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Charge Transfer Interactions of Zinc^{II} Tetraneopentoxyphthalocyanine with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Charge transfer interactions of zinc^{II} tetraneopentoxyphthalocyanine (ZnTnPc(2−)) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were investigated electrochemically and spectroscopically. DDQ oxidizes ZnTnPc(2−) by one electron to its cation radical, $[ZnTnPc(1-)]^+$, and is reduced to the semiquinone form, $[DDSq(1-)]^-$. A redox series of species were investigated by controlled-potential reduction and spectroelectrochemical methods. The possible existence of [ZnTnPc(1−)·DDSq(1−)], $[ZnTnPc(2-)\cdot DDSq(1-)]^-$, $[ZnTnPc(-2)\cdot DDCat(2-)]^{2-}$, and $[ZnTnPc(3-)\cdot DDCat(2-)]^{3-}$ is discussed. UV–vis, ESR, FTIR, cyclic and differential pulse voltammetry, and spectroelectrochemical data are presented. Bonding between the zinc metal of the phthalocyanine and the cyanide nitrogen of the quinone is proposed on the basis of AM1 calculations.

Introduction

Although charge transfer complexes involving porphyrins and phthalocyanines have been studied since the early 1960s,[1–4] it was not until the 1980s that the subject began to receive widespread attention.[5–16] Interest in the topic has largely been stimulated by the possibility to use these complexes as new semiconductive materials,[17] photocatalysts,[18] chemical gas sensors,[19,20] etc. While in a few cases the macrocyclic compounds were used as electron-accepting materials,[8,12,21] in most cases they acted as electron donors. Many acceptors have been employed to form charge transfer complexes with the phthalocyanines and porphyrins, including iodine,[5,11,22,23] chloride,[24] chloranil,[1,2] 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[25,26] trinitrofluorenone,[4] and others.[10,15,27] Surprisingly, although widely used as an acceptor in charge transfer interactions, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) has not been reported previously to complex with either phthalocyanines or porphyrins probably because of its extremely high electron-accepting ability. Maitrot et al.[14] prepared a film containing DDQ and bis(phthalocyaninato)-lutetium (Pc_2Lu) using a cosublimation technique and reported an increase of the film conductivity due to a p-type doping of the DDQ.

Among the many phthalocyanines, e.g. metal-free,[1,22] nickel,[2,5] manganese,[12,27] copper,[7,13] cobalt,[11,15] and palladium,[23] used for studying charge transfer interactions, zinc phthalocyanines (ZnPc) have received the most attention.[4,8,10,17,28–30] The zinc^{II} ion normally does not undergo any redox process, and hence ZnPc has frequently been chosen as a candidate for the study of ligand-related redox processes. Zinc phthalocyanines have been studied for their semiconductive,[17] photosensitive,[28,31] and gas-sensitive[32] properties. Kasuga et al.[29,30] recently reported the oxidation of ZnPc by DDQ, but to our knowledge, the formation of a complex between a ZnPc and DDQ has not been reported.

We have studied the charge transfer interaction between zinc^{II} tetraneopentoxyphthalocyanine (ZnTnPc(2−)) and DDQ, as a function of oxidation state of both species, seeking spectroscopic and/or electrochemical evidence for the possible existence of complexes between DDQ and ZnTnPc(2−) in their various oxidation states. $[DDSq(1-)]^-$ and $[DDCat(2-)]^{2-}$ are abbreviations for the first and second reduction products of DDQ.

Definitive evidence is presented for the formation of $[ZnTnPc(-2)\cdot DDCat(2-)]^{2-}$ and $[ZnTnPc(3-)\cdot DDCat(2-)]^{3-}$. A compound analyzing as [ZnTnPc(1−)·DDSq(1−)] contains the individual units, as described, but it is not possible to determine whether the two units are connected by a coordinate bond or if the species exists as a simple ion pair. No definitive evidence could be found for the existence of $[ZnTnPc(2-)\cdot DDSq(1-)]^-$ in solution.

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Experimental Section

Materials. (2,9,16,23-Tetraneopentoxyphthalocyaninato)zinc (ZnTnPc(2–)) was prepared following literature methods.[33,34] 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich) was recrystallized from a mixture of chloroform and dichloromethane (4:1), dried under vacuum at about 70 °C for 24 h, and then stored in a desiccator. Tetrabutylammonium perchlorate (TBAP, Kodak) was recrystallized from absolute ethanol and vacuum-dried at 50 °C for 2 days. 1,2-Dichlorobenzene (DCB, Aldrich, Gold Label, sealed under N_2) was used as supplied.

Spectroscopic and Electrochemical Methods. Solution electronic spectra were measured with a CARY 2400 UV–vis–near-IR spectrometer. Solid-state UV–vis spectra were collected with a Guided Wave Inc. Model 100 spectrum analyzer using a Nujol mull sample on either a KBr plate or quartz microslide. ESR spectra were recorded in the X-band frequency range with a Varian E4 EPR spectrometer calibrated with diphenylpicrylhydrazyl (DPPH). FTIR data were collected as KBr pellets or Nujol mulls on KBr window using a Nicolet 20SX instrument. Linear potential cyclic and differential pulse voltammetries were performed with a Princeton Applied Research (PARC) Model 173 potentiostat controlled by a PARC 175 universal programmer, and a PARC 174A polarographic analyzer. High scan rate cyclic voltammograms were recorded with a Cypress CS-1090-UPG computer-controlled electroanalysis system, software version 5.0. Rotating disk electrode (RDE) experiments were carried out with a PINE Instruments PIR rotator controlled either by the PARC Model 173 potentiostat or PINE Instruments RDE3 potentiostat. An optically thin cell[35] was used to collect spectroelectrochemical data with the CARY 2400 spectrometer and either the PARC or the PINE electrochemical system. Spectra were taken at potentials which were stepped with a magnitude of 50 mV in peak areas, and 100 or 200 mV in off-peak areas depending upon whether it was near off or far off. Normally, since the cell is very thin (about 0.25 mm thickness), 3–5 min was long enough to complete a bulk electrolysis at a specific potential; spectra were therefore usually recorded about 5 min after the potential had been stepped and when no further change in spectrum was occurring.

