meso–meso-*Linked Zn^{II} Diporphyrin*

Dihedral-Angle Modulation of *meso–meso*-Linked Zn^{II} Diporphyrin through Diamine Coordination and Its Application to Reversible Switching of Excitation Energy Transfer**

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Control of intramolecular excitation-energy transfer (EET) and electron transfer (ET) has been a subject of considerable attention in light of its importance in molecular electronics including artificial photosynthesis,[1] molecular sensing systems,[2] molecular devices,[3] and so forth. When the direction of an intramolecular EET reaction can be switched at will by external physical and/or chemical input, it provides a switching EET module as a component of molecular devices.[4]

Recently, we reported the synthesis of *meso–meso*-linked diporphyrins, whose Soret band is split into two bands by an exciton coupling but the conjugative electronic interaction between the porphyrin chromophores in the diporphyrin is weak because of the nearly perpendicular conformation, despite the direct *meso–meso* linkage.[5] Thus, a decrease in the dihedral angle of diporphyrin, from an average of 90° to an oblique geometry, is expected to lead to an enhancement in the electronic coupling within the diporphyrin, which has been confirmed by permanently distorted *meso–meso*-linked diporphyrins bridged by a strap of variable length.[6] Namely, the decrease in the dihedral angle between the porphyrin rings in the diporphyrin causes progressive lowering of the S_1-state energy and an increase in energy of the HOMO orbital in addition to the spectral changes from two Soret bands to four Soret bands, which is a consequence of symmetry change from D_{2d} to D_2.

Herein we report reversible switching of intramolecular EET direction on the basis of the dihedral angle control of *meso–meso*-linked Zn^{II} diporphyrin through 1,7-diaminohep-

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tane coordination. First, coordination behaviors of α,ω-diaminoalkanes ($H_2N(CH_2)_nNH_2$, ***n*DA**) to *meso–meso*-linked Zn^{II} diporphyrin **1** have been examined in terms of association ability and association mode, by changing the molecular length of ***n*DA**.[7] In the absence of an amine, the absorption spectrum of **1** exhibits split Soret bands at 416 and 451 nm in toluene.[5] Following the changes in the absorption spectra upon the addition of ***n*DA** to the corresponding solutions, we determined the association constants (K_a) on the basis of 1:1 complex formation (Table 1). A jump in K_a was

Table 1: Association constants of **1** with ***n*DA** in toluene at 25 °C. Association constants have been calculated assuming a 1:1 complex.

n	K_a [$\times 10^4$ M^{-1}]	*n*	K_a [$\times 10^4$ M^{-1}]
2	9.0	8	710
4	11	9	690
5	16	10	2600
6	10	12	910
7	160		

observed between 1,6-diaminohexane (**6DA**) and 1,7-diaminoheptane (**7DA**), and between 1,9-diaminononane (**9DA**) and 1,10-diaminodecane (**10DA**). Figure 1 shows typical contrasting coordination behaviors of 1,5-diaminopentane (**5DA**) and **7DA** towards **1**. The addition of **5DA** to a toluene solution of **1** caused the red shift of Soret bands to 424 and 459 nm with several isosbestic points (Figure 1a). These spectral changes, which are common for ***n*DA** shorter than **5DA** and for monoaminoalkanes, can be interpreted in terms of the coordination of two diamine molecules to **1** without affecting an averaged perpendicular conformation. Conversely, a similar addition of **7DA** to a toluene solution of **1** gave rise to markedly different spectral changes, from two Soret bands to four Soret bands (λ_{max} = 412 (shoulder), 427, 462, and 472 (shoulder) nm) as well as red shifts of Q bands from 540 (shoulder) and 553 nm to 554, 575, respectively, and the appearance of a band at 629 nm (Figure 1b). The resultant absorption spectral features of complex **7DA–1** are, both in the Soret band and Q band regions, quite similar to those of permanently distorted *meso–meso*-linked diporphyrin **2** bridged by a 1,4-dioxyteteramethylene strap (Scheme 1). It

