Aryloxo Derivatives of Phosphorus(V) Porphyrins. Synthesis, Spectroscopy, Electrochemistry, and Singlet State Properties

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Aryloxo derivatives of phosphorus(V) porphyrins of the type $[(TpTP)P(OR)_2]^+OH^-$ where TpTP is the dianion of tetra-*p*-tolylporphyrin and OR is an axial aryloxo (2,4-dimethylphenoxo, 4-methylphenoxo, phenoxo, 4-nitrophenoxo, 4-(4-nitrophenoxy)phenoxo, or 4-(2,4-dinitrophenoxy)phenoxo) ligand have been synthesized and fully characterized by FAB−mass, UV−vis, fluorescence, infrared, and nuclear magnetic resonance (^1H and ^{31}P) spectroscopies and cyclic voltammetric methods. Each new porphyrin shows a typical "normal UV−vis absorption spectrum" indicating the presence of a P(V) ion in the porphyrin cavity. The proton-decoupled ^{31}P NMR signal observed for these compounds, between −194 and −200 ppm, suggests that there exists an octahedral coordination around the phosphorus atom, and this supposition is further substantiated by the porphyrin ring-current-induced upfield shifts observed for protons on the two axial aryloxo ligands in the ^1H NMR spectra. Cyclic voltammetric studies reveal that each porphyrin undergoes two successive, one-electron reductions with the site of electron transfer being the porphyrin ring. The fluorescence quantum yield values of these porphyrins are found to be sensitive to the nature of the aryloxo ligand and also to the solvent polarity. The singlet state properties of these systems have been discussed in light of both the fluorescence and the redox potential data.

Introduction

The unique structural, spectroscopic, and redox properties of phosphorus(V) porphyrins (P(V) porphyrins) have attracted considerable attention over the past two decades.[1−21] While a majority of the early studies[1−10] on these bis axially ligated metalloid porphyrins have focused on their halide and hydroxide derivatives, recent studies[11−21] have, however, elaborated on the range of axial ligands coordinated at the phosphorus atom.

Specifically, preparation and spectral characterization of complexes of the type $[(por)P(L)_2]^+$, where por is the dianion of a *meso*-tetraarylporphyrin and L is an axially bound alkoxo, aryloxo, or arylamido ligand, have been recently reported by Brothers and co-workers[11] and also by Shimidzu and co-workers.[12−14,18,19] More recently, we[20] and also Susumu et al.[21] have designed and synthesized various "axial bonding" type hybrid porphyrin trimers in which a P(V) porphyrin has been linked, via aryloxy bridges, to free-base, phosphorus(V), zinc(II), or copper(II) porphyrins. Thus, more than a dozen P(V) porphyrins having organic axial ligands are currently available for study, but the spectral and redox properties of these systems have rarely been investigated in detail.[11,17,19] In this paper, we report on the spectral (FAB−mass, UV−vis, IR, and ^1H and ^{31}P NMR), electrochemical, and photochemical properties of a series of newly synthesized P(V) porphyrins having various aryloxo ligands coordinated to the central phosphorus ion. The structures of the investigated complexes are given in Figure 1. These complexes exist in ionic forms in solution and are represented as $[(TpTP)P(OR)_2]^+$, where OR is a 2,4-dimethylphenoxy $(O-o,p-C_6H_3(CH_3)_2)$, 4-methylphenoxy $(O-p-C_6H_4-CH_3)$, phenoxy (OC_6H_5), 4-(4-nitrophenoxy)phenoxy $(O-p-C_6H_4O-p-C_6H_4(NO_2))$, 4-(2,4-dinitrophenoxy)phenoxy $(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)$, or 4-nitrophenoxy $(O-p-C_6H_4(NO_2))$ group.

Experimental Section

Materials. The chemicals and solvents utilized in this study were purchased from either Aldrich Chemical Co. or B.D.H. (India). The solvents utilized for spectroscopic and electrochemical experiments were further purified using standard procedures.[22]

Synthesis. The *meso*-5,10,15,20-tetratolylporphyrin (H₂TpTP), [(TpT-P)PCl₂]⁺, and [(TpTP)P(O-*p*-C₆H₄CH₃)₂]⁺ were synthesized and purified according to the reported procedures.[11,23] [(TpTP)P(O-*o*,*p*-C₆H₃-

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(1) Sayer, P.; Gouterman, M.; Connell, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 1082.
(2) Carrano, C. J.; Tsutsui, M. *J. Coord. Chem.* **1977**, *7*, 79.
(3) Gouterman, M.; Sayer, P.; Shankland, E.; Smith, J. P. *Inorg. Chem.* **1981**, *20*, 87.
(4) Sayer, P.; Gouterman, M.; Connell, C. R. *Acc. Chem. Res.* **1982**, *15*, 73.
(5) Marrese, C. A.; Carrano, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1279.
(6) Mangani, S.; Meyer, E. F.; Cullen, D. L.; Tsutsui, M.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 400.
(7) Harriman, A. *J. Photochem.* **1983**, *23*, 37.
(8) Marrese, C. A.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 1858.
(9) Marrese, C. A.; Carrano, C. J. *Inorg. Chem.* **1984**, *23*, 3961.
(10) Pandian, R. P.; Chandrashekar, T. K.; Chandrasekhar, V. *Ind. J. Chem.* **1991**, *30A*, 579.
(11) Barbour, T.; Belcher, W. J.; Brothers, P. J.; Rickard, C. E. F.; Ware, D. C. *Inorg. Chem.* **1992**, *31*, 746.
(12) Segawa, H.; Kazuhiko, K.; Nakamoto, A.; Shimidzu, T. *J. Chem. Soc., Perkin Trans.* **1992**, 939.
(13) Segawa, H.; Nakayama, N.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1992**, 784.
(14) Kunimoto, K.; Segawa, H.; Shimidzu, T. *Tetrahedron Lett.* **1992**, *33*, 6327.
(15) Lin, Y.-H.; Lin, C.-C.; Chen, J.-H.; Zeng, W.-F.; Wang, S.-S. *Polyhedron* **1994**, *13*, 2887.
(16) Lin, Y.-H.; Sheu, M.-T.; Lin, C.-C.; Chen, J.-H.; Wang, S.-S. *Polyhedron* **1994**, *13*, 3091.
(17) Liu, Y. H.; Benassy, M.-F.; Chojnacki, S.; D'Souza, F.; Barbour, T.; Blecher, J. W.; Brothers, P. J.; Kadish, K. M. *Inorg. Chem.* **1994**, *33*, 4480.
(18) Segawa, H.; Kunimoto, K.; Susumu, K.; Taniguchi, M.; Shimidzu, T. *J. Am. Chem. Soc.* **1994**, *116*, 11193.
(19) Susumu, K.; Kunimoto, K.; Segawa, H.; Shimidzu, T. *J. Phys. Chem.* **1995**, *99*, 29.
(20) Rao, T. A.; Maiya, B. G. *J. Chem. Soc., Chem. Commun.* **1995**, 939.
(21) Susumu, K.; Segawa, H.; Shimidzu, T. *Chem. Lett.* **1995**, 929.

