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Synthesis, characterization and electrochemical properties of novel β 7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin substituted metal-free, Zn(II) and Co(II) phthalocyanines

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ABSTRACT

Novel metal-free (**4**), Co(II) (**5**) and Zn(II) (**6**) phthalocyanines bearing four 7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin substituents at peripheral (β) positions have been prepared by cyclotetramerization of 4-(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile. The compounds have been characterized by elemental analysis and IR, UV–Vis and MALDI-TOF mass spectroscopies. H-aggregation behaviour of the compounds has been investigated in different solvent media. Furthermore, the redox properties of the complexes were examined in dimethylsulfoxide and dichloromethane by voltammetry and *in situ* spectroelectrochemistry. In general, compounds **4** and **6** displayed ligand-based one-electron redox processes, while compound **5** showed both ligand- and metal-based processes, in addition to a couple corresponding to the reduction of the 7-hydroxy-4-(4-methoxyphenyl)-8-methylcoumarin substituents. Both electrochemical and *in situ* spectroelectrochemical data showed that the redox processes of these complexes are complicated by their high aggregation tendency.

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1. Introduction

Phthalocyanines (Pcs) have attracted much attention for many decades because they can be used in catalysts [1], chemical sensors [2], solar cells [3], colour filters for liquid crystal display devices, ink jet inks, data storage, infrared ray absorbents, electrophotographic photoreceptors, non-linear optical devices, deodorizers and photosensitizers used for photodynamic therapy [4,5]. The solubility of Pcs is very important for the investigation of their chemical and physical characteristics. Their properties are influenced not only by the nature of the substituents (i.e., their electron donating or electron withdrawing properties) on the ligand, but also by that of the metal ion in the core of the ligand. Thus, the solubility can be improved by introducing different kinds of solubility-enhancing substituents, such as alkyl, alkoxyl, phenoxyl and macrocyclic groups, into the peripheral of the Pc ring [6].

Numerous studies have been performed to modify Pcs with the goal of tuning their properties and optimizing the efficiency in their various applications. For the medical applications, Pcs conjugated with biological molecules are rare and only a few examples containing monosaccharides [7], amino acids [8], antibodies [9] and coumarins [10–12] have been described. Coumarins (2*H*-chromen-2-ones, 2*H*-1-benzopyran-2-ones) are among the best known

oxygen heterocyclics with a δ -lactone ring and comprise a very large class of compounds found throughout the plant kingdom [13]. When the lactone ring at the coumarin has been opened in strong alkaline media, water-soluble species occur. If alkyl groups are introduced into the coumarin compounds, the groups will induce the Pc solubility in organic solvents [14,15]. Therefore, we have combined coumarin and Pc materials into a single compound via a synthetic methodology to obtain novel Pcs.

The electrochemistry of Pcs has received considerable interest in recent years since there is a strong relationship between their redox properties and most of their industrial applications, such as semiconductors, photovoltaic cells, electrochromic displays and catalysts [16]. Small modifications in Pc molecules may remarkably influence their redox properties since these properties depend on various factors, such as the type of the central metal, solvent, axial ligands, substituents and aggregation [16-18]. It is well known that Pcs may dimerize and even form larger and more complex aggregates, owing to the extended π system [19– 21]. In most cases, the aggregation phenomenon is deleterious to the desired electrical [22], spectroscopic [23], photophysical [24] and electrochemical [25] properties of these compounds. On the other hand, the formation of well-defined Pc dimers and/or aggregates is useful in materials and catalytic applications where the self-assembly of Pc cores in close proximity is beneficial [26-28].

Voltammetry is the most widely used electrochemical method to determine the redox properties of Pcs compounds. However,





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in most cases, the nature of their redox processes cannot be distinguished thoroughly by voltammetric methods alone. A combination of spectroscopic and electrochemical techniques, i.e., *in situ* spectroelectrochemical measurements, allows us to determine whether the redox processes occur in the Pc ring or at the metal centre [29]. In addition, this technique makes the identification of the effect of aggregation phenomena on the redox processes possible since the aggregation processes can be probed using electronic spectroscopy.

In the present work, novel β -tetra substituted metal free, cobalt and zinc Pcs have been prepared from 4-(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile (Scheme 1) and characterized by elemental analyses, UV–Vis, IR and matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectroscopies. The aggregation behaviour of the newly synthesized compounds was investigated by UV–Vis spectroscopy in different solvents, such as toluene, chloroform, dichloromethane (DCM) and dimethylsulfoxide (DMSO). Moreover, the redox and aggregation behaviours of **4–6**, and the effect of aggregation phenomena on their redox behaviours have been examined by voltammetry and *in situ* spectroelectrochemistry.

