Novel Two-fold-macrocycle-substituted Phthalocyanines

Makbule Koçak, Ali I. Okur and Özer Bekaroglu *
Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

New metallophthalocyanines (M = Cu or Ni) substituted in peripheral positions with four 14-membered tetraaza macrocycles each attached to a 15-membered crown ether have been prepared in a multi-step reaction sequence. The *N*-tosylated derivatives are extensively soluble in apolar solvents and form adducts with alkali-metal cations. Detosylation of the macrocyclic aza groups provides donor sites for binding transition-metal ions (*e.g.* Ni^{II}) which leads to pentanuclear water-soluble complexes.

The self-assembly of supramolecular compounds bearing multiple binding sites is of great interest because of the wide range of applications such as to biosensors, molecular electronics and energy storage devices as well as the biomimicking of natural systems.[1] Phthalocyanines have sufficiently stable rigid cores to permit the task of organizing binding sites in a definite geometry.[2] The introduction of electron-donating substituents into them produces a bathochromic shift in absorption to the near-infrared region, thus providing a way to tune this absorption band.[3]

We have previously synthesised series of phthalocyanines substituted with oxa- and/or aza-macrocycles. Our first such contribution was the synthesis of crown ether-substituted phthalocyanines which showed extreme solubility in common organic solvents and a high tendency for alkali-metal-ion binding;[4–7] X-ray diffraction studies on these products indicated the formation of ion channels allowing the migration of alkali- or alkaline-earth-metal cations.[8] An additional advantage of using a monoazacrown ether substituent was the solubility in water obtained by quaternization of the aza function.[9] Phthalocyanines substituted with 14- or 15-membered tetraazamacrocycles provided donor sites for binding transition-metal ions, leading to pentanuclear complexes.[10,11] When trioxadiaza macrocycles were tried as substituents no alkali- or transition-metal complex could be isolated owing to lower stability.[12]

As a further step in the synthesis of macrocycle-substituted phthalocyanines, we have designed a new molecule carrying four 14-membered tetraazamacrocycles each attached to a 15-crown-5 unit as two-layered substituents. While the combination of these two donor rings is expected to result in the coordination of both alkali- and transition-metal ions, their solubilities will be different. We here report studies on the synthesis of phthalocyanines with eight macrocyclic substituents.

Results and Discussion

As a first step, the crown ether–tetraazamacrobicycle was prepared (Scheme 1 and Table 1). The ditosyl derivative **1** of 4′,5′-diaminobenzo-15-crown-5[13] (15,16-diamino-2,3,5,6,8,9,-11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) was treated with the hydrobromide salt of 2-bromoethylamine in dimethylformamide using potassium carbonate as the base to give the *N*,*N*′-bis(2-aminoethyl)-*N*,*N*′-ditosyl derivative **2**. The primary amine groups were then tosylated in pyridine at 130 °C. Under weak carbonate base conditions, 1,2-dibromo-4,5-bis(bromomethyl)benzene reacted with the 2-tosylaminoethyl groups of **3** to form the 14-membered tetraazamacrocycle **4a**. Treatment with water at the end of the reaction prevented any difficulty which might have arisen from the use of potassium carbonate as the base by decomposing any adduct formed between the crown ether unit and the alkali metal. The yield of the ring-closure reaction was reasonably high (*ca.* 32%) as encountered in the cyclization of similar tetraazamacrocycles from tosylamino derivatives and alkyl halides.[10,11,14] No 2:2 cyclization product was detected although molecular models revealed no steric constraints to this. The usefulness of the tosyl end group should be noted in that it enables the ring-closure reaction due to the restricted rotation of the tosylamide linkage and is stable.