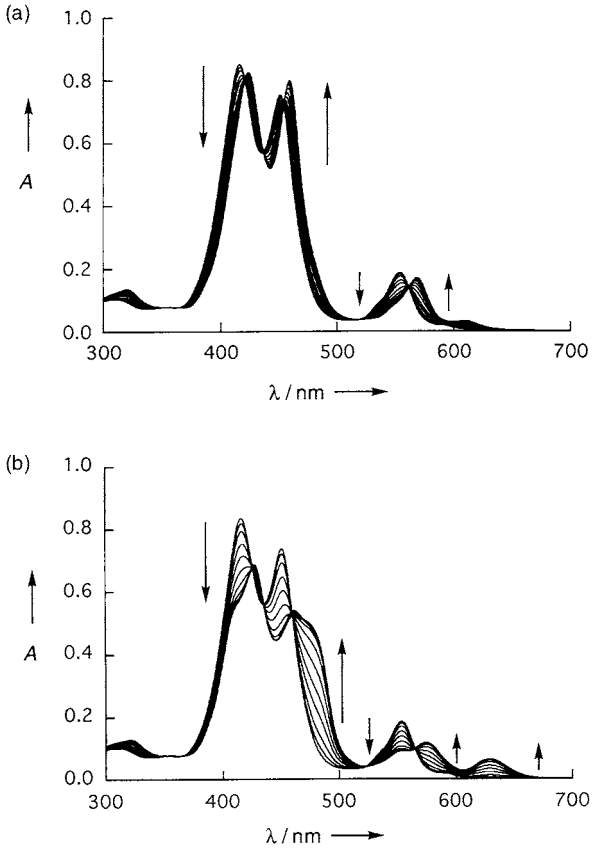
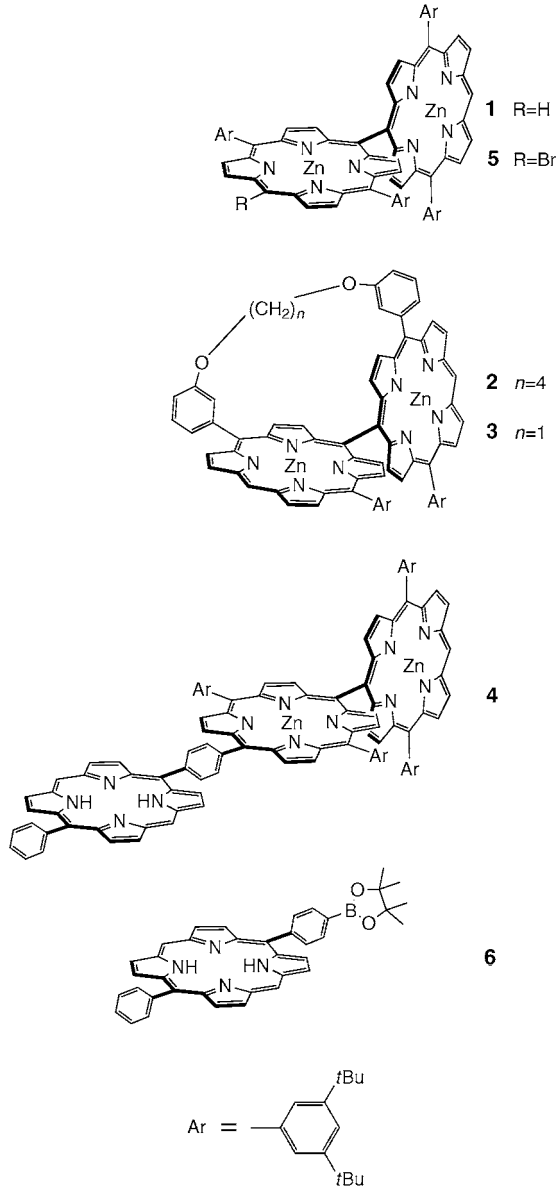


Figure 1. Absorption spectra of **1** (3.5×10^{-6} M) with **5DA** (a) and **7DA** (b) in toluene at 25 °C: [**5DA**] = 0–1.6×10^{-4} M; [**7DA**] = 0–3.5×10^{-5} M. *A* = absorption.



