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# Synthesis and electrochemical properties of crown ether functionalized coumarin substituted cobalt and copper phthalocyanines

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#### ABSTRACT

The synthesis of novel 6,7-[15-crown-5]-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (1)/6,7-[15-crown-5]-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (2) and their peripherally/non-peripherally cobalt and copper phthalocyanine complexes (3–6) have been prepared and characterized by elementel analysis, <sup>1</sup>H-NMR, MALDI-TOF, FT-IR and UV–Vis spectral data. Fluorescence intensity changes of compound 1 and 2 have been determined by addition of Na<sup>+</sup> or K<sup>+</sup> ions at 25 °C in THF. The effect of substitution type on the redox and aggregation behaviour of the compounds was investigated by voltammetry and *in situ* spectroelectrochemistry.

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#### 1. Introduction

Since their synthesis in the early 1930, phthalocyanines (Pcs) are known as excellent functional materials. Metallophthalocyanines (MPcs) have attracted a great deal of interest due to their high colouring property, extremely high thermal stability, chemical resistivity, electrical conductivity, photoconductivity and catalytic activity [1,2]. They have been studied in details for many years, especially with regard to their properties as pigments for printing inks, plastics [3] and in paints and coatings. Nowadays there is renewed interest in phthalocyanine chemistry, as Pcs and many of their derivatives exhibit noteworthy properties for applications in material science [4]. For example, Pcs are used in laser-beam printers and photocopiers [5,6], in nonlinear optics [7,8], as liquid crystals [9-11], as electrochromic substances [12], as carrier generation materials in near infrared (NIR) [13] and Langmuire Blodgett films [14]. Many substituted derivatives of Pcs behave like active components in various redox processes, for example, in photoredox reactions and photooxidations in solution [15,16] and for photodynamic cancer therapy (PDT) [17–19].

On the other hand, coumarins comprise a group of natural compounds found in a variety of plant sources. Coumarins have

important effects in plant biochemistry and physiology, acting as antioxidants, enzyme inhibitors and precursors of toxic substances. In addition, these compounds are involved in the actions of plant growth hormones and growth regulators, the control of respiration, photosynthesis, as well as defense against infection [20]. They have long been recognized to possess anti-inflammatory, antioxidant, antiallergic, hepatoprotective, antithrombotic, antiviral, and anticarcinogenic activities. The hydroxycoumarins are typical phenolic compounds and therefore, act as potent metal chelators and free radical scavengers [20–22].

The crown ethers are multidentate macrocyclic compounds, so called because of their appearance of space-filling models and their ability to "crown" cations. Their characteristic properties are the ability to solubilize inorganic compounds in organic solvents, and thus increase the range of their reactivities. The size of the cavity available in each crown ether varies and determines the type of cation which is bound most efficiently. Crown ether substituted phthalocyanines, which show a high tendency towards aggregation by polar protic solvents such as DMSO (dimethylsulfoxide) and DMF (dimethylformamide), i.e. and cations have been described [23]. They can be used for the colorimetric determination of alkali cations [24] as selective extracting reagents [25,26] and liquid crystals [27]. It has been proved that they are capable of forming ion channels and transport ions by arranging the pendant crown ether rings in stacks [28]. The main feature of the crown ether groups is that they can hold the alkali cations within their cavity. We have preferred these groups as substituent





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on the Pc ring; we think that they can penetrate easily into the cell for PDT activation.

Due to intermolecular interactions between the macrocycles, peripherally unsubstituted metallophthalocyanines are practically insoluble in common organic solvents, thereby minimizing their usefulness in applications. The solubility of phthalocyanines can be improved by introducing substituents on the periphery that increase the distance between the planar macrocycle rings carrying the  $\pi$ -electrons and making solvation easier. Starting compounds have formed from simple mono-functional substituents such as, diazatrioxa-, diazadioxa- and tetraaza-crown ether double layers have been introduced onto the periphery of the phthalocyanine nucleus [29]. These structures are capable of binding alkali metal ions and provide donor sites for binding transition metal ions, leading to homo- and heteronuclear complexes [30].

The understanding of the redox properties of the Pc complexes is important in terms of their applications in many areas. The redox or electron transfer processes of these complexes occur at either the Pc ring or the metal center. However, it is not possible to distinguish such processes by voltammetry alone. *In situ* spectroelectrochemistry provide additional support for the assignment of these redox processes. Moreover, spectroelectrochemical studies of Pcs are also important in identifying the effect of aggregation-disaggregation equilibrium of Pcs on their redox behaviour. Therefore, we also investigate the electrochemical and *in situ* spectroelectrochemical behaviour of the synthesized Pc complexes.