Table 1 Analytical data for the starting materials and the phthalocyanines*

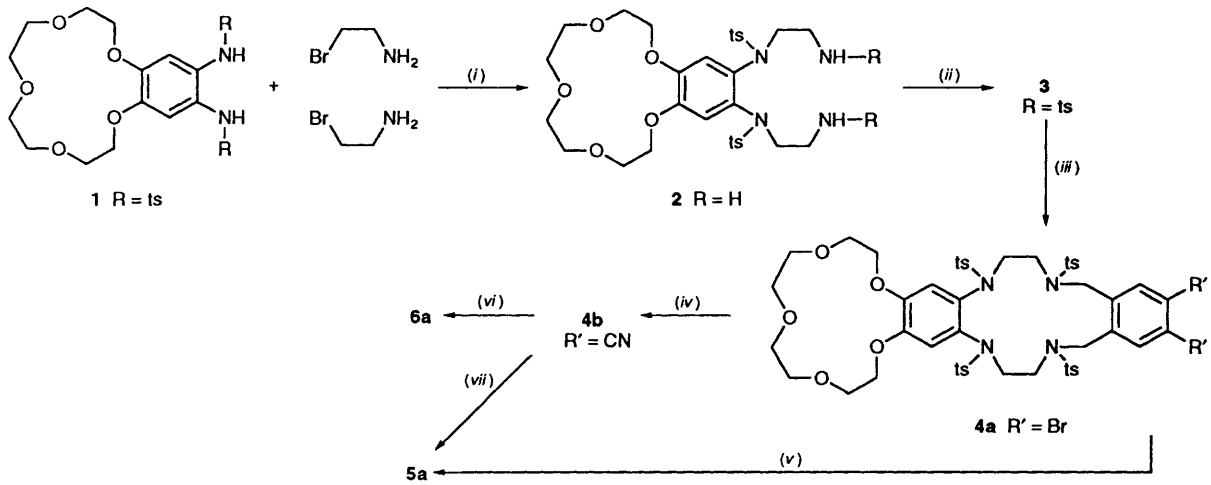
Compound	Analysis (%) C	H	N
1	55.70 (55.45)	5.90 (5.65)	4.55 (4.60)
2	55.65 (55.45)	6.30 (6.40)	8.10 (8.10)
3	55.25 (55.20)	5.40 (5.65)	5.40 (5.60)
4a	51.30 (51.45)	4.95 (4.80)	4.25 (4.45)
4b	58.30 (58.05)	5.25 (5.05)	7.30 (7.25)
5a	57.40 (57.50)	5.40 (5.20)	7.30 (7.20)
5b	60.50 (60.85)	6.95 (6.55)	14.85 (15.20)
5c	49.10 (49.30)	5.55 (5.30)	12.05 (12.30)
6a	57.55 (57.65)	5.20 (5.00)	7.10 (7.25)
5a·2KSCN	55.55 (55.70)	4.50 (4.95)	6.95 (7.50)

* Required values are given in parentheses.

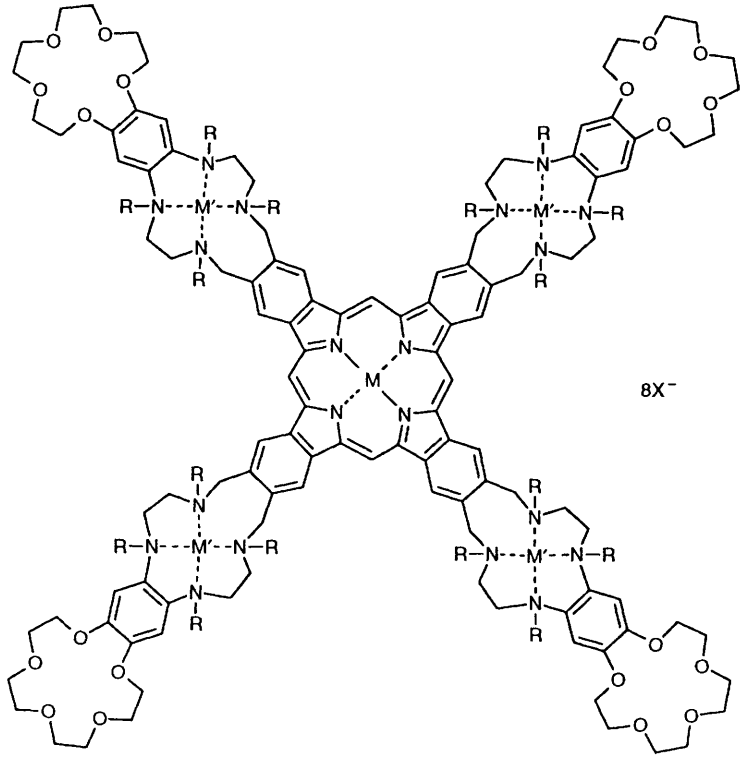
Phthalocyanine formation was accomplished either directly by the reaction of the dibromo derivative **4a** with copper(I) cyanide in pyridine, or by converting **4a** into the dicyano-derivative **4b** according to the Rosenmund von Braun reaction under milder conditions and then using this compound to prepare other metallophthalocyanines. The yields of these reactions were rather low, as encountered for phthalocyanines with other bulky groups.[7,12]

The most obvious feature of complexes **5a** and **6a** is their extensive solubility in common organic solvents, *e.g.* chloroform, dichloromethane, dimethyl sulfoxide (dmso), dimethylformamide (dmf), toluene, *etc.* The solubilities in chloroform are of the order of 5×10^{-3} mol dm^{-3} and are higher than those of corresponding complexes containing only crown ether[4,7] or tetraaza macrocyclic substituents.[10,11] The two-fold substitution results in a more bulky group, so the solubility is enhanced.

