

Through-Bond Excited Energy Transfer Mediated by an Amidinium–Carboxylate Salt Bridge in Zn–Porphyrin Free-Base Porphyrin Dyads

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Abstract: Excited energy-transfer processes were investigated for a supramolecular Zn–porphyrin free-base porphyrin dyad, ZnPA-2·FbPC-2, in which β -octaalkylated *meso*-diarylporphyrins are connected through an amidinium–carboxylate salt bridge. The rate of energy transfer in the dyad ($1.3 \times 10^9 \text{ s}^{-1}$) is substantially slower than that in the previously reported dyad, ZnPA-1·FbPC-1 ($4.0 \times 10^9 \text{ s}^{-1}$), in which *meso*-tetraarylporphyrins are connected through the same amidinium–carboxylate salt bridge. The Förster-type mechanism can explain only minor parts of

these rates (3.3×10^8 and $5.1 \times 10^8 \text{ s}^{-1}$, respectively). Thus, Dexter-type through-bond energy transfer may be invoked. Indeed, bridge-mediated electronic processes would be favored in ZnPA-1·FbPC-1 over ZnPA-2·FbPC-2 on the basis of steric and electronic factors. Sterically, the phenyl groups in ZnPA-2 and FbPC-2 are more closely

perpendicular to the porphyrin planes than those in ZnPA-1 and FbPC-1. Electronically, the energy and symmetry of the occupied frontier orbitals should favor ZnPA-1·FbPC-1 over ZnPA-2·FbPC-2 in terms of electronic interactions through the bridge. Therefore, the observed trend (ZnPA-1·FbPC-1 > ZnPA-2·FbPC-2), consistent with these considerations, lends further support to the through-bond mechanism. Thus, the amidinium–carboxylate salt bridge is effective in mediating through-bond energy transfer even though the bond is noncovalent.

Keywords: energy transfer • porphyrinoids • salt bridges • supramolecular chemistry • through-bond interactions

Introduction

Inspired by natural photosynthetic systems, attempts have been made to mimic the antenna function by using artificial chromophores, porphyrins in particular. These works aim not only at a better understanding of the energy-transfer processes but also at creating light-harvesting devices.^[1–9]

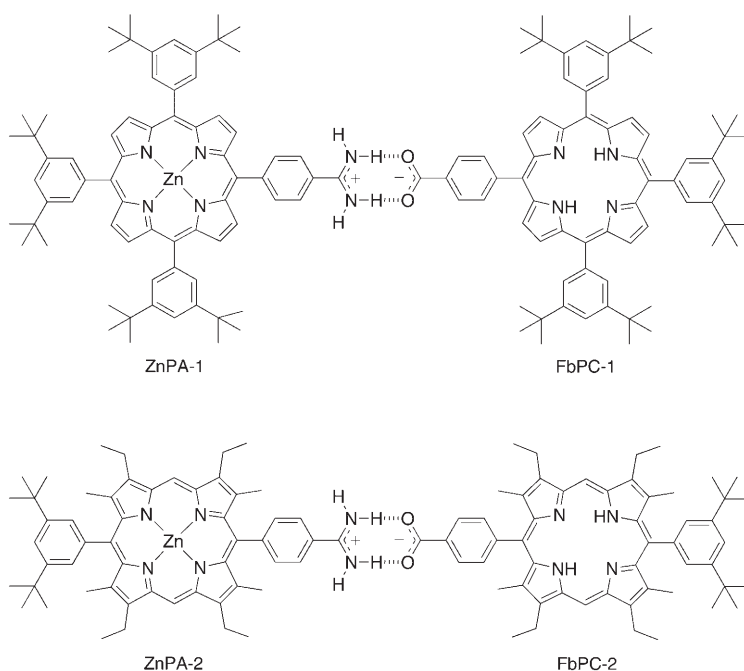
The supramolecular approach is a powerful methodology to construct complex yet well-defined multichromophore assemblies. In such assemblies, chromophores are joined together through noncovalent bonds, such as hydrogen bonds and coordination interactions. Therefore, it is important to know whether or not these noncovalent bonds can mediate excited energy migration from one chromophore to another within noncovalent assemblies. Energy transfer may take place by two mechanisms.^[10] One is the Förster mechanism which is due to Coulombic interactions of transition dipoles.^[11] This mechanism is also called the “through-space” mechanism because Coulomb interactions operate through space. The other is the Dexter mechanism, which is also called the exchange mechanism because it can be considered as an electron exchange process.^[12] It is called the “through-bond” mechanism as well, because the electron exchange process operates via the overlap of molecular orbitals, that is, through bonds.

We have previously reported the donor–acceptor dyad ZnPA-1·FbPC-1^[13] (Scheme 1; “ZnPA·FbPC” in the previous report), composed of a zinc-porphyrin and a free-base

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author and contains the Experimental Section and the coordinates of the optimized structures of the porphyrins.