(22) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Organic Chemicals*; Pergamon Press: Oxford, 1980.
(23) Fuhrhop, J.-H.; Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 769.
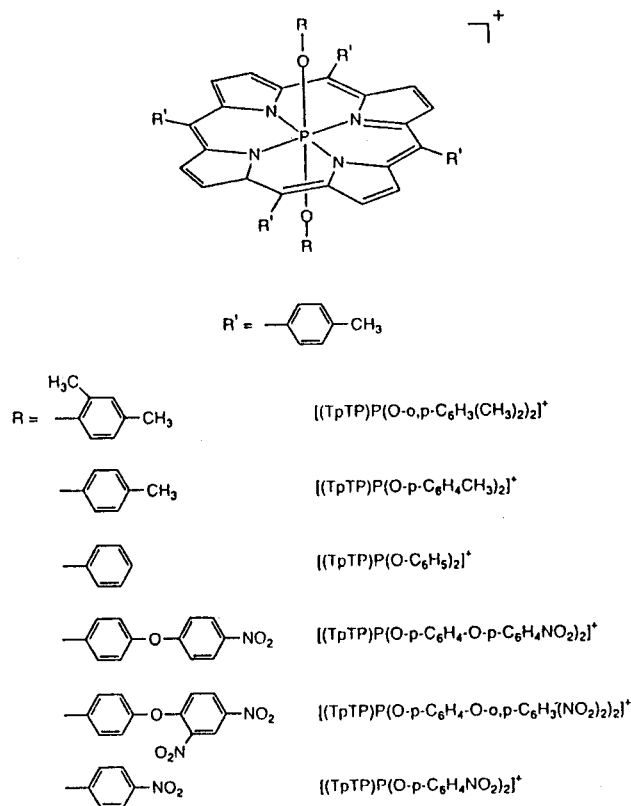
$R' = $ (phenyl)—CH_3

$R = $

(2,4-dimethylphenyl) $[(TpTP)P(O-o,p-C_6H_3(CH_3)_2)_2]^+$

(4-methylphenyl) $[(TpTP)P(O-p-C_6H_4CH_3)_2]^+$

(phenyl) $[(TpTP)P(O-C_6H_5)_2]^+$

(4-nitrophenoxyphenyl) $[(TpTP)P(O-p-C_6H_4\cdot O-p-C_6H_4NO_2)_2]^+$

(2,4-dinitrophenoxyphenyl) $[(TpTP)P(O-p-C_6H_4\cdot O-o,p-C_6H_3(NO_2)_2)_2]^+$

(4-nitrophenyl) $[(TpTP)P(O-p-C_6H_4NO_2)_2]^+$

Figure 1. Structures of the P(V) porphyrins investigated in this study.

$(CH_3)_2)_2]^+$, $[(TpTP)P(OC_6H_5)_2]^+$, and $[(TpTP)P(O-p-C_6H_4NO_2)_2]^+$ were synthesized starting from $[(TpTP)PCl_2]^+$ and 2,4-dimethylphenol, phenol, or 4-nitrophenol, respectively (yields $\cong$ 60%), adapting a procedure reported for the synthesis of $[(TpTP)P(O-p-C_6H_4CH_3)_2]^+$.[11] $[(TpTP)P(O-p-C_6H_4O-p-C_6H_4NO_2)_2]^+$ and $[(TpTP)P(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)_2]^+$ have been synthesized as detailed below.

A. Preparation of $[(TpTP)P(O-p-C_6H_4O-p-C_6H_4NO_2)_2]^+$ and $[(TpTP)P(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)_2]^+$. Hydroquinone (1.10 g, 0.01 mol) and K_2CO_3 (1 g) were stirred together in 20 mL of dry dimethylformamide for 45 min. 4-Nitrochlorobenzene (1.57 g, 0.01 mol) dissolved in 20 mL of dry dimethylformamide was slowly (ca. 0.5 h) added to this mixture, and the resulting solution was stirred overnight at 293 K. The solvents were removed by vacuum evaporation, and the residue was chromatographed on a silica gel column (200 g) using $CHCl_3$ as the eluent. The fractions containing the desired product, 4-(4-nitrophenoxy)phenol, were separated, and the solvents were removed under reduced pressure. The crude product was recrystallized twice from C_2H_5OH before use. Yield $\cong$ 60%. (Mp 169 $\pm$ 2 °C. Anal. Found: C, 62.24; H, 3.94; N, 6.58. Calcd for $C_{12}H_9O_4N$: C, 62.34; H, 3.90; N, 6.06.) Anal.

4-(2,4-Dinitrophenoxy)phenol was synthesized in an analogous manner with hydroquinone and 2,4-dinitrochlorobenzene. Yield $\cong$ 55%. (Mp 132 $\pm$ 2 °C. Found: C, 51.66; H, 2.75; N, 10.33. Calcd for $C_{12}H_8O_6N_2$: C, 52.17; H, 2.90; N, 10.14.)

$[(TpTP)PCl_2]^+$ (0.1 g) and either of the above two phenols (2 g) were dissolved in 25 mL of pyridine, and the resulting solution was refluxed for 1 h. The solvent was removed, and the crude product was chromatographed twice on silica gel. Elution with CH_2Cl_2 removed a faint red fraction containing H_2TpTP. Elution with $CH_3OH-CH_2Cl_2$ (1:9, v/v) removed either $[(TpTP)P(O-p-C_6H_4O-p-C_6H_4NO_2)_2]^+$ or $[(TpTP)P(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)_2]^+$ as a green band. The solvents were removed under reduced pressure, and the resulting solid was recrystallized twice from benzene–octane to give the pure product in each case (yield $\cong$ 50%).

It was noticed during the synthesis of these aryloxo P(V) compounds that the presence of trace amounts of water either in pyridine or in the chromatographic solvents/silica gel resulted in the formation of hydroxo salts along with the chloro salts. In order to be consistent with respect to an identity of the anion, each aryloxo derivative has been fully converted into the hydroxo salt either by refluxing the aqueous (5%)

pyridine solution containing the compound or by washing the $CHCl_3$ solution of it with dilute KOH solution.[11] The hydroxo salts thus obtained were rechromatographed and recrystallized. Tests for the presence of chloride ion proved negative.

B. Mass Spectral Data (*m/z*). $[(TpTP)P(O-o,p-C_6H_3(CH_3)_2)_2]^+$: $[M + H]^+$, 942; $[M - C_8H_9O]^+$, 820; $[M - 2(C_8H_9O)]^+$, 699 (base peak). $p(TpTP)P(O-p-C_6H_4CH_3)_2]^+$: $[M]^+$, 913; $[M - C_7H_7O]^+$, 806; $[M - 2(C_7H_7O)]^+$, 699 (base peak). $[(TpTP)P(OC_6H_5)_2]^+$: $[M + H]^+$, 885; $[M - C_6H_5O]^+$, 792; $[M - 2(C_6H_5O)]^+$, 699 (base peak). $[(TpTP)P(O-p-C_6H_4O-p-C_6H_4NO_2)_2]^+$: $[M]^+$, 1159; $[M - C_{12}H_8NO_4]^+$, 929; $[M - 2(C_{12}H_8NO_4)]^+$, 699 (base peak). $[(TpTP)P-(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)_2]^+$: $[M]^+$, 1249; $[M - C_{12}H_7N_2O_6]^+$, 974; $[M - 2(C_{12}H_7N_2O_6)]^+$, 699 (base peak). $[(TpTP)P(O-p-C_6H_4NO_2)_2]^+$: $[M]^+$, 975; $[M - C_6H_4NO_3]^+$, 837; $[M - 2(C_6H_4NO_3)]^+$, 699 (base peak).