Detosylation of complex **5a** was accomplished with highest yield at 125 °C by use of concentrated sulfuric acid for 5 h. While longer reaction times and higher temperatures resulted in decomposition to phthalimide derivatives, milder conditions



Scheme 1 ts = Tosyl (*p*-$MeC_6H_4SO_2$). (*i*) dmf, K_2CO_3; (*ii*) tosyl chloride, pyridine; (*iii*) dmf, K_2CO_3, 1,2-dibromo-4,5-bis(bromomethyl)benzene; (*iv*) dmf, CuCN; (*v*) pyridine, CuCN; (*vi*) dmf, $NiCl_2$; (*vii*) quinoline, CuCN



	M	M'	R	X
5a	Cu	–	ts	–
5b	Cu	–	H	–
5c	Cu	Ni	H	Cl
6a	Ni	–	ts	–

gave partially detosylated products. The solubility of the detosylated product **5b** in halogenated hydrocarbons was very low, but was enhanced in methanol and ethanol.

The interaction of alkali-metal picrates with the crown ether groups of complex **5a** was verified by extraction experiments.[4,15] This derivative was chosen owing to its higher solubility in chloroform. Amongst the alkali-metal cations the highest affinity was observed for K^+ which can be attributed to the sandwich-type adduct formation between two (15-crown-5) units and the cation. The stoichiometry of the complex isolated from a mixture of **5a** and KSCN was also found to be 1:2. The extremely low solubility of the latter product might be a result of sandwich-type adduct formation among crown ether groups of different molecules, leading to a network polymer structure.

An attempt to prepare a pentanuclear complex was made with the detosylated copper(II) phthalocyaninate **5b** and nickel(II) chloride in absolute methanol.[11] Elemental analysis indicated a 1:4 (**5b**:Ni^{II}) ratio as a consequence of encapsulation of one metal ion by each tetraaza macrocycle. The solubility of the product in water can be rationalized by the highly ionic character of the complex.

Spectral investigations on the newly synthesised intermediates and phthalocyanines are in accord with the proposed structures. Comparison of the IR spectra of each step gave some

Table 2 Proton NMR spectral data (δ) for the reactants and the phthalocyanines

Compound	Tosyl aromatic H	Aromatic H	CH_2 of aryl	CH_2O, CH_2N	NH_2, NH	Tosyl CH_3
1[a]	7.55–7.51 (4 H, d) 7.23–7.19 (4 H, d)	6.43 (2 H, s)	—	4.0–3.7 (16 H, m)	6.68 (2 H, s)[b]	2.38 (6 H, s)
2[c]	7.54–7.50 (4 H, d) 7.26–7.22 (4 H, d)	6.59 (2 H, s)	—	3.74–3.54 (24 H, m)	3.23 (4 H, s)[b]	2.33 (6 H, s)
3[c]	7.58–7.54 (8 H, d) 7.37–7.33 (8 H, d)	6.45 (2 H, s)	—	3.77–3.55 (24 H, m)	8.86 (2 H, s)[b]	2.36 (12 H, s)
4a[c]	7.77–7.73 (8 H, d) 7.45–7.44 (8 H, d)	7.40 (2 H, s) 6.51 (2 H, s)	4.66 (4 H, s)	3.84–3.54 (24 H, m)	—	2.42 (12 H, s)
4b[c]	7.76–7.72 (8 H, d) 7.41–7.37 (8 H, d)	7.90 (2 H, s) 6.61 (2 H, s)	4.75 (4 H, s)	3.87–3.59 (24 H, m)	—	2.41 (12 H, s)
6a[a,d]	7.7 (32 H) 7.4 (32 H)	7.9 (8 H, s) 6.5 (8 H, s)	4.8 (16 H, s)	3.9–3.5 (96 H, m)	—	2.38 (48 H, s)

[a] In $CDCl_3$. [b] Broad, D_2O exchangeable. [c] In $(CD_3)_2SO$. [d] Broad resonances.

