

Photoexcitations of Covalently Bridged Zinc Porphyrin Oligomers: Frenkel versus Wannier–Mott Type Excitons

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The effect of increasing chain length on the excited-state properties of two series of covalently linked zinc porphyrin oligomers has been investigated. One series has a 1,4-phenylene bridge, (PB)_n with $n = 1, 2, 3$, and 5, and the other series has a 1,4-butadiynylene bridge, (yPy)_n with $n = 1–6$. The two series differ dramatically in the nature of the porphyrin–porphyrin interaction. Flash-photolysis time-resolved microwave conductivity measurements (FP-TRMC) show that the excited singlet state (S₁) of the (PB)_n oligomers has a very small excess polarizability ($<20 \text{ \AA}^3$) which is characteristic of a tightly bound, Frenkel type exciton. In agreement with this, the optical absorption and emission spectra indicate that only electrostatic interactions occur between the transition dipoles of the porphyrin moieties. In contrast, very large excess polarizabilities are found for the S₁ state of the (yPy)_n series, which indicates that a high degree of electron exchange occurs between the porphyrin moieties. This is confirmed by the marked changes also observed in the optical absorption and emission spectra. The polarizability increases with increasing length of the oligomers up to a maximum of 960 \AA^3 indicative of a loosely bound, Wannier–Mott type exciton. In contrast, the triplet excited state of the (yPy)_n series has an excess polarizability of $<50 \text{ \AA}^3$, indicating that it is much more localized than the S₁ state.

Introduction

Research on excitons in multiporphyrinic arrays gained considerable momentum from the elucidation of the structure of the LH2 antenna complex of the photosynthetic purple bacterium *Rhodospseudomonas acidophila*.¹ Bacteriochlorophyll is the most abundant chromophore in LH2, and the circular arrangement of 18 of these porphyrin derivatives has attracted special attention.² To elucidate the underlying structure–property relation of these subtly organized arrays of chromophores a large variety of covalently bound multiporphyrinic arrays have been synthesized.^{3–5} To fully understand the relation between the three-dimensional structure and the photophysical properties a more thorough knowledge is required of the dependence of the photophysics of a multichromophoric array on the two possible kinds of interchromophoric interactions, electrostatic and electronic.⁶

The properties of photoexcitations of multichromophoric arrays are frequently discussed in terms of excitons by analogy with the theory of excitations in molecular crystals.^{7,8} An exciton is a neutral, bound electron–hole pair which has properties that differ from those of the excited state of an isolated chromophore. These differences result from a combination of electrostatic and electron-exchange interactions with other identical chromophores in the vicinity.

If electron exchange between chromophores is inhibited, that is, the exciton is localized almost exclusively on a single

chromophore, then the interchromophoric interactions will be mainly electrostatic in origin. Such a tightly bound electron–hole pair is referred to as a Frenkel exciton.^{8,9} Transfer of energy within a chromophoric array in this case occurs via the concerted recombination of the exciton on one chromophore and excitation of its neighbor, mediated via the transfer of a virtual photon. This mechanism of energy migration, which is usually referred to as Förster transfer,¹⁰ can result in “photonic-wire” characteristics of one-dimensional arrays.

Electronic interaction, either by direct overlap of the π -orbitals of the chromophores or mediated by the orbitals of the intervening bridge, allows electron exchange between individual chromophores to occur. As a consequence, the hole and electron, forming the exciton, are not necessarily localized on the same chromophore at any given moment. In molecular crystal theory such a weakly bound electron–hole pair is referred to as a Wannier–Mott exciton.^{8,11,12} The process of exchange of the electron and hole between chromophoric units offers an additional pathway for exciton migration which is not available to Frenkel excitons. If thermal energy suffices to overcome the Coulombic attraction between the electron–hole pair of a Wannier–Mott exciton, it can dissociate into separate mobile charge carriers.

The optical properties of Frenkel excitons only differ from those of an isolated chromophore by small red or blue shifts of absorption bands, which are the result of Davydov splitting.^{13,14} The size and sign of this purely electrostatic effect depends on the magnitude of the transition dipole moment associated with the particular excitation and the relative orientation of the chromophores involved, as described by Kasha et al.¹⁵ Wan-

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nier–Mott excitons, on the other hand, can display relatively large shifts to lower energies of the lowest absorption and emission bands because of the increased conjugation length and the creation of new charge-transfer states. In this case the effects are independent of the transition dipole moment of the original excitation, and they depend on the relative orientation only insofar as it affects the electronic coupling matrix element between chromophores.