#### 2. Experimental

#### 2.1. Materials

Acetonitrile, tetra ethyleneglycolditosylate, N,N-dimethylaminoethanol (DMAE), sodium carbonate, calcium chloride, anhydrous cobalt acetate, anhydrous copper acetate were purchased from Acros. DMSO and DMF were dried as described by Perrin and Armarego [31] before use. Methanol, *n*-hexane, chloroform, dichloromethane, tetrahydrofuran (THF), acetone and ethanol were freshly distilled. 4-Nitrophthalonitrile [32], 3nitrophthalonitrile [33], 6,7-dihydroxy-3-[p-(3'-4'-dicyanophenoxy)phenyl]coumarin and 6,7-dihydroksy-3-[p-(2'-3'-dicyanophenoxy)phenyl]-coumar-in [34,35] were synthesized according to reported procedures.

#### 2.2. Equipment

The IR spectra were recorded on a Shimadzu Fourier Transform FTIR-8300 using KBr pellets. Mass spectra were performed on a Bruker Daltonic Autoflex III MALDI-TOF spectrometer. Absorption spectra in the UV–Visible region were recorded with a Shimadzu UV-1601 spectrophotometers. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

#### 2.3. Synthesis

#### 2.3.1. 6,7-[15-Crown-5]-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (1)

6,7-Dihydroxy-3-[*p*-(3,4-dicyanophenoxy)phenyl]coumarin (1.0 g, 2.5 mmol) and tetra ethyleneglycolditosylate (1.26 g, 2.5 mmol) were dissolved in dry CH<sub>3</sub>CN (150 mL) under nitrogen atmosphere and anhydrous Na<sub>2</sub>CO<sub>3</sub> (0.53 g, 5 mmol) was added. After stirring for 7 days at 85–90 °C, the solvent was evaporated in vacuum. %37 HCl ( $1 \times 10^{-6}$  M) was added to the residue and the mixture was extracted with CHCl<sub>3</sub> (4 × 30 mL).

The combined organic extracts were washed with water, dried over CaCl<sub>2</sub> and evaporated in vacuum. Column chromatography of the crude products (silica gel 60, Merck) with chloroform gave pure chromenone crown ether. The compound is soluble in ethanol, methanol, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF and DMSO.

Yield: 0.215 g (17%). M.p.: 205–208 °C. IR *ν*(cm<sup>-1</sup>): 3073 (Ar–CH), 2930–2862 (aliphatic CH), 2231 (C≡N), 1708 (C=O), 1614–1573 (Ar C=C), 1250 (Ar–O–Ar). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 7.13 (s, 1H, Ar–H<sub>1</sub>), 7.07 (s, 1H, Ar–H<sub>2</sub>), 8.32 (s, 1H, lactone-H<sub>3</sub>), 7.86 (d, *J* = 8 Hz, 2H, Ar–H<sub>4</sub>), 7.32 (d, *J* = 8 Hz, 2H, Ar–H<sub>5</sub>), 8.21 (s, *J* = 8 Hz, 1H, Ar–H<sub>6</sub>), 7.47 (d, 1H, Ar–H<sub>7</sub>), 8.14 (d, *J* = 8 Hz, 1H, Ar–H<sub>8</sub>), 4.11 (m, 4H, OCH<sub>2</sub>), 3.83 (m, 4H, OCH<sub>2</sub>), 3.65 (m, 8H, OCH<sub>2</sub>). UV–Vis  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) (THF) (1 × 10<sup>-5</sup> M): 364 (4.20), 307 (3.94). Anal. calcd. for C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>: C 67.14; H 4.73; N 5.05%. Found: C 66.12; H 5.12; N 5.01%. MS (MALDI-TOF): *m/z* 554 [M]<sup>+</sup>.

#### 2.3.2. 6,7-[15-Crown-5]-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (**2**)

6,7-Dihydroxy-3-[*p*-(2,3-dicyanophenoxy)phenyl]coumarin (1.00 g, 2.5 mmol) and tetra ethyleneglycolditosylate (1.26 g, 2.5 mmol) were dissolved in dry CH<sub>3</sub>CN (150 mL) under nitrogen atmosphere and anhydrous Na<sub>2</sub>CO<sub>3</sub> (0.53 g, 5 mmol) was added. After stirring for 7 days at 85–90 °C, the solvent was evaporated in vacuum. %37 HCl ( $1 \times 10^{-6}$  M) was added to the residue and the mixture was extracted with CHCl<sub>3</sub> ( $4 \times 30$  mL). The combined organic extracts were washed with water, dried over CaCl<sub>2</sub> and evaporated in vacuum. Column chromatography of the crude products (silica gel 60, Merck) with chloroform gave pure chromenone crown ether. The compound is soluble in ethanol, methanol, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF and DMSO.

