A Porphyrin bearing Tetrahydrothiophene Pickets; Co-ordination Behaviour and Electron Transfer

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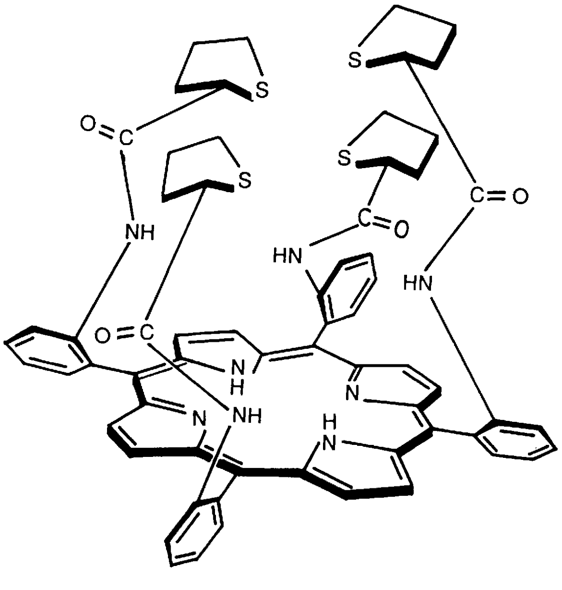
A novel 'picket-fence' porphyrin, 5,10,15,20-tetrakis[*o*-(tetrahydro-2-thenoylamino)phenyl]porphyrin (H_2L) with ligating tetrahydrothiophene rings disposed perpendicular to the porphyrin plane has been synthesised. Its zinc(II) derivative, [ZnL], binds two silver(I) ions co-operatively with a dissociation constant of 4.8×10^{-8} dm^3 mol^{-1}. Time-resolved fluorescence lifetime measurements reveal the presence of intramolecular photoexcited electron transfer in this donor–acceptor system.

Porphyrins bearing intramolecularly bound metal complexes provide the opportunity to study photoinduced electron-transfer reactions. A few examples of porphyrins containing ruthenium(III) pentamine complexes,[1] ferrocenium ion[2] and crown ether-complexed europium(III)[3] are known to display such reactions. Time-resolved spectroscopy of heterobimetallic porphyrins bearing zinc(II) and iron(III) and zinc(II) and manganese(III) revealed intramolecular electron transfer between photoexcited zinc(II) porphyrin and the trivalent metal ion in the porphyrin entity.[4] Recently, efficient charge separation has been reported within a polymetallic supramolecular system consisting of a porphyrin crowned by two cryptate entities and silver(I) ions.[5]

Picket-fence porphyrins bearing donor sites for metal co-ordination form important model systems for the study of intramolecular electron-transfer reactions. Here, we describe the synthesis of a novel molecular system, 5,10,15,20-tetrakis-[*o*-(tetrahydro-2-thenoylamino)phenyl]porphyrin, H_2L, and its co-ordination behaviour. Optical absorption and emission spectroscopy and cyclic voltammetric studies have shown that the zinc(II) derivative [ZnL] co-ordinates two silver(I) ions in a co-operative fashion. Interestingly, time-resolved fluorescence measurements of the silver(I) complex of [ZnL] indicate the existence of intramolecular electron transfer.

Results and Discussion

The compound H_2L obtained by condensing tetrahydrothiophene-2-carbonyl chloride and 'all *cis*' 5,10,15,20-tetra(*o*-aminophenyl)porphyrin was found to be spectroscopically pure. The ^{1}H NMR spectrum in $CDCl_3$ revealed a singlet at δ 8.67 characteristic of an 'all *cis*' orientation of the substituents at the *meso* phenyl rings of the porphyrin entity.[6] A multiplet at δ 7.46 arises from the *o*-protons of the phenyl ring, while the *m*- and *p*-protons together resonate as a multiplet at δ 7.84. The resonance of the amide group protons is at δ 5.29 based on deuteriation experiments. Triplets at δ 3.96 and a multiplet at δ 2.95 correspond to the proton resonances of tetrahydrothiophene rings, similar to the behaviour of free tetrahydrothiophene-2-carboxylic acid or its methyl ester. The inner imino protons of H_2L resonate as a singlet at δ −2.70. The complex [ZnL] exhibits proton resonances almost at the same positions as those observed for H_2L, except that the pyrrole proton resonances are deshielded by about 0.15 ppm. It may be noted that the β-pyrrole protons of [ZnL] resonate as a singlet indicating that the 'all *cis*' orientation is retained in the zinc(II) derivative. Interestingly, the ^{1}H NMR spectrum of the silver(I) complex of [ZnL] displays a complex multiplet centred at δ 8.87 arising from the β-pyrrole protons. The presence of a multiplet signifies the existence of different isomers in solution. Attempts to separate the different isomers using TLC/HPLC have not so far been successful. It may be noted that the proton resonances of the tetrahydrothiophene rings of [ZnL] are marginally deshielded on co-ordination with silver(I) ions.



