Articles

Phthalocyanines of a Novel Structure: Dinaphthotetraazaporphyrins with D_{2h} Symmetry

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Two naphthalene molecule-fused tetraazaporphyrins (TAPs) with D_{2h} symmetry have been synthesized, and some of their spectroscopic and electrochemical properties are reported. These compounds are structural isomers of phthalocyanines (Pcs) in the sense that four benzene units are fused to the TAP skeleton. In contrast to MPcs (M = metal) with D_{4h} symmetry, both the Q_{0-0} and Soret bands split into two as a result of the lowering of the molecular symmetry. Magnetic circular dichroism (MCD) shows Faraday *B* terms corresponding to the peaks and shoulders of the electronic absorption spectra, indicating that no degenerate state is included. The fluorescence quantum yield of the zinc complex is much smaller than in ZnPc with D_{4h} symmetry. The electronic absorption and electrochemical redox data of these complexes are reproduced by molecular orbital (MO) calculations within the framework of the Pariser–Parr–Pople (PPP) approximation. The results are compared with those of Pcs and mononaphtho-TAPs.

Introduction

Phthalocyanines (Pcs) are compounds in which a benzene ring is fused to each of the four pyrrole rings of tetraazaporphyrins (TAPs). In addition to traditional uses as dyes and in xerography, they are now rapidly increasing in importance in many fields such as batteries, photodynamic cancer therapy, chemical sensors, molecular metals, and liquid crystals.[1,2] Since metal (M) complexes of Pcs are generally obtained by the condensation of phthalonitriles or phthalic anhydride and urea in the presence of metals,[1a,b] the resultant MPcs have π-conjugated systems with D_{4h} symmetry, and no other Pc isomer has been reported to date. In this paper, we report, for the first time, the synthesis and spectroscopic properties of zinc and cobalt TAPs with two fused naphthalene units at the "*opposite*" pyrrole rings, *i.e.* Zn(DiNpTAP) and Co(DiNpTAP) (Figure 1). The π-conjugated aromatic cores of these compounds are structural isomers of Pc in the sense that they are TAPs containing four conjugated benzene units. The key point in their preparation is the use of 2,3-dicyano-1,4-diphenylnaphthalene as one of the two starting *ortho*-dinitriles. As demonstrated in our recent report on the preparation and characterization of a ZnPc with D_{2h} symmetry,[3] two 1,4-diphenylnaphthalene units are not expected to occupy the "*adjacent*" positions (Figure 1) in the resultant compounds because of the steric hindrance between the phenyl groups. Accordingly, the so-called "*opposite*" isomers with D_{2h} symmetry, *i.e.* Zn(DiNpTAP) and Co(DiNpTAP), are obtained preferentially. As will be shown below, their spectroscopic and electrochemical properties are quite different from those of general MPcs.
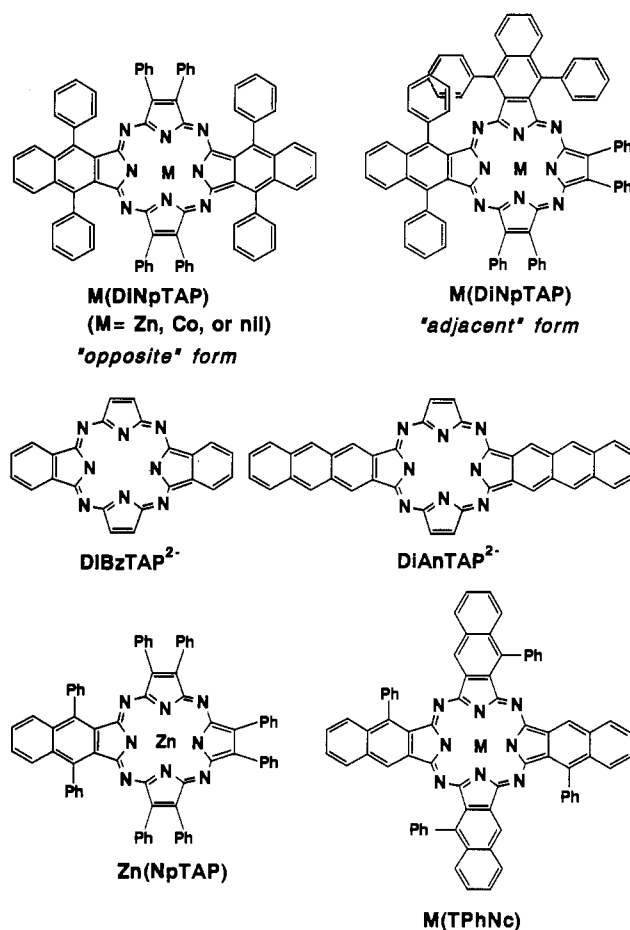
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(3) Kobayashi, N.; Ashida, T.; Osa, T. *Chem. Lett.* **1992,** 2031 (In this communication, 3,6-diphenylphthalonitrile was intentionally utilized as one of the two starting dinitriles in order to prevent formation of *adjacent* Pcs).

Figure 1. Structures and abbreviations of compounds treated in this study. Names of some of the compounds are introduced in the text.

