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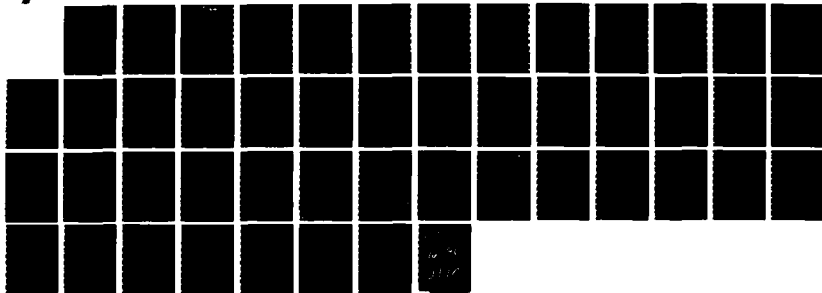
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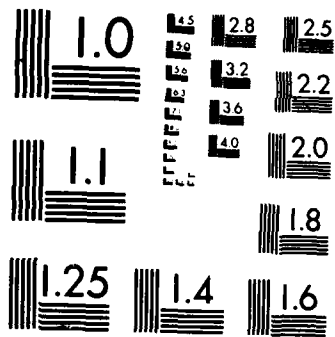
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Electrochemistry and Spectro-Electrochemistry of Mononuclear and Binuclear Cobalt Phthalocyanines

By

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ELECTROCHEMISTRY AND SPECTRO-ELECTROCHEMISTRY OF MONONUCLEAR AND BINUCLEAR COBALT PHTHALOCYANINES.

W.A. Nevin, M.R. Hempstead, W.Liu¹, C.C. Leznoff, and A.B.P. Lever*

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Abstract

The electrochemistry of [2,9,16,23-tetra(neopentoxy)phthalocyanato]cobalt, and some binuclear analogs, has been studied in dichlorobenzene and in dimethylformamide. The redox mechanisms and species on the electrode are discussed. Using an optically thin electrode, the electronic spectra of seven different oxidation states of the mononuclear derivative are reported. Data for a selection of oxidation states of several binuclear species are also presented.

Introduction

The electrochemistry and spectro-electrochemistry of metalloporphyrins have been extensively studied.²⁻¹⁶ However, relatively little spectro-electrochemistry has been carried out on phthalocyanines¹⁷⁻²⁵ due to their low solubilities in suitable solvents for electrochemistry which limits the use of optically transparent thin layer electrodes (OTTE). Such studies are desirable in view of the

potential use of phthalocyanines as electrocatalysts²⁶⁻²⁸, where an understanding of the nature of the redox processes of the phthalocyanine molecule is essential for the design of more efficient catalysts. The redox processes may occur at either the central metal atom or the phthalocyanine ring, but this cannot usually be distinguished using electrochemistry alone. Spectro-electrochemical studies of the phthalocyanines are also important with regard to their possible use as electrochromic materials.^{24,29,30}

Recently³¹⁻³³, we have reported the synthesis of a series of binuclear phthalocyanines formed by linking units of tri(neopentoxy) phthalocyanine (TrNpc) together through a benzene ring by bridges of 1,2,4 or 5 atoms. The three neopentoxy groups are randomly distributed in the 4 or 5 positions of the unlinked benzene rings and provide high solubility for the phthalocyanines in a wide range of organic solvents, such as toluene, o-dichlorobenzene (DCB), dichloromethane (DCM) and N,N-dimethylformamide (DMF). These complexes, and in particular the cobalt derivatives, have been the subject of recent investigations as oxygen reduction catalysts and as multi-electron redox catalysts.^{26, 34} We report here an electrochemical and spectro-electrochemical study on the cobalt derivatives of mononuclear and binuclear neopentoxy phthalocyanines in DCB and DMF.

The purpose of this work was to obtain, for the first time, the electronic spectra of a wide range of electrochemically generated CoPc redox species in organic solution, and, in addition, to determine any possible effects of coupling in the binuclear species on the redox processes and spectra. Several scattered reports on CoPc redox species exist in the literature; however these are incomplete and are either reported in the solid state where Davydov effects will distort the

spectra.

Spectra are presented here for a series of seven electrochemically generated redox species of the mononuclear derivative.

Of relevance to this presentation are the following species, with their abbreviations (Figure 1) (the number in parenthesis is the number of bridging atoms connecting the two phthalocyanine rings):

label

CoTNPc [3,9,16,23-tetra(neopentoxo)phthalocyanato]cobalt.

This is the mononuclear control molecule.

EtMeO(5)[CoTrNPc]₂ phthalocyanine rings linked via
-OCH₂C(Me)(Et)CH₂O-.

Cat(4)[CoTrNPc]₂ phthalocyanine rings linked via -O-C₆H₄-O-
(o-catechol).

C(2)[CoTrNPc]₂ phthalocyanine rings linked via -CH₂CH₂-.

O(1)[CoTrNPc]₂ phthalocyanine rings linked via a single oxygen
(ether) bridge.

These binuclear complexes can exist in various conformations depending upon the nature of the bridging unit.³⁵ The EtMeO(5) and Cat(4) species can close in a "clamshell" - like fashion (see Figure 1), while geometrical constraints of the bridge restrict the C(2) and O(1) species to an open conformation. Electronic coupling between the

phthalocyanine rings may occur through space or through the bridge.³⁵ For the series of binuclear cobalt derivatives, the degree of electronic interaction between the phthalocyanine rings has been found to increase in the order³⁴:



The nomenclature CoTNPC or [CoTrNPC]₂ is used for a general species of undefined oxidation state, while for specific compounds, the oxidation states of both metal and phthalocyanine are defined. The Pc(-2) state is the standard oxidation state for the phthalocyanine ring.^{36,37}

Experimental

The species H₂TNPc³¹, CoTNPC³¹, EtMeO(5)[CoTrNPC]₂³¹, Cat(4)[CoTrNPC]₂³², C(2)[CoTrNPC]₂³² and O(1)[CoTrNPC]₂³³ were prepared by the literature routes cited. N,N-dimethylformamide (DMF) (Aldrich, Gold Label, anhydrous, H₂O < 0.005%, packaged under nitrogen) o-dichlorobenzene (DCB) (Aldrich, Gold Label), dichloromethane (DCM) (Aldrich, Gold Label) and acetonitrile (Aldrich, Gold Label) were used as supplied. Tetrabutylammonium perchlorate (TBAP) (Kodak) was recrystallised from absolute ethanol and dried at 50° C under vacuum for two days. [Co(III)(CN)₂TNPc(-2)]K³⁸⁻⁴⁰ was prepared by adding a 10-fold excess of KCN to a solution of Co(II)TNPC(-2) in DCM/CH₃CN (2:1).

Electronic spectra were recorded with a Hitachi-Perkin Elmer Microprocessor model 340 spectrometer or a Guided Wave Inc. model 100-20 Optical Waveguide Spectrum Analyser with a WW100 fibre optic

probe. Electrochemical data were obtained using a Pine model RDE 3 double potentiostat, or with a Princeton Applied Research (PARC) model 173 potentiostat, or with a PARC model 174A Polarographic Analyser coupled to a PARC model 175 Universal Programmer. Cyclic voltammetry and differential pulse polarography were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Drilab using a conventional three-electrode cell. A platinum disc described by the cross-sectional area of a 27 gauge wire (area ca. 10^{-3} cm²), sealed in glass, was used as the working electrode in DCB solution, and a platinum wire in DMF solution. A platinum wire served as the counter electrode, and a silver wire was used as a quasi-reference electrode. Potentials were referenced internally to the ferrocenium/ferrocene (Fc⁺/Fc) couple (+0.16V vs SCE).⁴¹ All DMF solutions were prepared within the dry-box. The DCB solutions were prepared in air, degassed by repeated freeze-pump-thaw cycles, and then transferred to the dry-box.

Spectro-electrochemical measurements were made with an optically transparent thin layer electrode cell utilising a gold minigrad (500 lines/in)⁴², in conjunction with the Hitachi-Perkin Elmer spectrometer; or by using a bulk electrolysis cell, consisting of a platinum plate working electrode, platinum flag counter and silver wire quasi-reference electrode (reference and counter electrodes were separated from the working compartment by medium glass frits). Spectra were recorded during bulk electrolysis by immersing the Guided Wave fibre optic probe in the solution, degassed with argon.

Solutions for electrochemistry and spectro-electrochemistry contained 0.1-0.3M TBAP, as supporting electrolyte.

Results and Discussion

Electrochemistry in DCB Solution

Figure 2(a) shows a typical cyclic voltammogram of CoTNPc in DCB. The molecule undergoes two quasi-reversible one-electron reductions and three quasi-reversible one-electron oxidations within the limit of the solvent ($i_a = i_c$, $i \propto \sqrt{v}$). Half-wave potentials and peak separations at a scan rate (v) of 20 mV/s are given in Table I.

The binuclear $[\text{CoTrNPc}]_2$ complexes show very similar voltammetry to the mononuclear species, although the waves are generally broader and weaker. However, well defined peaks were obtained by differential pulse polarography; Figure 3 compares the results for $\text{O}(1)[\text{CoTrNPc}]_2$ with those of CoTNPc in DCB. Values of half-wave potentials measured for the binuclear complexes in DCB are given in Table I. Note that the potential of the second oxidation couple (II) is very sensitive to traces of anions which can coordinate to the cobalt atom.

