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# Photoinduced vectorial charge transfer in mixed Langmuir–Blodgett films of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin and its zinc(II) derivative

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Langmuir–Blodgett films containing 1 mol% 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (TBP) and its zinc(II) complex (ZnTBP) in a suitable matrix were prepared in an attempt to build a molecular-scale device capable of vectorial photoinduced electron transfer. The films were studied by absorption and fluorescence spectroscopies, and by the time-resolved measurement of Maxwell displacement charge (TRMDC) across the film. The latter experiments showed that photoinduced electron transfer takes place in the films and that its macroscopic direction can be controlled by the molecular orientation. The TRMDC signals were unusually long-lived.

## Introduction

The Langmuir–Blodgett (LB) technique is a well-known and inexpensive method for creating highly organized molecular structures.[1] It is often used in applications utilizing light harvesting and conversion functions of molecules similar to those found in natural photoreaction centres. Chromophores, responsible for a certain function, can be incorporated into a layer of supporting matrix molecules and transferred onto a solid support. The density of the chromophores in the LB films is high, which usually results in the formation of aggregates. On one hand, the aggregation can be considered as an advantage. The associate of an electron donor and an acceptor is an aggregate with a desirable property; the ability to transfer an electron fast and efficiently. On the other hand, extensive aggregation of the chromophores can open competitive channels for excitation relaxation and reduce the efficiency of the desired function.

A molecule widely used in the design of molecular electron transfer systems is porphyrin.[2–3] Numerous covalently linked donor–acceptor (DA) dyads[4–7] and more complex structures[8–10] have been synthesized and have proven to work well as light antennae and primary electron donors. Under certain conditions, free base porphyrins can be used as an intermediate or final electron acceptor.[11–13]

Different porphyrin derivatives have also been used in the preparation of thin films by the LB method.[14–19] Studies show that porphyrins can be incorporated into the film without significantly altering their light harvesting and electron transfer properties, although they can form low dimensional associates, like dimers.[18]

Previously we have shown that free base 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (TBP) can, when mixed with octadecylamine, be deposited as multilayer LB films.[18] The lifetime of its singlet excited state remains essentially long, a few nanoseconds, even at relatively high concentrations ($>10\%$). The TBP molecules are mainly present as monomers and face-to-face dimers whose macrocycles are parallel to the solid substrate. The relative dimer concentration is independent of the total concentration of the porphyrin, indicating that the dimers are formed because of a specific interaction between the *tert*-butyl groups and the matrix.

The tendency of TBP to form dimers in LB films offers a potential opportunity to construct a heterodimer of TBP and a suitably modified derivative in such a way that the final structure can perform electron transfer perpendicular to the plane of the film. In the present study, the electron-donating properties of the porphyrin macrocycle were enhanced by inserting a central metal, zinc, into TBP. The goal of the present work is to find out whether TBP–ZnTBP heterodimers are formed in LB films and whether they can perform photoinduced electron transfer. For the film to have practical use in the conversion of light signals to electrical signals, the electron transfer should have a macroscopic direction. This requires that the donor–acceptor (DA) structures, in the present study the TBP–ZnTBP dimers, should be uniformly oriented with respect to the plane of the film.

## Materials and methods

3,5-Di-*tert*-butylbenzaldehyde was synthesized by a literature method,[20] and pyrrole condensation[21] was used to obtain TBP, which was crystallised in a carbon tetrachloride–acetonitrile mixture. ZnTBP was obtained by metallating TBP as described in the literature.[22] *n*-Octadecylamine (ODA) was purchased from Sigma-Aldrich and used without further purification. Water was purified with a Milli-Q water de-ionising system (Millipore Corporation). A solution containing 1 mM $Na_2HPO_4$ and 0.2 mM $NaH_2PO_4$ (pH 6.5) was used as the subphase.

The LB films were prepared using a single- or a double-compartment Langmuir trough (LB 5000, KSV Instruments, Helsinki, Finland) with Wilhelmy plate surface balances interfaced to a computer with software supplied by the manufacturer. The monolayer was compressed at a rate of about 0.02 $nm^2\ min^{-1}\ molecule^{-1}$. The deposition speed was 10 $mm\ min^{-1}$. After the first withdrawal, the slides were allowed to dry for 1200 s and the subsequent dipping cycles were separated by 500 s pauses.

