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Excitonic Interactions in the Singlet and Triplet Excited States of Covalently Linked Zinc Porphyrin Dimers

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Abstract: The excess polarizability volumes, ΔV_p, of the relaxed S_1 and T_1 excited states of several covalently bridged zinc porphyrin dimers and their corresponding monomers have been measured using the flash photolysis time-resolved microwave conductivity technique. $\Delta V_p(S_1)$ increases from close to zero for a diaryl-substituted monomer up to a maximum value of 590 Å^3 for a dimer coupled by a 9,10-diethynylanthracene bridge, yPyAyPy. The particularly large excess polarizability of yPyAyPy is attributed to strong electronic coupling between the porphyrin moieties resulting from stabilization of the cumulenic quinoidal resonance structure of the bridge. The strength of the electronic interaction, as indicated by the magnitude of $\Delta V_p(S_1)$, increases in the following order of bridging units: 1,4-phenylene < single σ-bond < 1,4-diethynylbenzene < 2,5-diethynylthiophene ≈ butadiyne < 9,10-diethynylanthracene. The results provide an example of an inverse distance effect whereby the electronic interaction between porphyrin moieties actually increases with increasing length of the intervening bridge. The product of the intersystem crossing efficiency and the excess polarizability volume of the triplet state, $\phi_{isc}\Delta V_p(T_1)$, is more than an order of magnitude less than $\Delta V_p(S_1)$, indicating a much smaller degree of exciton delocalization in T_1 than in S_1. The microwave results are compared with results on the optical absorption and emission spectra which provide additional information on both the electronic and Coulombic excitonic interactions.

Introduction

Porphyrin derivatives are essential ingredients in all natural photosynthetic systems. In addition to being used as light-harvesting chromophores because of their broad range of optical absorption, covering the entire visible spectrum, porphyrin derivatives play a key role in the processes that direct the absorbed solar energy from the initial antenna complex to the reaction center, where they are also responsible for triggering the initial stages of transmembrane charge separation. These functions depend on collective interactions between two or more closely similar, or even identical, porphyrinic units juxtapositioned in organized assemblies, as in the "storage ring" arrays of bacterial antenna systems[1] or in the "special pair" of the reaction center.[2] In attempts to understand and reproduce these natural functions, a large number of porphyrinic arrays have been synthesized.[3−6]

The photophysical properties of an assembly of identical chromophores can be quite complex as a result of Coulombic and electronic interactions between neighboring monomeric units. Even in the absence of covalent bonding, pronounced differences in the optical absorption and emission spectra between the assembly and the corresponding monomer are often found. A qualitative explanation of such effects was first given by Kasha in terms of the Coulombic interaction between neighboring chromophores with isoenergetic electronic transitions.[7,8] Such dipolar exciton coupling can lead to the splitting of an energy level, generally referred to as "Davydov splitting", and is exemplified by either bathochromic or hypsochromic spectral shifts. The magnitude of the interaction, as measured by the excitonic splitting, δE, is related to the transition dipole moment, μ_{0n}, associated with a transition from the ground state, S_0, to an excited state, S_n, and to the distance between the chromophores, R_{cc}, according to

$$\partial E = K\frac{|\mu_{0n}|^2}{R_{cc}^3} \qquad (1)$$

The parameter K in (1) is dependent on the geometrical relationship between the chromophores and the spectral overlap. Dipolar coupling is also the basis of the Förster mechanism of energy transfer between chromophores, the rate of which obeys an inverse sixth power dependence on distance.[9]

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In the Kasha and Förster approaches to excitonic interactions, no electronic overlap or electron exchange between the chromophores is taken into account. While this may be a reasonable approximation for through-space interactions, since electronic overlap is expected to decrease exponentially with distance, it may break down for covalently bonded chromophores. In the latter case, through-bond interactions involving the σ,σ^* and π,π^* orbitals of the bridge can result in electronic interactions over much longer distances.[3,10-12] The resulting interchromophore coupling will then depend on the specific nature of the bridge, and a simple monotonic decrease with distance may no longer be assumed. This is clearly shown to be the case in the present work, where we have measured the extent of excitonic interactions in several zinc porphyrin dimers linked by a variety of covalent bridges and found that the electronic coupling can even *increase* with an increase in the length of the bridge.

In the past, evidence for excitonic interactions in molecular assemblies has been derived mainly from comparisons of the optical absorption and emission characteristics of assemblies with those of a model monomer molecule. In the present work we have used, in addition to optical methods, a modification of the flash photolysis time-resolved microwave conductivity method (FP-TRMC)[13-15] to measure the increase in molecular polarizability on formation of the relaxed excited singlet and triplet states. The method, which provides a direct measure of the extent of electron delocalization, has previously been used to study excitonic interactions in other symmetrical multichromophoric assemblies[16-19] and, more recently, in conjugated polymers.[15,20,21]

Experimental Section

The structures of the porphyrin dimers and corresponding model monomers studied in the present work are shown together with their pseudonyms in Figure 1. Their methods of synthesis and structural characterization have been given in previous publications,[22-25] which are listed in the last column of Table 1. All measurements were carried out on dilute solutions in benzene (Merck, Uvasol) to which 1 wt % 1,4-diazabicyclo[2,2,2]octane (DABCO; Aldrich 98%), was added to prevent aggregation by complexation with the central zinc atoms.

Optical absorption spectra were recorded on a Kontron Uvikon 940 double-beam UV−visible spectrophotometer. Emission spectra were recorded on a PTI quantamaster II spectrofluorometer equipped with a double-excitation and a single-emission monochromator. All samples were excited at a wavelength close to the maximum of their B-band. The absorbance at the excitation wavelength never exceeded 0.2.

