Electrochemical and optical aspects of cobalt meso-carbazole substituted porphyrin complexes

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1. Introduction

Looking for new organic materials for electronic molecular devices, like organic photovoltaic devices or sensors, but also for medical applications or catalysis, often involves analogues of natural pigments belonging to the vast family of molecules generally termed porphyrinoids [1–9]. Nowadays, the design and characterization of metal–organic complexes have become a field of immense interest [10–12]. The porphine ligand is a versatile building block for the synthetic chemist, especially due to its ability to accommodate several metal ions and form coordinatively unsaturated metal complexes [13–16]. The ample interest in cobalt-containing porphyrin ligands derives from the biological importance of cobalt-containing vitamin B12 and the unique characteristics of this metallocomplexes. Cobalt (II) form with porphyrin highly stable metal complexes exhibiting interesting catalytic, optical, and electrochemical properties [17–24]. What is important for practical applications, especially for sensors, is to understand the process involved in the charge transfer between the conjugated side and metal cation.

Early electrochemical studies on metalloporphyrins containing octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) in non-aqueous conditions have led to formulate diagnostic criteria for assigning the site of electron transfer. These include a constant electrochemical bandgap (2.25 ± 0.15 V) as the difference of potential between the first oxidation and the first reduction, independent of the central metal ion oxidation state, and a constant potential difference between the first and second macrocycle-centred oxidations (0.29 ± 0.05 V) or first and second macrocycle-centred reductions (0.42 ± 0.05 V). Most metal-centred redox processes have been reported to occur at potentials that are located between the formation of the macrocycle cation and anion radicals. These three potential differences continue to be used to distinguish macrocycle-centred reactions from metal-centred ones and often-quoted in publications reporting the electrochemistry of metalloporphyrins in non-aqueous media. However, more recent electrochemical studies of new porphyrins derivatives including nonplanar porphyrin containing copper, iron, cobalt or nickel and

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with macrocycles other than OEP or TPP, showed that previously utilized electrochemical diagnostic criteria might no longer be appropriate or useful. For instance, the potential separation between the two ring-centred oxidations of nonplanar nickel (II) porphyrin was often equal to 0 \([25-27]\). As for the electrochemistry of porphyrin cobalt (II), it is characterized by both metal and ring-centred processes. The most often observed metal-centred processes are the oxidation Co(II)/Co(III) and the reduction Co(II)/Co(I) reactions, which undergo at potentials easily accessible in most non-aqueous electrochemical solvents \([25,28,29]\). Porphyrin \(\pi\)-ring system can exhibit four redox waves in cyclic voltammetric experiments. During the electrochemical oxidation/reduction, the porphyrin ring undergoes only two one-electron transfers and involve the conversion of macrocycle to its cation/anion radical form followed at more positive/negative potentials by a conversion of the cation/anion radical to its dicationic/dianionic form \([25]\). The exact site of the first electron transfer in these complexes, both in the anodic and cathodic potential range, depends upon the structure of the compound and the solution conditions used to carry out the electrochemical measurements (the solvent, the strength of the counteranion, the presence of any coordinating ligands) \([24,25,27,30]\). Thus, for example, the first oxidation of cobalt (II) porphyrins can occur at the central metal ion to give cobalt (III) porphyrin with an intact \(\pi\)-system or at the conjugated macrocyclic leading to a cobalt (II) porphyrin cation radical product. Moreover, the d-block elements usually exhibit one-electron redox processes, hence the assignment of electron-transfer steps in such systems is not easy \([31]\). Whatever the site of electron transfer in the first one-electron oxidation, three successive one-electron abstractions of cobalt (II) porphyrins generate its dicaticonic form as cobalt (III) porphyrin dication \([\text{PCo}(\text{III})]^ {3+} [32]\).

In this work, we show synthesis and basic optical and electrochemical characterization of cobalt (II) \(\text{meso}\)-substituted porphyrin complexes containing one, two (syn and anti-substituted macrocycle), three or four carbazole units, in comparison with tetraphenylnporphyrin cobalt (II) derivative. The chemical structures of the investigated complexes are shown in Scheme 1. The relationship between structure and spectroscopic properties and the effect of substituents on the redox properties of these porphyrinoids are discussed.

