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Unsymmetrical phthalocyanines with alkynyl substituents

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Abstract

The synthesis of unsymmetrically substituted metallophthalocyanines (M = Zn, Ni, Co) bearing two phenylethyl moieties and six alkythio substituents was achieved by co-cyclotetramerization of two different phthalonitrile derivatives, namely 4,5-di(hexyl-thio)phthalonitrile and 4,5-di(phenylethynyl)phthalonitrile in the presence of zinc, cobalt or nickel salts. In contrast to the totally alkyne substituted phthalocyanines, these partially alkyne-containing derivatives are more soluble and their Q band absorptions are red-shifted when compared with all alkylthio phthalocyanines. Electrochemical properties of the phthalocyanines were studied by cyclic voltammetry.

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1. Introduction

Phthalocyanines are traditionally used as dyes and pigments. Phthalocyanine derivatives displaying photophysical properties, electron transfer ability and oxidoreduction capabilities are studied for applications in electrophotography, optical date-recording systems, electronic devices, photovoltaic cells, fuel cells and electrochromic displays. They are also promising materials for applications in gas sensors, nonlinear optical and optical limiting devices [1,2]. These properties are influenced both by the nature of the substituents (electron donating or electron withdrawing) on the ligand and by the nature of the metal ion in the core of the ligand.

In the synthesis and purification steps and also investigation of various properties, solubility of the phthalocyanines is of fundamental importance. By appropriate

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substitution with bulky or long-chain groups in the peripheral positions of the macrocycle, these compounds can be made soluble in common organic solvents, thus increasing the field of possible applications [3-8].

There has been a growing interest in unsymmetrical phthalocyanines which possess interesting properties in various areas like second order nonlinear optics [9], photodynamic therapy of cancer [10,11], liquid crystals [12] and Langmuir–Blodgett film formation [13]. Despite the variety of synthetic routes developed to prepare symmetrically substituted phthalocyanines, relatively few methods can be applied for preparing unsymmetrical ones [14]. The most simple approach to the preparation of phthalocyanines bearing different substituents is a mixed cyclization of two precursors with different substituents. The main problem with this method is the isolation of the desired phthalocyanines from a product mixture made up of components with similar physical and chemical properties. The second method is synthesis on a polymeric support developed by Leznoff and Hall [15], which consists in attaching a diiminoisoindoline

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or phthalonitrile to an insoluble polymer, making it react with a different diiminoisoindoline and, after removal of the symmetric phthalocyanine, releasing the unsymmetrical phthalocyanine from the polymer support. A third method has been described by Kobayashi and co-workers [16,17] and involves the ring expansion of a subphthalocyanine to a phthalocyanine using a phthalonitrile unit which bears a different type of substituent to that on the subphthalocyanine.

Over the past few years, palladium catalysed crosscoupling reactions provide a further and important means of functionalising the phthalocyanine ring with interesting grouping. This has produced various derivatives that include alkynyl and alkenyl functionalised phthalocyanines including some unsymmetrical phthalocyanines. Examples of some of these compounds and related structures have interesting NLO effects [18,19].

We have previously reported peripherally substituted symmetrical and unsymmetrical phthalocyanines [20– 22]. The incorporation of macrocyclic groups such as dioxadiaza and triaza-macrocycles has enhanced the solubility of these compounds [23,24]. A consequence of incorporating a sulfanyl function on the periphery has been a shift of the Q-band absorption to longer wavelengths [25]. This is preferred for a number of applications such as with IR absorbers and photosensitizers. In the present work, we report on the synthesis and characterization of unsymmetrical metallophthalocyanines which carry two peripheral hexylthio substituents on each of three of the benzenoid groups while the fourth one carries two phenylethynyl groups.

2. Experimental

IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ¹H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as an internal reference. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. 4,5-Dichlorophthalonitrile (1) [26] and 4,5-di(hexylthio)phthalonitrile (2) [27] were synthesized according to published methods.

