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REVIEW

Phthalocyanines Containing Macrocycles

Özer Bekaroğlu
Department of Chemistry, Faculty of Science, Technical University of Istanbul, 80626 Maslak–Istanbul, Turkey

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CONTENTS

1 INTRODUCTION

A phthalocyanine (pc) is a synthetic macrocyclic compound which was first reported in 1907 by Braun and Tcherniac, as a by-product of the preparation of *o*-cyanobenzamide from phthalamide and acetic anhydride at high temperature.[1] The copper complex of phthalocyanine (Cupc) was obtained by Diesbach and Von der Weid in 1927 by the reaction of *o*-dibromobenzene and CuCN in pyridine.[2] They also observed the exceptional stability of this compound.

The structures of the metal-free and metallophthalocyanines were published by Linstead and co-workers[3–6] in 1934 after a long study starting in 1929 and X-ray diffraction analyses by Robertson.[7–9] Since that time, and with almost all the metal ions in the Periodic Table, numerous metal phthalocyanines have been prepared. As excellent blue and green dyestuffs, phthalocyanines are an important article of commerce used in inks (ballpoint pens), dyestuffs for textiles and colouring for plastic and metal surfaces, and are produced at over 50 000 tons per year.

Recently they have been used as photoconducting agents in photocopying machines,[10, 11] as sensing elements in chemical sensors, as electrochromic display devices, as photodynamic reagents for cancer therapy, and for other medical applications. Other applications include uses for optical computer read–write disc and related information storage systems, as laser dyes, in liquid-crystal colour display applications, in photovoltaic cell elements, as catalysts for control of sulphur effluents, for oxidizing saturated hydrocarbons at low temperature, and for increasing the octane rate of gasoline.[12] This suggests that their potential usage in many fields of technology is likely to increase significantly. There are several methods of preparing phthalocyanines, depending on the starting materials.[10, 13, 14] Phthalocyanine and its metallated derivatives have been purified by sublimation and by dissolution in concentrated sulphuric acid followed by precipitation on ice. The extreme insolubility of most phthalocyanines makes the usual recrystallization, extraction and chromatographic methods inapplicable. The solubility of phthalocyanines can be enhanced by adding various groups to the benzene rings or by complexation with macrocyclic polyethers of the disodium and dipotassium phthalocyanines.[15, 16]

From another viewpoint, after the first publication by Pedersen on crown ethers,[17, 18] a large number of macrocyclic compounds capable of binding cations or anions have been prepared and

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investigated. Since the discovery of the crown ethers, host–guest or 'supramolecular' chemistry has grown enormously giving chemists many opportunities to design and to synthesize new compounds, and to investigate their applications. Many macrocyclic polyethers, polyamines, polythioethers and other related molecules contain central hydrophilic cavities with either electronegative or electropositive binding atoms and exterior flexible frameworks exhibiting hydrophobic behaviour. They are capable of binding a wide variety of alkali and alkaline-earth metal ions (hard cations) as well as transition-metal ions (soft cations) or anions and in many cases they undergo conformational changes during binding. The hydrophobic character of their exteriors allows them to solubilize ionic substances in non-aqueous solvents and in membrane media. The selective binding of certain of these cations results in their use as models for carrier molecules in the study of active ion transport phenomena in biological systems as well as in other applications.

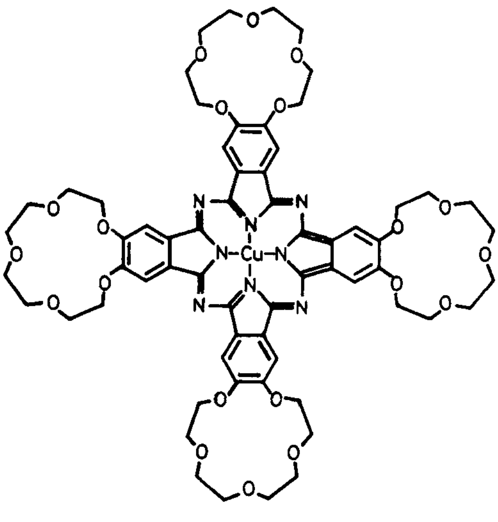
The present Review deals exclusively with phthalocyanines which combine with crown ethers or related macrocycles to form a new class of compounds. These phthalocyanines are able to bind hard and soft metal cations to form homo- or hetero-polynuclear complexes. These combinations usually affect not only the electronic or geometric properties but also the physical and chemical properties of the phthalocyanines.

2 PHTHALOCYANINES CONTAINING (O_n) MACROCYCLES

Copper phthalocyanine containing 15-crown-5 (Cucpc) in which crown ether units are integral parts of the molecule has been reported independently by three groups in a short time interval.[19–21] This copper phthalocyanine containing four benzo-15-crown-5 moieties in the molecule (**1**) was the first example of a novel class of soluble phthalocyanines.

Compound **1** was prepared by reaction of 4,5-dibromobenzo-15-crown-5 and CuCN in boiling quinoline in 8 h, or both compounds were reacted in pyridine in a sealed tube at 220 °C (48% yield) and purified by known procedures.

The compound was readily soluble in dichloromethane, chloroform, acetone, ethanol, methanol, pyridine, dimethyl sulphoxide and dimethylformamide. A sodium complex was obtained by simply mixing **1** with NaSCN in methanol according to a procedure given in the literature.[22] In order to measure the binding capability of Na^+ and K^+ ions of **1**, a liquid–liquid extraction of sodium and potassium picrates with **1** into dichloromethane was carried out. The result was that the extraction constant for potassium ions was about twice that of sodium ions. The higher potassium ion selectivity is generally considered to be due to the high extractability of the 2:1 potassium complex.[23] In this case a sandwich complex between two Cucpc and four potassium ions must be assumed, to explain the higher selectivity of this cation.

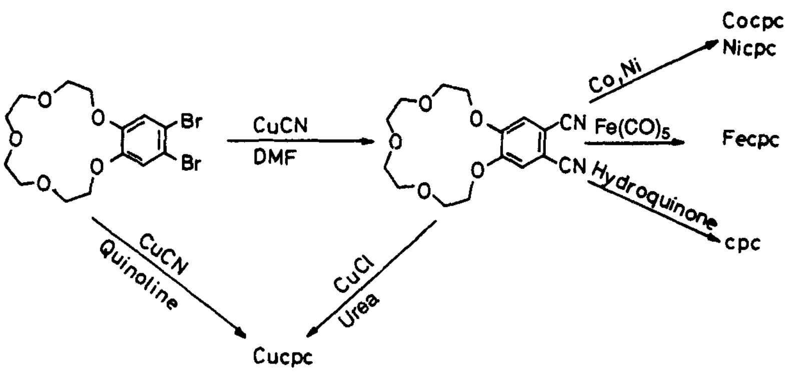


1

Metal-free phthalocyanines containing crown ether (cpc) can only be obtained by starting with reactants which already contain these groups. The metal-free cpc was synthesized by heating a mixture of dicyanobenzo-15-crown-5 with hydroquinone in a sealed tube (Scheme 1).[24]

Transition-metal complexes were also prepared from the dicyano compound and the corresponding metal salt, or carbonyl complex, in a high-boiling solvent. The IR spectra of cpc and metal-cpc (Cu, Ni, Co, Fe) are very similar. The only difference is the presence of ν(NH) and δ(NH) vibrations in the spectra of the free cpc molecule. These bands are absent in the spectra of the metal-cpc. There is little change in the absorptions due to the crown ether groups.

The ^{1}H-NMR spectrum of cpc indicates aromatic protons (δ 8.3 ppm) and aliphatic ether



Scheme 1. Synthesis of metal-free and metallo phthalocyanines containing benzo-15-crown-5.

protons (δ 3.9–3.2 ppm) as well as the protons of the internal NH groups (δ −4.8 ppm). The shift to higher field for NH protons is a result of the 18 π-electron system of the phthalocyanine ring. In contrast to the NH protons, aromatic protons were shifted to lower field because of the π-electron ring current of the phthalocyanine core, even after complexation with nickel(II).