2. Experimental

2.1. Measurements and characterization

The cyclic voltammetry (CV) measurements were performed in 0.1 M tetrabutylammonium tetrafluoroborate (Bu4NBF4) electrolyte solution in dichloromethane (DCM) at room temperature. Experiments were carried out in three-electrode electrochemical cell comprised of a 1 mm diameter platinum disk as a working electrode, platinum coil as counter electrode and silver wire as a quasi-reference electrode. The reference electrode potential was calibrated versus a ferrocene redox couple. CV investigations were performed in 1 mM concentrations of the investigated compounds using an Autolab PGSTAT101 potentiostat at a scan rate of 50 mV/s for oxidation processes and 300 mV/s for reduction behaviour and bandgap estimation. Photoluminescence spectra were collected using HITACHI spectrophotometer FL-2500, while UV–Vis spectra were registered using AVANTES Avalight-DH-S-BAL light and Avaspec-ULS2048XI, NIR512-1.7TEC detectors. Spectroscopy measurements were collected in eight solvents: dichloromethane, toluene, chloroform, tetrahydrofuran, cyclohexane, hexane, methanol, acetonitrile. The Grace Medium Pressure Liquid Chromatography with silica prepacked cartridge was used. NMR spectra were recorded on Bruker Avance 400 spectrometer. The following abbreviations were used: \(s = \text{singlet}, d = \text{doublet}, dd = \text{doublets of}

Scheme 1. Structures of the investigated complexes.
doublets, ddd = doublets of doublets of doublets, m = multiplet. All coupling constants J were measured in hertz (Hz). Chemical shifts are reported in parts-per-million (ppm). Tetramethylsilane was used as an internal reference. Mass spectra were recorded on Polaris Q or Hewlett Packard 5973.

2.2. Materials

The synthesis of the 5,10,15,20-tetraakis(3,5-dimethylphenyl) porphyrin (PCo), 1-octyl-3-carbazolaldehyde, 2,2’-(2,4,6-trimethylphenyl)meso-porphyrin were prepared according to previously published procedures [33–35]. The 1CbP2H, syn-2CbP2H and 3CbP2H were synthesized by using a statistical mixture of carbazole and benzaldehyde in Adler condition synthesis [36]. The compounds were chromatographically separated. The anti-2CbP2H has synthesized in 2 + 2 method because in the statistical mixture synthesis is usually produced in a small amount. Using mesityl peripheral substituents was necessary to prevent scrambling [37]. The 4CbP2H was synthesized by Lindsay’s method which usually gives higher yields [38]. The cobalt cation insertion was carried by a typical method using slight excess of cobalt (II) acetate with almost quantitative yield (see supplementary information). All other chemicals used in synthetic procedures were available commercially and used without additional purification, unless stated differently: dichloromethane RCI Labscan 99.8%, methanol Honeywell, hexanes Chem-Supply Analytical Grade, 99.9%, cobalt acetate tetrahydrate Sigma-Aldrich +98%, chloroform, tetrahydrofuran, cyclohexane, hexane, methanol, acetonitrile (Avantor Performance Materials Poland S.A., for HPLC).

Electrochemical studies were conducted in 0.1 M argon purged solutions of Bu₄NBФ₄, 99% (Sigma-Aldrich) in dichlormethane solvent, CHROMASOLV®, 99.9% (Sigma-Aldrich) at room temperature. All the solvents used for the spectroscopy measurements were commercially available and used without additional purification: dichloromethane (Sigma-Aldrich, Chromasolv for HPLC), toluene, chloroform, tetrahydrofuran, cyclohexane, hexane, methanol, acetonitrile (Avantor Performance Materials Poland S.A., for HPLC).

3. Results and discussion

Electrochemical studies have shown that all investigated cobalt (II) porphyrin derivatives are electroactive and undergo multiple redox processes. Anodic polarization of the PCo led to the registration of three clearly separated (Fig. 1a), quasi-reversible oxidation processes (peak-to-peak separation is scan-rate dependent, see Fig. S1) with maxima at 0.41 V, 0.58 V, 0.79 V (Table S1). This redox behaviour is similar to that described in the literature for other cobalt tetraarylporphyrins [24,30,39]. Each of oxidations tetraaryl-substituted cobalt (II) porphyrin is a one-electron process. Three oxidations are also observed for carbazole derivatives, however, these redox processes occur at lower potentials in comparison to PCo, which is directly related to the presence of carbazole substituents. Cyclic voltammograms showing the electrochemical oxidation involving three redox systems of all investigated compounds is presented in Fig. 1. Analysis of electrochemical behaviour and the data listed in Table S1 leads to the conclusion that oxidation potential depends directly on the number of carbazole substituents. With an increasing number of these units in the structure of the tetra substituted porphyrin, the potential of all determined oxidation systems decreases respectively from PCo (without carbazole substituent) to 4CbPco (four carbazole substituents). The first oxidation peak shifts to more lower potentials by 0.21 V, the second by 0.28 V, and the third by 0.32 V. Moreover with increasing the number of carbazole substituents, the separation of the first two electrode processes decreases. Both derivatives which contain two carbazole substituents, syn-2CbPco and anti-2CbPco (see Fig. 1b), show similar potentials of three oxidation processes. It has been noticed that the anti-substitution causes a slightly higher cathodic shift of two first oxidations of 0.02 V and anodic shift of the third oxidation which occurs for substitution of syn at a potential of 0.63 V, and for anti at 0.64 V, and as consequence a greater separation between the second and third peak of oxidation.

