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A molecular photoswitch based on an ‘axial-bonding’ type phosphorus(V) porphyrin

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Reversible isomerization of the two axial azobenzene subunits leads to modulation of the fluorescence due to the basal tetrapyrrolic chromophore in a new hexa-coordinated phosphorus(V) porphyrin 3, illustrating its utility as a molecular photoswitch.

‘Emitter–quencher’ assemblies based on porphyrin building blocks are attracting increasing attention because of their importance as either model compounds in photosynthetic research or photoswitches in the fabrication of molecular electronic/optical devices.[1,2] While a great variety of covalently or non-covalently bound porphyrin–acceptor motifs are now known to closely mimic the initial, photoinduced electron transfer (PET) events of natural photosynthetic reactions,[1] the utility of such motifs as photoswitches has not been firmly established. In this regard, it is interesting that a key recurring theme of most earlier attempts to construct porphyrin-based photoswitches involves intramolecular PET coupled to isomerization (*E*/*Z*) of the azobenzene group.[3–8] This theme is an appealing one, and especially so, in view of the ready availability of PET-based non-porphyrinic photoswitches that incorporate azobenzene moieties in their architecture.[2] However, barring a recent exception,[4] photoswitching function has not been demonstrated in any of the porphyrin–azobenzene conjugates reported so far. Herein, we describe the luminescence on/off behavior observed in a novel, metalloid porphyrin-based photoswitch **3**, which is constructed by utilizing the ‘axial-bonding’ capability of a phosphorus(V) porphyrin (Fig. 1).

The hydroxide salt of photoswitch **3** was synthesized in 70% yield by reacting [5,10,15,20-tetra(tolyl)porphyrinato]phosphorus(V) dichloride **1** and 4-hydroxyazobenzene (excess) **2**, in refluxing pyridine and purifying by column chromatography [silica gel, $CHCl_3$–MeOH 10 : 1, v/v)].[9] The ^1H 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,[10] with the magnitude of shift for a given proton being a function of its separation distance from the porphyrin π-plane (see Fig. 1). On the other hand, effects due to the substitution of axial chlorides by the aryloxo ligands are minimal for the porphyrin pyrrole-β and meso-aryl proton resonances. However, in the ^{31}P NMR spectrum, the signal due to the central phosphorus ion of **3** was seen to be shifted downfield (δ −194.9, 85% H_3PO_4 external reference) compared to that of **1** (δ −229.4) but is within the typical range expected for hexa-coordinated diaryloxo phosphorus(V) porphyrins.[9] Further support for the structural integrity of **3** arises from the appearance of its molecular ion peak at m/z = 1093 ([M]$^+$) in the FAB mass spectrum.

The UV/VIS spectrum of **3** is essentially a summation of the spectra of **1** and **2** (1 : 2 molar ratio), with the porphyrin Q- and B-bands [λ_{max}/nm (log ε): 610 (4.03), 566 (4.28), 436 (5.36)] clearly distinguishable from the absorption due to the two *trans* azobenzene moieties in their *E* isomeric form [λ_{max}/nm (log ε): 341 (4.86)] [Fig. 2 (top curve)]. These spectral features suggest that there is no electronic communication between the porphyrin and the azobenzene chromophores and, more importantly, that it is possible to individually address the photochemistry of these two subunits in this bichromophoric system. Accordingly, continuous irradiation of **3**$_E$ (5.9×10^{-5} M, MeCN) at 345 ± 5 nm resulted in the time-dependent decrease of its absorption band centered at 341 nm concomitant with a slight increase of absorption in the B-band region, suggesting isomerization of the porphyrin-bound azobenzene subunits to produce **3**$_Z$.[11] The reverse thermal reaction was also spectrally monitored and the *E* form could be recovered quantitatively (Fig. 2).