Electrochemical techniques were carried out with a Princeton Applied Research Model 273 potentiostat/galvanostat controlled by an external PC using the computer program HEADSTRT and utilising a three-electrode configuration at 25 ± 1 °C. An Origin 6.0 graph program was used to evaluate Headstrt software data, to draw voltammograms, and to analyse them. A Pt spiral wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode. The working electrode was a Pt plate with an area of 1.0 cm². Electrochemical grade tetrabutylammoniumperchlorate (TBAP) in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.1 mol dm⁻³. High purity N₂ was used for deaeration and to maintain a nitrogen blanket for at least 15 min prior to each run. For controlled potential coulometric (CPC) studies, a Pt gauze working electrode (10.5 cm² surface area), a Pt gauze counter electrode separated with a double bridge, a saturated calomel reference electrode (SCE) and a model 377/12 Synchronous stirrer were used. The potential of the working electrode was set to the E_p value obtained in the CV experiments. Then the solution was electrolysed with efficient stirring.

2.1. 4,5-Di(phenylethynyl)phthalonitrile (3)

To a solution of 1 g (5.10 mmol) of 1 dissolved in 100 ml of triethylamine was added 0.20 g (0.30 mmol) of bis(triphenylphosphine)palladium(II)chloride, 0.04 g (0.20 mmol)of copper(I)iodide and then 3.34 ml (30.45 mmol) of phenylacetylene. The reaction mixture was heated to 90 °C for 24 h under N2. As the reaction proceeded, a dark brown precipitate was formed. The resulting suspension was filtered off and the brown solid collected was washed with hexane. The yellow product was obtained by column chromatography with silica gel using CHCl₃/hexane (50:1) as eluent. Yield: 0.67 g, 40%; m.p. 190 °C. IR (KBr), v (cm⁻¹): 3080 (Ar–H), 2238(C=N), 2212 (C=C), 1600, 1523, 1446, 911, 782, 706 cm⁻¹; ¹H NMR (CDCl₃):*δ*: 7.92 (s, 2H, Ar-H), 7.59 (d, 4H, Ar–H), 7.42 (m, 6H, Ar–H); UV–Vis λ_{max} (nm) (log ε) in CHCl₃: 279 (4.62), 307 (4.70), 349 (4.34). Anal. Calc. for C₂₄H₁₂N₂: C, 87.79; H, 3.68; N, 8.53. Found: C, 87.07, H, 3.66; N, 8.33%.

2.2. 2,3,9,10,16,17-Hexakis(hexylthio)-23,24-bis(phenylethynyl)-29H, 31H-phthalocyaninato zinc (II) (4)

A mixture of 0.16 g of 2 (0.49 mmol), 0.53 g of 3 (1.46 mmol), 0.09 g of anhydrous Zn(CH₃COO)₂ (0.49 mmol), 32 µl of DBU and 5 ml of anhydrous *n*-pentanol was refluxed with stirring for 24 h under N_2 . The dark green mixture was cooled to room temperature and then diluted with ethanol until the crude product precipitated. The precipitate was filtered off and washed several times with hot ethanol and methanol to remove unreacted materials. Finally, the green precipitate was chromatographed on silica gel and eluted with CHCl₃/ CH₃OH (50:1). Yield: 0.10 g, 14%; m.p. > 200 °C. IR (KBr), v (cm⁻¹): 3080 (H–Ar), 2987–2870 (alkyl CH), 2212 (C=C) 1600, 1523, 1421, 1395, 1089, 987, 757, 706 cm⁻¹; ¹H NMR (CDCl₃): δ: 0.94 (t, 18H, CH₃), 1.62 (m, 36H, CCH₂C), 1.88 (qnt, 12H, SCCH₂), 3.18 (t, 12H, SCH₂),7.42–7.90 (m, 18H, Ar–H); UV–Vis λ_{max}

(nm) (log ε) in CHCl₃: 277 (4.68), 329 (4.80), 727 (4.93). Anal. Calc. for C₈₄H₉₆N₈S₆Zn: C, 68.41; H, 6.51; N, 7.60. Found: C, 68.28; H, 6.49; N, 7.47%.