2. Experimental

2.1. Materials and methods

Our starting compounds 7-hydroxy-4-(4-methoxyphenyl)-8methylcoumarin **1** and 4-nitrophthalonitrile **2** were prepared according to the reported procedures [30,31]. $Zn(OAc)_2 \cdot 2H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ were purchased from Aldrich Chemical Co., and were used as received. All reactions were carried out under a nitrogen atmosphere. All solvents were purified, dried and stored over molecular sieves (4 Å). The Pc compounds were purified succes-



Scheme 1. Synthesis of **3**, **4**, **5** and **6**. Reagents and conditions: i. K₂CO₃, N₂, DMSO, 50 °C, 24 h; ii. (a) 2-*N*,*N*-dimethylaminoethanol, N₂ 160 °C, 48 h, (b) Co(OAc)₂·4H₂O, N₂, 320 °C, 20 min, (c) Zn(OAc)₂·2H₂O, N₂, 320 °C, 20 min.

sively by washing with acetic acid, water, ethanol and acetonitrile in a soxhlet apparatus and by column chromatography. The melting points of the Pc compounds were found to be higher than 300 °C. The purity of the products was tested in each step by TLC (SiO₂). Chromatography was performed on silica gel 60. UV–Vis spectra were recorded on a Shimadzu UV-1601 UV–Vis spectrometer. IR spectra (KBr pellets) were recorded on a Shimadzu FT-IR-8300 spectrometer. ¹H NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. Mass spectra were acquired on an Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen UV-Laser operating at 337 nm and spectra were recorded in the reflectron mode with an average of 50 shots.

The electrochemical and *in situ* spectroelectrochemical measurements were monitored using a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three electrode configuration at 25 °C. UV-Vis absorption spectra were recorded by an Agilent 8453 diode array spectrophotometer equipped with a potentiostat/galvanostat. The electrochemical measurements were carried out in extra pure DMSO containing electrochemical grade tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a concentration of 0.10 mol dm⁻³. For cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements, the working electrode was a Pt plate with a surface area of 0.10 cm². A Pt spiral wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. High purity N₂ was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. Ferrocene was used as an internal reference, but the potentials were presented as the ones versus SCE. In situ spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of a thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was a transparent Pt gauze. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

2.2. Sample and matrix preparation

The matrix, α -cyano-4-hydroxycinnamic acid, was prepared in tetrahydrofuran (THF) at a concentration of 10 mg/mL as the matrix. The MALDI samples were prepared by mixing sample solutions (2 mg/mL in chloroform) and the matrix solution (1:10 v/v) in a 0.5 mL eppendorf[®] micro tube. Finally, 0.5 μ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

2.3. Syntheses

2.3.1. 4-(4-(4-Methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile (**3**)

7-Hydroxy-4-(4-methoxyphenyl)-8-methylcoumarin **1** (1.41 g, 5 mmol) and 4-nitrophthalonitrile **2** (0.86 g, 5 mmol) were dissolved in 20 mL anhydrous DMSO. After stirring for 10 min, finely ground anhydrous K_2CO_3 (2.07 g, 15 mmol) was added by stirring. The reaction mixture was stirred at 50 °C for 24 h under a N_2 atmosphere. After the K_2CO_3 salt was filtered off, the mixture was poured into ice water and the obtained precipitate was filtered off, washed with water and dried in a vacuum at 50 °C. The crude product was purified by column chromatography with silica gel eluting with chloroform, with a gradient of chloroform–THF from 0% to 5% THF.

Compound **3** is soluble in DCM, CHCl₃, THF, dimethylformamide (DMF) and DMSO. Mp: 205–208 °C. Yield: 1.86 g (91.18%). *Anal.* Calc. for C₂₅H₁₆N₂O₄: C, 73.52; H, 3.95; N, 6.86. Found: C, 73.41; H, 4.12; N, 7.03%. IR (KBr pellet) v_{max} (cm⁻¹): 524, 609, 825, 960, 1017, 1071, 1093, 1180, 1247, 1365, 1419, 1485, 1513, 1587, 1606, 1730, 2234, 2847, 2964, 3045, 3079. ¹H NMR (CDCl₃) δ , ppm: 2.30 (s, 3H), 3.80 (s, 3H), 6.35 (s, 1H), 6.82 (d, *J* = 8.98 Hz, 1H), 6.98 (dd, *J* = 8.99 Hz, *J* = 2.73 Hz, 2H), 7.18 (dd, *J* = 8.20 Hz, *J* = 2.35 Hz, 1H), 7.22 (s, 1H), 7.34 (dd, *J* = 8.98 Hz, *J* = 2.74 Hz, 2H), 7.42 (d, *J* = 8.59 Hz, 1H), 7.69 (dd, *J* = 8.20 Hz, *J* = 2.35 Hz, 1H). MALDI-TOF mass *m/z*: 393 (M–CH₃)⁺, 409 (M+H)⁺, 431 (M+Na)⁺, 447 (M+K)⁺.