The LB films for absorption and fluorescence spectroscopic studies were deposited as Y-type films on rectangular quartz slides ($36\times12\times1$ mm), which had been cleaned using a standard procedure.[23] The LB films for transient Maxwell

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displacement charge (TRMDC) studies were deposited on quartz slides with a vacuum-vaporized layer of indium tin oxide semiconductor (ITO) on one side. Before use, the slides were cleaned with chloroform. The slides were first covered with 9 or 10 layers of 100% ODA in order to insulate the ITO electrode from the active layers. Every second layer of the subsequent 20 was a porphyrin–ODA layer; the layers in between were 100% ODA layers. Finally, 10 100% ODA layers were deposited to provide insulation from the liquid metal electrode of the TRMDC instrument. For a given sample, all the layers containing porphyrin were deposited either upstroke or downstroke. If the DA structures (heterodimers) are formed on the floating monolayer and if they have a preferred orientation on the water surface, they should be uniformly oriented throughout the film in an ideal case.

UV–Vis absorption spectra were measured using a Shimadzu UV-2501PC instrument. Fluorescence spectra were recorded using a Fluorolog-3 spectrofluorometer equipped with an R928 photomultiplier detector from Instruments S.A., Inc. Fluorescence was collected at 90° to the excitation beam and the LB film slides were oriented so that the excitation light was reflected away from the detector. Fluorescence decay curves were measured with a time-correlated single photon counting instrument described elsewhere.[24] The samples were excited at 590 or 570 nm. The full width at half maximum (FWHM) of the instrumental response function was about 100 ps. At least $10^4$ counts were collected in the highest channel.

For decay-associated spectra (DAS), fluorescence decay curves were measured at several wavelengths over the fluorescence band. Counts were collected for 120 s for each curve. All the decay curves of a given sample were then fitted globally using a multiexponential decay model $I(t) = a_0 + \Sigma a_i \exp(t/\tau_i)$. The pre-exponential factors $a_i$ corresponding to different lifetimes $\tau_i$ were plotted as a function of wavelength.

The instrument for measuring time-resolved Maxwell displacement charge (TRMDC) has been described in detail earlier.[25–27] The samples were excited by a dye laser ($\lambda = 430$ nm), whose pulse width (20 ns) determined the time resolution of the system. One of the electrodes was the ITO layer on the quartz slide on which the LB film was deposited, the other was a droplet of indium–gallium liquid metal alloy gently touching the topmost layer of the film. The quality of the film and electrodes was checked by measuring the capacitance and resistance of the samples. Typically, the resistance was much higher than 10 GΩ. The capacitance $C_s$ of the samples was 50–100 pF. The pre-amplifier of the instrument had an input resistance $R_{in}$ of 100 MΩ or 10 GΩ. Consequently, $R_{in}$ and $C_s$ formed a circuit with a time constant $R_{in}C_s = 10$ ms or 1 s, respectively. Signals measured on time scales shorter than these were directly proportional to the charge displacement.

## Results

In this work, the functional units responsible for electron transfer in the LB films presumably consist of both TBP and ZnTBP. If such units are formed in statistically significant quantities, one can expect changes in the optical and electrical properties of the films compared with films containing only one type of porphyrin. Obviously, the two porphyrin molecules in such units should be close to each other. Therefore, the absorption and fluorescence properties of the functional units may be different from those of isolated porphyrins. In addition, electron transfer provides an alternative decay pathway for the excited states and decreases the fluorescence intensity. The Maxwell displacement charge measurements should directly reveal whether the films are capable of light-induced vectorial electron transfer.

### LB films

TBP[18] and ZnTBP do not form stable monolayers alone, but when mixed with an ODA matrix, stable films are formed. To avoid extensive aggregation, low molar fractions, 1–2%, of porphyrin in the films were used. In the porphyrin–ODA monolayers, the collapse pressure of the ZnTBP film is 15 mN m$^{-1}$, whereas for the TBP film it is 35 mN m$^{-1}$.[18]