The solubility of metal-cpc complexes (Mcpc) in various organic solvents enabled investigation of the electronic spectra of these compounds. These spectra showed a $\pi\rightarrow\pi^*$ Q-band transition at *ca* 670 nm and Soret-like $\pi\rightarrow\pi^*$ bands near 340 nm (Table 1). It can be seen that a progressive shift of the visible absorption bands to lower energy occurs in the order Co> Ni>Cu>Fe. The obvious effect of alkali-metal ions complexed in the crown groups on the Q-band transition of the phthalocyanine unit can be seen clearly. The broadening of this absorption, which was explained as the result of dimerization[13] as well as a hypsochromic effect, has been

Table 1 Electronic spectra and solubilities (in chloroform) of Mcpcs and their alkali-metal adducts[24]

Compounds	λ(nm)($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})[a]						Solubility[b] (mol dm^{-3})
cpc	348 (7.51)	420 (3.03)	601 (2.4)	644 (4.53)	661 (10.34)	701 (12.61)	3.9×10^{-3}
Cucpc	340 (3.71)	382 (2.04)	615 (2.03)	647 (2.13)	680 (4.41)		1.4×10^{-3}
Cocpc	328 (6.04)	398 (2.33)	604 (3.27)	639 (4.73)	669 (10.07)		0.8×10^{-3}
Nicpc	330 (4.13)	406 (2.21)	603 (2.7)	638 (3.51)	669 (12.38)		0.9×10^{-3}
Fecpc	350 (3.83)	412 (2.27)	606 (0.7)[c]	662 (2.06)[c]	682 (2.48)[c]	702 (3.31)	4.1×10^{-3}
cpc.$NaClO_4$	340 (4.71)	410 (1.89)		635 (3.69)			
cpc.2KSCN	332 (2.28)			640 (1.72)			
cpc.$2NH_4SCN$	352 (3.66)			660 (3.83)		700 (4.3)	
Cocpc.4NaSCN	360 (2.36)		612 (1.48)[c]			698 (2.69)	
Cocpc.2KSCN			628 (2.16)		675 (2.16)		
Cocpc.$2NH_4SCN$	355 (2.67)		620 (2.00)[c]		675 (2.73)		

[a] Where $c=A/\varepsilon l$ and $l=1$ cm.
[b] Saturated solution at 25 °C.
[c] Shoulder.

Table 2 Solvent extraction (percentage of extracted picrate) of alkali-metal picrates into the organic phase (chloroform) at 25 °C[24]

Complex	Li^+	Na^+	K^+
Benzo 15-crown-5	0.9	18.2	33.7
cpc	4.8	12.3	90.5
Cucpc	7.3	17.9	73.6
Cocpc	2.8	5.4	89.3
Nicpc	2.6	7.2	92.4
Fecpc	6.5	13.8	90.4

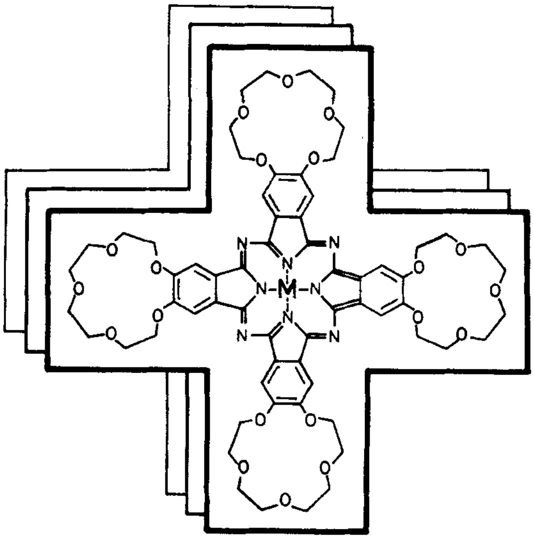
observed in the case of sodium and postassium. Since crown ethers form relatively stable, sandwich-type complexes with alkali-metal cations, dimerization is more easily accomplished when sodium or potassium cations are present. In the case of ammonium ions, similar changes occur in the spectra, but the shifts are not so distinct.

The alkali-metal binding ability of crown ether, cpc and metal-cpc complexes has been investigated by solvent extraction of alkali salts from water to chloroform[25] using picrate as the counteranion for all compounds (Table 2).

As can be seen in Table 2, all compounds exhibit their highest affinity for the potassium cation. The selectivity of Cocpc for the potassium cation is the highest and the influence of core transition metal ions on the binding properties of the crown ether groups is noteworthy.

Mass spectra using the FAB technique with thioglycerol, dichloromethane or trifluoroacetic acid as the matrix, gave molecular ion values which were in good agreement with predictions of theoretical isotopic distributions. The thermal stability of cpc and metal-cpc complexes has been investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), and it was found that the intial decomposition temperature decreased in the order $H_2>Co>Fe>Ni$. In spite of the high RMM (relative molecular mass) of the metal-cpc complexes, they could be sublimed in high vacuum without decomposition. This demonstrates that the combination of crown ethers with phthalocyanines forms stable molecules.[24]

Both cpc and Cu-cpc form mesophases containing ion channels. This property was found by X-ray determination at small angles which showed two types of condensed phases. Solid phases with orthorhombic structures were found for metal-free phthalocyanine and Cu-cpc. In these forms, two-dimensional rectangular arrays of substituted phthalocyanines lead to corrugated planes. Phthalocyanine moieties are superposed in an eclipsed conformation and the crown-ether macrocycles form channels (structure **2**).[26]



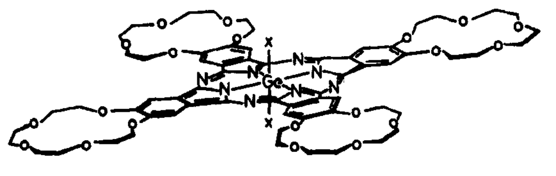
2

In the mesophase, the phthalocyanine rings and crown-ether macrocycles are approximately coplanar and form a two-dimensional square lattice. The phthalocyanine derivatives align with the crown-ether macrocycles in a staggered conformation. Ion channels still exist in the mesophases but the inter crown-ether distance is larger than in the crystalline form. In both cases, in the crystalline and mesomorphic forms, ion channels allowing the migration of alkali and alkaline-earth cations are formed.

This one-dimensional ion migration leads to information storage and transmission possibilities for ionoelectronics.[27, 28]

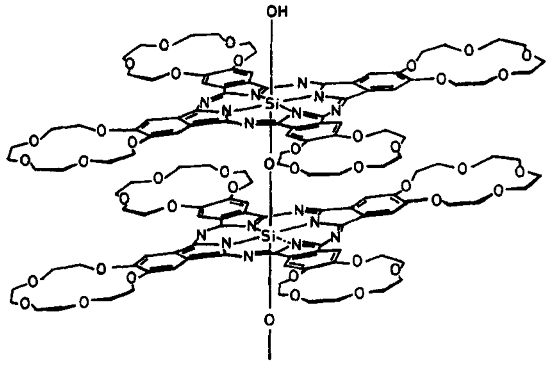
Films of the bis(phthalocyanine)s of lutetium containing crown ethers have been investigated by cyclic voltammetry.[29] It has been found that in films of $Lu(cpc)_2$ with potassium- or sodium-ion aqueous electrolytes, two reversible one-electron steps lead to the formation of the orange cation $Lu^+(cpc)_2$ and the blue anion $Lu^-(cpc)$.