The optical absorption spectrum of H_2L in MeCN exhibits four visible bands (Table 1) while the zinc(II) derivative exhibits a two-banded spectrum. Addition of silver(I) ions to [ZnL] results in a bathochromic shift of the Soret and visible bands (≈6 nm) accompanied by broadening of the absorption bands. The full width at half maximum of the Soret band was found to be increased by ≈225 cm^{-1} indicating complexation of [ZnL]. Similar studies of binding of silver(I) ions to H_2L could not be carried out since addition of silver(I) trifluoromethinesulfonate (triflate) protonates the inner imino nitrogens of H_2L as seen from the visible spectrum. The pK_a value of H_2L as found from optical absorption spectroscopy using CH_2Cl_2–MeOH (1:1 v/v) as solvent was found to be ≈1.0, similar to that found for other 'picket-fence' porphyrins.[7]

The cyclic voltammogram of H_2L and its zinc(II) derivative exhibit one two-electron oxidation of the porphyrin ring at 1.32

Table 1 Spectral data for the tetrahydrothiophene-appended porphyrin and its metal derivatives in MeCN at 298 K

	λ/nm		
Compound	Absorption[a]	Emission	Lifetime[b]/ns
H_2L	648 (3.01), 591 (3.12), 545 (3.60), 515 (4.01), 418 (5.60)	656, 721	1.89 (15.5), 11.3 (84.5)
[ZnL]	597 (3.71), 560 (4.23), 427 (5.63)	607, 656	1.26 (38.3), 2.60 (61.7)
$[ZnL]-Ag^+$	602 (3.64), 567 (4.12), 432 (5.49)	608, 658	0.96 (46.3), 2.24 (53.7)
H_2tpp	646 (3.56), 592 (3.74), 549 (3.72), 513 (4.16), 417 (5.76)	654, 720	8.96
[Zn(tpp)]	596 (3.84), 556 (4.30), 420 (5.82)	604, 652	1.87

[a] Values in parentheses are log ε. [b] Values in parentheses are the amplitudes. The goodness of the fit was judged from the χ^2 value found to be < 1.20.

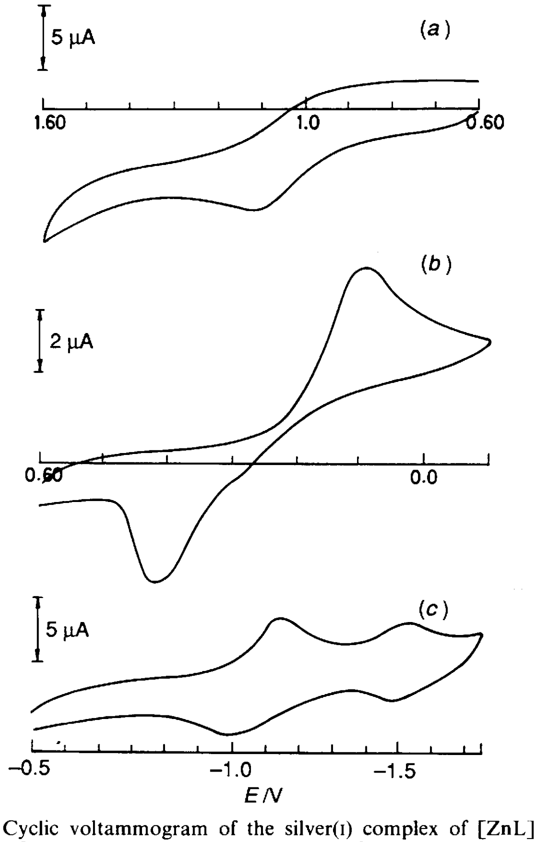


Fig. 1 Cyclic voltammogram of the silver(I) complex of [ZnL] (1 mmol dm^{-3}) in MeCN containing 100 mmol dm^{-3} tetrabutylammonium hexafluorophosphate at 25 °C. Scan rate 100 mV s^{-1}. Peaks occurring at different potential regions are shown in (a)–(c)