One way to study the possible formation of heterodimers in the TBP–ZnTBP–ODA monolayers is to measure the $\pi$–$A$ isotherms of monolayers containing different molar fractions of porphyrin. Therefore, a series of isotherms was recorded so that the TBP concentration was kept constant at 1% and the ZnTBP concentration was increased from 0 to 1.3% (Fig. 1). The mean molecular area can be calculated from $A_{mm} = x_p S_p + x_m S_m$, where $x_p$ and $x_m$ are the molar fractions, and $S_p$ and $S_m$ are the areas per molecule for the porphyrin and the matrix, respectively. Since $x_p + x_m = 1$, the expression for $A_{mm}$ can be rearranged to $A_{mm} = S_m + x_p(S_p - S_m)$. This implies that, because $S_p > S_m$, $A_{mm}$ should increase as ZnTBP is added and $x_p$ increases. This is indeed the case at low surface pressures (Fig. 1). However, as the surface pressure increases, three of the four TBP–ZnTBP isotherms come closer together until they cross each other at a surface pressure of about 30 mN m$^{-1}$. For these three isotherms, there is less ZnTBP than TBP in the monolayer. The fourth isotherm corresponds to a monolayer containing more ZnTBP than TBP and shows a larger $A_{mm}$ than the others at all surface pressures up to about 40 mN m$^{-1}$. In short, the added ZnTBP does not increase the total area of the monolayer at high surface pressures, as long as there is a sufficient amount of TBP in the film. This suggests that the surface pressure affects the formation of TBP–ZnTBP heterodimers. To confirm this by spectroscopic studies, LB films were deposited at various surface pressures ranging from 8 to 30 mN m$^{-1}$.

The two porphyrins deposited quite differently from porphyrin–ODA monolayers. The transfer ratios for TBP were about unity at surface pressures higher than 15 mN m$^{-1}$ and about 0.8 at 8 mN m$^{-1}$. ZnTBP could only be deposited below its collapse pressure, but even then, the transfer ratios varied from about 0.6 to 1. LB films deposited from monolayers containing 1% or 2% ZnTBP in ODA had virtually no porphyrin absorption, even if up to 21 layers were deposited. Absorption was only observed when the monolayer contained more than 5% ZnTBP. Apparently, ZnTBP is squeezed out of the monolayer at high surface pressures and, at low surface pressures, the matrix is not rigid enough to support ZnTBP during deposition. However, according to the optical studies (see below), ZnTBP was deposited from monolayers also containing TBP throughout the surface pressure range tested.

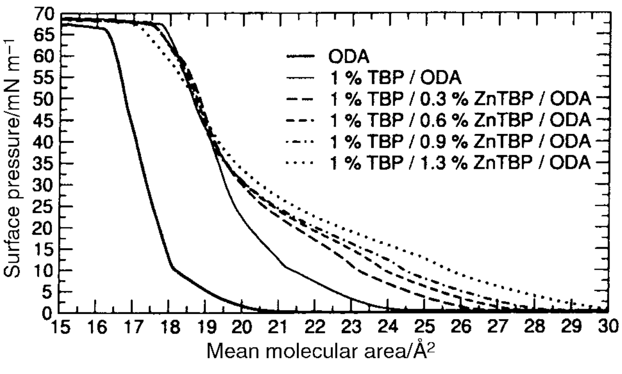

**Fig. 1** A series of $\pi$–$A$ isotherms from monolayers containing 1% TBP and 0–1.3% ZnTBP in an ODA matrix. The mean molecular area corresponds to all the porphyrin and matrix molecules in the film.

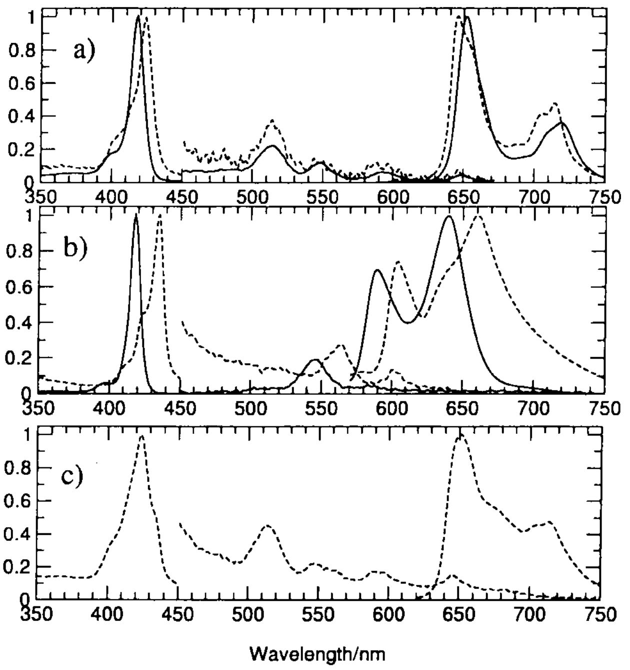

**Fig. 2** Absorption (left) and fluorescence (right) spectra of porphyrins in hexane (—) and in LB films mixed with ODA (- - -): (a) TBP, (b) ZnTBP, (c) 1% TBP–1% ZnTBP–ODA. All the spectra have been normalised to unity and the absorbances have been multiplied by 5 at wavelengths longer than 450 nm.

