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# Synthesis and electrochemical behavior of novel peripherally and non-peripherally substituted ball-type cobalt phthalocyanine complexes

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# ABSTRACT

The syntheses of new ball-type Co(II) phthalocyanines containing 4,4'-(9H-fluorene-9,9-diyl)diphenol substituents at non-peripheral (complex **6**) and peripheral (complex **7**) positions are presented. These complexes were characterized by UV–Vis, FT-IR, mass spectroscopy and electrochemical methods. Both complexes exhibit metal and ring based redox processes, typical of cobalt phthalocyanine complexes. For **6**, the metal based reduction was observed at -0.46 V followed by a ring based reduction at -1.40 V. The metal oxidation for **6** was observed at +0.16 V and the ring based oxidation at +1.05 V. For **7**, reductions are easier but the oxidations are more difficult. The metal based reduction for **7** was observed at -0.38 V followed by a ring based reduction at -1.03 V. The metal oxidation for **7** was observed at +0.20 V and the ring based oxidation at +1.35 V.

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### 1. Introduction

Metallophthalocyanines (MPcs) have been extensively studied due to their diversity of applications, which include molecular electronics [1], non-linear optics [2], liquid crystals [3], photosensitizers [4] and electrocatalysis [5,6]. Electrochemical studies of MPc complexes are also important with regard to their potential application as electrochromic materials where several colors are displayed depending on the applied potential on the electrode surface [7–9].

Cofacial or ball-type Pcs were published in the literature for the first time in 2002 [10,11]. However, studies on non-peripherally substituted CoPc ball-type derivatives containing bulky substituents (and hence less aggregated) are still limited. It has been reported that ball-type Pcs show spectroscopic and electrochemical properties which differ significantly from the parent monomer [12–25]. Ball-type Pcs have four bridged substituents on the peripheral positions of each benzene ring of the two Pc units, the latter are arranged cofacially, resulting in a ball-type structure. The electronic properties of ball-type Pcs can change dramatically depending on the bridging compounds or the central metal. The distance between the two Pc units affect the degree of interactions between the rings [12].

In this paper, we describe the syntheses, electrochemical and spectroelectrochemical properties of new symmetrically (peripherally and non-peripherally) substituted ball-type CoPcs (Scheme 1). We also discuss the influence of  $\alpha$  versus  $\beta$  substitution on the electrochemical properties of these complexes.

# 2. Experimental

# 2.1. Materials

3-Nitrophthalonitrile **1** and 4-nitrophthalonitrile **2** were synthesized as reported in the literature [26]. 4,4'-(9H-fluorene-9,9-*diy*l)diphenol **3** was obtained from commercial suppliers. Anhydrous potassium carbonate, cobalt(II) chloride and tetrabutyl-ammonium tetrafluoroborate (TBABF<sub>4</sub>) were purchased form Sigma-Aldrich. Dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and chloroform were obtained from Saarchem. Silica gel 60 for column chromatography was purchased from MERCK. All solvents were dried and purified as described by Perrin and Armarego [27]. All other reagents were used as received.

# 2.2. Equipment

UV–Vis absorption spectra were obtained using a Varian 500 UV–Vis–NIR spectrophotometer. IR spectra were obtained using a Perkin–Elmer 2000 FT-IR spectrometer. Elemental analysis was done using a Vario-Elementar Microcube ELIII. Mass spectral analysis was done using a Thermo Finnigan MAT LCQ or an ABI Voyager DE-STR MALDI-TOF instrument.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) data were obtained with an Autolab potentiostat PGSTAT 30 (Eco Chemie, Ultretch, The Netherlands) driven by the General Purpose



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Scheme 1. Synthesis of complex 6 and 7. (i) K<sub>2</sub>CO<sub>3</sub>, DMSO, rt, 3 days. (ii) CoCl<sub>2</sub>, 320 °C, 5 min.