The fluorescence decay times of the compounds P, PP, and PBP were determined from real-time transients using the 0.8-ns, 337-nm pulse of a Laser Photonics LN1000 nitrogen laser as excitation source and a Photek PMT-113-UHF channel-plate photomultiplier with a rise time of 150 ps as detector. For the remaining compounds the fluorescence decay time was determined by single photon counting using the 90-ps, 630-nm pulse from a cavity-dumped, mode-locked dye laser synchronously pumped by the second harmonic of a continuous-wave, mode-locked Nd:YAG laser. The decay times thus obtained, which were used as the singlet excited-state lifetime in the fitting procedure of the TRMC transients, are listed in Table 1.

For the TRMC experiments the solutes were photoexcited using single 7-ns, 308-nm unfocused pulses from a Lumonics HyperEX-400 excimer laser. The molar absorption coefficients of the solutes were ca. 1×10^4 M^{-1} cm^{-1} at the laser wavelength, and the absorbance of the solutions varied from ca. 0.2 to 0.9 for a 1-cm path length. Prior to use, the solutions were purged with CO_2 to remove oxygen and scavenge any free electrons which might be generated in low yield by multiphoton events. A maximum of 16 pulses were used for signal averaging. The power output of the laser was monitored routinely using a Scientec 365 power meter, and the actual fraction of photons entering the TRMC cell was determined using a solution of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) in benzene as an internal actinometer.[13,14,26] The average concentration of photons absorbed in the solutions was calculated to be ca. 10 μM per pulse for the absorbances used.

The solutions were contained in an X-band (8.2−12.4 GHz) resonant cavity. Transient changes in the power reflected by the cavity on flash photolysis, ΔR, were monitored at the upper and lower half-power frequencies, f_+ and f_-, of the cavity resonance at ca. 9.4 GHz. By addition and subtraction of the two transients, signals related to the change in the real, $\Delta\epsilon'$ (dielectric constant), and imaginary, $\Delta\epsilon''$ (dielectric loss), components of the complex permittivity of the solutions were obtained:[15,21]

$$\Sigma_{\pm} = (\Delta R_- + \Delta R_+) = B\Delta\epsilon'' \qquad (2)$$

$$\Delta_{\pm} = (\Delta R_- - \Delta R_+) = C\Delta\epsilon' + D\frac{d\Delta\epsilon'}{dt} \qquad (3)$$

Such "real" and "imaginary" transients are shown for all of the compounds investigated in Figures 2, 4, and 6.

The values of *B* and *C* in (2) and (3) can be calculated from the characteristics of the resonant cavity.[14] The differential term in (3) results from a nondissipative change in the energy stored within the cavity as a result of the fluctuations in ϵ'. This leads to an oscillatory component in the $\Delta_{\pm}$ transients. The value of *D* was determined by fitting transients for the formation of the highly polarizable triplet state of Michler's ketone.[27] Knowing *B*, *C*, and *D*, the absolute magnitude of the change in ϵ' and ϵ'' on flash photolysis can be determined. The signals actually observed have a noise level which corresponds to a fluctuation in the relative dielectric constant of less than 1 ppm in the irradiated volume of the cell.

A change in the complex permittivity of a solution on photoexcitation of the solute, $\Delta\epsilon$, can result from a change in the electronic polarizability, $\Delta\alpha$, or a change in the dipole moment, $\Delta\mu = \mu_* - \mu_0$, of the

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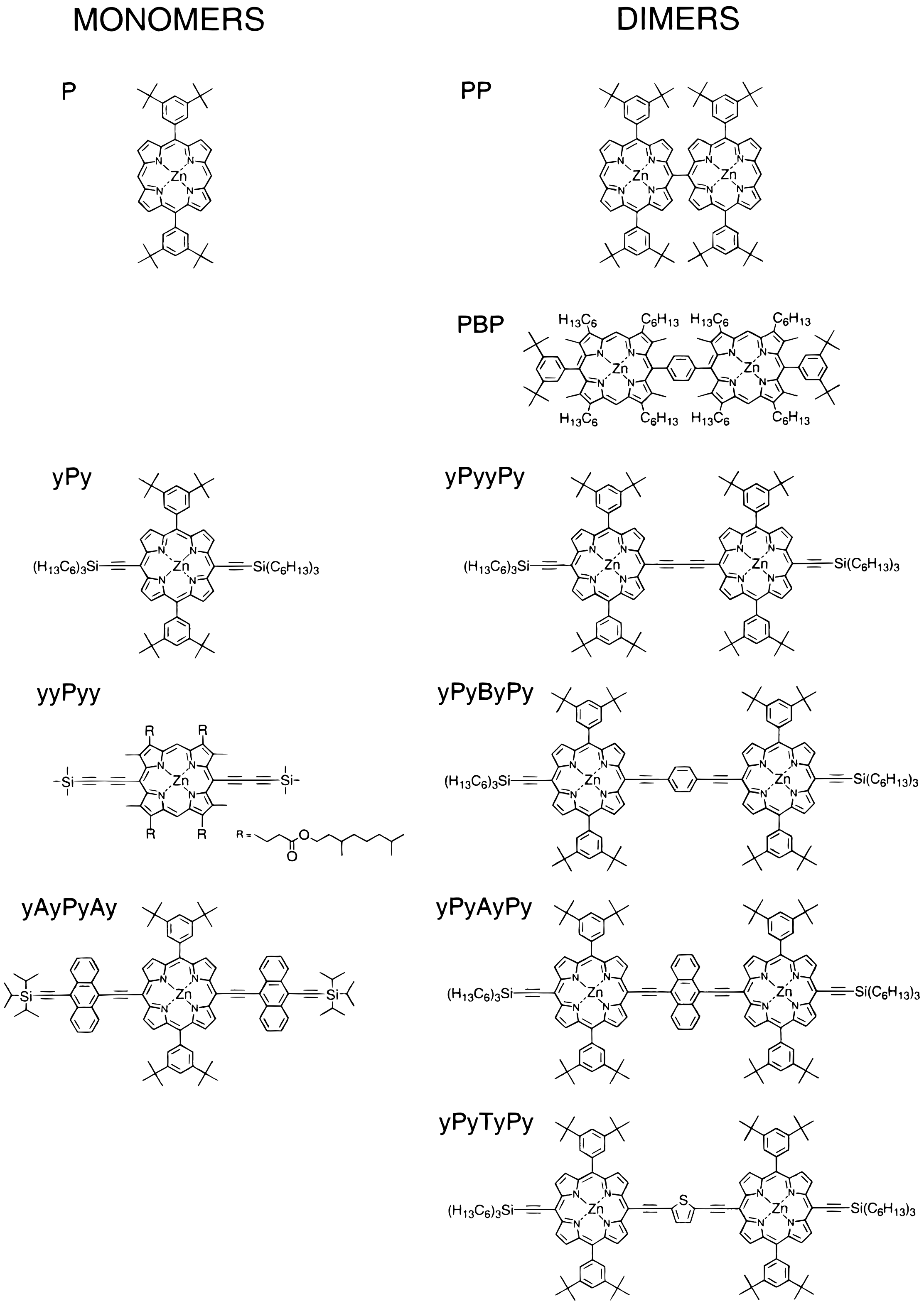

