

Synthesis and characterization of novel phthalocyanines with four tridentate NNS substituents and four chloro groups

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Received 27th September 1999, Accepted 25th October 1999

Two new 4,5-disubstituted phthalonitrile derivatives have been prepared from tridentate amine thiol reactants obtained by reducing directly two different benzothiazolines. Novel metal free phthalocyanines and divalent metal phthalocyanines carrying four tridentate NNS substituents in addition to four chloro groups on peripheral positions have been synthesized from the corresponding phthalonitrile derivatives in the presence of a suitable anhydrous metal salt [$\text{Zn}(\text{CH}_3\text{CO}_2)_2$ or NiCl_2] or 2-(dimethylamino)ethanol. A lutetium(III) bis(phthalocyaninate) complex that is highly soluble in most organic solvents has been synthesized from reaction of one of the phthalonitrile derivatives with anhydrous lutetium(III) acetate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) in 1-hexanol. The newly synthesized compounds have been characterized by elemental analyses, IR, ^1H , ^{13}C NMR, MS, UV/VIS, ESR, and atomic absorption spectroscopy. Cyclic voltammetric measurements of the novel compounds have been made.

The importance of the phthalocyanines in many fields including chemical sensors, solar cells, batteries, photodynamic therapy, semiconductive materials, liquid crystals, photosensitizers and catalysts is increasing rapidly as a result of newly synthesized compounds.¹⁻⁴ In addition to alkali or transition metal phthalocyanine complexes, rare-earth bisphthalocyanines, especially lutetium derivatives, are objects of intense investigation, mainly for their unique optical, conductive and redox properties. Lutetium(III) bis(phthalocyaninate) [LuPc_2] is a multifunctional compound having a sandwich structure and a wide range of applications: intrinsic semiconductivity, electrochromism, third-order optical non-linearity, and so on.⁵⁻⁷ Thus, they were examined for a wide variety of possible applications such as field-effect transistors (FETs) and displays.^{8,9} Like many phthalocyanine compounds, unsubstituted and some substituted [LuPc_2] are insoluble in most organic solvents.¹⁰⁻¹² An essential shortcoming of the phthalocyanines remains in their low solubility in organic solvents which hinders their application in solution. The introduction of different central metal ions or benzenoid rings turned out to be powerful means of modifying the chemical and physical properties of phthalocyanines.^{13,14} Our group has been actively engaged in the synthesis of phthalocyanines with macrocyclic, acyclic or heterocyclic substituents, the immediate consequences of which are enhanced solubility and additional donor sites for alkali and/or transition metal ions.¹⁵⁻²³ The substitution of the LuPc_2 subunit with various types of chains or macrocycles has been widely described.^{10,24,25}

Electrodonating substituents on phthalocyanine macrocycles, such as amino, phenylsulfanyl, alkoxy groups, strongly affect the position of the longwave absorption bands in the electronic spectra.²⁶⁻²⁸ In contrast, most peripheral substitution has very little effect on the Q band position.²⁹ The observed shift probably involves a subtle interplay of the inductive and mesomeric properties of the substituents and their location on the peripheral benzene ring. Phthalocyanines with sulfanyl substituents tend to exhibit shifts of the absorption bands to longer wavelengths in the near-IR than do unsubstituted or O-substituted ones.^{30,31} This is important in applications utilizing semiconductor lasers.³²

Electron-withdrawing substituents, such as chloro and bromo groups, quite significantly alter the redox potentials of the ring. The phthalocyanines bearing chloro³³ or bromo³⁴ groups at the peripheral positions have their reduction and

oxidation processes shifted to more positive potentials by the electron-withdrawing effect of these substituents.

Generally, while tetrasubstituted phthalocyanines obtained from 4-substituted phthalonitriles are a mixture of four isomers, the symmetrically octasubstituted ones (where all the eight substituents are the same) are a single product.^{27,35,36} The separation of all four isomers had been successful in the case of the 1,4-tetrasubstituted phthalocyanines using chromatographic methods (column chromatography and HPLC).³⁷ However, 1,4-tetrasubstituted phthalocyanines are easier to separate than 2,3-tetrasubstituted phthalocyanines, because they are distinguished by different steric interactions in the various constitutional isomers.³⁸ Hence, there can be different interactions between the various constitutional isomers and the stationary phase of the chromatographic column.³⁹ Recently, attempts were made to separate by chromatographic methods 2,3-tetrasubstituted phthalocyanines, but it was not possible to obtain a good separation with commonly available HPLC columns or by recrystallization.⁴⁰

Tetrasubstituted phthalocyanines usually exhibit higher solubilities than the symmetrically octasubstituted analogues. The great solubility of some tetrasubstituted phthalocyanines results not only from the steric bulk of the substituents preventing aggregation, but also from the presence of the very similar isomers.^{1,41} Thus, a mixture of similar isomers may practically be more useful than a single, less soluble isomer.⁴²

Compared to tetrasubstituted and symmetrically octasubstituted phthalocyanines, the octasubstituted phthalocyanines obtained from disubstituted derivatives with two different substituents in the 4,5 positions also give a mixture of positional isomers. This new class of substituted phthalocyanines are relatively less studied and only a few well characterized species are known. Attempts were made to separate the four possible isomers of one 2,3-octasubstituted phthalocyanine (*i.e.* two different substituents at 2,3 positions) with HPLC but the isomers were not separated.⁴³

The nucleophilic aromatic substituted reactions of 4,5-dicyano-1,2-dichlorobenzene with phenols, thiophenols or thiols give 4,5-disubstituted phthalonitriles in the presence of an excess of potassium carbonate in dimethylformamide.^{30,31} Phthalonitrile derivatives can be substituted by various long chains,⁴⁴ branched chains,³⁶ bulky groups^{18,23,45} or macrocycles.¹⁹

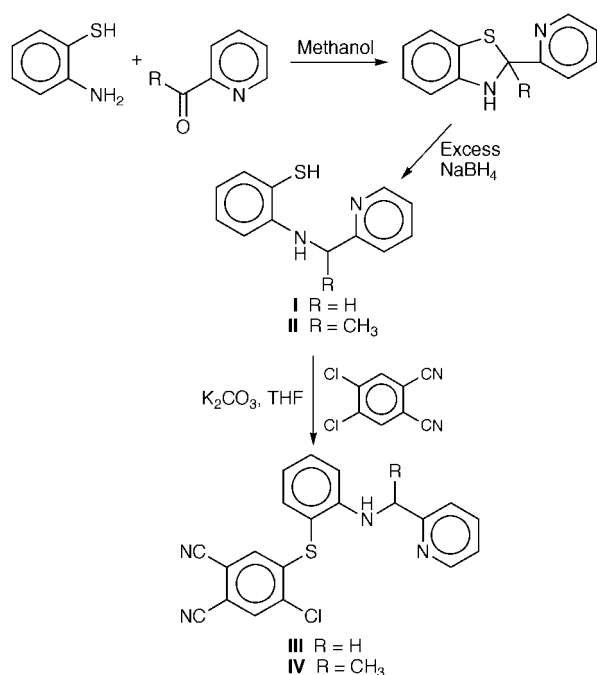
We report here for the first time the synthesis of two singly

substituted phthalonitriles with a branched bulky group in the 4 position using the substituted reaction method. In these displacement reactions one of two chloro groups was replaced only. Metal free and divalent metal phthalocyanines [$M = \text{Zn}^{\text{II}}$ or Ni^{II}] with four peripheral chloro groups and four tridentate NNS substituents have been synthesized from these phthalonitrile derivatives in addition to a green lutetium(III) bis(phthalocyaninate) complex which is in a non-protonated, one-electron ligand oxidized form where lutetium occupies the central position with eight co-ordinated nitrogen atoms of the two phthalocyanine moieties. This $[\text{LuPc}_2]$ complex is soluble in the two phthalocyanine moieties. This $[\text{LuPc}_2]$ complex is soluble in most common organic solvents. The redox properties of the prepared phthalocyanines with 2H , Zn^{II} and Lu^{III} in the phthalocyanine core were investigated by cyclic voltammetry.

