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Photocontrol of electron transfer from Zn-porphyrin to an axially bound stilbazole–pyromellitic diimide conjugate†

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A photochromic stilbazole unit has been incorporated into the bridge in a donor–bridge–acceptor scaffold constructed *via* a coordination interaction, wherein an efficient electron transfer occurs for the *cis* isomer of the bridge whereas no electron transfer is detected for the *trans* isomer.

Processing photons and electrons at the molecular or supramolecular level has received considerable attention in the past decade, which may lay the foundation for the development of molecule-based information processing devices.[1] Electron and energy transfer processes provide a means for electronic communication among molecular entities in the device. On–off switching of these processes in response to an external trigger is required to process information at the molecular level. Photochromic compounds have been used in photoswitchable electron transfer systems in view of their potential applications in photonic molecular devices.[2–4] In particular, incorporating a photochromic unit as the bridge in a donor–bridge–acceptor (D–bridge–A) scaffold is attractive, since the bridge can modulate the electronic coupling between D and A upon light irradiation, resulting in a change in the rate of electron or energy transfer from D to A.[3,4] Most of the examples demonstrated so far utilise electronic changes in the photochromic unit upon light irradiation, such as conjugation, absorption spectra and redox potentials, to switch the electron transfer paths.[2,3] In contrast, geometric changes associated with the photoreaction have rarely been utilised.[4] A large modulation of the electron transfer event is expected even with a relatively small geometry change, since the electron transfer rate generally decreases exponentially with the D–A distance. Herein we wish to report on a system exhibiting a large change in the electron transfer rate associated with a geometric change of the photochromic unit incorporated in the bridge in a D–bridge–A structure.

The stilbazole derivative containing a pyromellitic diimide unit, **1**, was prepared as the bridge–A unit (Fig. 1; for the preparation, see ESI†). Pyromellitic diimides quench the fluorescence of Zn-porphyrin by accepting the excited electron.[5] For the D–bridge connection, axial coordination to Zn-tetraphenylporphyrin (ZnTPP) was used, which is a facile method to construct well-defined porphyrin assemblies, although a large excess of ligand may be required due to a moderate binding strength.[6] One of the advantages of employing a noncovalent approach is that photoisomerisation is not inhibited by the proximate chromophore such as porphyrin, which, in covalent systems, could perturb the photochromic unit to an extent that the photoisomerisation no longer occurs.[2b]

Red-shifts in the Soret and Q-bands in the absorption spectrum of ZnTPP upon incremental addition of *trans*-**1** present clear evidence of axial coordination,[6] giving a value of 7200 (± 200) M^{-1} as the 1 : 1 binding constant (Fig. S1, see ESI†). During this titration, only a marginal decrease in fluorescence intensity was observed. Indeed, the magnitude of the decrease is about the same as that by 4-styrylpyridine, indicating that the quenching by electron transfer to the imide moiety in *trans*-**1** is negligible. This is in contrast to a previously reported case for pyromellitic diimide tethered to a pyridine group in place of the stilbazole group, thus having a shorter porphyrin–acceptor distance.[7]

The effect of the *trans*-to-*cis* isomerisation on porphyrin fluorescence was examined by irradiating light at 310 nm to a mixed solution of 10 μM ZnTPP and 1.5 mM *trans*-**1** in toluene. The decrease in absorbance at < 340 nm, as shown in Fig. 2a, shows that the conversion of *trans*-**1** into *cis*-**1** takes place. ^{1}H NMR measurements reveal that the final spectrum in this figure corresponds to a *trans* : *cis* ratio of 43 : 57. It is also noted that the Soret (~ 420 nm) and Q bands (not shown) of ZnTPP are invariant during irradiation, indicating that the photoisomerisation does not

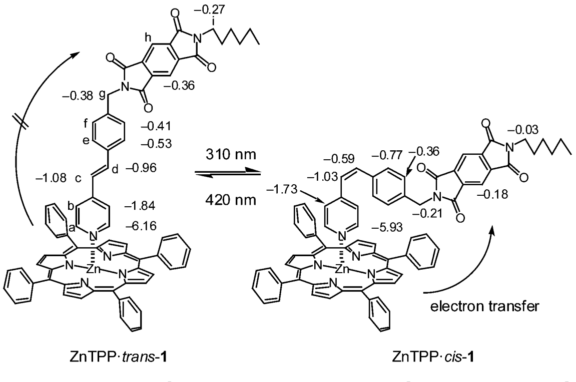

Fig. 1 Interconversion between ZnTPP·*trans*-**1** and ZnTPP·*cis*-**1**, and the limiting values of complexation-induced chemical shift changes in $CDCl_3$. Negative values indicate upfield shifts.