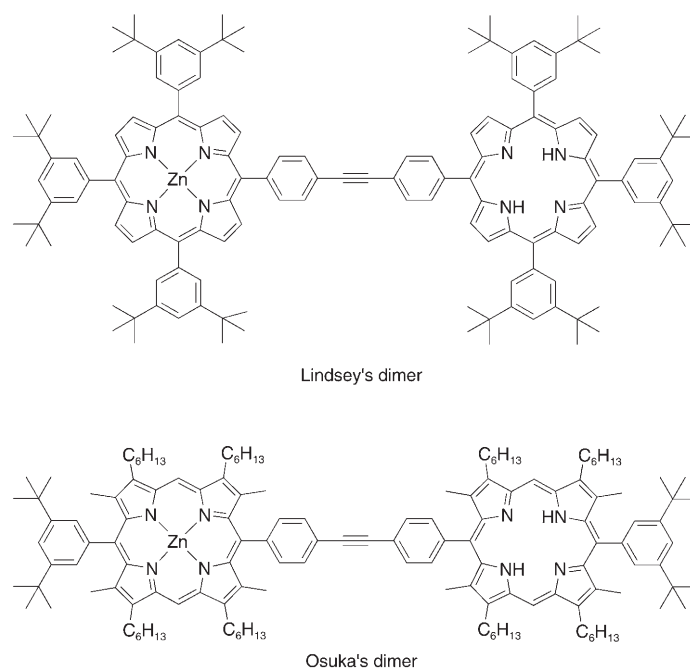


Scheme 1. The Zn-porphyrin free-base porphyrin dyads studied.

porphyrin connected through an amidinium-carboxylate salt bridge.^[13–23] The same intermolecular bond was also used for the construction of an antenna-type (donor)₄·(acceptor) complex. We found that the rates of excited energy-transfer processes in these supramolecules are much larger than expected from the Förster-type energy-transfer mechanism. In the dyad ZnPA-1-FbPC-1, the observed rate was $4.0 \times 10^9 \text{ s}^{-1}$, which is an order of magnitude larger than that calculated assuming the Förster mechanism ($5.1 \times 10^8 \text{ s}^{-1}$). We suggested a Dexter-type energy-transfer process as a possible explanation for the fast excited energy-transfer rate. This hypothesis has to invoke through-bond energy transfer through hydrogen bonds. Our literature survey indicated that energy-transfer rates were accounted for by the Förster mechanism for all noncovalent porphyrin assemblies reported so far.^[24–34] Although the through-bond mechanism through covalent bonds has been well documented, we did not find any example in which this mechanism was implied for noncovalent porphyrin assemblies, except our own case described above. Therefore, we decided to seek further support for the hypothesis that through-bond energy transfer can indeed be mediated by hydrogen bonds.

The rate of Dexter-type energy transfer is sensitive to the nature of frontier orbitals, as it is the electrons in these orbitals that are exchanged during the energy-transfer process. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of chromophores are the most critical orbitals, such that their overlap is important. Scheme 2 shows a pair of covalently connected Zn-porphyrin free-base porphyrin dyads with the same linker moiety. It was shown that the rates of energy transfer are quite different between these dyads due to the different

substituents on the porphyrin skeletons. The energy-transfer rate in Lindsey's dimer ($4.2 \times 10^{10} \text{ s}^{-1}$)^[34] is 17-fold larger than that in Osuka's dimer ($2.4 \times 10^9 \text{ s}^{-1}$).^[35] The difference was ascribed to different HOMOs for these porphyrins.^[36,37] Lindsey's dimer, which is of *meso*-tetraphenyl type, has an a_{2u} HOMO with a significant electron density on the *meso* carbon atoms, to one of which the linker is attached. On the other hand, the HOMO of Osuka's dimer is a_{1u} , which has nodes on the *meso* carbon atoms. Therefore, the conduit for an electron in the HOMO in the process of Dexter energy transfer is disconnected at the *meso* carbon atom in Osuka's dimer. Faster energy-transfer



Scheme 2. Two covalently connected Zn-porphyrin free-base porphyrin dyads with the same linker moiety.

processes for *meso*-tetraphenyl-type porphyrins than 5,15-diaryl- β -octaalkyl-type porphyrins were confirmed for related covalently linked porphyrin dyads as well.^[38,39] It is also likely that the mean angle made by the porphyrin plane and the *meso*-phenyl ring are different between these dyads. The β -methyl groups in Osuka's dyad would force its phenyl rings to orient in a more perpendicular manner to the por-

phyrin plane than those in Lindsey's dyad. This effect also favors Lindsey's dyad over Osuka's in terms of the energy-transfer process.

With this background, we set out to establish whether or not the Dexter-type energy transfer operates in the amidinium-carboxylate dyad, ZnPA-1·FbPC-1. We prepared a new dyad, ZnPA-2·FbPA-2, consisting of 5,15-diaryl- β -octaalkyl-type porphyrins, and investigated the energy-transfer process. Our working hypothesis was that if the Dexter-type energy transfer plays a major role in these dyads, then the observed rate for ZnPA-2·FbPA-2 would be significantly different from that observed for ZnPA-1·FbPC-1: 1) by a margin larger than what would be accounted for by the Förster-type energy-transfer process and 2) in a direction consistent with steric and electronic factors.

Results

Self-assembling behavior: From previous studies on systems containing both zinc-porphyrins and an amidine moiety, it has been established that the amidine axially coordinates to the zinc-porphyrin in noncoordinating solvents, such as toluene used in the present study.^[21] Therefore, molecules of ZnPA-2, which is a zinc-porphyrin with an amidine moiety, self-coordinate to form aggregates. This is apparent in toluene from its red-shifted Soret and Q-band peaks of the absorption spectrum (see below). This is not so much a complication, however, because FbPC-2 or any carboxylic acid, such as benzoic acid, once added binds to the amidine group much more strongly through amidinium-carboxylate salt bridge formation, thus disrupting the amidine-zinc-porphyrin association.