No splitting of the redox peaks was seen for any of the binuclear complexes, such as has been observed for the Co(II)/Co(I) couple of a "clamshell" cobalt porphyrin¹³ and the Co(II)/Co(I) and Co(III)/Co(II) couples of "face-to-face" cobalt porphyrins.^{13,14} This splitting is attributed to interactions between the two cobalt atoms which are held in close proximity by the ligand geometry, resulting in overlap of their d_{z^2} orbitals along the cobalt-cobalt axis. The size of the splitting is proportional to the magnitude of the interaction between the cobalt atoms. In the case of the binuclear phthalocyanines studied here,

however, the two CoTrNPc units of each molecule oxidise or reduce "simultaneously", even for those species known to exist in a closed "clamshell" conformation in solution. Either electronic coupling between the cobalt atoms is not sufficient to cause an observable splitting of the couples, or more likely, in a preliminary chemical step, the more coupled conformations rearrange to a less coupled conformation, prior to the electron transfer. The electronic coupling IS sufficient to be observed as a perturbation of the electronic spectra of these cobalt species.³⁴

Note that for the "clamshell" porphyrin¹³, linkage occurs via bridges between two benzene rings of each porphyrin ring thus giving a more rigid geometry than for the binuclear phthalocyanines reported here. The broadening of the redox waves of the binuclear compounds relative to CoTNPc may arise because of the mixture of isomers which is present, having slightly different redox potentials.

For comparison, half-wave potentials for the metal-free mononuclear complex, H₂TNPc, in DCB solution are also given in Table I. Two quasi-reversible one-electron reductions and two quasi-reversible one-electron oxidations are observed, corresponding to the first and second reductions and oxidations, respectively, of the phthalocyanine ring.

Spectro-electrochemistry in DCB Solution

Typical absorption spectra for Co(II)TNPc(-2), and the "closed" and "open" binuclear species, EtMeO(5)[Co(II)TrNPc(-2)]₂ and C(2)[Co(II)TrNPc(-2)]₂, respectively, are shown in Figure 4. The binuclear species show an additional band centred at ca. 50 nm to the

blue of the normal Q band as a result of interaction between the phthalocyanine rings through "exciton coupling".^{34,35} Spectroscopic data for CoTNpc species are given in Table II.

Polarisation of a solution of CoTNpc in DCB in the OTTLE at 200 mV negative of the first reduction couple (IV), results in the spectroscopic changes shown in Figure 5, and a change of colour from blue to yellow. Isosbestic points are observed at 325, 360, 395, 557 and 692 nm. The spectrum is typical of a Co(I)Pc(-2) species^{17,19,20,39,40,43,44}, characterised by the appearance of a strong band at 475 nm, assigned as a metal-to-ligand charge transfer from Co(I)Pc(-2)[d(xz,yz)] \rightarrow $\pi^*(1b_{1u})Pc(-2)$ ^{40,45,46}, and a red shift and decrease in intensity of the Q band. The reduced species is fully reversible to the starting material by oxidation positive of the first reduction couple.

Polarisation at 200 mV negative of the second reduction couple (V) results in a change from yellow to a pink solution, the spectrum of which is shown in Figure 6. The observed small red shift of the MLCT band and decrease in intensity of the Q band relative to the first oxidation product are similar to those obtained by Clack and Yandle²⁰ for the chemical formation of the species [Co(I)Pc(-3)]²⁻ in DMF, and by Le Moigne and Even⁴³ for a chemically reduced thin film of CoPc. In addition, a weak near ir band occurs at 950 nm. The appearance of a band in the region of 950 nm appears characteristic of the ligand-reduced species, as has been observed previously for a number of metallophthalocyanines.^{20,46} Re-oxidation at a potential positive of couple (IV) generates the starting material with ca. 20% decrease in the Q band intensity (no decomposition products absorbing in the region of 300-1600 nm were observed).

Oxidation of CoTNPC in DCB in the OTTLE at 200 mV positive of the first oxidation couple (III), results in a rapid decrease in the intensity of the Q band and the formation of a pale pink solution. The broad, low-intensity spectrum, shown in Figure 7, is unlike those observed for Co(III) phthalocyanine species^{34,39,40,47,48}, but is very similar in appearance to those reported for the ligand oxidations of phthalocyanines^{21,22,49} to form the Pc cation radical species, $[Pc(-1)]^+$. Since this redox couple is a one-electron process, it must correspond to the one-electron oxidation of the phthalocyanine ring, to give the species $[Co(II)TNPC(-1)]^+$. Similarly, a broadening and lowering of intensity of the bands in the visible region is typically observed for the ligand oxidation in metalloporphyrins.^{2,50-52} The results are in agreement with those of Gavrilov et al.²⁴, who reported the oxidation of Co tetra-4-t-butyl- phthalocyanine in DCB. In contrast, the first oxidation of cobalt tetraphenylporphyrin (CoTPP) in non-coordinating solvents has been shown to occur on the cobalt atom.³⁻⁵

Polarisation of the OTTLE at 200 mV positive of the second oxidation couple (II) results in the formation of a red-brown solution, with a spectrum shown in Figure 7. The broad, three-banded spectrum is typical of those found previously for chemically oxidised CoPc in $CHCl_3$ ⁴⁷ and as a thin film³⁷, and assigned to a $[Co(III)Pc(-1)]^{2+}$ species. Thus, the second oxidation occurs on the metal to give $[Co(III)TNPC(-1)]^{2+}$.

Polarisation of the OTTLE positive of the third oxidation couple (I) gives a decrease in absorption intensity to a broad spectrum with bands centred at 430 and 630 nm, as shown in Figure 7. Re-reduction of this solution positive of couple (III), formed the starting species with ca.

50% loss of the Q band intensity; however the spectrum was identical in shape to the initial spectrum and no decomposition products absorbing in the 300-1600 nm region were observed. To our knowledge, no report has previously been made of a phthalocyanine third oxidation product. In view of the similarity of the potential to that of the second ligand oxidation of H₂TNPc, and the fact that the electronic spectrum (Figure 7) is very different from the Pc(-1) species, it is likely that this is also the second ligand oxidation, to give [Co(III)TNPc(O)]³⁺, rather than [Co(IV)TNPc(-1)]³⁺.

Electrochemistry in DMF Solution

Figure 2(b) shows a typical cyclic voltammogram for CoTNPc in DMF, with half-wave potentials and peak separations at 20 mV/s given in Table I. The reduction processes are very similar to those found in DCB solution, having two quasi-reversible one-electron couples separated by ca. 1.15 V; however, marked changes are seen for the oxidation processes. The reversibility of the first oxidation wave (III) is strongly dependent both upon scan rate and the upper positive limit of the voltage sweep. If the voltage sweep is reversed at a potential negative of the second oxidation couple (II), a broad flat irreversible return wave is obtained at slow sweep rates, which increases in magnitude with increasing sweep rate, as shown in Figure 8(a).

Sweeping the potential positive of the second oxidation potential results in an increase in the return wave for a given sweep rate, although at very slow scan rates (2 mV/s) the return wave is still irreversible (Figure 8(b)). The second oxidation exhibits two anodic and two cathodic waves, as shown in Figure 8(b). At high sweep rates

(Figure 8(c)) (100 mV/s), the more positive wave is dominant, with only a shoulder occurring at ca. +0.3 V, and a single return wave. As the sweep rate is decreased, the contribution from the more negative couple increases, so that the return wave splits into two peaks. Before discussing the significance of these data, it is useful to review the spectro-electrochemical data.

Spectro-electrochemistry in DMF

Controlled potential electrolysis in the OTTLE of a solution of CoTNPc in DMF at 200 mV positive of the first oxidation couple (III) results in the spectroscopic changes shown in Figure 9, and the formation of a blue-green solution. This spectrum, characterised by a red-shift, increase in intensity and sharpening of the Q band and a red-shift of the Soret band relative to the starting spectrum, is similar to those observed for the Co(III)Pc species, $[\text{Co(III)(X)}_2\text{Pc(-2)}]^-$ (X = OH, F, Cl or Br)⁴⁷, $[\text{Co(III)(OH)}_2\text{TNPc(-2)}]^{-34}$, $[\text{Co(III)(CN)}_2\text{Pc(-2)}]^{-39,40,48}$ and $[\text{Co(III)(CN)}_2\text{TNPc}]^{1-}$ (this work). Thus, in DMF solution, the first oxidation (III) indeed occurs on the cobalt rather than the phthalocyanine ring.

Polarisation in the OTTLE at potentials positive of the oxidation couple (II) resulted in a fairly rapid loss of the phthalocyanine absorption. However, the spectrum of the oxidised species was obtained using the bulk cell/Guided Wave spectrometer arrangement. The spectrum was very similar to that of the second oxidation in DCB (see Table II), albeit with the bands red-shifted by 50 - 90 nm with respect to DCB solution. Thus couples (III) and (II) in DMF correspond to the

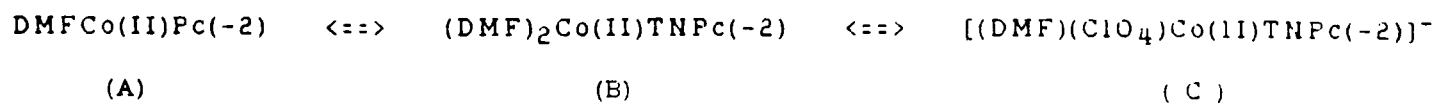
formation of $[\text{Co(III)TNPc(-2)}]^+$ and $[\text{Co(III)TNPc(-1)}]^{2+}$, respectively.