Yield: 0.215 g (17%). M.p.: 218–220 °C. IR  $ν(cm^{-1})$ : 3081 (Ar–CH), 2961–2869 (aliphatic CH), 2233 (C≡N), 1710 (C=O), 1614–1570 (Ar C=C), 1281 (Ar–O–Ar). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 7.13 (s, 1H, Ar–H<sub>1</sub>), 7.07 (s, 1H, Ar–H<sub>2</sub>), 8.21 (s, 1H, lactone-H<sub>3</sub>), 8.14 (d, *J* = 8 Hz, 2H, Ar–H<sub>4</sub>), 7.34 (d, *J* = 8 Hz, 2H, Ar–H<sub>5</sub>), 7.47 (d, *J* = 8 Hz, 1H, Ar–H<sub>6</sub>), 7.88 (t, 1H, Ar–H<sub>7</sub>), 7.41 (d, *J* = 8 Hz, 1H, Ar–H<sub>8</sub>), 4.11 (m, 4H, OCH<sub>2</sub>), 3.83 (m, 4H, OCH<sub>2</sub>), 3.38 (m, 8H, OCH<sub>2</sub>). UV–Vis  $λ_{max}$  (nm) (log ε) (THF) (1 × 10<sup>-5</sup> M): 362 (4.40), 316 (4.18). Anal. calcd. for C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>: C 67.14; H 4.73; N 5.05%. Found: C 66.12; H 5.12; N 5.01%. MS (MALDI-TOF): *m/z* 554 [M]<sup>+</sup>.

## 2.3.3. 2,9 (10),16 (17),23 (24)-Tetrakis[6,7-(15-crown-5)-3-(4-oxy-phenyl)coumarin]-phthalocyaninato cobalt and copper complexes (3) and (4)

6,7-[15-Crown-5]-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (1) (0.1 g, 0.18 mmol) Co(AcO)<sub>2</sub> (0.011 g, 0.045 mmol)/Cu(AcO)<sub>2</sub> (0.007 g, 0.040 mmol) and dry DMAE (2 mL) were refluxed with stirring under N<sub>2</sub> atmosphere for 24 h. After cooling to room temperature, the reaction mixture was treated with methanol and then the solid product was filtered off and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, acetone, acetic acid and diethyl ether. The compound is soluble in DMF and DMSO.

Compound **3**: yield: 0.035 g (34%), M.p.: >300 °C. IR  $\nu$ (cm<sup>-1</sup>): 3042 (Ar–H), 2918–2868 (alkyl-CH), 1715 (C=O lactone), 1614–1566 (C=C), 1234 (Ar–O–Ar). UV–Vis  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) (DMF) (1.3 × 10<sup>-5</sup> M): 362 (4.88), 665 (4.78). MS (MALDI-TOF), 2,5-dihydroxybenzoic acid as matrix: *m/z* 2275 [M + 1]<sup>+</sup>.

Compound **4**: Yield: 0.045 g (48%), M.p.: >300 °C. IR  $\nu$ (cm<sup>-1</sup>): 3100–3074 (Ar–H), 2958–2865 (alkyl-CH), 1714 (C=O lactone), 1613–1567 (C=C), 1233 (Ar–O–Ar). UV–Vis  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) (DMF) (1.3 × 10<sup>-5</sup> M): 362 (5.02), 677 (4.30). MS (MALDI-TOF), 2,5-dihydroxybenzoic acid as matrix: *m/z* 2280 [M + 1]<sup>+</sup>.

2.3.4. 1,8(11),15(18),22(25)-Tetrakis[6,7-(15-crown-5)-3-(4-oxyphenyl)coumarin]-phthalocyaninato cobalt and copper complexes (**5**) and (**6**)

6,7-[15-Crown-5]-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (**2**) (0.1 g, 0.18 mmol) Co(AcO)<sub>2</sub> (0.01 g, 0.040 mmol)/Cu(AcO)<sub>2</sub> (0.007 g, 0.040 mmol) and dry DMAE (2 mL) were refluxed with stirring under N<sub>2</sub> atmosphere for 24 h. After cooling to room temperature, the reaction mixture was treated with methanol and then the solid product was filtered off and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, acetone, acetic acid and diethyl ether. The compound is soluble in DMF and DMSO.

Compound **5**: Yield: 0.043 g (47%), M.p.: >300 °C. IR  $\nu$ (cm<sup>-1</sup>): 3100–3053 (Ar–H), 2980–2865 (alkyl-CH), 1713 (C=O lactone), 1613–1574 (C=C), 1248 (Ar–O–Ar). UV–Vis  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) (DMF) (1.3 × 10<sup>-5</sup> M): 360 (4.98), 681 (4.76). MS (MALDI-TOF), 2,5-dihydroxybenzoic acid as matrix: *m/z* 2275 [M + 1]<sup>+</sup>.