In addition to such distinguishing differences in optical properties, it should in principle be possible to differentiate Frenkel and Wannier–Mott type excitons by their polarizabilities. Thus, the strongly bound electron–hole pair of the former should be only weakly polarizable, whereas the weak binding of the latter should be apparent as a relatively large polarizability. Measurement of the polarizability of photoexcitations has recently become possible using the flash-photolysis time-resolved microwave conductivity technique (FP-TRMC)^{16,17} by which the changes in the real and imaginary components of the dielectric constant of a solution occurring on photoexcitation of the solute can be monitored. Changes in the molecular polarizability are observed as a change in the real part of the complex permittivity: the dielectric constant.^{18–21}

A previous article²² on covalently bridged porphyrin dimers showed that the type of interchromophoric interaction prevailing is strongly dependent on the nature of the intervening bridge. A 1,4-phenylene bridge, for example, allows only electrostatic interaction between the attached porphyrins because of steric hindrance, which forces the 1,4-phenylene unit out of coplanarity with the porphyrin rings^{23,24} and prevents efficient π -orbital overlap. On the other hand, electronic interactions dominate when a 1,4-butadiynylene bridge is used. The efficient electronic coupling via ethynylene bridges has been substantiated by theoretical calculations²⁵ and is ascribed to a cumulenonic resonance structure of the bridging unit in the excited state.^{26,27} In this article we have investigated the effect of increasing the number of porphyrin moieties in linear multiporphyrinic arrays on the polarizability and optical properties of the singlet and triplet excited states in relation to the prevailing interchromophoric interaction.

Experimental Section

In Figure 1 the molecular structures of the pentamers of the two series of porphyrin oligomers investigated are given to illustrate the major differences. The methods of synthesis and structural characterization of the compounds under investigation have been given in other publications,^{28–30} which are indicated in the last column of Table 1. The exact structures of the other oligomers investigated can be found in these references as well. Throughout this article the following pseudonyms are used: (PB)_n for the 1,4-phenylene-bridged compounds and (yPy)_n for the 1,4-butadiynylene-bridged compounds, where *n* equals the number of porphyrins in the oligomer.

All measurements were performed in benzene (Merck, Uvasol). The solute concentrations range between 10^{−5} and 10^{−4} M. To prevent aggregation 1 wt % 1,4-diazabicyclo[2,2,2]octane [DABCO (Aldrich 98%)] was added, which is equal to a concentration of 10^{−2} M. The large excess of DABCO ensures that only a negligible amount of solute molecules is present as ladders.²⁸

Optical absorption spectra were recorded on a Kontron Uvikon 940 spectrophotometer or a Perkin–Elmer Lambda 20 UV–Vis–NIR spectrophotometer. Emission spectra were recorded either on a PTI quantmaster II spectrofluorimeter equipped with a double-excitation and a single-emission mono-

chromator or on a FluoroMax-2 spectrofluorimeter fitted with a red-sensitive R928P photomultiplier. All samples were excited at a wavelength close to the maximum of their B-band. The optical density at the excitation wavelength never exceeded 0.2.

The fluorescence lifetimes of the (PB)_n series 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 (yPy)_n series the fluorescence lifetime was determined with a time resolution of less than 100 ps using the 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.

For the TRMC experiments the solutes were contained in an X-band (8.2–12.4 GHz) resonant cavity and were photoexcited at 308 nm using single unfocused 7-ns full width at half-maximum (fwhm) pulses from a Lumonics HyperEX-400 XeCl excimer laser. A maximum of 16 pulses was used for signal averaging. The optical densities of the solutions varied from ca. 0.3 to 0.9 for a 1-cm path length. Before use, the solutions were purged with CO₂ to remove oxygen. A pair of transients was recorded at the lower, *f*−, and upper, *f*+, half-power frequency. The real and imaginary contributions to the photoinduced changes of the complex dielectric constant, $\Delta\epsilon'$ and $\Delta\epsilon''$, can be obtained separately by subtraction and addition of the *f*− and *f*± transients, respectively. The procedure for the analysis of the data is given in previous publications.^{18,22}

Results and Discussion

TRMC Results. As mentioned in the previous section, changes in both the real and imaginary component of the complex permittivity, $\Delta\epsilon = \Delta\epsilon' - j\Delta\epsilon''$, resulting from photoexcitation of the solute molecules can be measured separately with the FP-TRMC technique. A change in the imaginary component or dielectric loss, $\Delta\epsilon''$, is related to the formation of mobile charges. This results from either translational motion of free-charge carriers or rotational motion of dipolar excited states. Changes in the real component or the dielectric constant, $\Delta\epsilon'$, indicate an increase in the polarizability of the solute molecules after excitation, $\Delta\alpha$. Out-of-phase motion of mobile charges can also contribute to $\Delta\epsilon'$. Therefore, it is possible to determine $\Delta\alpha$ from $\Delta\epsilon'$ only when an estimate of this contribution to $\Delta\epsilon'$ can be made from a knowledge of $\Delta\epsilon''$. For convenience of presentation the change in polarizability per excited molecule is expressed as the change in polarizability volume, $\Delta V_p (= \Delta\alpha/4\pi\epsilon_0)$.

The $\Delta\epsilon'$ and $\Delta\epsilon''$ transients for the pentamers of each series, (PB)₅ and (yPy)₅, are shown in Figure 1. No significant $\Delta\epsilon''$ transient is observed in either case. This is found for all of the oligomers investigated and shows unequivocally the absence of any contribution to $\Delta\epsilon'$ from mobile charges or dipolar excited states. It can be concluded therefore that only neutral excitons are formed and ΔV_p can be derived from $\Delta\epsilon'$ using eq 1.²²

$$\Delta V_p = \frac{9}{4\pi(\epsilon' + 2)^2 N^*} \Delta\epsilon' \quad (1)$$

In eq 1 *N** is the concentration of excited states and ϵ' is the dielectric constant of the solution.