In each case, a les intense peak at $m/z = [M + OH]^+$ was observed, confirming the presence of the hydroxyl counteranion in these systems.

Methods. The optical absorption and emission spectra were recorded with a Shimadzu model UV-160A spectrophotometer and a Jasco model FP 777 fluorescence spectrophotometer, respectively. The concentration of the porphyrins used for absorption spectral measurements ranged from ca. 2×10^{-6} to 5×10^{-5} M, and that used for emission measurements was $\cong 5 \times 10^{-7}$ M. (Optical density at λ_{exc} (430 nm) < 0.2.) The fluorescence quantum yields (ϕ) were estimated by integrating the areas under the fluorescence curves and by using (*meso*-5,10,15,20-tetraphenylporphyrinato)zinc(II) (ZnTPP) as the standard.[24] Refractive index corrections have been incorporated while reporting the fluorescence data in various solvents.[24–26] Infrared spectra were recorded (KBr pellets) with a Jasco model 5300 FT–IR spectrometer. The ^1H NMR spectra were recorded with a Bruker NR-200 AF-FT NMR spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. The proton-decoupled ^{31}P NMR spectra were also recorded with the same instrument, albeit with an operating frequency of 80.5 MHz and with 85% H_3PO_4 as an external standard. The FAB–mass spectra were recorded with a JEOL SX 102/DA-6000 mass spectrometer/data system. Cyclic- and differential-pulse voltammetric experiments (CH_3CN and 0.1 M tetrabutylammonium perchlorate, TBAP) were performed on a Princeton Applied Research (PAR) 174A polarographic analyzer coupled with a PAR 175 universal programmer and a PAR RE 0074 $x-y$ recorder, as detailed in our previous studies.[24–26]

Care was taken to avoid the entry of direct, ambient light into the samples in all the spectroscopic and electrochemical experiments. Unless otherwise specified, all the experiments were carried out at 293 $\pm$ 3 K.

Results

Each aryloxo P(V) porphyrin investigated in this study has been synthesized by closely following a procedure described earlier for the synthesis of $[(TpTP)P(O-p-C_6H_4CH_3)_2]^+$ and related aryloxo species.[11] All of these P(V) porphyrins are found to be stable in their solid state and also in a variety of organic solvents.

A. Spectroscopy. The wavelengths of maximum absorbance (λ_{max}) and molar extinction coefficient (log ϵ) values of all the aryloxo porphyrins are summarized in Table 1. Representative UV–vis spectra of $[(TpTP)P(O-p-C_6H_4CH_3)_2]^+$ and $[(TpTP)P-(O-p-C_6H_4O-o,p-C_6H_3(NO_2)_2)_2]^+$ are given in Figure 2. Both porphyrins show an intense Soret band and two less-intense Q-bands between 350 and 650 nm, and log ϵ values at the absorption maxima of these bands are found to be in a similar range, as seen in Figure 2 and Table 1. However, the log ϵ value of the peak at 314 nm of $[(TpTP)P(O-p-C_6H_4-o,p-C_6H_3-(NO_2)_2)_2]^+$ is higher than that of the corresponding peak (311 nm) of the 4-methylphenoxo analogue and this is due to an additional absorption by the dinitro aromatic chromophore

(24) Sirish, M.; Maiya, B. G. *J. Photochem. Photobiol., A* **1994**, *77*, 189.
(25) Rao, T. A.; Maiya, B. G. *Polyhedron* **1994**, *12*, 1863.
(26) Sirish, M.; Maiya, B. G. *J. Photochem. Photobiol., A* **1995**, *85*, 127.

Table 1. UV−Vis and IR Spectral Data of the Aryloxo P(V) Porphyrins[a]

	λ_{max}, nm (log ϵ)				
	Q-bands		B−band	UV	ν_{P-O}, cm^{-1}
compound					
(TpTP)P(O-o,p-C$_6$H$_3$(CH$_3$)$_2$)]$^+$	613 (3.81)	570 (4.11)	436 (5.01)	312 (4.16)	868
[(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$	610 (3.74)	566 (4.03)	439 (5.23)	311 (4.11)	889
[(TpTP)P(OC$_6$H$_5$)$_2$]$^+$	609 (3.97)	565 (4.25)	440 (5.32)	312 (4.34)	885
[(TpTP)P(O-p-C$_6$H$_4$O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$	611 (3.90)	566 (4.13)	440 (4.99)	309 (4.59)	870
[(TpTP)P(O-p-C$_6$H$_4$O-o,p-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$	616 (4.01)	570 (4.18)	444 (5.41)	314 (4.48)	870
[(TpTP)P(O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$	611 (3.94)	566 (4.16)	443 (5.39)	300 (4.52)	885

[a] UV−vis and IR spectra were taken in CH$_2$Cl$_2$ solutions and KBr pellets, respectively. Error limits: λ_{max}, ±1 nm; log ϵ, ±10%; ν_{P-O}, ±2 cm^{-1}.
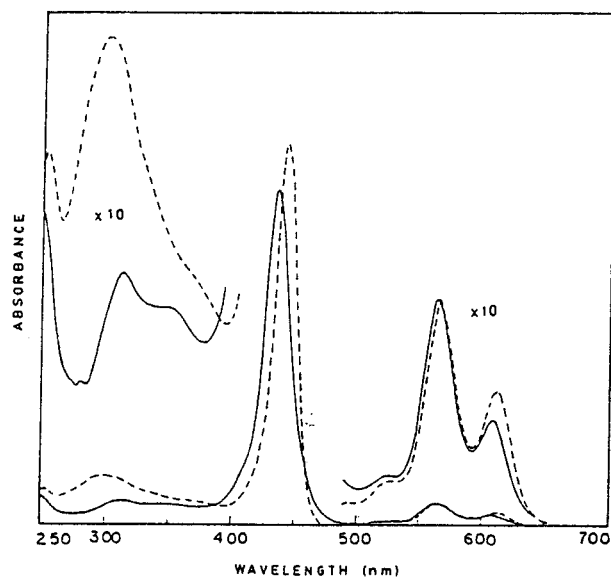
Figure 2. UV−vis spectra of [(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$ (—) and [(TpTP)P(O-p-C$_6$H$_4$O-o,p-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ (- - -) in CH$_2$Cl$_2$.

present on the former complex. The data on λ_{max} and log ϵ values given in Table 1 clearly suggest that the spectrum of each aryloxo derivative synthesized in this study also shows an intense Soret band and two less-intense Q-bands. A closer inspection of the data further suggests that these values are not very sensitive to the nature of axial aryloxo ligands. Nevertheless, as was the case with various metallo or metalloid porphyrins containing organic axial ligands,[4,11,27] the Soret bands of the aryloxo P(V) porphyrins reported here were also found to be broad and less intense in comparison with those of [(TpTP)PCl$_2$]$^+$ or [(TpTP)P(OH)$_2$]$^+$ (data not shown).

The band due to P−Cl stretching frequency (ν_{P-Cl}) observed at 425 cm^{-1} in the IR spectrum of [(TpTP)PCl$_2$]$^+$ was absent in the spectra of the aryloxo derivatives. The IR band due to ν_{P-O} for [(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$ has been reported[11] to occur at 885 cm^{-1}, and on the basis of this fact, the bands observed in the region of 868−889 cm^{-1} can be assigned to the ν_{P-O} for various aryloxo porphyrins investigated in this study (see Table 1).