Because various groups are attached to axial positions, some phthalocyanine complexes are capable of forming linear stacked polymers which may lead to metallomacrocyclic conductors.[30, 31] The Group 4A metal phthalocyanines containing crown ethers (**3–6**)



x = Cl, OH, SPh

3



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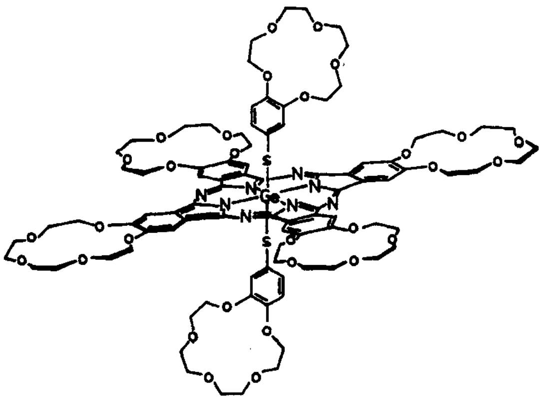

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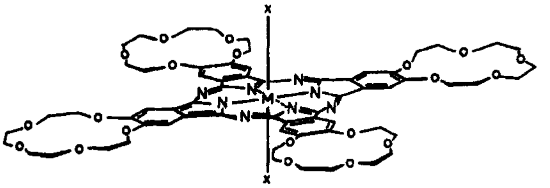
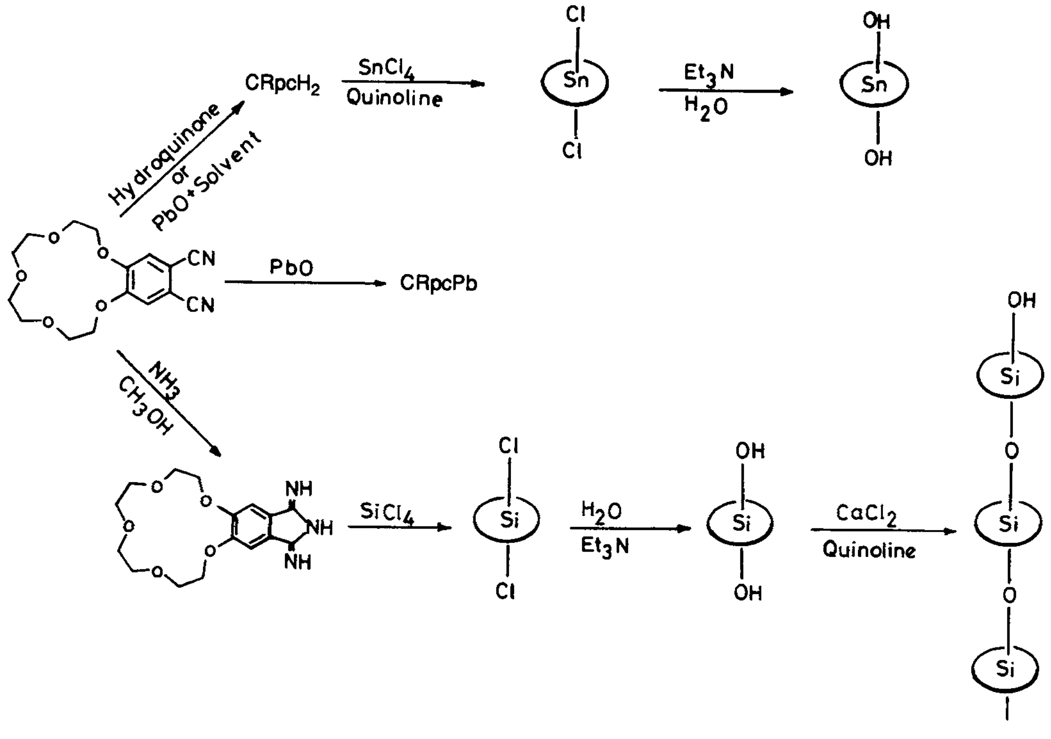
have been prepared.[32, 33] Synthetic routes to these compounds are given in Scheme 2.

The polycondensation of hydroxysilicon phthalocyanines to cofacially arrayed polymers has usually been carried out at a high reaction temperature of *ca* 400 °C.[34] However, thermal degradation of the crown-ether group occurs before this temperature is reached.[24] Therefore the catalytic use of water-free $CaCl_2$ in a high-boiling solvent should be employed to obtain polymerization degrees as indicated in the literature.[35] The average degree of polymerization was estimated by quantitatively determining in the IR spectra of the monomer and polymer, the well-characterized invariant modes of the crown-ether moieties.[34, 36] The average degree of polymerization was found to be around 25. The initial decomposition temperatures of these compounds decrease in the order $Pb > Sn(OH)_2 > SnCl_2 > Si(OH)_2 > H_2$. The thermal stability of Group 4A metal-cpc complexes is higher than that of the corresponding transition-metal cpc species. The phthalocyanines containing 18-crown-6 and 21-crown-7 macrocycles with silicon and their polycondensation products have also been prepared.[37]



M =	Si	Si	Sn	Sn	Pb	2H
x =	Cl	OH	Cl	OH	-	-

5

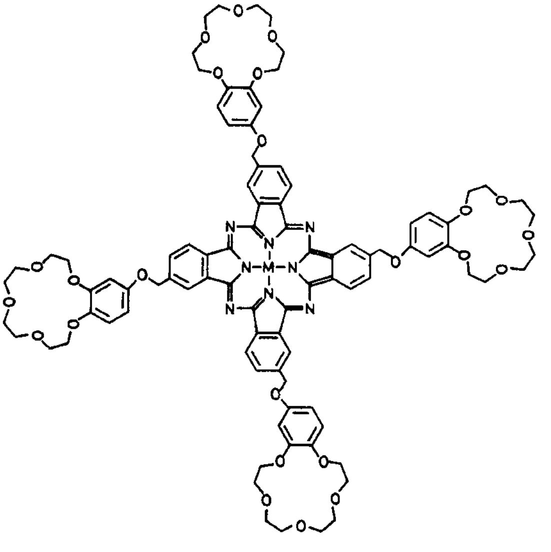


Scheme 2. Preparation routes of crown phthalocyanines with Group 4A metals.

3 PHTHALOCYANINES CONTAINING (O_n) MACROCYCLES THROUGH (O) AND (S) BRIDGES

This type of phthalocyanine contains crown ethers through flexible —CH_2—O— chains linked to the benzene rings insead of phthalocyanines having macrocyclic ethers as integral parts.

Starting from 1-bromomethyl-3,4-dibromobenzene and 4-hydroxy(benzo-15-crown-5), metal-free, copper and nickel complexes of phthalocyanines containing for crown-ether macrocycles (7) have been prepared.[38] The highest yield of metal-free phthalocyanine has been obtained by heating a mixture of the starting compounds with freshly sublimed hydroquinone in a sealed tube stirred at 180 °C. The expected isomers could not be separated using several column chromatography techniques. The ^1H-NMR and electronic spectra of this compound in different solvents showed that the aggregation is also effective in dilute solution. The alkali ion binding capability measurement of these phthalocyanines showed that the potassium ion, with the highest affinity, forms intermolecular sandwich complexes and follows the order Cupc>Nipc>H_2pc.



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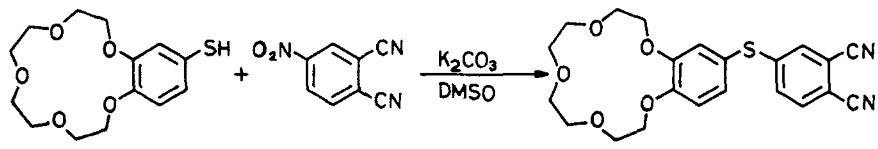
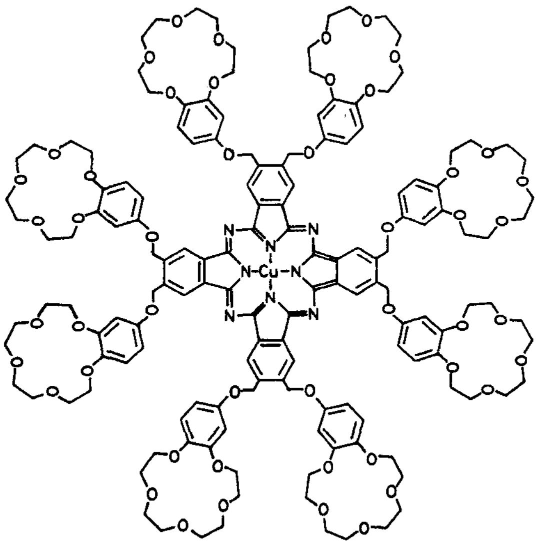
The detailed cyclic voltammetric measurement of these soluble metal-free and copper phthalocyanies showed two one-electron reduc-



Scheme 3. Preparation of sulphanyl-bridged dinitriles.