Values of ΔV_p of the excited states formed were derived from fits to the $\Delta\epsilon'$ transients. Because only neutral excited states are populated, only contributions from the lowest singlet, *S*₁, and the lowest triplet state, *T*₁, were taken into account. The

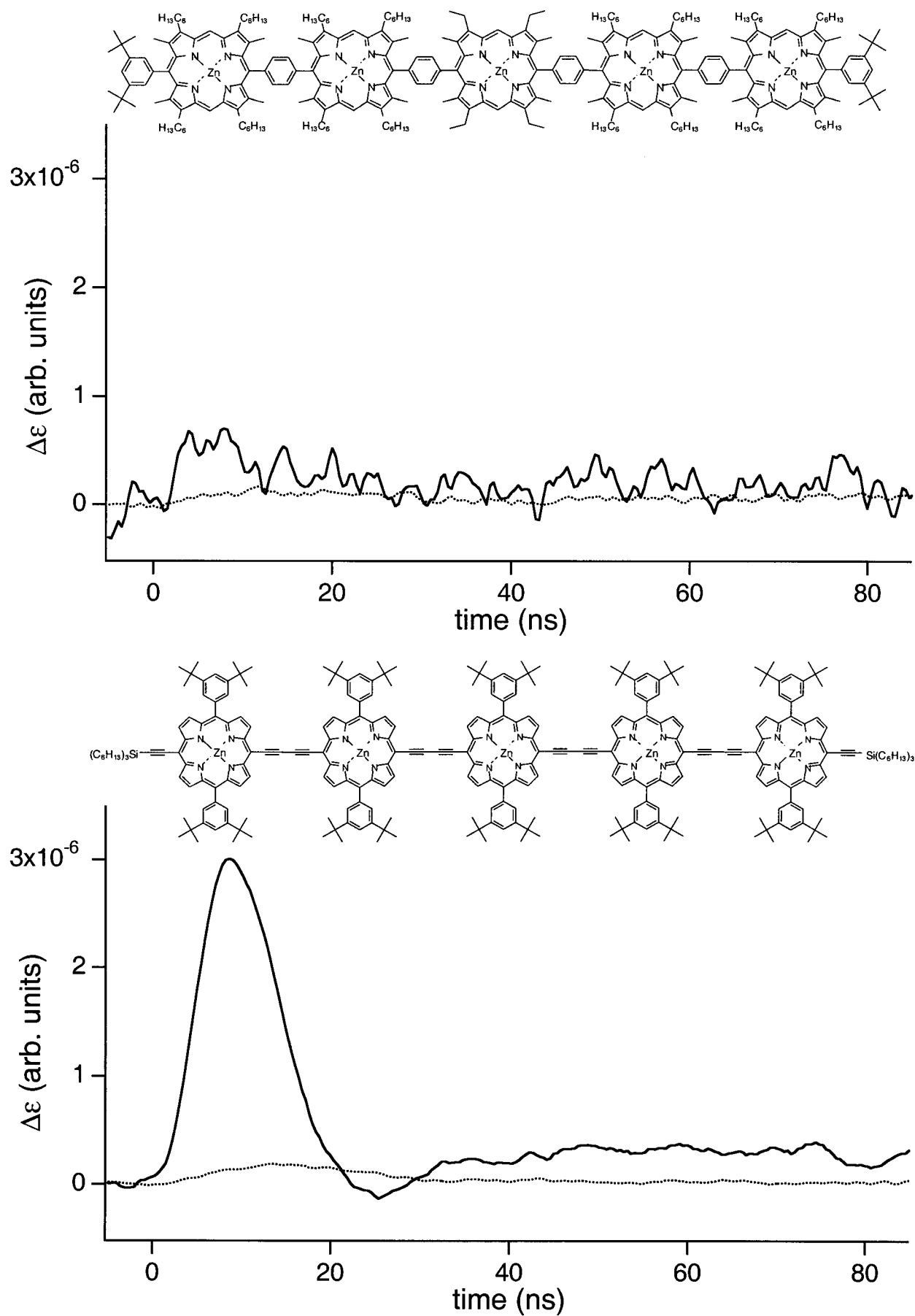


Figure 1. The molecular structure of (PB)₅ and (yPy)₅ shown together with their real (full line) and imaginary (dotted line) $\Delta\epsilon$ transient measured on dilute solutions in benzene with 1% DABCO.

TABLE 1: The Fluorescent Lifetime, $\tau(S_1)$, the Excess Polarizability Volume of the Singlet State, $\Delta V_p(S_1)$, the Product of the Intersystem Crossing Efficiency and the Excess Polarizability Volume of the Triplet State, $\phi_{isc}\Delta V_p(T_1)$, and the Maximum of the Fluorescence, $E_{fl,max}$

compound	$\tau(S_1)$ (ns)	$\Delta V_p(S_1)$ (Å ³)	$\phi_{isc}\Delta V_p(T_1)$ (Å ³)	$E_{fl,max}$ (eV)	ref ^a
(PB) ₁	1.30 ^b	<20 ^c	<5 ^c	1.91	29
(PB) ₂	0.90 ^b	<20 ^c	<5 ^c	1.89	30
(PB) ₃	0.75 ^b	<20 ^c	<5 ^c	1.90	30
(PB) ₅	0.65 ^b	<20 ^c	<5 ^c	1.89	30
(yPy) ₁	1.60	30 ± 20	<5 ^c	1.90	28
(yPy) ₂	1.25	400 ± 40	30 ± 5	1.64	28
(yPy) ₃	1.08	690 ± 70	20 ± 5	1.55	28
(yPy) ₄	0.89	920 ± 90	16 ± 5	1.51	28
(yPy) ₅	0.82	830 ± 80	12 ± 5	1.50	28
(yPy) ₆	0.86	960 ± 100	10 ± 5	1.49	28