What is quite important in the analysis of conjugated compounds, is that cyclic voltammetry is a transient method that allows determination of two crucial parameters of organic semiconductors: HOMO and LUMO levels, which are related to electrochemically estimated Ionization Potential (IP) and Electron Affinity (EA), respectively. For such estimation, usually, the first oxidation and first reduction process are taken into account. When it is assumed that the oxidation peak is associated with the HOMO level and the reduction peak with the LUMO level, the electrochemical bandgap is taken as the difference between the obtained electron affinity and ionization potential energy levels. These values determine the working parameters of optoelectronic devices and lead selection of active materials for those applications [40–42]. Incorporation of electron-donating or electron-withdrawing substituents directly onto the conjugated pathway is an effective way of perturbing the molecular orbitals through inductive, mesomeric effects. In general, electron-donating units raise the HOMO energy, while electron-withdrawing units lower the LUMO energy, resulting in a decreased bandgap. The energy of HOMO-LUMO difference also decreases when the length of conjugation increases [43]. Fig. S2 presents voltammograms recorded during the determination of the electrochemical band gap value for the solutions a) PCo and 1CbPco, b) syn-2CbPco and anti-2CbPco and c) 3CbPco and 4CbPco. The estimated values of redox potentials and determined parameters are collected in Table S2. With the increasing number of electron-donating substituents, the oxidation potential onsets decreases and the value of ionization potential increases. The same trend is observed in the reduction potentials onsets and the value of electron affinity, wherein anti-2CbPco exhibits values close to 4CbPco. Electrochemical band gaps are similar for all complexes and it ranges from 1.47 eV to 1.53 eV.

One of the more prominent features of porphyrins is their intense absorption of the visible region of the electromagnetic radiations, therefore UV–vis spectroscopy is the most feasible spectroscopic method to study these compounds. Indeed all naturally occurring and synthetic porphyrins are deeply coloured compounds. Hence, the name porphyrin originates from the Greek word porphura, meaning purple, as referring to the purple or violet colour of many of these compounds [15,44]. The highly intense colour of porphyrins is a consequence of the chromophoric properties of the expanded conjugated 18-π electron system [15]. The observed colour of the compound is a result of selective absorption of specific wavelengths of visible light (from range 380–780 nm) and simultaneous reflection of remaining wavelengths. Thus, the colour is determined by the reflected light, also described as complementary colour [8,45].

The spectroscopic UV–vis measurements of meso-substituted cobalt (II) porphyrin derivatives were carried out in dichloromethane used in electrochemical studies and spectra of the studied complexes are illustrated in Fig. 2 and a summary of the UV–vis bands and parameters are given in Table S3. Insert in Fig. 2 correspond to the enlarged spectral range of 480–680 nm. The solutions of the compounds in dichloromethane are intensely reddish-purple coloured and their spectra reveal a characteristic electronic absorption pattern of porphyrins [46], that consists of two distinct
absorption regions: in the visible and near UV.

As shown in Fig. 2 the derivative without carbazole (PCo) exhibits a sharp B band at 412 nm and weak Q band at 529 nm. Almost identical absorption spectra of similar derivatives have been reported by Sun and coworkers. Tetraaryl-derivatives containing para-CH3 or ortho-OCH3 substituents on four meso-benzene rings, show B and Q bands at 410 nm and 529 nm, and at 412 nm and 527 nm, respectively [30]. This indicates that the change of substituents at the meso-benzene rings of the macrocycle from e.g. CH3 to OCH3 cause only a slight perturbation to the electronic structure of porphyrin. The aryl substituents at the meso-positions of porphyrin are not in the same plane as porphyrin ring due to the intramolecular steric interactions between the hydrogen atoms in the ortho positions of the benzene rings and the β-hydrogens at the macrocycle (the large aryl–porphyrin dihedral angles) [15,47,48]. The electron effects of the aryl groups on the macrocycle rings are relatively weak, because of the minimal overlap of the aryls and porphyrin orbitals, therefore their influence to the B band is also weak. The UV–vis spectra of studied complexes are characteristic for porphyrin complexes in which cobalt ion exhibits the +2 oxidation state.

