Axial bis(terpyridoxy)phosphorus(V) porphyrin: Modulation of PET and EET by Zn^{2+} or Cd^{2+} ions†

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A novel phosphorus(V) porphyrin bearing two ptp [4′-(4-phenyloxy)-2,2′:6′,2″-terpyridine] groups was prepared and modulation of the intramolecular PET (λ_{ex} = 566 nm) and PET → EET (λ_{ex} = 300 nm) processes was studied from ptp to phosphorus(V) porphyrin by Zn^{2+} or Cd^{2+} ions.

Electron and energy transfer processes in porphyrin based donor–acceptor systems are receiving considerable attention because of their importance in photosynthetic research and molecular photo/electro-active devices.[1] In particular, much effort is currently devoted to regulating electron/energy-transfer reactions among the electroactive compounds through photoisomerisation, geometric changes and redox potentials.[2,3] A great variety of covalently or non-covalently bound porphyrin–terpyridine motifs are known to closely mimic the initial photoinduced electron transfer (PET) or excitation energy transfer (EET) events of natural photosynthetic reactions.[4] However, such studies were hitherto restricted to terpyridine ligand/s connected at meso-position/s of the porphyrin. In addition, it appears that no effort has been made so far to covalently connect the terpyridine donor at the axial site of a metal/metalloid porphyrin. To the best of our knowledge, this is the first example where terpyridine groups, strong chelating ligands towards the transition metal ions,[5] are covalently connected in the axial-position of a phosphorus(V) porphyrin, which has unique spectroscopic and redox properties.[6] In this paper we wish to report the modulation of PET and PET → EET by Zn^{2+} or Cd^{2+} ions observed in a novel and unique phosphorus(V) porphyrin based triad **L** {or **[P(ptp)$_2$]**$^+$}, Fig. 1.

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The hydroxide salt of triad **L** was synthesized in 55% yield by reacting 5,10,15,20-tetra(4-methylphenyl)porphyrinatophosphorus(V) dichloride **[PCl$_2$]**$^+$ with excess of 4′-(4-hydroxyphenyl)-2,2′:6′,2″-terpyridine **[OH-ptp]** in refluxing pyridine and further purification by column chromatography (silica gel, CHCl$_3$/CH$_3$OH 10 : 1, v/v). The ^{1}H NMR spectrum of this 'axial-bonding' type metalloid-porphyrin shows characteristic, porphyrin ring-current induced upfield shifts for the protons on the axial aromatic ligands.[7,8] However, in the ^{31}P NMR spectrum, the signal due to the central P(V) atom of **L** was seen to be shifted downfield (δ = −201.2 ppm) compared to that of **[PCl$_2$]**$^+$ (δ = −233.2 ppm) but, is within the typical range expected for hexa-coordinated diaryloxo P(V) porphyrins.[7a,7b] Further support for the structural integrity of **L** comes from the appearance of its molecular ion peak at m/z = 1365 ([M + OH]$^+$) in the MALDI mass spectrum.

In the absorption spectrum of **L**, the wavelength maxima of the Soret and Q bands [in DMSO, λ_{max}/nm (log ε): 615 (3.92), 570 (4.12), 445 (5.19), 287 (4.84)] are red shifted from respective bands in the 1 : 2 physical mixture spectrum of **[P(OH)$_2$]**$^+$ and **[OH-ptp]**, suggesting π–π interaction between axial **ptp** and porphyrin subunits (Fig. S1). Data given in Table 1 suggest that triad **L** is moderately/weakly fluorescent and peaks are broadened and red shifted compared to the **[P(OH)$_2$]**$^+$/OH-ptp. When excited at 555 nm in CH$_3$CN (porphyrin part), the emission of the porphyrin part was quenched (70 ± 10%) due to the PET from the ground state of **ptp** to the excited state of the porphyrin,[9] while on excitation at 280/300 nm (**ptp** part), the emission of the **ptp** was quenched due to both EET (∼ 61 ± 10%, Fig. 2a) and PET (∼37 ± 10%) from the excited state of **ptp** to the ground state of the porphyrin. The observed behaviour is in agreement with that reported for a number of axial aryloxy porphyrin derivatives.[2b,7a–7c,8]