Table 3 Electronic spectra of the phthalocyanines

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
5a[a]	672 (13.8), 640(sh) (2.6), 602 (2.8), 330 (5.3)
5b[b]	678 (8.9), 639(sh) (1.6), 607 (1.7), 335 (2.4)
5c[c]	668 (10.6), 637(sh) (3.8), 602 (4.1), 330 (6.2)
6a[a]	670 (15.1), 640(sh) (5.2), 605 (5.3), 340 (8.9)
5a·2KSCN[d]	682 (6.2), 640(sh) (1.55), 615 (1.36), 352 (2.3)

[a] In chloroform. [b] In methanol. [c] In water. [d] In dmso.

hints as to the nature of the products. In this context, we may cite the presence of SO_2 vibrations in the spectra of **1**–**3** and **4a** at 1340 and 1160 cm^{-1}, C≡N of **4b** at 2220 cm^{-1} and the SCN^- counter anion in **5a**·2KSCN at 2050 cm^{-1}. After detosylation the NH vibrations of **5b** appear at 3250 cm^{-1}. The ^{1}H NMR spectra of the intermediates show very small shifts when compared with the nickel(II) phthalocyaninate **6a** (Table 2). However, the rather broad bands in the case of **6a** are probably due to chemical exchange caused by aggregation–disaggregation equilibria which are effective at the high concentrations used in the NMR measurements.[6]

Changes occurring in the low-energy region of the UV/VIS spectra corresponding to the phthalocyanine core are especially important in identifying intermolecular interactions (Table 3). The spectrum of the *N*-tosylated copper-phthalocyaninate **5a** in chloroform is typical for phthalocyanines with bulky substituents such as crown ethers or long alkoxy chains;[4,16] the intense absorption at 672 nm is concentration dependent, decreasing at higher values, and gives rise to a shoulder at 640 nm indicating the presence of polymeric species.[17] Compared with the spectrum of **5a**·2KSCN in dmso, the shoulder around 638 nm is present to a lesser extent but shows no appreciable change with concentration. This can be used to support the interaction of crown ether units in **5a**·2KSCN where crown ethers from different molecules form sandwich-type adducts leading to network polymers rather than a dimer between two phthalocyanine molecules and four potassium ions. The spectra of the detosylated phthalocyanine **5b** were recorded in both chloroform and water; while the first spectrum was the same as that of **5a**, the polar solvent led to aggregation and the shoulder around 640 nm was intensified.[4,11,17] Complexation of four azamacrocycles with Ni^{II} did not lead to appreciable changes in the Q-band region in water, as expected from the low-intensity d–d transitions.

Experimental

Routine IR spectra were recorded on a Perkin Elmer 598 spectrophotometer as KBr pellets, electronic spectra on a Varian DMS 90 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TÜBITAK Marmara Research Center. Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer using $SiMe_4$ as the reference. 4′,5′-Diaminobenzo-15-crown-5 was synthesised according to the reported procedure.[13]

Preparations.—*Compound* **1**. 4′,5′-Diaminobenzo-15-crown-5 (2.98 g, 10 mmol) was dissolved in pyridine (80 cm^3) and a solution of toluene-*p*-sulfonyl chloride (4.19 g, 22 mmol) in pyridine (40 cm^3) was added dropwise over 2 h at −5 °C and stirred overnight. Then the solution was poured slowly on to a stirred mixture of concentrated HCl (150 cm^3) and ice (400 g). The precipitated ditosylate was filtered off and washed with water (500 cm^3). The yield of the creamy coloured ditosylate was 5.16 g (85%). It was very soluble in ethanol, chloroform, dichloromethane and dmf. ν_{max} 3220, 3090, 2920, 1510, 1340, 1210–1090, 680, 580 and 550 cm^{-1}.

Compound **2**. Compound **1** (6.06 g, 10 mmol) was dissolved in dry dmf (90 cm^3) containing finely ground anhydrous K_2CO_3 (12 g, excess) and stirred under nitrogen at 30 °C for 1 h. A solution of 2-bromoethylamine hydrobromide (6.147 g, 30 mmol) in dry dmf (70 cm^3) was added dropwise over 3 h and stirred at the same temperature for 3 d. When the reaction mixture was poured onto ice (500 g) the product was precipitated. It was filtered off, washed first with water until the filtrate was neutral and then with ethanol and diethyl ether, and dried. Yield: 5.68 (82%). ν_{max} 3420, 3230, 3060, 2940, 2910, 1600, 1510, 1340, 1210–1090 and 690 cm^{-1}.