Moreover, the electronic absorption and electrochemical experimental data are reproduced by molecular orbital calculations within the framework of the Pariser–Parr–Pople (PPP) approximation. In order to deepen our understanding, MO calculations were also performed for the dianion of normal Pc with D_{4h} symmetry (*i.e.* Pc^{2-}) and TAPs with two fused benzenes

or anthracenes at *opposite* pyrrole rings (hypothetical compounds abbreviated as DiBzTAP^{2-} and DiAnTAP^{2-}, respectively, in Figure 1) and experimental data on Zn(DiNpTAP) are compared with those of the known related compound containing one fused naphthalene, Zn(NpTAP) (Figure 1).[4]

Experimental Section

(i) Measurements. Electronic spectra were recorded with a Shimadzu UV-250 spectrophotometer, and magnetic circular dichroism (MCD) measurements were made with a JASCO J-400X spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields up to 1.17 T with parallel and then antiparallel fields. Its magnitude was expressed in terms of molar ellipticity per tesla, $[\theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}. Fluorescence and excitation spectra were recorded with a Shimadzu RF-500 spectrodichrometer with appropriate filters to eliminate scattered light. Fluorescence quantum yields were determined by the use of ZnPc in 1-chloronaphthalene ($\Phi_F = 0.30$) as a standard.[5] Data were obtained by a comparative calibration method with use of the same excitation wavelength and absorbance for Zn(DiNpTAP) and ZnPc and the same emission energies. Fluorescence decay curves were obtained at 20 °C by a Horiba NAES-550 series instrument, using combinations of glass filters and a monochromator for monitoring the emission. The lifetimes were determined from the decay curves by the use of the least-squares method. Sample solutions for fluorescence experiments were purged with argon before measurement.

Cyclic- and differential pulse voltammetry were conducted in *o*-dichlorobenzene (DCB) containing tetrabutylammonium perchlorate as an electrolyte (0.3 M) on a Yanaco Model P-1100 electric analyzer.

(ii) Synthesis. [2^1,2^6,12^1,12^6-tetraphenyldinaphtho[*b,l*]-7,8,17,18-tetraphenyl-5,10,15,20-tetraazaporphyrinato(2–)]zinc(II), Zn(DiNpTAP). Well-dried diphenylmaleonitrile[6] (230.3 mg, 1 mmol, 1 equiv) and 2,3-dicyano-1,4-diphenylnaphthalene[7] (991.2 mg, 3 mmol, 3 equiv) were mixed well and fused in the presence of Zn(OAc)$_2$ (143 mg, 1.21 mmol, 1.21 equiv) at 250–260 °C under a nitrogen atmosphere for *ca.* 20 min. After cooling, the residue was washed well with hot water and ethanol and placed on a basic alumina column using toluene as eluent. The second green fraction was collected and purified by gel-permeation chromatography using a Bio-beads SX-2 (Bio-rad) column and methylene chloride and finally recrystallized from toluene. The yield was 24 mg (*ca.* 2%), and the product showed the desired parent ion peak of *m/z* 1186 (M$^+$, 54) in addition to peaks at *m/z* 391 (15), 341 (64), and 273 (100 (relative intensity in parentheses) in its mass spectrum using a fast atom bombardement (FAB) technique. Anal. Calcd for C$_{80}$H$_{48}$N$_8$Zn: C, 80.97; H, 4.08; N, 9.44. Found: C, 80.70; H, 4.31; N, 9.17. ^{1}H NMR-(CDCl$_3$) δ: 7.0–8.3(m, 48H).

[2^1,2^6,12^1,12^6-tetraphenyldinaphtho[*b,l*]-7,8,17,18-tetraphenyl-5,10,15,20-tetraazaporphyrinato(2–)]cobalt(II), Co(DiNpTAP). This was similarly obtained in 2.5% yield using CoCl$_2$ in place of Zn(OAc)$_2$ in the preparation of Zn(DiNpTAP). FAB mass spectrum: *m/z* 1180 (M + 1, 68), 427 (98), 391 (100). Anal. Calcd for C$_{80}$H$_{48}$N$_8$Co: C, 81.39; H, 4.10; N, 9.49. Found: C, 81.06; H, 4.36; N, 9.22.