^a Reference to synthesis. ^b Fastest component of a two-component fit; in all cases a second component with a lifetime of ca. 5 ns was used. ^c Upper limit corresponding to the noise level.

lifetimes of the S_1 states used in the fitting procedure were obtained from fluorescence decay measurements and are given in Table 1. The lifetime of the T_1 state was not measured but, because no decay of the T_1 state is observed in the first 100 ns after excitation, it is expected to be at least several microseconds. In the fitting procedure it is sufficient to use an arbitrary lifetime of 1 μ s for all molecules investigated. The use of longer T_1 lifetimes in the fitting procedure does not yield significantly different results. The value of $\Delta V_p(S_1)$ could be obtained directly from the fits, because the quantum yield for formation of S_1 may be assumed to be unity. For the triplet state, however, only the product $\phi_{isc}\Delta V_p(T_1)$ could be obtained, with ϕ_{isc} the quantum efficiency for intersystem crossing. The values of $\Delta V_p(S_1)$ and $\phi_{isc}\Delta V_p(T_1)$ are given in Table 1.

(PB)_n Series. None of the $\Delta\epsilon'$ transients of any member of the (PB)_n series exceeded the noise level. Because of this, only an upper limit of 20 Å³ could be determined for $\Delta V_p(S_1)$. No measurable transient changes are observed for the longer oligomers of the (PB)_n series, just as for the monomer (PB)₁. Therefore, we conclude that the excited singlet state of the (PB)_n series is localized on a single chromophore and consists of a tightly bound electron–hole pair. This means that the S_1 excited state of the (PB)_n series can be characterized as a Frenkel type exciton.

Similarly, for the product $\phi_{isc}\Delta V_p(T_1)$ only an upper limit of 5 Å³ could be estimated. Because the quantum efficiency for intersystem crossing for zinc porphyrins is very high, that is, ϕ_{isc} is close to unity,^{31,32} $\Delta V_p(T_1)$ must be close to zero. This shows that the triplet state of the (PB)_n oligomers is also highly localized on a single porphyrin moiety.

(yPy)_n Series. FP-TRMC measurements show a completely different behavior of the (yPy)_n series. Figure 1 displays the large $\Delta\epsilon'$ transient observed for (yPy)₅. The transient consists of a short-lived component and a long-living tail, which is typical for a singlet and a triplet contribution, respectively. Comparable transients are obtained for all other members of the (yPy)_n series, except the monomer, (yPy)₁, whose triplet contribution fails to exceed the noise level. The values of $\Delta V_p(S_1)$ and $\phi_{isc}\Delta V_p(T_1)$ obtained from the fits to the transients are listed in Table 1.

The dramatic increase in $\Delta V_p(S_1)$ from 30 Å³ for the monomer, (yPy)₁, to 400 Å³ for the dimer, (yPy)₂, has been reported previously.²² As seen from the data in Table 1, $\Delta V_p(S_1)$ increases further on increasing the length of the oligomers, up to a value of 960 Å³ for the hexamer. This value is more

than twice the 400 Å³ of the dimer, indicating a delocalization of the exciton wave function over most of the available chromophores even in the longest oligomers. Therefore, the electron–hole pair on the (yPy)_n oligomers is only weakly bound and the exciton must be of the Wannier–Mott type. Because electron exchange between the porphyrin chromophores occurs, the required electronic interaction has to be mediated by the intervening bridge. This apparent efficacy of the 1,4-butadiynylene bridge in promoting electronic interactions between porphyrins previously has been attributed to the participation of cumulenic resonance structures in the excited state.^{22,25–27,33}

The development of the optoelectronic properties of linear molecular arrays with increasing chain length is frequently discussed in terms of the delocalization or correlation length of the excitonic state. This is a rather ill-defined property, however, which purports to give a measure of the physical extent of the excitonic wave function in terms of the number of monomer units. In the present case the values of the S_1 state polarizabilities, as given by $\Delta V_p(S_1)$ in Table 1, appear to saturate for a chain length of 4 or longer. The effective exciton delocalization length for the present compounds may therefore be concluded to be 3 to 4 monomer units.

Using perturbation theory, the exciton polarizability can be expressed in simple quantum mechanical terms, which relate the polarizability of the S_1 state to the coupling between S_1 and all other states in the singlet manifold according to

$$\alpha = \frac{2}{3} \sum_{n \neq 1} \frac{\mu_{n1}^2}{\Delta E_{n1}} \quad (2)$$

with μ_{n1} , the transition dipole matrix element, and ΔE_{n1} ($= |E_n - E_1|$), the energy gap between S_1 and S_n . For the frequently made simplification of a three-level system involving the ground-state, S_0 , the first excited state, S_1 , and a second state, S_2 , eq 2 becomes

$$\alpha = \frac{2}{3} \left(\frac{\mu_{21}^2}{\Delta E_{21}} - \frac{\mu_{01}^2}{\Delta E_{01}} \right) \quad (3)$$

A large exciton polarizability will result, therefore, from strong coupling between S_1 and an upper state which lies close in energy. In the present case this is probably a state with a high degree of charge-transfer character.

