9844 *J. Am. Chem. Soc.* **2000,** *122,* 9844−9845

Triplet Energy Transfer in Porphyrin Dimers: Comparison between π- and σ-Chromophore Bridged Systems

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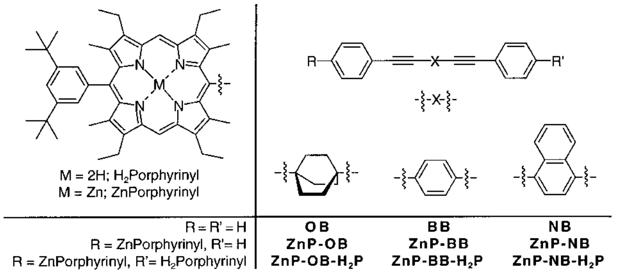
Received April 24, 2000
Revised Manuscript Received August 4, 2000

We report that triplet energy transfer occurs with unexpectedly high efficiency between zinc and free base porphyrin 19 Å apart (edge to edge) when held together by rigid π-conjugated chromophoric systems. In contrast, no triplet energy is transferred when the conjugation of the linking π-system is broken by σ-bonds although geometry and dimensions are kept the same.

Polychromophoric supermolecules have been suggested as molecular scale electronic and photonic devices. The operation of such devices will rely on the ability to control the flow of signals, i.e., flow of electrons or energy between molecular components within the supermolecule. The electronic interactions between molecular components that forms the basis for these transfer reactions have, therefore, experienced a rapidly growing interest in the past decades. In particular, the parameters and the factors of molecular bridges between components that govern such interactions. It was early shown that a bridge connecting two active components had far more intriguing functions than the passive role of controlling the relative orientation and distance between components.[1] The present work has focused on how the flow of triplet excitation energy, TET, depends on the electronic properties of the bridging molecule. This has further implications as photoinduced electron transfer and TET is governed by the same type of matrix elements.[2] General conclusions for TET[3] should therefore hold for electron transfer.

To investigate the influence of the intervening medium on the energy transfer processes we have designed and synthesized series of trichromophoric donor−bridge−acceptor (D−B−A) systems.[4,5] The systems are based on various porphyrin donors and acceptors linked with rigid hydrocarbon chromophores. The triplet and singlet energy transfer processes are conveniently studied in systems with free-base porphyrin (H_2P) as the acceptor and the corresponding zinc porphyrin (ZnP) as donor (Chart 1).[6] The rate of singlet energy transfer in these systems was found to have a significant dependence on the electronic structure of the connecting chromophore although the Förster (i.e. direct dipole−dipole coupling between the donor and acceptor) energy transfer was expected to be identical among the compounds.[5,7] In the study of singlet energy transfer, contributions from the Förster mechanism are unavoidable which might obscure the observation of mediation by the bridging chromophore. In contrast, triplet energy transfer should not occur in the studied systems unless there exists bridge mediation.



Fluorescence, measured in 2-methyltetrahydrofuran (MTHF) at 80 K, from the ZnP donor and H_2P acceptor is observed at wavenumbers between 17 500 and 14 250 cm^{-1} (Figure 1). The excitation light at 18400 cm^{-1} is predominantly absorbed by ZnP (88%, based on the room temperature molar absorption coefficients) and not absorbed by any of the bridging chromophores. At energies above 17 000 cm^{-1} the emission stems solely from ZnP and the large peak at 14 700 cm^{-1} is due to H_2P. When comparing the donor−acceptor systems with the reference compounds it is seen that the donor fluorescence is quenched while the acceptor shows sensitized fluorescence. This clearly indicates intramolecular singlet energy transfer, as previously reported.[5,7] At 80 K where the medium is rigid, phosphorescence from the ZnP chromophore is observed at wavenumbers below 14 250 cm^{-1} (Figure 1). No phosphorescence from H_2P was observed in accordance with earlier reports for similar free-base porphyrins.[8] The phosphorescence intensities of the D−B−A systems compared to the reference mixture are similar in magnitude for ZnP−OB−H_2P but are dramatically different for ZnP−BB−H_2P and ZnP−NB−H_2P. This shows that the lowest triplet state of ZnP is quantitatively quenched in the latter two D−B−A systems but not in the former.