and 1.16 V respectively characteristic of those observed for other 'picket-fence' porphyrins.[8] The first and second one-electron porphyrin reduction potentials of H_2L and [ZnL] occur respectively at −0.91 and −1.21 and −1.15 and −1.49 V corresponding to the formation of $L^{\bullet -}$ and L^{2-} species. Interestingly, the cyclic voltammogram of the silver(I) complex of [ZnL] revealed three one-electron reduction peaks at 0.26, −1.06 and −1.48 V (Fig. 1). These potentials are found to be quasi-reversible with the last two arising from successive one-electron porphyrin-ring reductions while the first corresponds to the reduction of complexed silver(I) ions. In order to demonstrate this, cyclic voltammetric measurements were carried out on the complexation properties of a model ligand, methyl tetrahydrothiophene-2-carboxylate, with silver(I) ions. Silver(I) triflate in MeCN solution exhibits a quasi-reversible one-electron reduction at 0.32 V (Fig. 2).[9] On increasing addition of the ester the reduction potential of silver(I) was found to shift cathodically and reach a limiting value of 0.26 V. This indicates that the complexed silver(I) is relatively more difficult to reduce due to co-ordination with sulfur atoms of the ligand. The cyclic voltammetric studies on complexation of [ZnL] with silver(I) closely parallel the model study, suggesting ligation of silver(I) ion.

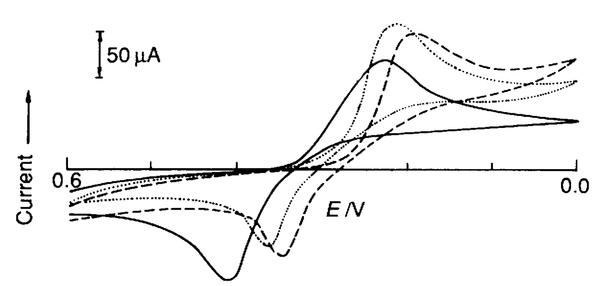


Fig. 2 Cyclic voltammogram of silver(I) triflate on increasing addition of methyl tetrahydrothiophene-2-carboxylate in MeCN containing 100 mmol dm^{-3} tetrabutylammonium hexafluorophosphate at 25 °C: ——, silver(I) triflate (1 mmol dm^{-3}); · · · ·, as (——) ester (1 mmol dm^{-3}); – – – –, as (——) ester (2.3 mmol dm^{-3}). Scan rate 100 mV s^{-1}

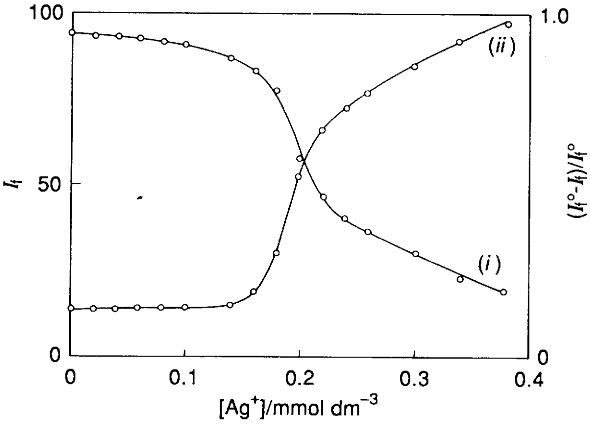


Fig. 3 (i) Effect of silver(I) triflate on the relative fluorescence intensity of [ZnL]. (ii) A saturation curve showing $(I_f^0 - I_f)/I_f^0$, where I_f^0 and I_f are the fluorescence intensities measured in the absence and presence of silver(I) triflate