2.3.2. 3,10,17,24-Tetra(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalocyanine (**4**)

Compound 3 (0.20 g, 0.5 mmol) was heated with 2 mL dry 2-N.N-dimethylaminoethanol in a sealed tube. The mixture was held at 160 °C for 48 h under a N₂ atmosphere. After cooling to room temperature, the reaction mixture was treated with dilute HCl and the mixture was filtered and washed with water until the filtrate became neutral. The raw green product was taken in a soxhlet apparatus then purified by washing with acetic acid, water, ethanol and acetonitrile for 12 h, respectively. The crude product was purified by column chromatography with silica gel, eluting with chloroform, with a gradient of chloroform-THF from 0% to 5% THF. The metal-free Pc 4 is soluble in chloroform, DCM, THF, DMF and DMSO. Mp >300 °C. Yield: 138.2 mg (67.70%). Anal. Calc. for C100H66N8O16: C, 73.43; H, 4.07; N, 6.85. Found: C, 73.31; H, 3.95; N, 6.99%. IR (KBr pellet) v_{max} (cm⁻¹): 531, 743, 834, 1019, 1083, 1175, 1248, 1366, 1470, 1511, 1596, 1728, 2837, 2916, 2963, 3064, 3287. MALDI-TOF mass m/z: 1632 (M⁺), 1655 (M+Na)⁺. UV–Vis (DCM): λ_{max} (nm), (log ɛ): 289 (5.532), 336 (5.586), 608 (5.149), 639 (5.307), 664 (5.550), 698 (5.585).

2.3.3. 3,10,17,24-Tetra(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalocyaninatozinc (II) and cobalt(II) (**5** and **6**)

A mixture of compound **3** (0.20 g, 0.5 mmol) and the metal salts [0.13 g, 0.5 mmol $Co(OAc)_2 \cdot 4H_2O$ or 0.13 g, 0.5 mmol $Zn(OAc)_2 \cdot 2H_2O$] was powdered in a quartz crucible and transferred to a reaction tube. DMF (0.30 mL) was added to this reaction mixture, and then the mixture was heated in the sealed glass tube for 20 min under dry N₂ atmosphere at 320 °C. After cooling to room temperature, 3 mL of DMF was also added to the residue to dissolve the product. The reaction mixture was precipitated by adding acetic acid. The precipitate was filtered and washed with acetic acid, water, ethanol and acetonitrile for 12 h respectively in a soxhlet apparatus. The crude product was purified by column chromatography with silica gel, eluting with chloroform, with a gradient of chloroform–THF from 0% to 5% THF.

Cobalt Pc **5** is soluble in chloroform, DCM, THF, DMF and DMSO. Mp >300 °C. Yield: 101.6 mg (49.03%). *Anal.* Calc. for C₁₀₀H₆₄Co-N₈O₁₆: C, 70.96; H, 3.81; N, 6.62. Found: C, 70.75; H, 3.99; N, 6.74%. IR (KBr pellet) v_{max} (cm⁻¹): 436, 752, 831, 959, 1084, 1176, 1249, 1367, 1411, 1469, 1512, 1595, 1726, 2837, 2932, 3072. MALDI-TOF mass: m/z 1691 (M⁺), 1714 (M+Na)⁺. UV–Vis (DCM): λ_{max} (nm), (log ε): 313 (5.934), 614 (5.116), 672 (5.332).

Zinc Pc **6** is soluble in chloroform, DCM, THF, DMF and DMSO. Mp >300 °C. Yield: 114.6 mg (55.10%). *Anal.* Calc. for C₁₀₀H₆₄ZnN₈O₁₆: C, 70.69; H, 3.80; N, 6.60. Found: C, 70.87; H, 3.64; N, 6.48%. IR (KBr pellet) v_{max} (cm⁻¹): 532, 565, 616, 696, 742, 761, 833, 863, 885, 960, 990, 1026, 1081, 1176, 1242, 1366, 1390, 1428, 1487, 1512, 1596, 1728, 2836, 2934, 3068. MALDI-TOF mass *m*/*z*: 1697 (M⁺), 1720 (M+Na)⁺. UV–Vis (DCM) λ_{max} (nm), (log ε): 288 (5.558), 347 (5.604), 613 (5.167), 680 (5.907).