It is interesting to compare our results on the polarizability of S_1 with the results from recent degenerate four-wave mixing (DFWM) experiments on the same (yPy)_n oligomers.³⁴ In the DFWM experiments, a dramatic increase in the second hyperpolarizability constant, γ , was found in going from the monomer to the dimer, 0.0063–0.48 in units of 10^{−45} m⁵/V², followed by successive substantial increases with further increase in the chain length up to $\gamma = 3.1$ for the pentamer. The value of γ can also be described in terms of electronic coupling using a three-state model, which results in eq 4 for nondipolar ground and excited states.

$$\gamma \propto \frac{\mu_{01}^2}{\Delta E_{01}^2} \left(\frac{\mu_{21}^2}{\Delta E_{02}} - \frac{\mu_{01}^2}{\Delta E_{01}} \right) \quad (4)$$

Both α and γ are seen to be large for large values of μ_{21} and to increase with decreasing energy difference between the states in the singlet manifold. The correlation between these two parameters, therefore, is to be expected for the present com-

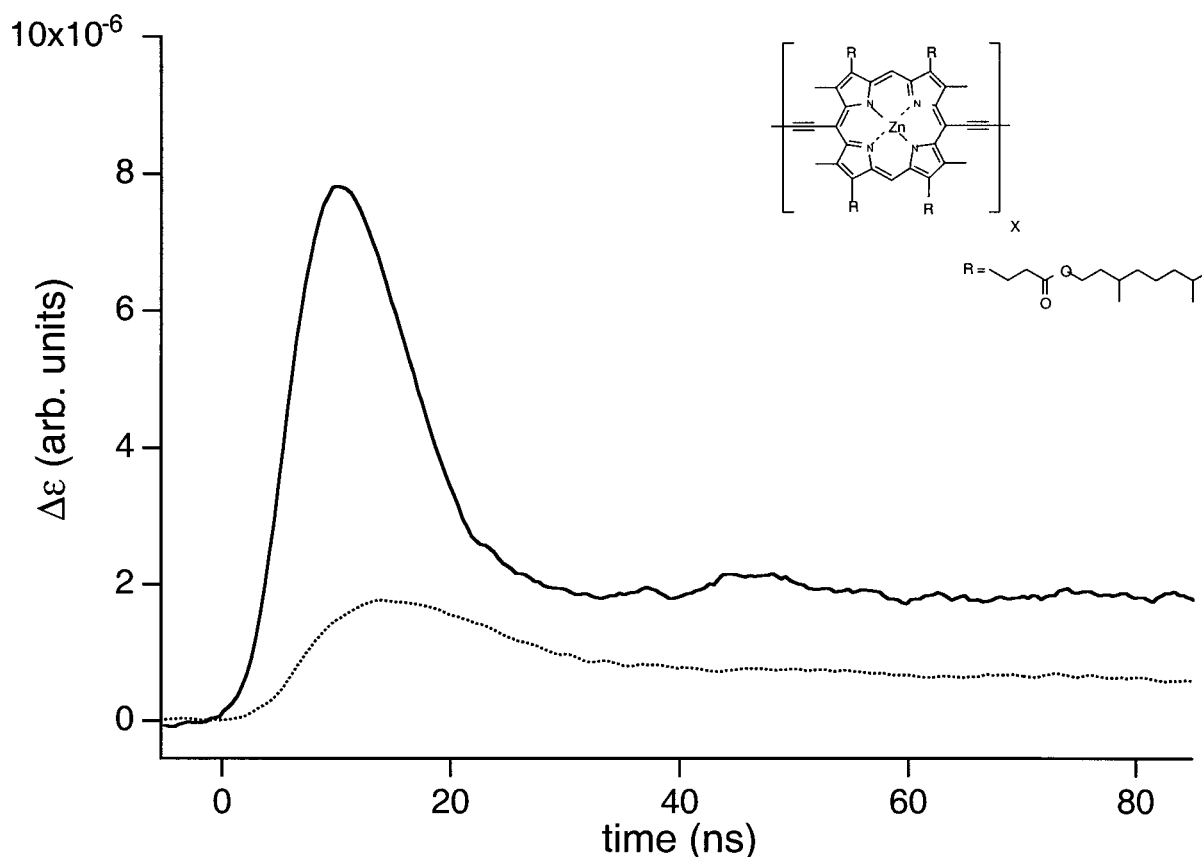


Figure 2. The real (full line) and imaginary (dotted line) $\Delta\epsilon$ transient of the short polymer $(yPy)_x$ measured in benzene with 1% DABCO, and as inset, the molecular structure of $(yPy)_x$ ($x > 10$).

pounds for which the transition energies decrease markedly with increasing chain length.