(iii) Computational Method. The M(DiNpTAP) structure was constructed using standard phthalocyanine X-ray structural data[8] and by making the ring perfectly planar and adopting D_{2h} symmetry. Molecular orbital (MO) calculations were performed for the dianion (deprotonated form) within the framework of the PPP approximation[9] using the semiempirical parameters recommended in a recent book.[10] These are as follows: atomic valence ionization potentials of 11.16 (carbon), 20.21 (central nitrogen), and 14.12 eV (imino nitrogen), together with atomic valence electron affinities of 0.03 (carbon), 5.32 (central nitrogen), and 1.78 eV (imino nitrogen). Since the calculation was
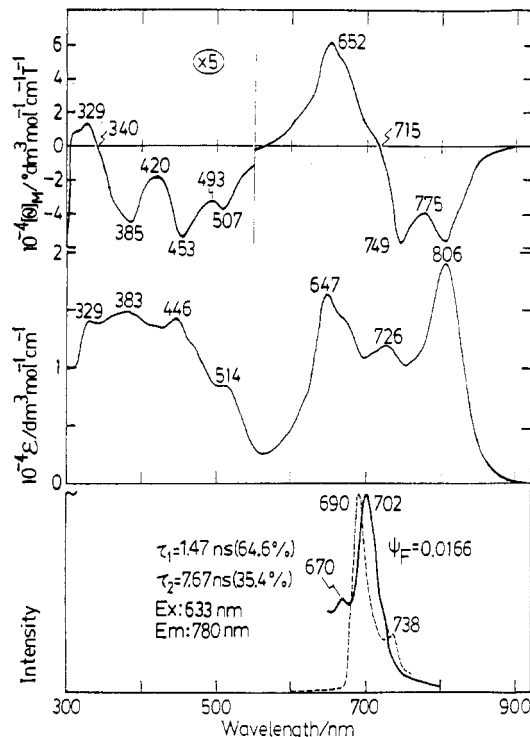

Figure 2. Electronic absorption (middle), magnetic circular dichroism (top), and fluorescence emission and excitation spectra (bottom) of Zn(DiNpTAP) in DCB.

performed for (pyrrole proton) deprotonated species, the central nitrogen atoms were assumed to be equivalent, supplying 1.5 electrons each to the π-system. In addition, σ polarizability was taken into account according to Hammond.[11] Resonance integrals were taken to be −2.48 (β_{CN}) and −2.42 eV (β_{CC}).[10] Two-center repulsion integrals were computed by the method of Mataga and Nishimoto.[12] The choice of configurations was based on energetic considerations, and all singly excited configurations up to 6 eV (56 458 cm^{-1}) were included. Separately, in order to answer the question raised by a reviewer, MO calculations were performed for DiNpTAP^{2-} and Pc^{2-} employing the parameters used by Gouterman and co-workers.[13] In this case, all singly excited configurations up to 7 eV were taken into account.

Results and Discussion

(i) Spectra of Zn(DiNpTAP) and Co(DiNpTAP). Figure 2 shows the absorption, fluorescence emission and excitation, and MCD spectra of Zn(DiNpTAP). Compared with the absorption spectra of common ZnPcs,[14] the Q band splits markedly, and the Q-band peak to the longest wavelength appears at 806 nm, much lower in energy than in ZnPc (670–700 nm). The Q-band absorption coefficients (ϵs) are also smaller. The energy differences among the three prominent Q-band peaks are 1367, 1682, and 3049 cm^{-1} for the peaks at 806 and 726, 726 and 647, and 806 and 647 nm, respectively. The value between 806 and 726 nm (1367 cm^{-1}) is appropriate as the spacing of vibrational bands in Pcs,[14] while the large energy difference of 3049 cm^{-1} between peaks at 806 and 647 nm has not been found in common MPcs[14] (as shown in Table 1, the peaks at 806 and 647 nm correspond to a split Q$_{0-0}$ band). The Soret band region also differs significantly from that in general MPcs, in that many peaks are observed over a wide wavelength range. In the MCD spectrum, minima and maxima are detected corresponding

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Table 1. Observed Energy Shifts and Splitting of the Q-Bands in 10^{-3} cm^{-1} Units[a]

compound	Q_1	Q_2	shift	splitting
ZnPc[b]	15.04	15.04	0.00	0.00
monobenzo-ZnPc[b]	14.43	14.68	−0.49	0.25
opposite dibenzo-ZnPc[b]	13.69	14.40	−0.99	0.71
octaphenylated ZnTAP[c]	15.77	15.77	0.00	0.00
mononaphtho-ZnTAP[c]	14.22	15.38	−0.97	1.16
opposite dinaphtho-ZnTAP	12.41	15.46	−1.84	3.05

[a] Shifts are given by either $(Q_1 + Q_2)/2 - 15.04$ (peak position of ZnPc) or $(Q_1 + Q_2)/2 - 15.77$ (peak position of octaphenylated ZnTAP). [b] Data from refs 19 and 22. [c] Data from ref 4.

roughly to the position of electronic absorption peaks and shoulders (*i.e.* Faraday *B* terms), suggesting that no degenerate states are included. The fluorescence emission spectrum also differs markedly from that of general Pcs[5,15] in that the position of the main S_1 peak lies at a wavelength shorter than the longest wavelength Q-band absorption peak,[16] although an approximate mirror-image relationship is seen with the excitation spectrum. Its quantum yield ($\Phi_F = 0.017$) is much smaller than is usual in ZnPc ($\Phi_F = 0.30$)[5] in good accord with our previous result[3,4] that Φ_F of the azaporphyrin S_1 emission becomes smaller with a departure of molecular symmetry from D_{4h}. Considering that the position of the S_1 emission peak is close to that of TAPs[17b] and that naphthalocyanines emit much more weakly than TAPs,[18] it is suggested that the inner TAP skeleton of the Zn(DiNpTAP) molecule may be mainly responsible for the above S_1 emission. With respect to the emission lifetimes, two values of 1.47 (64.6%) and 7.67 ns (35.4%) were obtained by biexponential fit of the fluorescence decay curve (not shown). In the case of mono-naphtho-fused ZnTAP, *i.e.* Zn(NpTAP) [$2^1,2^6$-diphenylnaphtho-[*b*]-7,8,12,13,17,18-hexaphenyl-5,10,15,20-tetraazaporphyrinato-(2−)]zinc(II)), a Φ_F of 0.03 and lifetimes of 1.31 (79%) and 7.15 ns (21%) have been measured in the same solvent.[4]