Compound **6**: Yield: 0.052 g (51%), M.p.: >300 °C. IR  $\nu$ (cm<sup>-1</sup>): 3112–3058 (Ar–H), 2992–2867 (alkyl-CH), 1714 (C=O lactone), 1613–1572 (C=C), 1249 (Ar–O–Ar). UV–Vis  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) (DMF) (1.3 × 10<sup>-5</sup> M): 363 (4.86), 695 (4.64). MS (MALDI-TOF), 2,5-dihydroxybenzoic acid as matrix: *m/z* 2280 [M + 1]<sup>+</sup>.

#### 2.4. Electrochemistry and in situ spectroelecrochemistry

The cyclic and differential pulse voltammetry measurements were carried out with a PAR VersoStat II Model potentiostat/ galvanostat controlled by an external PC and utilizing a threeelectrode configuration at 25 °C. The working electrode was a Pt plate with a surface area of  $0.10 \text{ cm}^2$ . The surface of the working electrode was polished with H<sub>2</sub>O suspension of Al<sub>2</sub>O<sub>3</sub> before each run. The last polishing was done with a particle size of 50 nm. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.10 mol  $dm^{-3}$ . High purity N<sub>2</sub> was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. In situ spectroelectrochemical measurements were carried out by an Agilent Model 8453 diode array spectrophotometer equipped with the potentiostat/galvanostat and utilizing an optically transparent thin layer (OTTLE) cell with three-electrode



Scheme 1. Synthesis route of the 6,7-[15-crown-4-ether-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (1)/6,7-[15-crown-4-ether-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (2)

and the chromenone crown ether substituted cobalt/copper phthalocyanine complexes (3-6).

configuration at 25  $^{\circ}$ C. The working electrode was transparent Pt gauze. Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The novel compounds (1–6) show good solubility in solvents such as DMF, DMSO and they have been characterized by elemental analysis (1 and 2), FT-IR, <sup>1</sup>H-NMR (1 and 2), UV–Vis and MALDI-MS spectroscopy. 6,7-Dihydroxy-3-[*p*-(3,4-dicyanophenoxy)phenyl] coumarin/6,7-dihydroxy-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin were reacted with tetraethylenglycol ditosylate in the presence of Na<sub>2</sub>CO<sub>3</sub> in dry CH<sub>3</sub>CN to give the compound **1/2** in 17% yield. The crude products were purified by column chromatography over silica gel using CHCl<sub>3</sub> as eluent (Scheme 1). The peripherally 2,9 (10),16 (17),23 (24)-tetrakis[6,7-(15-crown-5)-3-(4-oxyphenyl) coumarin]phthalocyaninatocobalt and copper complexes (3) and (4)/the non-peripherally 1,8(11),15(18),22(25)-tetrakis[6,7-(15crown-5)-3-(4-oxyphenyl)coumarin]-phthalocyaninatocobalt and copper complexes (5) and (6) have been prepared by cyclotetramerization of the novel 6,7-[15-crown-5]-3-[p-(3,4-dicyanophenoxy) phenyl] coumarin (1)/6,7-[15-crown-5]-3-[p-(2,3-dicyanophenoxy) phenyl]coumarin in  $\sim$  50% yield.

The FT-IR spectra of 1/2 showed two vibration peaks at ca. 2862 and 2930  $\text{cm}^{-1}/2869$  and 2961  $\text{cm}^{-1}$  for their C–H stretching frequency. The characteristic vibration peaks of the carbonyl group (C=O) and benzene ring were observed in the region  $1708 \text{ cm}^{-1}$  $1710 \text{ cm}^{-1}$  and  $1578-1614 \text{ cm}^{-1}/1570-1614 \text{ cm}^{-1}$ , respectively. One vibration peak was appeared in the range 1250 cm<sup>-1</sup> 1281 cm<sup>-1</sup> corresponding to C-O-C ether chain. Cyclotetramerization of the dinitril compounds to the cobalt (II) and copper (II) Pc complexes (3-6) was confirmed by the disappearance of the sharp  $\sim C \equiv N$  vibration at 2231 cm<sup>-1</sup>/2233 cm<sup>-1</sup>. The IR spectra of 3-4/5-6 showed vibration peaks at ca.  $3042 \text{ cm}^{-1}(3)$ - $3100-3074 \text{ cm}^{-1}$  (4)/3100-3053 cm<sup>-1</sup> (5)-3112-3058 cm<sup>-1</sup> (6) for aromatic C–H stretching, at 2918–2868 cm<sup>-1</sup> (**3**)–  $2958-2865 \text{ cm}^{-1}$  (**4**)/at  $2980-2865 \text{ cm}^{-1}$  (**5**)  $2992-2867 \text{ cm}^{-1}$  (**6**) for their aliphatic C–H stretching frequency. The characteristic vibration peaks of the carbonyl group (C=O) and C=C bonds at benzene rings were appeared in the region at  $\sim 1714 \text{ cm}^{-1}$  and at 1614–1566 cm<sup>-1</sup> for **3**, at 1613–1567 for **4**, at 1613–1574 for **5**, at 1613–1572 for 6 respectively. One vibration peak was also appeared in the range at  $1233 \text{ cm}^{-1}$  for **3**,  $1234 \text{ cm}^{-1}$  for **4**,  $1248 \text{ cm}^{-1}$  for **5**,  $1249 \text{ cm}^{-1}$  for **6** corresponding to C–O–C ether chain.