## Steady-state absorption and fluorescence

Selected absorption and fluorescence spectra of porphyrins in hexane and in LB films have been collected in Fig. 2. The spectra are typical for *meso*-substituted tetraphenylporphyrins. In hexane, the Soret absorption bands of the two porphyrins coincide. In LB films, however, the Soret band of ZnTBP is about 9 nm red shifted compared with that of TBP, possibly because of the complexation of ODA to ZnTBP. The Soret band of ZnTBP in hexane is gradually red shifted by 10 nm as ODA is added to the solution (not shown). Since the zinc atom in zinc porphyrins has a free coordination site and can form 1:1 complexes with various ligands, including organic amines,[28] the red shift of ZnTBP absorption in the films is most probably due to ODA.

The absorption spectra of TBP–ZnTBP–ODA films are slightly blue shifted relative to a model spectrum of a film containing equal amounts of the dyes (Fig. 3). The model spectrum was obtained as follows: the spectra of TBP–ODA and ZnTBP–ODA films were normalised to unity and multiplied by the molar absorption coefficients of the respective porphyrins at the wavelength of maximum absorption. The resulting spectra were superposed and the sum was normalised to unity.

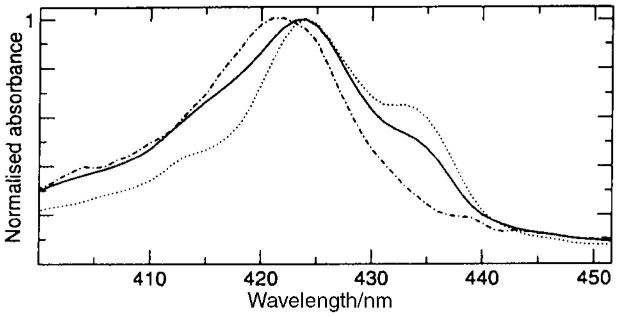

**Fig. 3** Normalised absorption spectra of 1% TBP–1% ZnTBP–ODA LB films deposited at either 8 (-··-) or 30 mN m$^{-1}$ (—). The dotted line (···) represents the calculated absorption spectrum for a film containing equal amounts of TBP and ZnTBP.

The spectra of the TBP–ZnTBP–ODA LB films depend weakly on the surface pressure at which the films are deposited (Fig. 3). The spectrum of the film prepared at the surface pressure of 8 mN m$^{-1}$ is more blue-shifted than the spectrum of the film deposited at 30 mN m$^{-1}$, for which the shift appears only as a blue shoulder. At 433 nm, the model spectrum has a distinct shoulder mainly caused by the ZnTBP–ODA complex. This shoulder is present in the spectrum of the film deposited at 30 mN m$^{-1}$, but not in the spectrum of the 8 mN m$^{-1}$ film.

The fluorescence emission spectra of the mixed TBP–ZnTBP–ODA films are clearly different from any possible linear combination of the component spectra (Fig. 4). The 600 nm band of the ZnTBP emission is completely absent, even when the samples are excited at 433 nm, the Soret maximum of the ZnTBP films. The deposition surface pressure clearly affects the shape of the spectra (Fig. 4). The spectra of films deposited at 20 mN m$^{-1}$ or higher have a broad shoulder centred at 680 nm. This shoulder does not appear in the spectra of TBP or ZnTBP films, or TBP–ZnTBP films deposited at 8 mN m$^{-1}$. In addition, the relative intensity in the red part of the spectrum is higher for the films deposited at higher surface pressures. The spectra are of similar shape, irrespective of whether the sample is excited at 422 nm, where both porphyrins absorb, or at 513 nm, where TBP absorbs almost exclusively.

## Time-resolved fluorescence

Time-resolved measurements allow separation of the fluorescence of species which have different lifetimes. The fluorescence of ZnTBP decays much faster than that of TBP (Fig. 5). The lifetimes for the mixed TBP–ZnTBP films are between those of TBP and ZnTBP, and decrease markedly as the deposition surface pressure increases.