The meso-carbazole substitution of the porphyrin macrocycle results in an overall redshift of the optical absorption spectrum associated with the reduction of the energy gap (see Fig. 2 and Table S3) [49]. Peripheral carbazole groups are also not co-planar with porphyrin core, but in contrast to aryl substituents, the electron-rich moiety can increase the electronic density at the porphyrin macrocycle [48]. With the increasing number of carbazole units, the stronger bathochromic shift in the absorption spectrum is observed. The overall magnitude of the B band shift is equal to 13 nm. As the number of carbazole-substituents increases, the intensity of both B and Q bands also increases. The most intense bands were observed for 4CbPCo, while the least for PCo (see Fig. 2 and Table S3). It can be noticed that the anti-substitution induces a stronger enhancement of the intensity of absorption bands than syn. In addition, the B band becomes broader as the number of carbazole groups increases at the meso-positions of the macrocycle. A similar observation has been presented for β-substituted porphyrins and this was interpreted based on configurational interactions [30,50].

Fig. 1. Cyclic voltammograms showing the electrochemical oxidation involving three redox systems of the meso-substituted cobalt (II) porphyrin derivatives a) PCo and 1CbPCo, b) syn-2CbPCo and anti-2CbPCo, c) 3CbPCo and 4CbPCo in 0.1 M Bu4NBF4/DCM. Sample concentration 10−3 M. Scan rate: 50 mV/s.
strength and a decrease in the B band intensity [51,52]. Furthermore, metalloporphyrins show additional absorption bands in the UV range between 230 and 360 nm (see Fig. 2), which are associated with the absorption of carbazole and/or aryl units (meso substituents). Their intensity increases with an increasing number of carbazole rings in the monomer structure. For PCo, two maxima are observed at 236 nm and 264 nm due to the presence in the structure only one type of meso-substituents: 3,5-diethylphenyl. According to the literature, carbazole moiety absorbs in the range of 290–350 nm and the bands observed around 350 nm are associated with the absorption of the carbazole ring, corresponding to its \(\pi-\pi^*\) transition. In the case of \textit{anti}-2CbPCo much weaker bands were recorded in the Q band range at 501 and 654 nm [53,54]. From the basic electrochemical analysis, we can estimate the electronic parameters i.e. HOMO, LUMO, bandgap energies, using UV–Vis spectroscopy we can calculate the optical band-gap and compare those results. Absorption maxima deliver information about the energies of electron transitions in the compound and, on the basis of UV–vis spectrum, an optical energy gap \(E_{\text{opt}}\) can be determined using the value of the low energy tail of the \(\pi-\pi^*\) absorption peak, denoted as \(\lambda_{\text{onset}}\) (see Table S3). The \(\lambda_{\text{onset}}\) rises with an increasing number of carbazole substituents in the monomer structure, resulting in a lower bandgap and in the bathochromic shift. For the investigated complexes, optical band-gap in dichloromethane is between 2.75 eV for 4CbPCo and 2.90 eV for PCo and is higher compared with electrochemically estimated band-gaps. In the optical method, the bandgap value is related to the electron transitions \(\pi-\pi^*\) of the macrocyclic ring, while the electrochemical bandgap was determined in relation to the two redox processes: the first oxidation which occurs on the macrocycle and the first reduction which corresponds to a reduction of the metal ion.

One of the most important factors for the optoelectronic application is the possibility of the organic compound to emit the light. The steady-state fluorescence spectra studies of investigated complexes were carried out in the same solvents as the UV–vis measurements (see supplementary information). No fluorescence signal was detected for the metalloporphyrins PCo, 1CbPCo, \textit{syn}-2CbPCo and 3CbPCo under the experimental conditions used. Excitation of the 4CbPCo in the carbazole absorption range resulted in the low-intensity fluorescence spectra in each of used solvent with maxima in the range of 345–370 nm. All recorded spectra have a vibronic structure. There is no significant and unequivocal effect of polarity of the solvents on the emission spectrum. The normalized fluorescence emission spectra of 4CbPCo in different solvents are shown in Fig. S3. However, the characteristic emission spectrum of the porphyrin core was not registered. Low-intensity fluorescence spectra were also recorded for \textit{anti}-2CbPCo. The normalized fluorescence emission spectra of \textit{anti}-2CbPCo in short-wave part in different solvents are shown in Fig. S4. Compared to the emission of 4CbPCo, spectra are bathochromically shifted by approximately 20 nm. There is no significant and unequivocal effect of polarity of the solvent on the emission spectrum. All recorded spectra have a vibronic structure with peaks between 365 and 390 nm. The excitation wavelength in the range of 270–300 nm was used. The \textit{anti}-2CbPCo emits in the ranges of 340–420 nm and 630–750 nm. It can exhibit energy transfer phenomena from the donor carbazole unit to the acceptor porphyrin core. The singlet–singlet Förster energy transfer for porphyrins derivatives was reported e.g. in Refs. [53,55]. As shown in Fig. 3, upon excitation at 299 nm, where carbazole unit absorbs, emission was observed from carbazole between 340 and 420 nm and characteristic emission was observed from porphyrin core with two bands Q (0,0) and Q (1,0) with maxima at 655 nm and 724 nm. When the excitation wavelength was used from the range 366–600 nm, it resulted in emission from the porphyrin ligand. Both registered signals are of low intensity. However, for the 5,10,15,20-tetrakis(3-(N-ethylcarbazoyl)porphyrin, the fluorescence spectrum of carbazole was not reported by Durantini and coworkers [55].