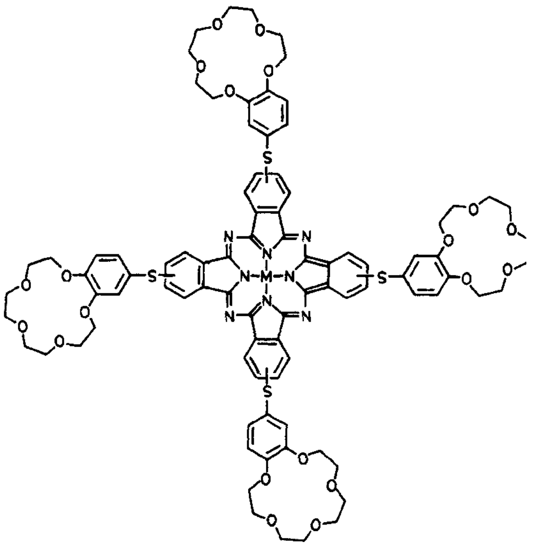
tion processes on sweeping to negative potentials. The addition of sodium or potassium ions to the solution results in a decrease in diffusion coefficients, which is a consequence of intermolecular complex formation in the presence of these two cations.[39]

A copper phthalocyanine with eight benzo-15-crown-5 moieties through —CH_2—O— chains (**8**) has been reported.[40] The alkali ion binding ability of **8** was measured by solvent extraction of alkali-metal picrates from water to chloroform. It was found that the highest affinity to alkali-metal ions was in the order $K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$. It was suggested that K^+ forms intramolecular sandwich complexes with benzo-15-crown-5 units rather than intermolecular pc dimers. The effect of alkali cations on the aggregation has been studied by means of visible spectra. There was no observable change in the spectra due to the various metal ions.



8

Recently, metal-free and nickel(II), copper(II), cobalt(II), zinc(II), lead(II) or tin(IV) complexes of phthalocyanines associated with four crown ethers through sulphanyl bridges (**9**) have been prepared.[41] By the well-known base-catalysed aromatic nitro displacement reaction, a suitable starting compound for the phthalocyanine was obtained (Scheme 3).



M=2H, Ni(II), Co(II), Cu(II), Zn(II), Pb(II), Sn(IV)

9

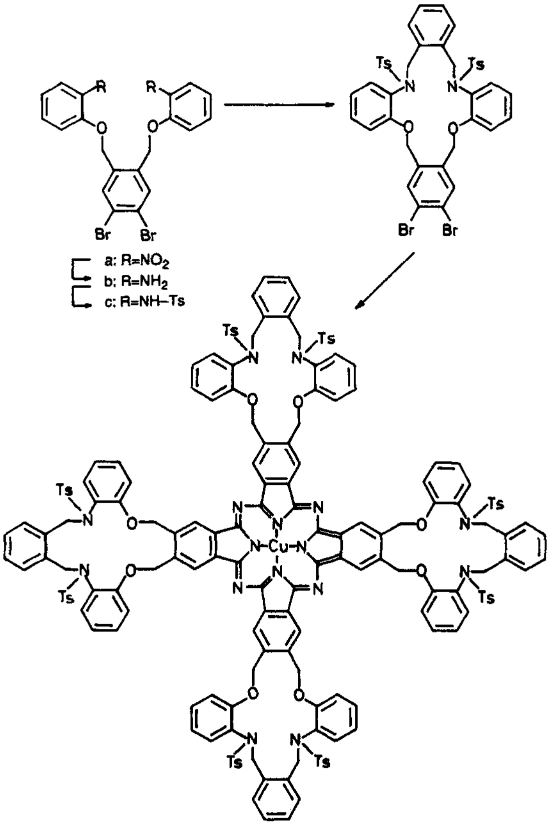
The usual cyclotetramerization in the presence of a reductant was used to obtain the metal-free phthalocyanine, while the metal salts Ni(II), Zn(II) or $SnCl_2$ and suitable solvents were required for the metallo-phthalocyanines. In the case of lead, PbO was added portionwise to melted **1**. All these phthalocyanines are soluble in various solvents, as are the other phthalocyanines containing crown-ether moieties.

The alkali-metal cation binding properties of all these phthalocyanines were tested by solvent extraction of alkali-metal picrates from water into chloroform. The highest binding was observed for potassium ion with all phthalocyanines forming intermolecular sandwich complexes. Investigation of the conductivity of the metal-free phthalocyanine and its complexes showed that the values found were in the range for semiconductors.

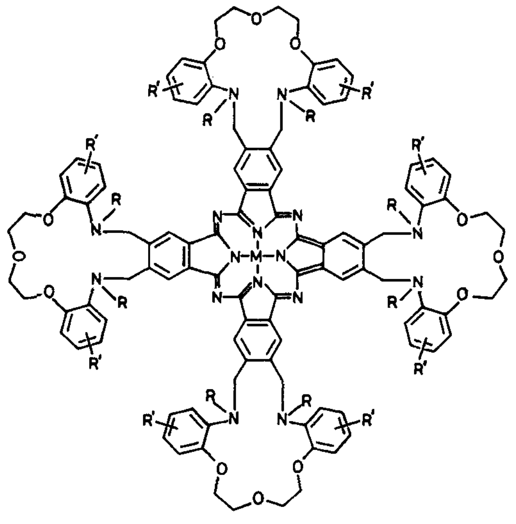
4 PHTHALOCYANINES CONTAINING (O_nN_n) MACROCYCLES

Starting from *o*-nitrophenol, 16-membered symmetrical tetrabenzodiazadioxa-macrocycles associated with a copper phthalocyanine have been synthesized[42] (Scheme 4).

The reaction sequences were followed by IR and NMR spectroscopy. These phthalocyanines were soluble in chloroform, dichloromethane, tetrachloroethane and dimethylformamide. All attempts to hydrolyse of tosylate groups by several methods were unsuccessful and therefore transition-metal complexes with diazadioxa-groups could not be prepared. The changes of the Q-band in the visible spectra revealed that increasing concentration results in the formation of aggregated species. Phthalocyanine complexes containing 17-membered trioxadiaza-marocycles (**10**) have been prepared and in addition to ^{1}H-NMR, IR and electronic spectra and thermogravimetric analysis, the electrical conductivities have also been investigated.[43]



Scheme 4. Synthetic route to copper phthalocyanine containing four 16-membered diazadioxa-macrocycles.



M=Cu, Ni, Zn, Co, 2H
R=Ts, H
R'= H, SO_3H, SO_3Na

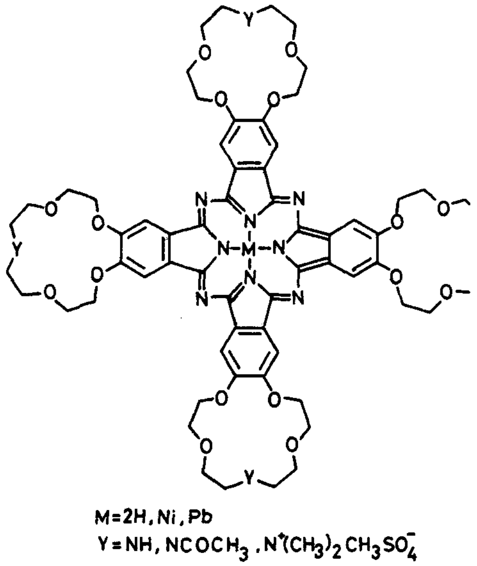
10

The yields reported were rather low and depended upon the metal ion. *N*-Tosyl derivatives are soluble in various organic solvents. Complete detosylation was carried out only with concentrated sulphuric acid at elevated temperature. However, this leads to products with sulphonyl groups on the aromatic rings of the macrocycle. The presence of eight SO_3H groups for each phthalocyanine gives a mixture of regioisomers along with four H_2SO_4 units bound to the aza groups. H_2SO_4 is easily removable by neutralization. Because of these polar groups, the phthalocyanines are soluble in water. Conversion of the eight SO_3H groups to SO_3Na groups with NaOH also resulted in extremely water-soluble products. Therefore the alkali-metal binding property was not determined. Transition-metal complexes of trioxadiaza-macrocycles could not be isolated.