3. Results and discussion

3.1. Syntheses and characterization

The starting material, 4-(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile **3**, was synthesized by the K_2CO_3 catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile 2 with 7-hydroxy-4-(4-methoxyphenyl)-8-methylcoumarin 1 [31-33]. The novel cobalt Pc 5 and zinc Pc 6 were prepared by a templated cyclotetramerization reaction from 4-(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile 3 and the metal salts [anhydrous $Co(OAc)_2 \cdot 4H_2O$ or $Zn(OAC)_2 \cdot 2H_2O$] in a little DMF (gel media) at 320 °C. The metal-free Pc 4 was synthesized by using the same starting material 3 in 2-N,N-dimethylaminoethanol at 160 °C under a N₂ atmosphere (Scheme 1). The β-tetra-[4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy]-substituted Pcs 4-6 were washed with water, acetic acid, ethanol and acetonitrile, respectively, in a soxhlet apparatus, and then purified by column chromatography. These novel Pcs are soluble in various solvents, such as toluene, chloroform, DCM, THF, DMSO and DMF. The characterization of the new products involved a combination of methods including elemental analyses, IR, UV-Vis and MALDI-TOF mass spectroscopy. Elemental analysis results and the spectral data of the newly synthesized compounds 3, 4, 5 and 6 are consistent with the proposed structures.

The FT-IR absorption spectrum of **3** exhibited a -C=C- double bond at 1606 cm⁻¹, coumarin carbonyl (lactone, -C=O) at 1730 cm⁻¹, $-CH_3$ at 2847 and 2964 cm⁻¹, and stretching frequencies for Ar–H at 3106 and 3079 cm⁻¹. The FT-IR spectrum clearly showed the formation of **3** with the appearance of a new absorption band at 2230 cm⁻¹ (-C=N) and additional bands at 1247 cm⁻¹ (Ar–O–Ar). The IR-spectra of the metal-free Pc **4**, the cobalt Pc **5** and the zinc Pc **6** are very similar, with the exception of **4** showing an N–H weak stretching band due to the inner core at 3287 cm⁻¹.

The molecular ion peaks $[M]^+$ of the ligand **3** and Pc compounds **4–6** were identified easily by using MALDI-TOF mass spectroscopy. For ligand **3**, the protonated molecular ion peak was observed at 409 Da. Besides the protonated molecular ion peak of the compound, three intense peaks were observed, one at 394 Da with a 15 Da mass difference (for the leaving CH₃ group) from the protonated molecular ion peak, the sodium adduct at 431 [M+Na]⁺ Da and the potassium adduct at 447 [M+K]⁺ Da. The molecular ion peaks of **4**, **5** and **6** were observed at 1632, 1691 and 1697 [M]⁺ Da, respectively. The sodium adducts were also observed at 1655, 1714 and 1720 [M+Na]⁺ Da. The experimental mass values for the molecular ions of **3–6** overlapped with the theoretical or calculated ones. The MALDI-TOF mass spectrum of **5** is shown as an example in Fig. 1.

The ¹H NMR spectra of **3** exhibited characteristic signals for methyl (–CH₃) and –OCH₃ protons at δ 2.30 and 3.80 ppm, respectively, each as a singlet. The peaks at δ 6.35 and 6.82–7.69 ppm indicate the presence of the proton at the lactone ring and the aromatic protons respectively.

3.2. Electronic absorption properties

The propensity of Pcs to self-aggregate through the coplanar association of the Pc rings to form dimers and higher order aggregates is well known [34,35]. In general, Pc aggregation is thought to reflect coplanar interactions involving the macrocycle ring. These interactions occur as a result of favourable van der Waals forces, π -stacking interactions and solvent effects. The aggregation process of Pcs can be easily probed using electronic spectroscopy. Upon formation of higher order complexes, the coupling between the electronic states of individual monomeric Pc units causes significant



Fig. 1. Positive ion in reflectron mode MALDI-TOF-MS spectrum of **5** obtained in α -cyano-4-hydroxycinnamic acid. Inset spectrum shows the expanded molecular ion and the sodium ion adducts mass region of the complex.