The binuclear cobalt phthalocyanines gave essentially similar spectro-electrochemistry to CoTNPc. The spectra of the redox products were those expected for complete oxidation or reduction of the two CoTrNPc units at each redox couple, with no evidence for the formation of any mixed valence states. As an example, the spectrum of the second reduction product of O(1)[CoTrNPc]_2 is shown also in Figure 6. Of note, the absorption of the ligand reduced species was rather more broad in the binuclear complexes, probably as a consequence of coupling.³⁴

Discussion of Electrochemical Behaviour in DMF

The bulk solute in DMF is expected to be the five coordinate DMFCo(II)TNPc(-2) based upon earlier studies which show the prevalence of five coordinate Co(II)Pc species.⁵³

Since the axial site is expected to be labile, there will be other species in equilibrium. The most important are likely to be:-

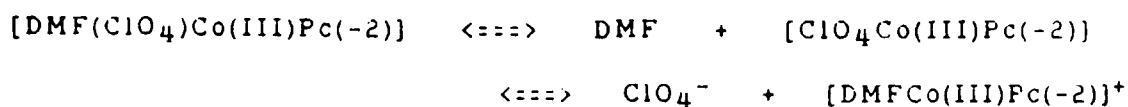


(1)

One may readily predict that species (C) will oxidise at the least positive potential.¹⁸ Thus in Figure 8 the anodic wave (IIa) corresponds to oxidation of species (C), formed very rapidly at the electrode in a CE reaction. Given that the $\text{ClO}_4^-:\text{Co(II)TNPc}$ ratio is so large, and that there is an axial site vacant on the phthalocyanine, the rate of perchlorate ion incorporation is probably diffusion

controlled.

When the switching potential lies between couples (II) and (III), the cathodic wave corresponding to (IIIa) diminishes in current quite dramatically with slower scan rate, and the ratio i_c/i_a is considerably less than unity (Table III). At higher scan rates, this ratio equals unity. Thus the couple is irreversible at very slow scan rates. These ratios are subject to some uncertainty given the close proximity of the next redox couple, so that calculation of rate constants therefrom would be unreliable. We note that, at a given scan rate, the i_c/i_a ratio increases with increasing perchlorate ion concentration, supporting the view that species (C) is involved as proposed. The product on the electrode after oxidation is the six coordinate $[\text{DMF}(\text{ClO}_4)\text{Co(III)TNPC}(-2)]$. This will participate in an equilibrium (2) in which either the DMF or perchlorato groups are lost to form a five coordinate species which is much more readily reducible to Co(II) than is the six coordinate species and thus has a redox potential positive of couple (III).



(2)

Although this five coordinate Co(III) species is likely to be formed in only minute amounts, the equilibrium should be sufficiently facile that during the time of the cathodic sweep positive of couple (III), some of the Co(III) species on the electrode is reduced and therefore does not contribute current to cathodic wave (IIIc). Clearly the slower the sweep, the greater the loss in cathodic current in (IIIc). Previous studies⁵⁴ show that although axial substitution of six coordinate Co(III) species is usually very slow indeed, axial sites on Co(III)

macrocycles are more labile.

Beyond (IIIa) the next process is oxidation to $[\text{DMF}(\text{ClO}_4)\text{Co}(\text{III})\text{TNPC}(-1)]^+$ reasonably associated with the major oxidation peak (IIa). Although in the spectro-electrochemical experiment, this species is unstable, it is evidently sufficiently stable in the much shorter time frame of the cyclic voltammetry experiment. There are two clearly identifiable cathodic peaks whose relative intensity changes with scan rate (Figure 8b). With increasing scan rate the more positive wave (IIc) grows at the expense of the less positive wave (II'c), and vice versa at slower scan rates. Moreover with increasing perchlorate ion concentration (0.1 - 0.3M), the less positive wave grows slightly, at the expense of the more positive wave. The most positive reduction wave, (IIc), must correspond with the reduction of $[\text{DMF}(\text{ClO}_4)\text{Co}(\text{III})\text{TNPC}(-1)]^+$. Wave (II'c) must involve additional perchlorate ion and is reasonably associated with reduction of $[(\text{ClO}_4)_2\text{Co}(\text{III})\text{TNPC}(-1)]$ formed by a slow substitution of DMF by perchlorate ion in $[\text{DMF}(\text{ClO}_4)\text{Co}(\text{III})\text{TNPC}(-1)]^+$.

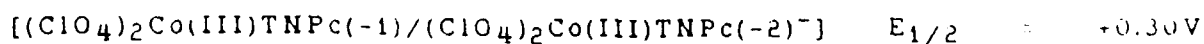
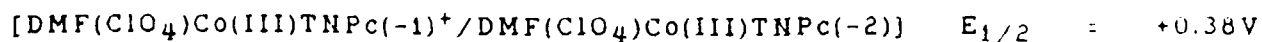
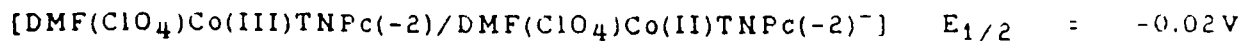
On the anodic component of couple (II), there is a very weak lower potential shoulder which is more evident at slow scan rates (Figure 8(b)) and is marginally enhanced by increasing perchlorate ion concentration. This is likely to be the anodic partner to (II'c) formed by very slow substitution of DMF by perchlorate ion in $[\text{DMF}(\text{ClO}_4)\text{Co}(\text{III})\text{TNPC}(-2)]$ formed on the electrode surface. The redox couple for the bis-perchlorato species (II') lies at a (slightly) lower potential than for the mono-perchlorato species, as would be anticipated because of the extra charge disposed onto the cobalt ion.¹⁸

When the switching potential is positive of couple (II), the cathodic return wave for couple (III) is not diminished except at

exceptionally slow scan rates, the i_c/i_a ratio remaining unity. Assuming that the above mechanism for irreversibility is correct, it follows that the species now on the electrode must be different from the previous switching situation and must dissociate a ligand rather more slowly. Indeed at the slow scan rates necessary to observe this phenomenon, the species on the electrode when switched beyond couple (II), will be $[(ClO_4)_2Co(III)TNPc(-2)]^-$ which must then have a slower dissociation rate. This bis-perchlorato species would be expected to have a somewhat less positive reduction potential than the $[DMF(ClO_4)Co(III)TNPc(-2)]$ species, yet this appears experimentally not to be the case. Possibly the difference is too small to be evident.

Previously, Kelly and Kadish¹² had shown that $DMF(Cl)Cr(III)TPP$ and $[(DMF)_2Cr(III)TPP]^+$ both reduce at the same potential, in DMF, and explain this by assuming that a CE reaction occurs, with chloride being replaced by DMF at the electrode in a reaction driven by the applied potential. This is the same argument being used here to infer which cobalt species is active at each couple.

Thus, in summary, the species involved in the region of couples (II) and (III) are (vs Fc^+/Fc):-



The overall redox behaviour is shown in Scheme I.

Rationalisation with the Literature.

There are scattered reports of the spectra of phthalocyanine anion and cation radical species in the literature, as referenced above, but this is the first study where the spectra of one species have been followed through seven oxidation states. Cation radical spectra have only rarely been reported in the solution state.

It is tempting to try to assign the spectra of the various oxidation species reported here and compare the data with those for related materials in the literature. Indeed we have previously predicted the type of spectra to be anticipated for metallo-phthalocyanines in various oxidation states⁴⁶; however, in the absence of supporting data such as MCD⁴⁹, it would be foolhardy to try and assign, in any detail, the rather broad and overlapping bands commonly observed for these various species (e.g. Figure 7).

Phthalocyanine cation radical (Pc(-1)) spectra are now known for a range of metal ions including Co(II), Co(III), Ru(II), Rh(III), Fe(III), Cr(III), Zn(II), Si(IV), H₂, Mg and Cu(II).^{21,22,37,46,47,49,55,56} These all appear to show medium intensity bands near 700-800nm and near 500nm. The former is assigned as a transition from a lower lying e_g π level into the hole in the HOMO π level.^{46,49,55} Charge transfer spectra from metal d levels to the hole in the HOMO level can be anticipated, but have not been identified.⁴⁹

The voltammetry of H₂TNPc and CoTNPc is summarised and compared with that of H₂TPP³,^{9,11,15,16,57-59} and CoTPP^{3-8,15,16,58} in the form of a redox potential state diagram in Figure 10. Complexation with cobalt (II) causes a negative shift in the potential of the first ligand reduction by ca. 500 mV in non-coordinating solvents for both

TNPc and TPP (Figure 10), as a result of the insertion of the cobalt d orbitals between the HOMO and LUMO orbitals of the ring. The potential of the first ligand oxidation also shifts negatively, but to a lesser extent, resulting in a net increase in separation between the first oxidation and reduction couples ($E[L^+/L] - E[L/L^-] = 2.1$ and 2.9 V for CoTNPc and CoTPP, respectively).^{3-5,7,8,58} Notably, the L/L^- , Co(II)/Co(I) and Co(III)/Co(II) couples of CoTNPc and CoTPP lie at similar potentials in non-coordinating solvents (Figure 10). For both compounds, the Co(II)/Co(I) couple lies positive of the first ligand reduction, so that the cobalt is reduced first. However, differences are seen in the oxidation processes. For CoTNPc, the separation between the HOMO and LUMO orbitals of the ring is small enough to leave the L^+/L couple negative of the Co(III)/Co(II) couple, so that oxidation occurs at the ring first. For CoTPP, however, the larger separation of the HOMO and LUMO orbitals results in the L^+/L couple lying positive of the Co(III)/Co(II) couple, even in non-coordinating solvents. The relative positions of the cobalt d orbitals and TNPc HOMO also results in a large increase in separation of the first and second ligand oxidations compared with the metal-free complex, while for porphyrins a small decrease in separation of the couples is seen.^{4,5,7,11,15,16}

In DMF, the Co(III)/Co(II) couple of CoTNPc shifts negatively by ca. 600 mV, as a result of the stabilisation of the Co(III) species in the presence of the axially coordinating solvent, while the L^+/L couple shifts positively by 300 mV, as a consequence of the presence of the highly polarising central ion (Co(III)).⁶⁰ Thus, the first oxidation now occurs at the cobalt atom. Similarly, the Co(III)/Co(II) couple shifts negatively by almost 800 mV for CoTPP on going from DCM to DMF solution.⁴ The potential of the Co(II)/Co(I) couple remains

approximately constant, as expected for the four-coordinate Co(I) species.