Electrochemical Systems data processing software (GPES, software version 4.9, Eco Chemie) using a three electrode set-up that consisted of a glassy carbon-working electrode (GCE, 3.0 mm diameter), Ag|AgCl wire pseudo reference electrode and a platinum wire counter electrode. The potential response of the Ag|AgCl pseudo reference under aqueous conditions was less than Ag|AgCl (3 M KCl) by 0.015 ± 0.003 V. The SWV settings were: step potential = 5 mV, pulse height = 25 mV, pulse frequency = 15 Hz. Prior to use, the electrode surface was polished with alumina on a Buehler felt pad and rinsed with excess Millipore water. All electrochemical experiments were performed in freshly distilled dry DMSO containing TBABF<sub>4</sub> as a supporting electrolyte. Solutions for the electrochemical studies were deaerated by bubbling argon before use and the electrochemical set-up was kept under argon atmosphere throughout the experiments. Spectroelectrochemical experiments were conducted using a home-made optically transparent thin-layer electrochemical (OTTLE) cell connected to a Bio analytical system (BAS) CV 27 voltammogram.

### 2.3. Syntheses

The target precursors were prepared by a nucleophilic aromatic substitution reaction between 3-nitrophthalonitrile **1** or 4-nitrophthalonitrile **2** and 4,4'-(9H-fluorene-9,9-diyl)diphenol **3** Scheme 1.

# 2.3.1. 3,3'-(4,4'-(9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy)di-phthalonitrile (**4**)

Compound **3** (2.22 g, 6.33 mmol) was dissolved in dry DMSO (15 mL) and **1** (2.19, 12.66 mmol) was added under an inert atmosphere. To this reaction mixture, finely ground anhydrous  $K_2CO_3$  (3.50 g, 12.66 mmol) was added. After 4 h of stirring at room temperature another batch of potassium carbonate (0.40 g, 2.88 mmol) was added, and this same amount was added again after 24 h of stirring. After a total of 72 h of stirring, the reaction mixture was poured into water (50 mL), resulting in the formation of a yellow precipitate. The crude product was centrifuged and was further purified by chromatography over a silica gel column using CHCl<sub>3</sub> as the eluent. The product was recrystallized from ethanol (EtOH)

and then the pure product was dried using phosphorous pentoxide. Yield: 2.1 g. IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3059 (Ar—CH), 2232 (C=N), 1573 (C=C), 1251 (C—O—C). <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$ , ppm: 7.97 (2H, d), 7.83 (2H, m), 7.51 (2H, d), 7.45 (2H, t) 7.38 (2H, t), 7.31 (2H, d), 7.26 (6H, d, Ar'—H), 7.16 (4H, d). *Anal.* Calc. for C<sub>41</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>: C, 81.71; H, 3.68; N, 9.31. Found: C, 81.92; H, 3.79; N, 9.96%. MS *m/z*: 602.64. Found [M]<sup>+</sup>: 602.18.

# 2.3.2. 4,4'-(4,4'-(9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy)diphthalonitrile (**5**)

Complex **5** was synthesized as described for **4** except complex **2** instead of **1** was employed. The amounts of reagents were the same. Yield: 2.1 g. IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3059 (Ar–CH), 2233 (C=N), 1575 (C=C), 1253 (C–O–C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$ , ppm 8.08 (2H, d), 7.97 (2H, d), 7.79 (2H, s), 7.51 (2H, d), 7.45 (2H, t), 7.38 (2H, t), 7.36 (4H, d), 7.26 (2H, d), 7.14 (4H, d). *Anal.* Calc. for C<sub>41</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>: C, 81.71; H, 3.68; N, 9.31. Found: C, 81.02; H, 3.56; N, 9.06. MS *m/z*: 602.64. Found [M+H<sub>2</sub>O]<sup>+</sup>: 621.19.

# 2.3.3. 1',11',15',25'-[Tetrakis(4,4'-(1,1'-binaphthyl-8,8'-diyl(oxy))diphenyl)]bis-phthalocyaninato dicobalt(II) (**6**)