spectral perturbations [36]. Different solvents and the concentration have a great influence on the aggregation behaviour of Pcs. Therefore, in this study, the effects of solvent and concentration on the aggregation behaviour and thus on the electronic absorption properties of the novel Pcs have been investigated. The relevant Qband and B-band absorption data of the compounds in toluene, CHCl₃, DCM and DMSO are summarized in Table 1. The variations in λ_{max} in Table 1 reveal how the central ions and the solvents provide a means of tuning the wavelength of the Q-band absorption. The UV–Vis spectrum of the metal-free Pc 4 exhibits a sharply split O-band absorption at 701 and 666 nm in toluene, at 697 and 664 nm in chloroform, and at 698 and 664 nm in DCM (Fig. 2A). Monomeric Pcs exhibit strong absorption bands in the 300 and 700 nm spectral regions, corresponding to the electronic transitions from π to π^* orbitals, termed the B- and Q-bands, respectively. However, for metal-free Pcs, the symmetry is usually D_{2h} and therefore the main Q-band absorption is split. Thus, the split Q-band absorptions of 4 in toluene, chloroform and DCM are attributed to π to π^* electronic transitions of its monomeric species, but not to the aggregated species. There are also vibrational absorptions as two shoulders at 638 and 606 nm in toluene, at 635 and 604 nm in CHCl₃ and at 639 and 608 nm in DCM. A partly split B-band of 4 also appears in the UV region at 337 and 291 nm, at 338 and 290 nm, and at 336 and 289 nm in toluene, CHCl₃ and DCM, respectively. Contrary to the situation in toluene, CHCl₃ and DCM, the UV-Vis spectrum of 4 in DMSO involves a broad Q-band between 650 and 725 nm, with maximum absorption at 678 nm, in addition to a very broad band at the higher energy side of the main Q-band at 617 nm with a relatively higher intensity (Fig. 2A). The B-band is observed at 321 nm as a single peak in DMSO. The presence of higher order Pc systems due to aggregation can be observed in the Q-band region of the electronic absorption spectrum. Typically, Pc aggregation results in a decrease in intensity of the components of the Q-band corresponding to the monomeric species, meanwhile a new, broader and blue-shifted band is usually seen to increase in intensity. This shift to lower wavelengths corresponds to H-type aggregates. Thus, the broad band at 617 nm can be assigned to Htype aggregates. The reason for the non-split broad main Q-band of **4** should also be aggregation. Aggregation behaviour of **4** in DMSO was also examined by the spectra monitored at different concentrations within the range between 3.0×10^{-6} and 0.38×10^{-6} mol dm⁻³ (Fig. 3A). At a concentration of 3.0×10^{-6} mol dm⁻³, the band with the higher energy at 617 nm is much stronger than the one with lower energy at 678 nm. However, as the concentration of **4** is decreased, the decrease in the absorption is more pronounced for the band at 617 nm, and thus their intensities become approximately equal when compound 4 is diluted to a concentration of 0.38×10^{-6} . This observation provides strong evidence for the assignment of the band at 617 nm to the H-type aggregates.

The cobalt Pc **5** shows only a single broad Q-band absorption for the $\pi-\pi^*$ transitions within the range 672–660 nm, with a weak vibrational band as a shoulder at around 605 nm in different solvents (Fig. 2B). While H-aggregation of metal-free Pc **4** in DMSO is observed by the appearance of a strong and broad band at the blue side of the main non-split Q-band, that of cobalt Pc **5** in the same solvent is observed by the remarkable broadening in its main Q-band absorption (Fig. 2B). A broad Q-band due to H-type aggregation is also observed in the spectra of **5** in chloroform and DCM. H-type aggregates in toluene, evidenced by a very weak band around 640 nm, appear to be very little. As shown in Fig. 3B, when the concentration of **5** is decreased from 3.00×10^{-6} to 0.38×10^{-6} , its aggregated species is still present, as evidenced by the continuing broadness of the Q-band absorption.

Similar to the situation for **4**, the electronic spectrum of the zinc Pc **6** involves a strong band at 632 nm at the blue side of the main Qband absorption at 673 nm, due to the presence of its H-aggregated species in DMSO (Fig. 2C). As shown in Fig 3C, as the concentration of **6** in DMSO is increased, the increase in the absorption is pronounced for the band at 632 nm. This observation confirms that the band at 632 nm results from the presence of aggregated species. It is clear from the sharp Q-band absorption that compound **6** does not form aggregated species in chloroform, while very weak peaks in its electronic spectra around 650 nm in DCM and toluene indicate that nearly all the molecules of **6** are in the form of monomeric species in these solvents, though a very small amount of aggregated species is present in the solution.

Table 1 UV-Vis spectral data for Pcs 4, 5 and 6 in various solvents at a concentration of 3.0×10^{-6} mol dm⁻³.