Compound **3**. Compound **2** (3.46 g, 5 mmol) was dissolved in pyridine (150 cm^3) under nitrogen and a solution of toluene-*p*-sulfonyl chloride (2.1 g, 11 mmol) in pyridine (20 cm^3) was added dropwise in 0.5 h at 130 °C. The reaction mixture was refluxed for 48 h and after cooling was poured onto a mixture of concentrated HCl (100 cm^3) and ice (500 g) and stirred for about 1 h. The viscous organic phase separated was extracted with chloroform (5 × 100 cm^3) and the organic layer treated with hydrochloric acid solution (10%) until free of any pyridine residue and then washed with water until neutral and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave an oily product which was treated with refluxing hexane to leave a solid product. Yield 3.26 g (65%), m.p. 65 °C. ν_{max} 3250, 3050, 2940–2890, 1610, 1500, 1340, 1220–1090 and 690 cm^{-1}.

Compound **4a**. Compound **3** (10.01 g, 10 mmol) was dissolved in dry dmf (100 cm^3) containing finely ground anhydrous K_2CO_3 (4 g, excess) and stirred under nitrogen at 35 °C for 1 h. A solution of 1,2-dibromo-4,5-bis(bromomethyl)benzene (5.2 g, 12.3 mmol) in dry dmf (75 cm^3) was added dropwise over 3 h and stirred at the same temperature for 48 h. The mixture was then poured onto ice–water (500 g) and stirred for 1 h. The precipitate was filtered off, washed with water until the filtrate was neutral and dried *in vacuo*. Recrystallization from acetic acid gave a creamy coloured product. Yield: 4 g (31.7%); m.p.

160 °C (decomp.). ν_{max} 3090, 2960–2880, 1510, 1340, 1205–1090, 670, 590 and 550 cm^{-1}.

Compound **4b**. Compound **4a** (0.504 g, 0.4 mmol), CuCN (0.179 g, 2 mmol) and anhydrous dimethylformamide were refluxed at 170 °C for 10 h with addition of a catalytic amount of pyridine. After cooling to room temperature the mixture was poured into aqueous NH_4OH (25%, 200 cm^3) and air was passed through the solution for 24 h. The creamy coloured precipitate was filtered off, washed first with NH_4OH solution (10%) and then with water until the filtrate was neutral and dried *in vacuo* at 50 °C. This crude product was dissolved in chloroform, filtered and the filtrate evaporated to dryness. Recrystallization from ethanol gave a creamy coloured product. Yield 0.28 g (60.7%), m.p. > 215 °C. ν_{max} 3070, 2960–2900, 2240, 1510, 1450, 1325, 1210–1060, 690, 580 and 555 cm^{-1}. ^{13}C NMR: (CCl_3) δ 21.57, 53.39, 68.82, 69.18, 70.27, 71.05, 112.65, 112.95, 114.77, 115.24, 127.43, 127.66, 129.76, 134.34, 134.79, 135.52, 135.79, 141.58, 144.72 and 147.81.

Complex **5a**. A mixture of dibromo compound **4a** (0.252 g, 0.2 mmol), CuCN (0.054 g, 0.6 mmol) and dry pyridine (1 cm^3) was heated and stirred at 190 °C under nitrogen in a sealed glass tube for 30 h. After cooling to room temperature the dark green mixture was diluted with EtOH (50 cm^3) and the precipitate centrifuged off. It was washed with ethanol until free of pyridine and then refluxed with a solution of NaCN in water–ethanol (1:2) (four times) to remove the excess of CuCN and filtered off. The crude product was dissolved in chloroform and filtered. The blue product was precipitated by addition of ethanol. Yield: 0.036 g (15.1%). ν_{max} 2960–2900, 1510, 1330, 1205–1095, 670 and 550 cm^{-1}.

Complex **6a**. A mixture of dicyano compound **4b** (1.153 g, 1 mmol), $NiCl_2$ (32.5 mg, 0.25 mmol) and anhydrous dimethylformamide (2 cm^3) was heated and stirred in a sealed glass tube for 3 d. After cooling, the reaction mixture was diluted with methanol (20 cm^3) and the precipitate was filtered off. It was treated with boiling methanol twice to dissolve any unreacted metal salt. Further purification was accomplished by column chromatography with neutral alumina and MeOH–$CHCl_3$ (1:20) as eluent. Yield: 65 mg (5.6%). ν_{max} 2960–2910, 1510, 1340, 1205–1095, 670 and 560 cm^{-1}.