Complex **4** (0.100 g) and CoCl<sub>2</sub> (0.100 g) were ground in a quartz crucible and heated in a sealed glass tube for 5 min under an argon atmosphere at 320 °C. After cooling to room temperature, the bluegreen reaction product was washed with hot methanol (MeOH) and hot water. The product was separated by column chromatography on silica gel with CHCl<sub>3</sub> and a gradient of CHCl<sub>3</sub>–MeOH up to 50%. Yield 0.015 g. Blue-green color. M.p. > 350 °C. UV–Vis (CHCl<sub>3</sub>)  $\lambda_{max}/nm$  (log  $\varepsilon/dm^{-3}$  mol<sup>-1</sup> cm<sup>-1</sup>): 688 (4.86), 323 (4.73). IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3055 (Ar–CH), 1579 (C=C), 1251 (C–O–C). *Anal.* Calc. for C<sub>164</sub>H<sub>88</sub>N<sub>16</sub>O<sub>8</sub>Co<sub>2</sub>: C, 77.90; H, 3.51; N, 8.86. Found: C, 78.57; H, 3.55; N, 9.16%. MALDI-TOF-MS *m*/*z* Calc.: 2528.42. Found [M–5H]<sup>+</sup>: 2523.0.

# 2.3.4. 2',10',16',24'-[Tetrakis(4,4'-(1,1'-binaphthyl-8,8'-diyl(oxy))diphenyl)]bis-phthalocyaninato dicobalt(II) (7)

Complex **7** was synthesized as described for **6**, except complex **5** instead of **4** was employed. The amounts of reagents were the same. Yield: 0.038 g. Blue-green color. M.p. > 350 °C. UV–Vis

(CHCl<sub>3</sub>)  $\lambda_{max}/nm$  (log  $\varepsilon/dm^{-3}$  mol<sup>-1</sup> cm<sup>-1</sup>): 664 (4.67), 325 (4.73). IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3054 (Ar–CH), 1579 (C=C), 1245 (C–O–C). *Anal.* Calc. for C<sub>164</sub>H<sub>88</sub>N<sub>16</sub>O<sub>8</sub>Co<sub>2</sub>: C, 77.90; H, 3.51; N, 8.86%. Found: C, 78.57; H, 3.10; N, 9.03%. MALDI-TOF-MS *m/z* Calc.: 2528.42. Found: [M+H<sub>2</sub>O]<sup>+</sup>: 2546.51, [M–11H]<sup>+</sup>: 2517.6.

#### 3. Results and discussion

#### 3.1. Syntheses and characterization

The substituted phthalonitriles were synthesized according to the synthetic route shown in Scheme 1. New binuclear, ball-type Co(II)Pcs (**6** and **7**) were prepared by the reaction of compound **4** or **5** with CoCl<sub>2</sub>. The structure and purity of the CoPc derivatives were confirmed by UV–Vis, IR, mass spectroscopies and elemental analyses. Complexes **6** and **7** are soluble in DMSO, THF and CHCl<sub>3</sub>, and are partially soluble in most other organic solvents.

The IR spectra of **6** and **7** show no C=N vibrational peak (2233 or 2232 cm<sup>-1</sup>) which was observed in the IR spectra of compounds **4** and **5**. This confirms the formation of the desired CoPc derivatives. The remaining IR spectra are very similar for compounds **4–7**. The IR spectra of **4–7** showed Ar–O–Ar vibrational band bands between 1235 and 1255 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of **5** shows a characteristic sharp singlet at 7.79 ppm, which is assigned to the peripherally positioned proton on the CN–Ar–H moiety. In both <sup>1</sup>H NMR spectra of **4** and **5** the total number of protons integrates to 22.

Elemental analysis results are also consistent with the proposed structures of **4–7**. The purified ball-type phthalocyanines were further characterized by mass spectra. The deprotonated molecular ion peaks were observed at m/z 2523.0 (for **6**) and 2546.51 and 2517.6 (for **7**), which concur with the theoretical calculated molecular ions (See Supplementary materials, Fig. 1). These results confirm that the complexes have been synthesized successfully.