Electrochemical data were collected with the usual three electrode setup, either under an atmosphere of N_2 within a Vacuum Atmospheres Drilab or with O_2-free Ar bubbling. At least 45 min was allowed for the Ar bubbling before any electrochemical data were collected. All potentials are reported against a AgCl/Ag/acetonitrile (MeCN) (saturated with AgCl) reference separated from the bulk solution by a glass frit. Cyclic voltammograms of the internal standard ferrocenium/ferrocene (Fc^+/Fc) couple were also obtained under the same experimental conditions.

Mixed solutions of ZnTnPc(2–) and DDQ with various molar ratios in DCB were generally prepared from stock ZnTnPc(2–) and DDQ solutions of about 10^{-4} M.

Preparation of ZnTnPc(2–)·DDQ complex. ZnTnPc(2–) (60.8 mg, 0.0659 mmol) was dissolved completely in dry benzene (15 mL) with stirring for 15 min. To the solution was added DDQ (30.7 mg, 0.135 mmol). The solution was stirred under Ar for 20 min at room temperature, transferred into a centrifuging tube, and then put into a refrigerator for half an hour. The frozen solution was warmed up at room temperature for about an hour, and the solution phase was removed by centrifuging. The remaining solid was washed with benzene/hexane (1:1 in vol) mixture four times, and finally dried under vacuum at about 75 °C for 3 days. Yield: 45 mg, 60%. Anal. Calcd for the 1:1 ZnTnPc·DDQ complex, $C_{60}H_{56}N_{10}O_6Cl_2Zn$: C, 62.69; H, 4.91; N, 12.19; O, 8.35. Found: C, 62.76; H, 5.05; N, 12.00; O, 8.40.

Results and Discussion

1. Solution Species. Cyclic Voltammetric Studies. 1.1 ZnTnPc(2–) Alone. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) data for ZnTnPc(2–) in DCB are shown in Figure 1a, and agree with earlier studies of zinc phthalocyanines[8,31,36] and for ZnTnPc(2–) itself.[37,38] Table 1 collects the relevant data and assignments.[37–39]

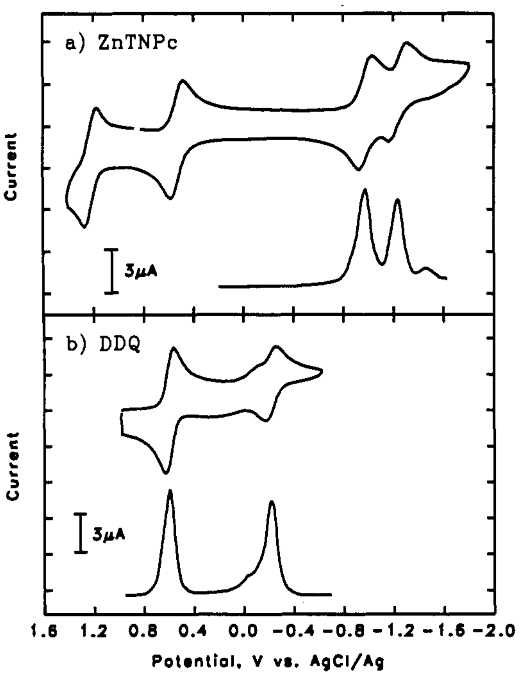

Figure 1. Cyclic voltammograms at 100 mV/s and differential pulse voltammograms at 2 mV/s of 3.08 × 10^{-4} M ZnTnPc(2–) (a) and 3.35 × 10^{-4} M DDQ (b) in 1,2-dichlorobenzene (DCB) containing 0.2 M TBAP, vs AgCl/Ag.

Table 1. Redox Potentials of ZnTnPc(2–), DDQ, and the ZnTnPc(2–)–DDQ Mixture in DCB Solutions vs AgCl/Ag

couples	assignments	electrons[a]	$E_{1/2}$, V[b]
I^{ZnPc}	$[ZnTnPc(0)]^{2+}/[ZnTnPc(1-)]^{+}$	1	1.23
II^{ZnPc}	$[ZnTnPc(1-)]^{+}/ZnTnPc(2-)$	1	0.55
III^{ZnPc}	$ZnTnPc(2-)/[ZnTnPc(3-)]^{-}$	1	–0.98
IV^{ZnPc}	$[ZnTnPc(3-)]^{-}/[ZnTnPc(4-)]^{2-}$	1	–1.24
I^{DDQ}	$DDQ/[DDSq(1-)]^{-}$ [c]	1	0.59
II^{DDQ}	$[DDSq(1-)]^{-}/[DDCat(2-)]^{2-}$ [c]	1	–0.22
I^{compd}	$[ZnTnPc(0)]^{2+}/[ZnTnPc(1-)]^{+}$	1	1.22
II^{comp}	$[ZnTnPc(1-)]^{+}/ZnTnPc(2-)$ + $DDQ/[DDSq(1-)]^{-}$	2	0.57
III^{comp}	$ZnTnPc(2-)$ + $[DDSq(1-)]^{-}/[ZnTnPc(2-)\cdot DDcat(2-)]^{2-}$	1	0.04
IV^{comp}	$[ZnTnPc(2-)\cdot DDcat(2-)]^{2-}/[ZnTnPc(3-)\cdot DDcat(2-)]^{3-}$	1	–1.06

[a] Obtained from RDE experimental results. [b] Under our experimental conditions, the Fc^+/Fc couple had an $E_{1/2}$ of 0.54 V against AgCl/Ag/MeCN. [c] $[DDSq(1-)]^-$ is an anion radical of semiquinone type, generated by one-electron reduction of DDQ. $[DDCat(2-)]^{2-}$ is a two-electron reduced dianion of DDQ of catechol type.