Figure 1 shows the ^1H NMR spectroscopic chemical shift changes of the aromatic protons in FbPC-2 on addition of ZnPA-2. Addition of ZnPA-2 affected the chemical shifts of the protons on the carboxyphenyl moiety but not of those on the di-*tert*-butylphenyl moiety, which is placed across the porphyrin core. This finding is consistent with the formation of an amidinium-carboxylate salt bridge. The chemical shifts changed until the added ZnPA-2 slightly exceeded one equivalent. The chemical shift changes are a combined effect of electronic changes associated with salt-bridge formation and the ring-current effect exerted by the ZnPA-2 molecule placed nearby. The slight scatter in the chemical shift values of the proton *ortho* to the carboxylic acid group (■) is due partly to some broadening of the resonance.

Absorption and fluorescence spectra: It was found that the absorption spectrum of ZnPA is concentration dependent. As its concentration became higher, the Soret band peak at 413 nm shifted to 426 nm and the Q-band peaks at 544 and 574 nm merged into a single broad band peaking at 552 nm. These spectral changes are accounted for by the self-association of ZnPA-2 molecules through coordination of the amidine group of one molecule to the zinc ion in another.^[20,21] Benzoic acid prevents this self-association of ZnPA-2 by

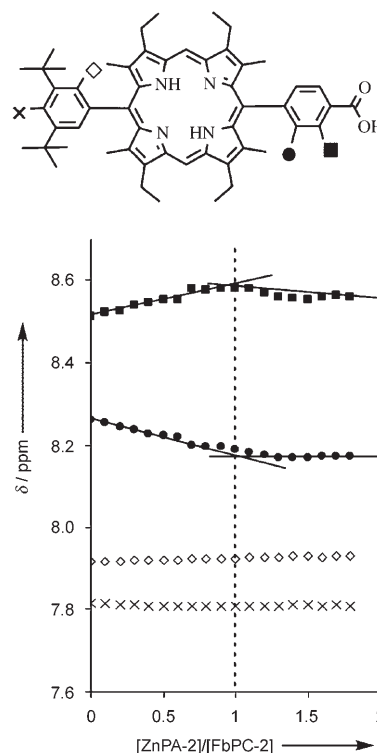


Figure 1. ^1H NMR spectroscopic chemical shifts of FbPC-2 (1 mM) with addition of ZnPA-2 in CDCl_3 .

forming the amidinium-carboxylate salt bridge with ZnPA-2. Thus, upon addition of benzoic acid to a solution of ZnPA-2, the spectrum reverted to the one for isolated ZnPA-2. Therefore, ZnPA-2-benzoic acid is more appropriate as a model of the ZnPA-2 moiety in the complex ZnPA-2·FbPC-2.

Figure 2a compares the absorption spectrum for the mixture of ZnPA-2 and FbPC-2 (—) and the sum of the spectra of individual species (×), that is, ZnPA-2·benzoic acid and FbPC-2. These two spectra almost completely coincide with each other. This observation for the mixture of ZnPA-2 and FbPC-2 indicates that 1) there is little ground-state electronic interaction between ZnPA-2 and FbPC-2, but 2) FbPC-2 does interact with ZnPA-2 in a way that prevents the self-association of ZnPA-2, that is, via the formation of the amidinium-carboxylate salt bridge.

Figure 2b compares the fluorescence spectra for ZnPA-2·benzoic acid (—×—), FbPC-2 (—○—), and the mixture of ZnPA-2 and FbPC-2 (—) with excitation at 555 nm, at which the free-base porphyrin exhibits a minimum absorption. There are several features that indicate energy transfer from ZnPA-2 to FbPC-2. The fluorescence intensity at 579 nm, at which only ZnPA-2 porphyrin emits fluorescence, is greatly decreased on mixing with FbPC-2. On the other hand, the intensity in the low-energy region is increased when compared to FbPC-2 alone. In particular, the increased fluorescence plateau around 700 nm indicates that the free-base fluorescence is increased in the presence of ZnPA-2. The excitation spectra, monitored at 697 nm,

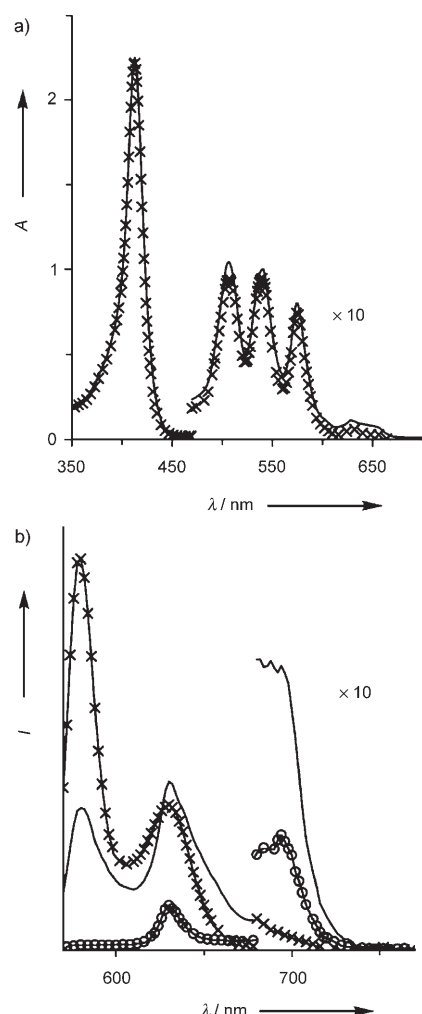


Figure 2. Comparison of spectra for a mixed solution of ZnPA-2 and FbPC-2 and those for the sum of individual species in toluene. a) Absorption spectrum for a mixture of ZnPA-2 and FbPC-2 ($4 \mu\text{M}$ each; —) and the sum of the spectra for ZnPA-2 ($4 \mu\text{M}$) in the presence of benzoic acid ($40 \mu\text{M}$) and that for FbPC-2 ($\times$). b) Fluorescence spectra ($\lambda_{\text{ex}}=555 \text{ nm}$) for a mixture of ZnPA-2 and FbPC-2 ($7 \mu\text{M}$ each; —), for ZnPA-2 ($7 \mu\text{M}$) in the presence of benzoic acid ($70 \mu\text{M}$; - $\times$ -), and for FbPC-2 ($7 \mu\text{M}$; - $\circ$ -).