Figure 1. Structures of the molecules investigated and the pseudonyms used throughout the text.

solute molecules. The overall change in permittivity is given by

$$\Delta\epsilon = \frac{(\epsilon(\infty) + 2)^2 N_*}{9\epsilon_0}\left(\Delta\alpha + \frac{(\mu_*^2 - \mu_0^2)}{3k_B T(1 + j\omega\Theta)}\right) \tag{4}$$

$$= \Delta\epsilon' - j\Delta\epsilon'' \tag{5}$$

In (4), N_* is the concentration of the excited state, $\epsilon(\infty)$ is the optical dielectric constant, k_B is the Boltzmann constant, T is the temperature, ω is the radian microwave frequency, Θ is the dipole relaxation time, ϵ_0 is the permittivity of vacuum, and j is $\sqrt{-1}$. In the present case of a nonpolar solvent ($\epsilon(\infty) = \epsilon'$) and solute molecules with zero dipole moment in the ground state, the individual changes in the real and imaginary components of ϵ are, from (4),

$$\Delta\epsilon' = \frac{(\epsilon' + 2)^2 N_*}{9\epsilon_0}\left(\Delta\alpha + \frac{\mu_*^2}{3k_B T(1 + \omega^2\Theta^2)}\right) \tag{6}$$

and

Table 1. Fluorescent Lifetime, $\tau(S_1)$, Excess Polarizability Volume of the Singlet State, $\Delta V_p(S_1)$, Product of the Intersystem Crossing Efficiency and the Excess Polarizability Volume of the Triplet State, $\phi_{isc}\Delta V_p(T_1)$, and Energy of the (0,0) Transition of the Fluorescence, E_{fl}

compound	$\tau(S_1)$ (ns)	$\Delta V_p(S_1)$ (Å^3)	$\phi_{isc}\Delta V_p(T_1)$ (Å^3)	E_{fl} (eV)	ref[b]
P	2.9	<20[a]	<5[a]	2.10	22
PP	2.1	50 ± 20	<5[a]	1.95	22
PBP	1.3	<20[a]	<5[a]	2.06	23
yPy	1.6	30 ± 20	<5[a]	1.90	24
yyPyy	1.9	50 ± 20	13 ± 5	1.84	25
yAyPyAy	0.8	330 ± 30	28 ± 5	1.68	24
yPyyPy	1.3	400 ± 40	30 ± 5	1.64	24
yPyByPy	0.8	270 ± 30	17 ± 5	1.78	24
yPyTyPy	0.8	390 ± 40	30 ± 5	1.71	24
yPyAyPy	1.1	590 ± 60	19 ± 5	1.61	24

[a] Upper limit corresponds to the noise level. [b] Reference to synthesis.

$$\Delta\epsilon'' = \frac{(\epsilon' + 2)^2 N_*}{27\epsilon_0 k_B T}\left(\frac{\omega\Theta\mu_*^2}{(1 + \omega^2\Theta^2)}\right) \qquad (7)$$

A change in the electronic polarizability is seen to result only in a change in ϵ', whereas a dipole moment change results in a change in both ϵ' and ϵ''. For the present molecules, no measurable change in ϵ'' could be observed, as can be seen from the results in Figures 2, 4, and 6, indicating that the excited states have no dipolar character, as might be expected on the basis of their symmetry. Therefore, any changes in ϵ' which are observed can be attributed entirely to changes in the electronic polarizability on photoexcitation, i.e.,

$$\Delta\epsilon' = \frac{(\epsilon' + 2)^2 N_*}{9\epsilon_0}\Delta\alpha \qquad (8)$$

As can be seen in Figures 4 and 6, the $\Delta\epsilon'$ transients are characterized by a combination of a fast component and a slow component, with the decay of the latter extending well into the microsecond regime. Since zinc porphyrins are known to undergo intersystem crossing with high efficiency, we ascribe the fast and slow components in the present measurements to the relaxed singlet and triplet states, S_1 and T_1, respectively. The data were therefore fitted using a convolution procedure with numerical calculation of the S_1 and T_1 concentrations during and after the pulse using the known laser pulse shape and intensity, the optical properties of the solution, and the S_1 lifetime determined from the fluorescence measurements. From the fits, values of the excess polarizability of the excited singlet state, $\Delta\alpha(S_1)$, and the product of the quantum yield and the excess polarizability of the triplet state, $\phi_{isc}\Delta\alpha(T_1)$, could be determined. For convenience of discussion, these values are given in Table 1 as the excess polarizability volume $\Delta V_p = \Delta\alpha/4\pi\epsilon_0$ in units of cubic angstroms.