Data for the binuclear species are somewhat disappointing given that they differ little from the mononuclear analog. The binuclear species are significantly, but not dramatically, more efficient for oxygen reduction²⁶, than the mononuclear control. More tightly coupled binuclear phthalocyanines are currently under investigation.

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Legends

Figure 1. Binuclear phthalocyanine compounds.

Figure 2. Cyclic voltammetry of CoTNPc (a) in DCB solution (Pt working electrode) and (b) in DMF solution (Pt wire working electrode). Scan rate = 50 mV/s, [CoTNPc] = 1×10^{-4} M, [TBAP] = 0.3M.

Figure 3. Differential pulse polarograms of (a) CoTNPc and O(1)[CoTrNPc]₂ in DCB solution (0.3M TBAP). Scan rate = 2 mV. [CoTNPc] = 1×10^{-4} M, [O(1)[CoTrNPc]₂] = ca. 5×10^{-5} M.

Figure 4. Electronic absorption spectra of Co(II)TNPc(-2) (—), EtMeO(5)[Co(II)TrNPc(-2)]₂ (----), and C(2)[Co(II)TrNPc(-2)]₂ (....) in [[Pc] x pathlength = constant]

Figure 5. Development of the electronic absorption spectra with time during the reduction of Co(II)TNPc(-2) at -1.1V vs Fc⁺/Fc in DCB (0.3M TBAP). [CoTNPc] = 1.2×10^{-4} M.

Figure 6. Electronic absorption spectra of electrochemically generated [Co(I)TNPc(-3)]²⁻ (—) and O(1)[Co(I)TrNPc(-3)]₂⁴⁻ (----) in DCB (0.3M TBAP). [CoTNPc] = 9×10^{-5} M, [O(1)[CoTrNPc]₂] = 4×10^{-5} M.

Figure 7. Electronic spectra of electrochemically generated [Co(II)TNPc(-1)]⁺ (----), [Co(III)TNPc(-1)]²⁺ (....) and [Co(III)TNPc(0)]³⁺ (—) species in DCB (0.3M TBAP). [CoTNPc] = 5×10^{-5} M.

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Figure 8. Cyclic voltammetry of CoTNPc in DMF (0.3M TBAP) at various scan rates and switching potentials. (a) The Co(III)/Co(II) couple at 2,5,10 and 20 mV/s, (b) Pc(-1)/Pc(-2) and Co(III)/Co(II) couples at 2,5,10 and 20 mV/s, and (c) Pc(-1)/Pc(-2) and Co(III)/Co(II) couples at 20,50 and 100 mV/s. [CoTNPc] = 1×10^{-4} M.

Figure 9. Development of the electronic absorption spectra with time during the oxidation of Co(II)TNPc(-2) at +0.2V vs Fc⁺/Fc in DMF (0.3M TBAP). [CoTNPc] = 2.3×10^{-4} M.

Figure 10. Summary of the electrochemistry of H₂TNPc and Co(II)TNPc(-2) comparison with H₂TPP and CoTPP.

Table I. Electrochemical Data for Mononuclear and Binuclear Neodentoxy
phthalocyanines.

Compound	$E_{1/2}$ V. (ΔE_p , mV) ^a				
	Oxidation			Reduction	
	I	II ^c	III	IV	V
H ₂ TNPc	+0.77		+0.28	-1.35	-1.70 (70)
CoTNPc	+0.87 (102)	+0.59 (90)	+0.03 (89)	-0.91 (70)	-2.07 (80)
CoTNPc ^b		+0.38 ^d	-0.02	-0.85 (85)	-1.99 (85)
EtMeO(5)[CoTrNPc] ₂	+0.87	e	+0.05 (165)	-0.93	-2.07 (85)
CaT(4)[CoTrNPc] ₂	+0.89	e	+0.03	-0.93	-2.07 (95)
C(2)[CoTrNPc] ₂ ^f	+0.87	+0.33	+0.03	-0.94	-2.07
O(1)[CoTrNPc] ₂ ^f	+0.91	+0.51	+0.04	-0.93	-2.07

^aDCB solution except for ^bDMF solution. Potentials are reported with respect to the ferrocenium/ferrocene couple. $E_{1/2}$ measured by cyclic voltammetry at 100, 50 and 20 mV/s [$E_{1/2} = (E_{pa} + E_{pc})/2$] or differential pulse polarography at 2 mV/s gave essentially identical potentials. Values of ΔE_p (= $E_{pa} - E_{pc}$) are given for a potential sweep rate of 20 mV/s. See text for assignment of couples I-V. ^cThe potential of this couple in DCB is very sensitive to traces of coordinating anions. ^dWeak shoulder at 0.30V, see text, labelled couple (II'). ^eNot resolved. ^fAdditional weak waves are seen at -1.36 and -1.7V as a consequence of aggregation.



Table II Electronic Absorption Maxima of CoTNPc Species

Species ^a	λ_{max} , nm ($\epsilon \times 10^{-4} \text{M}^{-1} \text{cm}^{-1}$)									
[Co(I)TNPc(-3)] ²⁻	315 sh	345 sh	480 (3.53)	520 sh	560 sh	640 (1.13)	703 (2.35)	955 (0.32)		
[Co(II)TNPc(-2)] ⁻	313 (5.79)	350 sh	435 sh	520 sh	560 vw	600 sh	643 (1.84)	675 sh	708 (4.50)	
[Co(III)TNPc(-2)]	330 (4.07)	380 (1.38)					612 (2.57)	645 sh	678 (7.21)	
[Co(III)TNPc(-1)] ⁻	320 sh	360 sh	405 sh	495 (1.40)	590 sh	620 (1.64)br		636 (1.76)		
[Co(III)TNPc(-1)] ²⁻	320 sh	380 (2.36)	400 (2.40)	520 (1.66)		580 sh		742 (1.15)		
[Co(III)TNPc(0)] ³⁻	330 sh	430 br, sh				620 br				
[Co(III)TNPc(-2)] ^b	326 (8.51)	380 sh				606 (3.89)		668 (10.96)		
[Co(III)TNPc(-2)] ^{-b}	340 sh	355 (6.31)				610 (3.72)		676 (14.79)		
[Co(III)TNPc(-1)] ^{2-b}	405 s		600 m			680 s		795 m		
[Co(III)(CN) ₂ TNPc(-2)] ^{-c}	355 sh	370 m	440 sh			610 w	645 sh	678 s		

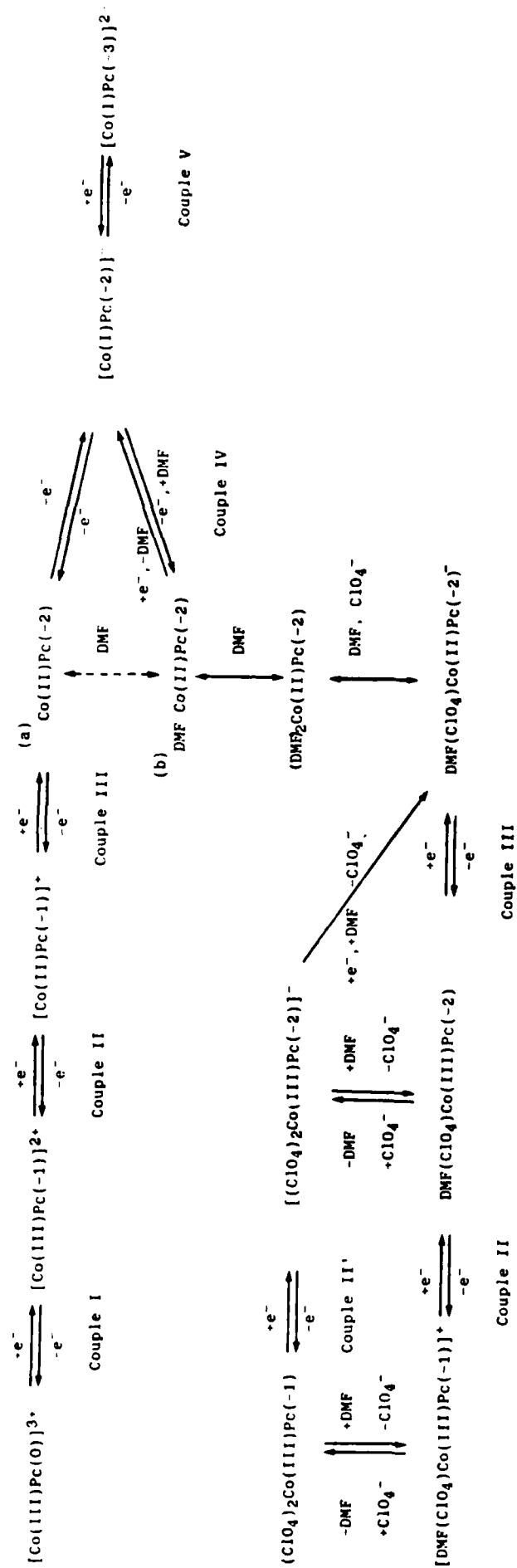
^aIn DCB solution with 0.3 M TBAP except for 0.3M TBAP and $\text{C}_6\text{H}_5\text{CN}$ solution. [CoTNPc] = 2×10^{-4} M. Note that at these concentrations of pthalocyanine and electrolyte substantial aggregation of the Co(II)TNPc(-2) species occurs. Values of λ_{max} ($\epsilon \times 10^{-4} \text{M}^{-1} \text{cm}^{-1}$) for $< 10^{-5}$ M Co(III)TNPc(-2) in pure DCB are 330 (6.54), 382 (2.49), 612 (3.45), 645 sh and 678 (13.5), nm.