Fig. 1. The positive ion and linear mode MALDI-TOF MS spectrum of 1  $([M+Na]^+:$  577 Da).

The <sup>1</sup>H-NMR spectra of **1/2** in DMSO-d<sub>6</sub> show the expected peak resonances and peak integrals due to the protons of chromenone crown ether derivative. The <sup>1</sup>H-NMR spectra of **1/2** showed characteristic signals for ether protons ( $-O-CH_2-CH_2-O-$ ) at  $\delta$  3.65–4.11 ppm/at  $\delta$  3.38–4.11 ppm each as multiplet. The singlet peaks at  $\delta$  8.32 ppm/8.21 ppm indicates the presence of lacton proton at the 4-position of coumarin moiety. In addition; the chemical shifts of the aromatic protons are observed at range of 7.13–8.21 ppm/7.07–8.14 ppm.

The mass spectra of newly synthesized compounds (1 and 2) confirmed the proposed structure. The mass spectral studies by the MALDI-TOF technique on the synthesized compounds identified at m/z: 554 [M]<sup>+</sup> for 1 (Fig. 1).

The UV–Vis spectra of cobalt (II)/copper (II) Pc complexes (3/4-5/6) showed characteristic absorptions in the Q band region at 665 nm/677 nm–681 nm/695 nm and the B band region was observed at around ~362 nm in DMSO. The spectrum showed monomeric behaviour evidenced by a single (narrow) Q band in the visible region which is typical for metallated phthalocyanine complexes [36].

With the aim of assessing the effect of alkali cations on the fluorescence intensity of the crown ether functionalized coumarin ligand by spectral methods, alkali metal salt (NaSCN or KSCN) solutions were added to compound **1**/**2** solution in THF. To avoid any effect arising from dilution due to the addition of the metal salt to the ligand solution, the compound **1**/**2** and metal salts were prepared at concentrations of  $1233 \times 10^{-5}$  M for NaSCN and  $1029 \times 10^{-5}$  M for KSCN in EtOH, respectively. However, the addition of NaSCN and KSCN to the compound **1**/**2** solutions caused decreasing of the fluorescence intensity of these compounds indicate that the entrance of the Na<sup>+</sup> or K<sup>+</sup> cations in the crown ether cavitiy (Fig. 2). The decreasing of the fluorescence intensity is



Fig. 2. The effect of alkali cations on the fluorescence intensity of the compound 1 by spectral methods, (a) during the gradual addition of NaSCN and (b) KSCN for 1 in THF.

Table 1			
Voltammetric data on	Pt in D	DMSO/TBAP	for <b>3–6</b> .

Complex	Ring oxidation	s	M <sup>II</sup> /M <sup>III</sup> 0.39	M <sup>II</sup> /M <sup>I</sup> -0.38	Ring reductions <sup>d</sup> $\Delta E_{1/2}$			
<b>3</b> (β-CoPc)	$E_{1/2} (V)^{a}$				-1.30			0.77
	$\Delta E_{\rm p} ({\rm V})^{\rm b}$		0.060	0.060	0.100			
<b>4</b> (β-CuPc)	$E_{1/2}$ (V) <sup>a</sup>				-0.73	-1.08	-1.64	
	$\Delta E_{\rm p} ({\rm V})^{\rm b}$				0.080	0.100	0.100	
<b>5</b> (α-CoPc)	$E_{1/2}$ (V) <sup>a</sup>		0.40	-0.37	-1.33			0.77
	$\Delta E_{\rm p} ({\rm V})^{\rm b}$		0.060	0.060	0.070			
<b>6</b> (α-CuPc)	$E_{1/2}$ (V) <sup>a</sup>	0.28 <sup>c</sup>			-0.73	-1.33		1.01
. ,	$\Delta E_{\rm p} ({\rm V})^{\rm b}$	0.200			0.060	0.080		

<sup>a</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$  at 0.025 V s<sup>-1</sup>.

<sup>b</sup>  $\Delta E_{\rm p} = E_{\rm pa} + E_{\rm pc}$  at 0.025 V s<sup>-1</sup>.

<sup>c</sup> The first oxidation couple of **6** ( $\alpha$ -CuPc) is observed at less positive potentials than those of Cu(II) phthalocyanines in literature [37], probably due to the adsorption of **6** on the platinum working electrode.