The UV–Vis spectra of **6** and **7** in CHCl<sub>3</sub> are in accordance with the trend found in the literature, Fig. 1. The phthalocyanines show typical electronic spectra with two main absorption bands in the UV region (320–350 nm, the *B*-bands) and the visible region (600–700 nm, the *Q*-band). The characteristic *Q*-band transition of metallophthalocyanines with  $D_{4h}$  symmetry is observed as a single band of high intensity in the visible region. Complexes **6** and **7** have *Q*-band absorption maxima at 688 and 664 nm in chloroform, respectively, as is shown in Fig. 1. It is well known that  $\alpha$  substitution results in red shifting of the spectra in MPcs [28,29], this is due to the electron density enhancement caused by the substitution at the non-peripheral position. The *B*-bands were observed at 323



Fig. 1. Absorption spectra of complexes 6 and 7 ( $4 \times 10^{-5}$  mol dm<sup>-3</sup>) in CHCl<sub>3</sub>.

and 325 nm for **6** and **7**, respectively. Typical of ball-type phthalocyanines, the intensity of the *B*-bands is high relative to the *Q*-band when compared to the monomer, and this may be due to intramolecular interactions between the Pc rings [30]. For example a CoPc tetra substituted at the non-peripheral positions with 3,4-(methylendioxy)-phenoxy substituents gave a log  $\varepsilon$  value for the *Q*-band of 5.39 compared to 4.75 for the *B*-band [31], whereas complex **7** shows a log  $\varepsilon$  value of 4.67 for the *Q*-band compared to 4.73 for the *B* band.

The aggregation behavior of a Pc is depicted as a coplanar association of rings, progressing from the monomer to a dimer and to higher order complexes, which are dependent on concentration, the nature of the solvent and substituents, metal ions and temperature [32]. Aggregation in MPcs is typified by broadened or split Qband, with the high energy band being due to the aggregate and the low energy band due to the monomer. As expected for balltype structures, complexes 6 and 7 have broad spectra [12-25,33]. A band near 620 nm in ball-type phthalocyanines has been associated with exciton coupling between the two Pc rings [33]. A strong intermolecular interaction between the Pc rings in ball-type Pc complexes is expected to result in a splitting of the molecular orbitals and hence a lowering of the symmetry, resulting in the splitting of the Q-band. The spectra of complexes 6 and 7 in chloroform shows bands in the 600 nm region, which could be a combination of vibronic bands and the band due to exciton coupling between the two rings. There is no clear splitting in the Q-band of both complexes, suggesting that the interactions are not very strong. The broadening is larger for 7, showing more intermolecular interactions and possibly aggregation. The peripherally substituted complex 7 is expected to show more aggregation than the non-peripherally substituted complex 6 [28].

## 3.2. Voltammetric studies

The electrochemistry of ball-type phthalocyanine complexes containing electroactive central metals is characterized by the formation of mixed valance species [12]. Multi-electron processes are known in the cyclic voltammetry of these complexes. The observation of one-electron processes in homo-dinuclear ball-type MPc complexes is attributed to a strong interaction between the rings, resulting in the splitting of the cyclic voltammetry peaks and the formation of mixed redox processes. The transfer of two electrons in each redox step suggests that there is no considerable interaction between the two Pc rings, and that the two rings are reduced and oxidized at the same potentials.

Complex **6** (Fig. 2) exhibited five redox processes, which are not reversible in some cases. The lack of reversibility of redox couples is typical behavior of ball-type MPc complexes and has been associated with interactions between the  $Co_2Pc_2$  units [12,34]. The reported electrochemistry of ball-type phthalocyanines is characterized by weak and often irreversible cyclic voltammograms [12,25]. The cyclic voltammograms observed in Figs. 2 and 3 are typical [12,25] of ball-type phthalocyanines.

Redox couple **III** in Fig. 2 is reversible, with a peak to peak separation ( $\Delta E$ ) of 80 mV ( $\Delta E$  = 85 mV for ferrocene standard). Processes **I**, **I'**, **II** and **IV** are not clearly reversible. The reversibility or relative intensities of the peaks could not be improved by changing the scanning direction or using a narrow potential window. Process **II** is only clearly observed on the square wave voltammogram at -0.46 V, Table 1, whereas process **I** is irreversible and is not observed on the square wave voltammogram, Fig. 2b, this is due to the extreme sensitivity of this technique to the reversibility of a couple and the chemical stability of the redox products. Using the known redox behavior of monomers and ball-type CoPc complexes, where the first reduction occurs on the central metal, process **II** is assigned to  $(Co^{II}Pc^{-2})_2/[(Co^{IP}c^{-2})_2]^{2-}$ . The assignment is



Fig. 2. (A) Cyclic and (B) square wave voltammograms of  $1\times 10^{-3}$  M complex 6 in freshly distilled DMSO containing 0.1 M TBABF\_4 supporting electrolyte.

