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Mediated Energy Transfer in Covalently Linked Porphyrin Dimers

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Donor−acceptor systems where the rate of radiationless electronic energy transfer is influenced by the electronic structure of the intervening medium are studied. In this paper we report the observation of mediated energy transfer in a series of geometrically well-defined porphyrin dimers. The dimers consist of a free base porphyrin (5,15-diphenyl-α,β-octaalkylporphyrin, H_2P) and the corresponding zinc porphyrin (ZnP) as acceptor and donor, respectively, connected by aryl chromophores with varying energies of the lowest excited states.

Introduction

Long-range electronic energy transfer, EET, is a very important photophysical process.[3] It is usually understood in terms of models: the Förster[4] and Dexter[5] models for very weak coupling between the acceptor and donor or the exciton coupling model for the so-called weak coupling case.[6] In the very weak coupling limit, the excitation is localized on either the acceptor or the donor and the energy transfer is incoherent (hopping). In the weak coupling model, the excitation is delocalized and the energy transfer is coherent.[7] It is expected to find systems which are not well described by either of these models but are intermediate in their coupling strength. In these intermediate cases, the donor and acceptor are well-separated chromophores that experience enhanced coupling through virtual states of the intervening medium.[8] The mediation of EET has recently been treated theoretically[9] on the basis of the so called through bond or superexchange mechanism[10] suggested for intramolecular electron transfer. There are several reports in the literature of long-range intramolecular EET[11] and electron transfer[12] mediated through rigid σ-bond spacers, but the influence of low-lying electronic excited states of the spacer groups has not yet been systematically investigated.[13] We believe that this is important for the understanding of the natural photosynthetic light-harvesting systems[14] and for the future construction of artificial photosynthetic complexes[15] and molecular photonic devices.[16]

Results and Discussion

The present porphyrin dimers are designed to answer specific questions about if and how the electronic structure of the bridge plays a role in the EET process. Therefore, other parameters that influence the rate of EET have been held constant in the series of donor−acceptor systems. The general structure of our porphyrin dimers is shown in Figure 1, where ZnP is the donor, H_2P the acceptor, and X is the central aromatic unit in the bridging chromophore, XB. A number of designing principles have been used in the construction of these dimers. (i) The distance between the donor and acceptor should be constant throughout the series. The distance between the donor and acceptor centers is estimated from MM+ optimized structures to be 25.3 Å.[17] (ii) Simple conjugation between the donor and the bridge as well as between the bridge and the acceptor should be suppressed. This is done by methyl substitution on the porphyrin rings at the β-position adjacent to the phenyl rings (Figure 1). The steric effect of the methyl group causes the porphyrin and phenyl planes to be nearly orthogonal, which is important in order to preserve the identity of the donor, acceptor, and bridge chromophores. The dihedral angle between the porphyrin plane and the adjacent phenyl was estimated to be 90 ± 25° from AM1 optimized structures of the phenyl-substituted porphyrins.[18] (iii) The relative orientation of the two porphyrin planes should be well defined. An almost uniform angular distribution is obtained by the use of acetylene connectors in the bridging chromophore. This simplifies the theoretical treatment in general and the comparison with the Förster model in particular. In addition, this flexibility, together with the presence of *tert*-butyl groups, increases the solubility.

The donor−acceptor systems were assembled by a palladium-catalyzed cross-coupling reaction[19] in a building block approach. The donor and acceptor were introduced at different points in the synthesis to secure the precise state of metalation in the systems. Solutions ($\sim 3 \times 10^{-6}$ M in CH_2Cl_2) of the dimers ZnP−BB−H_2P, ZnP−NB−H_2P, or ZnP−AB−H_2P (Figure 1) were prepared along with 1:1 mixtures of their reference compounds ZnP−BB/H_2P, ZnP−NB/H_2P, and ZnP−AB/H_2P. The absorption spectra of ZnP−BB−H_2P and ZnP−NB−H_2P could approximately be described as a 1:1:1 spectral mixture of their components ZnP/BB/H_2P and ZnP/NB/H_2P, respectively, or equally well as a 1:1 spectral mixture of their reference compounds ZnP−BB/H_2P and ZnP−NB/H_2P. Likewise, the absorption spectrum of ZnP−AB−H_2P is the spectral sum of its components or reference compounds in the Q-band region ($\lambda > 500$ nm), but significant deviations are observed in the Soret bands ($\lambda \approx 400$ nm) of the porphyrins. This is expected since in ZnP−AB−H_2P the Soret bands of the porphyrins overlap with the lowest absorption band of the bridging chromophore, AB, making the situation for electronic coupling perfect.