Fig. 6 shows the decay-associated spectra (DAS) for TBP and ZnTBP and for two TBP–ZnTBP films deposited at different surface pressures, 8 and 20 mN m$^{-1}$. To achieve a reasonable $\chi^2$ value, the decay profiles of the TBP film had to be fitted as a sum of two components, whereas the ZnTBP and TBP–ZnTBP films required a three-exponential fit. Although the fluorescence decays of the 1% TBP sample were bi-exponential, the component spectra (7.7 and 2.2 ns) have almost the same shape (Fig. 6a), and are characterized by two maxima at 650 and 715 nm. In the DAS of ZnTBP (Fig. 6b), the fastest (0.2 ns) component has two maxima at 610 and 650 nm, and dominates, especially on the short wavelength part of the spectrum. The other two components (0.5 and 2 ns) have a single maximum at 680 nm.

For the two TBP–ZnTBP films deposited at different surface

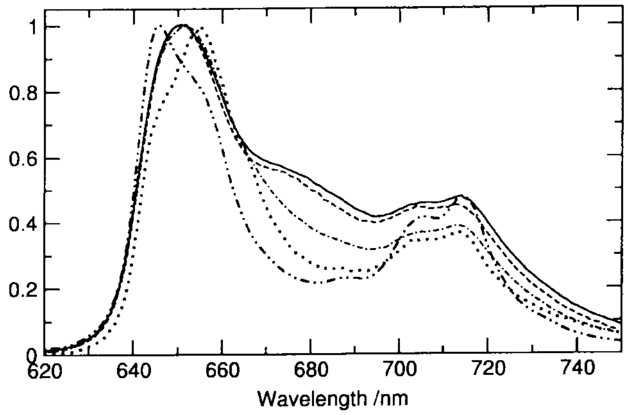

**Fig. 4** Normalised fluorescence emission spectra of 1% TBP–1% ZnTBP–ODA films deposited at surface pressures of 8 (-··-), 20 (---) and 30 mN m$^{-1}$ (—), and 1% TBP–ODA films deposited at 8 (···) and 30 mN m$^{-1}$ (-··-··).

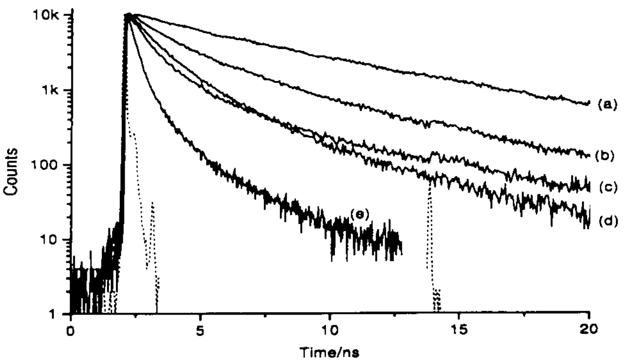

**Fig. 5** Fluorescence decay curves of porphyrin–ODA LB films, measured at the wavelength of maximum fluorescence intensity for each sample: (a) 1% TBP; 1% TBP–1% ZnTBP films deposited at surface pressures of (b) 8, (c) 20 and (d) 30 $\mathrm{mN\ m^{-1}}$ and (e) 5% ZnTBP. The dotted line shows the instrumental response function.

pressures, slightly different sets of lifetimes were obtained (Fig. 6c,d). However, the components with approximately similar lifetimes are supposed to be of the same origin. The components having lifetimes of about 6 and $<1$ ns have almost identical shapes, but different magnitudes at the different surface pressures. For the third component ($\tau \approx 2$ ns), the shape is also changed according to the surface pressure. It is therefore obvious that the 2 ns component causes the shoulder at 680 nm in the steady state emission spectra (Fig. 4) of the films deposited at high surface pressures.

### Maxwell displacement charge measurements

Because of the alternate deposition of the porphyrin-containing and insulating layers, the DA structures should, ideally, be uniformly oriented with respect to the ITO electrode. Therefore, the TRMDC signals measured from films deposited in opposite directions should have opposite signs. This was indeed observed. Fig. 7 shows the signals in three different time domains from microseconds to seconds. The signals are almost symmetrical with respect to the time axis. The charge-separated state is mostly formed on a time scale comparable to the width of the excitation pulse and has a very long lifetime. The apparent lifetimes of the order 0.6 s, obtained from the decay curves measured in the longest timescale in Fig. 7, are already limited by the input resistance of the measuring cell.