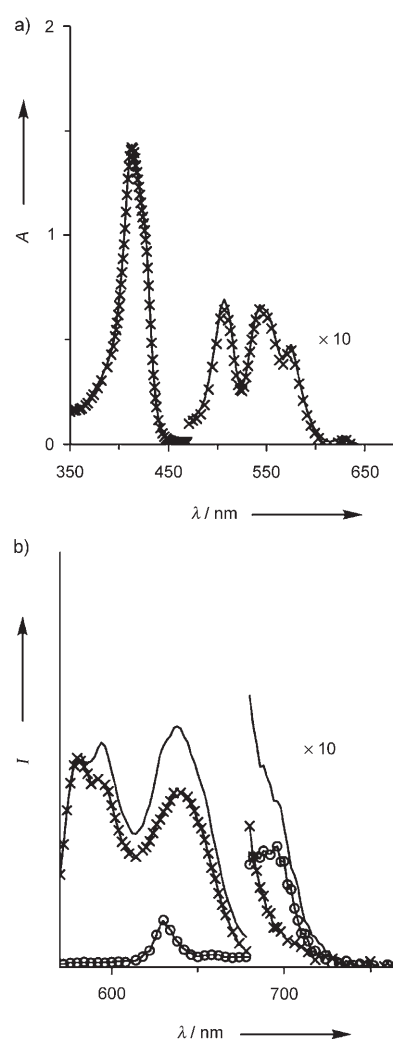


Figure 3. Comparison of spectra for a mixed solution of ZnPA-2 and FbPMe and those for the sum of individual species in toluene. a) Absorption spectrum for a mixture of ZnPA-2 and FbPMe ($4 \mu\text{M}$ each; —) and the sum of the individual spectra for ZnPA-2 and FbPMe ($4 \mu\text{M}$ each; $\times$). b) Fluorescence spectra ($\lambda_{\text{ex}}=555 \text{ nm}$) for a mixture of ZnPA-2 and FbPMe ($4 \mu\text{M}$ each; —), for ZnPA-2 ($4 \mu\text{M}$; - $\times$ -), and for FbPMe ($4 \mu\text{M}$; - $\circ$ -).

showed a sensitization by ZnPA-2 (data not shown). A least-squares curve fitting to the fluorescence intensity at 697 nm indicated that the association constant is around $9 \times 10^4 \text{ M}^{-1}$.

To provide evidence that the energy transfer occurs not through a diffusional encounter of the porphyrins but within a specific supramolecular complex, the methyl ester of FbPC-2, FbPMe, was employed in the same set of absorption and fluorescence experiments for comparison (see Figure 3). This compound cannot participate in the amidinium-carboxylate interaction. The observed absorption spectrum for the mixture of ZnPA-2 and FbPMe (—) nearly completely coincides with the calculated sum of the spectra of ZnPA-2 (without benzoic acid this time) and FbPMe ($\times$). The result indicates that the methyl ester, FbPMe, does not interrupt the self-association of ZnPA-2, which corroborates

the notion that the interaction of ZnPA-2 with FbPC-2 is through the amidinium-carboxylate salt bridge. The fluorescence of these sets of porphyrins was also investigated to see if there is any sign of energy-transfer processes. In this case, no quenching of ZnPA-2 fluorescence was observed even when FbPMe was present. Also, there was no sign of the sensitization of FbPMe by the presence of ZnPA-2. Compare the fluorescence intensities around 700 nm , a region where FbPMe emits more strongly than ZnPA-2; the observed fluorescence spectrum from the mixture of ZnPA-2 and FbPMe (—) coincides with the calculated sum of spectra of ZnPA-2 (- $\times$ -) and FbPMe (- $\circ$ -).

Time-resolved studies on excited energy transfer: Figure 4a shows the results of picosecond time-resolved fluorescence measurements. The decay of the fluorescence of ZnPA-2