Results and Discussion

As mentioned in the Introduction, the photophysical properties of identical chromophores in close proximity can be influenced by mutual Coulombic or electronic interactions. The former results in Davydov splitting of the energy levels, with the magnitude of the splitting being dependent on the relative orientation and distance between the chromophores, and the transition dipole moment associated with a particular transition as given in eq 1. In the case of porphyrins, the B-band in the 400−500-nm region is particularly sensitive to such effects because of the extremely large transition dipole moment associated with it. The Q-band of the porphyrins, on the other hand, has a much lower transition dipole and is correspondingly much less sensitive to Coulombic interactions. Spectral changes in the B-band absorption spectrum can therefore, in principle, be used as an indication of the magnitude of Coulombic interporphyrin interactions. The effect of the Coulombic interaction alone can, however, be obscured by other effects. Additional substituents on the porphyrin macrocycles, for instance, can lift the degeneracy of the two orthogonal B-band transitions, which can also lead to a splitting of the B-band.

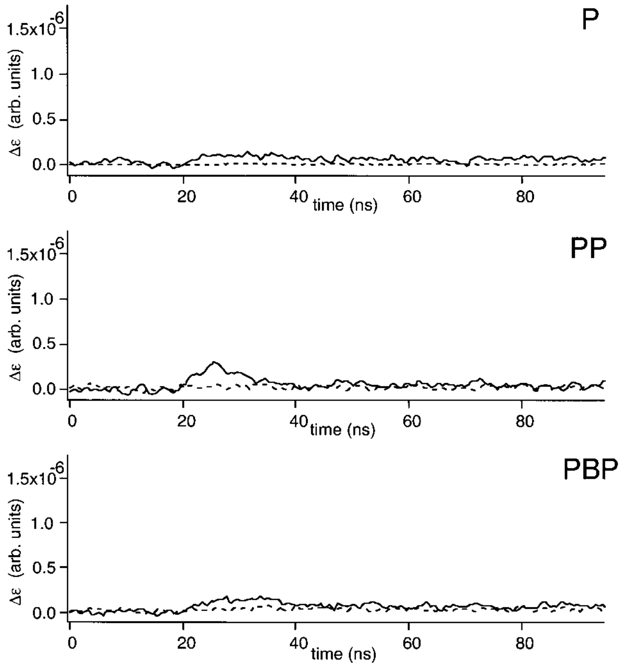

Figure 2. TRMC transients corresponding to changes in the imaginary (dashed line) and real (full line) components of the complex permittivity of dilute solutions of P, PP, and PBP in benzene to which 1 wt % DABCO was added.

Electronic interactions, either via direct orbital overlap or via electron exchange, are expected to lead to a reduction in the gap between the highest occupied molecular orbital (the HOMO) and the lowest unoccupied molecular orbital (the LUMO). This should, therefore, be observed as a bathochromic shift of the lowest energy Q-band and the (0,0) band of the fluorescence. Of particular relevance to the present work are the delocalization of the electronic wave function and the partial charge-transfer character of the S_1 excited state, which are consequences of electron exchange. This should be observable as an increase in the electronic polarizability of the molecule on excitation, an effect which is ideally suited to study by the present TRMC technique.

Considering the above, we divide the present compounds into three groups on the basis of their combined optical properties and excess polarizabilities: (1) the compounds P, PP, and PBP, which have extremely low excess polarizabilities but display B-band splitting in the dimeric compounds; (2) the monomer series P, yPy, yyPyy, and yAyPyAy, for which a gradual increase in excess polarizability is found with or without associated B-band splitting; and (3) the diethynyl-bridged dimers, denoted generally by yPyXyPy, all of which have large values of $\Delta V_p(S_1)$ and complex B-band spectra. These groups will be discussed separately below.

In addition to information on the relaxed excited singlet states of the present compounds, the TRMC technique is capable of providing information on the excess polarizability, and hence the degree of delocalization, in the triplet state. This will be discussed in a separate section after first considering the singlet state results.

(1) Singlet States of P, PP, and PBP. As can be seen in Figure 2, any change in ϵ' which may have occurred on photoexcitation of the monomer P was within the noise level

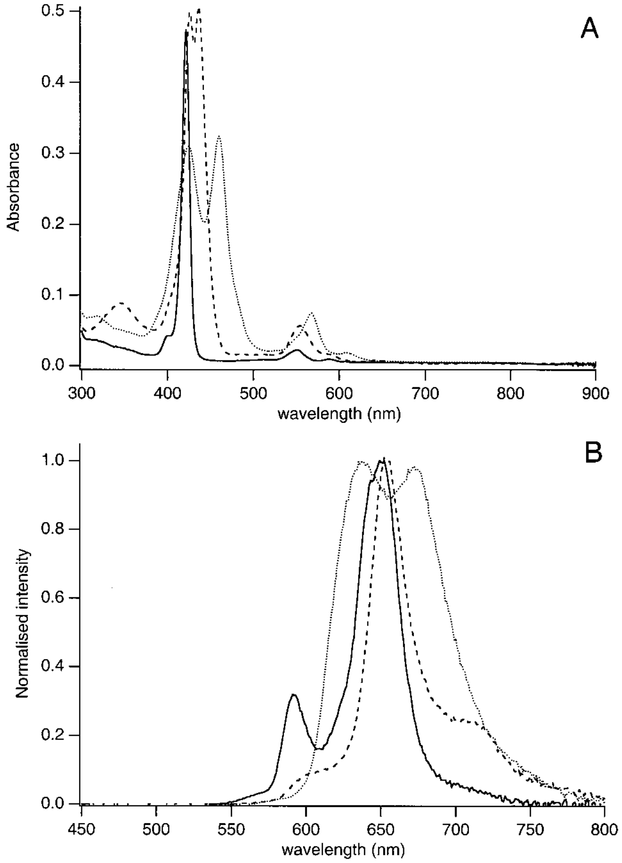

Figure 3. UV–visible absorption spectra (A) and fluorescence spectra (B) of the compounds P (full line), PP (dotted line), and PBP (dashed line) in benzene with 1 wt % DABCO added.

of the measurements, which corresponds to a value of $\Delta V_p(S_1)$ of approximately 20 Å^3. From this we conclude that excitation of an electron from the HOMO to the LUMO occurs with very little change in the degree of delocalization of the electronic wave function. The monomer P, therefore, provides an ideal reference point for monitoring the influence of substituents since any measurable value of $\Delta V_p(S_1)$ must arise from electron delocalization involving the molecular orbitals of the substituent.