Unfortunately, for the films deposited at 8 $\mathrm{mN\ m^{-1}}$, the TRMDC measurements were unsuccessful because of a high leak current between the electrodes. The ODA matrix is still in a liquid-expanded state at 8 $\mathrm{mN\ m^{-1}}$. Therefore, the resulting film is not tight enough to provide sufficient resistance, despite the many insulating layers. Thus, the electron transfer efficiencies of the samples deposited at different pressures cannot be compared.

To ensure that the TRMDC signals originated from the porphyrins, an action spectrum was recorded. The responses were recorded at different excitation wavelengths from 420 to 445 nm. The maximum amplitudes of the decay curves were divided by the excitation energy applied at the corresponding wavelength. The intensities obtained in this way were plotted as a function of the excitation wavelength (Fig. 8). The plot coincides well with the absorption spectrum, but its maximum is shifted to about 428 nm, halfway between the Soret maximum and the shoulder at 433 nm in the absorption spectrum.

## Discussion

The co-existence of different chromophore arrangements in the LB films complicates the analysis of the spectra. Fortunately, with the help of the decay-associated spectra (DAS), some of the molecular species can be identified. The photochemical processes considered between the chromophores are the energy and electron transfer. The latter must take place in the films to account for the observed TRMDC signals. The energy transfer $P_HP^*_{Zn} \rightarrow P^*_HP_{Zn}$ should be favourable because of the strong overlap of the TBP absorption and the ZnTBP fluorescence (Fig. 2), whereas the reverse reaction is energetically inefficient. To simplify the analysis, energy transfer is considered within the different associates but not between them or the monomers. This approximation is justified by the fact that the interchromophore energy transfer in the TBP–ODA films is negligible when the concentration of TBP is less than 3%,[18] as it is in the present study.

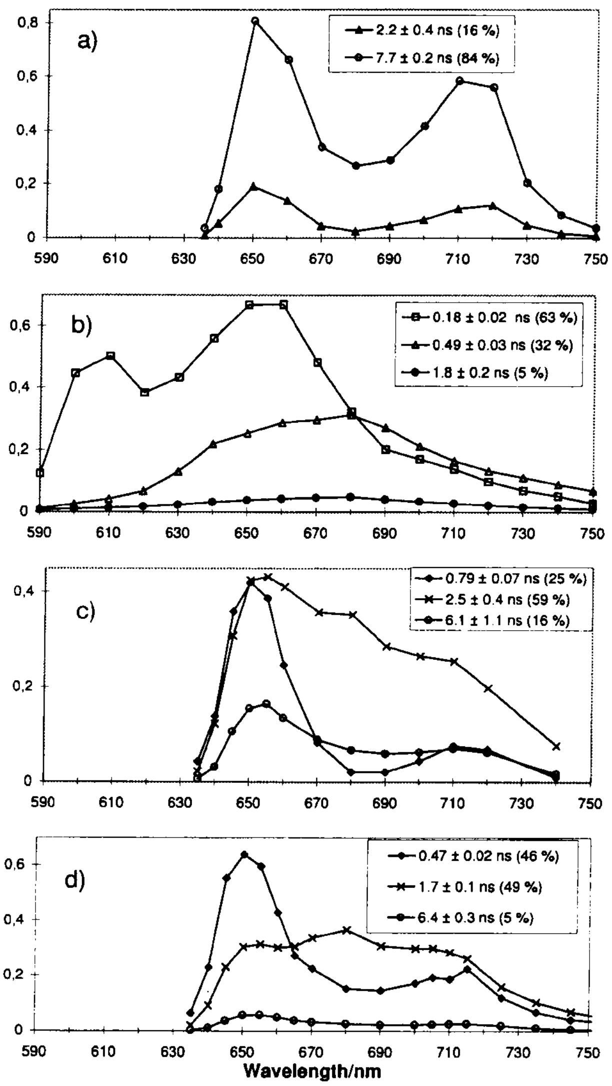

**Fig. 6** Decay-associated spectra (DAS) of porphyrin–ODA LB films with (a) 1% TBP and (b) 5% ZnTBP, and 1% TBP–1% ZnTBP deposited at (c) 8 and (d) 20 $\mathrm{mN\ m^{-1}}$. All the spectra are normalised so that the sum of all components has a maximum value of unity. The lifetimes and their standard deviations are shown in each inset. The overall relative magnitudes (the ratio of the area under the component spectrum to the area under the sum spectrum) of the components are given in parentheses.