1.2. DDQ Alone. Figure 1b shows the cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of DDQ as pure species in DCB. Redox couples in Figure 1 were assigned based on previous literature,[40–43] and are collected in Table 1. The couples DDQ/$[DDSq(1-)]^-$ (0.59 V) and $[DDSq(1-)]^-$/$[DDCat(2-)]^{2-}$ (–0.22 V) are about 500 mV more positive than an unsubstituted quinone ligand.[44] The DDQ/$[DDSq(1-)]^-$ couple is reversible with $i_c/i_a = 1$ and ΔE_p = 75 mV (ΔE_p refers

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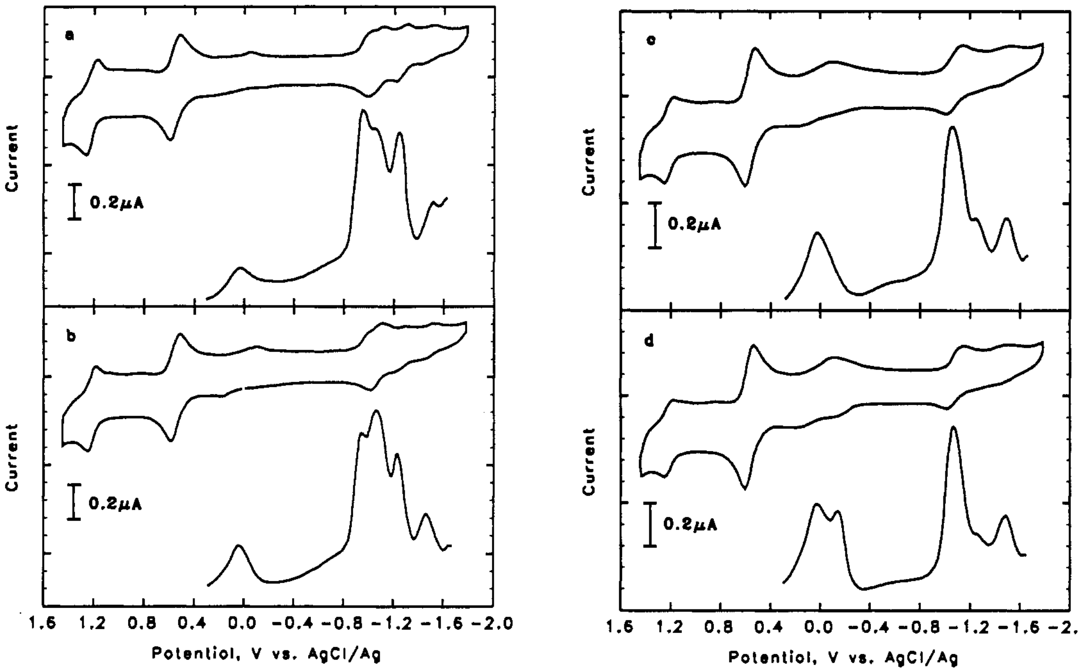

Figure 2. Cyclic voltammograms at 100 mV/s and differential pulse voltammograms at 2 mV/s, vs AgCl/Ag, of ZnTnPc(2–)/DDQ mixtures in DCB containing 0.2 M TBAP. The concentration of ZnTnPc(2–) and the ZnTnPc(2–)/DDQ ratio, in parentheses, are as follows: (a) 1.33 × 10^{-4} M (4:1); (b) 1.13 × 10^{-4} M (2:1); (c) 8.76 × 10^{-5} M (1:1); (d) 7.14 × 10^{-5} M (1:1.5).

to the potential difference between the anodic and cathodic peaks of the couple), the same ΔE_p value obtained for the Fc$^+$/Fc couple under the same condition, but the second reduction, [DDSq(1–)]$^-$/[DDCat(2–)]$^{2-}$, showed a reduced peak current (relative to the first reduction), larger peak to peak separation (95 mV), and a precathodic wave, lying about 150 mV positive of the main peak. Yamagishi[45] and Miller et al.[46] have reported the formation of an ESR silent dimer from anionic DDQ radicals. Hiromitsu et al.[47] found that [DDSq(1–)]$^-$ formed a dimer upon heating a DDQ doped fluoro(phthalocyaninato)aluminum(III) film. Thus, the prewave in Figure 1b is likely to be caused by dimerization of the [DDsq(1–)]$^-$ anion. Other possibilities, such as decomposition, or protonation of the [DDSq(1–)]$^-$ anion, were excluded after studying the RDE experiment results, scan rate dependence, solvent dependence, and H$^+$ effect.

1.3. ZnTnPc(2–)/DDQ Mixtures in Various Molar Ratios. The first reduction potential of DDQ (to [DDSq(1–)]$^-$, 0.59 V), is observed to be more positive than the first oxidation potential of ZnTnPc(2–) (to [ZnTnPc(1–)]$^+$, 0.55 V) (Figure 1 and Table 1). Therefore, thermodynamically, DDQ can chemically oxidize ZnTnPc(2–) in a homogeneous solution. This result is in accordance with the observations by Mu et al.[29] and Kasuga et al.[30] They reported that the potential of the first reduction step of DDQ was more positive than those of the first oxidation step of ZnPc(*t*-Bu)$_4$ and ZnPc(OC$_{12}$H$_{25}$)$_8$, resulting in the chemical oxidation of the ZnPc species by DDQ; however, they did not observe complex formation.

Different mixtures were made from the same ZnTnPc(2–)/DCB solution, to which calculated volumes of DDQ/DCB solution were added, to obtain specific ZnTnPc(2–)/DDQ molar ratios. Shown in Figure 2 are the cyclic and differential pulse voltammetry data for a series of ZnTnPc(2–)/DDQ mixed solutions, with molar ratios of ZnTnPc(2–) to DDQ ranging from 1:0.25 to 1:1.5.

Figure 2c is significantly different from Figure 1 and is not obtainable by superimposing the cyclic voltammogram of DDQ onto that of ZnTnPc(2–) with equal concentrations of the two species. Upon adding DDQ into the ZnTnPc(2–)/DCB solution, a new redox couple appears with an $E_{1/2}$ of –1.06 V, whose peak current, relative to the ZnTnPc(2–) reduction couples, increases with increasing DDQ (Figure 2a,b), and eventually, the new band dominates the region when DDQ is in excess of ZnTnPc(2–) (Figure 2c,d). With growth of the band at –1.06 V, the two couples at –0.98 and –1.24 V assigned to the sequential ring reductions of ZnTnPc(2–) decline in current and eventually disappear.

In the 0.0-V region, mixed solutions of ZnTnPc(2–)/DDQ, with ZnTnPc(2–) in excess show a couple at an $E_{1/2}$ of 0.04 V, whose current increases with DDQ concentration (Figure 2a–c). Both the –1.06 and 0.04 V couples are absent from the voltammetry of the individual components and must arise from a reaction product of these species. With DDQ in excess, a second band is observed at about –0.15 V (Figure 2d) corresponding to that observed in a solution of pure DDQ.