Results and discussion

As a first step, compound **II** was prepared in a one-pot synthesis from 2-acetylpyridine and 2-aminobenzenethiol. The condensation reaction yielded 2-methyl-2-(2-pyridyl)benzothiazoline⁴⁶ as an intermediate which was reductively opened with a large excess of NaBH_4 to form **II** in excellent yield, which could then be used without a purification step by a reported procedure for **I**.⁴⁷ The IR and ^1H NMR data of **II** are listed in the Experimental section. The simplest information obtained from the IR data is the presence of a $\nu(\text{SH})$ band at 2518 cm^{-1} .

4,5-Disubstituted phthalonitrile derivatives **III** and **IV** were synthesized from 1,2-dichloro-4,5-dicyanobenzene by displacement of the one chloro group with the SH function of the corresponding amine thiol reactants in tetrahydrofuran at reflux temperature (Scheme 1). In a previous study, when



Scheme 1 Synthesis of the phthalonitrile derivatives **III** and **IV**.

K_2CO_3 was used as a base, the chloro groups were only partially substituted. However, in the case of Na_2CO_3 , both of the chloro groups were substituted.⁴⁸ In the present study the same compounds were obtained in these reactions when either of these carbonates was used and the composition and structure of the singly substituted phthalonitrile derivatives are consistent with all analytical results. The displacement of only one chloro group might be a consequence of steric hindrance of the branched bulky group. The spectral and electrochemical properties and solubility of the phthalonitrile derivatives are almost identical. However, **III** has been obtained in better yield than **IV**.

Table 1 Analytical^a data for starting materials and the phthalocyanines

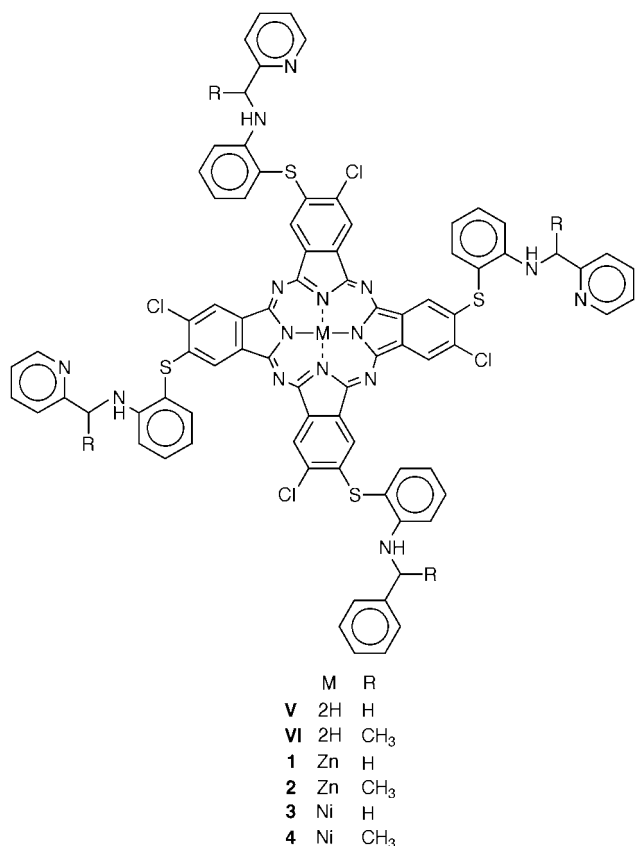
Compound	Formula (<i>M</i>)	Analysis (%)			
		C	H	N	M
II	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}$ (230)	67.83	6.09	12.17	
		(67.79)	(6.05)	(12.15)	
III	$\text{C}_{20}\text{H}_{13}\text{ClN}_4\text{S}$ (376.5)	63.74	3.45	14.87	
		(63.51)	(3.50)	(14.70)	
IV	$\text{C}_{21}\text{H}_{15}\text{ClN}_4\text{S}$ (390.5)	64.53	3.84	14.34	
		(64.55)	(3.86)	(14.36)	
V	$\text{C}_{80}\text{H}_{54}\text{Cl}_4\text{N}_{16}\text{S}_4$ (1508)	63.66	3.58	14.85	
		(63.60)	(3.55)	(14.87)	
VI	$\text{C}_{84}\text{H}_{62}\text{Cl}_4\text{N}_{16}\text{S}_4$ (1564)	64.45	3.96	14.32	
		(64.40)	(3.98)	(14.35)	
1	$\text{C}_{80}\text{H}_{52}\text{Cl}_4\text{N}_{16}\text{S}_4\text{Zn}$ (1571.37)	61.09	3.30	14.25	4.16
		(61.04)	(3.33)	(14.12)	(4.10)
2	$\text{C}_{84}\text{H}_{60}\text{Cl}_4\text{N}_{16}\text{S}_4\text{Zn}$ (1627.37)	61.94	3.68	13.76	4.02
		(61.89)	(3.72)	(13.72)	(3.97)
3	$\text{C}_{80}\text{H}_{52}\text{Cl}_4\text{N}_{16}\text{NiS}_4$ (1564.7)	61.37	3.35	14.31	3.75
		(62.01)	(3.40)	(13.89)	(4.01)
4	$\text{C}_{84}\text{H}_{60}\text{Cl}_4\text{N}_{16}\text{NiS}_4$ (1620.7)	62.19	3.70	13.82	3.62
		(61.57)	(3.48)	(13.01)	(3.98)
5	$\text{C}_{160}\text{H}_{104}\text{Cl}_8\text{LuN}_{32}\text{O}_8\text{S}_8$ (3187)	60.24	3.26	14.05	
		(59.97)	(3.30)	(13.89)	

^a Required values are given in parentheses.

In addition to the elemental analysis results (Table 1), the outcome of ^{13}C NMR spectral analysis is critical in determining whether the ratio of the precursors is 1:1 after substitution reactions. In the attached proton test (APT) ^{13}C NMR spectra the phthalonitrile derivatives showed ten different signals for protonated aromatic carbon atoms at δ 110–160 as a consequence of the unsymmetrical structure. While the chemical shifts of the other seven unsaturated carbon atoms, two arising from nitrile groups, are observed, the quaternary pyridine carbon atom is at lowest field as expected. In the ^1H NMR spectrum of **III** the deuterium (D_2O) exchangeable NH protons appeared as a singlet, whereas those of **IV** were doublets as a result of the interactions between the NH and methyl protons. A close investigation of the mass spectra of **III** and **IV** confirmed the proposed structures. In addition to molecular ion peaks m/z 377 and 391 for **III** and **IV**, respectively, fragment ions corresponding to the loss of $\text{C}_3\text{H}_5\text{N}$ ($[\text{M} - 79]^+$) were easily identified. Molecular ion species were observed in accord with isotopic distributions. The spectra of **III** and **IV** were obtained by the FAB technique using a HCO_2H and glycerine matrix.

The usual synthetic routes were applied to obtain the metal-free and the divalent metal phthalocyanines. Conversion of phthalonitrile derivatives **III** and **IV** into metal-free phthalocyanines **V** and **VI** was accomplished directly by refluxing these reagents in 2-(dimethylamino)ethanol to realize the cyclo-tetramerization.⁴⁹ The reaction of **III**, **IV** in a high-boiling solvent such as quinoline with the acetate of Zn^{II} and chloride of Ni^{II} gave the divalent metal phthalocyanines **1–4**.¹ In contrast to the case of complexes **1** and **2** which are soluble in dmf, dmsO and pyridine and can thus afford spectroscopic measurements, **3** and **4** are slightly soluble in these solvents, thus hindering further spectroscopic investigations.

As expected from disubstituted phthalonitriles containing two different substituents in the 4,5 positions, the metal free and metal phthalocyanines are a mixture of four positional isomers.⁴³ Our attempts to separate these isomers by column chromatography and, also HPLC methods using different solvents were not successful, but their presence could be verified by slight broadening encountered in the absorption bands of the ^1H NMR and electronic spectra when compared with those of symmetrically octasubstituted phthalocyanines comprised of a single product.³⁵



Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp $C\equiv N$ vibration at 2225 cm^{-1} . The NH groups in the inner core of the metal-free phthalocyanines gave an absorption at 3285 cm^{-1} . These protons were also very well characterized by the $^1\text{H NMR}$ which showed a peak at $\delta -4.3$ as a result of the 18 π -electron system of the phthalocyanine ring.¹⁵ The $^1\text{H NMR}$ spectra of metal-free phthalocyanines and zinc(II) phthalocyanines were almost identical, the only difference being the disappearance of the broad NH protons of **V** and **VI**. Chemical shifts due to the alkyl, aromatic and secondary amine group were the dominating signals in the spectra of **V**, **VI**, **1** and **2**. The presence of positional isomers due to the differently substituted benzo units leads to broad signals for the peripheral aromatic protons.⁵⁰ Also, aggregation of phthalocyanine molecules at the concentrations used for the NMR measurements may cause broadening of the aromatic signals.