 $^{d}$   $\Delta E_{1/2} = E_{1/2}$  (first oxidation) –  $E_{1/2}$  (first reduction). This value corresponds to the HOMO–LUMO gap for metallophthalocyanines having electro-inactive metal center, but it represents metal to ligand (MLCT) or ligand to metal (LMCT) charge transfer transition gap for metallophthalocyanines having redox active metal center.

higher for addition of Na<sup>+</sup> cation than K<sup>+</sup> because the size of the Na<sup>+</sup> ion is more suitable for the cavity of 15-crown-5 than the size of K<sup>+</sup> cation.

#### 3.2. Electrochemistry

Voltammetry and *in situ* spectroelectrochemistry of the complexes were carried out in de-aerated DMSO containing TBAP. The voltammetric data of **3–6**, including the half-wave redox potential value *vs.* SCE ( $E_{1/2}$ ), anodic-to-cathodic peak potential separation ( $\Delta E_p$ ) and the difference between the first oxidation and reduction potential ( $\Delta E_{1/2}$ ) are listed in Table 1. The number of electrons transferred is unity for all redox processes. Anyway, in monophthalocyanines, multi-electron processes occurring in one step are not common. The ratio of anodic to cathodic peak currents for the redox couples were usually near unity and anodic to cathodic peak separation  $\Delta E_p$  ranged 60–100 mV (except the oxidation couple of **6**), thus suggesting reversible to quasi-reversible behaviour ( $\Delta E$  of 80 mV at 0.025 V s<sup>-1</sup> was obtained for the ferrocene internal standard).

Fig. 3A shows typical cyclic voltammogram of beta-substituted CuPc, **4** at  $0.025 \text{ V s}^{-1}$  scan rate in DMSO/TBAP. It displays three reduction couples (R1-R3). It is clear from the well-known electrochemistry of metallophthalocyanines that Cu(II) at the center of Pc core is redox-inactive and thus, these reduction couples are Pc ligand-based [37]. As shown in Fig. 3A, the cathodic component of the first reduction couple, R1 is split into two peaks. This splitting implies that the electron transfer process is associated by aggregation-disaggregation equilibrium of 4 species. Spectroelectrochemical measurements in solution have a vital importance, not only in confirming the assignment of the redox processes but also in identifying the effect of aggregation phenomenon on the redox processes. Thus, in situ spectroelectrochemistry of 4 during the electrolysis of its solution in TBAP/DMSO at a potential slightly more negative than that of R1<sub>c</sub> peak was employed to provide support for the coupling of its electron transfer process by aggregation-disaggregation equilibrium. The concentration of the complexes was  $\sim 5.00 \times 10^{-5}$  mol dm<sup>-3</sup> in DMSO/TBAP for studies in OTTLE cell. In situ UV-Vis spectral changes during the first reduction process of 4 at -0.85 V versus SCE are shown in Fig. 3B. 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. Thus, the spectrum at the start of electrolysis indicates the presence of an equilibrium between the aggregated and monomer species, as judged by the splitting of Q band. It is clearly seen that the absorption of the band at 615 nm with higher energy dominates as compared to that of one

at 683 with lower energy. The aggregation of Pc molecules is usually as a coplanar association, which results mainly from the  $\pi-\pi^*$  interactions between the  $\pi$  electron clouds of adjacent Pc macrocycles [38]. Some functional groups in Pc molecules also enable aggregation, which results from additional specific interactions such as hydrogen bonding in Pcs containing carboxylic



**Fig. 3.** (A) Cyclic voltammograms of  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup> **4** in TBAP/DMSO. (B) *In situ* UV–Vis spectral changes during the controlled potential electrolysis of **4**.

groups [39], ester [40] or alkylamid [41]. The coumarins can also build aggregation at carboxyl groups. On the other hand, the lactone carbonyl of coumarins can coordinate metal cations such as  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  [42]. Upon first reduction at -0.85 V vs. SCE, the absorption of the all bands decreases while the absorption between 485 and 585 nm increases and a new band at 541 nm forms. Thus, isosbestic points are observed at 482 and 586 nm. The new band at 541 nm and the decrease in the O band absorption without shift are characteristic for Pc ring reduction [43,44]. The formation of isosbestic points at various wavelengths between 570 and 595 nm rather than at a specific wavelength implies that the reduction of both aggregated and monomer species occurs during the first reduction at -0.85 V versus SCE, and provide support for the presence of equilibrium between the aggregated and monomer species at the beginning. Fig. 4A and B displays cyclic and differential pulse voltammograms of alpha-substituted CuPc, 6. The redox behaviour of 6 at the cathodic side is similar to that of 4. However, the first reduction peak of 6 is not split and the second reduction of 6 occurs at more negative potentials than that of 4. Furthermore, on the contrary of 4, the first oxidation process of 6 can be observed, probably due to its high adsorption tendency on the platinum working electrode. Normally, this redox process is observed at relatively more positive potentials or cannot be observed within the available positive potential window. The peak current of the first oxidation process is much higher than those of other reduction processes. In addition, it is directly proportional to the scan rate at low scan rates. These observations provide strong support for high adsorption tendency of **6**. High adsorption tendency of copper phthalocyanines on platinum electrode was also reported previously by other studies [45–47]. Fig.4C displays in situ UV-Vis spectral changes monitored during the first reduction of 6 at -1.00 V vs. SCE in DMSO/TBAP. The unsplit and sharp Q-band absorption in the original spectrum monitored before the electrolysis shows that, on the contrary of **4**, the solution of **6** does not involve aggregated species. The absence of aggregated species in solutions of 6 in DMSO/TBAP may be attributed to the nonperipheral nature of alpha-substitution. It has been well established that nonaggregated Pcs are extremely important for their various applications [48-52]. The spectral changes in Fig.4C are characteristic for Pc ligand-based reduction with the decrease in the Q-band adsorption without shift and appearance of a new band between 500-600 nm [43,44].