In accordance with the previous work,[18] the 7.7 and 2.2 ns components in the DAS of the TBP film (Fig. 6a) are assigned to the TBP monomer and face-to-face dimer, respectively. As the shapes of the component spectra are almost identical, an average lifetime for the TBP singlet excited state over the entire fluorescence spectrum can be calculated. Using the values shown in Fig. 6a, an average lifetime of $\tau_{ave} = 0.16 \times 2.2\ \mathrm{ns} + 0.84 \times 7.7\ \mathrm{ns} = 6.8\ \mathrm{ns}$ is obtained. A component with an approximately similar lifetime and shape is found in the DAS of the TBP–ZnTBP films (Fig. 6c,d). It

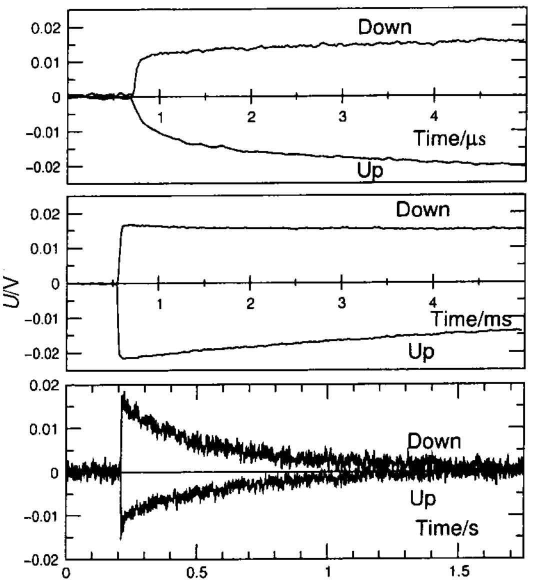

**Fig. 7** Maxwell displacement charge responses at different timescales from two 1% TBP–1% ZnTBP–ODA films, deposited in opposite directions, up or down, at a surface pressure of 30 mN m$^{-1}$.

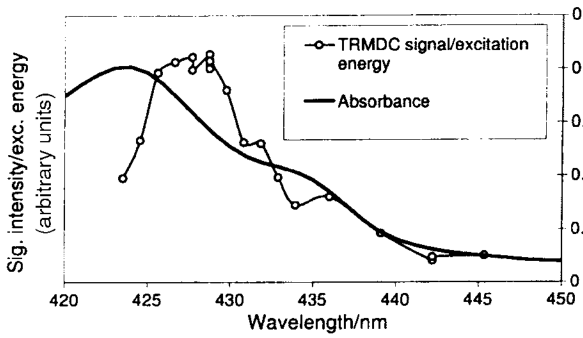

**Fig. 8** TRMDC action spectrum of a 1%TBP–1%ZnTBP–ODA LB film deposited at 20 mN m$^{-1}$ and the absorption spectrum of a similar film.

corresponds to TBP present mainly as monomers and in small part dimers.

The DAS of the ZnTBP film (Fig. 6b) reveals the presence of at least three fluorescing species. One of the components has an approximately similar shape and lifetime to the 2 ns component in the DAS of the TBP–ZnTBP films (Fig. 6c,d). However, these components cannot be of the same origin. As stated in the Results section, the 2 ns component causes the shoulder at 680 nm in the steady-state emission spectra of the mixed films (Fig. 4). This shoulder is present even if the sample is excited at a wavelength specific for TBP. In that case, ZnTBP cannot be excited, even indirectly, because the energy transfer $P^*_H P_{Zn} \rightarrow P_H P^*_{Zn}$ is unfavourable.

The fluorescing species producing the 2 ns component in the DAS of the TBP–ZnTBP films must consist of both TBP and ZnTBP, because no similar species was found in the films containing only one type of porphyrin. The molecules in the associate have a common excited state and a unique fluorescence spectrum, which is sensitive to the surface pressure (Fig. 6c,d). In contrast, the 6 ns component in the DAS is mostly due to the emission from TBP monomers, and the surface pressure does not affect its spectral shape. Since the chromophores in the associate are not covalently bonded, the surface pressure is likely to affect their mutual separation and orientation and, consequently, change the energy levels of the associate.