Solvent	Pcs	Q-band, λ_{max} (nm)	logɛ	B-band, λ_{max} (nm)	log ε
Toluen	4	701, 666, 638, 606	5.611, 5.551, 5.212, 5.035	337, 291	5.463, 5.460
CHCl ₃	4	697, 664, 635, 604	5.574, 5.548, 5.296, 5.511	338, 290	5.561, 5.524
DCM	4	698, 664, 639, 608	5.585, 5.551, 5.307, 5.149	336, 289	5.586, 5.532
DMSO	4	678, 617	5.231, 5.381	321	5.733
Toluen	5	670, 606	5.332, 5.116	311	5.884
CHCl ₃	5	662, 600	5.432, 4.885	328	5.512
DCM	5	672, 614	5.332, 5.116	313	5.934
DMSO	5	660, 600	5.504, 5.169	320	5.746
Toluen	6	680, 650, 612	5.892, 5.068, 5.113	350	5.461
CHCl ₃	6	682, 616	5.702, 5.009	343, 312	5.476, 5.468
DCM	6	680, 613	5.907, 5.167	347, 288	5.604, 5.558
DMSO	6	673, 632	5.672, 5.646	344, 287	5.837, 5.754



Fig. 2. The UV–Vis spectra of (A) 4, (B) 5 and (C) 6 in various solvents with a concentration of 3.0×10^{-6} mol dm⁻³.

Finally, the UV–Vis spectral changes were monitored during the gradual addition of trifluoroacetic acid (TFA) into a 3.5×10^{-6} M solution of each Pc compound in chloroform. On the contrary to their behaviour in the above mentioned solvents, the Pc compounds exhibit protonated species in chloroform, as evidenced by the appearance of a red-shifted band at 740 nm for **4**, 720 nm for **5** and 721 nm for **6**. The UV–Vis spectral changes of **6** are shown as an example in Fig. 4.

3.3. Electrochemical and in situ spectroelectrochemical measurements

Redox properties of the Pc compounds **4–6** in solution were studied by CV and DPV on a platinum working electrode in DMSO/TBAP. Table 2 lists the voltammetric data of the complexes, which include the half-peak potentials ($E_{1/2}$), the peak to peak potential separations (ΔE_p) and the difference between the half-peak

potentials of the first oxidation and reduction processes ($\Delta E_{1/2}$). The number of electrons transferred is usually unity for the redox processes, except the last reduction couples of **5** and **6**. Typically Pc compounds undergo successive one-electron reduction and one-electron oxidation to yield the anion and cation radicals, and multi-electron processes occurring in one-step are not common.

Fig. 5 shows the cyclic and differential pulse voltammograms of metal-free Pc **4**. Compound **4** gives two one-electron reduction processes. These redox processes are ring-based since compound **4** is a metal-free Pc. The separation between the first and second ring reductions was found to be approximately 0.32 V. This peak separation value is in agreement with the reported ones for redox processes in metal-free Pcs [37]. A comparison of the redox potentials of **4** in DMSO with those of the relevant unsubstituted Pcs in a similar coordinating solvent, DMF, in the literature [37] shows clearly that the redox potentials of the former shifts to relatively



Fig. 3. The UV-Vis spectra of (A) 4, (B) 5 and (C) 6 in DMSO at different concentrations.

more positive potentials, probably due to the 7-hydroxy-4-(4methoxyphenyl)-8-methylcoumarin substituents, suggesting that the redox potentials and thus the efficiency of the Pcs in various applications can be changed remarkably by the peripheral substituents. For instance, the efficiency of MPcs in electrocatalytic applications is closely related to their redox potentials. The first oxidation process of **4** is out of the available potential range of the DMSO/TBAP medium, probably as a result of the shifting the redox potentials towards more positive potentials by the 7-hydroxy-4-(4-methoxyphenyl)-8-methylcoumarin substituents. However, both waves of the first reduction couple (R1) are somewhat rounded, which implies the presence of aggregated species in solution. The peaks of the second reduction couple (R2) are also rounded. The broadness of the redox peaks of **4** is probably due to the presence of its aggregated species and an equilibrium between monomeric and aggregated species. The aggregation of Pc molecules is usually by coplanar association, which results mainly from the π - π * interactions between the π electron clouds of adjacent Pc macrocycles. The presence of both aggregated and nonaggregated Pc species in equilibrium results generally in a broadening of the redox signals or their splitting, due to the differences in the redox potentials of these species. The presence of aggregated species in solution in the case of β -substitution should be due to its peripheral nature, leading to planarity of the complex.

Fig. 6A shows cyclic and differential pulse voltammograms of **6**. It undergoes five reductions and two oxidations (inset B). The oxidation processes could be identified only by DPV, due to their high positive potentials within the available potential range (inset B in



Fig. 4. UV–Vis spectral changes observed during the addition of TFA into a $2.50\times 10^{-6}\,mol\,dm^{-3}$ solution of 6 in CHCl3.