Fig. 5 shows the cyclic and differential pulse voltammograms of 3 in DMSO/TBAP. The redox potentials of **3** are considerably different in comparison with those of 4 and 6 (Table 1). The first reduction of 3 occurs at a potential less negative (-0.38 V vs. SCE) than those of 4 and 6 (-0.73 V vs. SCE). This difference in the voltammetric behaviour is due to the fact that MPcs, such as MnPc, CoPc and FePc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the Pc ligand, in general exhibit redox processes centred on the metal [37,53–57]. For CoPc complexes, the first oxidation and first reduction processes usually occur on the metal center in polar solvents such as DMF and DMSO. However the first oxidation process usually occurs on the Pc ring in nonpolar solvents such as DCM and THF. Therefore, the first reduction (R1) and the first oxidation (O1) processes of **3** may be assigned to the [Co(II)Pc(-2)]/ $[Co(I)Pc(-2)]^-$  and  $[Co(II)Pc(-2)]/[Co(III)Pc(-2)]^+$  redox couples, respectively. The second reduction process (R2) is probably ligandbased and can be assigned to  $[Co(I)Pc(-2)]^{-}/[Co(I)Pc(-3)]^{2-}$  [37]. The separation between the first oxidation and the first reduction potentials of the metal center for the Co(II) complex, 3 (0.77 V) is comparable with the relevant values in the literature [37,53–57], and does not reflect the HOMO-LUMO gap. As shown in Fig. 5, the anodic component of the first reduction couple, R1 and the cathodic component of the second reduction couple are split into two peaks, which implies that the electron transfer process is associated by aggregation–disaggregation equilibrium of **3** species. *In situ* spectroelectrochemical measurements in TBAP/DMSO provided strong support for both the assignment of the redox processes of **3** and the coupling of its electron transfer processes by



**Fig. 4.** (A) Cyclic and (B) differential pulse voltammograms of  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup> **6** in TBAP/DMSO. (C) *In situ* UV–Vis spectral changes during the controlled potential electrolysis of **6**.



Fig. 5. Cyclic (A) and differential pulse (B) voltammograms of  $2.5\times 10^{-4}$  mol dm  $^{-3}$  3 in TBAP/DMSO.

aggregation-disaggregation equilibrium. Fig. 6A represents in situ UV–Vis spectral changes during the first reduction of 3 at -0.75 V vs. SCE corresponding to the redox process labeled R1. The concentration of the complexes was  $\sim 5.00 \times 10^{-5} \, mol \, dm^{-3}$  in DMSO/TBAP for studies in OTTLE cell. The spectrum at the start of electrolysis indicates the presence of an equilibrium between the aggregated and monomer species, as judged by remarkably broad Q-band absorption. The broad O-band at 663 nm decreases and shifts 670 nm, while a new band at 705 nm appears. At the same time, the B band shifts from 388 to 410 nm. The red shifting of the Q-band and the formation of a new band at 705 nm indicate the formation of [Co(I)Pc(-2)]<sup>-</sup> species, confirming the voltammetric assignment of the couple R1 to  $Co(II)Pc(-2)/[Co(I)Pc(-2)]^-$  process [58,59]. However, the Q-band obtained after the first reduction process is still broad and the accompanied spectral changes don't have welldefined isosbestic points at specific wavelengths. Furthermore, the characteristic Co(I)Pc(-2) band around 475 nm could not be observed clearly although the absorption within the range of 450-500 nm increased. All these observations imply that the species obtained upon the reduction of aggregated species probably do not disaggregate after the first reduction process and thus, there is also equilibrium between aggregated and monomeric forms of mono-reduced species. During the second reduction, the Q band



