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Non-covalent switch for intramolecular energy transfer†

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The axially coordinated complex of phenylazopyridine and a Zn-porphyrin/free-base porphyrin conjugate provides a switch for intramolecular energy transfer, with reversible complexation/decomplexation as a switching protocol.

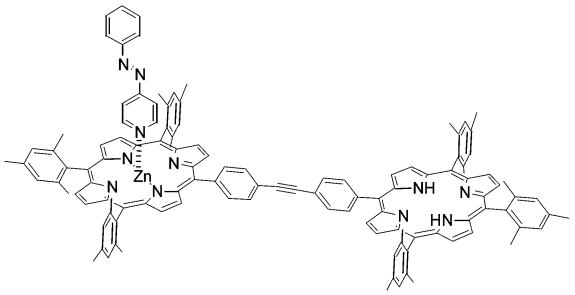
The development of molecular photonic/electronic devices rests on the realisation of electronic communication and its switching among suitably placed photo/electro-active molecule-based components.[1] Although covalent linkages, especially rigid conjugated ones, promise well-defined arrangements of components, multi-step preparations would pose increasingly serious obstacles as the system becomes more and more elaborate. Non-covalent assembly using programmed intermolecular interactions may provide a means to overcome this problem.[2]

We previously showed that a non-covalent assembly, which is composed of a light emitting centre (Zn-tetraphenylporphyrin; ZnTPP) and a quenching component (4-(phenylazo)pyridine; PhNNPy) connected *via* kinetically labile but structurally well-defined axial coordination,[3] functions as an electron- and proton-responsive photoswitch.[4] In this switch, the fluorescence of ZnTPP is turned on and off by external triggers, which means that the excited state lifetime is controlled. This suggests the possibility of controlling processes which follow the excited state, such as electron and energy transfer. Here we show that energy transfer is indeed switched on and off with this strategy being applied to a Zn-porphyrin/free-base porphyrin conjugate, ZnFbU.[5] This work provides a photonic gate[6] with a switching means unique to the non-covalent approach.

The conjugate molecule, ZnFbU, prepared according to the literature,[5a] has the following properties. Firstly, the absorption spectrum of ZnFbU is essentially a summation of the spectra of the Zn and Fb units, suggesting that the interchromophore interactions are weak in the ground state and allowing the estimation of the proportion of light absorbed by each chromophore at a given wavelength.[5b] Secondly, the intramolecular energy transfer efficiency in this molecule is 0.99, the rate of energy transfer being $k_{ET} = 4.2 \times 10^{10}$ s^{-1} in toluene at 25 °C.[5b] Therefore, the fluorescence from this molecule is almost exclusively from the Fb unit; the fluorescence spectrum of ZnFbU is nearly identical to that of the Fb unit (Fig. S1, see ESI†).[5b]

We have examined whether PhNNPy effectively hinders the intramolecular energy transfer process from the Zn unit to the Fb unit. This requires that the quenching of the excited state of the Zn unit by PhNNPy is extremely efficient with the quenching rate sufficiently larger than k_{ET} to compete with the fast energy transfer process.

Upon the addition of PhNNPy to a solution of ZnFbU in CH_2Cl_2, the Q-band absorption spectrum by the Zn unit exhibited a red-shift characteristic of axial coordination as shown in Fig. 1. The presence of clear isosbestic points in this change at wavelengths of 557, 584 and 590 nm indicates that a well-defined 1 : 1 adduct, wherein PhNNPy axially coordinates



to Zn in ZnFbU, is formed.[3a] The association constant in CH_2Cl_2 at 25 °C has been determined as $K_{PhNNPy} = 1.2 \times 10^4$ M^{-}.‡

The fluorescence intensity of PhNNPy·ZnFbU was found to be 21%‡ of that of ZnFbU, when excited at 647 nm where only the Fb unit is excited, indicating PhNNPy directly quenches the fluorescence of the Fb unit through long-range interactions. On the other hand, when excited at an isosbestic 557 nm where the ratio of light absorbed by the Zn unit and the Fb unit is 82 : 18, the fluorescence intensity of PhNNPy·ZnFbU was 7%‡ of that of ZnFbU. More than half of this fluorescence intensity (~4% = 0.18 × 0.21) is accounted for by the direct excitation of the Fb unit, leaving only ~3% being originated from the excited state of the Zn unit through energy transfer, which indicates that the energy transfer process is largely hindered by the coordination of PhNNPy.