br = broad, sh = shoulder, vw = very weak, m = medium, s = strong

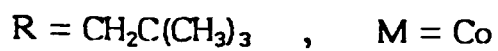
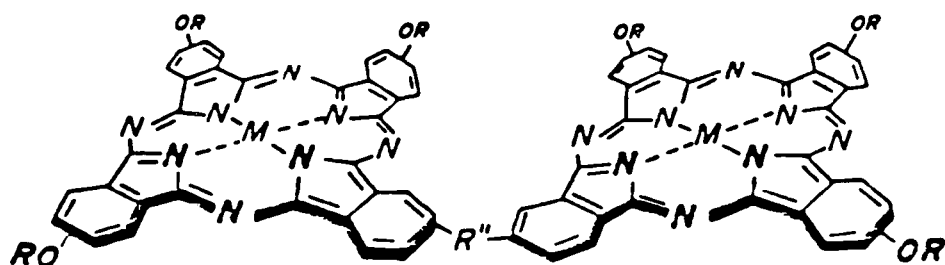
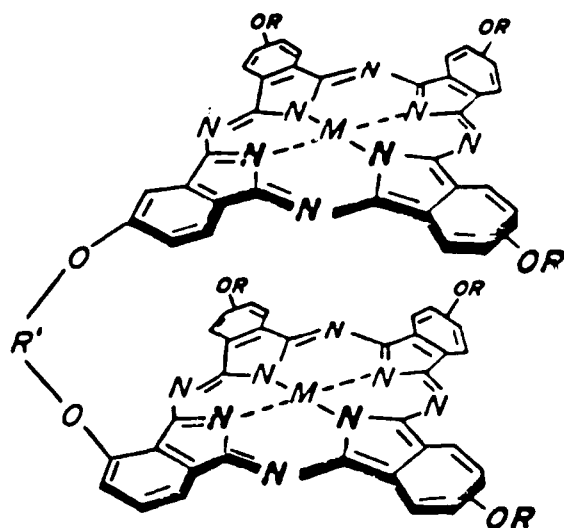
 Table III Cathodic - Anodic Peak Ratios for CoTNPc Redox Couple III in DMF Solution at Various Scan Rates.^a

Scan Rate	[TBAP]	i_c/i_a	[TBAP]	i_c/i_a
10 mV/s			0.3 M	0.78
20 mV/s	0.1 M	0.76	- 0.3	0.81
50	0.1	0.77	- 0.3	0.83
100	0.1	0.82	- 0.3	0.86
200	0.1	0.87		
500	0.1	1.00		

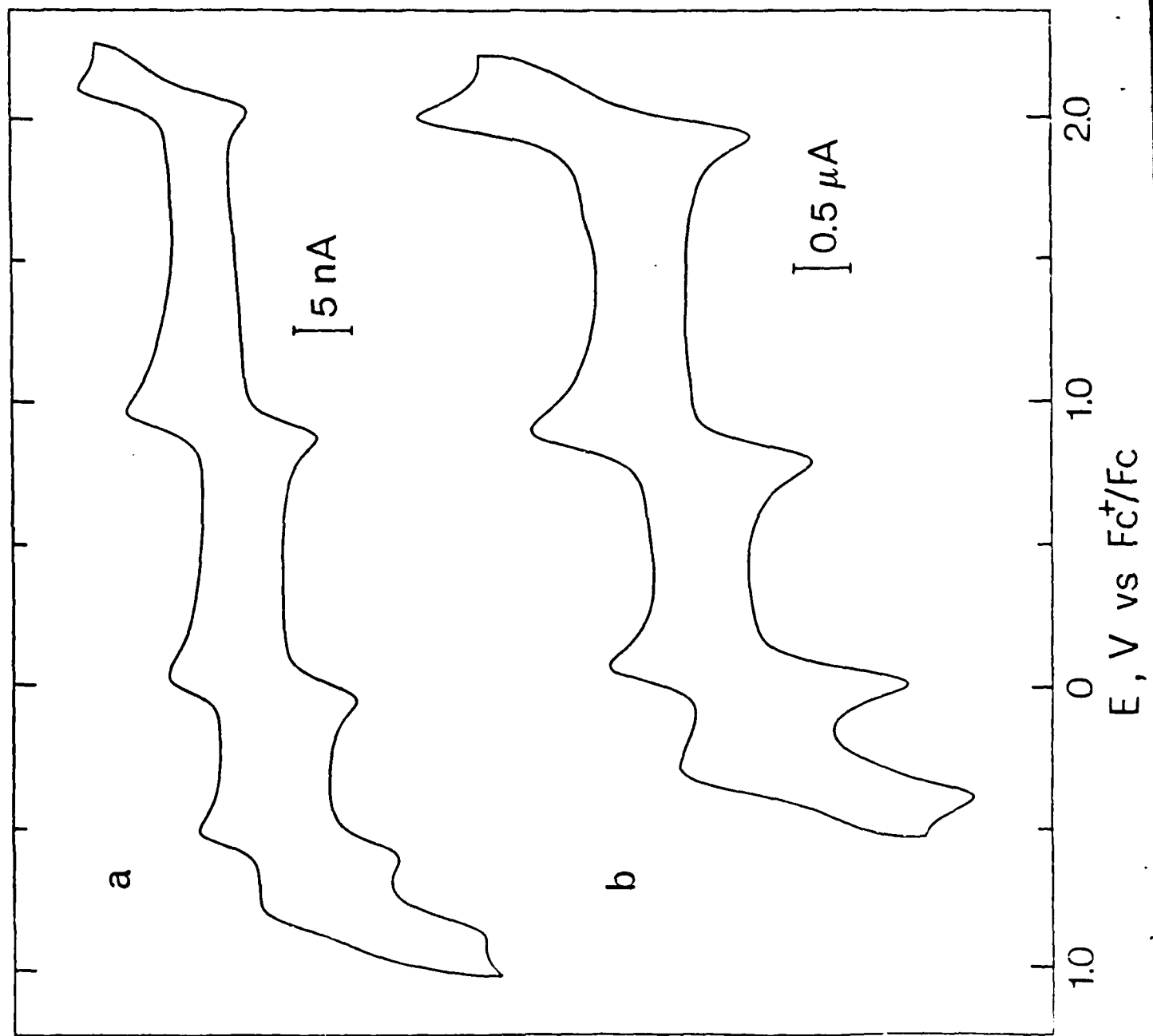
^a[CoTNPc] = 1×10^{-4} M. Positive switching potential lies between couples II and III.

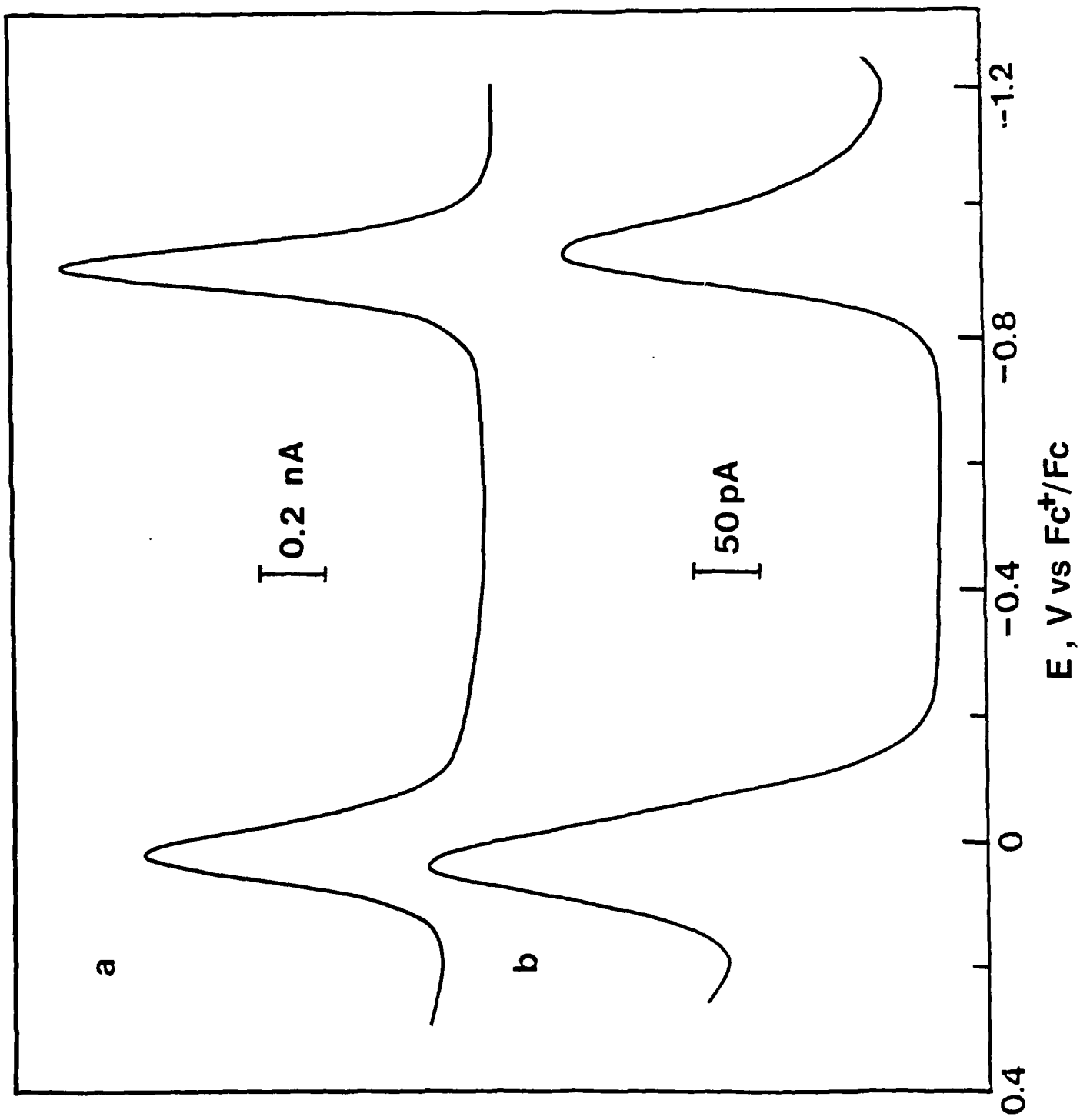


Scheme 1. Redox equilibria of CoTPc: (a) in DCB solution, (b) in DMF solution (Pc-TNpc).