Scheme 1. Structure of the porphyrins referred to.

is thus conceivable that the association of **7DA** with **1** takes place through two amino groups coordinated to the two zinc centers, hence forcing a tilt of the two porphyrins from a dihedral angle of about 90° to a decreased dihedral angle. Association constants of **1** with longer diamines such as **10DA** and **12DA** are apparently larger than that with **7DA**, but the resulting complexes exhibit an absorption spectra similar to that of the **5DA–1** complex, thus suggesting that these long diamines have sufficient molecular length to form a 1:1 complex without affecting the average perpendicular conformation of the *meso–meso*-linked Zn^{II} diporphyrin. Job plots indicate a 1:1 molecular ratio for the formation of complexes **7DA–1** and **10DA–1** (Supporting Information). Different association modes between complexes **5DA–1** and **7DA–1** are also evident in the fluorescent spectra (Figure 2), which feature modest spectral changes in the former, and a distinct red shift and intensity enhancement in the latter. The fluorescence spectrum of complex **7DA–1** (Figure 2b) is reminiscent of that of the distorted diporphyrin **2** coordinated with amine, which again indicates a change in the dihedral angle of **1** upon the association of **7DA**. Among the α,ω-diaminoalkanes examined, **7DA** is the most effective in inducing the distorted conformation as judged from the optical properties of the complexes formed. Judging from the X-ray crystal structure of the Cu^{II} analogue of **2**, the coordination of **7DA** reduces the dihedral angle from nearly 90° to 60–70°.[6b] The absorption and fluorescence spectra of **7DA–2** complex are quite similar to those of more distorted diporphyrin **3** bridged by a dioxymethylene strap, in which the dihedral angle is estimated to be less than 50°.[6b] Therefore, it is likely that **7DA** is ideally suited for changing the dihedral angle of the *meso–meso*-linked Zn^{II} diporphyrin and the additional torsional strain imposed by the coordination of **7DA** is effective for the modulation of the interporphyrin electronic interaction. Furthermore it is noteworthy that the addition of acetic acid to a solution of complexes **7DA–1** or **7DA–2** restores the original absorption and fluorescence spectra of **1** or **2**, plausibly through a simple acid–base reaction without affecting the Zn^{II} metallation. Thus these torsional changes can be effected in a reversible manner.

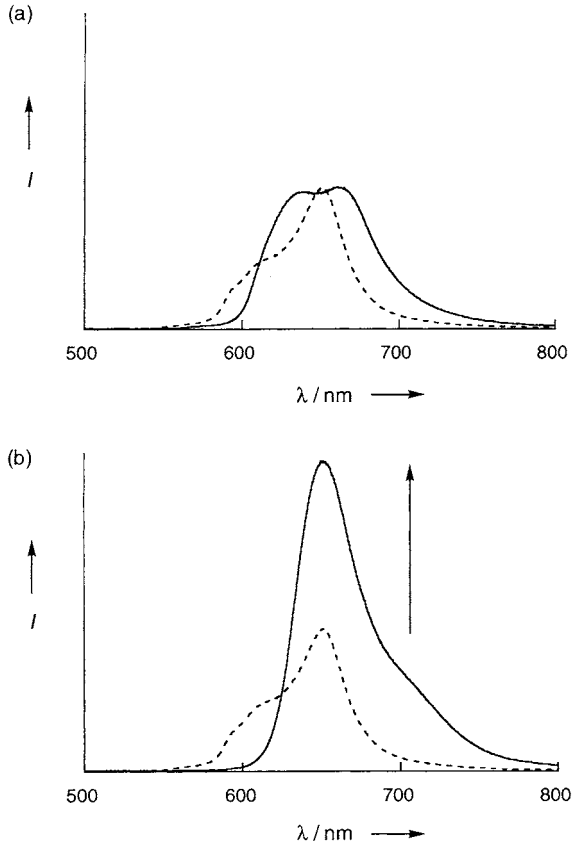


Figure 2. Fluorescence spectra of **1** (3.5×10^{-6} M) with **5DA** (a) and **7DA** (b) in toluene at 25 °C: $\lambda_{ex}=435$ nm, [**5DA**] = 0 (-----) or 2.9×10^{-4} M (——); [**7DA**] = 0 or 8.0×10^{-6} M. *I* = intensity (arbitrary units).