Direct comparison between the phosphorescence intensities to estimate the triplet energy transfer quantum yields is problematic due to differences in singlet energy transfer rates. However, directly measuring the lifetime of the ZnP triplet gives the rate constant for triplet energy transfer from, $k_{\mathrm{TET}} = 1/\tau - 1/\tau_0$, where τ and τ_0 are the ZnP phosphorescence lifetimes of the D−B−A systems and the corresponding reference compounds (ZnP−XB), respectively. The phosphorescence decays[9] at 80 K for ZnP−OB−H_2P and ZnP−OB are shown in Figure 1 as an inset and lifetimes are collected in Table 1. The two single exponential decays are identical within the accuracy of the measurements. This shows that *no or very slow* ($k_{\mathrm{TET}} \leq 0.1$ s^{-1})[10] *triplet energy transfer occurs at 80 K in the ZnP−OB−*H_2P *system held together*

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(1) (a) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Flemming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652. (b) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Cotsaris, E.; Hush, N. S. *Chem. Phys. Lett.* **1988**, *143*, 488. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

(2) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(3) (a) Zimmerman, H. E.; MacKelvey *J. Am. Chem. Soc.* **1971**, *93*, 3638. (b) Gust, D.; Moore, T. A.; Moore, A. L.; Krasnovsky, A. A., Jr.; Liddell, P. A.; Nicodem, D.; DeGraciano, J. M.; Kerrigan, P.; Makings, L. R.; Pessiki, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 5684. (c) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516. (d) Asano-Someda, M.; Kaizu, Y. *Inorg. Chem.* **1999**, *38*, 2303. (e) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Ventura, B.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Inorg. Chem.* **1999**, *38*, 661. (f) Tan, Z.; Kote, R.; Samaniego, W. N.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem. A* **1999**, *103*, 7612. (g) Levanon, H.; Regev, A.; Das, P. K. *J. Phys. Chem.* **1987**, *91*, 14.

(4) Kajanus, J.; van Berlekom, S. B.; Albinsson, B.; Mårtensson, J. *Synthesis* **1999**, 1155.

(5) Kilså, K.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. B* **1999**, 103, 7329.

(6) The D−B−A molecules are designed to behave as tri-chromophoric systems. Therefore direct conjugation between donor and bridge, and bridge and acceptor is minimized by sterically forcing the porphyrin planes to be perpendicular to the adjacent phenyl planes of the bridging chromophore. Please see refs 5 and 7 for further details.

(7) Jensen, K. K.; van Berlekom, S. B.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. A* **1997**, *101*, 2218.

(8) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; pp 41−42.

(9) Phosphorescence decays were measured using a SPEX Fluorolog 3 equipped with a phosphorimeter (SPEX 1934D3) with time gated detection at 715 nm following pulsed xenon lamp excitation at 544 nm.

(10) This rate constant is estimated from the phosphorescence lifetimes (85 ms), with the maximum difference in decay times for ZnP−OB−H_2P and ZnP−OB estimated as no larger than 1 ms.