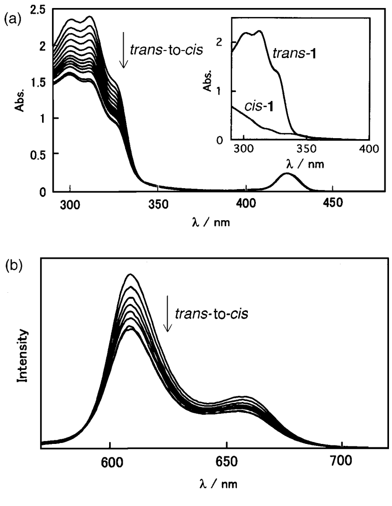

Fig. 2 Spectral changes upon 310 nm irradiation to a solution of ZnTPP (10 μM) and *trans*-**1** (1.5 mM) in toluene at 25 °C. (a) Absorption spectra for diluted (1/20) samples taken from the irradiated solution. The absorption bands of **1** and ZnTPP appear at < 360 nm and ~ 420 nm, respectively. Inset: absorption spectra for *trans*- and *cis*-**1** (75 μM). (b) Accompanying fluorescence changes (not diluted), λ_{ex} = 555 nm.

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† Electronic supplementary information (ESI) available: preparation of **1** and titration of ZnTPP with *trans*-**1**. See http://www.rsc.org/suppdata/cc/b4/b403991b/

affect the binding of **1** with ZnTPP. Fluorescence intensity (λ_{ex} = 555 nm) decreased at the same time as shown in Fig. 2b, suggesting that the electron transfer quenching is more efficient in ZnTPP·*cis*-**1** than in ZnTPP·*trans*-**1**.

The fluorescence lifetime measurements were consistent with the above mentioned steady-state measurements. The observed lifetime of the singlet excited-state of ZnTPP (10 μM) in the presence of *trans*-**1** (1.5 mM) in toluene, wherein 92% of porphyrin is complexed, was 1.66 ns,[8] slightly shortened from that of ZnTPP alone (2.03 ns).[9] The slight change in the fluorescence lifetime is due to axial coordination, since the lifetime was the same (1.66 ns) when **1** was replaced by 4-styrylpyridine. On the other hand, the fluorescence time profile of ZnTPP in the presence of a mixture of *trans*- and *cis*-**1**, produced by light irradiation at 310 nm, consisted of two decaying components. The longer lifetime (τ_0), 1.82 ns, is comparable to that of ZnTPP·*trans*-**1**, whereas the shorter lifetime component (τ), 0.42 ns, is assigned to ZnTPP·*cis*-**1**. The fractions obtained in the lifetime and ^{1}H NMR measurements agreed with each other, supporting the assignment. The electron transfer rate (k_{et}) and efficiency (Φ_{et}) for ZnTPP·*cis*-**1** are determined from the equations, $k_{\mathrm{et}} = \tau^{-1} - \tau_0^{-1}$ and $\Phi_{\mathrm{et}} = k_{\mathrm{et}}\,\tau$, as 1.83×10^9 s^{-1} and 0.77, respectively. Thus, it has been demonstrated that an efficient electron transfer occurs in ZnTPP·*cis*-**1**, whereas no electron transfer is detected for ZnTPP·*trans*-**1**.

Subsequent irradiation of 400–435 nm light to the mixture of ZnTPP, *trans*-**1** and *cis*-**1** resulted in the reversal of the absorption and fluorescence intensity changes as well as the increase of the fraction of the longer lifetime component, indicating the reversibility of the photoisomerisation process. It is known that the *cis*-to-*trans* isomerisation of stilbazole derivatives is sensitized by Zn-porphyrins through the triplet energy transfer.[10]

To probe the mechanism of the modulation of electron transfer rate, the ^{1}H NMR spectra of ZnTPP·*trans*-**1** and ZnTPP·*cis*-**1** were compared. By recording chemical shifts upon addition of incremental amounts of ZnTPP into a solution of *trans*- and *cis*-**1** in $CDCl_3$, the limiting complexation-induced chemical shift changes were obtained, which are displayed in Fig. 1. The upfield shifts as much as ~6 ppm for H_a are clear evidence for axial coordination to ZnTPP *via* the pyridine-*N*.[6,11] The upfield shifts for H_a, H_b and H_c are similar in both *trans*-**1** and *cis*-**1**, while the shift for H_d in *cis*-**1** is smaller by *ca.* 0.4 ppm than that in *trans*-**1**, suggesting that H_d in *cis*-**1** is located more off centre with respect to the porphyrin macrocycle. As for *trans*-**1**, the magnitudes of upfield shifts decrease regularly as the separation between the relevant protons and the pyridine-*N* increases. On the other hand, for *cis*-**1**, the upfield shift for H_e is larger than that of H_d, which suggests that H_e is closer to the porphyrin macrocycle than H_d is, due to the U-shaped *cis*-configuration at the double bond. The remaining protons (H_f, H_g, H_h and H_i) in *cis*-**1** exhibit smaller upfield shifts than those in *trans*-**1**, although these protons in *cis*-**1** should be closer to ZnTPP, since these protons lie over the peripheral region of ZnTPP.

Stable conformations for *trans*-**1** and *cis*-**1** were exhaustively searched with molecular mechanics calculations by systematically rotating the phenylene-*C*–CH_2 and CH_2–imide-*N* bonds, while the stilbazole part was fixed according to the crystal structures.[12] Two especially stable conformations were found for each of *trans*-**1** and *cis*-**1**. Ring-current shifts for these conformations were calculated based on the Abraham mode,[11] and the results were qualitatively consistent with the observation described above. Assuming that **1** coordinates to ZnTPP in a perpendicular fashion,[13] the distances between the centre of ZnTPP and the centre of the imide ring in *trans*-**1** and *cis*-**1** are estimated to be *ca.* 16.5 Å and 10–13 Å, respectively.