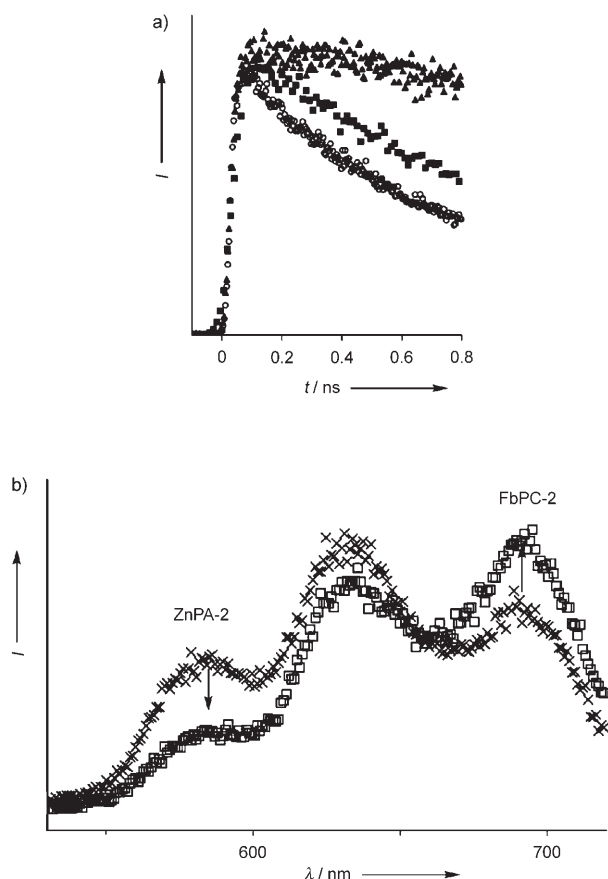


Figure 4. Time-resolved fluorescence measurements (toluene; each porphyrin 25 μM ; $\lambda_{\text{ex}}=410\text{ nm}$). a) Decays of ZnPA-2 fluorescence at 580–620 nm in the absence ($\blacksquare$) and presence ($\circ$) of FbPC-2. The time profile of FbPC-2 fluorescence monitored at 690–720 nm in the mixture is also shown ($\blacktriangle$). b) Time-resolved spectra for the mixture in time domains of 0–0.9 and 1.1–2.4 ns.

alone ($\blacksquare$) was fitted by a single exponential function, which gave a lifetime of $\tau_0=1.6\text{ ns}$. The lifetime was not altered by the addition of excess (100 μM) benzoic acid to ZnPA-2. On the other hand, the decay for an equimolar mixture of ZnPA-2 and FbPC-2 ($\circ$) was fitted by two exponential functions with lifetimes of 1.58 (45 %) and 0.53 ns (55 %). As the former value is identical with that of ZnPA-2 alone, it was attributed to noncomplexed ZnPA-2 in the mixture. Therefore, the latter value was ascribed to the complex, ZnPA-2·FbPC-2. From the association constant estimated from steady-state fluorescence titration ($9\times 10^4\text{ M}^{-1}$), the fraction of ZnPA-2 incorporated in the dyad under the present conditions is 52 %, which is in good agreement with the above results. We attributed the shortened lifetime to an energy-transfer process from the singlet excited state of ZnPA-2 to FbPC-2 within the complex on the basis of the observed sensitized fluorescence in the steady-state measurements.

Further support for the energy transfer comes from the delayed rise in the fluorescence intensity collected at 690–720 nm ($\blacktriangle$), in which the fluorescence of FbPC-2 dominates in the time-resolved measurements (Figure 4a). This is more

clearly seen in Figure 4b, which shows time-resolved spectra for the mixture in time domains of 0–0.9 and 1.1–2.4 ns. It is clearly seen that the fluorescence of ZnPA-2 in the shorter-wavelength region is replaced by that of FbPC-2 in the longer-wavelength region. No such time dependence of the spectral profile was observed when FbPC-2 was replaced by FbPCM, which is the methyl ester of FbPC-2, thus confirming that the amidinium–carboxylate salt bridge is indispensable for energy transfer. The rate of the energy-transfer process was calculated to be $1.26\times 10^9\text{ s}^{-1}$ according to the equation $k_{\text{obs}}=\tau^{-1}-\tau_0^{-1}$.

Rate of Förster-type energy transfer: The rate of Förster-type energy transfer, k_{F} (in s^{-1}), may be calculated by using Equation (1), in which κ^2 is an orientation factor, Φ and τ are the fluorescence quantum yield and lifetime (in s) of ZnPA-2, respectively, in the absence of FbPC-2,^[40] J_{F} is the spectral overlap term (in M^{-1}cm^3), n is the refractive index of the solvent, and r is the donor–acceptor center-to-center distance (in cm). In Equation (2), $F(\nu)$ is the fluorescence spectrum of the donor and $\varepsilon(\nu)$ is the absorption spectrum of the acceptor.

$$k_{\text{F}} = \frac{8.81 \times 10^{-25} \kappa^2 \Phi J_{\text{F}}}{n^4 \tau r^6} \quad (1)$$

$$J_{\text{F}} = \frac{\int F(\nu) \varepsilon(\nu) \nu^{-4} d\nu}{\int F(\nu) d\nu} \quad (2)$$

The value of $\kappa^2=1.01$ was used as the orientation factor,^[41] which is based on the assumption that the two porphyrin planes are in a coplanar conformation. This assumption would give the upper limit because there are some rotatable single bonds along the linkage between the *meso* carbon atoms connecting the two porphyrin macrocycles. The perpendicular porphyrins would give rise to $\kappa^2=0.81$, as the lower limit value. The center-to-center separation, $r=2.28\times 10^{-7}\text{ cm}$, was estimated from the crystal structures of a 5,15-diphenyloctaalkylporphyrin^[42] and an amidinium–carboxylate complex.^[43] The quantum yield, $\Phi=0.011$, was obtained by comparing the fluorescence intensities integrated over the entire reciprocal centimeter range with those of zinc-*meso*-tetraphenylporphyrin (quantum yield: 0.030^[34]). Other parameter values used in the calculation were $n=1.51$ (toluene) and experimentally obtained values of $J_{\text{F}}=3.94\times 10^{-14}\text{ M}^{-1}\text{cm}^3$ and $\tau=1.6\times 10^{-9}\text{ s}$. The rate of Förster-type energy transfer was obtained as $k_{\text{F}}=3.3\times 10^8\text{ s}^{-1}$ by using these parameter values. This accounts for about a fourth of the observed rate, $k_{\text{obs}}=1.26\times 10^9\text{ s}^{-1}$.