For the simplest, directly covalently linked dimer, PP, a TRMC transient slightly outside of the noise level is observed in Figure 2 which corresponds to $\Delta V_p(S_1) = 50$ Å^3. On the basis of this, we conclude that there is a small but significant degree of electronic coupling between the two porphyrin moieties. This is also apparent in Figure 3 as a small bathochromic shift of 0.15 eV in both the Q-band absorption and the emission. A much more pronounced effect is seen on the B-band absorption, which is split by 0.25 eV as observed previously.[22,28] We conclude, therefore, that for PP the interaction between the two chromophores is dominated by Coulombic effects, with electronic coupling playing only a minor role. The weakness of the electronic interaction can be ascribed to the lack of coplanarity of the macrocycles induced by steric hindrance.[22,29]

For the 1,4-phenylene-bridged dimer, PBP, both Coulombic coupling and electronic coupling are found to be much smaller than those for PP. The former effect is shown in Figure 3 by the considerably reduced (but still observable!) splitting of the B-band of only 0.09 eV.[22,28] The much reduced Kasha-type exciton coupling for PBP is to be expected on the basis of the increased distance between the porphyrin units, as given by eq 1.

The lack of significant electronic interaction in PBP is indicated by the absence of a measurable $\Delta\epsilon'$ transient in Figure 2 and the lack of a substantial red shift in the fluorescence maximum compared with that for the monomeric compound, as shown in Figure 3. The fact that the porphyrin macrocycles can adopt a coplanar arrangement in PBP would appear to be insufficient to compensate for the negative effect on the electronic coupling of the larger interchromophore separation. The present results lead, therefore, to the conclusion that the excitation energy is almost completely localized on a single porphyrin unit in PBP. This is in agreement with resonance Raman measurements on a nickel analogue of PBP, which indicated that hardly any electronic interaction is mediated via the intervening 1,4-phenylene bridge.[30]

As mentioned in the Introduction, distance cannot be used as the only criterion in discussing electronic coupling in bridged dimers since through-bond coupling can play an important role. In this regard, one would tend to conclude from the present results for PBP that the 1,4-phenylene unit is, in fact, a very weak coupling agent. Previous experiments on phenylene-bridged porphyrins have also indicated that the coupling efficiency of the 1,4-phenylene unit is weak.[31–33] The lack of efficiency of the 1,4-phenylene bridge is attributed, at least in part, to the forced noncoplanarity between the phenylene and porphyrin ring systems caused by steric hindrance.[23,31] This reduces the orbital interactions between the chromophore and the bridge necessary for through-bond coupling. As will be shown below, a bridge consisting of a phenylene unit interposed between two ethynyl groups can act as an efficient coupling agent. In that case, the phenylene ring *can* adopt a conformation in which it is coplanar with both porphyrins.

(2) Singlet States of P, yPy, yyPyy, and yAyPyAy. In Figure 4, the TRMC transients for all of the monomeric porphyrin derivatives are compared. The magnitude of the transients and the corresponding $\Delta V_p(S_1)$ values given in Table 1 are seen to increase gradually with increasing complexity of the substituents at the opposing meso positions, up to a relatively large value of 330 Å^3 for yAyPyAy. As shown in Figure 5, the Q-band absorption and the (0,0) band of fluorescence undergo corresponding bathochromic shifts within the series. Clearly, there is a substantial degree of electron delocalization from the porphyrin ring into the substituents in the S_1 state of the monomeric ethynyl-containing derivatives and, in particular, for the 9,10-diethynylanthracene substituent. These conclusions are in agreement with the results of Beljonne et al.[34] on compounds very similar to yPy and yyPyy and LeCours et al.[35] on *meso*-arylethynyl derivatives. These workers, together with Wang et al.,[36] have also carried out theoretical calculations which substantiate the delocalization of the LUMO wave functions

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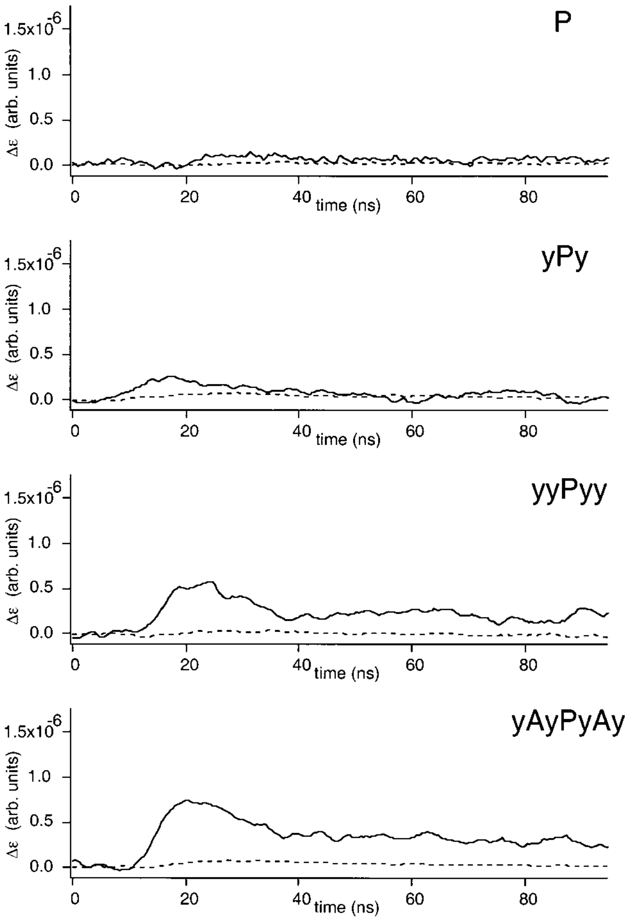

Figure 4. TRMC transients corresponding to changes in the imaginary (dashed line) and real (full line) components of the complex permittivity of dilute solutions of the series of monoporphyrinic compounds in benzene to which 1 wt % DABCO was added.

into the *meso* substituents. In particular, the low-lying singlet states of the arylethynyl derivatives were found to be highly polarized, which would explain the large polarizability found in the present work for yAyPyAy.