Each P(V) porphyrin reported here was also investigated by the ^{31}P NMR spectroscopic method, and the chemical shift data are summarized in Table 2. The proton-decoupled ^{31}P NMR signal observed for each compound is between −194 and −200
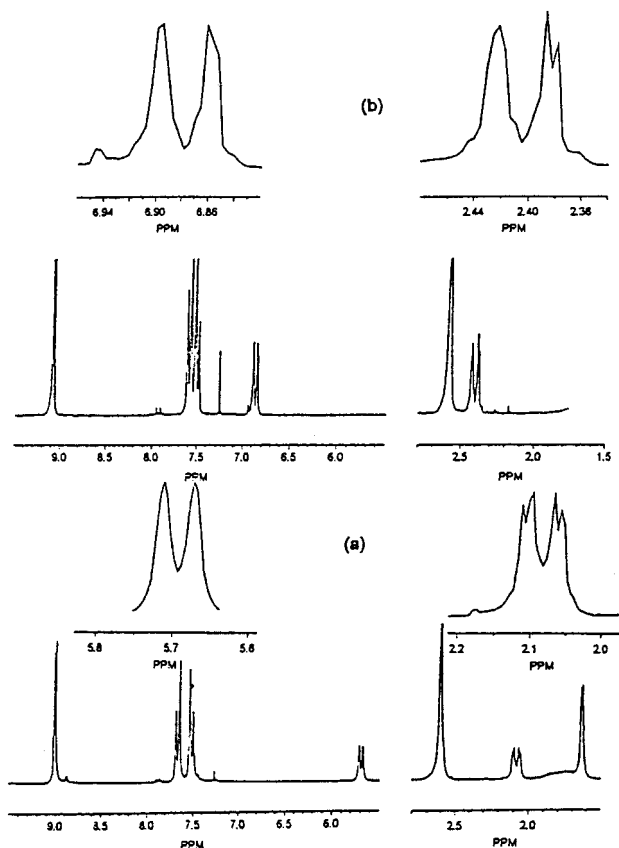

Figure 3. ^{1}H NMR spectra of (a) [(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$ and (b) [(TpTP)P(O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$ in CDCl$_3$ (resonances due to axial ligand protons have been expanded in each case).

ppm, and this range is typical of that expected for six-coordinate phosphorus compounds.[28]

The ^{1}H NMR spectra of [(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$ and [(TpTP)P(O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$ are compared in Figure 3. The spectrum of the chloride salt of [(TpTP)P(O-p-C$_6$H$_4$CH$_3$)$_2$]$^+$ has been reported earlier,[11] and the spectrum obtained in this study for the hydroxo salt of the same species is consistent with the reported spectrum. Therefore, proton assignments for the peaks seen in the spectrum of [(TpTP)P(O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$ can be made on the basis of the known data of the 4-methylphenoxo analogue. Thus, peaks appearing at 9.09 ppm (d, $^4J_{PH}$ = 3.8 Hz), 7.60 ppm (d, $^3J_{HH}$ = 8.1 Hz), and 7.51 ppm (d, $^3J_{HH}$ = 8.1 Hz) in the spectrum of [(TpTP)P(O-p-C$_6$H$_4$NO$_2$)$_2$]$^+$ (Figure 3b) have been assigned to the pyrrole-β and the o- and m-tolyl

(27) Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1987**, *64*, 205.

(28) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 369.

Table 2. ^{1}H and ^{31}P NMR Spectral Data of the Aryloxo P(V) Porphyrins

	peripheral protons			axial ligand protons					^{31}P NMR data[b]
compound	H_β ($^4J_{PH}$)	H_o, H_m ($^3J_{HH}$)	CH_3	H_o/CH_3 ($^3J_{HH}$, $^4J_{PH}$) [$\Delta\delta$]	H_m ($^3J_{HH}$, $^5J_{PH}$) [$\Delta\delta$]	H_p/CH_3 ($^3J_{HH}/^7J_{PH}$) [$\Delta\delta$]	$H_{o'}$ ($^3J_{HH}$) [$\Delta\delta$]	$H_{m'}$ ($^3J_{HH}$, $^4J_{HH}$) [$\Delta\delta$]	
(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)$_2$]$^+$	9.02(d)[c] (3.5)	7.49(s) (7.5)	2.60(s)	0.75(d), −0.86(s) (8.3) [6.24] [3.21]	5.46(d), 5.73(s) (8.3) [1.53] [1.06]	1.64			−197
[(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$	9.01(d) (3.1)	7.66(d), 7.52(d) (7.9) (7.9)	2.61(s)	2.08(dd) (7.8, 2.9) [4.99]	5.69(d) (7.8) [1.08]	1.64 [0.71]			−194
[(TpTP)P(OC$_6$H$_5$)$_2$]$^+$	9.02(d) (3.6)	7.66(d), 7.52(d) (8.0) (8.0)	2.61(s)	2.20(dd) (7.7, 1.7) [5.06]	5.92(m) (7.7) [0.98]	1.64 (2.9) [0.67]			−195
[(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$	9.10(d) (3.1)	7.76(d), 7.55(d) (8.0) (8.0)	2.63(s)	2.32(dd) (8.1, 2.0) [4.61]	5.68(dd) (8.1, 1.8) [1.25]	6.11(m) (7.2, 1.7) [0.79]	6.31(d) (8.9) [0.62]	7.91(d) (8.9) [0.27]	−195
[(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$	9.10(d) (3.8)	7.74(d), 7.55(d) (7.9) (7.9)	2.62(s)	2.35(dd) (9.2, 2.3) [4.62]	5.74(dd) (9.2, 1.5) [1.23]		6.17(d) (9.3) [0.80]	8.00(dd), 8.61(d) (9.3, 3.4), (2.4) [0.29] [0.22]	−195
[(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$	9.09(d) (3.8)	7.60(d), 7.51(d) (8.1) (8.1)	2.59(s)	2.41(dd) (8.8, 1.7) [4.51]	6.87(d) (8.8) [1.31]				−199

[a] Spectra were measured in CDCl$_3$ using TMS as an internal standard; J values are in hertz; $\Delta\delta$ values indicate the differences between the δ values of the free and bound ligands. Error limits: δ, ±0.01 ppm. [b] Spectra were measured in CDCl$_3$ using 85% H$_3$PO$_4$ as an external standard. Error limits: δ, ±2 ppm. [c] Multiplicities are given in parentheses following chemical shift.
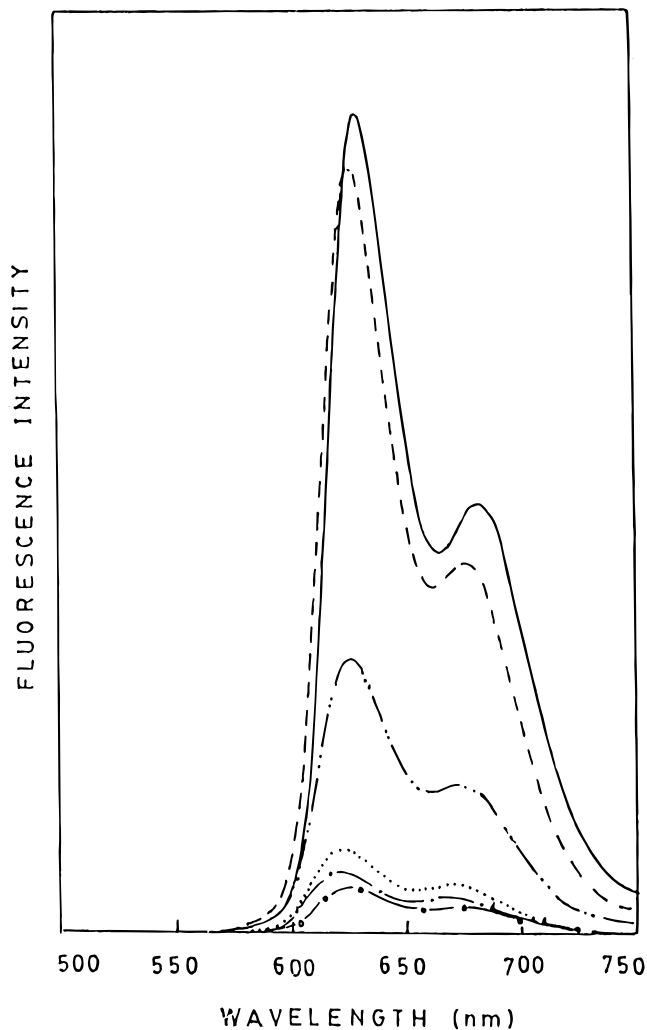
Figure 4. Fluorescence emission spectra of equiabsorbing (OD = 0.12) solutions of (bottom to top) [(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)$_2$]$^+$, [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$, [(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$, [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$, [(TpTP)P(OC$_6$H$_5$)$_2$]$^+$, and [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ in CH$_2$Cl$_2$; λ_{exc} = 430 nm in each case.