Of the several spectroscopic features of Zn(DiNpTAP) described above, the electronic absorption spectra alone can be related reasonably to those of octaphenylated ZnTAP and octaphenylated mononaphtho ZnTAP (Zn(NpTAP)).[4] That is to say, according to the symmetry-adapted perturbation method recently developed,[19] the effect of substituent groups on the spectra of porphyrins and Pcs can be systematically understood on the basis of the number and position of the substituent groups. Two important factors are the shift of the Q band from the Q-band position of the parent molecule and the splitting of the Q band of the resultant molecules. If Δ(shift) represents the Q-band shift of a monosubstituted type porphyrinic compound from the Q band of a parent molecule with D_{4h} symmetry, the Q-band shift of *opposite* type disubstituted porphyrins or Pcs becomes 2Δ(shift). Similarly, theoretically, the splitting of the Q band (Δ(splitting)) of *opposite* (D_{2h}) type disubstituted porphyrins is twice that of a monosubstituted C_{2v} type compound. In contrast, no splitting of the Q band is observed for *adjacent* (C_{2v}) type disubstituted porphyrinic compounds. Since octaphenylated ZnTAP shows a Q_{0-0} band at 634 nm, while octaphenylated mononaphtho-ZnTAP produces split Q_{0-0} peaks at 650 and 703 nm,[4] Δ(shift) and Δ(splitting) of the Q bands can be summarized, as shown in Table 1, assuming further that the 806 and 647 nm peaks correspond to the split Q_{0-0} band of Zn(DiNpTAP). Concerning the Δ(shift), the value for Zn(DiNpTAP) is twice
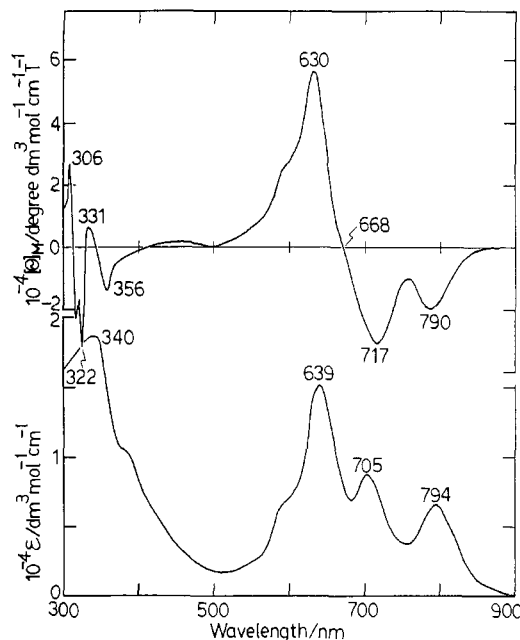
Figure 3. Electronic absorption (bottom) and magnetic circular dichroism spectra (top) of Co(DiNpTAP) in DCB.

that for Zn(NpTAP), consistent with prediction from theory.[19,20] Although the Δ(splitting) of Zn(DiNpTAP) is 2.6 times that of Zn(NpTAP), slightly inconsistent with theory,[21] this is exactly the same phenomenon as observed between *opposite* type dibenzo-ZnPc and monobenzo-ZnPc.[19,22] Thus, the results in Table 1 strongly support the view that we are dealing with *opposite* (D_{2h}) type TAP derivatives, not *adjacent* (C_{2v}) TAPs. For comparison, values in ZnPc and benzo-substituted ZnPc systems[19] are also included in Table 1. Both the Δ(shift) and Δ(splitting) values are much larger for TAP systems than Pc systems, consistent with the data that substituent effects appear more pronounced in smaller porphyrins.[4,23] For example, the Δ(splitting) of Zn-(DiNpTAP) is about 4.3 times larger than that of "*opposite*" type dibenzo-ZnPc.[19,22]

Spectra of Co(DiNpTAP), shown in Figure 3, are similar to those of Zn(DiNpTAP). The lowest energy Q band lies at shorter wavelength than that in Zn(DiNpTAP), and the absorption intensity of the Q band relative to the Soret band is smaller for Co(DiNpTAP) than Zn(DiNpTAP), as also seen in ordinary Co- and ZnPc systems.[14] The energy difference (3055 cm^{-1}) between the first and the third Q-band peaks from the longer wavelength side is almost exactly the same as in the Zn(DiNpTAP) system (3049 cm^{-1}), indicating that these two intense Q-band peaks are characteristic of M(DiNpTAP) systems (*i.e.* the split Q_{0-0} band). In the Soret band region, at least one peak and shoulder (around 385 nm) are discernible. The shape of the MCD spectra resembles that of Zn(DiNpTAP), again showing the contribution of Faraday *B* terms.