The mass spectrometry studies by the FAB technique¹⁵ on the newly synthesized phthalocyanines gave molecular ion species only for **VI** and **2**. Values for the molecular ions show good agreement with the calculated values for metal-free **VI** [M]⁺ peak (m/z 1564) and zinc phthalocyanines [$M + 2$]⁺ peak (m/z 1629). In addition to molecular ion peaks, the fragment ions corresponding to the loss of $4C_5H_5N$ [$M - 316$]⁺ were easily identified.

The most revealing data for a phthalocyanine system are given by their UV/VIS spectra in solution (Table 2). The electronic absorption spectrum of metal-free phthalocyanines **V**, **VI** exhibited a partly split Q band absorption which is due to the $\pi \rightarrow \pi^*$ transition of this completely conjugated 18 π electron system. The consequence of the lower symmetry introduced by two different substituents on each benzene group together with the solvent effect was a single intense Q band absorption in dmsO at 695 nm with a shoulder around 719 nm.⁵¹ The characteristic Q band transitions of metal phthalocyanines were observed as a single band of high intensity in the visible region for **1** and **2**. For all the phthalocyanines, the effect of S-substitution in addition to chloro groups was a shift in

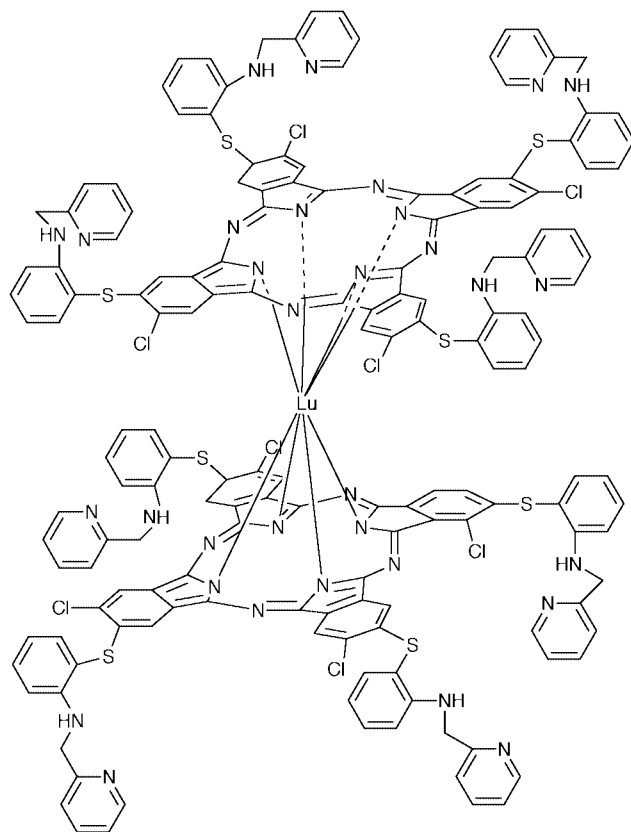
Table 2 Electronic spectra of the phthalocyanines

Compound	$\lambda_{\text{max}}/\text{nm}$ ($10^{-4}\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)
V ^a	719 (10.12), 695 (12.53), 661 (8.68), 345 (13.29), 311 (14.70)
VI ^a	718 (13.19), 694 (15.02), 660 (7.36), 352 (10.78), 309 (11.38)
1 ^a	699 (6.12), 632 (1.51), 370 (3.35)
2 ^a	699 (12.39), 630 (2.65), 369 (5.31)
3 ^b	835 (4.99), 741 (1.57), 392 (1.41), 311 (5.73)
4 ^b	790 (12.28), 701 (4.05), 401 (4.28), 308 (10.13)
5 ^c	699 (19.45), 667 (3.13), 630 (3.48), 427 (1.47), 363 (8.18)

^a In dmf. ^b In H_2SO_4 . ^c In chloroform.

these intense Q bands to longer wavelengths when compared with those of the unsubstituted or alkyl substituted derivatives.^{22,30,31,35} Concentrated H_2SO_4 , today, provides a new means by which to characterize the spectral properties of phthalocyanines.¹ The spectra of the nickel phthalocyanines **3** and **4** dissolved in concentrated H_2SO_4 without decomposition exhibited a red-shifted Q band. The position of the Q band in the H_2SO_4 spectrum should be a measure of the basicity of the unco-ordinated bridging nitrogen atoms.^{33,52,53}

The reaction of the phthalonitrile derivative **III** with anhydrous lutetium acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) in 1-hexanol gave the lutetium bis(phthalocyaninate) complex **5** in approximately 40% yield. Purification was achieved by column chromatography (silica gel).^{54,55} After chromatography, **5** was recovered as a pure green powder, as shown by elemental analysis. The most obvious feature of it is its high solubility in common organic solvents, e.g. chloroform, dichloromethane, thf, acetone, dmf and dmsO.



The IR spectrum of the lutetium complex **5** was very similar to those of other metal phthalocyanines. A characteristic band at 1472 cm^{-1} was observed, with various intensities, between the 1452 and 1472 cm^{-1} in the spectra of unsymmetrically substituted complexes.^{11,12} The band observed at 820 cm^{-1} , absent for

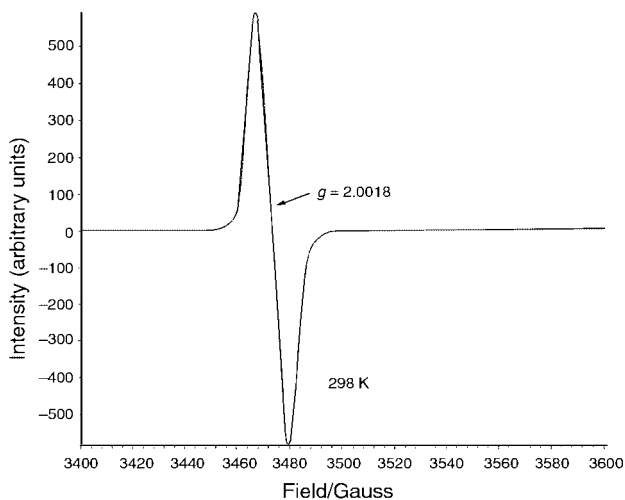


Fig. 1 The X-band ESR spectra of complex **5** at 298 K.

the metal-free phthalocyanine **V**, is usually attributed to the central ion–ligand vibration.^{56,57}

Only a few NMR data concerning lutetium bis(phthalocyaninates) are available from the literature,^{55,58} most of them dealing with the reduced forms.^{11,59} For all neutral forms, the paramagnetism of the [LuPc₂] perturbs the proton signals situated in the vicinity of the aromatic core. The good solubility of lutetium complex **5** in chloroform enabled us to record ¹H NMR spectra. The broad signals in the aromatic region could be attributed to the aromatic protons in the substituent group. While the D₂O exchangeable proton for the NH group was observed at δ 5.95, the CH₂ protons were at δ 4.44. Integration values were consistent with this interpretation.

The electronic spectrum of green, neutral complex **5** contained a Q band at 699 nm, a Soret band at 363 nm and a typical radical phthalocyanine anion band as a shoulder in the 400–500 nm region.^{34,60,61} The λ_{max} value (Q band) shows that the electronic transitions are effected by the nature and the number of substituents, as expected. A bathochromic shift was also observed for **5**, with a shift if the Q band toward longer wavelengths compared to those of alkyl, alkoxy or *tert*-butyl substituted bisphthalocyanines.^{34,55,58–60}

FAB mass spectroscopy has been extensively used to characterize various sandwich complexes.^{11,12,55,62–64} However, as has been described elsewhere, the spectra of the lutetium sandwich complexes vary drastically with the matrix used.^{63,64} Thus, FAB-MS gave only fragmentation peaks for the present compound.