(peripheral) protons of the compound, respectively. The resonances ascribable to the axial ligand protons of [(TpTP)P-(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$ and [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ show expected integrated intensities for eight protons and, moreover, are found to be typically shifted upfield of their normal ranges due to the porphyrin diamagnetic ring-current effect.[29] For example, the ortho and meta (with respect to the hydroxy substituent) resonances of 4-nitrophenol, which were occurring at 6.92 (d) and 8.18 (d) ppm, now appear at 2.41 (dd) and 6.87 (d) ppm, respectively, when this ligand is axially bound to the central phosphorus atom in [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$. The change in the chemical shift ($\Delta\delta$) observed for the ortho protons ($\Delta\delta$) = 6.92 − 2.41 = 4.51 ppm) is more than that for the meta protons ($\Delta\delta$ = 8.18 − 6.87 = 1.31 ppm). Furthermore, ortho protons of the axial ligands resonate as a "doublet of a doublet" in [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ due to a three-bond coupling with the adjacent meta protons ($^3J_{HH}$ = 8.8 Hz) and a four-bond coupling with the central phosphorus atom ($^4J_{PH}$ = 1.7 Hz).

The data given in Table 2 suggest that this case is similar with the remaining aryloxo P(V) porphyrins in that they all show a doublet β-pyrrolic proton resonance, a pair of doublet

(29) Abraham, R. J.; Bedford, G. R.; McNeillie, D.; Wright, B. *Org. Magn. Reson.* **1980**, *14*, 418.

Table 3. Fluorescence Data of the Aryloxo P(V) Porphyrins

	λ_{max}, nm $\phi_f{}^a$				Stokes shift $(\Delta v)^b$ (eV)	$E^{S\ c}$ (eV)
compound	toluene	CH$_2$Cl$_2$	CH$_3$CN	DMSO		
(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)]*	618, 667	619, 669	618, 667	620, 668	0.052	2.016
	0.004	0.002	0.003	0.001		
[(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$	618, 668	623, 669	619, 669	620, 670	0.052	2.016
	0.010	0.004	0.005	0.003		
[(TpTP)P(OC$_6$H$_5$)$_2$]$^+$	627, 670	627, 677	626, 674	631, 678	0.058	2.008
	0.027	0.037	0.025	0.021		
[(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$	622, 667	626, 672	623, 669	628, 670	0.049	2.005
	0.003	0.003	0.002	0.001		
[(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$	619, 670	624, 672	621, 670	623, 670	0.050	2.000
	0.025	0.013	0.012	0.006		
[(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$	633, 683	630, 682	630, 680	634, 684	0.058	1.999
	0.033	0.040	0.030	0.028		

^{a} Measured using ZnTTP as the fluorescence standard. Error limit: ±10%. ^{b} Calculated using the data on absorption and emission maxima. Error limit: ±10%. ^{c} 0−0 spectroscopic transition energy of the compound.

resonances due to peripheral *p*-tolyl substituents, and upfield-shifted resonances due to the coordinated axial aryloxy substituents. In each case, resonances due to the peripheral β-pyrrolic protons and ortho protons of the axial ligand both show a four-bond coupling with the central phosphorus atom. In a few cases, $^5J_{PH}$ and $^7J_{PH}$ coupling constants were also noticed, and these values are listed in Table 2. Finally, the $\Delta\delta$ values for the protons on the axial aryloxo ligands are also given in Table 2.

Each aryloxo P(V) porphyrin investigated in this study shows a two-banded fluorescence spectrum in CH$_2$Cl$_2$ (Figure 4) that is typical of the emission of a metallo porphyrin. The energies of the singlet states (E^S) and the Stoke's shifts (Δv) of these porphyrins (see Table 3) are in the same range as the corresponding parameters of [(TpTP)PCl$_2$]$^+$ (E^S = 2.00 eV, Δv = 0.035 eV). However, the quantum yield (ϕ) values of most of these aryloxo derivatives are found to be quite low compared to the ϕ of [(TpTP)PCl$_2$]$^+$ ($\phi \cong 0.035$). As seen from the data given in Table 3, the quantum yield values follow a trend with respect to the nature of the ligated aryloxy group as follows: [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ > [(TpTP)P(OC$_6$H$_5$)$_2$]$^+$ > [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ > [(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$ ≥ [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ ≈ [(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)$_2$]$^+$. In addition, the solvent polarity also seems to have an influence on the fluorescence properties of these porphyrins, and in general, except for [(TpTP)P(O-*p*-C$_6$H$_4$-NO$_2$)$_2$]$^+$, the quantum yields follow the order toluene > CH$_2$-Cl$_2$ > CH$_3$CN > DMF (see Table 3).

B. Electrochemistry. Figure 5 gives the cyclic voltammetric traces obtained for each aryloxo P(V) porphyrin investigated in this study in CH$_3$CN and 0.1 M TBAP at 293 ± 3 K, and Table 4 summarizes the redox potential data obtained at both 293 ± 3 and 273 ± 3 K. Except for [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ and [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ (Figure 5) which show three reduction peaks, each investigated porphyrin was found to undergo two stepwise reduction reactions. Wave analysis suggested that most of these electrode processes represent reversible (i_{pc}/i_{pa} = 0.9−1.0) and diffusion-controlled ($i_{pc}/v^{1/2}$ = constant in the scan rate (v) range 50−500 mV/s) one-electron transfer (ΔE_P = 60−70 mV; ΔE_P = 65 ± 3 mV for ferrocene$^+$/ferrocene couple) reactions.[30] On the other hand, the second reduction steps of [(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)$_2$]$^+$, [(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$; and [(TpTP)P-(OC$_6$H$_5$)$_2$]$^+$ and also the third reduction steps of [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ and [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ are found to be either quasi-reversible ($E_{pa} - E_{pc}$ = 90−200 mV and i_{pc}/i_{pa} = 0.2−0.7 in the scan rate (v)

over the range of 100−500 mV s^{-1}) or totally irreversible. On the basis of the redox potential data reported earlier for various P(V) porphyrins of the type [(por)P(X)$_2$]$^+$ (where por = either a *meso*-tetraarylporphyrin or the octaethyl porphyrin and X = Cl, OH, O(Si(CH$_3$)$_3$), or OCH$_3$)[5,8,9,17] and also on the basis of the diagnostic criteria developed by Fuhrhop, Kadish, and Davis[31] for porphyrin ring reduction ($\Delta E_{1/2}$ (i.e., the difference in potential between the first one-electron and second one-electron addition) = 0.42 ± 0.05 V; see Table 4 where $\Delta E_{1/2}$ = 0.52 − 0.41 V), the first two reduction waves observed for the hydroxide salts of the aryloxo P(V) porphyrins investigated here can be assigned to successive, one-electron additions to the porphyrin ring. The third reduction peaks observed for [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ and [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ can be assigned to electron additions to the bound nitro aromatic axial ligands in each case. Interestingly, these observed potentials are close to those of the corresponding free phenolic precursors (see Table 4).