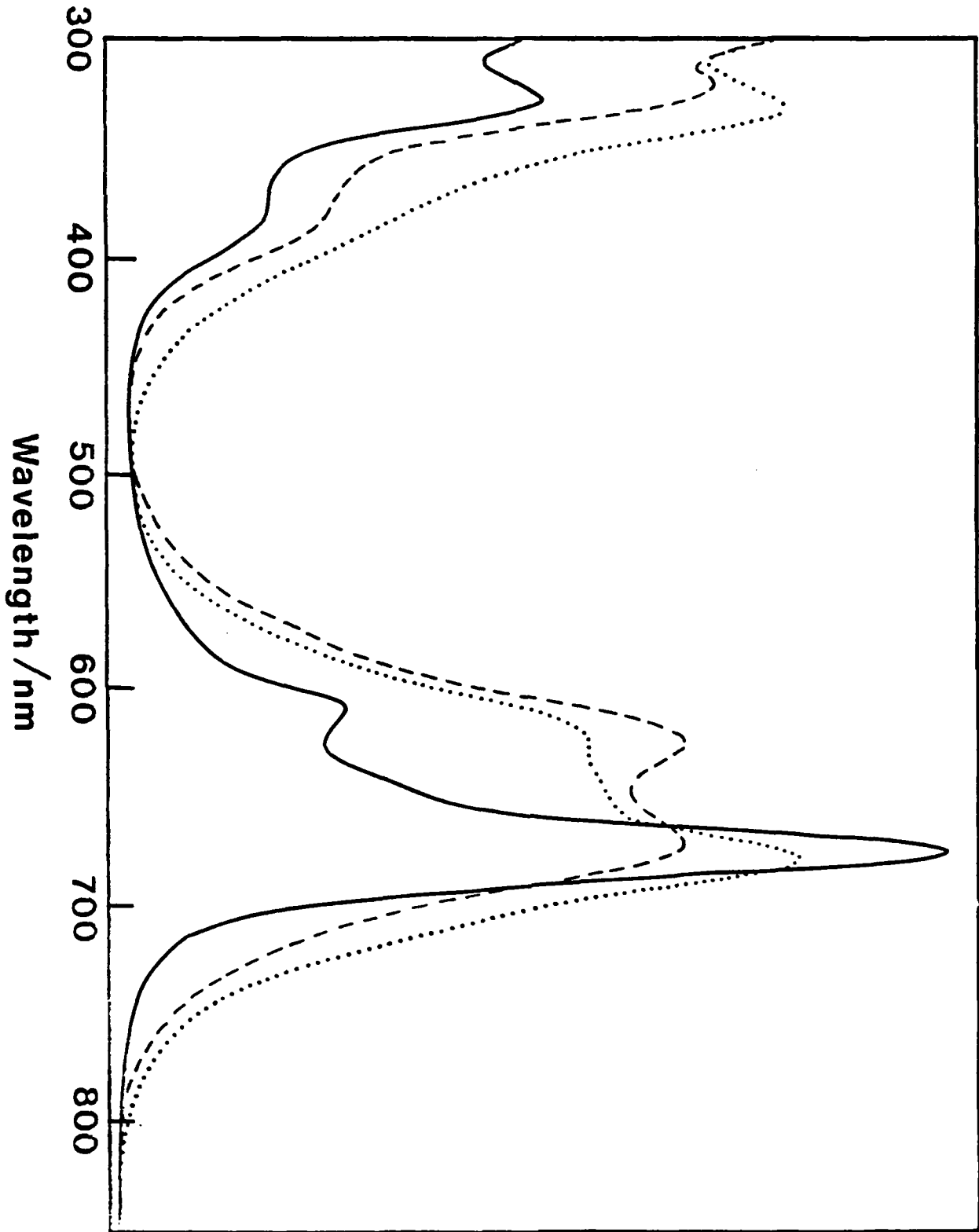


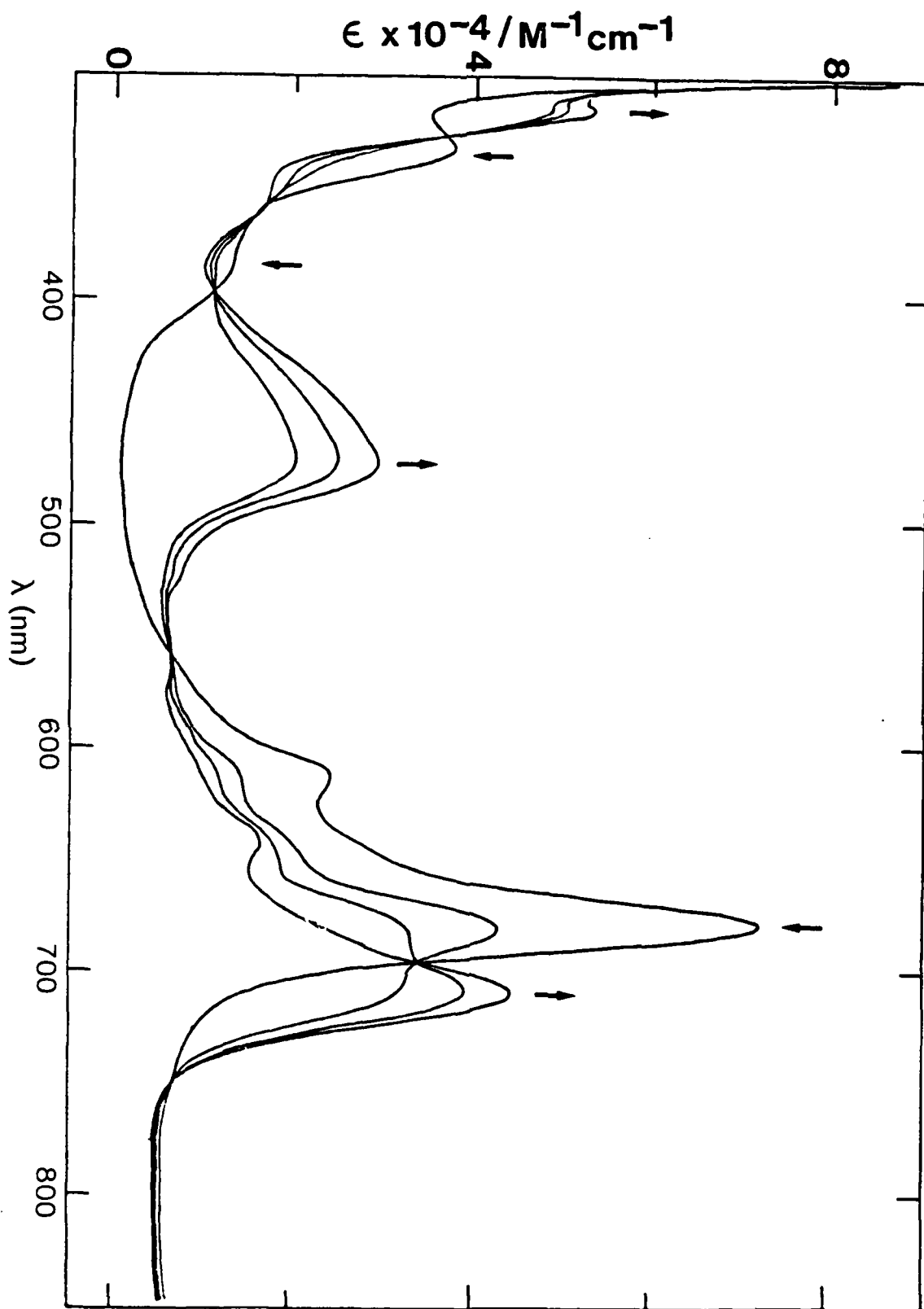
- A
- EtMeO(5) [CoTrNPc]₂, $R' = \text{CH}_2\text{C}(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{CH}_2$
- Cat(4) [CoTrNPc]₂, $R' = \text{o-phenylene}$
- B
- C(2) [CoTrNPc]₂, $R'' = \text{CH}_2\text{CH}_2$
- O(1) [CoTrNPc]₂, $R'' = \text{O}$