Figure 2 shows fluorescence emission spectra of the dimers ZnP−BB−H_2P, ZnP−NB−H_2P, and ZnP−AB−H_2P compared to the emission from a 1:1 mixture of ZnP−BB and H_2P. The optical density at the excitation wavelength of all samples were matched in order to facilitate immediate comparison. The donor, ZnP, dominates the emission between 550 and 600 nm while the acceptor, H_2P, dominates the emission above 680 nm. It is clearly seen in Figure 2 that the donor emission decreases and the acceptor emission increases in the covalently connected porphyrin dimers when compared to the 1:1 mixture of ZnP−

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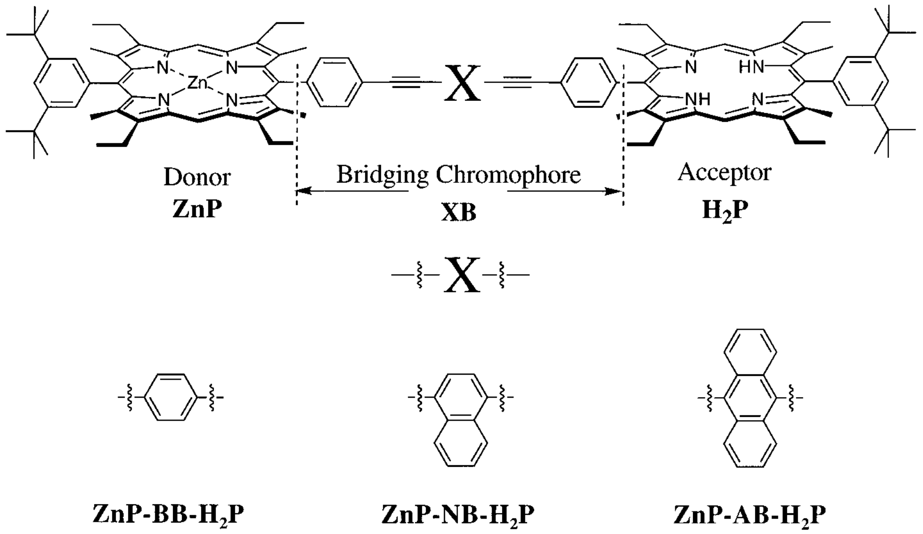

Figure 1. Structure of the studied donor−acceptor systems. The systems are denoted ZnP−XB−H_2P, and the corresponding reference compounds are denoted ZnP−XB. XB is the bridging chromophore, where X is the central aromatic unit, which is either benzene, B, naphthalene, N, or anthracene, A.

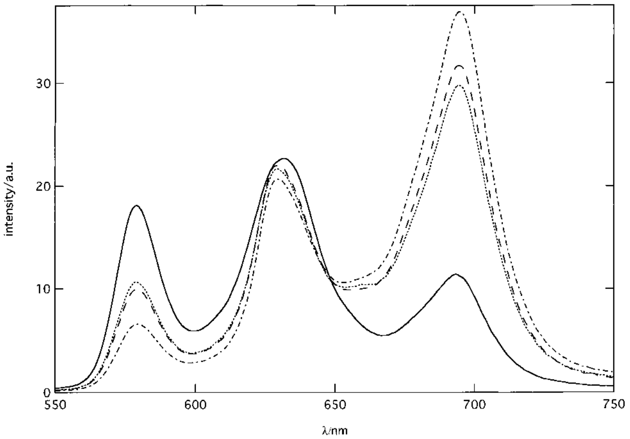

Figure 2. Steady state fluorescence emission spectra of the bridged porphyrin dimers (ZnP−BB−H_2P ···, ZnP−NB−H_2P - - -, ZnP−AB−H_2P −•−) compared to a 1:1 mixture of ZnP−BB and H_2P (−). Measurements were performed at 20 °C in CH_2Cl_2 solution, and the optical densities of all samples were matched at the excitation wavelength, 538 nm.

BB and H_2P. This is consistent with intramolecular EET as the source for donor emission quenching. It should be noted that the donor emission is more efficiently quenched in ZnP−AB−H_2P than in either of the other two dimers indicating a more efficient energy transfer process in the former one.

The lifetime[20] of the donor fluorescence was also measured for the dimers and the reference compounds. The EET efficiencies, *E*, were calculated from the steady state and lifetime measurements as $E = 1 - I/I_0 = 1 - \tau/\tau_0$, where I and I_0 are the donor emission intensities of the dimers and the 1:1 mixtures of the reference compounds, respectively, and τ and τ_0 are the corresponding fluorescence lifetimes. The EET rate constants are calculated as $k_{EET} = E/\tau_0(1 - E)$. These results are compiled in Table 1. Both steady state emission spectra and the kinetic measurements clearly show that the rate of EET is about two times higher in the dimer with the anthracene bridging chromophore, ZnP−AB−H_2P, compared to the dimers with the naphthalene or benzene bridging chromophores.

