylmercapto)-4,5-dicyanobenzane [20] and 4-[(4-methylphenyl)sulfonyl]-1,7-dioxa-4,10-diazacyclododecane [21] were synthesized according to reported procedures.

4,5-Bis-{2-[10-(toluene-4-sulfonyl)-1,7-dioxa-4,10-diaza-cyclododec-4-yl]-ethylsulfonyl}-phthalonitrile

A round-bottom flask containing dry acetonitrile (100 cm^3) and fitted with a condenser was evacuated, refilled three times with dry nitrogen and connected to a vacuum line. Under dry nitrogen, the flask was charged with **2** (1.97 g, 6 mmol), **1** (1.76 g, 3 mmol) and an excess amount of finely ground anhydrous K_2CO_3 (4.14 g, 30 mmol) and the mixture was refluxed under argon for six days. The reaction was monitored by thin layer chromatography (eluent chloroform:petroleum ether:methanol 7:2:1). At the end of this period, the mixture was cooled to room temperature and filtered to separate any inorganic residue such as salts of potassium tosilate and unreacted K_2CO_3 and washed with acetonitrile. The major liquor and washing solvent were combined and evaporated to dryness to give an oily residue product under reduced pressure. Crushed ice (200 g) was added to the oily residue and stirred for 3 h and the resulting product was filtered off, washed with water and then dried *in vacuo*. The brown solid formed was chromatographed on silica gel (eluent chloroform:petroleum ether: methanol 7:2:1). The eluent was evaporated to dryness under reduced pressure and the solid product crystallized from methanol. Yield 2.1 g (78%); mp 98–100°C. IR (KBr pellets, cm^{-1}): 3060, 2923–2855, 2228, 1597, 1564, 1456, 1337, 1159, 1112, 815. ^{1}H NMR ($CDCl_3$): δ 7.70 (m, 4H, ArH), 7.50 (s, 2H, ArH), 7.32 (m, 4H, ArH), 3.88–3.58 (m, 16H, OCH_2), 3.26 (m, 12H, NCH_2), 2.91 (m, 4H, SCH_2), 2.74 (m, 8H, NCH_2), 2.42 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): 144.25 (Ar-tos), 143.28 (ArCS), 135.71 (ArC), 129.71 (ArCH), 128.45 (ArCH), 127.25 (ArCH), 115.69 (ArC), 111.14 (C≡N), 70.33–68.76 (OCH_2), 55.58 (NCH_2), 51.15 (NCH_2), 31.15 (SCH_2), 21.51 (CH_3). Anal. Calcd. for ($C_{42}H_{56}N_6O_8S_4$)(%): C, 56.00; H, 6.22; N, 9.33. Found: C, 55.84; H, 6.33; N, 9.13. MS (FAB positive); m/z 923 $[M + Na]^+$.

Metal-free Phthalocyanine (4)

A mixture of the dicyano derivative (**3**) (0.99 g, 1.1 mmol), dry *n*-pentanol (10 cm^3) and five drops of DBU was placed a stoppered Schlenk tube under a dry nitrogen atmosphere and heated gently, and then heated for 24 h at 160°C. After being cooled to room temperature, the dark green solid product was filtered off, washed with ethanol (25 cm^3) and diethylether (40 cm^3) and then dried *in vacuo*. The solid product was passed through on a short neutral alumina column using chloroform:pyridine (8:2) as eluent. The eluent was evaporated to 10 cm^3 under reduced pressure and 30 cm^3 of petroleum ether was added to the solution to give a green product. Yield 0.12 g (17%); mp 292–294°C. IR (KBr pellets, cm^{-1}): 3341, 3054, 2926–2846, 1637, 1596, 1568, 1445, 1160, 1122, 813. ^{1}H NMR (d_6-DMSO): δ 7.67–7.45 (m, 24H, ArH), 7.30 (m, 16H, ArH), 3.63 (m, 64H, OCH_2), 3.33 (m, 48H, NCH_2), 3.09 (m, 16H, SCH_2), 2.68 (m, 32H, NCH_2), 2.42 (s, 24H, CH_3). ^{13}C NMR (d_6-DMSO): δ 154.15 (C=N), 143.00 (Ar-tos), 139.36 (ArCS), 135.14 (ArC), 129.70 (ArCH), 126.92 (ArCH), 125.87 (ArCH), 116.64 (ArC), 69.25–68.41 (OCH_2), 54.56 (NCH_2), 49.83 (NCH_2), 29.13 (SCH_2), 20.84 (CH_3). UV–Vis [(in chloroform) λ_{max}/nm 10^{-5} ε(mol^{-1} cm^{-1})]: 727 (4.83), 706 (4.82), 635 (4.08), 361 (4.48), 299 (4.87), 265 (4.89). Anal. Calcd. for ($C_{168}H_{226}N_{24}O_{32}S_{16}$)(%): C, 55.96; H, 6.27; N, 9.32. Found: C, 55.77; H, 6.05; N, 9.44. MS (FAB positive: m/z 3626.2 $[M + Na + 1]^+$.