Scanning the potential in the positive range (0−1.8 V) for solutions containing these porphyrins gave ill-defined voltammograms with a large background current. However, all of the phenols employed here for the synthesis of the aryloxo P(V) porphyrins could be irreversibly oxidized (E(Ph-OH$^+$/Ph-OH)) in CH$_3$CN (0.1 M TBAP). These data are summarized in Table 4.

Discussion

The aryloxo P(V) porphyrins investigated in this study are readily-synthesizable and stable species as was the case with similar compounds previously reported by us[20] and by other research groups.[11,21] These porphyrins show what is called a "normal UV-vis absorption spectrum" with one intense Soret band and two less-intense Q-bands. This fact indicates the presence of a P(V) species (and not a P(III) which shows a "hyper" spectrum) in the porphyrin core for all of them.[4,17] The absence of the band due to P−Cl stretching and the appearance of a new band that is ascribable to the P−O stretching in the IR spectra of these complexes suggest that the two axial ligands are attached to the central P(V) atom. This supposition is also supported by the ^{31}P NMR spectroscopic data; the chemical shift range in which the ^{31}P NMR signals appear for these compounds suggests that there exists an octahedral coordination around the phosphorus atom in each case.[20,28] Further support is provided by an analysis of the ^{1}H NMR results. The observation that the resonances due to ortho and meta protons of the four peripheral *p*-tolyl substituents on each porphyrin (cf, Figure 3)

(30) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(31) Fuhrhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.
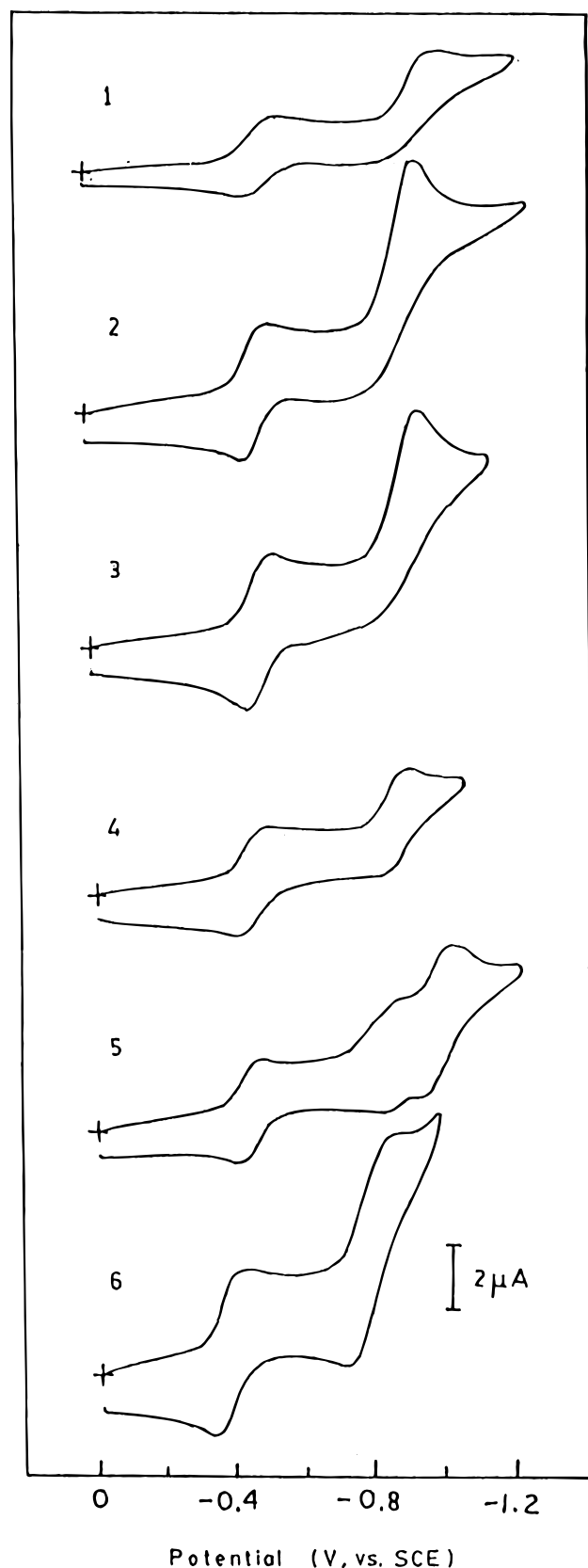
Figure 5. Cyclic voltammograms of (top to bottom) [(TpTP)P(O-*o,p*-C$_6$H$_3$(CH$_3$)$_2$)$_2$]$^+$ (1), [(TpTP)P(O-*p*-C$_6$H$_4$CH$_3$)$_2$]$^+$ (2), [(TpTP)P(OC$_6$H$_5$)$_2$]$^+$ (3), [(TpTP)P(O-*p*-C$_6$H$_4$O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ (4), [(TpTP)P(O-*p*-C$_6$H$_4$O-*o,p*-C$_6$H$_3$(NO$_2$)$_2$)$_2$]$^+$ (5), and [(TpTP)P(O-*p*-C$_6$H$_4$NO$_2$)$_2$]$^+$ (6) in CH$_3$CN (0.1 M TBAP) at 293 ± 3 K.

appear as a pair of doublets in the ^{1}H NMR spectra is indicative of either a rapid rotation of the *p*-tolyl groups on the NMR time scale or a complex with two equivalent axial ligands.[11] An

analysis involving resonance positions and integrated intensities of the ^{1}H NMR signals due to protons on the axial ligands supports the fact that there are two axial aryloxy ligands present in each case.[32] Finally, the trend observed for the Δδ values of the axial aryloxo ligands indicates that the farther a given proton is from the porphyrin π-plane, the smaller is the Δδ value for it. We note that this observation is consistent with the porphyrin ring-current model.[29]

A close inspection of the data given in Tables 1 and 2 suggests that the UV-vis, IR, and ^{1}H and ^{31}P NMR spectroscopic features of these porphyrins do not appreciably vary with respect to the electron-donating or electron-withdrawing nature of the axial ligands. However, this is not the case as far as the electrochemical redox potentials and the fluorescence quantum yields of these complexes are concerned, as discussed below.