As a comparison the EET rate constant was estimated from the Förster theory[4]

$$k_{EET}^{\text{Förster}} = 8.79 \times 10^{-25} \frac{k_D \kappa^2 J}{n^4 R^6} \text{ s}^{-1}$$

TABLE 1: Observed Donor Fluorescence Lifetimes (τ), Intensities (I), Calculated EET Efficiencies (E), and Rate Constants (k_{EET})

compound	τ^a/ns	$I_{rel}{}^b$/au	E^c	$k_{EET}{}^c$/ns^{-1}
ZnP−BB	1.30	18.2		
ZnP−BB−H_2P	0.76	10.7	0.41	0.54
ZnP−NB	1.30	17.3		
ZnP−NB−H_2P	0.74	9.9	0.43	0.58
ZnP−AB	1.21	15.7		
ZnP−AB−H_2P	0.57	6.6	0.55	1.0

[a] ZnP fluorescence lifetimes. The samples were excited at 530 nm, and emission was collected through a 540 nm cutoff filter. The observed demodulations and phase shifts were fitted to a biexponential model for the dimers were one component was essentially constant and corresponded to the free base emission decay (9.1 ns), and the other was interpreted as the ZnP fluorescence decay. All the reference compounds had single-exponential decays. The goodness-of-fit was evaluated by comparing the fit of the model to the measured data points. [b] Relative fluorescence intensity observed at 579 nm with excitation at 538 nm. [c] Average values calculated from the decrease in donor fluorescence lifetime and intensity.

where for all three dimers $J = 3.1 \times 10^{-14}$ M^{-1} cm^{-3} is the spectral overlap integral, $R = 25.3 \times 10^{-8}$ cm (25.3 Å) is the donor−acceptor distance,[17] $n = 1.42$ is the solvent refractive index,[21] $\kappa^2 = {}^5/_6$ is the average orientation factor,[22] and $k_D = \phi_D/\tau_D = 2.3 \times 10^7$ s^{-1} is the radiative rate constant for the donor fluorescence. The EET rate constant is, within the Förster approximation, the same for all three dimers, $k_{EET}^{\text{Förster}} = 4.9 \times 10^8$ s^{-1}. This value agrees with the observed rate constants for the dimers with benzene or naphthalene bridging chromophores but not for the dimer with the anthracene bridging chromophore. This indicates that the EET is of "normal" Förster type in the former two and that the coupling is enhanced in the latter.

The lowest singlet excitation energies of the benzene, naphthalene, and anthracene bridging chromophores are 31 000, 27 500, and 21 600 cm^{-1}, respectively. These should be compared to the lowest singlet excitation energies for ZnP (17 500 cm^{-1}) and H_2P (16 000 cm^{-1}). The energy splitting between the donor and bridge chromophores and between the bridge and acceptor chromophores is expected to be an important parameter in modeling the mediated EET.[9] Here it suffices to stress that the splitting is large enough to prevent stepwise transfer ZnP → XB → H_2P at room temperature, which would be a trivial cause for the enhanced EET. Furthermore, it should be noted that the triplet−triplet energy transfer could be substantial from the ZnP donor to the anthracene bridging chromophore but not to the benzene or naphthalene bridging chromophores because the triplet state of anthracene (14 700 cm^{-1})[23] is close in energy to the lowest triplet state of ZnP (14 000 cm^{-1}). However, this is not expected to contribute to the observed singlet−singlet EET, since no delayed fluorescence from ZnP has been observed and we have not observed any difference in the EET efficiencies between air-saturated and argon-bubbled solutions.

In this paper long-range EET has unequivocally been shown to increase due to mediation through a chromophore that does not take part as an intermediate excitation site. This effect is presumably related to the energy gap between the lowest excited state energies of the donor/acceptor and the bridging chromophore. As such it might be possible to selectively tune the rate of energy transfer and possibly to build “molecular switches” based on rapid changes in mediation potential of the bridging medium.

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(18) AM1 model Hamiltonian as implemented in the program package MOPAC 6.0. The angular deviation at room temperature was estimated from the Boltzmann distribution by varying the dihedral angle between the porphyrin and phenyl planes, optimizing the structure, and calculating the potential energy at these fixed dihedral angles.

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