Metallophthalocyanines (5,6)

The dicyano derivative **3** (0.40 g, 0.44 mmol), dry *n*-pentanol (5 cm^3), five drops of DBU and 2.2 mmol of the corresponding metal acetate salts [copper(II) acetate (0.40 g) or zinc(II) acetate dihydrate (0.41 g)] were placed in a standard Schlenk tube under a dry nitrogen atmosphere and held at 150°C for 8 (**5**) or 43 h (**6**), respectively. The reaction was monitored by TLC using chloroform:methanol (9:1) as eluent. After cooling to room temperature, diethylether was added until a cloudy precipitate appeared, then the mixture was filtered off, the precipitate washed with a few cm^3 of water, cold ethanol and diethylether, and then dried *in vacuo*. The green solid was chromatographed on silica gel using chloroform:methanol (9:1) (**5**) or chloroform:ethanol (100:1) (**6**) as eluent. The eluent was evaporated to dryness and the product stirred with methanol (20 cm^3) (**5**) or 30 cm^3 a mixture of ethanol:petroleum ether (1:1) (**6**) until precipitation was complete. The dark (**5**) or pale (**6**) green solid was filtered off, washed with diethylether and then dried *in vacuo*.

CuPc (5)

Yield 0.136 g (33%); mp $>$ 300°C. IR (KBr pellets, cm^{-1}): 3060, 2925–2855, 1634, 1598, 1562, 1443, 1335, 1158, 1088, 814. UV–Vis [(in chloroform) λ_{max}/nm $10^{-5}\,\varepsilon$ ($mol^{-1}\,cm^{-1}$)]: 717 (4.53), 690 (4.33), 620 (4.05), 365 (4.48), 305 (4.86), 274 (4.92). Anal. Calcd. for ($C_{168}H_{224}N_{24}O_{32}S_{16}Cu$)(%): C, 55.02; H, 6.11; N, 9.17; Cu, 1.73. Found: C, 55.19; H, 6.34; N, 8.95; Cu, 1.61. MS (FAB positive): m/z 3686.3 $[M + Na]^+$.

ZnPc (6)

Yield 0.15 g (38%), mp $>$ 300°C. IR (KBr pellets, cm^{-1}): 3084, 3047, 2927–2849, 1646, 1594, 1570, 1445, 1323, 1159, 1127, 814. ^1H NMR (d_6-DMSO): δ 7.61–7.42 (m, 24H, ArH), 7.38 (m, 16H, ArH), 3.58 (m, 64H, OCH_2), 3.30 (m, 48H, NCH_2), 3.12 (m, 16H, SCH_2), 2.57 (m, 32H, NCH_2), 2.42 (m, 24H, CH_3). UV–Vis [(in chloroform) λ_{max}/nm $10^{-5}\,\varepsilon$ ($mol^{-1}\,cm^{-1}$)]: 715 (4.70), 688 (4.18), 625 (4.00), 375 (4.49), 303 (4.83), 269 (4.90). Anal. Calcd. for ($C_{168}H_{224}N_{24}O_{32}S_{16}Zn$)(%): C, 55.00; H, 6.11, N, 9.16; Zn, 1.78. Found: C, 55.26; H, 5.93; N, 8.98; Zn, 2.01. MS (FAB positive): m/z 3689.2 $[M + Na + 1]^+$.

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References

[1] Moser, F. H.; Thomas, A. L. *The Phthalocyanines*; CRC Press: Boca Raton, 1983.

[2] Leznoff, C. C., Lever, A. B. P., Eds.; *Phthalocyanines: Properties and Applications*; VCH: New York, 1989 and 1993; Vols 1 and 2.

[3] Bekaroğlu, Ö. *Appl. Organomet. Chem.* **1996**, *10*, 605.

[4] de la Torre, G.; Torres, T. *J. Porph. Phthalocyan.* **1997**, *1*, 221.

[5] Hamuryudan, E.; Bayır, Z. A.; Bekaroğlu, Ö. *Dyes Pigments* **1991**, *43*, 77.