(ii) Molecular Orbital Calculations. According to group theory[19,20] and experimental data on benzo-substituted Pcs,[22] the Q band of *adjacent* C_{2v} type porphyrins and Pcs does not split while that of *opposite* D_{2h} types does split. However, in order to enhance our interpretation of the spectra, MO calculations have been performed within the framework of PPP approximation[9] for DiNpTAP^{2-} and, for comparison, Pc^{2-} and the related TAPs^{2-}

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(16) In order to confirm that this is the S_1 emission, the excitation wavelength was changed every 10 nm between 800 and 560 nm.

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(21) The symmetry-adapted perturbation theory adopted in ref 19 is a kind of first-order perturbation theory, and this slight discrepancy may be ascribed to the limit of the theory.

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shown in Figure 1. For Pc^{2-}, the Q and Soret bands are calculated to lie at 662 and 332 nm respectively, consistent with previously reported experimental data (approximately 660–690 and 330–335 nm, respectively),[14,23] therefore demonstrating the reliability of the parametrization. In the case of DiNpTAP^{2-}, the two split Q bands of comparative intensity are calculated to lie at 691 and 608 nm, which are shorter wavelengths than the experimental data. A large part of this discrepancy in the Q-band wavelengths between our M(DiNpTAP) systems (around 800 and 640 nm) and the calculated values (691 and 608 nm), however, can be explained as a substituent effect of the phenyl groups. Although the Q band shifts to longer wavelength in proportion to the number of substituent groups when the same substituent groups are used,[24] the effect of phenyl groups is particularly large when they are directly attached to the TAP skeleton. For example, MgTAP without substituent groups[17a] and tetra-*tert*-butylated MgTAP[17b] show Q$_{0-0}$ bands at 587 and 592 nm, respectively, while the Q$_{0-0}$ band of octaphenylated MgTAP[17b] occurs at 636 nm in pyridine. In this way, the effect of phenyl groups on the shift of the Q band (*ca.* 6 nm per phenyl) is about 5 times larger than that of butyl groups (*ca.* 1.2 nm per butyl). Accordingly, the attachment of four phenyl groups to the TAP skeleton would shift the Q band by roughly 25 nm to longer wavelengths. Our M(DiNpTAP)s additionally contain four phenyl groups attached to benzene rings fused directly onto the TAP skeleton, so that this substituent effect also has to be estimated. For this purpose, the most useful compounds to compare are metallonaphthalocyanines (MNcs) without substituent groups and 2^1,7^1,12^1,17^1-tetraphenyl MNcs (for this structure, see the compound abbreviated as M(TPhNc) in Figure 1).[23] Compared with the Q-band position of the former compounds, those of the latter are shifted to lower wavelengths by *ca.* 30–33 nm when M = VO or Cu in noncoordinating solvents such as 1-chloronaphthalene and *o*-dichlorobenzene (*i.e.* 8 nm per phenyl)[23] Accordingly, it is anticipated that the Q band of a M(DiNpTAP) π-system *without substituent groups* would lie at roughly 55–60 nm[25] to shorter wavelengths compared to the present Zn(DiNpTAP) and Co(DiNpTAP) systems. Thus, the calculated values are not extraordinarily short and appear to be fairly realistic. In fact, the calculated Q-band positions (662 nm for Pc^{2-} and 691 and 608 nm for DiNpTAP^{2-}) suggest that the two Q-band peaks of *opposite* type D$_{2h}$ M(DiNpTAP)s appear at both sides of the Q-band peak of MPcs with D$_{4h}$ symmetry, and this is indeed recognized when comparison is made among the Q-band positions of Zn(DiNpTAP) and/or Co(DiNpTAP) (i.e. ca. 800 and 640 nm) and octaphenylated MPcs: octaphenylated MPcs show the Q$_{0-0}$ bands at around 700–720 nm.[23]

We have compared our calculations with the results of MO calculations employing Gouterman's parameters,[13] which have