Due to the fact that the porphyrin should not emit the red light when it is excited at 299 nm, we concluded that intramolecular energy transfer from carbazole to the macrocyclic core is taking place. Normalized fluorescence spectra of \textit{anti}-2CbPCo in the long-wave part in different solvents are shown in Fig. S5. The emission spectra are located in the range of 630–750 nm. There is no significant effect of polarity of the solvents on the emission spectrum of the porphyrin core. The maximum of Q band (0,0) for different solvents shift around 2 nm range. The emission peaks of the metal-free porphyrins H2TPP reported in Refs. [46,53,56] (in different solvents) were situated at \(\approx 650\) and \(\approx 715\) nm which were almost the same positions as determined for \textit{anti}-2CbPCo.

During follow-up electrochemical studies, where the PCo was compared to the carbazole-derivatives, a clear additional redox system in the anodic potential range with a maximum above 0.80 V is observed. Fig. 4 shows four redox systems of studied compounds containing carbazole unit in comparison with three redox PCo systems. Additional oxidation peak registered for all carbazole-

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**Fig. 2.** Absorption spectra of a dilute solution of investigated compounds determined in dichloromethane. Sample concentration \(10^{-6}\) M.
derivatives is irreversible. In this case, a cathodic shift of the oxidation maxima is also observed (Table S1). The lowest oxidation potential of carbazole unit (0.84 V) was recorded for 4CbPCo complex and the potential difference between the maxima of the fourth oxidation of 1CbPCo and 4CbPCo is equal to 0.22 V. The obtained results indicate that the carbazole substituent/s exert an electron-donating effect on the redox behaviour of the porphyrin molecule, which is apparent in the successive shifts of the oxidation potentials to more negative (easier to oxidize) potentials with increasing number of carbazole substituents as compared to the PCo. The electron-donating properties of this heterocycle cause increasing the electron density in the porphyrin macrocycle,
thereby facilitating compound oxidation. The fourth oxidation peak potentials are lower than the oxidation potential of carbazole, showing the influence of porphyrin connection and expanded conjugation [10,40,55]. The carbazole units oxidation of anti-2CbPCo and 3CbPCo occur at a similar potential at 0.89 V and 0.88 V respectively, while these units oxidation of dicarbazole-substituted derivatives were recorded at different potentials. The carbazole units of syn-2CbPCo are difficult to oxidize than of anti-2CbPCo and the potential difference is equal to 0.08 V. This can come as a result of higher conjugation on anti-substituted compound than syn-derivative and also close to the conjugation of the derivative with three carbazole substituents. The oxidation of carbazole in 1CbPCo was recorded at 1.06 V. The potential difference between the oxidation potentials of carbazole-substituted compounds indicates the formation of the carbazole radical cation more difficult for 1CbPCo and syn-2CbPCo. The values of all measured redox potentials and the separation between oxidation processes are presented in Table S1.