consistent with the UV-Vis spectrum (Fig. 1) which does not show splitting, and hence shows that there are no strong interactions between the two rings, suggesting a two electron transfer process. This assignment will be confirmed below using spectroelectrochemistry. The irreversible process I (at -0.9 V), is then assigned to the subsequent ring reduction  $(Co^{1}Pc^{-2})_{2}]^{2-/[(Co^{1}Pc^{-3})_{2}]^{4-})}$  for complex 6, in comparison also with complex 7 below, which confirms a process in this potential range to be ring reduction, Table 1. Process I' is then assigned to further ring reduction and the formation of  $(Co^{I}Pc^{-2})_{2}$ <sup>4-</sup>/[ $(Co^{I}Pc^{-4})_{2}$ <sup>6-</sup>, Table 1. Process III shows a much higher intensity compared to II. This process could reflect on the overlap of two processes. Again using the literature [34], we assigned couple III (at 0.16 V) to  $[(Co^{III}Pc^{-2})_2]^{2+}/[Co^{II}Pc^{-2})_2$ . Process IV (at 1.05 V) is at the limit of solvent-electrolyte system, and hence it is not well refined. However this process may be assigned to a subsequent ring oxidation ( $[(Co^{III}Pc^{-2})_2]^{2+}/[(Co^{III}Pc^{-1})_2]^{4+}$ ). Table 1 compares the redox processes for the complexes reported here with those of monomers peripherally and non-peripherally substituted with substituents containing oxygen bridges. Oxidation seems to occur more easily for the ball-type complexes compared to monomers. However this is a tentative suggestion since the substituents are not exactly the same in the two systems.

Complex **7** exhibited five redox processes (Fig. 3), more clearly visible on the square wave voltammogram, especially process **III**. Process **II** was reversible, but the remaining processes exhibited a lack of reversibility, typical of ball-type MPc complexes [34]. An additional process (compared to complex **6**) at 0.44 V (labeled **III**') was observed for complex **7**, which could be due to aggregated species or the presence of mixed valance processes. The observation of process **III** having a higher intensity than the remaining processes for **6** and the observation of an extra peak for **7** suggest a separation of the redox peaks **III** and **III**' for **7** which were



**Fig. 3.** (A) Cyclic and (B) square wave voltammograms of  $1\times 10^{-3}$  M complex 7 in freshly distilled DMSO containing 0.1 M TBABF\_4 supporting electrolyte. Insert to B: SWV at a narrower potential window.

overlapped as **III** for **6**. For complex **6**, which is non-peripherally substituted, there is less splitting of the orbitals hence less splitting of the redox process compared to **7**. Less splitting of the orbitals suggests that there are lower interactions of the rings in **6**, as also observed in the UV–Vis spectra in Fig. 1, which shows more broadening in **7** compared to **6**. The assignments of the processes for **7** are similar to those of **6** (Table 1). Complex **6** is easier to oxidize and more difficult to reduce compared to complex **7**.

# 3.3. Spectroelectrochemical studies

The nature of the redox couples was probed via spectroelectrochemistry to confirm the above mentioned assignments. Fig. 4A shows the application of potentials more negative than couple II for complex 7. The starting spectrum in Fig. 4A is broader than observed in Fig. 1 and shows a blue shifted band near 620 nm due to aggregation at the concentrations used for the OTTLE cell. The spectral changes in Fig. 4A shows a shift in the Q-band from 662 to 703 nm. This is accompanied by the formation of new peak centered at 469 nm, which is characteristic of Co<sup>I</sup>Pc species [29]. Also the shift in the O-band to the red without a decrease in intensity is typical of metal based processes in MPc complexes [29]. The spectral changes in Fig. 4A show diffuse isosbestic points near 329, 380, 560 and 690 nm, suggesting more than two species in solution. The spectral changes are attributed to central metal reduction in balltype complexes, where reduction occurs in both Pc units as follows:  $(Co^{II}Pc^{-2})_2/[(Co^{I}Pc^{-2})_2]^{2-}$  [34].