From the above considerations, we propose that the change in the D–A distance associated with the photoisomerisation of the stilbazole unit is the primary cause of the modulation of the electron transfer rate.[14] This work also highlights the importance of a direct electron transfer path from the donor to the acceptor without the involvement of the bridging part in ZnTPP·*cis*-**1**, possibly mediated by solvent molecules,[15] since electron transfer does not occur in ZnTPP·*trans*-**1** which has exactly the same atomic connectivity but only in a more extended fashion.

In conclusion, we have constructed a new noncovalent D–bridge–A system, in which a photochromic unit is incorporated into the bridging part. It has been demonstrated that an efficient electron transfer occurs in ZnTPP·*cis*-**1**, whereas no electron transfer is detected for ZnTPP·*trans*-**1**, representing a photoswitchable photo-induced electron transfer system based on a geometric change.

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Notes and references

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*b*) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541–548; (*c*) A. P. de Silva and N. D. McClenaghan, *Chem. Eur. J.*, 2004, **10**, 574–586.

2 (*a*) D. R. Reddy and B. G. Maiya, *Chem. Commun.*, 2001, 117–118; (*b*) A. J. Myles and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 177–178; (*c*) P. A. Liddell, G. Kodis, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 2002, **124**, 7668–7669; (*d*) Y. Terazono, G. Kodis, J. Andreasson, G. Jeong, A. Brune, T. Hartmann, H. Dürr, A. L. Moore, T. A. Moore and D. Gust, *J. Phys. Chem. B*, 2004, **108**, 1812–1814; (*e*) X. Guo, D. Zhang and D. Zhu, *J. Phys. Chem. B*, 2004, **108**, 212–217.

3 (*a*) S. L. Gilat, S. H. Kawai and J.-M. Lehn, *Chem. Eur. J.*, 1995, **1**, 275–284; (*b*) S. Fraysse, C. Coudret and J.-P. Launay, *Eur. J. Inorg. Chem.*, 2000, 1581–1590; (*c*) J.-P. Launay, S. Fraysse and C. Coudret, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 125–132; (*d*) H. Port, A. Hartschuh, M. Hennrich, H. C. Wolf, J. M. Endtner and F. Effenberger, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 145–150.

4 S. Tsuchiya, *J. Am. Chem. Soc.*, 1999, **121**, 48–53.

5 (*a*) Thus, we assume that the quenching of the ZnTPP excited state by **1** is due to electron transfer: A. Osuka, S. Nakajima, K. Maruyama, N. Mataga and T. Asahi, *Chem. Lett.*, 1991, 1003–1006; (*b*) A. Osuka, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.*, 1996, **118**, 155–168.

6 J. Otsuki, *Trends Phys. Chem.*, 2001, **8**, 61–72.

7 (*a*) C. A. Hunter, J. K. M. Sanders, G. S. Beddard and S. Evans, *J. Chem. Soc., Chem. Commun.*, 1989, 1765–1767; (*b*) J. Otsuki, K. Harada, K. Toyama, Y. Hirose, K. Araki, M. Seno, K. Takatera and T. Watanabe, *Chem. Commun.*, 1998, 1515–1516.

8 This value should be a convolution of the similar lifetimes of fluorescence from ZnTPP·*trans*-**1** and residual free ZnTPP.

9 J.-S. Hsiao, B. P. Krueger, R. W. Wagner, T. E. Johnson, J. K. Delaney, D. C. Mauzerall, G. R. Fleming, J. S. Lindsey, D. F. Bocian and R. J. Donohoe, *J. Am. Chem. Soc.*, 1996, **118**, 11181–11193.

10 (*a*) D. G. Whitten, P. D. Wildes and I. G. Lopp, *J. Am. Chem. Soc.*, 1969, **91**, 3393–3394; (*b*) P. D. Wildes and D. G. Whitten, *J. Am. Chem. Soc.*, 1970, **92**, 7609–7610; (*c*) M. Brink and O. Wennerström, *J. Photochem. Photobiol., A*, 2001, **143**, 201–208.

11 (*a*) R. J. Abraham, S. C. M. Fell and K. M. Smith, *Org. Magn. Reson.*, 1977, **9**, 367–373; (*b*) R. J. Abraham, G. R. Bedford, D. McNeillie and B. Wright, *Org. Magn. Reson.*, 1980, **14**, 418–425.

12 S. Hirose, S. Hayami and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2059–2066.

13 D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, 1970, **92**, 3761–3771.

14 Cyclic voltammetry in CH_2Cl_2 showed that the reduction potentials of *trans*- and *cis*-**1** are the same at −1.36 V *vs.* Fc/Fc$^+$.

15 N. R. Lokan, M. N. Paddon-Row, M. Koeberg and J. W. Verhoeven, *J. Am. Chem. Soc.*, 2000, **122**, 5075–5081.