The free-radical nature of the green LuPc₂ complexes is confirmed by ESR spectrum.⁶⁵ The spectrum of a solid sample of the lutetium complex **5** at room temperature, which shows a strong signal at $g = 2.0018$ with a bandwidth of 9 G, confirms the presence of an unpaired spin and is consistent with the occurrence of a phthalocyanine radical (Fig. 1).⁶⁶ The structure may have both phthalocyanine ligands symmetrically attached to the central metal atom. An intramolecular charge transfer with the free electron hopping between the two phthalocyanine rings was suggested in the green form of LuPc₂.^{61,67}

Electrochemical measurements

The difference of one methyl group between the two types of phthalocyanines would have a negligible effect on the electrochemical properties, therefore cyclic voltammetric measurements were carried out only for **V**, **1** and **5**.

Cyclic voltammetry of compounds V, 1 and 5 in dimethyl sulfoxide. Cyclic voltammetry data for compounds **V**, **1** and **5** in dmsO are shown in Table 3. Both **V** and **1** display two reversible one-electron reduction peaks with the peak separations (ΔE_p) of

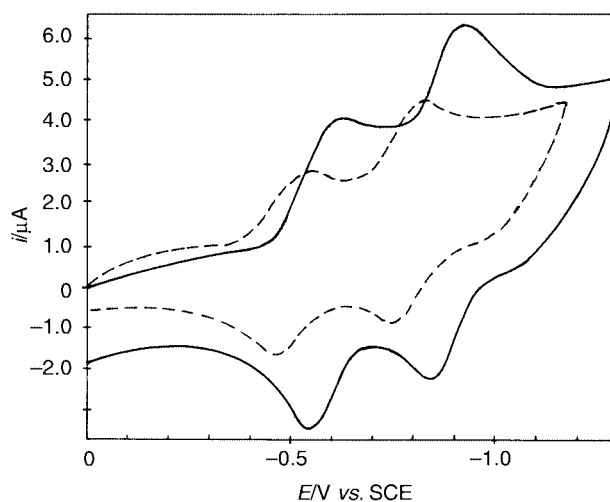


Fig. 2 Cyclic voltammograms of compounds **V** [(---), $\nu = 50 \text{ mV s}^{-1}$] and **1** [(—), $\nu = 100 \text{ mV s}^{-1}$] ($2.5 \times 10^{-4} \text{ M}$) in dmsO.

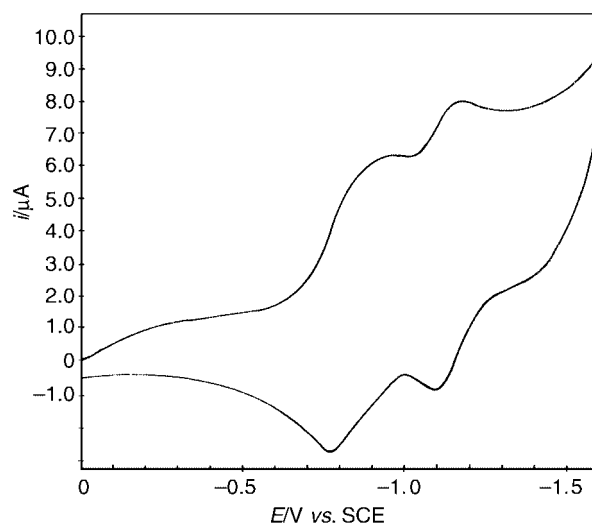


Fig. 3 Cyclic voltammogram of complex **5** ($2.5 \times 10^{-4} \text{ M}$) in dmsO at $\nu = 100 \text{ mV s}^{-1}$.

0.060 V (Fig. 2). The values of $I_{pc}/\nu^{1/2}$ were constant suggesting diffusion-controlled processes. The reduction of these compounds is thought to be ligand-based as reported for similar compounds with different substituents.^{52,67–72} The displacement of two protons by Zn^{II} shifts the first reduction potential of the phthalocyanine (Pc) ring to more negative values (–0.52 V for **V** and –0.61 V for **1**). This voltammetric behaviour has been observed previously with various metal-free and metal phthalocyanines^{69,72–76} and may be attributed to the increase in the negative charge of the Pc ring as a result of the strong coordination of nitrogen atoms to the metal ion. The π -back donation of the filled d_{π} of the metal ion into the empty Pc π^* orbitals and the polarization of the ligand due to the E_g symmetry with the displacement of protons by metal ion was previously reported⁷⁷ as providing an additional support for the negative shift in the reduction potential of the ring. On the other hand the reduction of free and zinc(II) phthalocyanines synthesized in this work was found to occur at considerably less negative potentials with respect to unsubstituted free and zinc(II) phthalocyanines whose reduction potentials were reported previously.^{69,74,78–80} The shift in reduction potentials can be attributed to the electron withdrawing chloro substituent which decreases the negative charge on the phthalocyanine ring.³³

Lutetium complex **5** shows a highly different voltammetric behaviour compared with those of **V** and **1**, giving two reduction peaks with the corresponding anodic waves (Table 3) as

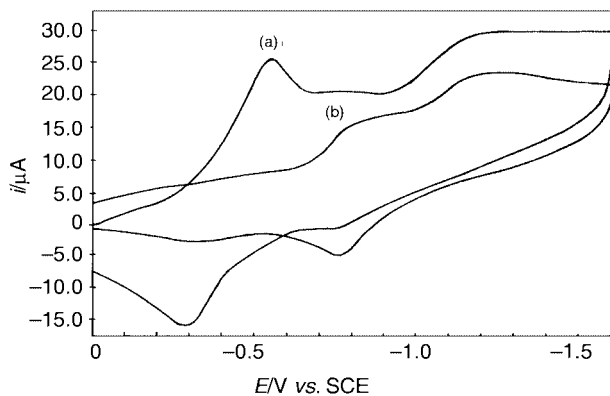


Fig. 4 Cyclic voltammograms of complex **5** (2.5×10^{-4} M) recorded in dmsu at $\nu = 250 \text{ mV s}^{-1}$ during the continuous potential cycle [(a) the first voltammogram recorded with the platinum electrode stood in complex solution previously, (b) the voltammogram recorded after 20 sweeps].

shown in Fig. 3. The voltammogram was recorded immediately after dipping the platinum working electrode into the complex solution. Voltammograms recorded after leaving the platinum electrode in the solution for 15–30 min had remarkable differences, especially during the continuous potential cycle (Fig. 4). While Fig. 4(a) shows the first voltammogram recorded with the working electrode previously stood in solution, Fig. 4(b) indicates that recorded after twenty sweeps. At first the reduction of the complex occurs at -0.54 V with continuous cycling, and the first reduction peak of the complex decreases in height and its peak potential shifts to more negative values. This type of behaviour suggests that **5** is adsorbed on the surface of the platinum electrode and is reduced more easily than that in solution. However **5** cannot form a stable adsorbed layer since the peak heights of the subsequent voltammograms were observed to decrease with continuous cycling. This was easily proven by taking the electrode out of the solution (after the electrode had stood in it for 30 min) and running the cyclic voltammogram in a solution involving only the solvent and electrolyte. It was not possible to observe the related peak in voltammograms recorded in this manner. The first reduction peak currents of the voltammograms recorded at different scan rates after dipping the working electrode into the complex solution were found to be directly proportional to $\nu^{1/2}$. On the other hand, the steady-state peak currents of the voltammograms recorded by first standing the platinum electrode in the complex solution for 30 min were directly proportional to the scan rate.