The electrical conductivity (measured on the compressed microcrystalline powder) was found to be in the order of 10^{-12} S m^{-1}. This was expected for these complexes with bulky peripheral substituents.[44,45]

Cyclic voltammetry studies of Cu(II) and Co(II) complexes of this phthalocyanine were carried out in both aqueous and dimethyl sulphoxide solutions.[46] The cyclic voltammograms of these phthalocyanines were characterized by two cathodic waves which were not observed on the positive scan, even at higher sweep rates. Such behaviour strongly suggests that electron transfer from these metallo-phthalocyanines is electrochemically undirectional, i.e. totally irreversible. The values of the diffusion coefficients obtained for these two phthalocyanines were low, which is consistent with the large size of the molecules. The acqueous voltammogram of these phthalocyanines was different from the non-aqueous behaviour. These waves were more likely to involve the phthalocyanine rings.

A phthalocyanine with monoazabenzo-15-crown-5 (acpc) (**11**) was synthesized starting from the dibromo compound with excess CuCN in pyridine in a sealed tube at 205–210 °C. Methylation of **11** with dimethyl sulphate gives the quaternary ammonium salt which forms the quaternized copper phthalocyanine.[47] The common feature of these two phthalocyanines is that both of them are soluble in DMSO, and the quaternized phthalocyanine is very soluble in water. The most interesting feature of this copper phthalocyanine is that it is an effective catalyst for oxidation of saturated and unsaturated hydrocarbons at relatively low temperatures and pressures, and also increases the octane rating of gasoline.[48]



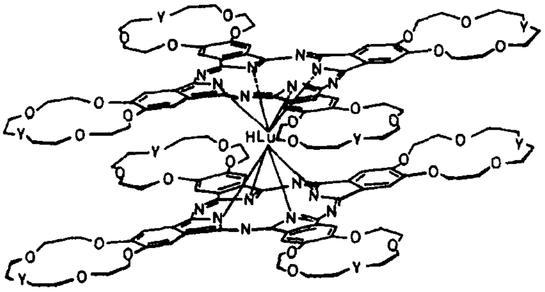
M=2H, Ni, Pb

Y = NH, $NCOCH_3$, $N^+(CH_3)_2CH_3SO_4^-$

11

More detailed work was carried out for the synthesis of water-soluble phthalocyanines containing various quaternized monoaza crown ethers. Moazabenzo-15-crown-5, after bromination, gave the dibromo compound which was treated either with dimethyl sulphate in acetonitrile in the presence of sodium carbonate to obtain the quaternary ammonium salt, or with acetic anhydride to protect the amino group in the phthalocyanine reaction. The bromo substituent was converted into dicyano groups by the Rosenmund–von Braun reaction.[49,50] From the dinitrile with suitable metal salts, a water-soluble phthalocyanine (acpc) was obtained in rather low yields. A more convenient way to isolate a water-soluble phthalocyanine is to start the reaction from the *N*-acetyl dinitrile compound to obtain an *N*-acetylphthalocyanine which can be methylated directly with dimethyl sulphate in chloroform to give the quaternized acpc. In this way, metal-free, nickel(II) and lead(II) complexes of acpcs were prepared and their ^1H-NMR, IR and electronic spectra were reported.[51]

The first water-soluble lutetium-$(acpc)_2$ was also synthesized as **12**.[51]



Y=NH, $NCOCH_3$, $N^+(CH_3)_2 \cdot CH_3SO_4^-$

12

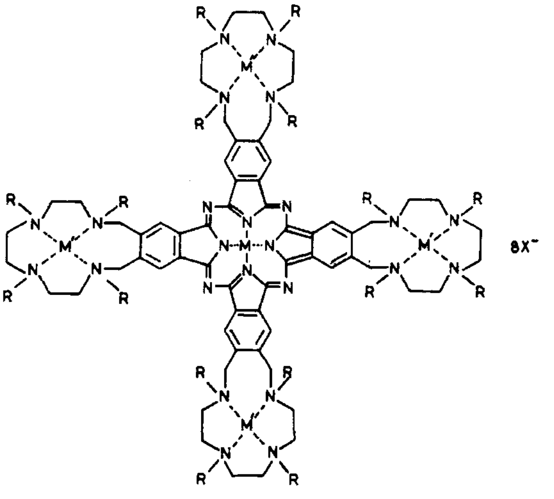
From the electrochemical point of view, $Lu(pc)_2$ is the first known intrinsic molecular semiconductor.[52,53] The neutral $Lu(pc)_2$ is green, the one-electron-oxidized cation is orange and the one-electron-reduced anion is blue. The colour of solutions of $Lu(acpc)_2$ complexes (in chloroform and in water) were green, indicating that these complexes are in the neutral Lu(III) form.

Conductivity measurement of (monoaza crown ether)-associate metal-free, metallo derivatives of phthalocyanines, together with the alkali-metal adducts and partially oxidized derivatives of Cu-acpc and also $Lu(acpc)_2$ compounds, have been investigated in detail.[54]

5 PHTHALOCYANINES CONTAINING (N_n) MACROCYCLES

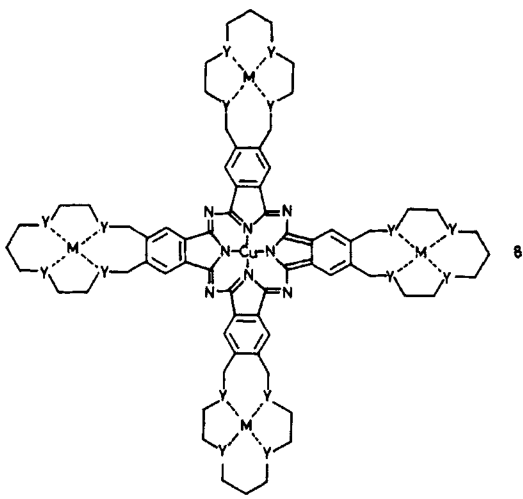
The synthesis of Cu(II), Ni(II), Co(II) and Sn(IV)-cpcs containing four 14- and 15-membered tetra(aza)-macrocycles (**13**, **14**) from dibromo compounds has been described.[55–57]

In the case of crown ethers as substituents, the molecules possess the capability of forming ion channels allowing the migration of alkali and alkaline-earth cations.[19, 24, 26] Phthalocyanines containing polyaza-macrocycles can form homo- and hetero-pentanuclear transition-metal complexes. Tetra(aza)dibromobenzene, which was cyclotetramerized with tetramethylurea in the presence of CuCN, gave a copper phthalocyanine containing four tetra(aza)-macrocycles (Cu-tapc), **13**. The tosyl groups in **13**, hydrolysed by heating in concentrated H_2SO_4 for 3 h at 100 °C. After neutralization with acqueous NaOH, complex **13b** was obtained as a dark blue product soluble in ethanol. Treatment of this Cu-tapc with the stoichiometric amount of $NiCl_2$ in absolute ethanol led to the precipitation of a heteronuclear complex which is soluble in water (**13c**) and **14h**. Visible absorption spectra of **13c** and **14h** in ethanol and water were similar. The Ni(II) tetra(aza)–macrocycle does not have absorptions that are as intense as the B- and Q-bands of phthalocyanines.[58]



	R	M	M′	X
a	Ts	Cu	-	-
b	H	Cu	-	-
c	H	Cu	Ni	Cl
d	Ts	N	-	-
e	Ts	Co	-	-
f	Ts	$SnCl_2$	-	-

13



	Y	M	X
a	N(Ts)	-	-
b	NH	-	-
c	$NH_2^+ .\frac{1}{2} SO_4^{2-}$	-	-
d	$NMe_2^+ , MeOSO_3$	-	-
e	NMe_2^+ , ClO_4	-	-
f	NH	Co^{II}	Cl
g	NH	Co^{II}	ClO_4
h	NH	Ni^{II}	Cl
i	NH	Ni^{II}	ClO_4
j	NH	Cu^{II}	Cl
k	NH	Cu^{II}	ClO_4
l	NH	Zn^{II}	Cl

14

In the case of the phthalocyanine substituted with four 15-membered tetra(aza)-macrocycles, **14**, Cu(II)- and Zn(II)-containing pentanuclear complexes were prepared and their IR and electronic spectra and thermogravimetric analyses were investigated.