The relevant excitation spectra have been compared to confirm this contention as shown in Fig. S2, see ESI.† All peak positions of the excitation spectrum of PhNNPy·ZnFbU (λ_{fl} = 712 nm) nearly agree with those of 5,10,15,20-tetramesitylporphyrin (TMP) as a Fb model. If the energy transfer occurred from the coordinated Zn unit in PhNNPy·ZnFbU, the excitation spectrum would show red-shifted peaks corresponding to the red-shift of absorption peaks. The excitation spectra of DMAP·ZnFbU (DMAP = 4-(*N*,*N*-dimethylamino)pyridine) is

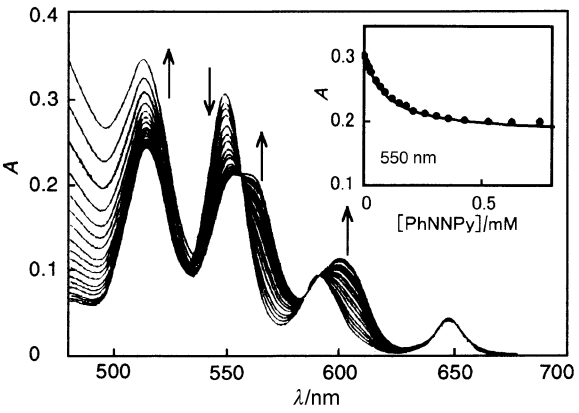


Fig. 1 Changes in the absorption spectrum of ZnFbU (10 μM) induced by the addition of PhNNPy (0–0.9 mM) in CH_2Cl_2 at 25 °C. The absorption by PhNNPy appears at <540 nm. Inset: changes in absorbance at 550 nm.

† Electronic supplementary information (ESI) available: fluorescence spectra and excitation spectra. See http://www.rsc.org/suppdata/cc/b2/b212912d/

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shown for comparison, as DMAP coordinates to ZnFbU without quenching much of the excited state of the Zn unit. Although a difference in intensity is noted for the peak at 549 nm between the excitation spectra of PhNNPy·ZnFbU and TMP, when the latter is normalised at 645 nm where only the Fb unit is excited, this is due to residual uncoordinated ZnFbU. Thus, the coordination of PhNNPy hinders the energy transfer process below the detection limit by the excitation spectra, realising the switched-off state of energy transfer.

The switch may be turned on by removing PhNNPy from ZnFbU. This can be effected by the addition of acid or a competitively coordinating ligand. Upon the addition of DMAP (0.3 mM) to a mixed solution of PhNNPy (1 mM) and ZnFbU (10 μM) in CH_2Cl_2, the absorption spectrum showed a slight change with an isosbestic point at 566 nm and the fluorescence of ZnFbU increased, as DMAP replaced PhNNPy from ZnFbU (Fig. S3, see ESI†). Since the association constant of DMAP and ZnFbU (K_{DMAP} = 2.9 ×10^5 M^{-1})‡ is more than 20 times larger than K_{PhNNPy}, the predominant species in solution under this condition was DMAP·ZnFbU. Turning the switch on again is effected by the addition of acid. To the above solution containing PhNNPy, ZnFbU and DMAP, dichloroacetic acid (0.3 mM) was added. Due to a large difference in pK_a values of the conjugate acids of PhNNPy (3.5)[7] and DMAP (10.1),[8] DMAP is preferentially protonated, leaving ZnFbU and thus allowing for PhNNPy to coordinate again to ZnFbU. This coordination turns off the energy transfer process. Further switching on and off are effected by the alternate addition of DMAP and dichloroacetic acid. This scheme works quite reversibly and its on/off ratio is reasonably large as shown in Fig. 2.§