A comparison of the electrochemical properties of the aryloxo P(V) porphyrins reported in this study with those of the previously studied P(V) porphyrins is interesting. Whereas [(TpTP)P(Cl)$_2$]$^+$ has been reported to undergo a series of chemical reactions following electron transfer in CH$_2$Cl$_2$ (0.1 M TBAP) at 295 K, the alkoxo analogue [(TpTP)P(OCH$_3$)$_2$]$^+$ has been shown to be relatively stable with respect to electroreduction under similar experimental conditions.[17] By comparison, except for the second one-electron reduction peaks of the three complexes mentioned above, the electrochemical reduction steps of the aryloxo P(V) complexes reported here are reversible within the voltammetric time scale in CH$_3$CN (0.1 M TBAP) at 293 ± 3 K. Low-temperature (273 ± 3 K) voltammetric behavior of these investigated compounds was found to be essentially similar to that obtained at the room temperature (see Table 4). Interestingly, as was the case with the previously studied P(V) porphyrins having "oxo" type ligands ([(TpTP)P(OH)$_2$]$^+$ and [(TpTP)P(OCH$_3$)$_2$]$^+$), all of the aryloxo P(V) porphyrins reported here are more difficult ($E_{1/2}$(I) = −0.36 to −0.51 V) to reduce than the dichloro complex ($E_{1/2}$([(TpTP)PCl$_2$]$^+$) = −0.33 V) under similar experimental conditions.[8,9,17] In addition, the reduction potentials of these porphyrins seem to follow a trend that is consistent with the electron-donating ability of the axial ligands.[19]

It has been well established that for many different metallo porphyrins $E_{1/2}$(ox) − E$_{1/2}$(red) (i.e., the potential difference between the first ring oxidation and first ring reduction) is in the range of 2.1−2.2 V.[33] Aryloxo P(V) porphyrins are also expected to confine to this rule, and in such a case, the first one-electron oxidation peaks for these porphyrins can occur at potentials more positive than ca. 1.8 V. Similarly, the fact that all of the phenols utilized here for the synthesis of the aryloxo P(V) porphyrins could be oxidized between 0.92 and 1.35 V (see Table 4) suggests that peaks due to oxidation of the bound aryloxo ligands can be expected during the positive potential scan for solutions containing these porphyrins. However, as mentioned above, neither the porphyrin ring-oxidation potentials nor the oxidation potentials of the bound aryloxo ligands could be measured under our experimental conditions. Nonetheless, the low ring reduction potentials and the high ring oxidation potentials of these aryloxo P(V) porphyrins suggest that, in principle, it is easier to add an electron to their excited states than to abstract one from them.

A. Singlet State Properties. A variety of excited state processes including enhanced internal conversion and intersystem crossing, ion-association, excitation energy transfer (EET),

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(32) The mass spectral fragmentation pattern (see Experimental Section) is also consistent with the presence of two equivalent axial ligands on these porphyrins.

(33) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, 435.

Table 4. Redox Potential Data of the Aryloxo P(V) Porphyrins and the Axial Ligands in CH_3CN (0.1 M TBAP)[a]

| | porphyrin ring | | | | | axial ligand[b] | | | |
| | 293 K | | | 273 K | | | | | |
compound	$-E_{1/2}$(I)	$-E_{1/2}$(II)	$\Delta E_{1/2}$[c]	$-E_{1/2}$(I)	$-E_{1/2}$(II)	$-E_{1/2}$	$E_{1/2}$[d]	E_{CT}(1)[e] (eV)	E_{CT}(2)[f] (eV)
(TpTP)P(O-o,p-$C_6H_3(CH_3)_2$)]$^+$	0.51	1.00[g]	0.49	0.51	0.98[g]		0.92	>3.1	1.43
[(TpTP)P(O p-$C_6H_4CH_3$)$_2$]$^+$	0.49	0.94[g]	0.45	0.50	0.95[g]		0.92	>3.1	1.41
[(TpTP)P(OC$_6$H$_5$)$_2$]$^+$	0.48	1.00[g]	0.52	0.49	0.95[g]		1.12	>3.1	1.60
[(TpTP)P O-p-C_6H_4O-p-$C_6H_4NO_2$)$_2$]$^+$	0.45	0.87	0.42	0.45	0.87	1.28 (1.22)[h]	1.21	>3.1	1.66
[(TpTP)P(O-p-C_6H_4O-o,p-$C_6H_3(NO_2)_2$)$_2$]$^+$	0.44	0.85	0.41	0.43	0.86	0.90 (0.98)[h]	1.35	>2.7	1.79
[(TpTP)P(O-p-$C_6H_4NO_2$)$_2$]$^+$	0.36	0.77	0.41	0.37	0.77	1.02	1.33	>2.8	1.69

[a] Error limits: ±0.02 V. [b] Redox potentials are for the free phenols. [c] $\Delta E_{1/2}$ is the difference between the first and the second reduction potentials (V vs SCE). [d] Peak potentials obtained from differential-pulse voltammetry. [e] E_{CT}(1) is the energy of the charge transfer state P(V)$^+$ − OR (see text, eq 1, and ref 36). [f] E_{CT}(2) is the energy of the charge transfer state P(V)$^-$−OR$^+$ (see text, eq 2, and ref 36). [g] Irreversible/quasi-reversible (see Figure 5). [h] These values are for the bound aryloxo ligands.

photoinduced electron transfer (PET), etc., can be thought of to be operative in the quenching of fluorescence observed for the aryloxo P(V) porphyrins in various solvents. Obviously, it is not going to be easy to estimate the contribution from each of these excited state processes based only on the steady state fluorescence data. However, an intramolecular EET from the singlet P(V) porphyrin to the appended aryloxo ligand is less likely to occur[34] and hence, the contribution of this process to the overall decrease in the ϕ values is considered to be the minimum for these complexes. Similarly, the observed general dependence of the ϕ values on the electron-donating/withdrawing ability of the axial ligand and also on the solvent polarity (see Table 3) indicates that it is difficult to rationalize these trends solely on the basis of differences in the rates of internal conversion and intersystem-crossing reactions of the aryloxo porphyrins among themselves and also in relation to the dichloro analogue. Ion-association is another phenomenon that is imminent in these charged species, and the extent of this process is expected to be dependent on the solvent properties and also on the structure of the fluorophore. Currently, no direct or indirect evidence exists to show the correspondence between the trends observed for the ϕ values and the extent of ion-association in these complexes. Finally, as far as the PET-based mechanisms are concerned, two types of reactions can be envisaged here (eqs 1 and 2), where P(V)*−OR represents

$$P(V)*-OR \rightarrow P(V)^+-OR^- \quad (1)$$

$$P(V)*-OR \rightarrow P(V)^--(OR)^+ \quad (2)$$
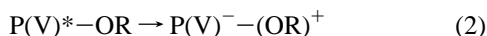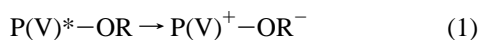
the singlet state of the aryloxo P(V) porphyrins and P(V)$^+$−OR$^-$ and P(V)$^-$−OR$^+$ represent the charge-separated species.[35] Calculations based on the available redox potential data of these systems suggest that while the energies of the charge transfer states corresponding to P(V)$^+$−OR$^-$ (i.e., $E_{P(V)^+-OR^-}$) are all greater than at least ca. 2.7 eV, those of the P(V)$^-$−OR$^+$ states (i.e. $E_{P(V)^--OR^+}$) range between 1.79 and 1.41 eV (see Table