The room-temperature conductivities of these phthalocyanines conformed to expectations, as for substituted phthalocyanines.[54, 59, 60] Especially for the parent tosylated (Cu-tapc) **14**, conductivity is lowest in vacuum. The bulky toxyl groups probably prevent the interaction of delocalized π-electrons in the phthalocyanine plane. Consequently detoxylation leads to a small increase in conductivity.

The pentanuclear nickel(II), copper(II), Zinc(II) and cobalt(II) complexes of **14** have been investigated in dimethyl sulphoxide solution using cyclic voltammetric and coulometric methods. The cyclic voltammogram of Cu-tapc revealed one cathodic wave which had a totally irrreversible nature. The pentanuclear copper(II) complex of Cu-tapc showed quasi-reversible behaviour with four one-electron reduction waves. The ratio of the anodic to cathodic peak currents demonstrated the presence of coupled chemical reactions which are important for the oxido–reduction couple. On the other hand, for the pentanuclear Ni(II) complex of Cu-tapc, two one-electron reduction waves (one reversible and the other quasi-reversible) were observed.[61]

The zinc(II) complex of Cu-tapc showed one cathodic irreversible and two anodic (first, quasi-reversible; second, irreversible) waves. These are one-electron oxido–reduction waves. For the cobalt(II) analogue two one-electron quasi-reversible reduction waves were observed.[62]

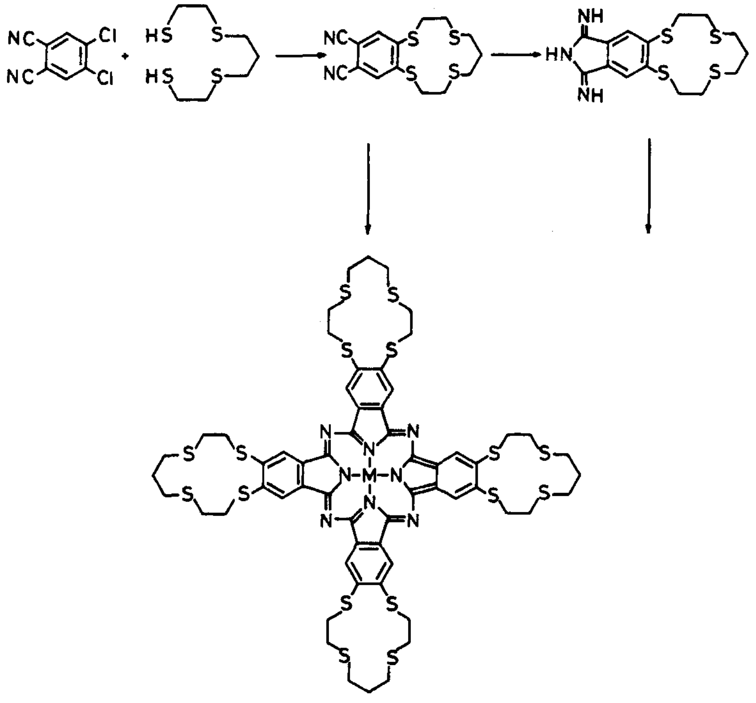
6 PHTHALOCYANINES CONTAINING (S_n) MACROCYCLES

A new fused-phthalocyanine derivative with a tetra(thia)-macrocycle (ttpc) (**15**) has been reported recently.[63] The synthetic route to this phthalocyanine was different from the case of other fused phthalocyanines, starting with 1,2-dibromo functions on the benzene moiety of the macrocycle. The dibromo derivative could not be converted either into a phthalocyanine in a high-boiling point solvent in a sealed tube, or into a dinitrile by the Rosenmund–von Braun reaction. This phthalocyanine containing tetra-(thia)-macrocycles (**15**) has been prepared using the nucleophilic displacement reaction[64, 65] of 4,5-dichlorophthalonitrile with a dithiol, as outlined in Scheme 5.

In contrast to tetra(aza)-macrocycle- or (crown ether)-substituted analogues, this phthalocyanine is not soluble in common solvents. Only **15b** and **15d** are soluble to a certain extent in pyridine. Using suspensions of **15c** and **15d**, Pd(II) complexes and an Ag(I) complex of **15d**, all having one metal ion for each tetra(thia)-macrocycle, have been prepared.

7 PHTHALOCYANINES CONTAINING BOTH (N_n) AND $(O_n($MACROCYCLES

As a further step in the synthesis of macrocycle-combined phthalocyanines, a phthalocyanine



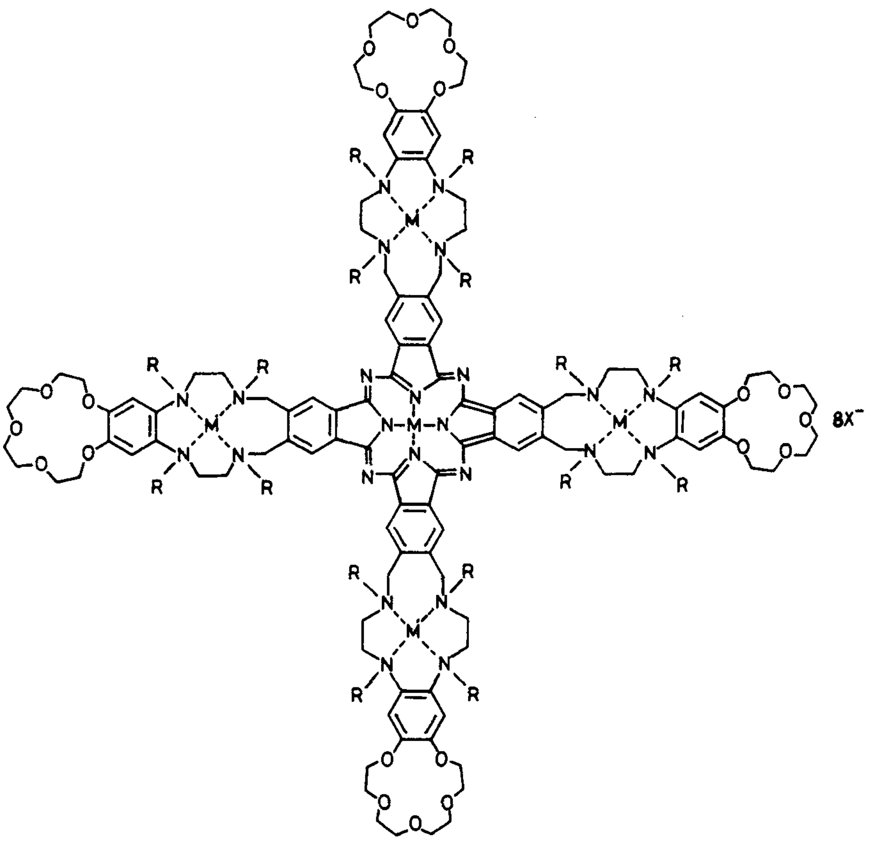
15 a:M=2H
b:M=Co
c:M=Ni
d:M=Zn

Scheme 5. Synthesis of phthalocyanines containing tetrathia-macrocycles.

carrying four 14-membered tetra(aza)-macrocycles each attached to a 15-crown-5 unit (**16**) was synthesized.[66] The combination of these two donor macrocycles gave phthalocyanines the ability to form coordinate ion compounds of both alkali- and transition-metal ions whose solubilities are different.

The interaction of alkali-metal picrates with crown ether groups of complex **16a** was carried out in chloroform. Among the alkali-metal cations, the highest affinity was observed for K^+, which could be attributed to sandwich-type adduct formation between two 15-crown-5 units and a potassium ion. This complex was isolated from a mixture of **16a** and KSCN, and the stoichiometry of the complex was found to be 1:2. The extremely low solubility of the complex should be a result of sandwich type adduct formation among crown-ether groups of different molecules, leading to a network polymer structure. Detosylation of complex **16a** was accomplished with the highest yield at 125 °C by use of concentrated H_2SO_4 for 5 h. The solubility of the detosylated complex **16b** in halogenated hydrocarbons was very low, but was enhanced in methanol and ethanol. A pentanuclear complex of **16b** was formed with nickel(II) chloride in absolute methanol, **16c**.