10.1021/ja001409r CCC: $19.00

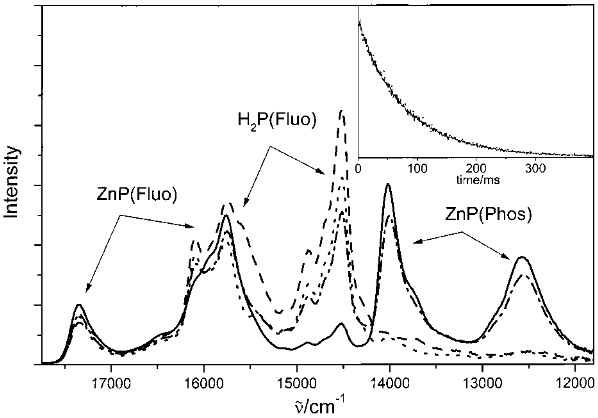

Figure 1. Steady-state emission spectra in MTHF at 80 K for ZnP−OB−H$_2$P (- • -), ZnP−BB−H$_2$P (•••), and ZnP−NB−H$_2$P (- - -) compared to a 1:1 mixture of ZnP−OB and H$_2$P (—). The optical densities were matched and below 0.1 to facilitate comparison and to avoid inner-filter effects, respectively. Inset: Phosphorescence decays for ZnP−OB−H$_2$P (•••) and ZnP−OB (—); excitation at 18 400 cm^{-1} and emission monitored at 14 000 cm^{-1}.

Table 1. ^{3}ZnP Lifetimes and Rate Constants for Triplet Energy Transfer

	80 K		150 K	
compd	τ_{ZnP}/s	k_{TET}/s^{-1}	τ_{ZnP}/s	k_{TET}/s^{-1}
ZnP−OB−H$_2$P	$(85 \pm 1) \times 10^{-3}$	$<0.1^{a}$	$(2.4 \pm 0.1) \times 10^{-3}$	$<20^{a}$
ZnP−BB−H$_2$P		4×10^{4b}	$(1.38 \pm 0.05) \times 10^{-6}$	0.72×10^{6}
ZnP−NB−H$_2$P		2×10^{5b}	$(0.28 \pm 0.05) \times 10^{-6}$	3.6×10^{6}
ZnP−OB	$(85 \pm 1) \times 10^{-3}$		$(2.4 \pm 0.1) \times 10^{-3}$	
ZnP−BB	$(86 \pm 1) \times 10^{-3}$		$(2.6 \pm 0.1) \times 10^{-3}$	
ZnP−NB	$(86 \pm 1) \times 10^{-3}$		$(2.4 \pm 0.1) \times 10^{-3}$	

[a] Estimated from the uncertainty in lifetime. [b] Extrapolated value, see ref 11.

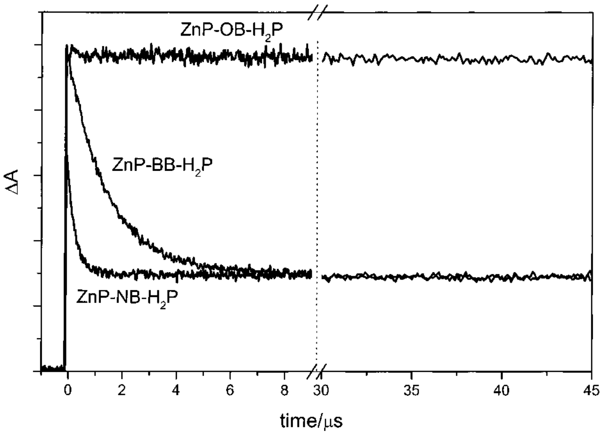

Figure 2. Triplet state decays for the studied D−B−A systems in MTHF at 150 K. Pump wavelength 532 nm; probe wavelength 470 nm. Please note the broken time axis.

by a framework of σ-bonds. Time-resolved phosphorescence measurements on the quenched D−B−A compounds did not yield meaningful lifetimes since the residual emission at 14 000 cm^{-1} was dominated by small amounts of impurities with the same lifetime as the reference compounds (i.e. 85 ms).

The triplet energy transfer process could be quantitatively studied with transient absorption measurements on the ZnP triplet states also in fluid solution. At the excitation wavelength, 532 nm, ZnP absorbs about 75% of the light and the triplet states (^{3}ZnP and ^{3}H$_2$P) are formed within nanoseconds in high yields at 150 K (Figure 2). Monitoring the triplet state dynamics at 470 nm, where absorption from ^{3}ZnP dominates, directly yields the triplet energy transfer rates (Table 1). At a different monitoring wavelength (434 nm), where the ^{3}H$_2$P absorption dominates, the corresponding rise-times are observed (not shown) establishing that triplet energy transfer between ZnP and H$_2$P is the reason for the rapid deactivation of the ZnP triplet state. The difference in decay kinetics between the systems held together by π-conjugated chromophores and ZnP−OB−H$_2$P is striking but there is also a significant difference between ZnP−BB−H$_2$P and ZnP−NB−H$_2$P. In Table 1 it is seen that the rate constants for triplet energy transfer differ by at least a factor of 10^5 for structurally very similar but electronically different D−B−A systems. This difference could be even larger since only an upper limit for the TET rate of the ZnP−OB−H$_2$P system was available. For ZnP−BB−H$_2$P and ZnP−NB−H$_2$P the rate constants at 80 K (Table 1) are extrapolated from measurements at higher temperatures.[11]