2.3. 2,3,9,10,16,17-Hexakis(hexylthio)-23,24-bis(phenylethynyl)-29H,31H-phthalocyaninatonickel (II) (5)

A mixture of 0.40 g of 2 (1.22 mmol), 1.32 g of 3 (3.66 mmol), 0.16 g of anhydrous NiCl₂ (1.22 mmol) and 80 µl of DBU was refluxed in 13 ml of anhydrous n-hexanol with stirring for 36 h under N_2 . The resulting suspension was cooled to room temperature and the crude product was precipitated by addition of ethanol. It was filtered off and washed first with hot ethanol, then with methanol. The green product was isolated on a silica gel column first with hexane/THF (5:1) and then with THF/ DMF (5:1) as eluent. Yield 0.09 g, 5%. Melting point > 200 °C. IR (KBr), v (cm⁻¹): 3080 (H–Ar), 2987-2870 (alkyl CH), 2212 (C=C) 1600, 1523, 1421, 1395, 1089, 989, 756, 706 cm⁻¹; ¹H NMR (CDCl₃ 250 MHz): 0.97 (t, 18H, CH₃), 1.66 (m, 36H, CCH₂C), 1.93 (qnt, 12H, SCCH₂), 3.22 (t, 12H, SCH₂), 7.38-7.91 (m, 18H, Ar–H), 7.78 (s, 2H); UV–Vis λ_{max} (nm) (log ε) in CHCl₃: 322 (4.89), 703 (4.83). Anal. Calc. for C₈₄H₉₆N₈S₆Ni: C, 68.72; H, 6.54; N, 7.63. Found: C, 68.53; H, 6.41; N, 7.33%.

2.4. 2,3,9,10,16,17-Hexakis(hexylthio)-23,24-bis(phenylethynyl)-29H,31H-phthalocyaninatocobalt (II) (6)

A mixture of 0.30 g of **2** (0.92 mmol), 0.99 g of **3** (2.75 mmol), 0.12 g of anhydrous CoCl₂ (0.92 mmol) was refluxed in 10 ml anhydrous *n*-pentanol in the presence of 60 µl of DBU under N₂ with stirring for 24 h. The reaction mixture was cooled and the crude product was precipitated by addition of ethanol. It was filtered off and washed several times with hot ethanol and acetone. The green product was chromatographed on silica gel with hexane/THF (2:1) as eluent. Yield 0.11 g, 8%. Melting point > 200 °C. IR (KBr), ν (cm⁻¹): 3080m (H–Ar), 2987–2870 (alkyl CH), 2212 (C=C) 1600, 1523, 1421, 1395, 1089, 987, 757, 706 cm⁻¹; UV–Vis λ_{max} (nm) (log ε) in CHCl₃: 270 (3.98), 329 (4.19), 711 (4.00). *Anal.* Calc. for C₈₄H₉₆N₈S₆Co: C, 68.71; H, 6.54; N, 7.63. Found: C, 68.35; H, 6.36; N, 7.50%.

3. Results and discussion

3.1. Synthesis and characterisation

Different strategies to synthesise unsymmetrically substituted phthalocyanines (A_3B) have been reported, the most common one being the statistical condensation reaction between two different phthalonitriles or diimi-

noisoindolines. Statistical considerations predict that reaction of two different phthalonitriles of the same reactivity in a 3:1 ratio will afford a mixture of products in the following percentages: A_4 (33%), A_3B (44%), other cross-condensation products (23%) [14]. Using phthalonitriles with different solubility characteristics may permit separation of the unsymmetrical phthalocyanines by virtue of the different solubilities of the compounds present in the resulting statistical mixture. The attachment of alkylthio groups at the peripheral positions of one of the starting compounds facilitates the isolation of the A_3B product, as this substituent confers solubility in organic solvents and disfavours aggregation of the macrocycles [28].