The number of electrons was calculated to be approximately two, using Eq. (1)

Table 1	
Peak potentials ( $E_p$ or $E_{\frac{1}{2}}$ ) for the redox processes of complexes <b>6</b> and <b>7</b> in DMSO containing 0.1 M TBABF <sub>4</sub> .	

Complex 6	Complex 7	Complex <b>8</b> <sup>a</sup>	Complex <b>9</b> <sup>b</sup>
$\begin{array}{c} -1.40 \ (I') \\ [(Co^{IP}c^{-3})_2]^{4-}/[(Co^{IP}c^{-4})_2]^{6-} \\ -0.90 \ (I) \\ [(Co^{IP}c^{-2})_2]^{2-}/(Co^{IP}c^{-3})_2]^{4-} \\ -0.46 \ (II) \\ (Co^{IIP}c^{-2})_2/[(Co^{IP}c^{-2})_2]^{2-} \\ +0.16 \ (III) \\ [(Co^{IIP}c^{-2})_2]^{2+}/(Co^{IIP}c^{-2})_2 \\ +1.05 \ (IV) \\ [(Co^{IIIP}c^{-1})_2]^{4+}/[(Co^{IIP}c^{-2})_2]^{2+} \end{array}$	$\begin{array}{l} -1.03 \ (I) \\ [(Co^{I}Pc^{-2})_{2}]^{2-}/[(Co^{I}Pc^{-3})_{2}]^{4-} \\ -0.39 \ (II) \\ (Co^{II}Pc^{-2})_{2}/[(Co^{I}Pc^{-2})_{2}]^{2-} \\ +0.2 \ (III) \ and +0.44 \ (III') \\ [(Co^{II}Pc^{-2})_{2}]^{2+}/(Co^{II}Pc^{-2})_{2} \\ +1.35 \ (IV) \\ [(Co^{III}Pc^{-1})_{2}]^{4+}/[(Co^{III}Pc^{-2})_{2}]^{2+} \end{array}$	$\begin{array}{c} -1.36 \\ (Co^{I}pc^{-2})^{-}/(Co^{I}pc^{-3})^{2-} \\ -0.27 \\ Co^{II}pc^{-2}/(Co^{I}pc^{-2})^{-} \\ +0.56 \\ (Co^{II}pc^{-2})^{*}/Co^{II}pc^{-2} \\ +1.03 \\ (Co^{III}pc^{-1})^{2+}/(Co^{III}pc^{-2})^{*} \end{array}$	$\begin{array}{c} -1.45 \\ (Co^{l}Pc^{-2})^{-}/(Co^{l}Pc^{-3})^{2-} \\ -0.38 \\ Co^{ll}Pc^{-2}/(Co^{l}Pc^{-2})^{-} \\ +0.49 \\ (Co^{ll}Pc^{-2})^{+}/Co^{ll}Pc^{-2} \\ +0.92 \\ (Co^{ll}Pc^{-1})^{2+}/(Co^{ll}Pc^{-2})^{+} \end{array}$

<sup>a</sup> The data for non-peripheral tetra 3,4-(methylendioxy)-phenoxy substituted cobalt phthalocyanine monomer are from Ref. [31] and in DMF containing 0.1 M TBABF<sub>4</sub>.



**Fig. 4.** UV-Vis spectral changes observed for the reduction of complex **7** at potentials of: (A) couple **II** (-0.40 V); (B) couple **I** (-1.1 V); (C) process **III** (0.50 V); (D) process **IV** (1.4 V). The initial spectrum (dashed line) of D is the final spectrum of C. The dotted line shows the first spectrum in all figures. Solvent: DMSO containing 0.1 M TBABF<sub>4</sub> supporting electrolyte.

 $Q = nFVC \tag{1}$ 

where *n*, *F*, *V* and *C* are the number of electrons transferred, Faraday's constant, volume and concentration of the electroactive species respectively. For the calculation of the number of electrons, three independent experiments were performed, giving an average of two electrons. The observation of two-electron processes in the homo-dinuclear ball-type CoPc complex **7** suggests that there is no considerable interaction between the two Pc rings and that the two rings are reduced and oxidized at the same potentials. However, the lack of clear isosbestic points suggests that there some unresolved splitting of the redox processes, resulting in some mixed valence complexes which absorb at slightly different wavelengths. The unresolved splitting suggests some interaction between the rings, as evidenced also by the broadening of the UV–Vis spectra in Fig. 1, for **7** in particular. Application of a zero potential regenerated 80% of the original complex, which emphasises the reversibility of this process.