The bathochromic shift in the Q-bands and in the fluorescence of the ethynyl-substituted monomers is accompanied by a considerable red shift in the B-band, as shown in Figure 5. In addition, there is clear evidence of B-band splitting for yPy and yAyPyAy, whereas yyPyy displays only a single sharp band. These results for the monomeric compounds illustrate the care that must be taken in interpreting such B-band effects in terms of excitonic interactions alone. The splitting in the case of the first two compounds and its absence for yyPyy may be related to the fact that the former compounds have additional 3,5-di-*tert*-butylphenyl substituents at the 10,20-*meso* positions whereas yyPyy has none. A full discussion of these interesting differences is outside the scope of the present work.

(3a) Singlet State of yPyyPy. The $\Delta V_p(S_1)$ value of 400 Å^3 for the butadiyne dimer, yPyyPy, derived from the $\Delta\epsilon'$ transient displayed in Figure 6, is much larger than the values of ca. 30 and 50 Å^3 found for the monomeric yPy and yyPyy compounds. This is direct evidence that strong electronic coupling between the two porphyrin moieties is mediated by the intervening butadiyne bridge. A large degree of interchromophore interaction is also indicated by the pronounced bathochromic shift of the dimer fluorescence shown in Figure 7, which corresponds to a decrease in the HOMO−LUMO gap from 1.90 eV for the yPy monomer to 1.64 eV. The present results support the conclusion that a butadiyne bridging unit provides efficient interaction between porphyrin moieties, which was drawn previously on the basis of the optical properties of the closely related compound yyPyyPyy.[34]

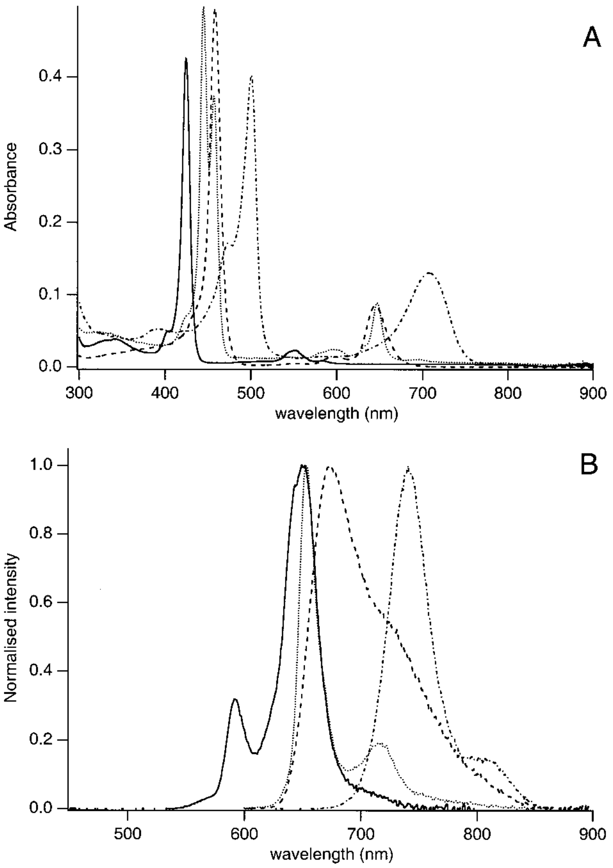

Figure 5. UV−visible absorption spectra (A) and fluorescence spectra (B) of the compounds P (full line), yPy (dotted line), yyPyy (dashed line), and yAyPyAy (dotted-dashed line) in benzene with 1 wt % DABCO added.

In addition to $\Delta V_p(S_1)$ for the yPyyPy dimer being much larger than for the model monomers, it is also very much larger than the values found for the PP and PBP dimers, despite the fact that the edge-to-edge distance between the porphyrin moieties in yPyyPy is larger. It could be argued that the larger excitonic interaction observed for yPyyPy than for PP is the result of the freedom of rotational motion of the chromophoric units provided by the butadiyne bridge, which allows the porphyrin macrocycles to adopt a coplanar arrangement. Conformational relaxation in S_1 to form a coplanar emitting state has been found to occur within ca. 30 ps for a PyP-type dimer.[37] Coplanarity alone, however, cannot be the sole cause of the large coupling, since this is also possible in the case of PBP, for which no significant excess polarizability could be observed.

It has been suggested that the explanation of the highly efficient electronic coupling provided by oligoethynyl chains lies in the adoption, in the excited state, of a cumulenic structure,[34,38] as illustrated in Figure 8. Theoretical calculations on 1,4-diphenylbutadiyne have shown that the degree of bond alternation in the butadiyne unit does, in fact, decrease considerably in the excited state.[34] Such cumulenic structures introduce

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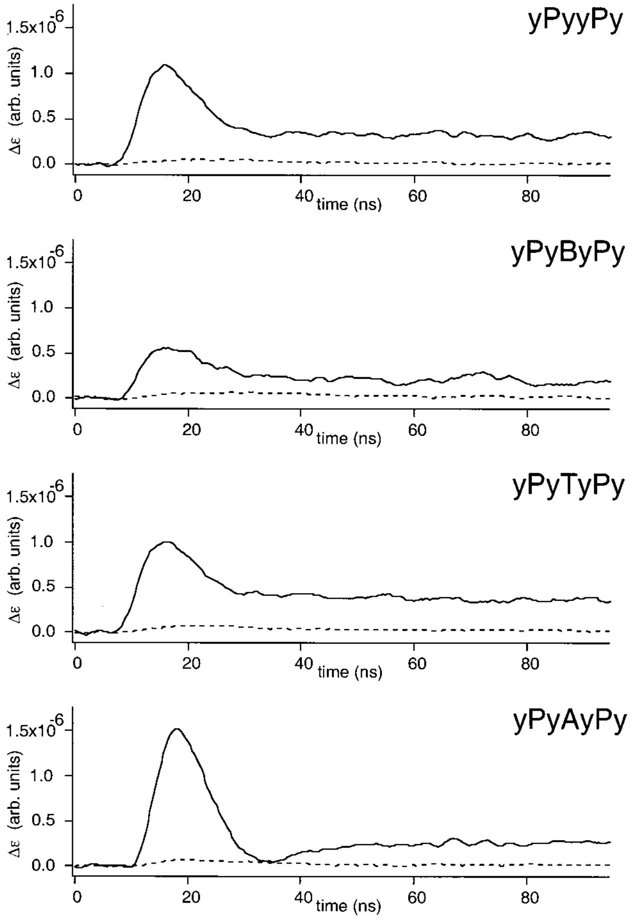