Fig. 6A). It is clear that all redox processes of 6, except the last reduction couple, are ligand-based since the Zn(II) ion is redoxinactive in zinc Pcs. The peak currents of the last reduction couple are much higher than those of the other redox couples, suggesting that it corresponds to the reduction of the four coumarin substituents. In general, zinc Pcs display a maximum of two or three ligand-based reductions within the available potential range in a coordinating solvent such as DMSO or DMF [37]. The appearance of five reductions for **6** strongly implies that the splitting of the redox processes of **6** occurs due to the presence of aggregated species and reduction of aggregated species at different potentials compared to that of the monomer species. For this reason, in situ spectroelectrochemical measurements during the controlled-potential electrolysis of the complex at -0.75 V versus SCE were also carried out to provide additional support for the identification of possible aggregation effects. The two groups of in situ spectroelectrochemical changes during the controlled-potential electrolysis of 6 at -0.75 V versus SCE are shown in Fig. 6B and C. As shown in Fig. 6B, the Q-band absorption in the spectrum at the start of the electrolysis is split, although the spectroelectrochemical measurements were carried out at relatively low concentrations $(5.00 \times 10^{-5} \text{ mol dm}^{-3})$ as compared to that in the voltammetric measurements (5.00×10^{-5} mol dm⁻³). It is clear that there is still an equilibrium between the aggregated and monomer species since aggregation in MPc complexes is typified by a broadened or split Q-band, with the high energy band being due to the aggregate and the low energy band due to the monomer. As shown by the first group of spectral changes in Fig. 6B at -0.75 V versus SCE, upon reduction, the absorption of the band at 636 nm, correspond-



Fig. 5. Cyclic and differential pulse (inset) voltammograms of $5.0\times10^{-4}\,mol~dm^{-3}$ 4 in TBAP/DMSO.

ing to aggregated species, decreases while that of the main Q-band at 675 nm increases with a red shift to 683 nm. On the other hand, the Q-band decreases without shift and a new band at 574 nm appears during the second group of spectral changes, which is accompanied by a decrease in the B-band absorption at 343 nm (Fig. 6C). These spectral changes indicate clearly that the aggregation equilibrium shifts towards the monomer species before the ligandbased first reduction process.

Fig. 7A shows the cyclic voltammogram of 5. It undergoes a oneelectron oxidation and two one-electron reductions, in addition to a further reduction involving the transfer of more than one electron. The $\Delta E_{\rm p}$ parameter of the phthalocyanine-based redox couples takes values within the range 0.060–0.100 V at 0.050 V s^{-1} scan rate, indicating reversible or quasi-reversible character of the electron transfer processes (Table 2). The $\Delta E_{1/2}$ value of **5** is 0.66 V, which is much lower in comparison with those of 6 and 4, although the first oxidation couple of 4 is out of the available solvent-limited potential range. Thus, it is reduced and oxidized more easily than the other products. This distinctive behaviour of 5 can be attributed to the fact that the Co(II) centre has accessible d orbital levels lying between the HOMO and the LUMO gap of the Pc species. In that case, metal centre can be oxidized and reduced before the ring-based redox processes. This type of Pc complexes can vary their electrochemical behaviour according to their environment, depending on whether there are any available coordinating species that would stabilize the Co(II) centre. The main difference lies in whether the metal or the ring is oxidized first. Donor solvents strongly favour Co(III)Pc(-2) by coordinating along the axis to form six coordinate species. If such solvents are absent, then oxidation to Co(III) is inhibited and ring oxidation occurs first. Thus,

Table 2			
Voltammetric da	ata on Pt in	TBAP/DMSO	for 4–6 .

Complex		Ring oxid	dations	M ^{II} /M ^{III}	M ^{II} /M ^I	Ring reductions		Substituent reduction	$\Delta E_{1/2}^{\mathbf{d}}$
4 (H ₂ Pc)	$E_{1/2}^{b}(V)$					-0.56	-0.88		
	$\Delta E_{\rm p}^{\rm c}$ (V)					0.090	0.080		
5 (CoPc)	$E_{1/2}^{b}(V)$			0.35	-0.31	-1.24		-1.63	0.66
	$\Delta E_{\rm p}^{\rm c}({\rm V})$			0.060	0.060	0.100		0.220	
6 ^a (ZnPc)	$E_{1/2}^{b}(V)$	1.06	0.96			-0.55 (-0.70)	-0.81 (-1.07)	-1.65	1.51
	$\Delta E_{\rm p}^{\rm c}({\rm V})$					0.060	0.200 (0.18)	0.200	

^a The redox behaviour of **6** was complicated by aggregation phenomenon and thus its redox couples were split in general. Phthalocyanine redox potentials were determined by differential pulse voltammetry.

^b $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.050 V s⁻¹.

^c $\Delta E_{\rm p} = E_{\rm pa} + E_{\rm pc}$ at 0.050 V s⁻¹.

^d $E_{1/2} = E_{1/2}$ (first oxidation) $-E_{1/2}$ (first reduction).