Now, what is the reason for the very large difference in triplet energy transfer rates? Stepwise transfer, D → B → A, is not a possible mechanism because the triplet energies of the bridging chromophores are too high in comparison to the porphyrin triplets.[12] Direct coupling through space between the triplet states of the porphyrins is negligible since the distance is too large (19 Å edge to edge). Thus, the observed TET must solely be due to coupling via the bridge between D and A, and the large observed difference in transfer rates shows how sensitive this coupling is to the properties of the bridge.

Clearly π-conjugation is possible in the aromatic bridging chromophores whereas the conjugation is broken in the bicyclooctane bridge. This can have a strong influence on the electronic coupling between the porphyrin moieties. However, an attempt was made to minimize the direct conjugation between the chromophore subunits (cf. ref 6). The observed enhanced electronic coupling might be due to a mixing of the donor and bridge triplet states which would yield a slightly delocalized triplet. This also explains why the effects of the two aromatic bridges are different; the mixing with the naphthalene bridge is more efficient due to its lower lying triplet manifold. Theoretically, this mixing should be related to the so-called superexchange mechanism of electron transfer,[2] which predicts the electronic coupling, or the square root of the transfer rate, to be proportional to the inverse energy difference between the donor and the relevant bridge states. In recent reports this mechanism has been suggested as one of the reasons for the differences between TET rate constants within sets of structurally similar donor−acceptor compounds.[13] The two systems with π-conjugated bridges are in reasonably good agreement with this theory,[14] but the bicyclooctane-containing bridge seems to behave differently. This is not unexpected since the degree of delocalization in the lowest triplet state of the OB-bridge might be different from the lowest triplet states of BB- and NB-bridges. A simple correlation guided by only the energy splitting between donor and bridge states is, therefore, not sufficient.

In conclusion, we have shown that triplet energy can be transferred over 19 Å (25 Å center to center) in less than 300 ns via a π-conjugated spacer while being essentially localized for a slightly modified spacer. This enormous difference in transducing efficiency caused by a small electronic modification implies possible technological applications, such as in a molecular switch.

Acknowledgment. This work was supported by grants from the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Sciences (TFR).

JA001409R

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(11) The activation energies for TET are estimated to be 1 kcal/mol for both the ZnP−BB−H$_2$P and ZnP−NB−H$_2$P systems based on measurements in the temperature range 250−120 K (Andréasson, J.; Kyrychenko, A.; Mårtensson, J.; Albinsson, B. Unpublished material).

(12) The triplet energies are experimentally determined from the 0−0 phosphorescence transitions to be 14 000 (ZnP), 17 500 (NB), 20 000 ^{1} (BB), and 25 500 cm^{-1} (OB). The triplet energy for H$_2$P was estimated from the triplet energies of other free-base porphyrins with similar substitution pattern (ref 8) to be 13 000−11 700 cm^{-1}.

(13) (a) El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 185. (b) Harriman, A.; Romero, F. M.; Ziessel, R. Benniston, A. C. *J. Phys. Chem. A* **1999**, *103*, 5399. (c) Grosshenny, V.; Harriman, A.; Hissler, M. Ziessel, R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2223.

(14) The energy splitting between the lowest triplet states of ZnP and NB or BB is 3500 and 6000 cm^{-1}, respectively, and the rate constant for TET is about 4× larger for ZnP−NB−H$_2$P than for ZnP−BB−H$_2$P (Table 1).