Figure 6. TRMC transients corresponding to changes in the imaginary (dashed line) and real (full line) components of the complex permittivity of dilute solutions of the series of bis-ethynylenic linked porphyrin dimers in benzene to which 1 wt % DABCO was added.

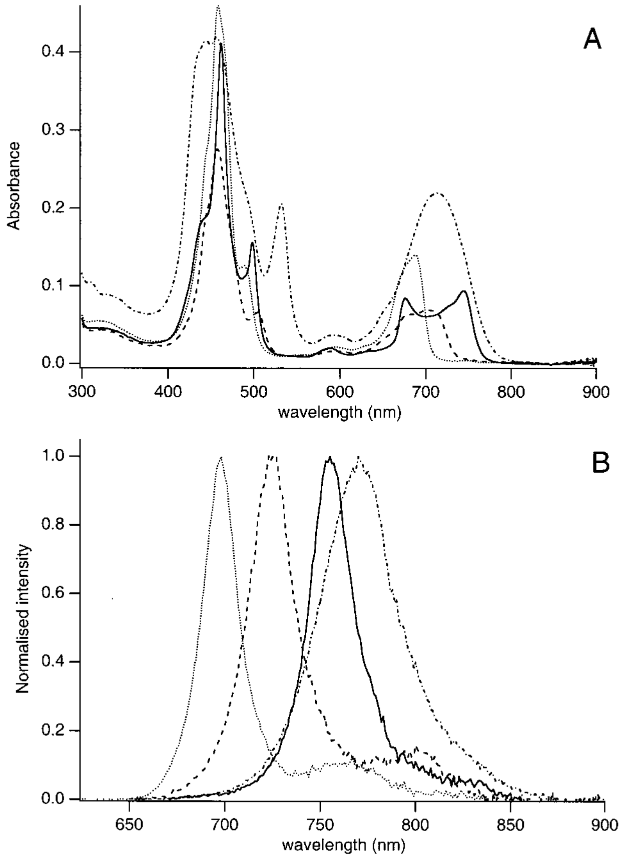

Figure 7. UV−visible absorption spectra (A) and fluorescence spectra (B) of the compounds yPyyPy (full line), yPyByPy (dotted line), yPyTyPy (dashed line), and yPyAyPy (dotted-dashed line) in benzene with 1 wt % DABCO added.

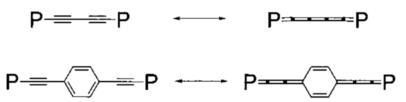

Figure 8. Ethynylenic and cumulenic resonance structures of the yy bridging unit (top) and aromatic ethynylenic and quinoidal cumulenic resonance structures of the yXy (X = B or A) bridging unit (bottom).

the possibility of charge-transfer states which may lie close to the locally excited state. Strong electronic coupling between the local and charge-transfer states could explain the very large excess polarizability found for yPyyPy.

(3b) Singlet States of the yPyXyPy Series. Interposing a 1,4-phenylene moiety in the butadiyne bridge to give yPyByPy results in a decrease in the interaction between the chromophores, as shown by the considerable decrease in $\Delta V_p(S_1)$ from 400 to 270 Å^3 and the increase in the HOMO−LUMO gap from 1.64 to 1.78 eV. A substantial decrease in coupling efficiency would have been expected simply on the basis of the considerably increased interchromophore distance. On the basis of the weak coupling found for PBP, it is, in fact, surprising that the decrease is not even larger. This can be explained, at least in part, by the removal of the steric hindrance to rotation of the phenylene ring by the presence of the intervening ethynylenic units. This allows the central aromatic ring to adopt a coplanar orientation with respect to the porphyrin moieties. In such a coplanar conformation, increased conjugation would be favored by an increased contribution from a combined cumulenic quinoidal resonance structure,[24] as illustrated in Figure 8.

Evidence for the importance of a cumulenic quinoidal resonance structure is provided by the results for yPyAyPy. Thus, even though the interporphyrin distance remains constant compared with yPyByPy, the value of $\Delta V_p(S_1)$ increases by almost a factor of 2. Since the energy difference between an aromatic and a quinoidal structure is considerably smaller for anthracene than for benzene, substitution of a 9,10-anthrylene unit for the 1,4-phenylene group should favor the formation of a cumulenic quinoidal structure[39−41] and hence result in an increase in the coupling efficiency of the bridge, as is observed. Not only is the excess polarizability for yPyAyPy larger than that for yPyByPy, it is even larger than that for the much shorter bridge compound yPyyPy! The 9,10-diethynylanthracene moiety appears, therefore, to be an exceptionally good agent for the electronic coupling of porphyrinic chromophores, as was previously concluded on the basis of the optical properties of these compounds.[24] The series PBP, yPyyPy, and yPyAyPy provides, therefore, a good illustration of the inverse effect of an *increase* in electronic coupling accompanying an *increase* in interchromophore distance.

The optical properties of yPyAyPy are themselves of interest. Thus, while the lowest energy absorption band of this compound is higher in energy than that for yPyyPy, its highest

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energy fluorescence band is lower in energy. The large Stokes shift for yPyAyPy is further evidence that a substantial structural change occurs after photoexcitation. This is in agreement with the bond rearrangement required for the formation of the cumulenic quinoidal structure in the relaxed S_1 state.