Cyclic voltammetry of complex 5 in dichloromethane. Complex **5** showed highly interesting voltammetric behaviour in CH_2Cl_2 . The voltammogram on sweeping to positive potentials (Fig. 5) displayed an oxidation peak at a potential of 0.86 V vs. SCE with the corresponding reduction wave. The first oxidation potentials of lutetium octa-4-phenyldipthalocyanine [$\text{LuPc}_2^{\text{Ph}}$] and lutetium octa-3-bromo-octa-5-*tert*-butylphthalocyanine [$\text{LuPc}_2^{\text{tBr}}$] were reported as 0.44 and $0.82 \text{ V (vs. Ag-AgCl)}$ respectively.³⁴ The oxidation potential of [$\text{LuPc}_2^{\text{tBr}}$] was observed to increase with the inductive effect of the bromo substituent in related work. The value of 0.86 V vs. SCE measured in this work is consistent with the previously reported literature value and indicates the acceptor nature of the chloro substituent.³³

The cyclic voltammetry of complex **5** in CH_2Cl_2 -tetrabutylammonium perchlorate involved very high currents which increased with continuous sweep and reached a steady state with sufficient cycling (approximately 20 cycles). When the platinum electrode was taken out of the solution after a steady-state voltammogram had been achieved a film with a distinct green colour was observed. On sweeping to negative potentials a reduction process with a very small re-oxidation peak was

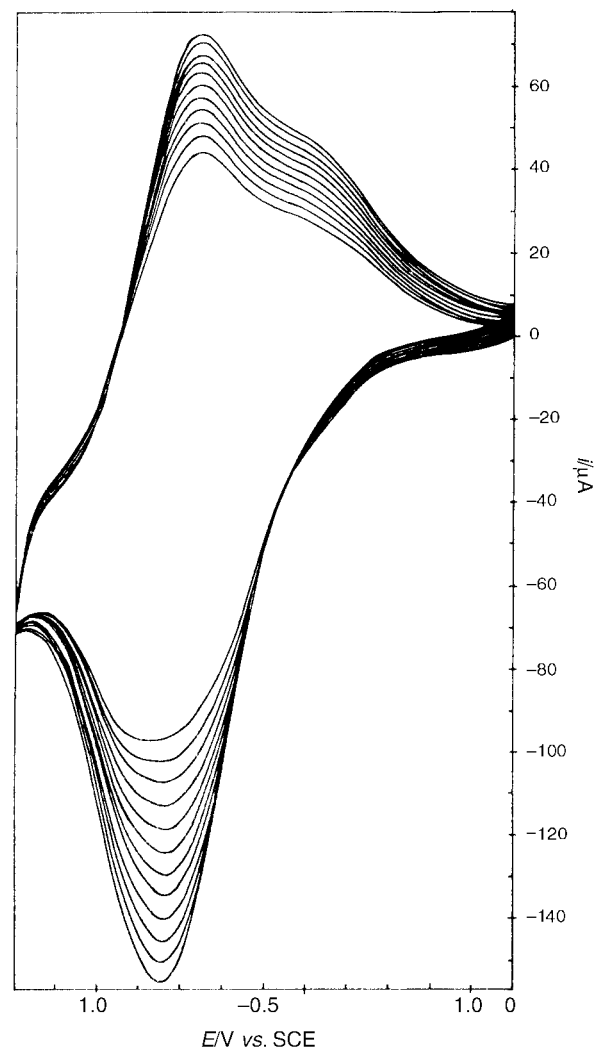


Fig. 5 Cyclic voltammograms of complex **5** (2.5×10^{-4} M) on sweeping to positive potentials in CH_2Cl_2 at $\nu = 50 \text{ mV s}^{-1}$.

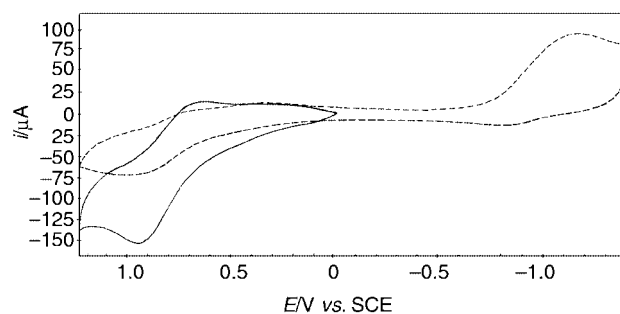


Fig. 6 Cyclic voltammograms of complex **5** (2.5×10^{-4} M) in CH_2Cl_2 with $\nu = 50 \text{ mV s}^{-1}$ in the potential ranges 0 – 1.25 V (—) and 1.25 to -1.40 V (---).

observed at -1.1 V , but the height of the oxidation peak decreased considerably (Fig. 6) when the lower potential limit was changed from 0 to -1.4 V after sufficient cycling between 0 and 1.25 V to achieve steady-state conditions. The value of -1.1 V is also consistent with the potential reported for [$\text{LuPc}_2^{\text{tBr}}$] by Rodriguez-Mendez and Aroca.³⁴ The oxidation peak currents of the voltammograms recorded at different scan rates immediately after dipping the working electrode into the [LuPc_2] solution and after sufficient cycling to achieve steady-state conditions were directly proportional to the scan rate showing that the relevant peak involves the oxidation of adsorbed species. On the other hand, adsorption or the formation of a film on the working electrode was not observed when the electrode had

Table 3 Redox potentials of compounds **V**, **1** and **5** in dmsO

Compound	Redox couple	$E_{pc}^a(\Delta E_p)^b/V$ vs. SCE	$E_{1/2}^c/V$ vs. SCE
V	$H_2Pc(-2)-[H_2Pc(-3)]^-$	-0.52 (0.060)	-0.49
	$[H_2Pc(-3)]^--[H_2Pc(-4)]^{2-}$	-0.81 (0.060)	-0.78
1	$[ZnPc(-2)]-[ZnPc(-3)]^-$	-0.61 (0.060)	-0.58
	$[ZnPc(-3)]^--[ZnPc(-4)]^{2-}$	-0.92 (0.060)	-0.89
5	$[LuPc_2]-[LuPc_2]^-$	-0.94 (0.120)	-0.88
	$[LuPc_2]-[LuPc_2]^{2-}$	-1.16 (0.060)	-1.13

^a Cathodic peak potential. ^b Peak splitting (V) evaluated by $\Delta E_p = E_{pa} - E_{pc}$. ^c Half-wave potential estimated by $E_{1/2} = (E_{pa} + E_{pc})/2$.

stood in the solution for a long time and then been taken out. These observations indicate that adsorption or the formation of a film occurs only during the continuous potential sweep.

Electrochromic properties of complex **5** were observed with the naked eye by running the cyclic voltammogram in a solution involving only CH_2Cl_2 and NBu_4ClO_4 with the platinum working electrode covered with the green phthalocyanine film as explained before. The cyclic voltammograms recorded in this manner were identical in shape to those recorded in solution, but the peak currents for both oxidation and re-reduction were lower. During the potential cycle between 0 and 1.25 V the film was observed to change from green to orange at potentials more positive than 0.90 V and from orange to green at potentials less positive than 0.80 V. The green film was so electrochemically stable during the potential cycles between 0 and 1.25 V that it was possible to observe this change in colour even after 50 cycles without a decrease in the peak currents and also without a change in the shape of the voltammogram. The film was also very stable chemically because it did not dissolve even when the electrode was shaken in CH_2Cl_2 . The electrochemical stability may be attributed to the charge balancing effect of the perchlorate ions after the oxidation of the $[LuPc_2]$ in the film. However, the green film probably dissolves and passes into solution after the lower potential limit is changed from 0 to -1.4 V and the working electrode is allowed to have potentials more negative than -1.10 V at which the reduction peak is observed. During the potential cycle between 1.25 and -1.4 V both oxidation and reduction peaks disappeared and the reversible change in colour could not be observed although a green film still appeared on the electrode. Unfortunately, we could not observe a colour change from green to blue. This is probably owing to the fact that tetrabutylammonium cation, which has a considerable size, cannot penetrate into the film to balance the negative charge of the reduction product. So the destruction of the film occurs. However, **5** is an interesting complex which forms an electrochemically and chemically stable film on a platinum electrode without using any special method (*e.g.* rotation, vapour deposition) and electrode material (*e.g.* ordinary pyrolytic graphite, glassy carbon, highly oriented pyrolytic graphite, ITO glass).

Experimental

Routine IR spectra were recorded on a ATI Unicomp-Mattson 1000 spectrophotometer as KBr pellets, electronic spectra on a ATI Unicomp UV/Vis spectrometer UV2, ¹H and ¹³C NMR spectra on a Bruker 200 MHz spectrometer, mass spectra on a VG Zabspec GS-MS spectrometer and ESR spectra using a Bruker 380 EMX spectrometer operated at X-band. The metal contents of the complex were determined with a Hitachi-180-80 atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in concentrated HCl and concentrated HNO₃ (3:1) solution followed by dilution in water.