**Fig. 6.** *In situ* UV–Vis spectral changes during the controlled potential electrolysis of **3** upon (A) the first reduction at -0.75 V vs. SCE, (B) the second reduction at -1.50 V vs. SCE and (C) the first oxidation at 0.80 V vs. SCE in TBAP/DMSO.

decreases slightly without shift (Fig. 6B) and the absorption within the range of 500–600 nm increases. These spectral changes at the potential of the couple R2 are characteristic for a ring-based second reduction in Co(II)Pc complex,  $[Co(I)Pc(-2)]^{-}/[Co(I)Pc(-3)]^{2-}$ . The Qband is still broad, suggesting the presence of doubly reduced aggregated species. Fig. 6C displays *in situ* UV–Vis spectral changes during the first oxidation process. The broad Q band at 663 nm increases in intensity with red shift to 676 nm and becomes sharp. At the same time, the B bands decrease. The increase of the Q band with red shift is typical of a metal-based oxidation in CoPc complexes [58–63], and thus confirms the voltammetric assignment of Co(II) Pc(-2)/[Co(III)Pc(-2)]<sup>+</sup> for couple O1 of **5**. In addition, the formation of a sharp Q-band after the first oxidation process implies that mono-oxidized species are not aggregated, i.e., disaggregation occurs immediately after the oxidation of aggregated species.

Fig. 7 shows cyclic and differential pulse voltammograms of alpha-substituted CoPc 5. The redox potentials of beta-substituted CoPc, 3 and alpha-substituted CoPc, 5 are very similar to each other with small shifts. However, on the contrary of the reduction couples of **3**, those of **5** are not split due to the absence of aggregated species. It is known that the shape of the alpha-substituted Pc molecules deviate from planarity, which should be responsible for the absence of aggregated species since aggregation usually results from the  $\pi - \pi^*$  interactions between the  $\pi$  electron clouds of adjacent Pc macrocycles [38]. Fig. 8A and B displays in situ UV-Vis spectral changes during the first reduction and the first oxidation processes of **5** at suitable potentials, respectively. The spectrum at the start of the electrolysis in Fig. 8A or B indicates the absence of aggregated species, as judged by relatively sharper Q-absorption band at 680 nm, in comparison with the corresponding one for **3** in Fig. 6A or C. During the first reduction process, the Q-band at 680 nm and its shoulder at 614 nm decrease first, and then disappear while new bands at 650 and 716 nm appears (Fig. 8A). The result is 36 nm red shift of each band. At the same time, a weak



Fig. 7. Cyclic (A) and differential pulse (B) voltammograms of  $2.5\times10^{-4}$  mol dm $^{-3}$  5 in TBAP/DMSO.



**Fig. 8.** In situ UV–Vis spectral changes during the controlled potential electrolysis of **5** upon (A) the first reduction at -0.75 V vs. SCE and (B) the first oxidation at 0.80 V vs. SCE in TBAP/DMSO.

band at 471 nm appears and the B band decreases with small red shift from 358 to 363 nm with the appearance of a new band at 317 nm. These spectral changes have well-defined isosbestic points at 399, 578 and 704 nm. The formation of a new band at 475 nm and red shifting of the Q band indicate the formation of  $[Co(I)Pc(-2)]^-$  species, confirming the CV assignment of the first reduction process, R1 to  $Co(II)Pc(-2)/[Co(I)Pc(-2)]^-$  process [58,52]. Upon the first oxidation process, the Q band at 680 nm increases slightly in intensity with red shift to 6692 nm (Fig. 8B). At the same time, the B band decreases considerably. The increase of the Q band with red shift is typical of a metal-based oxidation in CoPc complexes [58–63], and thus confirms the voltammetric assignment of Co(II) Pc(-2)/[Co(III)Pc(-2)]^+ for the first oxidation process, 01, of **5**.

#### 4. Conclusion

In conclusion, the novel 6,7-[15-crown-5]-3-[p-(3,4-dicyanophenoxy)phenyl] coumarin (1)/6,7-[15-crown-5]-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (2) and their cobalt (II)/ copper (II) phthalocyanine complexes (**3**–**6**) have been synthesized and characterized for the first time in this study. The fluorescence intensity changes of compounds **1** and **2** are investigated by addition of the Na<sup>+</sup> or K<sup>+</sup> ions. The fluorescence intensity decreasing is higher by addition of Na<sup>+</sup> cation than K<sup>+</sup> cation due to the different size of these cations. The size of the Na<sup>+</sup> cation is more suitable than bigger size K<sup>+</sup> cation for cavity of 15-crown-5.

Voltammmetric and in situ spectroelectrochemical measurements indicated that aggregation tendency of beta-substituted phthalocyanine complexes in TBAP/DMSO is much higher than that of alpha-substituted ones. The huge difference in aggregation tendency of compounds can be attributed to the deviation from planarity in alpha-substituted molecules as a result of the nonperipheral substitution.

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