DFT calculations: It is known that the HOMO and HOMO–1 of the porphine π system are nearly degenerate.^[44] They respectively span the symmetry species A_{1u} and A_{2u} in the D_{4h} point group. This near degeneracy is lifted upon substitution on the core. When electron-donating substituents, such as alkyl groups, are introduced to the β positions, the a_{1u} orbital energy becomes higher, as this orbital has a larger density on the β -carbon atoms. As a conse-

quence, the a_{1u} orbital becomes the HOMO. On the other hand, the introduction of electron-donating substituents, say phenyl groups, to the *meso* positions raises the a_{2u} orbital energy, as this orbital has a larger density on the *meso* carbon atoms. In these circumstances, the a_{2u} orbital becomes the HOMO.

DFT geometry optimization and molecular orbital calculations (B3LYP/6-31g*) were performed on the porphyrins to obtain the energy and symmetry of frontier molecular orbitals on the porphyrin core. Calculations were separately carried out for a ZnPA-benzoic acid pair and a FbPC-benzamidine pair to represent the ZnPA and FbPC moieties, respectively, in the ZnPA-FbPC dyad. Table 1 shows the frontier orbitals obtained, while Figure 5 shows their orbital energies. For all porphyrins the LUMO and the LUMO+1 are nearly degenerate, as expected, within 0.002 eV. In contrast, the ordering of the HOMO and HOMO–1 and the energy gap between these orbitals depends on the substituent patterns on the porphyrin core more sensitively than the unoccupied orbitals. For ZnPA-1 and FbPC-1, the HOMOs are of an a_{2u} -like symmetry, the energies of which are higher than those of the HOMO–1 (a_{1u}) by 0.006 and 0.011 eV, respectively. On the other hand, for ZnPA-2, the energy of the a_{1u} orbital is raised relative to that of the a_{2u} orbital. As a consequence, the ordering is reversed and the HOMO of ZnPA-2 is now the a_{1u} orbital. Likewise, the energy of the a_{1u} orbital is raised for FbPC-2 and the energy gap between the HOMO and HOMO–1 is appreciably narrowed to 0.002 eV, only a little short of the reversal of energy ordering.

Discussion

As reported previously, the observed energy-transfer rate in dyad ZnPA-1-FbPC-1 was $k_{\text{obs}} = 4.0 \times 10^9 \text{ s}^{-1}$ and the estimated Förster rate, $k_F = 5.1 \times 10^8 \text{ s}^{-1}$, could only account for a minor part of the energy-transfer rate.^[13] We suggested a

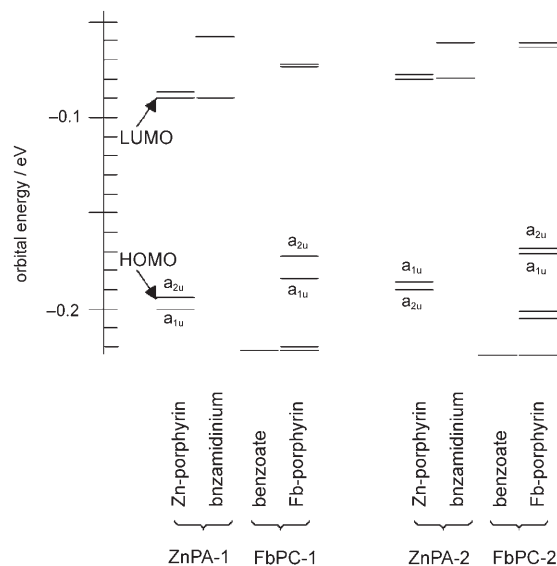


Figure 5. Orbital energies, indicated by horizontal bars. Orbital localization (i.e., on the porphyrin core or on the bridge) is also indicated by the horizontal positions.

Table 1. Frontier molecular orbitals.^[a]

	ZnPA-1-benzoic acid	Benzamidine-FbPC-1	ZnPA-2-benzoic acid	Benzamidine-FbPC-2
LUMO+1				
LUMO				
HOMO				
HOMO–1				

[a] *t*Bu groups are omitted in the calculations.

Dexter-type energy transfer to account for the remaining major part of the energy-transfer process ($k_{\text{obs}} - k_{\text{F}} = 3.5 \times 10^9 \text{ s}^{-1}$). However, there was no precedent in which a Dexter-type through-bond energy transfer was implicated for supramolecular porphyrins connected through noncovalent interactions.^[24–34] To strengthen our point, we prepared a new dyad, ZnPA-2-FbPC-2, and measured the energy-transfer rate in the present study. This dyad was designed to have similar spectroscopic properties to the previous one to minimize the effect on Förster-type energy-transfer processes. On the other hand, the substitution pattern on the porphyrin core was largely changed to have a significant impact on the energetics of frontier orbitals, which would then have a large effect on Dexter-type energy-transfer processes, if they were involved. Thus, if the observed rate for the new dyad is significantly different from that observed for ZnPA-1-FbPC-1 in the right direction, it becomes more certain that a Dexter-type energy-transfer process is indeed in operation.