Cyclic voltammetric measurements were performed with an

instrument (PAR model 273 potentiostat, controlled by an external computer) utilizing a three-electrode configuration and an X-Y recorder (RE 0091). A platinum wire served as the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. The working electrode was a platinum plate. The surface of the latter was polished with a water suspension of Al_2O_3 before each experiment. The last polishing was done with a particle size of 50 nm. The SCE was separated from the solution by a double bridge containing saturated KCl adjacent to the SCE and solvent, and carrier adjacent to the solution. Dimethyl sulfoxide and dichloromethane, which was dried over molecular sieves, were employed as the solvents. Electrochemical grade NBu_4ClO_4 in dmsO and extra pure Na_2SO_4 (Merck) in water were used as the supporting electrolytes in 0.1 M concentration. Solutions were deaerated by bubbling nitrogen for at least 30 min prior to each voltammetric measurement.

All reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego.⁸¹ The solvents were stored over molecular sieves (4 Å). The homogeneity of the products was tested in each step by TLC (SiO_2). 1,2-Dichloro-4,5-dicyanobenzene³¹ and 2-(2-pyridylmethylamino)benzenethiol **I**⁴⁷ were prepared by the literature methods.

Preparations

2-(2-Pyridylethylamino)benzenethiol II. 2-Aminobenzene-thiol (4.91 g, 39.21 mmol) was dissolved in methanol (40 cm³) under nitrogen. A solution of 2-acetylpyridine (4.75 g, 39.2 mmol) in methanol (40 cm³) was added dropwise. The reaction mixture was heated to reflux for 2 h and then cooled to room temperature. The salt $NaBH_4$ (14.8 g, 390 mmol) was added in small portions with stirring. The solvent was removed in a rotary evaporator and the solid residue suspended in 100 cm³ of ice-water and neutralized carefully with glacial acetic acid. The greenish yellow emulsion was extracted four times with 50 cm³ of dichloromethane each time. The combined extracts were washed with water (50 cm³) and dried over Na_2SO_4 . Then the solvent was reduced *in vacuo*. Analytically pure product which was treated with refluxing light petroleum (bp 40–60 °C) remained as a yellow oil. Yield 6.44 g (71%). $\tilde{\nu}_{max}/cm^{-1}$ 3390 (NH), 3058, 3010, 2924–2850 (alkyl CH), 2518 (SH), 1588–1568 (pyridine C=N), 1501, 1473, 1446, 1426, 1353, 1286, 1230, 1137, 1106, 1085, 1040, 995, 957, 786, 746 and 665. ¹H NMR (d_6 -dmsO): δ 1.40 (d, 3 H, CH_3), 4.63 (p, 1 H, NCH), 6.65–7.79 (m, 7 H, aryl-H) and 8.53 (d, 1 H, pyridine H_a). MS (EI): m/z 230 (36, M⁺), 229 (77, M - 1) and 228 (89%, M - 2).

1-Chloro-3,4-dicyano-6-[2-(2-pyridylmethylamino)phenylsulfanyl]benzene III. Compound **I** (1.45 g, 6.73 mmol) and 1,2-dichloro-4,5-dicyanobenzene (0.66 g, 3.36 mmol) were dissolved in absolute tetrahydrofuran (150 cm³) under nitrogen. After stirring for 10 min finely ground anhydrous potassium carbonate (3.33 g, 24.15 mmol) was added with stirring. The reaction mixture was stirred under nitrogen at reflux temperature for 48 h. After cooling the yellowish mixture was filtered and the solvent evaporated to dryness. Diethyl ether (100 cm³) was added to the oily residue and the precipitate obtained was filtered off, washed with water several times, then with EtOH and Et₂O and dried *in vacuo*. Compound **III** is soluble in chloroform, dichloromethane, acetone, thf, dmf and dmsO. Yield 1.00 g (40%), mp 174 °C. $\tilde{\nu}_{max}/cm^{-1}$ 3390 (NH), 3079, 3058, 3003, 2983–2890 (alkyl CH), 2225 (C≡N), 1589–1568 (pyridine C=N), 1501, 1480, 1445, 1425, 1366, 1292, 1225, 1121, 933, 785, 750, 708, 700 and 665. ¹H NMR (d_6 -dmsO): δ 4.45 (d, 2 H, CH_2), 6.47 (s, 1 H, NH), 6.67–7.71 (m, 9 H, aryl-H) and 8.47 (dd, 1 H, pyridine H_a). ¹³C NMR (APT) (d_6 -dmsO): δ 22.43 (CH_2), 107.94 (aromatic C), 111.94 (aromatic CH), 113.72 (aromatic C), 115.17–115.48 (C≡N), 117.64, 121.30, 122.50,

129.48, 133.46, 134.33 (aromatic CH), 135.27 (aromatic C), 137.17–137.84 (aromatic CH), 145.42 (aromatic C), 149.00 (aromatic CH), 149.56 (aromatic C) and 158.74 (pyridine C). MS (FAB): m/z 377 (100, M^+), 298 (3, $M - C_5H_5N$), 249 (1) and 183 (10%).

1-Chloro-3,4-dicyano-6-[2-(2-pyridylethylamino)phenyl-sulfanyl]benzene IV. Compound **II** (1.00 g, 4.62 mmol) and 1,2-dichloro-4,5-dicyanobenzene (0.46 g, 2.32 mmol) were dissolved in tetrahydrofuran (120 cm³) under nitrogen. After stirring for 10 min finely ground anhydrous potassium carbonate (1.15 g, 8.26 mmol) was added with stirring. The reaction mixture was stirred under nitrogen at reflux temperature for 48 h. After cooling the yellowish green mixture was filtered and the solvent evaporated to dryness. The resulting oily residue was extracted with *n*-hexane (3 × 25 cm³). The combined extracts were kept at -30 °C for 24 h. The cold mother-liquor was decanted off the yellow precipitate which was dried *in vacuo* at room temperature. Compound **IV** is soluble in chloroform, dichloromethane, ethanol, acetone, thf, Et₂O, dmf and dmsO. Yield 0.36 g (20%), mp 124 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3395, 3390 (NH), 3074, 3004, 2956, 2918, 2866 (alkyl CH), 2225 (C≡N), 1589–1566 (pyridine C=N), 1501, 1480, 1445, 1425, 1366, 1292, 1225, 1121, 933, 785, 750, 708, 700 and 667. ¹H NMR (d₆-dmsO): δ 1.40 (d, 3 H, CH₃), 4.76 (qnt, 1 H, NCH), 5.88 (d, 1 H, NH), 6.69–7.72 (m, 9 H, aryl H) and 8.41 (pyridine H_a). ¹³C NMR (APT) (d₆-dmsO): δ 22.43 (CH₃), 53.35 (NCH), 108.60 (aromatic C), 112.78 (aromatic CH), 113.72 (aromatic C), 115.12–115.50 (C≡N), 118.82–120.75, 122.53, 129.65, 133.47, 134.39 (aromatic CH), 135.70 (aromatic C), 137.28–137.88 (aromatic CH), 146.10 (aromatic C), 149.04 (aromatic CH), 149.40 (aromatic C) and 162.73 (pyridine C). MS (FAB): m/z 391 (100, M^+), 312 (7, $M - C_5H_5N$) and 106 (25%).

Metal-free phthalocyanines V and VI. A solution of complex **III** (0.188 g, 0.50 mmol) or **IV** (0.200 g, 0.50 mmol) in dry 2-(dimethylamino)ethanol (1 cm³) was refluxed under nitrogen for 2 h. After cooling, ethanol (10 cm³) was added in order to precipitate the product. The green product was filtered off and refluxed several times with ethanol to remove unreacted organic materials. The crude products were purified by column chromatography (silica gel, CH₂Cl₂-*n*-hexane 5:2). The products were soluble in dmf and dmsO. Yield of **V** 0.039 g (21%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3390 (NH), 3285 (NH), 3079, 3009, 2983–2890 (alkyl CH), 1600, 1588, 1566 (C=N), 1501, 1482, 1446, 1425, 1368, 1290, 1225, 1120, 934, 790, 757, 708, 700 and 667. ¹H NMR (d₆-dmsO): δ -4.29 (s, 2 H, NH), 4.40 (s, 8 H, CH₂), 5.40 (s, 4 H, NH), 6.47–8.26 (m, 40 H, aryl H). Yield of **VI** 0.040 g (20%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$: 3395–3390 (NH), 3285 (NH), 3049, 3004, 2954, 2908, 2858 (alkyl CH), 1600, 1587, 1566 (C=N), 1502, 1462, 1424, 1412, 1366, 1293, 1224, 1120, 933, 786, 757, 708, 700 and 665. ¹H NMR (d₆-dmsO): δ -4.29 (s, 2 H, NH), 1.36 (s, 12 H, CH₃), 4.78 (s, 4 H, NCH), 5.40 (s, 4 H, NH), 6.42–8.23 (m, 40 H, aryl H). MS (FAB): m/z 1564 (8, M^+) and 1248 [18%, $M - 4(C_5H_5N)$].