[6] Matlaba, P.; Nyokong, T. *Polyhedron* **2002**, *21*, 2463.

[7] McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, 1998.

[8] Yu, S.-Y.; Luo, O.-H.; Shen, M.-C.; Huang, X.-Y.; Yang, W.-H.; Zhang, Z. *Inorg. Chim. Acta* **1994**, *223*, 181.

[9] Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19.

[10] Lukyanets, E. *J. Porph. Phthalocyan.* **1999**, *3*, 424.

[11] Sanchez, M.; Fache, E.; Bonnet, D.; Meunıer, B. *J. Porph. Phthalocyan.* **2001**, *5*, 867.

[12] Gürek, A.; Ahsen, V.; Gül, A.; Bekaroğlu, Ö. *J. Chem. Soc., Dalton Trans.* **1991**, 3367.

[13] Koçak, M.; Okur, A. İ.; Bekaroğlu, Ö. *J. Chem. Soc., Dalton Trans.* **1994**, 323.

[14] Koçak, M.; Gürek, A.; Gül, A.; Bekaroğlu, Ö. *Chem. Ber. 127* **1994**, 355.

[15] Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

[16] Gokel, G. W.; Korzeniowski, S. H. *Macrocyclic Polyether Syntheses*; Springer-Verlag: Berlin, 1982.

[17] Kumar, A.; Mageswaran, S.; Sutherland, I. O. *Tetrahedron* **1986**, *42*, 3291.

[18] Anelli, P. L.; Montanari, F.; Quici, S. *J. Org. Chem.* **1988**, *53*, 5292.

[19] Quici, S.; Manfredi, A.; Buttafava, M. *J. Org. Chem.* **1996**, *61*, 3870.

[20] Gürek, A. G.; Bekaroğlu, Ö. *J. Porph. Phthalocyan.* **1997**, *1*, 227.

[21] Anelli, P. L.; Montanari, F.; Quici, S. *J. Org. Chem.* **1988**, *53*, 5392.

[22] Yıldız, S. Z.; Gök, Y. *N. J. Chem.* **1998**, 1365.

[23] Gök, Y.; Kantekin, H.; Değir-Mencioğlu, I. *Supramol. Chem.* **2003**, *15*, 335.

[24] Hanack, M.; Heckmann, H.; Polley, R. *Methods of Organic Chemistry*; Georg Thieme Verlag: Stuttgart, 1998; Additional Supplementary Volume, p 776.

[25] van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957.

[26] Bilgin, A.; Ertem, B.; Gök, Y. *Tetrahedron Lett.* **2003**, *44*, 3829.

[27] Cheney, J.; Lehn, J. M.; Sauvage, J. P.; Stubbs, M. E. *J. Chem. Soc., Chem. Commun.* **1972**, 1100.

[28] Arraud-Neu, F.; Almasio, M. C.; Spiess, B.; Schwing-Weill, M. J.; Sullivan, S. A.; Lehn, J. M. *Helv. Chim. Acta* **1985**, *68*, 831.

[29] Alberts, A. H.; Lehn, J. M.; Parker, D. *J. Chem. Soc., Dalton Trans.* **1985**, 2311.

[30] Yılmaz, i̇; Bekaroğlu, Ö *Chem. Ber.* **1996**, *129*, 967.

[31] Whalley, M. J. *J. Chem. Soc.* **1961**, 866.

[32] Kroenke, W.; Kenney, M. E. *Inorg. Chem.* **1964**, *6*, 1587.

[33] Gürek, A. G.; Bekaroglu, Ö. *J. Chem. Soc., Dalton Trans.* **1994**, 1419.

[34] Sielcken, O. E.; van Tilborg, M. M.; Hendricks, R.; Drenth, W.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1987**, *109*, 4261.

[35] Cuellar, E. A.; Marks, T. *Inorg. Chem.* **1981**, *20*, 3766.

[36] Gök, Y.; Kantekin, H.; Bilgin, A.; Mendil, D.; Değirmencioğlu, i̇ *J. Chem. Soc., Chem. Commun.* **2001**, 285.

[37] Bilgin, A.; Gök, Y. *Tetrahedron Lett.* **2002**, *43*, 5343.

[38] Takahashi, K.; Kawashima, M.; Tomita, Y.; Itoh, M. *Inorg. Chim. Acta* **1995**, *232*, 69.

[39] Stillman, M. J.; Nyokong, T. In Chapter 3, *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 1, p 3.

[40] Kobayashi, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1987**, *109*, 7433.