With these reversible modulations of the optical properties of **1** at our disposal, we have explored a molecular system that enables reversible switch in direction of the EET. We designed triporphyrin **4**, in which a *meso–meso*-linked Zn^{II}-diporphyrin unit is covalently linked to a 5,15-diaryl free-base porphyrin through a 1,4-phenylene bridge. Model **4** was prepared by the Suzuki coupling reaction of bromide **5** with boronate **6** ($[Pd(PPh_3)_4]$, K_2CO_3, toluene) in 81 % yield.[8] The absorption spectrum of **4** is almost identical to the sum of those of **1** and the monomer of 5,15-diaryl free-base porphyrin, thus indicating negligible electronic interaction in the ground state. The steady-state fluorescence spectrum of **4** arises only from the 5,15-diaryl free-base porphyrin, thus indicating the nearly quantitative EET from the *meso–meso*-linked Zn^{II}-diporphyrin subunit to the free-base porphyrin subunit. The addition of **7DA** to a toluene solution of **4** caused distinct spectral changes in the absorption spectra, which are essentially the same as those observed for **1**, thus suggesting a similar decrease in the dihedral angle of the *meso–meso*-linked diporphyrin. Interestingly, the fluorescence spectrum of **4** exhibits a clear change of the emitting chromophore, from the 5,15-diaryl free-base porphyrin in free **4** to the *meso*–meso-linked Zn^{II}-diporphyrin in **7DA–4** complex (Figure 3a). These results indicate that the intramolecular EET direction can be switched upon the addition of **7DA**. Furthermore, the addition of acetic acid to complex **7DA–4** recovers the original absorption and fluorescence spectra of the free **4** (Figure 3b), hence restoring the intramolecular EET from the Zn^{II} diporphyrin to the free base porphyrin, probably through liberation of **7DA** from the Zn^{II}-diporphyrin moiety.[9]

The intramolecular EET processes have been examined by picosecond time-resolved transient absorption spectroscopy. Figure 4a shows the transient absorption spectra of free **4** taken by excitation at 580 nm, mainly pumping the *meso–meso*-linked Zn^{II}-diporphyrin part of the molecule. The spectrum at 1 ps delay time indicates strong bleaching bands at 450 and 555 nm because of the formation of the singlet excited state of the Zn^{II} diporphyrin. These bleaching bands disappear rapidly with $\tau = 5.5$ ps (Supporting Information) followed by an increase of a new bleaching band at 500 nm arising from the formation of the singlet excited state of the free base porphyrin with $\tau = 5.0$ ps as can be seen in the spectrum at 50 ps delay time and the temporal profile at