The potentials of the redox couples for a 1:1 (ZnTnPc(2–)/DDQ) mixture (Figure 2c) are given in Table 1, with the couples labeled as I$^{\mathrm{comp}}$, II$^{\mathrm{comp}}$, III$^{\mathrm{comp}}$ and IV$^{\mathrm{comp}}$; couple II$^{\mathrm{comp}}$ is a 2-electron couple while the others are 1-electron.

According to Figure 1, at a potential around 0.0 V, the phthalocyanine should be in its neutral form and quinone in its one-electron reduced form, the [DDSq(1–)]$^-$ radical. Then, with the potential scanning negatively, the phthalocyanine should remain unchanged and the [DDSq(1–)]$^-$ radical becomes a dianion, [DDCat(2–)]$^{2-}$, beyond –0.2 V. In Figure 2a–c, however, there is no couple seen at –0.22 V; instead, a new couple at $E_{1/2}$ = 0.04 V appears, which is assigned to the [DDSq(1–)]$^-$/[DDCat(2–)]$^{2-}$ process, but positively shifted from the original potential, due to formation of a complex between ZnTnPc(2–) and DDQ. Such a shift could arise through a complex being formed with [DDSq(1–)]$^-$ and/or [DDCat(2–)]$^-$.

However there is no other direct evidence for the existence of [ZnTnPc(2–)·DDSq(1–)]$^-$; the electronic spectrum of a solution purportedly containing this species (*vide infra*) is indistinguishable from that of ZnTnPc(2–). Further, and more critically, a solution of ZnTnPc(–2):DDQ = 1:0.75, was reduced to the mixture ZnTnPc(2–) + [DDSq(1–)]$^-$ by controlled-potential reduction at 0.1 V and yielded an ESR spectrum typical only of free

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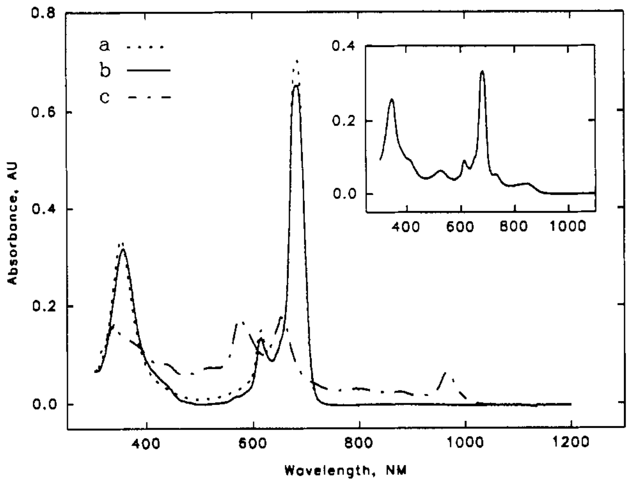

Figure 3. Equilibrium UV–vis spectra of a ZnTnPc(2–)/DDQ (1:1) mixture in DCB (1.57×10^{-4} M) containing 0.2 M TBAP in an optically transparent thin cell (0.025 cm of optical pathlength) at the following potentials: (inset) open-circuit; (a) 0.2 V; (b) –0.4 V; (c) –1.2 V, respectively, against AgCl/Ag/MeCN reference.

uncoordinated [DDSq(1–)]$^-$. Since we anticipate that binding of this species to Zn will occur by the CN group (*vide infra*), its ESR spectrum would change dramatically, losing the equivalence of the two N atoms; since no such change is observed, we conclude that no complex is formed between ZnTnPc(2–) and [DDSq(1–)]$^-$ in solution. Accordingly the couple at 0.04 V is assigned to reaction 1 (couple III$^{\mathrm{comp}}$ in Table 1).

$$\mathrm{ZnTnPc(2–)} + [\mathrm{DDSq(1–)}]^- + e^- \rightleftharpoons [\mathrm{ZnTnPc(2–)\cdot DDCat(2–)}]^{2-} \; (E_{1/2} = 0.04\ \mathrm{V}) \quad (1)$$

Thus, the reduction of [DDSq(1–)]$^-$ is favored by complexation of the reduced species, [DDCat(2–)]$^{2-}$ to ZnTnPc(2–). Assuming that the [DDSq(1–)]$^-$ does not form a complex with ZnTnPc(2–) then the stability constant for formation of the [ZnTnPc(2–)·DDCat(2–)]$^{2-}$ species can be deduced from the potential shift discussed above, using[48]

$$\Delta E_{1/2} = -(RT/nF)\ln(1/\beta_{\mathrm{red}}) \quad (2)$$

where $\Delta E_{1/2}$, the shift due to complexation is equal to $E_{1/2}$(complex) – $E_{1/2}$ (uncoordinated species), and β_{red} is the formation constant for the reduced ([ZnTnPc(2–)·DDCat(2–)]$^{2-}$) species. Substitution of the experimental data into eq 2 yields $\beta_{\mathrm{red}} = 10^{4.4}$ L mol.$^{-1}$.

In all the cases discussed above, those redox processes which lie sufficiently far from their neighbors for adequate study were shown to be diffusion controlled, to have current proportional to square root of the scan rate (cyclic voltammetry), and to have approximately equal cathodic and anodic currents.

2. Spectroelectrochemistry of ZnTnPc(2–), DDQ, and Mixed Systems. Spectroelectrochemical studies were carried out with the 1:1 ZnTnPc(2–)/DDQ mixed solution. Figure 3 shows the equilibrium spectra recorded at 0.2 V vs AgCl/Ag/MeCN (curve a), –0.4 V (curve b), and –1.2 V (curve c), respectively. The spectrum of the same solution in an open-circuit cell is shown in the inset of the figure, wherein bands at 683 nm (Q-band) and 347 nm (Soret band) indicate the presence of the neutral zinc phthalocyanine species, and bands at 845, 730, and 523 nm confirm a one-electron oxidized phthalocyanine cation radical[31,49,50] (both being present in solution).