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(25) We feel this value is the minimum estimate from the following argument. An additivity of the substituent effect on the Q-band position of Pcs exists when a substituent is introduced at the same position of different benzene rings. For example, the energy difference of the Q$_{0-0}$ band of (2^2,7^2,12^2,17^2-tetra-*tert*-butylbenzo[*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)zinc from that of unsubstituted ZnPc is four times larger than that between (2^2-*tert*-butylbenzo[*b*]tribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)zinc and unsubstituted ZnPc.[24] However, we have found recently for several Pcs (our unpublished data) that this additivity does not strictly hold when the second substituent group is introduced at the *para* positions of each benzene ring. In this case, the effect of the second substituent group is larger than that of the first substituent group. For example, the Q$_{x(0-0)}$ bands of (i) unsubstituted H$_2$Pc, (ii) 2^1,7^1,12^1,-17^1-tetrabutoxytetrabenzo[*b*,*g*,*l*,*q*]-5,10,15,20-tetraazporphyrin, and (iii) 2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4-octabutoxytetrabenzo[*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrin, appear at 694.5, 728, and 768 nm, respectively, in *o*-dichlorobenzene. The energy difference between (i) and (ii) is 662.6 cm^{-1} while that between (ii) and (iii) is 715.4 cm^{-1}. Thus, the effect of the second group is 1.08 times larger than the first group. Since our M(DiNpTAP)s contain two phenyl groups as substituents at *para* positions of each naphthalene ring, our estimate of the shift due to four phenyl groups (30–33 nm, *i.e. ca.* 8 nm per phenyl) may be smaller than in the real systems. Accordingly, the calculated Q-band position may be a little shorter than the real systems, but appears not to be markedly short.
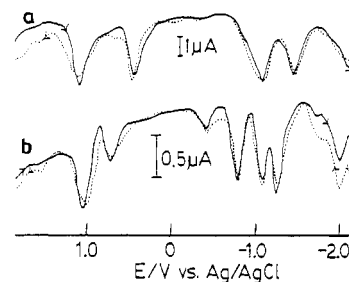
Figure 4. Differential pulse voltammograms of Zn(DiNpTAP) (curves a) and Co(DiNpTAP) (curves b) in DCB containing tetrabutylammonium perchlorate (0.3 M). Scan rate = 5 mV/s. Area of electrode = 0.07 cm^2. Concentration = *ca.* 1 mM for Zn(DiNpTAP) and *ca.* 0.25 mM for Co(DiNpTAP).

been adopted by many researchers. With his parameters, the Q and Soret bands of dianion of Pc with D$_{4h}$ symmetry (*i.e.* Pc^{2-}) were calculated to lie at 669 (*f* = 0.93) and 320 (*f* = 2.39) nm. Since, as described above, the Q and Soret bands of transition metal Pcs appear typically at 660–690 and 330–335 nm, respectively,[14,23] these values are also reproducing the hitherto accumulated experimental data. On the other hand, the calculated split Q bands of the DiNpTAP dianion (*i.e.* DiNpTAP^{2-}) were at 699 (*f* = 0.66) and 598 (*f* = 0.88) nm, revealing much shorter wavelengths than in our experimental M(DiNpTAP) systems. Here again, the calculated Q band of Pc^{2-} (669 nm) appeared approximately midway between the split Q bands (699 and 598 nm) of DiNpTAP^{2-}. Thus, a large part of discrepancy in the Q-band position between our calculations and the M(DiNpTAP) systems appears to be attributable to a substituent effect of the phenyl groups, not to a failure of the parametrization.

A summary of the calculations is given in Table 2. This table predicts several things. (i) In a one-electron description, the Q band to lower energy corresponds to a transition from the HOMO to the LUMO, while that to higher energy corresponds to one from the HOMO to the second LUMO. These transitions become purer the longer the molecule which fuses to the TAP skeleton. Under D$_{2h}$ symmetry, these bands are assigned to a transition from a$_u$ to b$_{2g}$ orbitals, and to one from a$_u$ to b$_{3g}$ orbitals, respectively. (ii) The splitting of the Q band increases with increasing ratio of long to short axis of the molecule, since the calculated Q-band splitting energies for DiBzTAP^{2-}, DiNpTAP^{2-}, and DiAnTAP^{2-} are 1507, 1976, and 2340 cm^{-1}, respectively. (iii) The Soret band also splits into two and shifts to longer wavelengths compared with the position of Pc. They are, however, no longer described in a one-electron description, since they appear to be mixtures of several configurations. (iv) Both the Soret and Q bands shift to longer wavelength and the Q band gains intensity with the expansion of the π-system, *i.e.* in the order DiBzTAP^{2-}, DiNpTAP^{2-}, and DiAnTAP^{2-}. (v) In M(DiNpTAP), several frontier orbitals appears to be naphthalene-centered orbitals. Although not shown, the second and fourth HOMO and the third LUMO have larger LCAO coefficients in the naphthalene moiety than in the central TAP moiety. However, as Table 2 suggests, these naphthalene-centered orbitals do not contribute to transitions in the Soret and Q-band regions.

(iii) Voltammetry and Spectroelectrochemistry. Redox potentials of Zn(DiNpTAP) and Co(DiNpTAP) were measured in DCB (Figure 4). Four couples at 1.06, 0.46, −1.06, and −1.55 V vs Ag/AgCl of the former (curves a) are attributed to the second and first oxidation, and the first and second reduction of the ligand, respectively. For comparison, those of the tetraneopentoxy-Pc–zinc complex (ZnTNPc), having approximate D$_{4h}$ symmetry, occur at 1.23, 0.57, −1.07, and −1.45 V in the same solvent.[26] The potential difference (ΔE) between the first oxidation and reduction in Zn(DiNpTAP) (1.52 V) is 120 mV

(26) Manivannan, V.; Nevin, W. A.; Leznoff, C. C.; Lever, A. B. P. *J. Coord. Chem.* **1988**, *19*, 139.