The NMR titrations were carried out for **L** using Zn(OTf)$_2$ in CH$_3$CN-d_3. The spectrum clearly shows the appearance of the
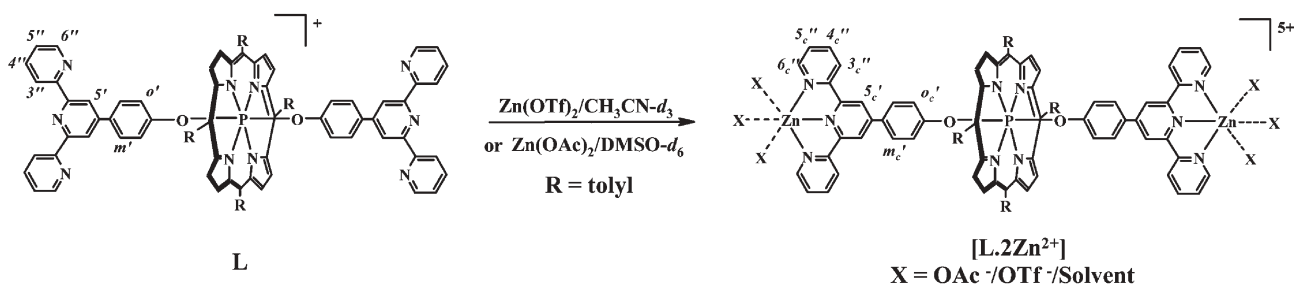

Fig. 1 Complexation of **L** with Zn(OTf)$_2$ in CH$_3$CN-d_3 or Zn(OAc)$_2$ in DMSO-d_6.

Table 1 Redox potential and fluorescence data[a]

Compound	$E_{1/2}$/V		ΔG_{PET}/eV	ϕ_f (% Q)[f]	
	Ox	Red		λ_{ex} = 555 nm	λ_{ex} = 280/300 nm
OH-ptp[b]	1.00	—	—	—	0.20
[P(OH)₂][+]	—	−0.57, −0.97	—	0.054, 0.06[b]	—
L or **[P(ptp)₂]**[+]	1.70	−0.22, −0.78	1.60[c], −0.08[d], −1.83[e]	0.016 (70), 0.026 (58)[b]	0.003 (98)

[a] Solvent, CH₃CN, 0.1 M TBAP. Error limits: $E_{1/2}$, ±0.03 V. [b] Measured in DMSO, 0.1 M TBAP. [c] λ_{ex} = 555 nm, ΔG(P⁺ptp⁻), in this calculation the oxidation potential of the phosphorus(V) porphyrin and the reduction potential of the **ptp** subunit are assumed to be anodic to +1.80 V and cathodic to −1.80 V, respectively (solvent limit). [d] λ_{ex} = 555 nm, ΔG(P⁻ptp⁺). [e] λ_{ex} = 280/300 nm, ΔG(P⁻ptp⁺). E_{0-0} values for **P** and **ptp** were 2.00 eV and 3.75 eV, respectively. [f] Error limits, ±10%.
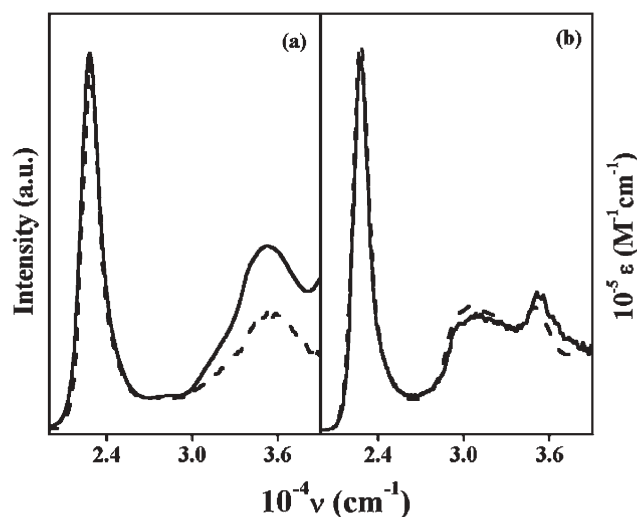