4,5-Di(hexylthio) phthalonitrile (2) and 4,5-di(phenylethynyl)phthalonitrile (3) were chosen as starting materials for this study. 2 was prepared from 4,5-dichlorophthalonitrile and hexanethiol in DMF. K₂CO₃ was used as the base for this nucleophilic aromatic displacement [27]. Leznoff and Suchozak [29] have reported the synthesis of 3 from 4,5-diiodophthalonitrile. In the present work, 3 was synthesised from 4,5-dichlorophthalonitrile which is easily obtained from commercially available 4,5-dichloro-1,2-benzenedicarboxylic acid in four steps [26]. Under typical Sonogashira reaction conditions [30], the cross-coupling reaction between an excess of phenylacetylene and 4,5-dichlorophthalonitrile in triethylamine with bis(triphenylphosphine)palladium(II)chlorideand copper(I)iodide as catalysts at 90 °C under nitrogen atmosphere produced 3 in 40% yield.

Mixed condensation of 4,5-di(phenylethynyl)phthalonitrile with 4,5-di(hexylthio) phthalonitrile in the presence of the corresponding metal(II) salt afforded the unsymmetrical zinc-, nickel- and cobalt-substituted complexes **4**–**6**. Some experiments with different molar ratios were carried out to raise the yield of the desired unsymmetrically substituted phthalocyanines **4**–**6**. A 1:3 ratio of the two precursors was found to be the most appropriate for dinitriles **2** and **3**. The unsymmetrical phthalocyanines were separated by column chromatography from the corresponding totally symmetrical octahexylthiophthalocyanine formed in the statistical condensation. The unsymmetrical phthalocyanines **4**–**6** show good solubility in common organic solvents such as dichloromethane, chloroform and tetrahydrofuran (see Scheme 1).

The spectroscopic characterisation of the newly synthesised compounds included ¹H NMR, IR and UV–Vis. Spectral investigations and the results are in accord with the proposed structures. In the IR spectrum of **3** the intense absorption band at 2238 cm⁻¹, corresponding to C=N vibrations, disappears after its conversion into the phthalocyanines. The ¹H NMR spectrum of **3** indicates aromatic protons at δ 7.92, 7.59 and 7.42 ppm.

The ¹H NMR spectra of the unsymmetrical phthalocyanines **4** and **5** are in excellent agreement with the



proposed structures. The dominant features in the NMR spectra of 4 and 5 are the hexylthio group resonances. These resonances are shifted downfield by the phthalocyanine ring current relative to the precursor compound 2 [27]. ¹H NMR spectrum of 4 exhibited the aromatic protons at around δ 7.42–7.90 ppm as multiplets, the SCH₂, SCCH₂ protons at δ 3.18 and 1.88 ppm as a triplet and a quintet, respectively, and the aliphatic CH₃ protons as a triplet at δ 0.94 ppm. The ratio of aromatic to aliphatic protons appears to show that the benzo groups with two different substituents are present in a 3:1 ratio. The presence of alkylthio side chains in 4 was also confirmed by IR spectroscopy which showed an intense aliphatic C–H stretching at 2987–2870 cm⁻¹. The ¹H NMR spectrum of **5** is similar to that of **4**.

The UV–Vis spectra of **4–6** recorded in chloroform show the typical pattern of phthalocyaninatometal complexes. They are dominated by the π – π * transitions within the heteroaromatic 18- π -electron system. The electronic absorption spectra of **4–6** exhibit a Q band absorption at 727, 703 and 711 nm, respectively. B bands of these phthalocyanines appear in the UV region at about 329 nm. The Q-bands of octakis alkylthio-substituted phthalocyanines are above 700 nm [27], the replacement of one of the benzenoid rings by a phenylethynyl ring gives rise to a bathochromic shift. The different Q band absorptions of **4–6** are attributable to the nature of the central metal ion.

In conclusion, unsymmetrical metallophthalocyanines **4–6** substituted with one phenylethynyl and three hexylthio groups were synthesised by a statistical condensation route. Their spectral properties in a given solvent depends strongly on the central metal ion.