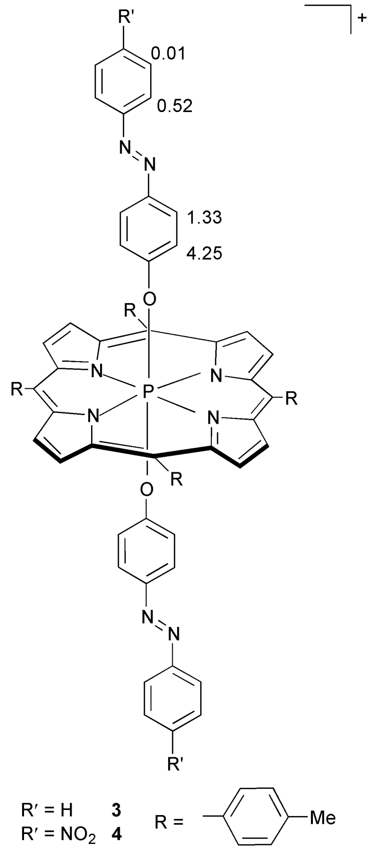

Fig. 1 Molecular structure of photoswitches investigated in the present study. The numbers indicated adjacent to protons on the azobenzene moiety are the corresponding porphyrin ring-current-induced ^1H NMR chemical shifts [*i.e.* $\Delta\delta$ (free − bound)] observed for **3**$_E$.

Excitation of a MeCN solution of **3**$_E$ at 345 nm resulted in no fluorescence emanating from the azo chromophore as is the case with the precursor **2**. On the other hand, the porphyrin component of the complex showed a fluorescence spectrum (λ_{exc} = 465/565 nm) typical of a hexa-coordinated phosphorus(V) porphyrin.[9] The fluorescence quantum yield [Φ_f, estimated using (5,10,15,20-tetraphenylporphyrinato)zinc(II), Zn^{II}TPP, as the standard] of **3**$_E$ (0.01) is less than that of [5,10,15,20-tetra(tolyl)porphyrinato]phosphorus(V) dihydroxide {[P^V(TTP)(OH)$_2$]$^+$, Φ_f = 0.045}. Interestingly, the fluorescence intensity due to **3**$_Z$ (produced by continuous irradiation at 345 ± 5 nm) is only 60 ± 5% of that due to **3**$_E$, and the thermal back reaction regenerates the fluorescence of **3**$_E$ as illustrated in Fig. 2 (inset). This *E*/*Z* interconversion was repeated 5–6 times

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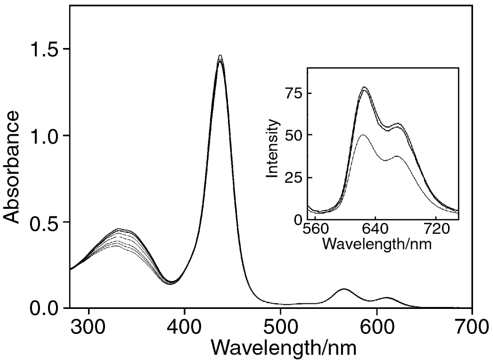

Fig. 2 Time-dependent UV/VIS spectral changes observed upon continuous irradiation of $\mathbf{3}_E$ (solvent: MeCN, $[\mathbf{3}_E] = 5.9 \times 10^{-5}$ M). Top curve represents the initial spectrum with the subsequent lower ones resulting from continuous irradiation of the solution at 345 ± 5 nm at 25 °C for 1, 2, 5, 7, 9, 12 and 16 min, respectively (PTI 150 W Xe-arc lamp model A1010, PTI model 1366-MONO monochromator). The dotted curve close to the top curve is the spectrum obtained after keeping the irradiated solution in the dark for several hours. Inset: fluorescence spectra of (——) unirradiated $\mathbf{3}_E$, (– – –) $\mathbf{3}_Z$ obtained upon irradiating $\mathbf{3}_E$ and of (· · · ·) $\mathbf{3}_E$ resulting from the back thermal reaction of $\mathbf{3}_Z$ (solvent: MeCN; $\lambda_{\mathrm{exc}} = 465$ nm).

with < 5% loss of the material (UV/VIS and fluorescence), thus establishing the ability of **3** to be an effective and stable photoswitch.