DFWM measurements on a related short polymer, $(yPy)_x$ with x between 10 and 15, showed again a very large increase in the third-order polarizability in comparison with the longest oligomer.^{34,35} In line with the above-given parallel dependences of α and γ on chain length, a very large $\Delta\epsilon'$ transient is measured for $(yPy)_x$, which is shown in Figure 2. Unfortunately, a complication arises for $(yPy)_x$ that prevents the determination of $\Delta V_p(S_1)$ and $\phi_{isc}\Delta V_p(T_1)$ from the $\Delta\epsilon'$ transient. In a previous publication we reported a significant long-lived $\Delta\epsilon''$ transient after excitation for $(yPy)_x$. This transient, which is also shown in Figure 2, was attributed to the formation of mobile charges by low-yield exciton dissociation.³⁶ This was substantiated by the nonexponential decay of the transient. Because the contribution of the mobile charge carriers to the $\Delta\epsilon'$ transient is not known, eq 1 no longer holds and the value of $\Delta V_p(S_1)$ cannot be determined. However, from the large $\Delta\epsilon'$ transient in Figure 2 it is clear that the primarily formed S_1 state is highly polarizable. A small amount of these Wannier–Mott-like excitons must decay by exciton dissociation to explain the mobile charge carriers responsible for the $\Delta\epsilon''$ transient.

To compare the polarizability volumes of the S_1 and T_1 states, a knowledge of the intersystem crossing efficiency is required to calculate $\Delta V_p(T_1)$ from $\phi_{isc}\Delta V_p(T_1)$. As mentioned in the previous section, ϕ_{isc} for zinc porphyrin derivatives are in general large³¹ and a value of 0.80 has been determined³² for $(yPy)_2$. Using this value $\Delta V_p(T_1)$ is calculated to be 38 \AA^3 , which is an order of magnitude smaller than $\Delta V_p(S_1)$ of the same molecule. Therefore, the T_1 state must be much more localized than the S_1 state of $(yPy)_2$ or any other members of the $(yPy)_n$ series. Actually, the value is very close to the value of 30 \AA^3 found

for the S_1 state of the monomer, indicating that the T_1 state must be considered to be localized on a single porphyrin moiety. This is in agreement with electron paramagnetic resonance (EPR) experiments on a related ethynylene bridged porphyrin dimer and a trimer.³⁷

In view of this, it seems justifiable to conclude that $\Delta V_p(T_1)$ is independent of chain length and has a value close to the 38 \AA^3 determined for $(yPy)_2$. Using this value to calculate ϕ_{isc} from $\phi_{isc}\Delta V_p(T_1)$, a steady decrease in ϕ_{isc} with increasing oligomer length is found: 0.52 for $n = 3$, 0.42 for $n = 4$, 0.32 for $n = 5$, and eventually 0.26 for $n = 6$. Thus, with increasing chain length intersystem crossing becomes increasingly less favorable as a decay pathway for the S_1 state.

Optical Measurements. The ultraviolet–visible (UV–Vis) absorption spectra of monomeric zinc porphyrins are characterized by two main features in the visible range: the Q-band (S_0 -to- S_1 transition) and the B-band (S_0 -to- S_2 transition). The B-band is an extremely intense and sharp absorption band in the 400–500-nm region of the spectrum. The Q-band is considerably weaker than the B-band. It also displays vibrational structure. The emission band of a monomeric zinc porphyrin is usually a mirror image of the Q-band.

The extremely large transition dipole moment of the B-band can strongly interact electrostatically with other porphyrin B-band transition dipole moments in its vicinity. Because the B-band actually consists of two degenerate transitions, which are orthogonal, their respective transition dipole moments can interact differently. If this occurs, the B-band will split. This phenomenon, first recognized as such by Kasha et al., is an example of Davydov splitting^{14,15} and is a clear indication of an electrostatic interaction. Because of the much weaker

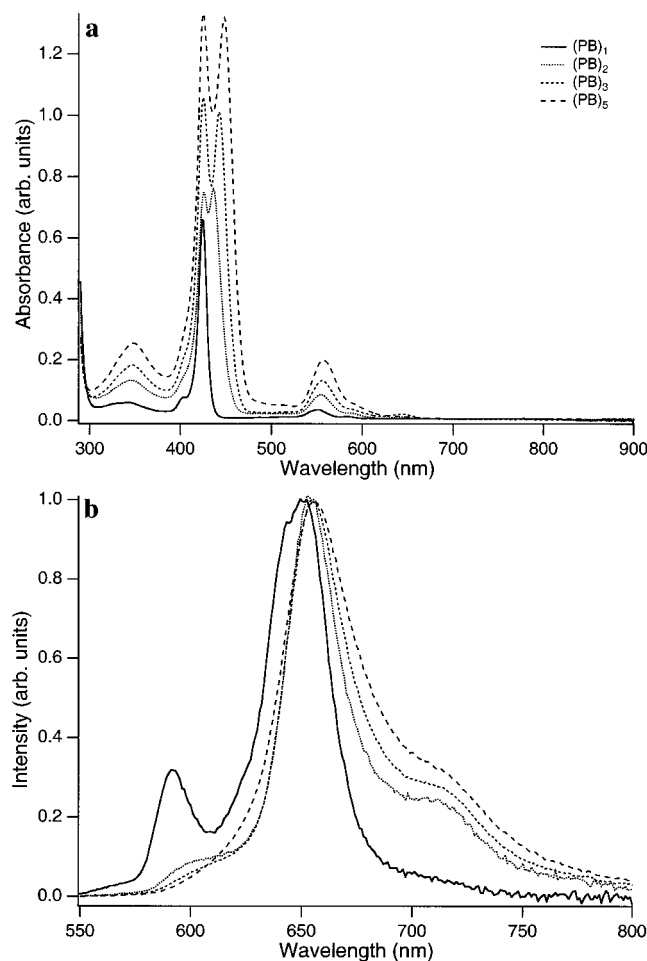


Figure 3. The UV-Vis absorption (top) and emission (bottom) spectra of the (PB)_n series in benzene with 1% DABCO.