On the basis of the excess polarizability value of 390 Å^3 for yPyTyPy, the 2,5-diethynylthiophene bridge, yTy, is seen to have a coupling efficiency intermediate between those of yBy and yAy and close to that for the butadiyne group alone. This is in agreement with the ordering of the fluorescence emissions and the positions of the B- and Q-band absorptions shown in Figure 7. In the case of yPyTyPy, a cumulenic semiquinoidal structure may be taken to be responsible for the highly efficient coupling. It would appear that the bent nature of the yTy bridge does not have a significant negative influence on the electronic coupling efficiency.

The B-bands of the yPyXyPy compounds are seen in Figure 7 to be complex, with in all cases multiple splitting occurring, as has been observed previously for similar ethynyl-bridged dimers.[42,43] Compared to the corresponding monomers described in the previous section, this splitting is much more pronounced and, therefore, cannot solely be attributed to the asymmetric substitution around the porphyrin macrocycle. For instance, from the spectrum of yPyyPy, we estimate a splitting of ca. 0.2 eV, which is similar in magnitude to that of the directly coupled dimer PP. This is a surprising result, since the Coulombic interactions responsible for the B-band splitting would be expected to be much weaker for the large interchromophore distance in yPyyPy. We are tempted to conclude that the strong electronic interaction between the porphyrin chromophores has the additonal effect of extending the range of the Coulombic coupling considerably in the yPyXyPy compounds.[42]

Arnold and co-workers[43] recently put forward an alternative explanation for the complex B-band of covalently linked bisporphyrinic compounds solely based on electronic interaction. The four-orbital model of Gouterman[44,45] for a single porphyrin is the starting point of what they have called the eight-orbital model. This model evolves from the two set of four orbitals by a process best described as the linear combination of molecular orbitals (LCMO). Nonzero overlap between two isoenergetic orbitals of neighboring porphyrins generates a new pair of orbitals, consisting of a bonding and an antibonding orbital with an energy difference dependent on the strength of the interporphyrin interaction. Notwithstanding its simplicity, this model succeeds amazingly well in describing the complex shape of the B-band and the red shift of the Q-band in the electronic spectrum of covalently linked porphyrinic dimers such as PyyP as well as those of their mono- and dianion, which is clearly related to the ethynylenic bridged dimers we have investigated.

Most important for this paper is that regardless of which explanation is used, the same conclusion is reached: the broadest B-band indicates the strongest electronic coupling between the porphyrin moieties. The trend in porphyrin−porphyrin interactions shown by the splitting of the B-band in the optical data is therefore in agreement with the outcome of the TRMC measurements.

(4) Triplet States. Zinc porphyrins are known from transient optical absorption and EPR experiments to have high efficiencies for intersystem crossing to form relatively long-lived triplet states, ϕ_{isc}.[46] The value of ϕ_{isc} for a derivative very similar to yyPyy has, for example, been determined to be 0.8.[47] We therefore attribute the long-lived TRMC transients observed for some of the ethynyl derivatives in the present experiments to the formation of T_1 states with a polarizability larger than that of the ground-state molecules. The values of $\phi_{isc}\Delta V_p(T_1)$ derived from the transients are listed in Table 1. If we assume the intersystem crossing efficiency to be similar to that given above, then the actual values of $\Delta V_p(T_1)$ would be only approximately 20% larger than the products given in Table 1. A general qualitative conclusion that can immediately be drawn from the data is that the T_1 state has a considerably lower polarizability, by approximately an order of magnitude, than S_1. This indicates a much smaller degree of delocalization, which is in agreement with EPR measurements on the triplet state of a series of ethynylic bridged multiporphyrin arrays by Angiolillo et al.[48] By comparing the results for monomeric porphyrins similar to P, yPy, and yyPyy with those for oligomers of the types PyP, PyyP, and PyPyP, these authors concluded that the electron spins associated with T_1 were strongly localized on a single chromophore of the oligomer.

The absolute values of $\phi_{isc}\Delta V_p(T_1)$ for the diethynyl-substituted compounds indicate that there may be some delocalization of the triplet wave function into the substituent groups. There is, however, no definite trend in the values similar to that found for the excited singlet states.

Conclusions

The interaction in the excited singlet state between two zinc porphyrin moieties joined together by a covalent bridge is strongly dependent on the nature of the bridging unit. For linkage via a single σ-bond or a 1,4-phenylene group, the interaction is mainly Coulombic and is much weaker for the latter, as evidenced by the influence on the B-band absorption. Bridges containing ethynyl groups lead to strong electronic coupling between the porphyrins, as evidenced by a large polarizability change on photoexcitation, $\Delta V_p(S_1)$, and a large bathochromic shift in the Q-band absorption and fluorescent emission. The order of the strength of the electronic coupling for the different bridges (with $\Delta V_p(S_1)$ in parentheses) is the following: 1,4-phenylene ($<$20 Å^3) $<$ σ-bond (50 Å^3) $<$ 1,4-diethynylbenzene (270 Å^3) $<$ 2,5-diethynylthiophene (390 Å^3) $\approx$ butadiyne (400 Å^3) $<$ 9,10-diethynylanthracene (590 Å^3). The strong electronic coupling for butadiyne and the ethynyl-containing units is attributed to the contribution of cumulenic and cumulenic quinoidal resonance structures in the excited state. Interestingly, the strong electronic coupling in these ethynylenic coupled dimers appears to extend the effective range of the Coulombic interaction. The relatively weak electronic coupling for the σ-bond and 1,4-phenylene linkages is attributed, at least in part, to steric hindrance, preventing coplanarity of the porphyrin macrocycles in the former case and the central phenylene ring in the latter case.

The excess polarizabilities associated with triplet state formation are approximately an order of magnitude less than those

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for the S_1 state, indicating a much greater degree of localization for the former.

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