3.2. Electrochemical measurements

The electrochemical properties of metallophthalocyanine (MPc) complexes are well known [31-44]. Reduction and oxidation reactions can occur at either the Pc ring or central metal or both. Oxidation at the Pc ring in MPc(-2) occurs by successive loss of one or two electrons from the highest occupied molecular orbital (HOMO) resulting in the formation of the $[MPc(-1)]^+$ or $[MPc(0)]^{+2}$ cations, respectively. Reduction of the Pc ring occurs by the successive gain of one to four electrons by the lowest unoccupied molecular orbital (LUMO) of the MPc complex, resulting in the formation of MPc(-3), MPc(-4), MPc(-5) and MPc(-6) species, as commonly shown to indicate the oxidation states of the phthalocyanine ligand in the literature related with the electrochemistry of this compounds [1,6,31,40-44].

It has been demonstrated that substituents on the periphery of the phthalocyanine ligand strongly influence the solution redox chemistry of these materials. Electron-donating groups lead to a negative shift of the redox potentials and electron-withdrawing groups to a positive shift. This has been observed with both redox inactive metals like nickel, copper and zinc and redox active metals like cobalt [1].

Cyclic voltammograms of CoPc (6) (Fig. 1) show four well-defined redox couples (I–IV) within the available potential range of the TBAP/DCM solvent system at -0.313 and 0.644 V, easily attributed to Co^{II}/Co^I (I)

and Co^{II}/Co^{III} (IV), and at 0.327 and -1.247 V at 0.100 V s⁻¹ scan rate easily attributed to Pc^{2-}/Pc^{3-} (II) and Pc^{2-}/Pc^{1-} (III) redox couples, respectively. It is clearly indicated that first-row transition metallophthalocvanines differ from those of the main-group metallophthalocyanines due to the fact that metal "d" orbitals may be positioned between the HOMO and LUMO of the phthalocyanine (Pc^{2-}) ligand. This has been well established by several papers published by Lever et al. [1,42–44]. According to these studies, electrochemistry of metallophthalocyanines containing a redox active metal center such as Mn, Fe and Co can conveniently be split into two sections, that referring to non-donor solvents, and that referring to donor solvents. For CoPc complexes, donor solvents or coordinating counter anions strongly favour Co(III)Pc by coordinating along the axis to form a six-coordinate L₂Co(III)Pc species. If a donor solvent is not present, such as DCM used in this study, then oxidation to Co(III)Pc is inhibited and ring oxidation occurs first. So in this study, it is possible to assign the first oxidation of the CoPc species at 0.33 V to the ring oxidation and the second one at 0.64 V to the metal center. According to this behaviour of CoPc in DCM, the electron transfer sequence would be [Co(III)/(II)]Pc(1-) > Co(II)[Pc(1-)/(2-)] > [Co(II)/(I)]Pc(2-) > Co(I)[Pc(2-)/(3-)].

The separation between the first reduction and first oxidation processes (640 mV) of **6**, which reflects the HOMO–LUMO gap of the complexes, is smaller than that in the reported CoPc papers [1,31–44]. This is not very surprising since extended π -conjugation of **6** may cause a decrease in the HOMO–LUMO gap of the complex. This voltammetric data was confirmed by the shifting of the Q band towards a longer wavelength in the



Fig. 1. Cyclic voltammogram of 1.0×10^{-3} mol dm⁻³ CoPc (6) in 0.1 mol dm³ TBAP/DCM at 100 mV s⁻¹ scan rate.

Table 1
The cyclic voltammetric data of the complexes with the related MPc derivatives reported in the literature

