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Ultrafast charge transfer in phytochlorin–[60]fullerene dyads: influence of the attachment position

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Abstract

A femtochemistry study has been performed on two phytochlorin–[60]fullerene donor–acceptor dyads, in which the fullerene moiety is linked via a pyrrolidine bridge either to the position 3 or 7 of the phytochlorin ring. Both dyads form an emissive intramolecular exciplex in less than 1 ps, but only the former dyad relaxes to the ground state via a charge transfer (CT) state. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Fullerene based donor–acceptor (DA) systems have received great attention during the past decade [1–12]. Though the electron accepting capability of fullerene is comparable with that of traditional acceptors, such as benzo- and naphthoquinones, its unusual geometry, extensive conjugated π-electron system, and the capability to accept more than one electron, make it an attractive candidate for chemical engineering. Combinations of a fullerene acceptor with a porphyrin or chlorin-like donor are excellent model systems for detailed investigations of the intramolecular photoinduced electron transfer (ET) [5–12].

Numerous synthetic efforts have been undertaken to design porphyrin–fullerene [1,3,5–7,9–12] and chlorin–fullerene compounds [8,13,14]. Studies of these compounds have proven that the dyads can undergo an efficient photoinduced ET. A close look at the photochemical processes taking place in the dyads has revealed that there are two important excitation relaxation channels, which can influence the efficiency of the long-distance (complete) ET capability of the systems. These are the intramolecular energy transfer from either porphyrin or chlorin to fullerene [5,6] and the formation of an intramolecular exciplex [8,15]. Though the excitation energy does not relax completely, the remaining amount of the energy may be too low for the dyad to perform a complete ET reaction. Tuning of each relaxation channel is important in order to understand the mechanism and to achieve an efficient ET.

The present work is a comparative study of two phytochlorin–bridge–fullerene dyads (Fig. 1), in which the pyrrolidine bridge–fullerene system is linked either to the position 3 or 7 of the

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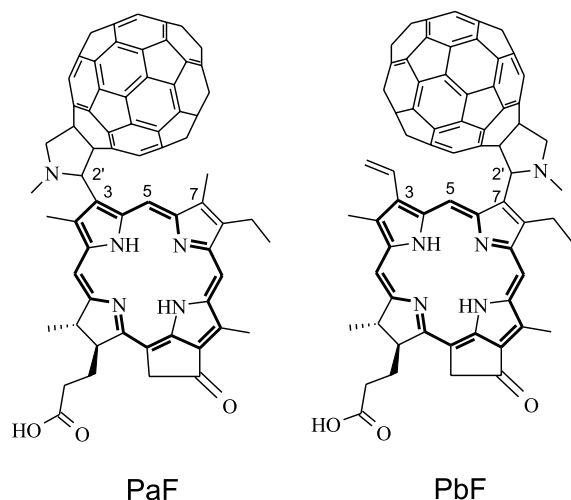
Fig. 1. The structures of PaF and PbF dyads. The aromatic 18-π-electron delocalization pathway is drawn in bold.

phytochlorin ring. The photochemistry of PaF (fullerene linked to the position 3) is described in detail earlier [8], whereas the photoprocesses of PbF (fullerene at the position 7) have not yet been reported. The different position of the fullerene in PbF does not change the photochemistry completely: most of the principal steps of the excitation relaxation, such as the intramolecular energy transfer and the exciplex formation [8], are common for both dyads and are characterized by similar rates. However, the complete ET, which was previously observed for the PaF dyad in polar solvents [8], e.g. benzonitrile, does not occur in the PbF dyad under the same conditions. This difference is attributed mainly to the difference in the electronic coupling between the exciplex and the complete ET states. In the PaF dyad, the C_{60} acceptor moiety is linked to the position 3, which belongs to the aromatic 18-π-electron [18]-diaza-annulene delocalization pathway of the chlorin ring, whereas, in the PbF dyad, the C_{60} is linked to the position 7, which lies outside the aromatic delocalization pathway (Fig. 1) [16,17].