transition dipole moment of the Q-band, Davydov splitting has never been observed for this absorption band for porphyrin derivatives.

Electronic interactions between an orbital of a single chromophore and an orbital close in energy of, for instance, the intervening bridge or an identical chromophore in its neighborhood will replace these two localized orbitals by a pair of new and more extended orbitals. The energy difference between these new orbitals will be proportional to the magnitude of the interaction. If the interaction involves a pair of the highest occupied or lowest unoccupied orbitals the energy gap between the ground state and the excited state will be reduced. A bathochromic shift of the affected absorption band will result. Therefore, substantial changes in the position and shape of absorption bands with increasing chain length suggest electronic interactions between at least some of the chromophores of an oligomer.

Considering the different effects to be expected for electrostatic and electronic interchromophoric interactions on the optical properties of multiporphyrinic arrays, as outlined in the previous paragraphs, it was of interest to compare the FP-TRMC results with the concomitant changes in the optical absorption and emission spectra.

(PB)_n Series. The optical absorption and emission spectra for the (PB)_n series are shown in Figure 3. As expected for Frenkel excitons, the optical data show no indication of electronic interaction between the chromophores. Apart from the splitting of the B-band the spectra of the three oligomers strongly resemble each other, and even the spectrum of the

monomer, (PB)₁. The position and shape of the Q-band is completely unaffected by the successive addition of porphyrin subunits within the entire series. This shows that the lowest excited state is unaltered compared with an isolated zinc porphyrin. This is corroborated further by comparison of the emission spectra displayed in Figure 3b. The position of the maximum of the emission spectra, see also Table 1, shows almost no dependence on the number of chromophores. Only a slight bathochromic shift of the maximum and a change in the shape of the spectrum is observed on going from (PB)₁ to (PB)₂. A further shift of the emission maximum with an additional increase in the number of monomer units is completely absent.

The splitting of the B-band, which is observed for all members of the (PB)_n series except the monomer, increases with the number of porphyrin subunits in the chain. Similar behavior has been observed for a closely related (PB)_n series in 1,2-dichlorobenzene as solvent.³⁸ The splitting of the B-band of the oligomers results in two bands of almost identical magnitude and similar width. The highest energy band has a maximum at 2.92 ± 0.01 eV, independent of the number of monomer units and equal to that found for the monomer itself. The lower energy band is shifted bathochromically with respect to the higher energy band by 0.07, 0.11, and 0.15 eV for $n = 2, 3$, and 5 , respectively. This is characteristic for Davydov splitting. According to the Kasha treatment, the bathochromic shift indicates that the main electrostatic interaction involves the transition dipole in the oligomer chain direction. In agreement with this, the evolution of the shift with increasing monomer units is close to that expected, that is, $\Delta E \propto (n - 1)/n$, for in-line dipoles.^{39,40} The lack of an appreciable blue shift of the higher energy band indicates that the electrostatic interaction between the transition dipole moments orthogonal to the chain direction is extremely weak.

(yPy)_n Series. Evidence for strong electronic interactions in the (yPy)_n series, as indicated by the polarizability measurements, is apparent from the marked dependence of the position of the Q-band on the length of the oligomer, as shown in Figure 4a. In addition to the marked shift of the Q-band to lower energy, its shape is also altered considerably. The structured Q-band with its two maxima typical for a zinc porphyrin is replaced by a broad band that consists of several Gaussian subbands. The different bands can be readily observed as shoulders in the Q-band of the trimer and tetramer. In the longest oligomers they merge completely into a single broad and structureless band.

A pronounced bathochromic shift and broadening is also observed in Figure 4b for the emission spectra of the (yPy)_n series. The shift of the emission is more pronounced than that of the Q-band absorption. This means that the Stokes' shift increases with chain length. For two short *meso-to-meso* ethynylene-bridged porphyrin oligomers, Kumble et al. showed that the Stokes' shift of these oligomers is considerably larger than that of a single porphyrin.³³ They hypothesized that the increase in Stokes' shift in these molecules could result from a relaxation process that forces the porphyrin rings of a single oligomer to adopt a coplanar geometry in the excited state. In this coplanar geometry the conjugation extends over all chromophores and a highly delocalized excited state results, which was expected to be highly polarizable. The hypothesis of Kumble et al. is corroborated by the present TRMC measurements, which unequivocally show this large excited-state polarizability. Therefore, in line with this hypothesis, we think it is reasonable to relate the increase of the Stokes' shift with increasing chain length to the increase in the number of bridges