Complex	Redox processes ^e												Solvent	Reference
	IV			III			Ι			II				
	^a E _{1/2} (mV)	$^{b}\Delta E_{p}$ (mV)	^c I _{pc} / I _{pa}	${}^{a}E_{1/2}$ (mV)	$^{b}\Delta E_{p}$ (mV)	$^{\rm c}I_{\rm pc}/I_{\rm pa}$	^a E _{1/2} (mV)	$^{b}\Delta E_{p}$ (mV)	$^{\rm c}I_{\rm pc}/I_{\rm pa}$	$^{a}E_{1/2}$ (mV)	$^{b}\Delta E_{p}$ (mV)	^c I _{pc} / I _{pa}		
ZnPc (4)	814	98	0.94	633	75	1.1	-780	149	1.2	-1027	191	0.75	DCM	tw
NiPc (5)	837	109	0.97	576	87	0.60	-817	186	0.98	-1032	154	0.93	DCM	tw
CoPc (6)	644	92	0.78	327	147	0.57	-313	287	1.1	-1247^{a}	157	0.58	DCM	tw
ZnPc(SC ₆ H ₄ CH ₃) ₈				750			-680			-1050			DMF	45
$ZnPc(SC_4H_9)_8$				620			-830			-1180			DMF	45
$ZnPc(OC_6H_4C(CH_3)_3)H_7$				550			-1080			-1560			DMF	46
$ZnPc(SC_6H_{13})_8$	850			645			-830			-1150			DCM	31
CoPc(CH ₃ OC ₆ H ₁₃) ₈ ^d	730			-160			-490			-670			DMSO	32
ZnPc(SC ₆ H ₄ NH ₂) ₄ Cl ₄ ^d							-713			-1105			DMSO	33
CoPc(SC ₆ H ₄ NH ₂) ₄ Cl ₄ ^d	950			605			-609			-1037			DMSO	33
NiPc(SC ₆ H ₄ NH ₂) ₄ Cl ₄ ^d							-615			-1210			DMSO	33
$ZnPc(SC_4H_9)_8$	1270			620			-830			-1180			DMF	34
CoPc(SC ₂ H ₄ OH) ₈							-340			-1220			DCM	35

^a Cathodic peak potential for reduction, anodic peak potential for oxidation for irreversible processes.

^b $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$ at 0.100 V s⁻¹ scan rate.

^c I_{pa}/I_{pc} for reduction, I_{pc}/I_{pa} for oxidation at 0.100 V s⁻¹ scan rate.

^d Complexes also have extra reduction and oxidation couples.

^e For CoPc (6) and study in [35], redox processes; I: M(II)Pc(-2)/M(I)Pc(-2), II: M(I)Pc(-3), III: M(II)Pc(-2)/M(II)Pc(-1), IV: M(II)Pc(-1)/M(II)Pc(-1). For CoPc complexes studied in [32,33], redox processes; I: M(II)Pc(-2)/M(I)Pc(-2), II: M(I)Pc(-2)/M(II)Pc(-3), III: M(II)Pc(-2)/M(II)Pc(-3), III: M(II)Pc(-2)/M(II)Pc(-3), III: M(II)Pc(-2)/M(II)Pc(-3), III: M(II)Pc(-2)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3)/M(II)Pc(-3), III: M(II)Pc(-3)/M

UV–Vis spectrum of the complex. The separation between the metal based reduction and the ring reduction was found to be 0.930 V, which is in agreement with the separation reported for CoPc's [31–45]. In Table 1, the CV data, cathodic to anodic peak separation (ΔE_p) and peak current ratios (I_{pa}/I_{pc}) of **6** are listed together with those of ZnPc (**4**), NiPc (**5**) and MPc's containing a similar metal centre and substituents reported in the literature.

The observation of two closely spaced reduction peaks (I' and I) has been attributed to the presence of both the aggregated and unaggregated forms of 6in solution. At the concentration employed for voltammetric studies in this work, aggregation of the CoPc derivatives is expected and was confirmed by a shoulder of the Q band in the UV-Vis spectra of 6 [46]. Characterisation of this couple could not be done as a result of the splitting of the reduction peak. The process II recorded at -1.247 V was quasi-reversible in that it shows a more enhanced forward (cathodic) peak compared to the return (anodic) peak and a large $\Delta E_{\rm p}$ value (200 mV at 100 mV s⁻¹). Peak current ratios $(I_{\rm pa}/I_{\rm pc})$ of this couple were smaller than unity at slow scan rates and approached unity with increasing scan rates. This behaviour of the process indicated the existence of a chemical reaction following the electron transfer reaction (EC mechanism) [47-49]. Both of the oxidation processes (III and IV) of 6 exhibited a quasi-reversible peak character with moderate $\Delta E_{\rm p}$ values (157 and 147 mV at 100 mV s⁻¹, respectively). For

these processes, the anodic peak currents increased linearly with the square root of the scan rates for scan rates ranging from 10 to 500 mV s⁻¹, indicating that the electrode reaction is purely diffusion-controlled. For both the III and IV couple, peak current ratios (I_{pa}/I_{pc}) were smaller than unity at slow scan rates, but move towards unity by increasing the scan rates, indicating the complication of the mass transport mechanism of the complex probably with a proceeding or succeeding chemical reaction.