For comparison, spectroelectrochemical data were also collected on pure ZnTnPc(2–)/DCB and DDQ/DCB solutions. For DDQ, the spectra of the anion radical [DDSq(1–)]$^-$ and dianion [DDCat(2–)]$^{2-}$ were obtained at 0.1 V (vs AgCl/Ag/MeCN) and –0.6 V. For ZnTnPc(2–), spectra of neutral ZnTnPc(2–) (open circuit), one-electron reduced [ZnTnPc(3–)]$^-$ anion radical (at –1.15 V vs AgCl/Ag/MeCN), and two-electron reduced [ZnTnPc(4–)]$^{2-}$ dianion (at –1.5 V) were obtained. Two sets of isosbestic points were observed corresponding to the two processes ZnTnPc(2–)/[ZnTnPc(3–)]$^-$ and [ZnTnPc(3–)]$^-$/[ZnTnPc(4–)]$^{2-}$. The spectrum of a one-electron oxidized [ZnTnPc(1–)]$^+$ cation radical was also obtained. Table 2 summarizes the spectroelectrochemical results of the ZnTnPc(2–)/DDQ (1:1) mixture, pure ZnTnPc(2–), and pure DDQ. The [ZnTnPc(1–)]$^+$ cation radical is in equilibrium with its dimer,[37] giving rise to a band at about 720 nm, consistent with our observation of the 727-nm band in the cation radical spectrum (Table 2). Thus, a mixture of monomer (845 nm) and dimer (727 nm) was likely obtained upon oxidizing ZnTnPc(2–) to [ZnTnPc(1–)]$^+$ electrochemically.

Figure 3a shows the electronic spectrum of a solution polarized at a potential where ZnTnPc(2–) exists with [DDSq(1–)]$^-$; the electronic spectrum (Table 2) is indistinguishable from that of ZnTnPc(2–), supporting the view that no complex forms in solution between these species.

Figure 3b shows the spectrum of ZnTnPc(2–) in the presence of [DDCat(2–)]$^{2-}$. The small decrease in Q-band intensity from part a to part b is likely caused by axial ligation of [DDCat(2–)]$^{2-}$ to ZnTnPc(2–) (see further discussion below).

The data in Figure 2 clearly indicate that the pair of waves corresponding with the formation of the mono- and dianion of ZnTnPc(2–) are replaced by a single wave at –1.06 V (IV$^{\mathrm{comp}}$), which corresponds with formation of the [ZnTnPc(–3)·DDCat(2–)]$^{3-}$ anion radical (eq 3) as proven by its electronic spectrum (Figure 3c).

$$[\mathrm{ZnTnPc(2–)\cdot DDCat(2–)}]^{2-} + e^- \rightleftharpoons [\mathrm{ZnTnPc(3–)\cdot DDCat(2–)}]^{3-} \; (E_{1/2} = -1.06\ \mathrm{V}) \quad (3)$$

Here, the shift of the redox couple upon complexation is the reverse of that observed with equilibrium 1 and is indicative of the stabilization of the ZnTnPc(2–) moiety against formation of the anion radical, relative to the uncomplexed species, presumably because of the build up of negative charge. In this case the shift in potential translates to a ratio of formation constants (oxidized to reduced) of $10^{1.4}$, and hence a formation constant for [ZnTnPc(3–)·DDCat(2–)]$^{3-}$ of $10^{4.4}/10^{1.4}$, or 10^3 L mol^{-1}.

The electronic spectrum of the [ZnTnPc(3–)·DDCat(2–)]$^{3-}$ species (Figure 3c), obtained by controlled potential reduction at –1.2 V, profiles the major features of the spectrum of [ZnTnPc(3–)]$^-$ with, however, a weak band at 519 nm, which is absent from the pure [ZnTnPc(3–)]$^-$ species (see also Table 2). To display the new band at 519 nm more clearly, Figure 4 shows the spectra of [ZnTnPc(3–)·DDCat(2–)]$^{3-}$ (Figure 4a), [ZnTnPc(3–)]$^-$ (Figure 4b), and [DDCat(2–)]$^{2-}$ (Figure 4c), and a differential spectrum in part d (=a – (b + c)), where the band at 519 nm is evident. The 519-nm band could be assigned to a charge-transfer transition from a lower lying orbital of [DDCat(2–)]$^{2-}$ to [ZnTnPc(3–)]$^-$ since such a band is not observed in the spectra of the separated species.[51]

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Table 2. Electronic Absorption Maxima for DDQ, ZnTnPc(2–), and Mixed ZnTnPc(2–)/DDQ (1:1) DCB Solutions,[a] All Containing 0.2 M TBAP

species[b]	λ_{max},[c] nm ($10^{-4}\epsilon$, mol^{-1} cm^{-1})					
DDQ	334 (0.29)					
[DDSq(1–)]$^-$	348 (0.56)	458 (0.40)	553 (0.36)	592 (0.37)		
[DDCat(2–)]$^{2-}$	428 (0.66)	478 sh				
[ZnTnPc(1–)]$^+$	336 (5.38)	386 (3.32)	520 (2.51)	727 (2.21)	845 (1.46)	
ZnTnPc(2–)	352 (8.29)	614 (3.73)	682 (17.8)			
[ZnTnPc(3–)]$^-$	338 (4.10)	442 sh	575 (4.84)	653 (4.96)	966 (1.88)	
[ZnTnPc(4–)]$^{2-}$	324 (3.53)	533 (5.19)				
[ZnTnPc(2–)·DDCat(2–)]$^{2-}$ [d]	356 (8.07)	434 sh	614 (3.41)	682 (16.6)		
[ZnTnPc(3–)·DDCat(2–)]$^{3-}$ [d]	338 (4.18)	441 w	519 w	576 (4.42)	654 (4.46)	965 (1.62)

[a] The concentrations are 5.68×10^{-4} M for DDQ, 2.17×10^{-4} M for ZnTnPc(2–), and 1.57×10^{-4} M for mixed ZnTnPc(2–)/DDQ (1:1) solutions; the spectroelectrochemical data were obtained with an optically transparent thin cell of 0.025-cm path length. [b] See text for the potentials to produce various species. [c] Key: sh = shoulder, w = weak. [d] Also see Figure 3.

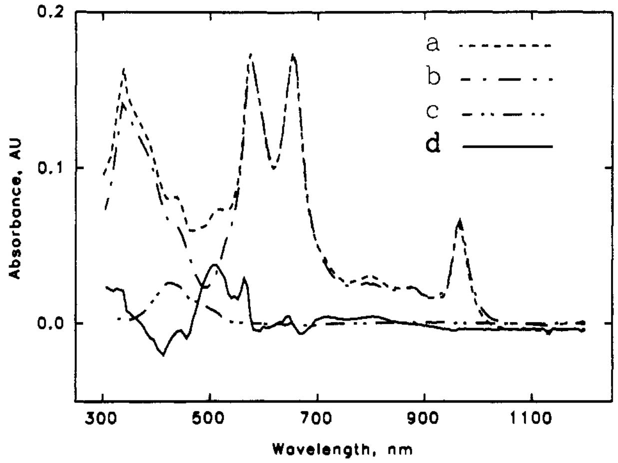

Figure 4. Differential treatment of UV–vis spectra: (a) [ZnTnPc(3–)·DDCat(2–)]$^{3-}$; (b) [ZnTnPc(3–)]$^-$; (c) [DDCat(2–)]$^{2-}$; (d) subtraction of the sum of (b) and (c) from (a) after correction for concentration.