Zinc(II) phthalocyanines 1 and 2. A mixture of compound **III** (0.193 g, 0.514 mmol) or **IV** (0.200 g, 0.512 mmol), anhydrous zinc acetate (0.023 g, 0.128 mmol) and quinoline (0.5 cm³) was heated and stirred at 175 °C in a sealed glass tube for 5 h under nitrogen. After cooling to room temperature, ethanol (5 cm³) was added in order to precipitate the product. The dark green product was filtered off and then washed several times successively with hot water, hot EtOH, hot chloroform and diethyl ether. It was isolated by silica gel column chromatography with chloroform-methanol (20:1 v/v) as eluent. These products are soluble in dmf, dmsO and pyridine. Yield of **1** 0.104 g (52%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3390 (NH), 3080, 3009, 2978–2876 (alkyl CH), 1600, 1588, 1570 (C=N), 1522, 1497, 1446, 1421, 1395, 1290, 1220, 1140, 961, 790, 757, 706 and 667.

¹H NMR (d₆-dmsO): δ 4.48 (s, 8 H, CH₂), 5.54 (s, 4 H, NH), 7.10–8.75 (m, 40 H, aryl H). Yield of **2** 0.094 g (45%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3395–3390 (NH), 3080, 3008, 2978, 2902, 2876 (alkyl CH), 1600, 1585, 1575 (C=N), 1525, 1495, 1445, 1420, 1395, 1280, 1210, 1140, 960, 790, 757, 705 and 667. ¹H NMR (d₆-dmsO): δ 1.24 (d, 12 H, CH₃), 4.21 (t, 4 H, NCH), 5.54 (s, 4 H, NH), 6.82–8.57 (m, 40 H, aryl H). MS (FAB): m/z 1629 [5, ($M + 2$)⁺] and 1311 [12, $M - 4(C_5H_5N)$].

Nickel(II) phthalocyanines 3 and 4. A mixture of compound **III** (0.200 g, 0.0531 mmol) or **IV** (0.200 g, 0.512 mmol), anhydrous NiCl₂ (0.0179 g, 0.131 mmol) and quinoline (5 cm³) was heated and stirred at 175 °C for 5 h under nitrogen. After having cooled to 60 °C, it was filtered and the dark green precipitate refluxed several times with water, ethanol, chloroform and acetone to remove unchanged materials. The solid was heated at 60 °C with dmf (2 × 10 cm³) and dmsO (2 × 10 cm³) and filtered off. Finally the dark green **3** and **4** were obtained by washing with ethanol and diethyl ether, then, dried *in vacuo* at 100 °C. These compounds are slightly soluble in dmf, dmsO and pyridine. Yield of **3** 0.06 g (29%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3390 (NH), 3074, 3004, 2975–2866 (alkyl CH), 1600, 1589, 1566 (C=N), 1530, 1465, 1431, 1390, 1150, 970, 780, 757, 704 and 665. Yield of **4** 0.0399 (19%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3395–3390 (NH) 2978–2865 (alkyl CH), 1600, 1588, 1567 (C=N), 1535, 1470, 1420, 1380, 1150, 975, 790, 757, 700 and 665.

Lutetium(III) bis(phthalocyaninate) 5. A mixture of compound **III** (0.200 g, 0.531 mmol), anhydrous lutetium(III) acetate (0.032 g, 0.264 mmol) and dbu (0.317 g, 2.112 mmol) in 1-hexanol (1.5 cm³) was heated at reflux under nitrogen for 20 h. After cooling to room temperature, it was treated with ethanol (5 cm³) and the dark green precipitate filtered off and then washed with hot ethanol several times. The crude product was extracted with chloroform (5 × 20 cm³). The remaining green solid was identified by visible spectroscopy as being the free phthalocyanine. The green solution was reduced in volume on a rotary evaporator and then chromatographed on a column of silica gel using CH₃OH-CH₂Cl₂ (1:20, v/v) as eluent. The green product is soluble in chloroform, dichloromethane, acetone, thf, dmf and dmsO. Yield of **5** 0.085 g (40%), mp > 200 °C. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3390 (NH), 3055, 3009, 2953–2827 (alkyl CH), 1600, 1588, 1574 (C=N), 1523, 1497, 1485, 1472, 1446, 1421, 1395, 1290, 1220, 1140, 961, 820, 790, 757, 706 and 667. ¹H NMR (d₆-dmsO): δ 4.44 (s, 16 H, CH₂), 5.95 (s, 8 H, NH) and 6.97–8.25 (m, 64 H, aryl H).

Acknowledgements

The authors thank A. R. Özkaya for cyclic voltammetry measurements. Ö. B. is grateful to the Turkish Academy of Science (TUBA) and the Research Fund of the Technical University of Istanbul for their support.

References

- 1 C. C. Leznoff and A. B. P. Lever (editors), *Phthalocyanines Properties and Applications*, VCH, New York, 1989–1996, vols. 1–4.
- 2 P. Gregory, *High Technology Applications of Organic Colorants*, Plenum, New York, 1991.
- 3 I. Rosenthal, *Photochem. Photobiol.*, 1991, **53**, 859.
- 4 Z. Z. Öztürk, R. Zhou, U. Weimar, V. Ahsen, Ö. Bekaroğlu and W. Göpel, *Sens. Actuators, B*, 1995, **26–27**, 208.
- 5 M. Maitrot, G. Guillaud, B. Boudjema, J. J. Andre, H. Strzelecka, J. Simon and R. Even, *Chem. Phys. Lett.*, 1987, **133**, 59.
- 6 Y. Liu, K. Shigehara, M. Hara and A. Yamada, *J. Am. Chem. Soc.*, 1991, **113**, 440.
- 7 J. S. Shirk, J. R. Lindle, F. J. Bartoli and M. E. Boyle, *J. Phys. Chem.*, 1992, **96**, 5847.
- 8 M. M. Nicholson, *Ind. Eng. Chem. Prod. Res. Dev.*, 1982, **21**, 261.
- 9 C. Piechocki, J. Simon, J. J. Andre, D. Guillon, P. Petit, A. Skoulios and P. Weber, *Chem. Phys. Lett.*, 1985, **122**, 124.