Application of more negative controlled potentials (-1.1 V, process I) for **7**, Fig. 4B, show a collapse in the Q-band with a shift in the band at 469 to 491 nm and formation of new bands between 500 and 600 nm. The formation of new weak bands in the 500–600 nm area is characteristic of ring based reduction and the formation of Pc<sup>-3</sup> species [35]. There is a lack of clear isosbestic points in Fig. 4B, showing the involvement of more than two species as discussed for process II above. We suggest that the spectral changes are due to the reduction of both rings, forming the [(Co<sup>I</sup>Pc<sup>-3</sup>)<sub>2</sub>]<sup>4–</sup> species [34]. The number of electrons transferred



**Fig. 5.** UV/Vis spectral changes observed for the reduction of complex **6** at potentials of: (A) couple II (-0.50 V); (B) process III (0.30 V); (C) process IV (1.1 V). The initial spectrum (dashed line) of C is the final spectrum of B. The dotted line shows the first spectrum in all figures. Solvent: DMSO containing 0.1 M TBABF<sub>4</sub> supporting electrolyte.

was found to be two using Eq. (1), and again using three independent experiments.

To investigate the oxidation couples, a new sample was injected in the OTTLE cell and a controlled potential (+0.50 V) was applied to confirm the assignment of the redox couple **III**, Fig. 4C. The UV/Vis spectral changes consist of a shift of the Q-band from 662 to 674 nm, with an increase in intensity. The spectral changes are typical of metal oxidation in CoPc electrochemistry [29]. Clear isosbestic points were observed at 662, 490 and 340 nm, suggesting the involvement of only two species. The total number of electrons was calculated to be two at the end of the electrolysis. We assign process **III** to  $[(Co^{II}Pc^{-2})_2]^{2+}/[Co^{II}Pc^{-2})_2$ .

Upon proceeding to more positive potentials (1.4 V), all the bands decreased in intensity, with only a small increase in the 500 nm area, typical [35] of ring oxidation, Fig. 4D. It was not possible to calculate exactly the number of electrons involved. However the irreversible process **IV** may tentatively be assigned to the redox couple  $[(Co^{III}Pc^{-2})_2]^{2+}/[(Co^{III}Pc^{-1})]^{4+}$ , where both rings are being oxidized.

Fig. 5A shows the spectral changes observed on application of the potentials of couple **II** for complex **6**. The *Q*-band shifts from 682 to 709 nm, but with diffuse isosbestic points. The lack of clear isosbestic points suggest that there are more than two species in solution, and hence imply the presence some unresolved splitting of the redox processes and the possibility of some mixed valence complexes which absorb at slightly different wavelengths, as observed for complex 7. We assign process II to  $(Co^{II}Pc^{-2})_2/$  $[(Co^{1}Pc^{-2})_{2}]^{2-}$ . The subsequent reduction will be at the ring. Fig. 5B shows the spectral changes observed on application of the potentials of process III for complex 6. The spectral changes consist of a shift in the Q-band from 684 to 693 nm, with an increase in intensity. These spectral changes are typical of metal oxidation in CoPc complexes [30]. There are clear isosbestic points at 684. 500 and 339 nm, showing that only two species are present in solution. The number of electrons obtained following the oxidation was still two, suggesting that the two rings are oxidized at exactly the same potential for 6. Fig. 5C shows the spectral changes observed on application of the potentials of process IV for 6. There is a decrease in the Q-band and the formation of a weak band near 500 nm, confirming ring oxidation.

#### 4. Conclusions

The syntheses and electrochemical properties of new symmetrically substituted (at non-peripheral (**6**) and peripheral (**7**) positions) ball-type CoPc derivatives are presented. The effects of the position of the substituent on these properties were explored. Both complexes exhibits ligand and metal based redox processes. Complex **6**, which is non-peripherally substituted, is easier to oxidize and more difficult to reduce than **7**. The interaction between the two CoPc rings is less severe for **6** as compared to **7**.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.11.028.

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