Further reduction to the [ZnTnPc(4–)·DDCat(2–)]$^{4-}$ species was not observed in the potential range studied. The build-up of negative charge on the molecule again may serve to shift this process to rather more negative potentials. The weak couple at –1.47 V (Figure 2) is not believed to correspond to this reduction process since its current remains unchanged from part a to part d in Figure 2. The source of this couple is not clear. Thus, in summary, there is convincing evidence for the formation of [ZnTnPc(2–)·DDCat(2–)]$^{2-}$ and [ZnTnPc(3–)·DDCat(2–)]$^{3-}$. To determine the bonding site of the quinone moiety to the zinc ion, an AM1 semiempirical calculation was performed comparing a PcZn–oxygen (DDCat) bond and a PcZn–nitrogen (CN) (DDCat) bond. The complex with the PcZn–nitrogen bond is lower in energy than that of the PcZn–oxygen bond by 8 kcal/mol. Therefore, we propose that one of the cyano groups of quinone acts as a ligand towards the ZnTnPc(2–) unit, binding to the zinc atom, as postulated elsewhere for a DDSq-containing metal complex.[52]

We assume that only one DDQ molecule is associated with the ZnTnPc(2–) species, though there is no evidence to exclude two DDQ molecules per zinc except for the known tendency of ZnPc species to be five coordinate.[53]

There remains the question of whether a complex is formed in an open-circuit cell with the ZnTnPc(2–)/DDQ (1:1) mixed system. On the basis of the redox potentials of II^{ZnPC} and I^{DDQ} (see Table 1), in a potential region between 0.55 V and 0.59 V, [ZnTnPc(1–)]$^+$ (which would be a strong Lewis acid) exists in the presence of [DDSq(1–)]$^-$. These may remain as separate ions in solution or may form a complex [ZnTnPc(1–)·DDSq(1–)] which could be axially coordinated or conceivably a π-type charge transfer complex.

Solution electrochemical measurements failed to show any evidence for formation for the [ZnTnPc(1–)·DDSq(1–)] species. As shown in Figure 2 and Table 1, couple II^{comp} is a two-electron process, identical to the sum of couples II^{ZnPc} and I^{DDQ} in terms of shape, current, and $E_{1/2}$ values. I^{comp} shows no shift from I^{ZnPC} and likely represents exactly the same process as I^{ZnPc}. Therefore, at a potential more positive than 0.6 V, there is no complex in solution but, instead, isolated [ZnTnPc(1–)]$^+$ and DDQ species. This is not unreasonable since DDQ is likely a very poor ligand.

The open circuit electronic spectrum also failed to show any characteristics which could be attributed to a new complex. Thus we suppose that no such complex exists in solution.

3. Solid-State Studies. Individually, both ZnTnPc(2–) and DDQ are very soluble in benzene. Upon mixing the two species, a precipitate was formed, referred to as the *complex*. Elemental analysis of the product suggests that a molecular complex has been formed between ZnTnPc(2–) and DDQ in 1:1 molar ratio. Since the open-circuit solution will contain [ZnTnPc(1–)]$^+$ cations and [DDSq(1–)]$^-$ anions, the product in the solid state may be a simple salt containing these species. On the other hand, the difference forces operating in the solid state, relative to solution, may permit formation of an axially coordinated complex or a π-complex.

3.1. UV-Vis Spectrum of the Solid *Complex*. A Nujol mull sample of the solid *complex* was used to obtain the UV–vis spectrum shown in Figure 5a. Absorption bands are observed at 350, 383, 513, 692, and 860 nm with a shoulder at 745 nm, clearly associated with the [ZnTnPc(1–)]$^+$ cation radical.[31] The Nujol mull sample was then dissolved in dry benzene, and the resultant solution provided the spectrum shown in Figure 5b. There is much correspondence in the peak positions between Figures 5b and 5a. The sharp Q-band at 685 nm of the benzene solution (Figure 5b) is greatly broadened in the solid state spectrum (Figure 5a) due to intermolecular coupling (solid-state coupling), which could also be responsible for some shifts in peak position. While the spectroscopic features of the [ZnTnPc(1–)]$^+$ radical cation can be observed, absorption due to the [DDSq(1–)]$^-$ unit is weak and obscured.

A pure solid ZnTnPc(2–) sample shows a significantly different spectrum (Figure 5c) from the solid *complex* (Figure 5a). There is a strong absorption at 630 nm, which, absent in Figure 5a, arises from strong Pc--Pc aggregation.[54] The broadness of the bands is attributed to the intermolecular coupling in the solid state.

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(51) An estimate of the energy of this transition is given by the difference of potentials, [DDSq(1–)]$^-$/[DDCat(2–)]$^{2-}$ – [ZnTnPc(3–)]$^-$/[ZnTnPc(4–)]$^{2-}$ = 1.04 V. (Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.). However the observed transition is significantly higher in energy and may therefore reflect a transition from a lower lying orbital of [DDCat(2–)]$^{2-}$. The band predicted near 1.04 V will be weak and broad, and is probably obscured by phthalocyanine absorption.

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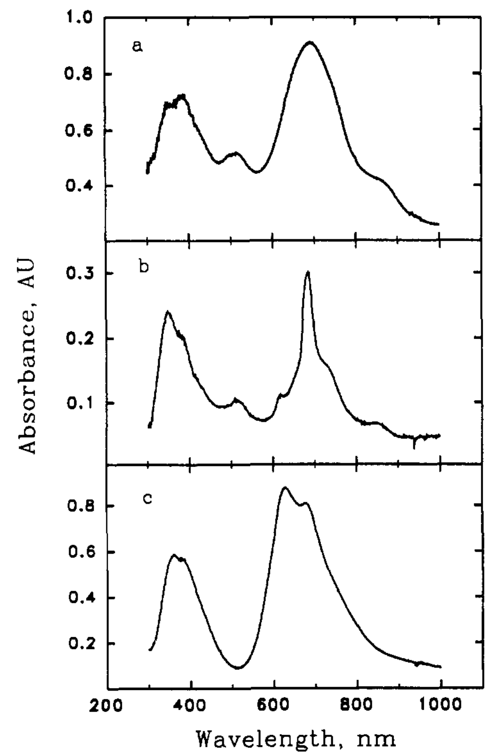

Figure 5. Electronic spectra of (a) [ZnTnPc(1–)·DDSq(1–)] as a Nujol mull sample, (b) benzene solution of the [ZnTnPc(1–)·DDSq(1–)] Nujol mull sample (unknown concentration), and (c) pure ZnTnPc(2–) as a Nujol mull sample, made in the same fashion as that in part a.