We infer electron transfer as a possible mechanism of the quenching based on energetic considerations. The free energy change from PhNNPy·^{1}ZnFbU* to PhNNPy$^-$·ZnFbU$^{\cdot+}$ is estimated as *ca.* –0.26 eV, which is negative enough to allow rapid electron transfer. This value has been derived from the first oxidation potential of ZnFbU (0.41 V *vs* Fc/Fc$^+$),[5c] the first reduction potential of PhNNPy·ZnTPP (−1.47 V *vs* Fc/Fc$^+$), the excited state energy of axially-coordinated ZnTPP (2.04 eV),[9] and the fact that axial coordination induces negative shift of the first oxidation potential of Zn porphyrins by *ca.* 0.1 V (thus, the oxidation potential of PhNNPy·ZnFbU is estimated as *ca.* 0.31 V *vs* Fc/Fc$^+$).[9]

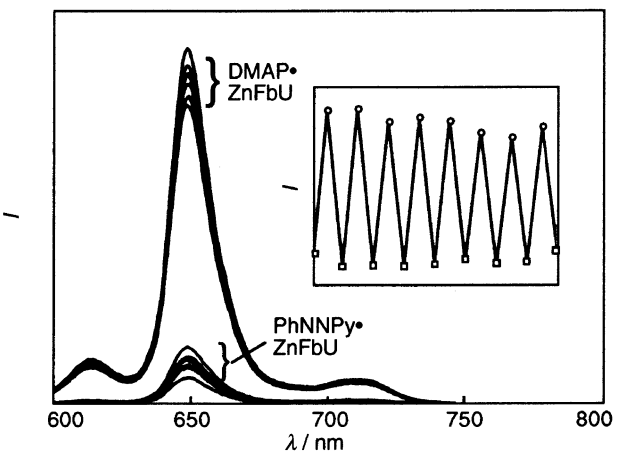

Fig. 2 Fluorescence response of a solution of PhNNPy (1 mM) and ZnFbU (10 μM) in CH_2Cl_2 at 25 °C, upon the alternate addition of DMAP (circle) and dichloroacetic acid (square). The excitation wavelength is isosbestic 566 nm.

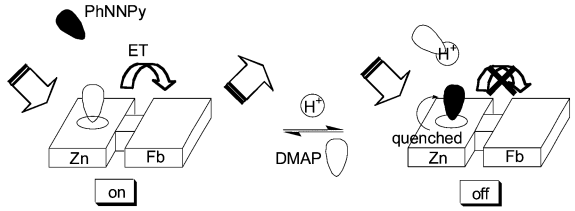

Fig. 3 Reversible switching of intramolecular energy transfer in ZnFbU by the complexation and decomplexation of PhNNPy (black lobe) effected by the alternate addition of base (DMAP; white lobe) and acid (dichloroacetic acid; H$^+$).

Fig. 3 schematically summarises the *modus operandi* of this switch. In conclusion, we have shown that a switch (or a gate) for intramolecular energy transfer is conveniently constructed by metal–ligand interactions involving a quencher and an energy-transfer component. Turning the switch on and off has been realised by using complexation and decomplexation of the assembly, which is a protocol unique to systems in which components are connected in a reversible fashion.

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Notes and references

‡ Association constants were determined by a non-linear least square procedure. The conditional standard deviations were within 3%. The fluorescence intensity of complexes were obtained by the same procedure and the limiting values (*i.e.* complete complexation) are given.

§ A comment may be warranted about the use of DMAP and dichloroacetic acid. PhNNPy can be removed from ZnFbU by the addition of acid as was done in our previous photoswitch.[4] However, excess or stronger acid is needed to protonate PhNNPy, since PhNNPy is a weak base, which tends to cause demetallation of the Zn unit. On the other hand, an almost equivalent amount of acid is enough to protonate DMAP. Non-protonated PhNNPy keeps the medium basic all the time during the switching experiments. No evidence of demetallation was observed during the experiments shown in Fig. 2.

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