The electronic spectrum of this water-soluble complex showed that complexation of four azamacrocycles with Ni(II) did not lead to appreciable changes in the Q-band region in



	M	M	R	X
a	Cu	-	Ts	-
b	Cu	-	H	-
c	Cu	Ni	H	Cl
d	Ni	-	Ts	-

16

water, and gave (as expected) low-intensity *d*–d transitions.

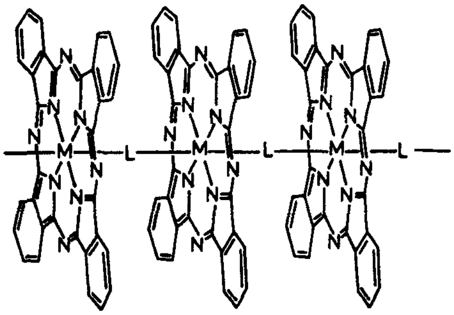
8 POLYMERIC PHTHALOCYANINES CONTAINING MACROCYLES

The phthalocyanines can form mainly two types of polymers: one is cofacial in face-to-face oriented polymers. These stacked and bridged phthalocyaninato–metal complexes can be obtained by the reaction of metal phthalocyanines with other bifunctional organic and inorganic reagents.

Because conducting and photoconducting organic and inorganic compounds are of considerable interest as candidates for optical, electronic, photoelectric and electrochemical applications, research into cofacially stacked phthalocyanines has grown rapidly during the past few years.

Phthalocyaninato-(Si, Ge, Sn) oligomers linked face-to-face (**17**) which have been doped with iodine produce electrically conductive polymers with a wide range of iodine stoichiometries. Halogen doping of the stacked polymers was accompanied by electrical conductivity increases as large 10^7 ohm^{-1} cm^{-1}.[67–81]

The first examples of silicon and tin complexes of (15-crown-5)-associated phthalocyanines were prepared from the corresponding dicyano- or iminoisoindoline compounds. The axial dichloro ligands of these complexes have been converted into the dihydroxy form by hydrolysis in aqueous triethylamine. The catalytic effect of water-free $CaCl_2$ in quinoline was used for polycondensation of dihydroxysilicon–phthalocyanine to cofacially stacked one-dimensional polymers.[33]



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The second type of phthalocyanine polymer is the network polymers; such polymers are ideally formed from bis(phthalonitrile) monomers. However two different conceptual approaches exist that might allow networks or peripheral polymeric phthalocyanine systems to be prepared. This polymerization was first studied using 3,3′, 4,4′-tetracyanodiphenyl ether in a heterogeneous fusion reaction.[82] It has also been found that the metal-free phthalocyanine compounds can be prepared in high yield from phthalonitriles in the presence of an appropriate proton-donating organic reducing agent such as hydroquinone and that such co-reactants are useful for curing bis(phthalonitrile) to phthalocyanine polymers.[83] However the polymerization progresses beyond the dimer and trimer stages only with difficulty.[82]

Synthesis of polymers consisting of fused phthalocyanine rings are usually based on the template polymerization of tetrabrombenzene, tetracyanobenzene or pyromellitic anhydride. Although soluble, high-molecular-mass polymers of this type have been reported, most compounds of this type are insoluble.[84] To overcome such a problem, several research groups have prepared alternative polymers in which phthalocyanine units were linked covalently to a soluble polymer. Methods used for the phthalocyanine linkage include the Friedel–Crafts alkylation[85] or dicyclohexylcarbodi-imide or cyanuric chloride coupling to an organic polymer.[86] It is known that replacement of the peripheral hydogen atoms in phthalocyanine itself by bulky substituents increases the solubility dramatically.

Several polyphosphazene–phthalocyanines have been prepared by a synthetic approach different from those mentioned above. It involves the synthesis of polyphosphazenes that bear side-group structures which function as phthalocyanine precursors, such as *o*-dicyanoaryl residues.[87] It was also realized that steric factors would probably place a definite limit on the number of phthalocyanine units that could be attached to a given polymer chain. One-dimensional and two-dimensional phthalocyanine polymers have been prepared and their electrochemical properties have been investigated.[88] Theoretical studies of such complexes have also been accomplished.[89]

The first examples of (crown ether)-associated metal-free and metal-containing network polymer phthalocyanines (**18**) have been synthesized from tetrabromodiobenzo-18-crown-6.[90–92] Polymerization reactions were carried out in a sealed tube with pyridine as solvent. In order to see the effect of the tetrabromo/CuCN ratio on the degree of polymerization, three different ratios were applied. The yields of the isolated polymers showed an increase in the order of increasing excess of CuCN. The ratios of the absorption intensities of the end groups (nitrile) to those of another intense group (Ar—O—C) in the IR spectra were used to estimate the number of end groups per molecule.

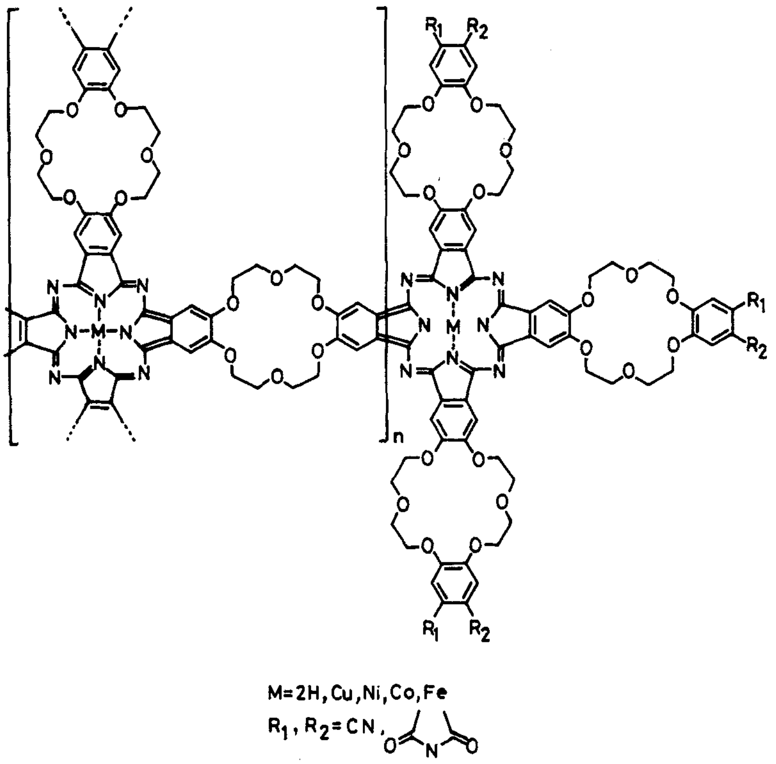
The alkali-metal ion binding ability of one compound was investigated with sodium and potassium picrates in a relatively polar solvent, THF. The results of these measurements confirmed that dibenzo-18-crown-6 units showed a higher tendency to form complexes with K^+ rather than with Na^+.[88]

Starting from **18**, condensation of **19** gave **20** (Scheme 6) which gave, with CuCN in a high-boiling solvent, the tetranitrile derivative **21**. By the cyclotetramerization reaction of **21** in the presence of a metal salt, the two-dimensional network polymers **22a**–**22e** were prepared.[93]

The metal-free phthalocyanine network polymer **22a** was obtained directly from the reaction of **21** with freshly sublimed hydroquinone in the absence of solvent. In the case of **22c** and **22d** the compounds were souble in the presence of alkali hydroxides, so these two compounds were purified by dissolving in alkali hydroxide and reprecipitating by neutralization. The electrical conductivities of the phthalocyanines **22a**–**22e** have been measured in air and at room temperature, and found to have lower values than those of phthalocyanines with bulky substituents.[54, 59]

9 UNSYMMETRICAL PHTHALOCYANINES CONTAINING MACROCYCLES

Among the classical phthalocyanines, unsymmetrical ones are important goals in the development of new methods of synthesis and