What is the origin of weak fluorescence observed for **3** and what is the mechanism of its photoswitching function? Among the various possible mechanisms considered by us,† an intramolecular PET from the axial azobenzene donors to the singlet excited state of the basal phosphorus(v) porphyrin seems to be the most probable pathway for the quenching of fluorescence in $\mathbf{3}_E$. This interpretation is consistent with not only the exoergicity for such a PET reaction ($\Delta G_{\mathrm{PET}} = -0.16 \pm 0.03$ eV‡), but also a similar interpretation made earlier for the quenching observed in a series of aryloxo phosphorus(v) porphyrins reported by us.[9b] Moreover, Φ_f for complex $\mathbf{4}_E$ (Fig. 1), which is endowed with the electron withdrawing nitro group at the axial azobenzene ligand, was seen ($\Phi_f = 0.035$) to be more than that of $\mathbf{3}_E$.§ Thus, accepting that PET is occurring between the axial ligand and the singlet porphyrin in this donor–acceptor complex, the photoswitching function demonstrated here can be rationalized in terms of the distance dependence of PET. As schematically represented in Fig. 3, the distance between the basal porphyrin and the axial ligand in $\mathbf{3}_Z$ is shorter than that in $\mathbf{3}_E$ explaining the additional fluorescence quenching observed for the former isomer.

Recently, electro-switch and proton-switch properties of an supramolecular ensemble comprising of Zn$^{\mathrm{II}}$TPP and *axially* ligated 4-(phenylazo)pyridine has been reported but, the effect of *E/Z* isomerization on the luminescence properties of this system was not observed.[3] Similarly, studies on the covalently connected azobenzene–porphyrin conjugates reported by Hunter and Sarson revealed that photochemistry of the porphyrin components of these novel chromophoric assemblies is essentially unaltered but, the photochemical isomerization of their azobenzene components could not be detected.[5] On the other hand, fluorescence properties of the early azobenzene–porphyrin systems reported by several groups were not investigated in detail.[6–8] While this work was in progress, photoswitching features of an azobenzene-linked diporphyrin complex have been described.[4] However, because of the extensive absorption by the two dissimilar porphyrin chromophores in the UV/VIS region, spectral detection of the *E/Z* isomerization in this system was not as facile as demonstrated here for **3**.

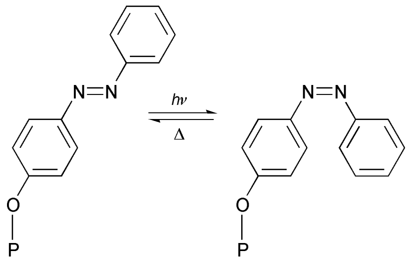

Fig. 3 Reversible *E/Z* isomerization in **3** (P = porphyrin).

In summary, the new phosphorus(v) porphyrin **3** is an effective and stable photoswitch. Its photoswitching ability is a result of the isomerization-induced modulation of the PET between the axial azobenzene subunits and the basal porphyrin scaffold. Further studies on **3** and other closely related 'axial-bonding' type photoswitches are currently in progress.

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Notes and references

† Excitation of **3** at 345 nm resulted in weak fluorescence in the range 550–750 nm but control experiments have suggested this to be entirely due to the residual absorption by the porphyrin chromophore. Moreover, the excitation spectrum of the compound (emission collected at the porphyrin fluorescence band maximum) did not show absorption corresponding to the azobenzene chromophore. In a separate set of experiments, neither the fluorescence of $[\mathrm{P(TTP)(OH)_2}]^+$ was found to be quenched by compound **2** nor was any rate enhancement observed for the thermal back reaction of $\mathbf{3}_Z$ in the presence of externally added **2**. Thus, fluorescence quenching observed here for **3** is not due to the energy transfer between the azobenzene and porphyrin subunits or the photochemical disscociation of azobenzene ligands.

‡ Estimation of ΔG_{PET} is based on the electrochemical redox potential data [E_{ox} (axial ligand) = 1.52 V, E_{red} (basal porphyrin) = −0.35 V] and singlet energy of the porphyrin (2.03 eV[9c]).

§ The presence of an electron withdrawing nitro group on the axial ligand is expected to decrease its donor capacity. Indeed, ΔG_{PET} for **4** is close to 0.0 eV, consistent with its high Φ_f value.

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