Table 2. Calculated Transition Energies, Oscillator Strength (f), and Configurations for DiBzTAP^{2-}, DiNpTAP^{2-}, and DiAnTAP^{2-} [a]
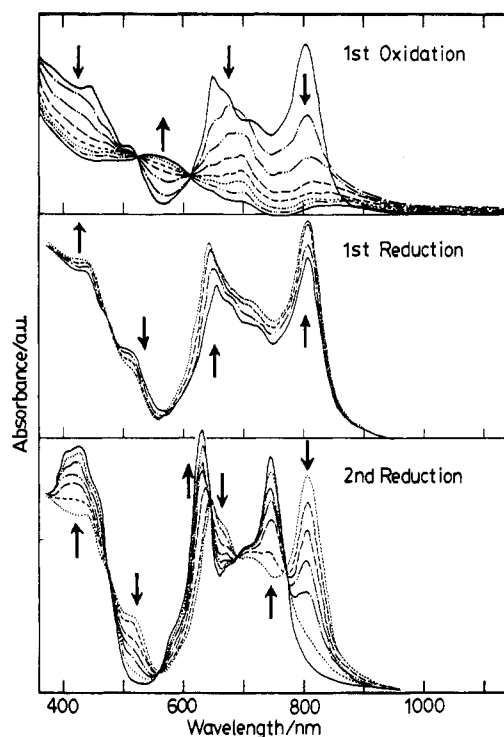
energy/eV (nm)	f	configurations			
		DiBzTAP^{2-}			
1.90604 (650)	0.58	17 → 18 (85%)	16 → 19 (15%)		
2.09351 (592)	0.39	17 → 19 (76%)	16 → 18 (23%)		
3.34142 (371)	0.94	11 → 18 (46%)	16 → 18 (21%)	13 → 18 (21%)	17 → 19 (11%)
3.66684 (338)	2.27	16 → 18 (51%)	11 → 18 (17%)	13 → 18 (16%)	17 → 19 (12%)
3.91309 (317)	1.78	16 → 19 (65%)	17 → 18 (13%)	11 → 19 (11%)	
4.33110 (286)	0.40	13 → 19 (68%)	16 → 19 (11%)	11 → 19 (10%)	
4.43939 (279)	0.52	17 → 18 (56%)	17 → 18 (24%)	17 → 18 (12%)	
		DiNpTAP^{2-}			
1.79505 (691)	0.69	21 → 22 (88%)	19 → 23 (12%)		
2.04014 (608)	0.67	21 → 23 (80%)	19 → 22 (18%)		
3.20293 (387)	1.98	19 → 22 (41%)	14 → 22 (34%)	21 → 23 (13%)	
3.49928 (354)	1.15	14 → 22 (52%)	19 → 22 (23%)	16 → 22 (12%)	
4.05736 (306)	1.70	19 → 23 (71%)			
4.15874 (298)	0.34	16 → 22 (44%)	18 → 23 (28%)	19 → 22 (12%)	
		DiNpTAP^{2-} by Gouterman's Parameter			
1.77373 (699)	0.66	21 → 22 (89%)			
2.07536 (597)	0.88	21 → 23 (83%)	18 → 22 (13%)		
3.36839 (368)	2.58	18 → 22 (49%)	14 → 22 (19%)	19 → 23 (15%)	
3.55064 (349)	0.36	14 → 22 (66%)	16 → 22 (12%)	18 → 22 (10%)	
3.89030 (319)	1.14	19 → 23 (26%)	18 → 22 (20%)	17 → 24 (13%)	16 → 22 (13%)
4.22391 (294)	1.40	18 → 23 (68%)			
		DiAnTAP^{2-}			
1.72920 (717)	0.71	25 → 26 (89%)			
2.01846 (614)	0.87	25 → 27 (82%)	22 → 26 (16%)		
3.08686 (402)	2.43	25 → 27 (12%)	23 → 27 (17%)	22 → 26 (46%)	18 → 26 (17%)
3.43613 (361)	0.34	23 → 27 (10%)	18 → 26 (74%)		
3.89794 (318)	1.09	23 → 27 (42%)	22 → 26 (28%)		
4.13415 (300)	2.68	22 → 27 (69%)			

[a] Excited states with energy less than 4.5 eV and f greater than 0.3 are shown.

or about 0.2 V smaller than that in ZnTNPc (1.64 V) and general ZnPcs ($\Delta E = ca.$ 1.7 V),[27] in accord with the red-shifted Q$_{0-0}$ band position of Zn(DiNpTAP) (806 nm). In addition, since one naphthalene ring-fused Zn(NpTAP) shows the corresponding couples at 1.17, 0.06, −1.07, and −1.39 V in the same solvent,[4] it is seen that the D_{2h} type ring expansion causes mainly a lowering of the first and second oxidation potentials, and therefore destabilization of the HOMOs. In contrast, the first reduction potential practically does not differ between Zn(NpTAP)[4] and Zn(DiNpTAP), implying that the LUMO energies are similar in the two systems.