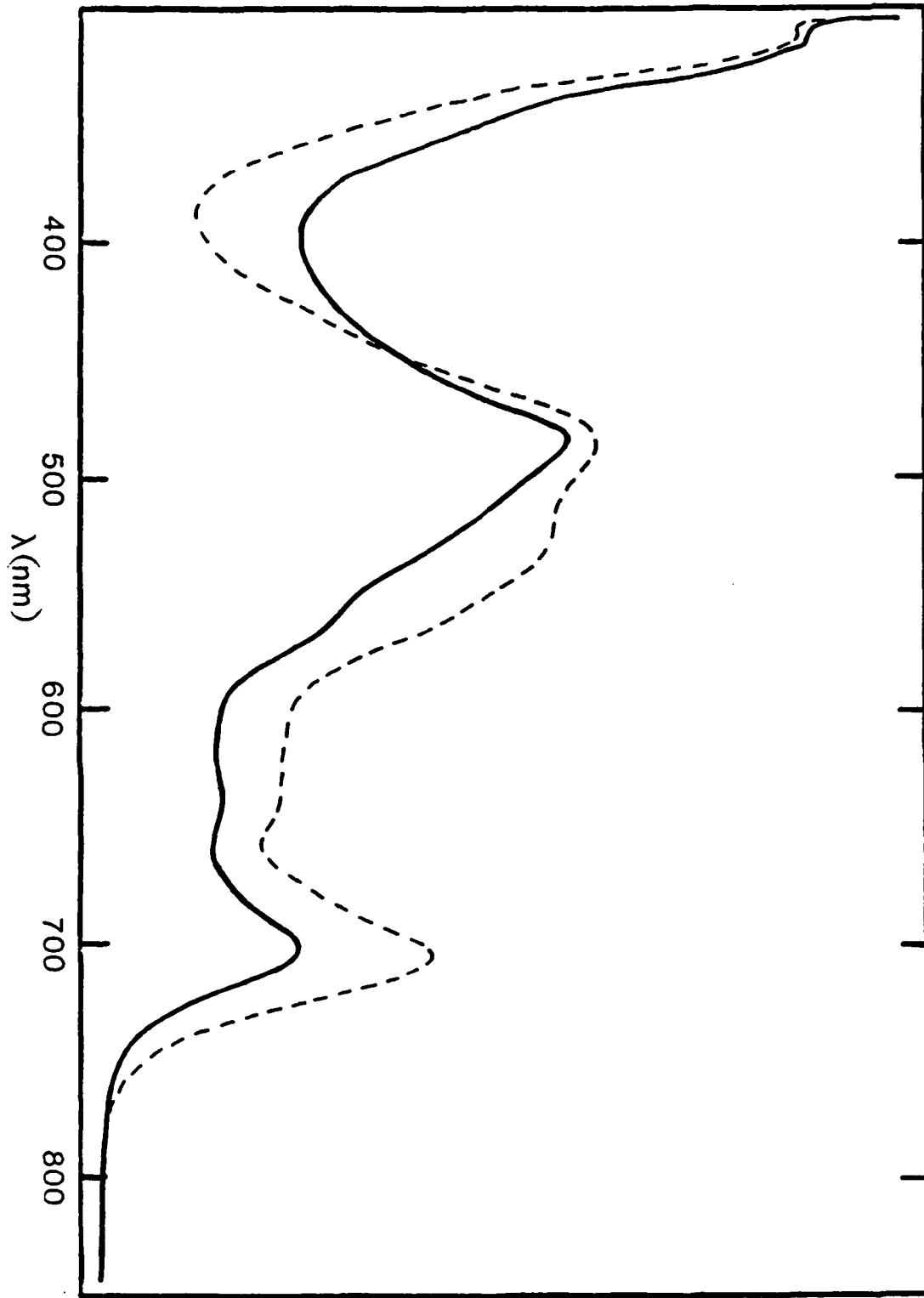


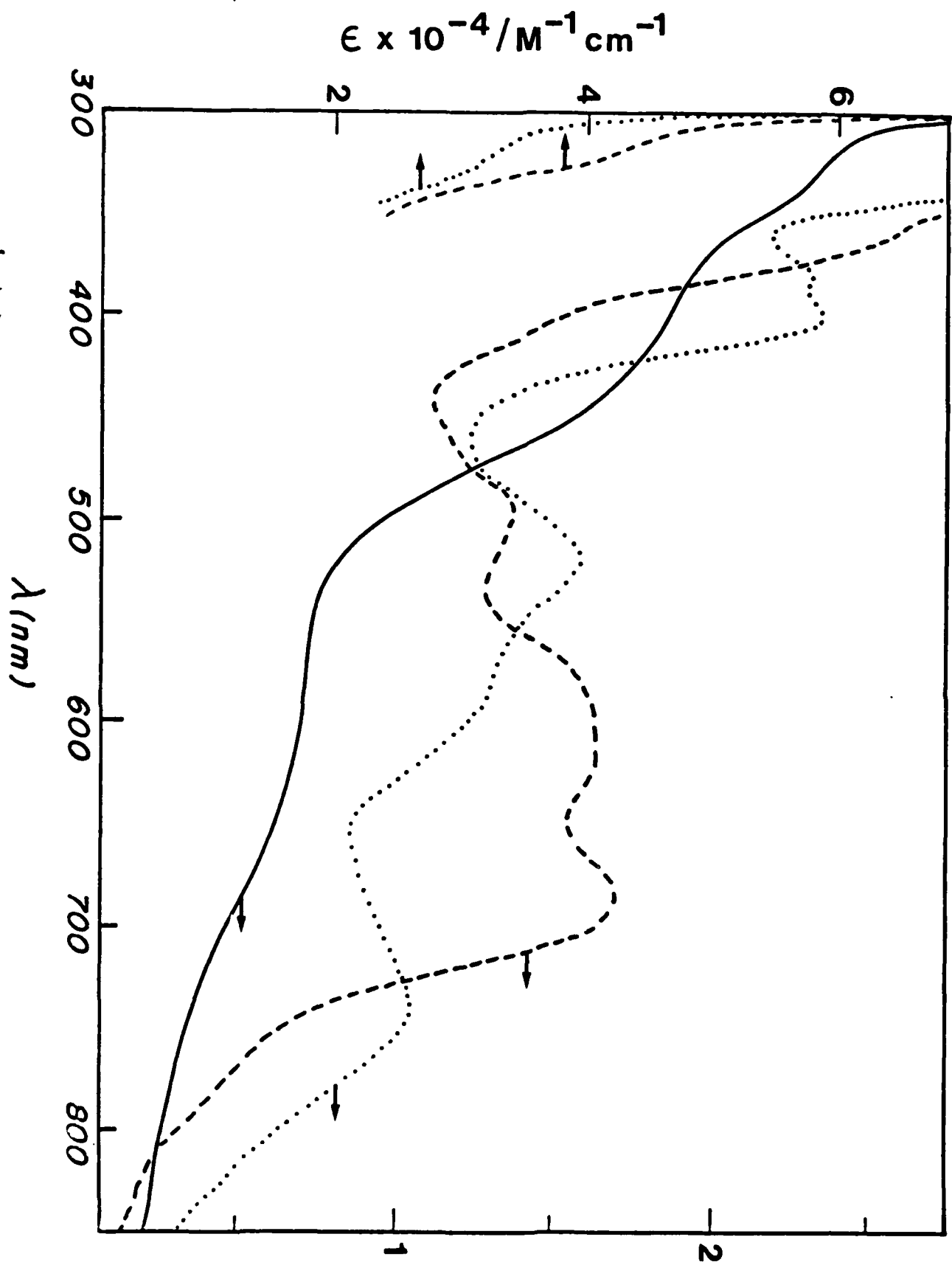
Absorbance

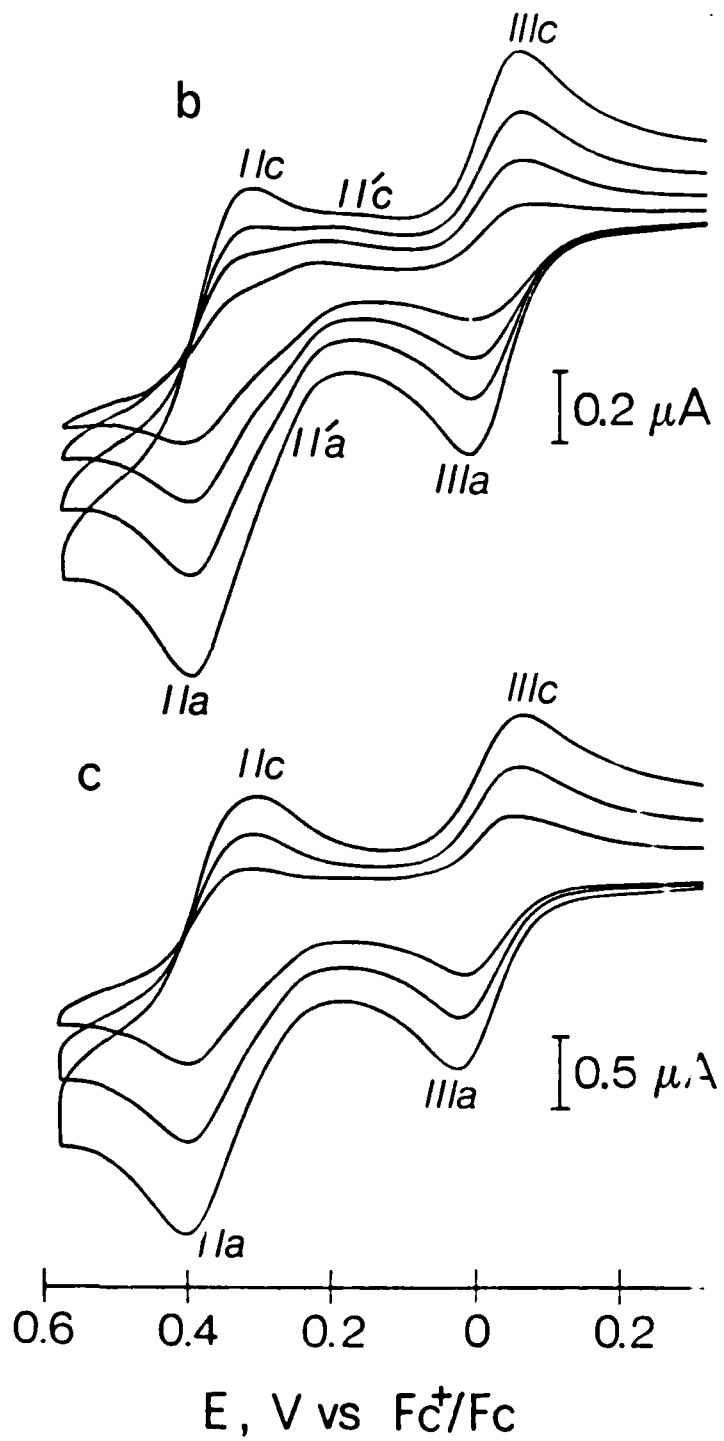
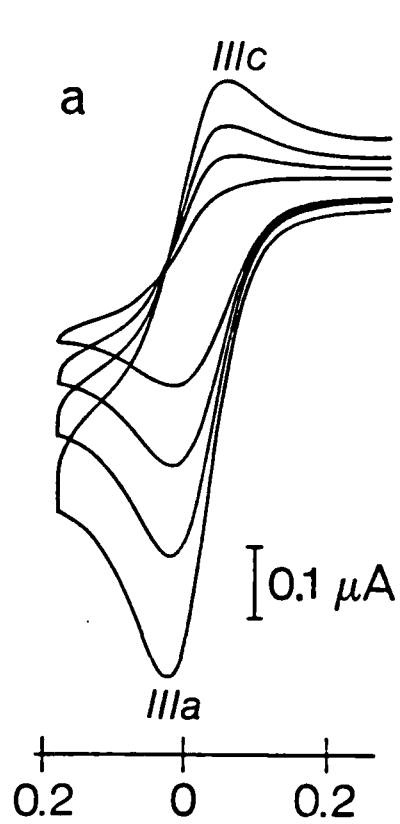