The observed rate of energy transfer for dyad ZnPA-2-FbPC-2 was $k_{\text{obs}} = 1.26 \times 10^9 \text{ s}^{-1}$, which was only about a third of the rate for dyad ZnPA-1-FbPC-1. The Förster-type energy-transfer rate for dyad ZnPA-2-FbPC-2 was estimated to be $k_{\text{F}} = 3.3 \times 10^8 \text{ s}^{-1}$. This value can only account for a fourth of the observed rate of energy transfer. The remaining major part of the rate ($k_{\text{obs}} - k_{\text{F}} = 9.3 \times 10^8 \text{ s}^{-1}$) for ZnPA-2-FbPC-2 is only about a fourth of the corresponding rate for ZnPA-1-FbPC-1 ($3.5 \times 10^9 \text{ s}^{-1}$). The appreciable difference in these rates between the dyads is in favor of the involvement of Dexter-type energy-transfer processes, if the difference is in the right direction. We discuss in the following whether or not the difference in the rates is consistent with the difference in the molecular structures when a Dexter-type energy-transfer process is assumed.

The Dexter-type energy-transfer rate k_{D} is given by Equation (3):

$$k_{\text{D}} = \frac{2\pi}{\hbar} V^2 J_{\text{D}} \quad (3)$$

in which $\hbar$ is Planck's constant, V is the electronic coupling matrix element, and J_{D} is the overlap integral. The electronic coupling matrix element represents the magnitude of electronic interaction, while the overlap integral corresponds to the Franck–Condon weighted density of states. The overlap integral can be determined by using the following expression [Eq. (4)]:^[12]

$$J_{\text{D}} = \frac{\int F(\nu)\varepsilon(\nu)\text{d}\nu}{\int F(\nu)\text{d}\nu \int \varepsilon(\nu)\text{d}\nu} \quad (4)$$

in which $F(\nu)$ is the fluorescence spectrum of the donor and $\varepsilon(\nu)$ is the absorption spectrum of the acceptor. For the absorption spectrum in this case, the Q band of the free-base porphyrins may be used, as the relevant transition is the $S_0 \rightarrow S_1$ transition. The values of the overlap integrals were obtained as $J_{\text{D}} = 7.1 \times 10^{-5}$ and $1.1 \times 10^{-4} \text{ cm}$ for ZnPA-

1-FbPC-1 and ZnPA-2-FbPC-2, respectively, from relevant spectroscopic data.

If we assume that the energy-transfer rates which are unaccounted for by the Förster-type mechanism are due to Dexter-type processes, that is, $k_{\text{D}} = 3.5 \times 10^9$ and $9.3 \times 10^8 \text{ s}^{-1}$ in ZnPA-1-FbPC-1 and ZnPA-2-FbPC-2, respectively, the electronic coupling matrix element for ZnPA-1-FbPC-1 and ZnPA-2-FbPC-2 would have to be $V^2 = 41$ and 7.2 cm^{-1} , respectively. Thus, the value of V^2 for ZnPA-2-FbPC-2 is only about a sixth of that for ZnPA-1-FbPC-1. Now the problem of whether or not the electronic interaction represented by V^2 in ZnPA-2-FbPC-2 is smaller than that in ZnPA-1-FbPC-1 is reasonably explained by the difference in the molecular structures.

There are steric and electronic factors to be considered. With regard to steric factors, we examined the rotation of the *meso*-phenyl rings. In the case of ZnPA-1-FbPC-1, the angle made by the porphyrin plane and the *meso*-phenyl ring was 65° in the optimized structure.^[45] However, the *meso*-phenyl group may nearly freely rotate with respect to the porphyrin plane in solution.^[46,47] For ZnPA-2-FbPC-2, the angle of the phenyl ring with respect to the porphyrin plane is more restricted to approximately 90° because the phenyl group is flanked by the β -methyl groups, although the rotation may not be completely hindered.^[47,48] It is evident that these steric factors favor ZnPA-1-FbPC-1 over ZnPA-2-FbPC-2 in a through-bond interaction. Thus, the Dexter mechanism is consistent with the steric considerations.

As for the electronic factors, we consider the energetics and symmetry of the frontier orbitals, as it is the electrons in these orbitals that are exchanged during the Dexter process. The DFT calculations (Figure 5 and Table 1) show that the LUMO and LUMO+1 of every porphyrin are nearly degenerate, with their energy difference within 0.002 eV. Thus, the symmetry difference in these two orbitals is insignificant in determining electronic interactions between ZnPA and FbPC. On the other hand, for occupied frontier orbitals, the ordering of the HOMO and HOMO–1 and the energy gap between these orbitals would be important in determining the electronic coupling through the bridge. The lowest singlet excited state of porphyrins is a mixture of HOMO $\rightarrow$ (LUMO, LUMO+1) and HOMO–1 $\rightarrow$ (LUMO, LUMO+1) transitions due to configuration interactions, the contribution of the former transition being larger. However, the relative contribution of the latter increases as the energy gap between the HOMO and HOMO–1 is narrowed.^[37] As a guiding principle, a stronger electronic interaction is expected when the HOMO is a_{2u} because the a_{2u} orbital is heavily populated at the *meso* carbon atoms, one of which is just on the bridge connecting the porphyrins, whereas a weaker interaction is expected when the HOMO is a_{1u} because the a_{1u} orbital has virtually no electron density at the *meso* carbon atoms. It should be noted, however, that the symmetry of HOMO–1 plays an increasingly larger role as the energy gap between the HOMO and HOMO–1 becomes smaller.