The number of carbazole substituents affects the separation between oxidation processes, however, the magnitude of the substituent effect on the redox potentials is not the same for all oxidations (see Table S1). It has been noticed that the peaks separation of the first and the second oxidation decreases from well-separated processes of PCo by 0.17 V to the weakest separated and almost superimposed peaks of 4CbPCo by 0.10 V (Figs. 1 and 4). The two oxidations becomes overlapped for 4CbPCo because the first process shifts negatively by 0.21 V and the second changes by 0.28 V in the same direction. The strongest positive induction effect of the carbazole substituent is observed for 1CbPCo. The introduction of one carbazole substituent in the macrocycle meso position decreases the peak separation by 0.04 V, meanwhile incorporation each additional carbazole unit to complex structure reduces the peak separation, systematically by 0.01 V. For syn or anti substitution the same separation of the first and second oxidation peak was observed (0.12 V) which means that the generation of second oxidation form is achieved with the same effort. The separation potential between the second and third peak of complexes contrasts with the former separation peaks, where for most complexes this value is in the range 0.17–0.18 V, except PCo and anti-2CbPCo (0.21 V). Analysis of the peak separation value leads to the conclusion that the transformation of PCo and anti-2CbPCo to dicationic form is slightly more difficult compared to the other complexes. The strongest positive induction effect of the carbazole substituent is observed for 1CbPCo since the introduction of one carbazole substituent decreases the peak separation by 0.03 V. The largest separation of the fourth and third oxidations maxima was recorded for 1CbPCo (0.39 V) and the smallest for anti-2CbPCo (0.25 V). The registered peaks of syn-2CbPCo and 3CbPCo are separated by an identical value of 0.34 V and a similar value was obtained for the 4CbPCo (0.37 V). The anti-2CbPCo combines the electrochemical properties of syn-2CbPCo and 3CbPCo, the first three oxidation peaks are similar to the syn-derivative, and the fourth peak appears almost at the same potential as for the derivative with three carbazole substituents. According to diagnostic criteria for assigning the site of electron transfer [25,26] a constant potential difference between the first and second macrocycle-centred oxidations should be around 0.29 ± 0.05 V. The potential difference between the first and the third oxidation of carbazole-derivatives is ~0.30 V and may lead to conclusion that this two processes can be related to macrocycle oxidation. Durantini and co-workers [55,57] remarked that the carbazole groups can be conjugated with porphyrin macrocycle, therefore charge delocalization on the macrocycle and/or the peripheral substituents is possible during oxidation. Charge delocalization has also been observed in porphyrin containing triphenyl-amine groups attached to the macrocycle at meso position [55]. The electron-donating effect of carbazole on redox potentials of complexes was observed during CV experiments. It was demonstrated that the investigated complexes do not behave as a compound formed by independent units i.e. porphyrin macrocycle, metal ion, carbazole and/or aryl units, but like a whole molecule with all these groups connected and interacting which could affect the electrochemical properties.

The first electron abstraction from Co (II) porphyrins most often involve metal ion leading to the formation of a Co (III) complex. However, for cobalt (II) tetraphenylporphyrin and its derivatives, the initial oxidation can be assigned as the ring-centred and the generating a Co (II) porphyrin cation radical has been observed in dry non-coordinating solvents e.g. CH2Cl2 containing weakly coordinating anions. Axial ligation of solvent molecules, e.g. pyridine, dimethyl sulfoxide, or trace water at the metal centre stabilizes the cobalt ion and facilitates the oxidation of cobalt to the third oxidation state, and hence the oxidation of Co (II) is metal-centred and occurs at markedly lower potentials than in non-coordinating solvents [25,26,30,39]. Scheme 2 presents the possible oxidation and reduction electron-transfer steps of the investigated metallocomplexes on the example of PCo.

The effects on redox processes and their potential separation will depend not only upon the electronic properties of the substituents on the meso-positions but also upon the planarity of the macrocycle and steric hindrance of peripheral groups [26,55].

A scan of the anode potential achieved by increasing potential range above the fourth oxidation allows to register an additional redox process, associated with the carbazole unit transition to a higher oxidation degree and the formation of dication. The recorded voltammograms for syn-2CbPCo - 4CbPCo monomers are shown in Fig. 5. Maximum peaks of this process are located at 1.12 V, 1.05 V, 1.06 V and 1.13 V, for syn-2CbPCo, anti-2CbPCo, 3CbPCo, 4CbPCo, respectively. The separation of the maxima between 4th and 5th redox systems is equal to 0.15 V, 0.16 V, 0.18 V and 0.29 V. For the 1CbPCo this process can occur above the electrochemical potential window of used electrolyte.

Electrochemical studies reveal that all investigated complexes are electroactive in both anodic and cathodic potential range. Each porphyrin derivative undergoes two reductions in CH2Cl2 containing 0.1 M Bu4NBF4 as seen in Fig. 6. Cyclic voltammograms show the electrochemical reduction of investigated compounds including the first reduction process (dashed line) and two reduction processes (solid line). The reduction potentials and their potential separation are summarized in Table S4. The increasing the number of carbazole units in the compound structure pushes the reduction potentials to lower values and make complexes more
difficult to reduce compared to PCo, owing to the positive inductive
effect of carbazole substituents. The obtained results indicate that the
incorporation of carbazole at the meso position has an effect not
only on the oxidation processes but also on the reduction proper-
ties of the cobalt (II) porphyrin. Among the investigated com-
pounds, the dicarbazole-substituted anti-2CbPCo exhibits
exceptional behaviour (Fig. 6d). In this case, the first reduction was
recorded with a minimum at the potential \(-1.59\) V, similar as
4CbPCo (\(-1.61\) V), meanwhile, the second process was obtained at
almost identical potential as in the case of monomer 3CbPCo
\((-1.98\) V, \(-2.00\) V, respectively).