Fig. 2 Overlay of excitation (- - - -) and absorption (——) spectra of (a) **L** and (b) **[L·2Zn²⁺]** in CH₃CN at λ_{em} = 670 nm. The excitation spectra were corrected for the instrument response function and were normalized with respect to the absorption spectra between 1.5×10^4 – 1.7×10^4 cm⁻¹.

complex accompanied by the disappearance of the uncomplexed **ptp** peaks (Fig. S2) exactly at a **L** : Zn²⁺ ratio of 1 : 1. From these data the formation of coordination polymer can be inferred.[10] Interestingly, the addition of an excess amount of Zn(OTf)₂ gives rise to a second process in which the polymer complex is dissociated again in favour of an open form (**L·2Zn²⁺**) with the Zn²⁺ ion only attached to one **ptp** subunit with its other coordination sites presumably saturated by solvent molecules, Fig. 1. When **L** was titrated with Zn(OAc)₂ in DMSO-d_6, similar chemical shifts were observed except that it goes directly to an open form.[11] The ³¹P NMR signals due to the central P(V) atom in **L·2Zn²⁺** complex appear at −197.9 and −197.0 ppm with Zn(OTf)₂ and Zn(OAc)₂, respectively. Similar results were observed even in the case of Cd(OAc)₂ titrations. UV-visible titrations show that there is a slight decrease in the ε value of the porphyrin Soret band whereas the Q-bands (λ > 500 nm) are almost unchanged upon complexation with Zn²⁺/Cd²⁺ ions in DMSO/CH₃CN. At shorter λ (250–300 nm), characteristic ligand-centered **ptp** band intensity decreases with a red shift. Simultaneously, a new band emerges between 300–400 nm, which is attributed to **ptp** complexation, Fig. S3.

Interestingly, in the emission titrations (λ_{ex} = 566 nm), enhancement of the porphyrin fluorescence and a red shift in the spectral maximum were observed with the addition of Zn(OTf)₂ in CH₃CN, Fig. 3. At the saturation point, the calculated fluorescence quantum yield is 0.048, which is nearly 84% recovery with respect to the reference compound **[P(OH)₂]⁺** (ϕ_f = 0.054 in CH₃CN). The same trend was observed when **L** was titrated with Zn(OAc)₂ in DMSO, but enhancement was relatively less when compared to that of Zn(OTf)₂ titrations. At saturation point, the ϕ_f was found to be 0.041, which is ∼43% fluorescence recovered with respect to that of reference compound **[P(OH)₂]⁺** (ϕ_f = 0.06 in DMSO). Similar fluorescence enhancement was observed with Cd(OAc)₂ titrations. This fluorescence enhancement is due to the fact that PET between the ground state of **ptp** and excited porphyrin is inhibited by the complexation of the **ptp** moiety. After forming the complex with metal, **ptp** becomes electron deficient,[12] resulting in an increase in the oxidation potential of the **ptp** (> 1.70 V), Fig. S4.[13] The free energy change (ΔG_{PET}) becomes positive or endergonic, inhibiting the reductive electron transfer and enhancing the porphyrin fluorescence emission.