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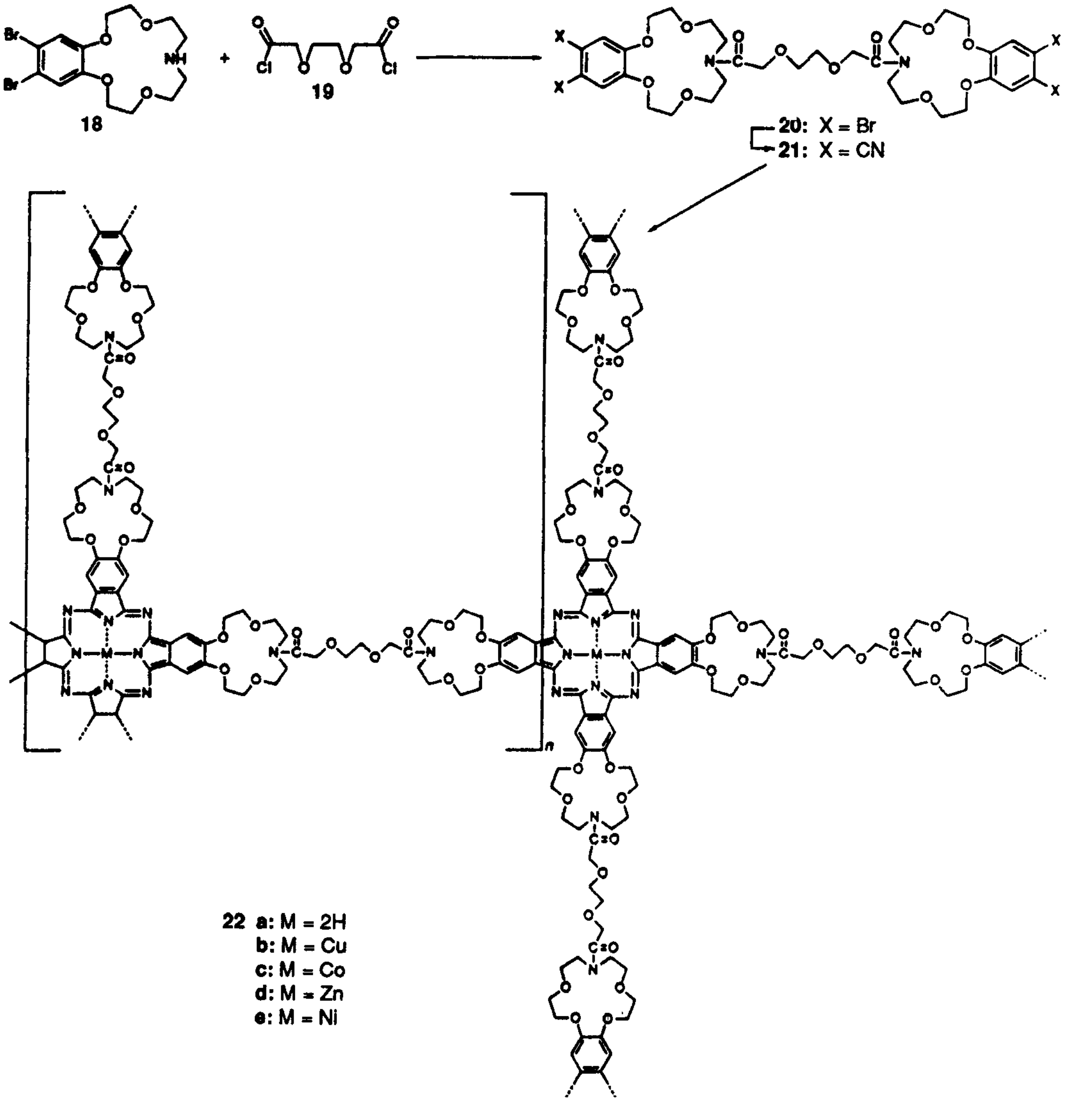
separation. The synthesis of unsymmetrical phthalocyanines can currently be divided into three methods according to the route used.

(1) The polymer support route, which is not suitable for large-scale preparation of unsymmetrical phthalocyanines.[94–97]

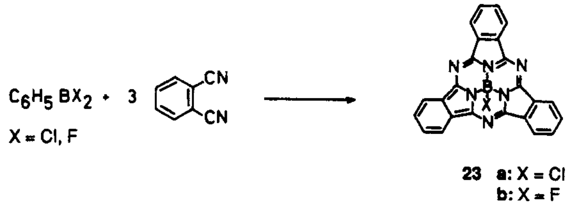
(2) The homogeneous mixed condensation route, which is the ordinary method of forming unsymmetrical phthalocyanines by condensation of different phthalonitriles. The statistical mixture of phthalocyanines is separated with difficulty by common chromatographic methods.[96, 98, 99]

(3) The subphthalocyanine route, which is not suitable for the preparation of alkoxy-substituted phthalocyanines. This method goes back to the synthesis of the hexa(aza)boron complex **23** which was obtained from the reactions of haloboranes and organohaloboranes with phthalodinitrile[100] (Scheme 7).

Starting from this subphthalocyanine (**23**) with iminoisoindoline compounds at 80–90 °C in a mixture of dimethyl sulphoxide and either chlorobenzene, *o*-dichlorobenzene, 1-chloro-



Scheme 6. Synthesis of bridged network polymers of phthalocyanines containing monoaza crown ether groups.

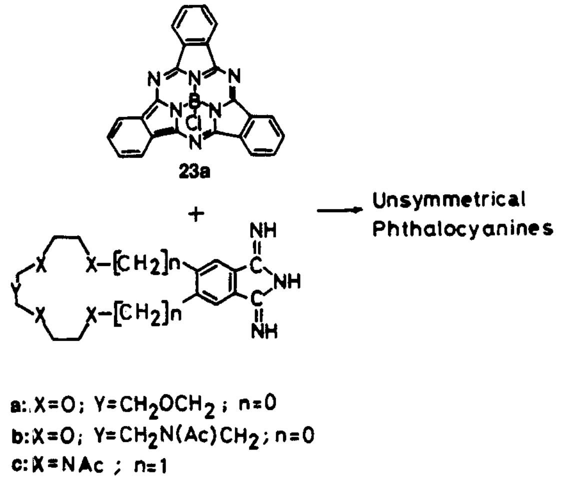


Scheme 7. Synthesis of hexa(aza)boron complexes.

naphthalene or 2-chloronaphthalene, some new unsymmetrical phthalocyanine derivatives were obtained.[101]

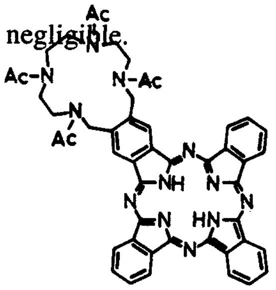
Unsymmetrical phthalocyanines containing a single macrocyclic substituent have been synthesized by the reaction of the boron complex (**23a**) with the iminoisoindoline derivatives of 15-crown-5, monoaza-15-crown-5 and tetra-(aza)-cyclotetradecane[102] (Scheme 8).

All unsymmetrical phthalocyanines were precipitated from the 1-chloronaphthalene–dimethyl sulphoxide medium by the addition of water and isolated by filtration. Except for **24**, which is sufficiently soluble in chloroform, the phthalocyanines showed a rather low solubility in organic solvents when compared with tetra-substituted phthalocyanines carrying similar macrocycles. The NMR spectrum of the soluble compound **24** could be recorded, and confirmed the structure. The alkali-ion binding property of (crown ether)-containing compound **25a** was verified by the formation of the compound–**25** NaSCN adduct. The IR spectrum in ethanol exhibited a characteristic SCN^- vibration. However, enhancement of solubility by adduct formation was negligible.

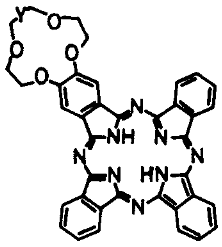


Scheme 8. Synthesis of unsymmetrical phthalocyanines containing 15-crown-5 and monoaza-15-crown-5 macrocycles.

24



25 a: $Y=CH_2OCH_2$
b: $Y=CH_2N(Ac)CH_2$



In contrast to the tetra(monoaza-crown ether)-containing phthalocyanine,[47] quaternization of compound **25b** with dimethyl sulphate, even under extreme conditions, could not be achieved. The visible absorption spectra showed that the splitting pattern of the Q-bands around 680 nm is very similar in both symmetrical and unsymmetrical compounds. The loss of symmetry appeared to cause no appreciable splitting of the visible absorption.

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