- 10 T. Komatsu, K. Ohta, T. Fujimoto and I. Yamamoto, *J. Mater. Chem.*, 1994, **4**, 533.
- 11 A. Pandoven, Y. Cozien and M. L'Her, *New. J. Chem.*, 1991, **15**, 515.
- 12 A. Pandoven, Y. Cozien and M. L'Her, *New. J. Chem.*, 1992, **16**, 711.
- 13 M. Hanack, S. Deger and A. Lange, *Coord. Chem. Rev.*, 1988, **83**, 115.
- 14 S. A. Mikhalenko, S. V. Barkanova, O. L. Lebedev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1971, **41**, 2735.
- 15 A. R. Koray, V. Ahsen and Ö. Bekaroğlu, *J. Chem. Soc., Chem. Commun.*, 1986, 932; V. Ahsen, E. Yilmazer, M. Ertaş and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1988, 401; V. Ahsen, A. Gürek, E. Musluoğlu, A. Gül and Ö. Bekaroğlu, *Helv. Chim. Acta*, 1990, **73**, 174.
- 16 M. Koçak, A. Cihan, A. I. Okur and Ö. Bekaroğlu, *J. Chem. Soc., Chem. Commun.*, 1991, 578; A. Gürek, V. Ahsen, A. Gül and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1991, 3367.
- 17 G. Gümüş, Z. Öztürk, V. Ahsen, A. Gül and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1992, 2485.
- 18 I. Yılmaz and Ö. Bekaroğlu, *Chem. Ber.*, 1996, **129**, 967.
- 19 M. Koçak, A. I. Okur and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1994, 323.
- 20 A. Gürek and Ö. Bekaroğlu, *Helv. Chim. Acta*, 1994, **77**, 1616.
- 21 A. G. Gürek and Ö. Bekaroğlu, *J. Porph. Phthalocyan.*, 1997, **1**, 227.
- 22 Z. Altuntaş Bayır, E. Hamuryudan, A. G. Gürek and Ö. Bekaroğlu, *J. Porph. Phthalocyan.*, 1997, **1**, 349.
- 23 M. Kandaz and Ö. Bekaroğlu, *Chem. Ber.*, 1997, **130**, 833.
- 24 E. Musluoğlu, V. Ahsen, A. Gül and Ö. Bekaroğlu, *Chem. Ber.*, 1991, **124**, 2531.
- 25 Z. Z. Öztürk, E. Musluoğlu, V. Ahsen, A. Gül and Ö. Bekaroğlu, *J. Mater. Sci.*, 1992, **27**, 6183.
- 26 S. A. Mikhalenko, V. M. Derkacheva and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1981, **51**, 1650.
- 27 M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson and K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2453.
- 28 W. Eberhardt and M. Hanack, *Synthesis*, 1997, 95.
- 29 N. B. McKeown, *Phthalocyanine Materials, Synthesis, Structure and Function*, Cambridge University Press, 1998.
- 30 H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, Y. Suda, K. Shigehara and A. Yamada, *Proc. SPYE-Int. Soc. Opt. Eng.*, 1990, **105**, 1337.
- 31 D. Wöhrle, M. Eskes, K. Shigehara and A. Yamada, *Synthesis*, 1993, 194.
- 32 S. Hayashida and N. Hayashi, *Chem. Lett.*, 1990, 2137.
- 33 M. N. Golovin, P. Seymour, K. Jayaraj, Y. Fu and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1719.
- 34 M. L. Rodriguez-Mendez and R. Aroca, *Chem. Mater.*, 1993, **5**, 933.
- 35 I. Gürol, V. Ahsen and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1994, 497.
- 36 A. Gürek and Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.*, 1994, 1419.
- 37 M. Hanack, G. Schmid and M. Sommerauer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1422; *Angew. Chem.*, 1993, **105**, 1540.
- 38 G. Schmid, M. Sommerauer, M. Geyer and M. Hanack, in *Phthalocyanines: Properties and Application*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1996, vol. 4, p. 83.
- 39 M. Hanack and M. Lang, *Chemtracts-Org. Chem.*, 1995, **8**, 131; *Adv. Mater.*, 1994, **6**, 822.
- 40 M. Sommerauer, C. Rager and M. Hanack, *J. Am. Chem. Soc.*, 1996, **118**, 10085.
- 41 C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever and K. B. Tomer, *Can. J. Chem.*, 1985, **63**, 623.
- 42 C. C. Leznoff, M. Hu, C. R. McArthur, Y. Qin and J. E. Van Lier, *Can. J. Chem.*, 1994, **72**, 1990.
- 43 P. Haisch and M. Hanack, *Synthesis*, 1995, 1251.
- 44 D. Masural, C. Sirlin and J. Simon, *New. J. Chem.*, 1987, **11**, 455.
- 45 K. Takahashi, M. Kawashima, Y. Tomito and M. Itoh, *Inorg. Chim. Acta*, 1995, **232**, 69.
- 46 M. Hossain and S. Ghosh, *Transition Met. Chem.*, 1997, **497**, 22.
- 47 U. Brand and H. Vahrenkamp, *Chem. Ber.*, 1996, **129**, 431.
- 48 A. G. Gürek and Ö. Bekaroğlu, *J. Porph. Phthalocyan.*, 1997, **1**, 67.
- 49 J. F. van der Pol, E. Neeleman, J. C. van Miltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Macromolecules*, 1990, **23**, 155.
- 50 S. Gaspard and P. Maillard, *Tetrahedron*, 1987, **43**, 1083.
- 51 G. Gümüş, A. Gül and Ö. Bekaroğlu, *J. Chem. Res. (S)*, 1994, 430.
- 52 D. Wöhrle and V. Schmidt, *J. Chem. Soc., Dalton Trans.*, 1988, 549.
- 53 D. Wöhrle and B. Schulte, *Makromol. Chem.*, 1988, **189**, 1167.
- 54 H. Tomoda, S. Saito, S. Ogawa and S. Shiraishi, *Chem. Lett.*, 1980, 1277.
- 55 T. Toupance, P. Bassoul, L. Mineau and J. Simon, *J. Phys. Chem.*, 1996, **100**, 11704.
- 56 C. Clarisse and M. T. Riou, *Inorg. Chim. Acta*, 1987, **130**, 139.
- 57 H. F. Shurvell and L. Pinzutti, *Can. J. Chem.*, 1966, **44**, 125.
- 58 T. Toupance, V. Ahsen and J. Simon, *J. Am. Chem. Soc.*, 1994, **116**, 5352.
- 59 H. Konami, M. Hatano and A. Tajiri, *Chem. Phys. Lett.*, 1989, **160**, 163.
- 60 M. L. Rodriguez-Mendez and R. Aroca, *Chem. Mater.*, 1992, **4**, 1017.
- 61 D. Battisti, L. Tomilova and R. Aroca, *Chem. Mater.*, 1992, **4**, 1323.
- 62 F. Guyon, A. Pandoven, P. Guenot and M. L'Her, *Inorg. Chem.*, 1994, **33**, 4787.
- 63 M. Bouvet and J. Simon, *Chem. Phys. Lett.*, 1990, **172**, 299.
- 64 F. Guyon, A. Pandoven, J. Kerbaol and M. L'Her, *Inorg. Chem.*, 1998, **37**, 569.
- 65 A. De Cian, M. Moussavi, J. Fischer and R. Weiss, *Inorg. Chem.*, 1985, **24**, 3162.
- 66 C. Piechocki and J. Simon, *J. Chem. Phys. Lett.*, 1985, **122**, 124.
- 67 G. A. Coker, B. Grant and N. J. Clecak, *J. Electrochem. Soc.*, 1979, **126**, 1339.
- 68 T. Nyokong, *Polyhedron*, 1993, **12**, 375.
- 69 R. H. Campbell, G. A. Heath, G. T. Hefter and R. C. S. McQueen, *J. Chem. Soc., Chem. Commun.*, 1983, 1123.
- 70 A. Giraudeau, A. Louati, M. Gross, J. J. Andre, J. Simon, C. H. Su and K. M. Kadish, *J. Am. Chem. Soc.*, 1983, **105**, 2917.
- 71 J. T. S. Irvine and B. R. Eggins, *J. Electroanal. Chem., Interfacial Electrochem.*, 1989, **271**, 161.
- 72 A. R. Özkaya, A. I. Okur, A. Gül and Ö. Bekaroğlu, *J. Coord. Chem.*, 1994, **33**, 311.
- 73 L. D. Rolmann and R. T. Iwamoto, *J. Am. Chem. Soc.*, 1968, **90**, 1455.
- 74 A. Giraudeau, F. F. Fan and A. J. Bard, *J. Am. Chem. Soc.*, 1980, **102**, 5137.
- 75 A. R. Özkaya, A. G. Gürek, A. Gül and Ö. Bekaroğlu, *Polyhedron*, 1997, **16**, 1877.
- 76 A. R. Özkaya, I. Yılmaz and Ö. Bekaroğlu, *J. Porph. Phthalocyan.*, 1998, **2**, 483.
- 77 A. Rosa and A. J. Baerends, *Inorg. Chem.*, 1994, **33**, 584.
- 78 D. W. Clack, N. S. Hush and I. S. Woolsey, *Inorg. Chim. Acta*, 1976, **19**, 129.
- 79 D. Lexa and M. Reix, *J. Chim. Phys.*, 1974, **71**, 511.
- 80 E. Ough, T. Nyokong, K. A. M. Creber and M. J. Stillmann, *Inorg. Chem.*, 1988, **27**, 2724.
- 81 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980.

Paper 9/07747B