Steady-state and time-resolved fluorescence studies have been carried out to probe the excited-state interactions in the superstructural entities. The fluorescence spectra of H_2L and [ZnL] exhibit two bands corresponding to the Q(0,0) and Q(1,0) transitions (Table 1). The fluorescence of [ZnL] (0.08 mmol dm^{-3}) in CH_2Cl_2–MeOH (1 : 1 v/v) is efficiently quenched on addition of a low concentration of silver(I) ions (< 0.2 mmol dm^{-3}). Under identical conditions, the fluorescence of [Zn(tpp)] (H_2tpp = 5,10,15,20-tetraphenylporphyrin) is not quenched on addition of Ag^+. This suggests that the decrease in fluorescence intensity of [ZnL] is not due to any intermolecular process since the low concentration of Ag^+ cannot quench the short-lived excited singlet state of [ZnL]. The sigmoidal nature of the fluorescence titration curve (Fig. 3) indicates co-operative binding of Ag^+ by the [ZnL] moiety. The dissociation constant and the stoichiometry of the complex (n) were calculated using Hill's method[10] as 4.8×10^{-8} dm^3 mol^{-1} and 2.1. The magnitude of n suggests that [ZnL] complexes two silver(I) ions. The four tetrahydrothiophene rings disposed perpendicular to the porphyrin plane offer four thioether (sulfur donor) sites for co-ordination to Ag^+. It is known that the cyclic tetrathiaether, 1,4,8,12-tetrathiacyclotetradecane (L′) binds two silver(I) ions effectively to form stable [Ag_2L'] complexes.[11] It is suggested that the two thioether entities co-ordinate to one Ag^+ which facilitates subsequent binding of another Ag^+ thereby displaying co-operative binding of Ag^+ by [ZnL]. This is an important feature of the conformational mobility of pickets (bearing sulfur donors, tetrahydrothiophene rings) around the porphyrin for co-ordination to Ag^+. The greater affinity of thioether (of [ZnL]) co-ordination to Ag^+ is revealed by the low dissociation constant (10^{-8} dm^3 mol^{-1}) compared to that of the corresponding silver(I)-tetrahydrothiophene complex ($\approx 10^{-4}$ dm^3 mol^{-1}).

The singlet lifetimes of H_2L and [ZnL] have been measured in deaereated MeCN solution using an excitation wavelength of 565 nm. Both compounds exhibit decay curves which could best be fitted with a biexponential function. The goodness of fit is established by the low χ^2 values.[12] The magnitude of the lifetime along with the amplitude is given in Table 1. The lifetimes did not reveal any changes within the concentration range (0.5–5 μmol dm^{-3}) of the porphyrins. This indicates absence of aggregation at the concentration employed. The two lifetime components observed for the synthesised 'picket-fence' porphyrins in contrast to the single lifetime found for H_2tpp and [Zn(tpp)] in the same solvent and concentration range imply the possible existence of different conformers. Non-equilibrating conformers have been observed for other picket-fence porphyrins.[13] The possibility of any fluorescence impurity or accidental presence of fluorescence quenchers in the test solution is best avoided by repetitive measurements with different synthetic samples and the complete absence of oxygen. Interestingly, the silver(I) complex of [ZnL] revealed a biexponential decay with diminished lifetime components relative to that observed for [ZnL] alone. That the decrease in both the lifetime components of the silver(I) complex of [ZnL] is not due to any artifacts was confirmed by measurement of the lifetime of [Zn(tpp)] in the presence of silver(I) ions. Addition of a 10-fold excess of silver(I) ions (10 μmol dm^{-3}) to [Zn(tpp)] (1 μmol dm^{-3}) does not result in any decrease in lifetime of [Zn(tpp)] and the decay remained monoexponential. Similar results obtained from steady-state emission studies indicate the absence of any intermolecular quenching. The quenched lifetime components of [ZnL]–Ag^+ could arise from electron transfer or intersystem crossing to the excited triplet state through spin–orbit coupling of Ag^+ (heavy-atom effect). An estimate of the rate of electron transfer (k_{ET}) can be made using expression (1) where τ_1 and τ_2 represent the corresponding lifetime components of [ZnL] and its silver(I) complex. The k_{ET} values arising from the long and short lifetimes are found to be 0.5×10^8 and 1.5×10^8 s^{-1}. It is believed that the usage of an average lifetime should be avoided since the lifetimes originate from different isomers, the nature of which remains uncertain. The rate of intersystem crossing (k_{isc}) estimated from the known spin–orbit coupling parameter of Ag^I is found to be $\approx 10^7$ s^{-1}, an order of magnitude lower than the observed k_{et}. Moreover, electron-transfer quenching from the excited triplet of the porphyrin seems less likely owing to the weakly exergonic nature of the parameter ΔG_{et} (change in free energy for electron transfer). On the other hand, the ΔG_{et} value estimated from the electrochemical redox potential data and the energy of the excited singlet state of the porphyrin is found to be -1.13 eV (*ca.* 1.80×10^{-19} J). This suggests that the electron transfer from the excited singlet state of the porphyrin is the dominant pathway for quenching of the lifetimes. Steady-state photolysis experiments on acetonitrile solutions containing [ZnL] and Ag^+ have revealed the formation of the porphyrin radical cation ($\lambda_{max} = 660$ nm) and silver(0) ($\lambda_{max} = 390$ nm)[14] as products of the electron-transfer reaction. This is in accord with the intramolecular electron transfer occurring within the superstructural donor–acceptor entity.