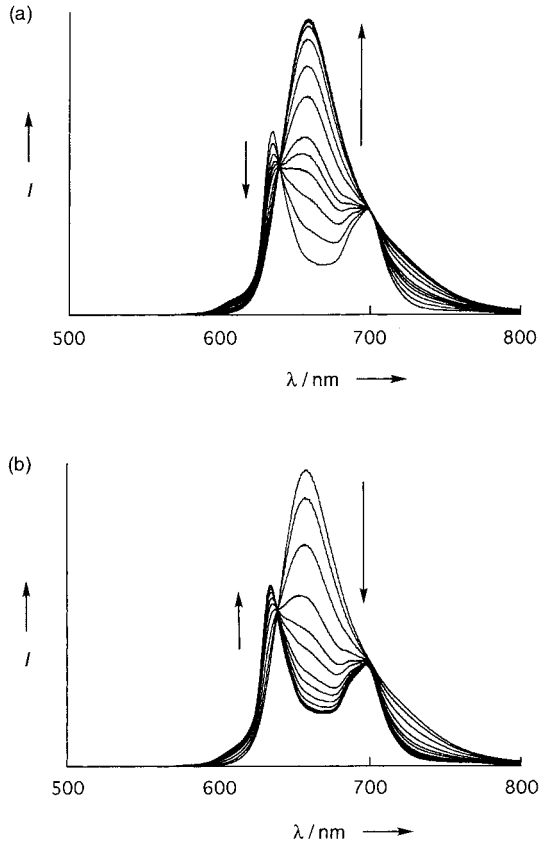


Figure 3. Fluorescence spectra of **4** (1.8×10^{-6} M) with **7DA** in toluene at 25 °C: $\lambda_{ex}=468$ nm, [**7DA**] = 0–1.7×10^{-5} M, (a). Fluorescence spectra of **4** (1.8×10^{-6} M) and **7DA** (6.7×10^{-6} M) plus acetic acid, [acetic acid] = 0–2.6×10^{-2} M, (b).

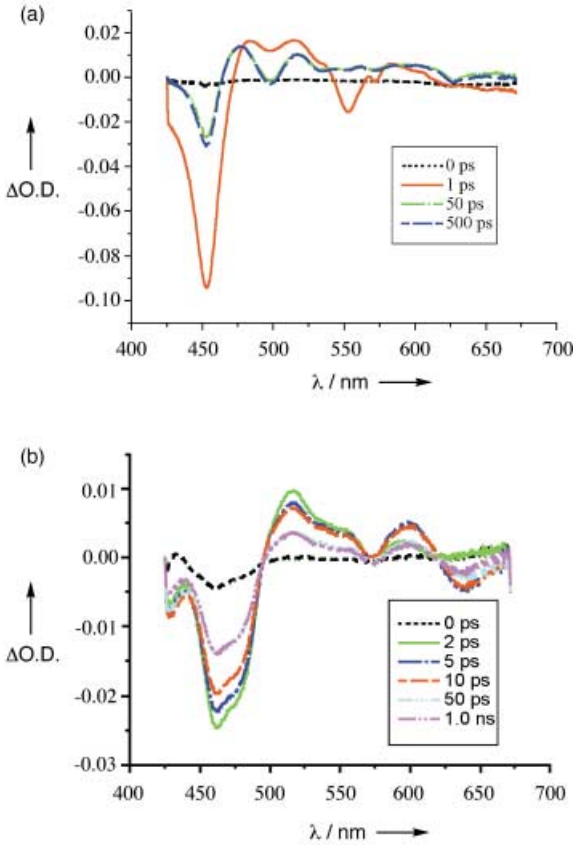


Figure 4. Transient absorption spectra of **4** in toluene by excitation at 580 nm (a) and of **7DA–4** complex by excitation at 400 nm (b). O.D. = optical density.

500 nm (Supporting Information). These results unambiguously indicate the efficient intramolecular EET from the Zn^{II}-diporphyrin to the free base porphyrin part with $k_{EET}=2\times10^{11}\ s^{-1}$. The resultant singlet excited state of the free-base porphyrin has a lifetime of about 9 ns, as determined by the fluorescence lifetime measurement, and thus is not quenched by the Zn^{II}-diporphyrin moiety. This result provides firm evidence for the occurrence of EET, not electron transfer. The reverse EET in **7DA–4** complex was more difficult to detect owing to larger absorbance of the Zn^{II}-diporphyrin in comparison with that of the free-base porphyrin unit, which did not allow a selective excitation of the latter. Figure 4b shows the transient absorption spectra of complex **7DA–4** taken by excitation at 400 nm that corresponds to the pumping of the Zn^{II} diporphyrin and the free base porphyrin roughly in a 1:1.5 ratio. At 462 nm, at which the bleaching arises from the superposition of the singlet excited states of the Zn^{II} diporphyrin complexed with **7DA** as well as from the free base porphyrin, the temporal profile has revealed a rapid recovery with $\tau\approx10$ ps, which is assignable to the EET from the free base porphyrin to the Zn^{II} diporphyrin.