For ZnPA-1 and FbPC-1, the HOMOs are a_{2u} -like while the HOMO-1s are a_{1u} , the energy gaps between them being substantial (0.006 and 0.011 eV, respectively). Accordingly, the orbital ordering is favorable for a strong electronic interaction. For ZnPA-2, the orbital ordering is reversed; the HOMO is a_{1u} whereas the HOMO-1 is a_{2u} , the energy gap being 0.005 eV, which is unfavorable for an electronic interaction through a bridge via the *meso* position. For FbPC-2, the HOMO is a_{2u} -like whereas the HOMO-1 is a_{1u} . This situation is favorable for an electronic interaction. However, the energy gap between these two orbitals is only 0.002 eV. Therefore, in the lowest excited state, there should be a substantial component of HOMO-1 $\rightarrow$ (LUMO, LUMO+1) being mixed into the transition HOMO $\rightarrow$ (LUMO, LUMO+1). This mixing works unfavorably for the electronic interaction through the *meso* carbon atoms. Taken together, the DFT calculations indicate that the frontier orbitals in ZnPA-1·FbPC-1 are more favorable than those in ZnPA-2·FbPC-2 for electronic interactions through the *meso* carbon atoms. Thus, the through-bond mechanism is also consistent with the electronic considerations. In conclusion, steric as well as electronic features of the dyads ZnPA-1·FbPC-1 and ZnPA-2·FbPC-2 are consistent with the experimentally observed trend of energy-transfer rates (ZnPA-1·FbPC-1 > ZnPA-2·FbPC-2) when the Dexter mechanism is assumed.

As the Zn- and free-base porphyrins are spatially separated in the dyad, direct electronic interactions between these two chromophores is unlikely. Instead, a bridge-mediated superexchange mechanism may be invoked.^[49–51] In the superexchange mechanism for the present system, the electronic coupling matrix element may be represented as [Eq. (5)]:

$$V = \frac{V_{\text{ZnP-A}} V_{\text{A-C}} V_{\text{C-FbP}}}{\Delta E_{\text{DB}}^2} \quad (5)$$

in which V is the electronic coupling matrix element between the chromophores designated in the subscripts (A and C represent benzamidinium and benzoate moieties, respectively) and ΔE_{DB} is the gap between the excited energies of the donor and the bridge. Thus, a larger electronic coupling between consecutive components and a smaller energy gap are more favorable for a superexchange-based energy-transfer process.

The role of the energy gap was nicely demonstrated by Albinsson and co-workers who examined singlet excited energy-transfer rates in covalent Zn-porphyrin/bridge/free-base porphyrin triads, in which the bridge is varied among bicyclo[2.2.2]octane, benzene, naphthalene, and anthracene.^[52] They found a linear relation between $k_{\text{D}}^{1/2}$ and $\Delta E_{\text{DB}}^{-1}$ for the series. In our case, ΔE_{DB} could be estimated as approximately 14000 cm⁻¹ from the absorption edges for ZnPA-2-benzoic acid (590 nm) and for benzamidinium/benzoate (320 nm). However, as the HOMO/LUMO energies are significantly offset between the benzamidinium and benzoate moieties (see Figure 5), charge-transfer-type (ben-

zoate $\rightarrow$ benzamidinium) low-energy excited states might be involved to decrease the effective ΔE_{DB} value, although corresponding optical transitions were not detected by absorption measurements. It is also noted that the benzamidinium moiety contributes significantly to low-lying virtual orbitals in ZnPA-1 and ZnPA-2 (Figure 5). Indeed, the LUMOs are delocalized on both the porphyrin core and the benzamidinium moiety. In addition, the LUMO+2 is a $\pi\pi^*$ orbital localized on the benzamidinium moiety. For the free-base porphyrins, on the other hand, the HOMO-3 (FbPC-1) and HOMO-4 (FbPC-2) are delocalized orbitals over the porphyrin core and the benzoate moiety. The delocalization may contribute to the coupling terms $V_{\text{ZnP-A}}$ and $V_{\text{C-FbP}}$. Of course, as the overall rate is likewise dependent on the coupling through the term $V_{\text{A-C}}$, the observation that the through-bond energy transfer occurs at a significant rate suggests that the through-hydrogen-bond electronic coupling represented by the term $V_{\text{A-C}}$ is also significant.

Conclusion

The observed energy-transfer rates in dyads ZnPA-1·FbPC-1 and ZnPA-2·FbPC-2 were 4.0×10^9 and 1.3×10^9 s⁻¹, respectively. The results corroborate the notion that the exchange mechanism does operate in the energy-transfer processes for the following reasons. First, these values are substantially larger than those calculated assuming the Förster mechanism (5.1×10^8 and 3.3×10^8 s⁻¹, respectively). Second, the larger energy-transfer rate in ZnPA-1·FbPC-1 than in ZnPA-2·FbPC-2 is consistent with the through-bond mechanism, as the former dyad is more favorable for the through-bond mechanism in terms of symmetries and energies of frontier molecular orbitals as well as less encumbrance around the phenyl groups along the linkage. These factors would not exert any influence on the Förster energy transfer except for a slight variation in the orientation factor. Thus, this work has made it more certain that the exchange energy transfer does operate in these dyads connected by hydrogen bonds, or more specifically, the amidinium-carboxylate salt bridge. This conclusion means that hydrogen bonds can provide an effective pathway for energy-transfer processes via a through-bond mechanism. It has become clear that the choice of noncovalent intermolecular linkage is important not only in terms of structural aspects, but also in terms of an electronic aspect for the design of supramolecular systems in which efficient energy transfer is desired.

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