Comparing compounds containing two carbazole substituents,
syn-2CbPCo and anti-2CbPCo, with refer to the potentials recorded for
1CbPCo, a stronger cathodic peak shift was found for a com-
pound with the opposite arrangement of carbazole units, the first
reduction anti-derivative is more shifted towards negative value by
0.18 V and the second by 0.07 V than syn. This can comes as a result
of stronger positive inductive effect of the electron-donating units at
the anti-position, increasing the electron density at the porphyrin
macrocycle and making reduction process more difficult. Pco exhibit
two irreversible reductions located at \(-0.87\) and \(-1.38\) V. The potential difference between reductions of com-
pounds Pco and 4CbPCo is equal to 0.25 V (the first process) and
0.21 V (the second process). The reduction processes of Pco and
1CbPCo were obtained at similar potentials as the carbazole unit
has a slight impact and shifted both processes by 0.02 V. Sym-
metrical shift of both redox processes were also observed for syn-2CbPCo and 3CbPCo, while asymmetrical shift is shown for the
anti-derivative and containing four carbazole substituents as the second
process is shifted by a lower value. The mesityl substituent
should be more electron-donating than ethyl group, however, due
to increasing of steric hindrance overlapping of orbitals is smaller
and its positive inductive effect is lowered. Kadish and co-workers
reports that Co(II) porphyrins can undergo either a metal-centred
reduction to give a Co(I) porphyrin (an intact/unreduced \(\pi\)-sys-
tem) or reduction at the conjugated \(\pi\)-system to give a Co(II)
porphyrin anion radical (see Scheme 2) [25,30]. As previously
mentioned the porphyrin ring can undergo up to two one-electron
reductions. Both ligand-centred reductions of Co(II) porphyrins are
not common but have been reported for easily reducible complexes
containing multiple electron-withdrawing groups on the macro-
cycle, such as CN4TPPCo. The reduction of the cobalt ion i.e. the
Co(II)/Co(I) transition takes place at the potentials available in most
non-aqueous electrochemical solvents [25]. The introduction of
metal ion (e.g. cobalt) in the macrocycle cavity usually leads to a
shift of the first ring reduction potential to a more negative value as
a result of the \(\pi\)-back donation of the filled \(d_{\alpha}\) of the metal ion into
the empty porphyrin \(\pi^*\) orbitals [19,44,58]. Ye and co-workers re-
ports that the first reversible redox process is usually assigned to
a cobalt (II) porphyrin radical anion, while the first irreversible
reduction is assigned to the formation of cobalt(I) porphyrin [24].
The first reduction electron transfer of studied complexes is quasi-
reversible for Pco, 1CbPCo and syn-2CbPCo and irreversible for others,
however, it is irreversible for all when the scanning rate is
used below 300 mV/s. Currents for the second reduction in CH2Cl2
are higher than those for the first reduction and this process is
irreversible for all six investigated compounds. Furthermore when
potential scan is terminated below second redox system the reox-
idation peak take at \(-1.37\) V, \(-1.42\) V, \(-1.45\) V, \(-1.48\) V, \(-1.51\) V and
\(-1.50\) V is observed for Pco, 1CbPCo, syn-2CbPCo, anti-2CbPCo,
3CbPCo and 4CbPCo respectively. This behaviour is assigned to
metal-centred processes, leading to the formation of a Co(I) prod-
uct after the first reduction in CH2Cl2. This low valent complex is
highly reactive and quickly reacts with alkyl and aryl halides (RX)
to yield the corresponding alklycobalt(III) tetraphenylporphyrin
(RCoTPP). As a result, the Co-\(\sigma\)-C bond is formed between the
complex and the alkyl halide generating \(\sigma\)-bonded Co(III) product.
The reductions processes determined during CV tests are well-
separated (Table S4). The smallest separation between the
minima of reduction processes is observed for anti-2CbPCo
(0.41 V), a greater separation determined for 4CbPCo by 0.05 V,
while for the remaining compounds estimated an identical value
equal to 0.50 V (Table S2). The potential difference of both processes
may suggest the activity of electrogenerated cobalt (I) complexes in
the alkylation reaction with dichloromethane.