Complex 4 and 5 exhibited very similar voltammetric behaviours. Fig. 2 shows the cyclic voltammograms of4 recorded at 100 mV s⁻¹ scan rate. As shown in the figure, two well-defined reduction processes, (I and II) at -0.780 and -1.027 V attributed to the Pc^{2-}/Pc^{3-} and Pc^{3-}/Pc^{-4} redox couples, and two well-defined oxidation processes, (III and IV) at 0.633 and 0.814 V attributed to the Pc^{2-}/Pc^{1-} and Pc^{1-}/Pc^{0} redox couples, are observed. Since the central Zn(II) metal is redox inactive, all oxidation and reduction processes observed are ring-based [38]. Ring-based redox potentials of complex 4 are considerably different to those of complex 6. The potential of the [Pc(2-)/(1-)] couple of complex 4 is shifted to positive potentials compared with that of complex 6. The potential of the [Pc(2-)/(1-)] couple of complex 4 is 0.63 V and the [Pc(2-)/(1-)] couple of 6 is 0.33 V. Similar behaviour was observed for the ring reduction potentials of the complexes. The [Pc(2-)/(3-)]couple of 4 is shifted to a more positive potential compared with that of the 6. The difference between the first



Fig. 2. Cyclic voltammogram of 1.0×10^{-3} mol dm⁻³ ZnPc (4) in 0.1 mol dm³ TBAP/DCM at 100 mV s⁻¹ scan rate.

and second reduction processes for 4 is 0.244 V, which is compatible with the average value for the separation of the first and second reduction processes of similar metal phthalocyanine complexes [1]. The potential separation between the first ring oxidation and the first ring reduction (ΔE), which corresponds to the magnitude of the energy difference between the HOMO and LUMO, is approximately between 1.5 and 1.8 V [1,31]. However, the ΔE value of ~1.413 V for **4** is smaller than the range reported for similar complexes. Exchange of one hexylthio substituent of ZnPc bearing an octakis(hexylthio) substituent (ΔE value = 1.475 V) [31] with the diphenylethynylgroup cause a decrease in the ΔE value of 4 of about 62 mV. This is perhaps the result of the decreasing HOMO–LUMO gap by the effect of the extended π -conjugation of the complex. The cyclic voltammograms of 5 also gave two one-electron diffusion controlled quasi-reversible reduction processes at -0.817 and -1.032 V vs. SCE, attributed to the Pc^{2-}/Pc^{3-} and Pc^{3-}/Pc^{-4} redox couples, and two one-electron diffusion controlled quasi-reversible oxidation processes at 0.536 and 0.837 V, attributed to the Pc^{2-}/Pc^{1-} and Pc^{1-}/Pc^{0} redox couples. The difference between the first and second reduction processes (0.215 V) and the small ΔE value (1.393 V) for 5 is compatible with those of 4. Moreover, the individual potentials for the first reduction and the first oxidation of 4 and 5 varied remarkably due to the function of the polarising power of the central metal ion. In general the more polarising the central metal ions, the easier it is to reduce the ring, and the more difficult to oxidise the ring.

During controlled potential coulometric (CPC) studies, complete electrolysis of the solution at the working electrode at constant potential (E_{pc} of the redox couple) was achieved, and the time integration of the electrolysis current was recorded. The electroactive species in the solution were depleted during the electrolysis, and the charge, *Q*, at the end of the electrolysis was calculated using the current-time response of solution. *Faraday*'s law was used to estimate the number of electrons transferred. The CPC studies indicated that the number of electrons transferred for all electron transfer reactions of the compounds studied is one.

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