The broad band centered at 692 nm (Figure 5a) could indicate some contamination of the *complex* by the neutral ZnTnPc(2–) species which is also evident in the spectrum of the solid *complex*/benzene solution (Figure 5b), where a sharp Q-band is observed at 685 nm. The presence of the neutral ZnTnPc(2–) is ascribed to the sensitivity of the *complex* to moisture, i.e., the *complex* tends to decompose partially when dissolved in solvent in the air.

Therefore, we conclude from the comparison of part a of Figure 5 with parts b and c that the *complex* is indeed [ZnTnPc(1–)·DDSq(1–)].

3.2. Electron Spin Resonance Spectra of the Solid ZnTnPc(1–)·DDSq(1–) *Complex*. ESR spectra were collected on the solid species (Figure 6a), on a suspension in toluene (in which the *complex* is only sparingly soluble) and in a solution in acetone (Figure 6b), in which the *complex* is very soluble.

The solid displays a broad unstructured signal at $g = 2.001$ as does the toluene suspension except for a small difference in line width, being 4.2 and 6.2 G for the solid and toluene solution, respectively.

In acetone solution two signals were observed $g = 2.005$ and 2.002, respectively, with the former showing a quintet hyperfine structure (Figure 6b). Table 3 lists the parameters obtained from Figure 6. Also given in Table 3 are the spin Hamiltonian parameters of the [DDSq(1–)]$^-$ anion and [ZnTnPc(1–)]$^+$ cation radicals for comparison. The ESR spectra of the two radicals are shown in Figure 6c ([DDSq(1–)]$^-$) and 6d ([ZnTnPc(1–)]$^+$), respectively. Figure 6 shows that, for the ZnTnPc·DDQ *complex*, the g value is smaller, there is no hyperfine structure, and the line width is about half that of the [ZnTnPc(1–)]$^+$ signal alone.

The ESR spectrum of a [DDSq(1–)]$^-$ anion[46,55,56] normally consists of hyperfine interactions of the unpaired electron with two equivalent ^{14}N nuclei ($S = 1$), a quintet ($a_N = 0.63$ G), and two or three of the four types of ^{13}C atoms ($S = {}^1/_2$) (Figure 6c).

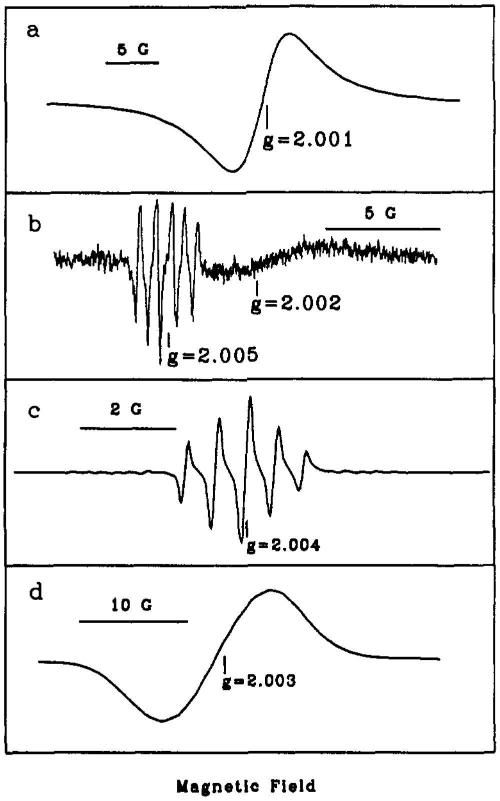

Figure 6. ESR spectra of [ZnTnPc(1–)·DDSq(1–)] *complex* at room temperature: (a) powder sample; (b) acetone solution; (c) [DDSq(1–)]$^-$/DCB (5.68 × 10^{-4} M, 0.2 M TBAP) solution, which had been used for CV measurements prior to the ESR studies; (d) [ZnTnPc(1–)]$^+$/DCB (ca. 5 × 10^{-4} M, 0.2 M TBAP) solution, produced electrochemically by bulk electrolysis at 0.8 V vs AgCl/Ag/MeCN reference.

Table 3. Experimental ESR Parameters

species	g[a]	LW,[b] G	a_N,[c] G
[ZnTnPc(1–)·DDSq(1–)][d]	2.001	4.2	
acetone solution[e]	2.005, 2.002	0.3, 8	0.62
[DDSq(1–)]$^-$ [f]	2.004	0.2	0.63
[ZnTnPc(1–)]$^+$ [g]	2.003	9.9	

[a] g values have an experimental error of about 0.0005. [b] LW = line width. [c] a_N = nuclear splitting constant of DDQ nitrogen atoms. [d] Solid state. [e] *Complex* dissolved in acetone; two signals observed. [f] DCB solution containing 0.2 M TBAP; [DDSq(1–)]$^-$ was produced by controlled-potential reduction. [g] DCB solution containing 0.2 M TBAP; [ZnTnPc(1–)]$^+$ was generated by bulk electrolysis at 0.8 V vs AgCl/Ag/MeCN.

The ESR signal for [ZnTnPc(1–)]$^+$, as shown in Figure 6d, matches some typical features of phthalocyanine radical ESR spectra, broadness and lack of hyperfine structure.

The *complex* [ZnTnPc(1–)·DDSq(1–)], has two unpaired electrons, one on each of the two radicals. Depending upon the interaction between the two electrons, one might obtain an ESR silent singlet species (antiferromagnetic coupling) or a triplet species (ferromagnetic coupling).