Complex **5b**. Complex **5a** (0.100 g, 0.02 mmol) was treated with concentrated H_2SO_4 (10 cm^3) at 125 °C for 5 h. After cooling, the mixture was poured into cold ethanol and centrifuged. Washing with ethanol was repeated three times to remove the excess of H_2SO_4. The protonated product (0.075 g) was dissolved in water (40 cm^3) and the mixture raised to pH 12 by addition of aqueous NaOH solution (2 mol dm^{-3}) which resulted in partial precipitation of the phthalocyanine. The whole mixture was extracted with chloroform (3 × 30 cm^3) and evaporation of the combined extracts after drying over anhydrous Na_2SO_4 gave the dark green phthalocyanine **5b** with a purple lustre. Yield: 31 mg (66%). ν_{max} 3250, 2960–2900, 1600, 1510, 1450, 1410, 1300, 1220–1100, 1030, 900, 750 and 710 cm^{-1}.

Adduct **5a**·2KSCN. Complex **5a** (140 mg, 0.03 mmol) was dissolved in chloroform (30 cm^3), a solution of KSCN (14 mg, 0.144 mmol, excess) in ethanol (5 cm^3) added and the mixture refluxed for 15 h. The precipitated product was filtered off, washed with chloroform and dried *in vacuo*. Yield: 80 mg (54.9%). ν_{max} 2960–2900, 2050, 1510, 1340, 1210–1100, 670 and 550 cm^{-1}.

Complex **5c**. To a stirred solution of complex **5b** (22 mg, 0.01 mmol) in absolute methanol (10 cm^3) was added a solution of $NiCl_2$ (13 mg, 0.1 mmol) in absolute methanol (5 cm^3). The mixture was refluxed for 5 h under nitrogen. The dark green precipitate was filtered off, washed with absolute methanol and dried *in vacuo*. Yield 20 mg (74%). ν_{max} 3240, 2960–2900, 1600, 1510, 1430, 1240–1100, 980, 750 and 710 cm^{-1}.

Acknowledgements

We thank the Research Fund of the Technical University of Istanbul for financial support.

References

1 J. M. Lehn, *Chem. Scr.*, 1988, **28**, 237.
2 C. Piechocki and J. Simon, *Nouv. J. Chim.*, 1985, **9**, 159.
3 M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson and K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2453.
4 A. R. Koray, V. Ahsen and Ö. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932; V. Ahsen, E. Yilmazer, M. Ertas and Ö. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, 1988, 401.
5 V. Ahsen, E. Yilmazer, A. Gürek, A. Gül and Ö. Bekaroglu, *Helv. Chim. Acta*, 1988, **71**, 1616.
6 A. I. Okur, A. Gül, A. Cihan, N. Tan and Ö. Bekaroglu, *Synth. React. Inorg. Metal-Org. Chem.*, 1990, **20**, 1399.
7 S. Sarigül and Ö. Bekaroglu, *Chem. Ber.*, 1989, **122**, 291.
8 C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yilmazer and Ö. Bekaroglu, *Chem. Phys. Lett.*, 1987, **139**, 362.
9 V. Ahsen, A. Gürek, E. Musluoglu and Ö. Bekaroglu, *Chem. Ber.*, 1989, **122**, 1073; E. Musluoglu, V. Ahsen, A. Gül and Ö. Bekaroglu, *Chem. Ber.*, 1991, **124**, 2531.
10 M. Koçak, A. Cihan, Ali Okur and Ö. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1991, 578.
11 A. Gürek, V. Ahsen, A. Gül and Ö. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, 1991, 3367.
12 G. Gümüs, Z. Z. Öztürk, V. Ahsen, A. Gül and Ö. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, 1992, 2485.
13 A. Gül, A. I. Okur, A. Cihan, N. Tan and Ö. Bekaroglu, *J. Chem. Res.*, 1986, (*S*) 90; (*M*) 881; A. Gül, A. I. Okur, S. Can and Ö. Bekaroglu, *Chem. Ber.*, 1986, **119**, 3870.
14 F. Chavez and A. D. Sherry, *J. Org. Chem.*, 1989, **54**, 2990.
15 A. H. Haines, I. Hodgkisson and C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1983, 311.
16 J. Vacus, P. Doppelt, J. Simon and G. Memetzidis, *J. Mater. Chem.*, 1992, **2**, 1065.
17 M. J. Stillman and T. Nykong, in *Phthalocyanines Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1989, p. 133.

Received 10*th June* 1993; *Paper* 3/03351A