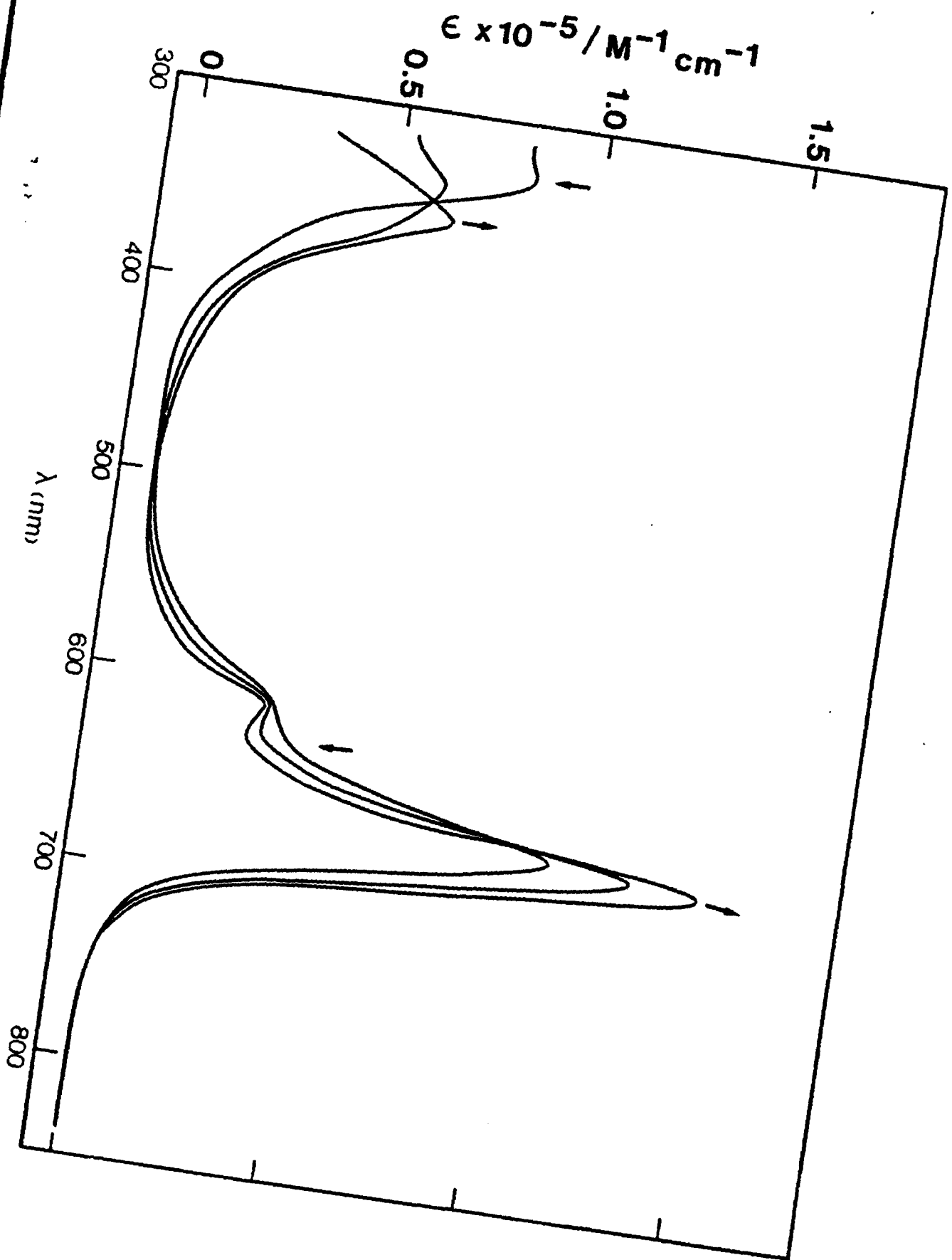


Absorbance

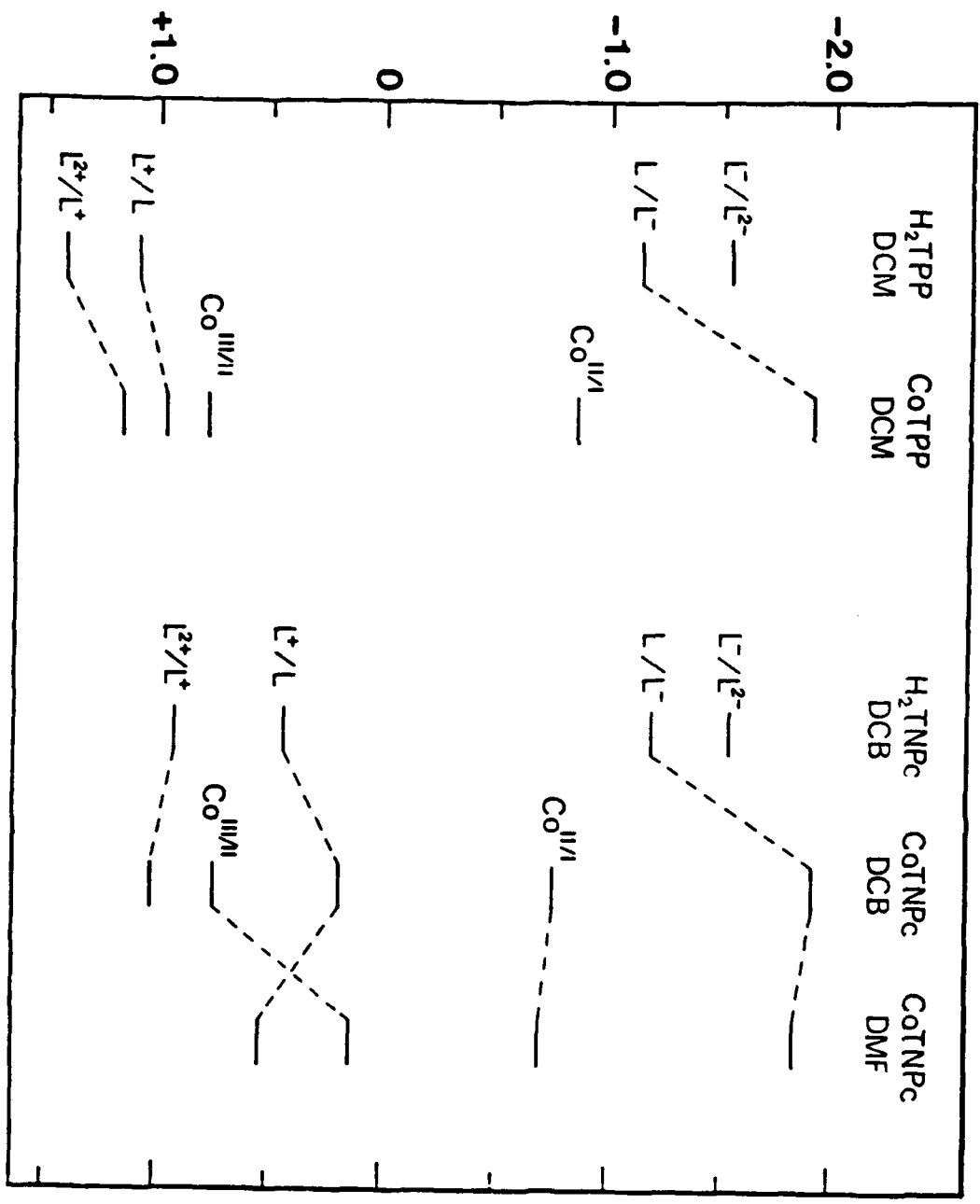








E, V vs SCE



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