Since face-to-face dimers were proposed for TBP films,[18] it is reasonable to assume that the TBP–ZnTBP associates responsible for the 2 ns component are face-to-face heterodimers oriented parallel to the substrate plane. Such structures could take a smaller surface area than individual, separated porphyrins. Therefore, the formation of the heterodimers explains the observed behaviour of the isotherms in Fig. 1 well. For face-to-face porphyrin dimers, a blue shift of the Soret band due to exciton splitting is often observed.[29] The Soret band of the TBP–ZnTBP films is indeed blue shifted (Fig. 3).

The shortest-living component in the DAS of the TBP–ZnTBP films also has a spectral shape similar to those found in the DAS of TBP. Its lifetime ($<1$ ns) is, however, much shorter than the shortest measured for the TBP film (2.2 ns). Therefore, this component corresponds probably to the singlet excited state of TBP with a shortened lifetime. The added compound in the film is ZnTBP, which obviously acts as a quencher. The most probable quenching mechanism is the electron transfer $P^*_H P_{Zn} \xrightarrow{k_{el}} P^-_H P^+_{Zn}$ because the energy transfer $P^*_H P_{Zn} \rightarrow P_H P^*_{Zn}$ was shown above to be inefficient.

For convenience, the TBP–ZnTBP arrangement capable of the electron transfer is called a "pair". The molecules in the pair are very close to each other, but they do not have a common excited state like they do in the heterodimers. Instead, ZnTBP interacts with the excited state of TBP. The porphyrin macrocycle acts both as an electron donor and acceptor. Therefore, to achieve vectorial electron transfer normal to the plane of the film, the majority of the donors should lie either below or above the acceptors. The difference in the redox potentials of the porphyrins suggests that the charge transfer state is $P^-_H P^+_{Zn}$. This assumption and the measured polarity of the displacement charge indicate that, in the floating monolayer, ZnTBP is closer to the water surface than TBP.

Because of the rearrangement of the chromophores, the deposition surface pressure affects the optical properties of the TBP–ZnTBP films (Fig. 3–6). The absorbance at 435 nm, which is the absorption maximum of the ZnTBP–ODA complex, is relatively higher for the film deposited at 30 mN m$^{-1}$ than for the 8 mN m$^{-1}$ film (Fig. 3). In addition, the blue shift of the Soret band, which is attributed to the heterodimers, is less pronounced for the 30 mN m$^{-1}$ film. Apparently, at a low surface pressure, the complexation of the ZnTBP molecules with ODA is inhibited, possibly because of the formation of heterodimers. In covalently bound zinc porphyrin dimers, the π–π interaction can reduce the affinity of zinc for external ligands.[29] At a surface pressure higher than 15 mN m$^{-1}$, some of the heterodimers are rearranged in a way that allows ODA to again complex with ZnTBP. The rearrangement may involve a reorientation or even dissociation of the heterodimers. Possibly, some of the heterodimers are converted to pairs capable of electron transfer.

The increasing surface pressure decreases the fluorescence lifetime of the TBP–ZnTBP films significantly (Fig. 5). The relative amount of the longest-living species, the TBP monomers, is reduced from 16 to 5% as the surface pressure is changed from 8 to 20 mN m$^{-1}$ (Fig. 6c,d). In addition, the overall fraction of the 2 ns component is somewhat reduced, in accordance with the proposed dissociation of the heterodimers. Consequently, the amount of short-lived ($\tau < 1$ ns) pairs is almost doubled.

Because the rate of formation of the charge transfer state is not well resolved in the TRMDC measurements, it cannot be compared with the fluorescence decay times. The lifetime of the charge transfer state is unusually long, 0.6 s (Fig. 7), when the lifetimes of CT states in DA dyads are usually shorter than a microsecond. More complex structures, such as triads, may have a longer CT state lifetime. There is, however, no evidence for the formation of more complex and well-ordered structures than heterodimers or pairs.

## Conclusion

LB films containing both TBP and ZnTBP can perform vectorial photoinduced electron transfer, the direction of which can be controlled by the fabrication method. TBP and ZnTBP probably form heterodimers with their macrocycles parallel to the solid substrate. However, the geometry of the structures responsible for the electron transfer remains unknown.

## Acknowledgements

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