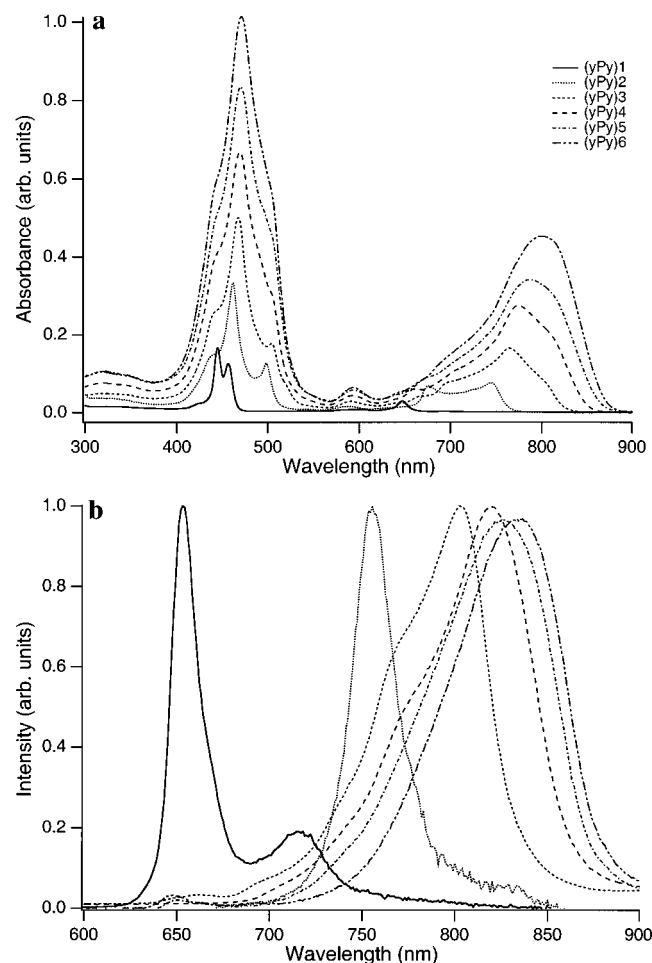


Figure 4. The UV–Vis absorption (top) and emission (bottom) spectra of the (yPy)_n series in benzene with 1% DABCO.

which must adopt a partial cumulenonic bond length pattern to allow the extensive delocalization typical for Wannier–Mott excitons.

In contrast to the Q-band, the position of the B-band is hardly affected by the number of repeat units in the oligomers. A marked change is observed, however, on going from the monomer to the dimer; there is a substantial shift of the maximum and a change in the splitting pattern. From the trimer onward, only minor shifts of the maximum are observed with increased oligomer length, and the shape of the band hardly alters between (yPy)₂ and the longest oligomer, (yPy)₆. Only a gradual broadening of the individual subbands appears to occur with increasing chain length.

The two maxima of the B-band of the monomer (yPy)₁ indicate that the two orthogonal B-band transitions are no longer degenerate in the (yPy)_n series. It is tempting to simply attribute this to the unequal substitution at the two pairs of opposite *meso*-positions, but it is unclear if this is indeed the reason. The splitting pattern of the other members of the (yPy)_n series can be understood from the spectrum of (yPy)₁ by assuming electrostatic interactions between neighboring chromophores.

In a recent article, Arnold and co-workers introduced a model that seemed to explain the complex shape of the entire UV–Vis spectra of the neutral and the mono- and bis-anion of a butadiynylene-bridged porphyrin dimer from electronic interactions alone.⁴¹ An important prediction of their “eight orbital model” is that pronounced changes in the Q-band should be accompanied by similar changes in the B-band. Figure 4a shows unequivocally that this is not the case for the longer oligomers.

Therefore, in contrast to the Q-band of the (yPy)_n series, the B-band is affected mainly by electrostatic interactions.

Conclusion

The photophysics of an array of porphyrins depends strongly on the type of interaction between the chromophores. The two series investigated in this article confirm that these properties are determined to a large extent by the nature of the bridge in linear covalently linked arrays.

The 1,4-phenylene bridging unit of the (PB)_n series electronically isolates the porphyrin chromophores. The optical data of all oligomers investigated strongly resemble that of a single porphyrin. The only difference between the spectra is Davydov splitting of the B-band, which results from electrostatic interaction between porphyrins. On excitation only Frenkel excitons are formed. The strongly bound character of the electron–hole pair is shown by the FP-TRMC technique, that is, on photoexcitation a negligible increase in polarizability is observed.

The 1,4-butadiynylene bridging unit of the (yPy)_n series mediates electronic interaction between the porphyrin chromophores via a cumulenonic resonance structure. A substantial bathochromic shift of the Q-band is observed with increasing number of porphyrin units in an oligomer. The FP-TRMC technique shows the formation of a neutral but highly polarizable excited state. This kind of behavior is in agreement with the formation of a weakly bound electron–hole pair characteristic of a Wannier–Mott-like exciton. The delocalization of the exciton is seen to increase with increasing chain length, even up to 6 porphyrin units. For a polymeric (yPy)_x derivative with $x > 10$, evidence is found for dissociation of the Wannier–Mott type exciton into separate mobile charges.

For both oligomer series the T₁ state is localized on a single porphyrin unit.

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