$$k_{ET} = (1/\tau_2) - (1/\tau_1) \qquad (1)$$

Experimental

5,10,15,20-Tetra(*o*-aminophenyl)porphyrin was prepared by reducing the corresponding nitro derivative with tin(II) chloride.[15] The isomeric 'all *cis*' compound was separated by column chromatography using silica gel, and a chloroform–acetone solvent mixture as eluent.[16] Tetrahydrothiophene-2-carboxylic acid was synthesised by the reduction of thiophene-2-carboxylic acid (Riedel-de Haen Chemicals) using mercury amalgam.[17] The reduced compound was converted into the acid chloride on treatment with thionyl chloride. This was immediately used for further condensation reactions. Silver(I) triflate was used as a source of Ag^+.

Preparation of 5,10,15,20-*Tetrakis*[o-(*tetrahydro*-2-*thenoylamino*)*phenyl*]*porphyrin*, H_2L.—To a solution of 5,10,15,20-tetra(*o*-aminophenyl)porphyrin (30 mg) in CH_2Cl_2 (50 cm^3) containing pyridine (2 cm^3) was added dropwise tetrahydrothiophene-2-carbonyl chloride (50 mg) in CH_2Cl_2 (15 cm^3). The resulting solution was refluxed for 10 min and stirred for 30 min at room temperature under an argon atmosphere. The solvent was removed under vacuum and the residue dissolved in CH_2Cl_2 (25 cm^3). The solution was washed twice with water (50 cm^3) and dried over anhydrous Na_2SO_4. The compound was purified on a silica gel column using CH_2Cl_2 and MeOH (3%) as eluent. Its purity was confirmed by TLC and HPLC. Yield 10% (Found: C, 67.35; H, 5.25; N, 9.85. Calc. for $C_{64}H_{58}N_8O_4S_4$: C, 67.95; H, 5.15; N, 9.90%). The fast atom bombardment mass spectrum revealed a peak at *m*/*z* 1133.0 ± 1 (calc. 1132.0).

The compound [ZnL] was prepared by treating H_2L (25 mg) in CH_2Cl_2 (50 cm^3) with zinc(II) acetate tetrahydrate (50 mg) in MeOH at room temperature under argon. The compound was purified on a silica gel column using CH_2Cl_2 as eluent (Found: C, 63.95; H, 4.55; N, 9.25. $C_{64}H_{56}N_8O_4S_4Zn$ requires C, 64.35; H, 4.70; N, 9.40%). The [ZnL]–Ag^+ complex was prepared by treating [ZnL] with silver(I) triflate. Several attempts to isolate the complex in the solid state have not been successful. Hence only a solution study of the silver(I) complex is reported.

All the spectral measurements were carried out on instruments described elsewhere.[18] The cyclic voltammograms of the synthesised compounds were recorded on a BAS 100-A electroanalytical working station. A three-electrode assembly consisting of a glassy carbon working electrode, a platinum-wire auxiliary electrode and Ag–AgCl reference electrode was used. Fluorescence lifetimes were measured using the picosecond laser excitation time-correlated single-photon counting method.[19] The fluorescence decay was analysed by the non-linear least-squares method using iterative reconvolution and the Marquardt procedure for optimization of parameters.

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