The MO calculations succeeded in producing data which support the above electrochemical results. The reduction of the HOMO–LUMO energy gap on going from Pc^{2-} to DiNpTAP^{2-} is reasonably explained, since this value in the former system is 3.7427 eV while in the latter it is 3.5450 eV. The difference of $ca.$ 0.2 eV corresponds to what we observed. The destabilization of the HOMO on going from NpTAP^{2-} to DiNpTAP^{2-} is understandable, since the first HOMO energies in these systems are predicted at −8.1318 and −7.7185 eV, respectively. In contrast, the energies of the first LUMOs in the two systems were very close to each other (−4.1172 and −4.1735 eV, respectively), again supporting the similar first reduction potentials observed by experiment.

Voltammograms of cobalt porphyrins and Pcs differ generally from those of zinc complexes in showing redox couples due to cobalt oxidation and reduction (Figure 4, curves **b**). Within the limit of solvent breakdown, in DCB, Co(DiNpTAP) shows seven redox couples at 1.03, 0.75, −0.40, −0.77, −1.12, −1.25, and −2.05 V vs. Ag/AgCl, in contrast to five couples in CoTNPc. By comparing literature data,[17b,28] we tentatively assign these couples

(27) (a) Rollman, L. D.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455. (b) Lever, A. B. P.; Licoccia, S.; Magnell, K.; Minor, P. C.; Ramaswamy, B. S. *ACS Symp. Ser.* **1982**, *No. 201*, 237 and several references cited therein.
(28) Nevin, W. A.; Hempstead, M. R.; Liu, W.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 570.

Figure 5. Spectroscopic changes observed during electrolysis of a DCB solution of Zn(DiNpTAP) at 0.9 (top), −1.3 (middle), and −1.9 (bottom) V vs Ag/AgCl.

to Co$^{III/II}$, first ligand oxidation, Co$^{II/I}$, and first, second, third, and fourth ligand reductions, respectively.

Figure 5 shows the spectroscopic changes observed on the formation of monocationic and mono- and dianionic Zn(DiNpTAP). In the oxidation, the intensity of both the Q and Soret regions decreases. Concomitantly, the initial green solution

turned to a pale yellow solution. In the case of a ZnPc with D_{4h} symmetry, a similar spectroscopic change was observed except that an intensity increase occurred in the shorter wavelength region of the Soret band.[26] This similarity in the Zn(DiNpTAP) and ZnPc systems may reflect the removal of an electron from orbitals of similar symmetry, where an electron is removed from nondegenerate a_u (the former) or a_{1u} (the latter) orbitals. In contrast, the spectroscopic changes observed on reduction are quite different from general MPcs with D_{4h} symmetry. On first reduction, tetracoordinated Mg-, Ni-, and CuPcs show spectra with a weak peak at *ca.* 900–1000 nm and two intense peaks at 550–650 nm.[29] In Zn(DiNpTAP), the first reduction intensifies both the Soret and Q bands but no near-IR peak appears. The different behavior between Zn(DiNpTAP) and MtPc can be attributed to the difference in shape of the molecular orbitals to which the electron is added. In MPc with D_{4h} symmetry, an electron is accepted by doubly degenerate e_g oribitals, while in Zn(DiNpTAP) having D_{2h} symmetry it is added to a non-degenerate b_{2g} orbital. The spectroscopic changes observed in the second reduction are very pronounced. Both the Q and Soret bands shift to shorter wavelength and intensify, and the splitting of the Q band decreases by approximately one-third. Thus, the introduction of the second electron appears to weaken the effective D_{2h} symmetry.

Spectroelectrochemistry of Co(DiNpTAP) was performed in DCB, but its low solubility prevented the measurement of definitive spectra. On the first oxidation, however, a decrease of the Q-band intensity was observed, consistent with the above assignment that the first oxidation is a ligand-centered process.

Conclusions

Tetraazaporphyrins (TAPs) containing two naphthalene molecules at the *"opposite"* pyrrole rings were synthesized and characterized. They are structural isomers of Pcs, and their D_{2h} molecular symmetry was supported by the so-called symmetry-adapted perturbation theory, but they differ from general MPc in that they show a markedly split Q_{0-0} and Soret band. The spectroscopic changes observed by fusing two naphthalene molecules at the *"opposite"* positions of TAP were much larger than those seen by fusing two benzene molecules at the *"opposite"* positions of Pc. In voltammetry, the potential difference between the first oxidation and reduction was found to be smaller than in general Pcs, in accordance with the results inferred from the position of the Q band. The spectrum of the first reduction product differed markedly from that of D_{4h}-type Pcs, probably reflecting the difference of the symmetry of the first LUMO. These spectroscopic and electrochemical features have been reproduced by MO calculations using the PPP approximation.

To date, mainly the size of π-conjugation systems and the number and kind of peripheral substituent groups have been changed in Pc-related compounds in order to alter or adjust the position of the absorption bands and redox potentials. The present study has demonstrated, however, that a change of molecular symmetry to D_{2h} is also very effective for these purposes.

(29) (a) Dott, J. W.; Hush, N. S. *J. Chem. Soc.* **1964**, 4607. (b) Sidorov, A. N. *J. Struct. Chem. USSR (Engl. Transl.)* **1973**, *14*, 229.