On the other hand, when excited at 300 nm (isosbestic point), fluorescence enhancement was observed in porphyrin emission bands with addition of Zn(OTf)₂ in CH₃CN, Fig. S5. The enhancement in fluorescence intensity is accounted for by the combined effect of direct excitation of porphyrin (due to the small amount of porphyrin absorption at 300 nm) and excitation energy transfer from **ptp** to the porphyrin moiety. When emission was recorded at the porphyrin emission maximum (670 nm), the
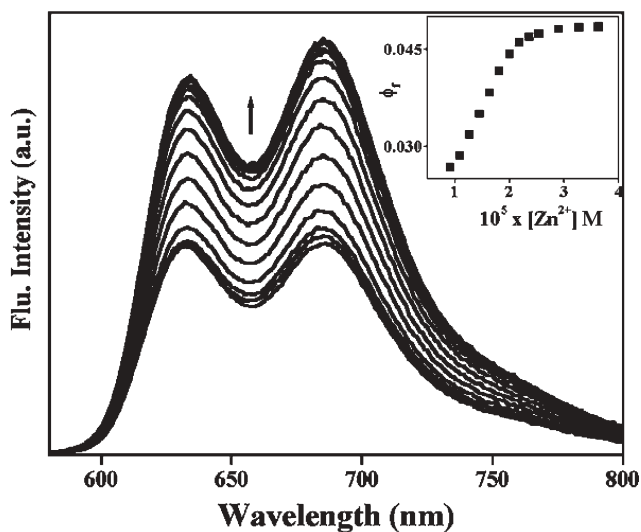
Fig. 3 Fluorescence titration of **L** (1.78×10^{-5} M) with Zn(OTf)₂ (9.11×10^{-4} M) at λ_{ex} = 566 nm; the inset shows fluorescence quantum yield upon addition of Zn(OTf)₂.

excitation spectrum showed bands characteristic of complexed **ptp** absorption. Fig. 2b shows the corrected and normalized excitation spectrum overlaid with the corresponding absorption spectrum in CH_3CN indicating almost $\sim 100 \pm 10\%$ energy transfer efficiency. But according to the fluorescence properties of triad **L**, upon excitation of **ptp** the fluorescence was quenched by EET ($\sim 61 \pm 10\%$, Fig. 1a) and the remaining $37 \pm 10\%$ could be due to PET. These results suggest that due to complexation of **ptp** subunits, the EET is dominant over the PET. To confirm this hypothesis, titration of **OMe-ptp** with $Zn(OTf)_2$ in CH_3CN at $\lambda_{ex} = 300$ nm was carried out and it was found that the fluorescence intensity increased with a large red shift (~ 80 nm) in the fluorescence maximum, Fig. S5. This implies that the spectral overlap integral (J) between emission of **ptp** and the absorption of porphyrin in this D–A system **L** is considerably enhanced with complexation. According to both the Forster[14] and Dexter[15] mechanisms, the rate of energy transfer is proportional to the spectral overlap integral (J) of the donor emission and acceptor absorption. An analysis based on these mechanisms suggests that the energy transfer rate increases with J and it reaches $\sim 100 \pm 10\%$ at the saturation point.

Finally, in both mechanisms the axial **ptp** subunits act as a donor and P(v) porphyrin as an acceptor. In fluorescence titrations it was found that the PET and EET reactions are modulated by metal coordination with **ptp** subunits. A schematic representation of these PET and EET processes is shown in Fig. 4. When excited at 566 nm in the presence of Zn^{2+} or Cd^{2+}, the PET process was inhibited from the ground state of the **ptp** subunit to the excited state of the porphyrin, resulting in an enhancement of porphyrin fluorescence. On the other hand, when excited at the isosbestic point at 300 nm, PET was suppressed and EET from the excited **ptp** subunit to the ground state of the porphyrin was enhanced. Further studies on **L** with other metal ions are currently in progress.
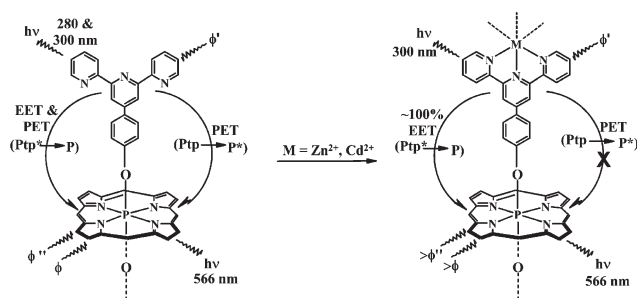
Fig. 4 A schematic diagram shows the modulation of PET and EET by Zn^{2+} or Cd^{2+} ions. Where ϕ, ϕ' and ϕ'' are fluorescence quantum yield of P(v) porphyrin ($\lambda_{ex} = 566$ nm), **ptp** ($\lambda_{ex} = 280/300$ nm) and P(v) porphyrin ($\lambda_{ex} = 280/300$ nm), respectively.

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