Fig. 6. (A) Cyclic and differential pulse (insets) voltammograms of 5.0×10^{-4} mol dm⁻³ **6** in TBAP/DMSO. (B) The first and (C) the second groups of *in situ* UV–Vis spectral changes during the controlled potential electrolysis of **6** at -0.75 V vs. SCE in TBAP/DMSO.

the first oxidation and the first reduction processes of **5** are probably metal-based and correspond to $Co(II)Pc(-2)/[Co(III)Pc(-2)]^+$ and $Co(II)Pc(-2)/[Co(I)Pc(-2)]^-$ redox couples, respectively, since the voltammetric measurements were carried out in DMSO/TBAP. On the other hand, it is also well known from the literature that the second reduction process is ring-based [37]. The peak currents of the last reduction couple are much higher than those of the other redox couples, as also observed for **6**. This behaviour implies that it corresponds to the reduction of the four coumarin substituents. Spectroelectrochemical measurements were also carried out to assign especially the first reduction and the first oxidation processes of 5 with certainly. Fig. 7B shows the in situ UV-Vis spectral changes during the first reduction of 5 at -0.75 V versus SCE, corresponding to the redox process labelled R1 in Fig. 7A. The considerably broad Q-band absorption in the UV-Vis spectrum of 5 in DMSO/TBAP indicates the presence of aggregated species, although the cyclic voltammogram of 5 does not show any evidence for these species. Upon the first reduction, the broad shoulder on the Q-band at 616 nm, corresponding to aggregated species, nearly disappears, while the main Q-band at 669 nm shifts to 705 nm and a new band appears at 475 nm with a shoulder around 437 nm. The spectral changes have well-defined isosbestic points at 411 and 550 nm. However, these changes form various isosbestic points at different wavelengths within the ranges 678-694 and 725-733 nm, rather than ones at specific wavelengths, due to the formation of different reduced species produced from the reduction of aggregated and monomer species of 5. It is probable that the reduction of aggregated species is followed by the disaggregation of the reduction product, giving the same species as those produced from the monomer reduction. The band at 475 nm and the shifting of the Q-band indicate the formation of $[Co(I)Pc(-2)]^{-}$ species, confirming the CV assignment of the couple R1 to the $Co(II)Pc(-2)/[Co(I)Pc(-2)]^{-}$ process [31,38-40]. During the second reduction at -1.40 V versus SCE, the Q-band at 705 nm decreases without shift and the absorption at 475 nm increases slightly in intensity with a red shift to 482 nm, while the absorption between 500 and 600 nm increases (Fig. 7C). These spectral changes at the potential of the couple R2 are characteristic for a ring-based reduction in Co(II)Pc complexes and confirm our voltammetric assignment of this process to $[Co(I)Pc(-2)]^{-1}$ $[Co(I)Pc(-3)]^{2-}$.

Fig. 7D displays the *in situ* UV–Vis spectral changes during the first oxidation process at 0.60 V versus SCE. The Q-band at 669 nm increases in intensity with a red shift to 678 nm. The increase of the Q-band with a red shift is typical of a metal-based oxidation in CoPc complexes and thus, confirms the CV assignment of $Co(II)Pc(-2)/[Co(III)Pc(-2)]^+$ for the couple O1 of **5** in Fig. 7A [31,38–40].

4. Conclusions

The novel metal free Pc **4** and metallo Pcs **5** and **6** have been synthesized from 4-(4-(4-methoxyphenyl)-8-methylcoumarin-7-oxy)phthalonitrile **3**. The complexes were characterized by elemental analysis, UV–Vis, IR and MALDI-TOF mass spectroscopies. The effect of solvent and concentration on the aggregation behaviour of the novel Pcs and thus on their spectroscopic properties were investigated. H-aggregation behaviours of the compounds suggested that the formation of their aggregated species can be controlled by changing the solvent medium. It was observed in the UV–Vis spectra of the Pcs that they exhibit protonated species in acidic medium in chloroform.

The compounds **4–6** displayed redox processes located at the ring and/or metal centre. A general trend for the compounds was their aggregation character, implied by splitting or broadening of the redox waves. In some cases, it was not possible to identify the nature of the redox processes and also to understand the possible aggregation effects on these processes with great detail on the basis of electrochemical measurements alone. *In situ* spectroelectrochemical measurements during controlled-potential electrolysis



Fig. 7. (A) Cyclic voltammogram of 5.0 × 10⁻⁴ mol dm⁻³ 5 in TBAP/DMSO. In situ UV–Vis spectral changes during the controlled potential electrolysis of 5 (B) at -0.75 V (C) at -1.40 V and (D) at 0.60 V vs. SCE in TBAP/DMSO.

of the complexes at suitable potentials allowed us to provide additional support for the assignment of the redox processes and to identify the aggregation effects.

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