If the *complex* were a π complex with parallel [DDSq(1–)]$^-$ and [ZnTnPc(1–)]$^+$ rings, then strong antiferromagnetic coupling would be anticipated and there should be no ESR signal. While the solid may contain ion pairs with no close contacts between Zn and [DDSq(1–)]$^-$ it seems more likely that the [DDSq(1–)]$^-$ acts as a ligand toward the strongly Lewis acidic [ZnTnPc(1–)]$^+$ species, coordinating perpendicularly through the zinc atom. In this fashion the electron spins on each fragment are essentially orthogonal and electron-electron coupling is expected to be weak or nonexistent. The room-temperature ESR spectrum is consistent with this model. However there is a decrease in signal intensity with decreasing temperature implying that some degree of coupling becomes more important at lower temperatures.

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Table 4. FTIR Data[a,b] for H_2TnPc(2−), ZnTnPc(2−), [ZnTnPc(1−)·DDSq(1−)], and DDQ

H_2TnPc[c]	ZnTnPc(2−)[c]	*complex*[c,d]	DDQ[e]
436 w	434 w	425 w	454 m
	567 w	500 w	719 s
650 w	654 w		761 w
746 s	746 s	754 m	800 s
822 m	823 m	823 w	894 s
921 m	924 m	919 w	1009 w
1016 s	1012 s	1009 s	1069 w
1054 s	1057 s	1049 s	1173 s
1096 s	1092 s	1083 m	1215 w
1163 w	1176 w	1161 w	1267 s
1237 s	1232 s	1232 s	1513 w
1279 w	1278 m	1282 m	1524 w
1343 m	1334 s	1332 s	1552 s
1363 m	1362 m	1363 w	1674 s[f]
1393 s	1394 s	1394 s	2230 m[g]
1425 m			2722 w
1473 s	1474 s	1471 s	
		1554 w[f]	
1610 s	1607 s	1608 s	
		2209 w[g]	
2954 s	2953 s	2955 s	

[a] Data in wavenumbers, cm^{-1}. [b] Key: s = strong; m = medium; w = weak. [c] KBr pellet. [d] Solid [ZnTnPc(1−)·DDSq(1−)]. [e] Nujol mull. [f] ν_{CO}. [g] ν_{CN}.

The *complex* is not very soluble in the very weakly polar solvent toluene, nor can toluene break the [ZnTnPc(1−)·DDSq(1−)] bond. The ESR spectrum of a toluene solution hence resembles the solid spectrum. With a more polar solvent such as acetone, however, the *complex* is very soluble and the Pc(1−)–Sq(1−) bond is broken, releasing the two radicals into solution. Therefore, two signals (Figure 6b), resulting from the two separated [DDSq(1−)]$^-$ anion (the quintet signal) and [ZnTnPc(1−)]$^+$ cation radicals (single broad signal), are observed.

3.3. FTIR Studies of the Solid ZnTnPc(1−)·DDSq(1−) *Complex*. The FTIR spectrum of the ZnTnPc(1−)·DDSq(1−) *complex* (KBr pellet) is presented in Table 4. For comparison, FTIR data are also collected in Table 4 for KBr pellets of pure metal-free H_2TnPc and ZnTnPc(2−) and the Nujol mull of DDQ.

Table 4 shows that the FTIR spectrum of the *complex* is primarily composed of a ZnTnPc species, which is understandable considering the relative molecular weights of ZnTnPc and DDQ. Nevertheless, bands due to the DDQ moiety, namely, –C≡N (cyano) stretching and >C=O (carbonyl) stretching, were observed, both shifted to lower energy relative to free DDQ (in its quinone oxidation state). The strong C–Cl (carbon–chlorine) stretching vibration, which appears at 800 cm^{-1} in DDQ, was not observed in either KBr pellet or Nujol mull samples of the ZnTnPc–DDQ *complex*.

Miller et al.[57] and Matsunaga[58] have reported that, upon the reduction of DDQ to [DDSq(1−)]$^-$, there is approximately a 30 cm^{-1} red shift in the (C≡N) stretching (from 2234 cm^{-1} to 2206 cm^{-1}) and more than 100 cm^{-1} shift in (C=O) (from 1701 cm^{-1} to 1562 cm^{-1}). In our FTIR studies, the (C≡N) and (C=O) stretching vibrations in the DDQ species appeared at 2230 and 1674 cm^{-1}, respectively. For the *complex*, the two stretching vibrations occured at 2209 and 1554 cm^{-1}, about 20 and 120 cm^{-1} red-shifted from DDQ, consistent with the semiquinone formulation.

Finally, the strong C–Cl stretching band of DDQ, at 800 cm^{-1}, was not observed in the *complex*. The X-ray results of Miller et al.[46] showed that the C–Cl bond length was elongated from 1.715 Å in DDQ to 1.724 Å in [DDSq(1−)]$^-$. Therefore the C–Cl stretching will shift to the red where perhaps it was obscured by phthalocyanine vibrations.

The above UV–vis, ESR, and FTIR results suggest that the solid *complex* has the molecular formula [ZnTnPc(1−)·DDSq(1−)], most probably with an axially bound [DDSq(1−)]$^-$ unit though this cannot be confirmed.

Concluding Remarks

The reaction of ZnTnPc(2−) with DDQ leads to formation of a complex [ZnTnPc(1−)·DDSq(1−)] existing in the solid state, probably as a ligated [DDSq(1−)]$^-$ nitrogen bonded to the zinc ion of the [ZnTnPc(1−)]$^-$ radical cation, supported by UV–vis, ESR, and FTIR data. There is no evidence that this complex exists in solution. Oxidation appears to yield DDQ and [ZnTnPc(1−)]$^+$ as independent entities.

There is no evidence for the existence of [ZnTnPc(2−)·DDSq(1−)]$^-$ existing in solution, upon reduction of a 1:1 mixture of ZnTnPc(2−) and DDQ. Definitive electrochemical and spectroscopic evidence is reported for both [ZnTnPc(2−)·DDCat(2−)]$^{2-}$ and [ZnTnPc(3−)·DDCat(2−)]$^{3-}$ upon reduction of a 1:1 mixture of ZnTnPc(2−) and DDQ, both species being assumed to involve DDQ cyanide nitrogen to zinc binding. Stability constants are reported for these last two [DDCat(2−)]$^{2-}$-containing species.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington) for financial support. We also thank Prof. W. J. Pietro for help in the semiempirical calculations and Dr. W. Torres for useful discussions.

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