4. Conclusions

In this work, a series of carbazole-substituted cobalt porphyrins
were synthesized and their electrochemical and optical properties
were studied.

The effect of the number and position of carbazole groups on the
redox potentials were analysed, and comparisons were made to
structurally similar compounds containing benzene-based groups
at the meso-position. All investigated molecules demonstrate
ambipolar behaviour, undergoing both oxidation and reduction
processes. Up to seven redox reactions can be observed depending
upon the positive and negative potential limits of the utilized sol-
vent/supporting electrolyte system. On the basis of the potential
separations, so-called diagnostic criteria, the first and the third
oxidation of carbazole-derivatives were assigned to macrocycle
oxidation. The electron-donating effect of carbazole on redox po-
tentials of complexes was observed during CV experiments. It was
demonstrated that the investigated complexes do not behave as a
compound formed by independent units, but like a whole molecule
with all component, groups conjugated.

The \(E_g\) values determined by the optical method differ sig-
ificantly from the values obtained by the electrochemical method. In
the optical method, the \(E_g\) value is related to the electron	transitions \(\pi^*\) of the macrocyclic ring, while the electrochemical
\(E_g\) was determined in relation to the two redox processes:

Fig. 5. Cyclic voltammograms showing redox systems of syn-2CbPCo, anti-2CbPCo,
3CbPCo and 4CbPCo in wide range of anodic potentials in 0.1 M Bu4NBF4/DCM. Sample
collection 10\(^{-3}\) M. Scan rate: 50 mV/s.
Fig. 6. Cyclic voltammograms showing the electrochemical reduction of investigated compounds a) PCo, b) 1CbPCo, c) syn-2CbPCo, d) anti-2CbPCo, e) 3CbPCo and f) 4CbPCo, including the one reduction process (dashed line) and two reduction processes (solid line). Black line correspond to the first CV scan, while red color denotes the second CV scan. Sample concentration $10^{-3}$ M. Scan rate: 300 mV/s. Electrolyte: 0.1 M Bu4NBF4/DCM. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
the first oxidation which occurs on the macrocycle and the first reduction which corresponds to a reduction of the metal ion.

The electron donor effect of the carbazole group on the meso-position produced a small effect on the UV–vis spectra when compared with the derivative without carbazole unit. Overall the effect of the addition of carbazole groups at the meso-position resulted in a red-shift of the B band and the Q band from tetra-phenyl PCo to tetra-carbazole derivative 4CbPCo. The B and the Q bands both arise from π-π* electrons’ transitions of the porphyrin macrocycle system. Low-intensity fluorescence spectra were registered for anti-2CbPCo and 4CbPCo upon excitation in the carbazole absorption range. In the case of anti-derivative was observed a characteristic vibronic signal of porphyrins core with two bands, both upon excitation at wavelengths where carbazole unit and metalloporphyrin absorb. It can exhibit singlet–singlet Förster energy transfer phenomena from the donor carbazole unit to the acceptor porphyrin core.

Electron-transfer reactions of the investigated cobalt porphyrins can occur at the conjugated ring system of the porphyrin macrocycle(s), the metal central ion or, in the case of oxidations, additionally at the electroactive carbazole unit. It was proposed that all monomers undergo metal-centred reduction to give Co(I) porphyrin complexes, which is highly reactive and react with CHCl₃ to generate π-bonded Co(III) product. With the increase in the number of electron-donating substituents in the compound structure, the reduction potential is shifted towards more negative value. This can comes as a result of stronger positive inductive effect of carbazole units, increasing the electron density and making reduction process more difficult.

The investigated complexes contain an extensively conjugated π-system and exhibit extensive optical absorption in the visible spectrum, which renders them suitable for light-harvesting and makes them a good candidate as the photoactive layer for an organic solar cell application, e.g. DSCC. Since the carbazole unit is known to possess electron-donating character, it allows for greater electron delocalization. An anticipated red-shift of the B band is observed by increasing the number of the donor unit. Moreover, the metallocomplexes possess the energy of LUMO orbitals above the conduction band of TiO₂ and the HOMO level below the redox couple of the electrolyte redox couple 1V/1+/. However, the most prominent perspective application of investigated small molecules is electrocatalysis or sensing due to the central metal ions are redox-active. The cobalt porphyrins can be tested in the electrocatalytic oxidation of several important molecules such as thiols, nitric oxide, as well as they can be used as catalysts for oxygen reduction reactions for potential application in the field of fuel cells or CO₂ reduction.

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Appendix A. Supplementary data

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References