As demonstrated above, the dihedral angle between the two porphyrins in the *meso–meso*-linked Zn^{II} diporphyrin can be modulated effectively upon the addition of **7DA** through the 1:1 coordination at both Zn^{II} centers. This mechanical torsion gives rise to a decrease in the S_1-state energy in the *meso–meso*-linked Zn^{II}-diporphyrin subunit, which, in turn, can be erased upon the addition of acetic acid in a reversible manner. This sequence, when applied to the triporphyrin model **4**, nearly completes the switch in the direction of the intramolecular EET. Further extension of this methodology is currently being investigated in our laboratories.

Experimental Section

Triporphyrin **4**: *meso*-Brominated *meso–meso* Zn^{II} diporphyrin **5** (10 mg, 0.006 mmol), porphyrin boronate **6** (30 mg, 0.051 mmol), K_2CO_3 (44 mg, 0.32 mmol), and $Pd(PPh_3)_4$ (1.2 mg, 0.001 mmol) were dissolved in dry toluene (7 mL). The solution was degassed by three freeze–pump–thaw cyles and then heated to 80 °C for 17 h under argon. The reaction mixture was cooled to room temperature, and the solvent was removed by evaporation. The desired porphyrin was separated by silica-gel column chromatography (eluent; CH_2Cl_2:hexane = 1:1) and was further purified by recrystallization from CH_2Cl_2 and MeOH to give **4** as a violet solid. Yield; 10 mg, 81 %. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=10.45$ (s, 2H, *meso*), 10.41 (s, 1H, *meso*), 9.62 (d, $J=5$ Hz, 2H, Por-β), 9.60 (d, $J=5$ Hz, 2H, Por-β), 9.53 (d, $J=5$ Hz, 2H, Por-β), 9.51 (d, $J=5$ Hz, 2H, Por-β), 9.48 (d, $J=5$ Hz, 2H, Por-β), 9.26 (d, $J=5$ Hz, 2H, Por-β), 9.21 (d, $J=5$ Hz, 2H, Por-β), 9.15 (d, $J=5$ Hz, 2H, Por-β), 8.80 (d, $J=5$ Hz, 2H, Por-β), 8.77 (d, $J=5$ Hz, 2H, Por-β), 8.78 and 8.73 (d-d, $J=8$ Hz, 4H, Phenylene), 8.35–8.32 (m, 2H, Ph), 8.22 (d, $J=5$ Hz, 2H, Por-β), 8.19 (d, $J=2$ Hz, 4H, Ar), 8.16 (d, $J=5$ Hz, 2H, Por-β), 8.14 (d, $J=2$ Hz, 4H, Ar), 7.86–7.84 (m, 3H, Ph), 7.76 (t, $J=2$ Hz, 2H, Ar), 7.73 (t, $J=2$ Hz, 2H,

Ar), 1.50 ppm (s, 36H, *t*Bu), 1.48 (s, 36H, *t*Bu); MALDI-TOF MS *m*/*z* 1955, calcd for $C_{128}H_{122}N_{12}Zn_2$ 1955; UV/Vis (toluene): $\lambda_{max}(\log\varepsilon) =$ 410(5.64), 458(5.49), 500(4.59), 541(4.65), 558(4.82), 601(4.05), and 633(3.52) nm; fluorescence (toluene): $\lambda_{max} = 634$ and 698 nm.

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[9] The observed fluorescence upon addition of acetic acid was the same as that of nonprotonated free-base porphyrin, thus excluding the formation of dicationic species in toluene solution. As about 1000-fold excess of acetic acid was needed to recover the fluorescence of the free base porphyrin in **7DA**–**4**, therefore the switching cycle only occurs once at the present stage.