4).[36] Interestingly, the P(V)$^+$−OR$^-$ state of each complex lies above the E^S (= 2.008 ± 0.008 eV, Table 3) of the P(V) porphyrin, and thus, an electron transfer from the singlet porphyrin to the axially bound aryloxo subunit is not possible on the thermodynamic grounds for these systems. On the other hand, the $E_{P(V)^--OR^+}$ values are all less positive than the E^S values, suggesting that charge transfer from the axial aryloxo subunits to the P(V) porphyrin is thermodynamically favorable in each case. We analyze that the relaxation of the singlet state to this thermodynamically accessible charge transfer state can, in principle, rationalize the observed fluorescence quenching of the porphyrin chromophore in these compounds. Consistent with this analysis is the fact that the fluorescence due to [(TpTP)P(O-o,p-$C_6H_3(CH_3)_2$)$_2$]$^+$ and [(TpTP)P(O-p-$C_6H_4(CH_3)_2$)$_2$]$^+$ (which possess electron-donating methyl groups) is quenched much more than that due to [(TpTP)P(O-p-$C_6H_4NO_2$)$_2$]$^+$ and [(TpTP)P(O-p-C_6H_4O-o,p-$C_6H_3(NO_2)_2$)$_2$]$^+$ (which possess electron-accepting nitro groups). The observed decrease of ϕ values with increasing polarity of the solvent is also consistent with the participation of a charge transfer state in the excited state deactivation for these compounds.[19,24−26] In this regard, it can be noted here that recent fluorescence studies, which include those on a series of "wheel-and-axle" type dimeric and oligomeric P(V) porphyrins,[18,19] on bis axially ligated "oligothiophenoxy" derivatives of P(V) porphyrins[13] and on P(V) porphyrin-based, aryloxo-ligand bridged, hybrid porphyrin trimers[20,21] all have indicated that the relaxation of the singlet excited states of these complexes involves significant contribution from the charge transfer states. Despite these, we note that it is not generally correct to consider exclusively a PET-based mechanism relying only on the thermodynamic criteria and the solvent dependence of the ϕ values. Thus, it is reasonable to expect that contribution from a PET-based mechanism is the maximum for a compound having a highly electron-donating axial ligand

(34) While the singlet state energy of the "porphyrin part" of each aryloxo P(V) porphyrin is 2.008 ± 0.008 V, that of the aromatic axial ligands is expected to be ca. >3.0 V in each case (see, Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York: 1973. Turro, N. J. *Modern molecular photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.)

(35) The positive charge present on the P(V) porphyrin has been omitted for clarity in the presentation at these equations. Thus, P(V)$^+$−OR$^-$ possesses a porphyrin "dication radical" and an anion radical of the aryloxo ligand. Similarly, P(V)$^-$−OR$^+$ possesses a "neutral" porphyrin radical species and a cation radical of the aryloxo ligand.

(36) $E_{P(V)^+-OR^-} = E(P(V)^+/P(V)) − E(Ph−OH/Ph−OH^-)$ and $E_{P(V)^--OR^+} = E(Ph−OH^+/Ph−OH) − E(P(V)/P(V)^-)$, where $E(P(V)^+/P(V))$ and $E(P(V)/(PV)^-)$ are the ring oxidation and ring reduction potentials of the P(V) porphyrin and $E(Ph−OH^+/Ph−OH)$ and $E(Ph−OH/Ph−OH^-)$ are the oxidation and reduction potentials of the phenolic precursors, respectively. $E(P(V)/P(V)^-)$ and $E(Ph−OH^+/Ph−OH)$ for all the porphyrins and $E(Ph−OH/Ph−OH^-)$ for [(TpTP)P(O-p-C_6H_4O-o,p-$C_6H_3(NO_2)_2$)$_2$]$^+$, [(TpTP)P(O-p-C_6H_4O-p-$C_6H_4NO_2$)$_2$]$^+$ and [(TpTP)P(O-p-$C_6H_4NO_2$)$_2$]$^+$ are taken from Table 4. $E(Ph−OH/Ph−OH^-)$ values for rest of the porphyrins are expected to be more negative than those observed for these two complexes.[37] As discussed earlier, $E(P(V)^+/P(V))$ values are more positive by at least 1.8 V. It should be noted here that the energies of the charge transfer states estimated here are only "apparent" values. This is because we have employed oxidation potentials of the precursor "free" phenols and not those of the bound aryloxo ligands in the calculation and, in addition, the exact oxidation potentials of the P(V) porphyrins are not known with certainty.

and the minimum for a compound having a highly electron-withdrawing axial ligand in this series of P(V) porphyrins.

In summary, six aryloxo P(V) porphyrins have been synthesized and fully characterized by various spectroscopic methods. Thermodynamic considerations based on the electrochemical and fluorescence data indicate that a charge transfer state of the type $P(V)^--OR^+$ can participate in the excited state deactivation of these compounds. In this sense, these investigated aryloxo P(V) porphyrins can be considered as the rarely encountered and newly emerging[18-21] examples of porphyrin-based donor−acceptor (D−A) (in fact, D_2−A triads) compounds in which the axial sites of a porphyrin, rather than its *meso*-phenyl or the pyrrole-β position, have been utilized for covalently linking the donor moiety.[38] The results obtained in this study thus testify to the powerful oxidizing ability of the excited states of P(V) porphyrins and further suggest that the porphyrin derivatives investigated here are well suited as

components of porphyrin-based supramolecular arrays[39,40] and as photosensitizers for the photodynamic therapy of tumors.[48]

(37) AM1 calculations (Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P.; Zoebisch, E. G. *J. Am. Chem. Soc.* **1985**, *107*, 3902) suggest that the electron affinity values (eV) of axial ligands follow the order 0.442, 2,4-dimethylphenol > 0.424, 4-methylphenol > 0.402, phenol > −1.065, nitrophenol > −1.121, 4-(4-nitrophenoxy)phenol > −1.694, 4-(2,4-dinitrophenoxy)phenol.

(38) In comparison with a vast body of literature available that deals with PET reactions from the porphyrin to an appended electron acceptor,[39,40] only a few studies have examined electron transfer to a porphyrin from an attached donor.[41-43] More importantly, studies on PET reactions involving porphyrin excited states and axially ligated organic/organometallic electron donors or acceptors are scarce in the current literature.[19-21,44-47]

(39) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(40) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198.
(41) Harriman, A.; Hoise, R. *J. Photochem.* **1981**, *15*, 163.
(42) Wasielewski, M. R.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559.
(43) Loppnow, G. R.; Melamed, D.; Hamilton, A. D.; Spiro, T. G. *J. Phys. Chem.* **1993**, *97*, 8957 (and references therein).
(44) Recently, "vertically" linked D−A type porphyrin trimers have been reported: (a) references 20 and 21 of this manuscript. (b) Kimura, A.; Funatsu, K.; Imamura, T.; Kido, H.; Sasaki, Y. *Chem. Lett.* **1995**, 207.
(45) Crouch, A. M.; Sharma, D. K.; Langford, C. H. *J. Chem. Soc.*, *Chem. Commun.* **1988**, 307.
(46) Maiya, B. G.; Barbe, J.-M.; Kadish, K. M. *Inorg. Chem.* **1989**, *28*, 2524.
(47) Zakrzewski, J.; Giannotti, C. *Coord. Chem. Rev.* **1995**, *140*, 169.
(48) Saito, T.; Kitamura, M.; Tanaka, M.; Morimoto, M.; Segawa, H.; Shimidzu, T. *Nucleosides Nucleotides* **1995**, *13*, 1607.