2. Methods and materials

The structures of the PaF and PbF dyads are presented in Fig. 1. The solvents used for the synthesis were of analytical grade and dried over 4 Å molecular sieves. Chloroform was distilled through a Vigreux column prior to use. α, β-3-((2′ R,S)-N-methyltetrahydro[60]fullereno[c]pyrrol-2′-yl)-3-deethylphytochlorin (PaF) was prepared as described previously [13]. Buckminsterfullerene C_{60} (>98%) and N-methylglycine (>99%) were purchased from Fluka (Buchs, Switzerland).

$3^1,3^2$-didehydro-7-((2′ R, S)-N-methyltetrahydro[60]fullereno[c]pyrrol-2′-yl)-7-demethylphytochlorin (PbF). Pyropheophorbide b (3^1, 3^2-didehydro-7-demethyl-7-formylphytochlorin, 30 mg, 0.054 mmol) and N-methylglycine (30 mg, 0.35 mmol) were dissolved in a mixture of dry toluene (30 ml) and 1,4-dioxane (15 ml). A solution of 40 mg of C_{60} (0.056 mmol) in 40 ml of dry toluene was added to the reaction mixture. The resulting mixture was refluxed under argon atmosphere and the progress of the reaction was monitored by TLC on silica (eluent $CHCl_3$–MeOH 15:1 (v/v)). After 47 h of refluxing the mixture was cooled to room temperature, the solvent was evaporated, and the residue was chromatographed on a silica gel column (silica gel 60, ASTM, Merck, Darmstadt, Germany; 230–400 mesh; height of the layer 280 mm; 300 × 45 mm ID column; elution with $CHCl_3$–MeOH–CH_3COOH 20:1:0.01 (v/v)). The main fraction was collected, washed with distilled water, dried over anhydrous Na_2SO_4, and evaporated to dryness to give 31 mg (43% yield) of dyad PbF. The structure of the PbF was confirmed by NMR (300 MHz Varian INOVA).

Absorption spectra of the compounds were recorded on a Shimadzu UV-2501PC spectrophotometer. Fluorescence spectra were measured using a Fluorolog-3 fluorimeter (SPEX) and were corrected to the instrument wavelength sensitivity. The time-resolved fluorescence upconversion and pump–probe systems and the data analysis procedures used in the experiments have been described in detail earlier [8]. In short, the samples were placed in a 1-mm thick rotating cuvette and excited by the second harmonic of the Ti:sapphire pulsed laser system at 410–415 nm yielding the second excited singlet state of the phytochlorin moiety, $P^{2S}F$. The time resolution was approximately 150 fs for both instruments.

3. Results and discussion

The absorption spectra of $3^1,3^2$-dide-hydrophytochlorin (P), two phytochlorin–fullerene dyads (PaF and PbF), and [60]fullerene (C_{60}) in toluene are shown in Fig. 2. The difference between the spectra of the dyads arises from the fact that the electron withdrawing fullerene moiety is attached to a different position relative to the phytochlorin macrocycle.

The fluorescence of the DA compounds originates mainly from the phytochlorin moiety. The fluorescence spectra of P, PaF, and PbF in toluene solution are shown in Fig. 3a. As compared with the reference compound P, the fluorescence intensities of the dyads PaF and PbF were quenched to 1/200 and 1/50, respectively, and the spectra of the dyads show a broadening in the near-infrared (NIR) region (750–900 nm). The broadening for PaF is more intense than that for PbF and, for both dyads, it is less intense in benzonitrile than in toluene. Because neither phytochlorin nor fullerene emits in this spectral region, the new emission bands are attributed to exciplex emissions [8]. Exciplex-like emission has been observed also in porphyrin–fullerene systems [18–20].

The time-resolved fluorescence measurements were carried out using the fluorescence up-conversion technique. The fluorescence decays were followed at 670 nm, the maximum of the emission intensity of the phytochlorin moiety. After the excitation to the second excited singlet state, the
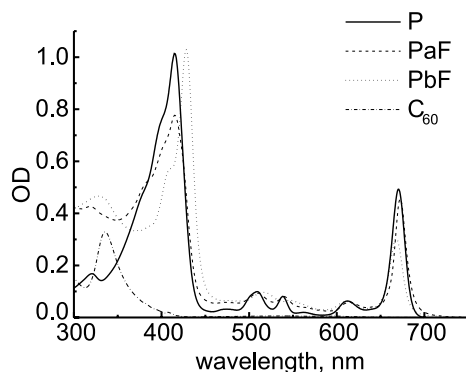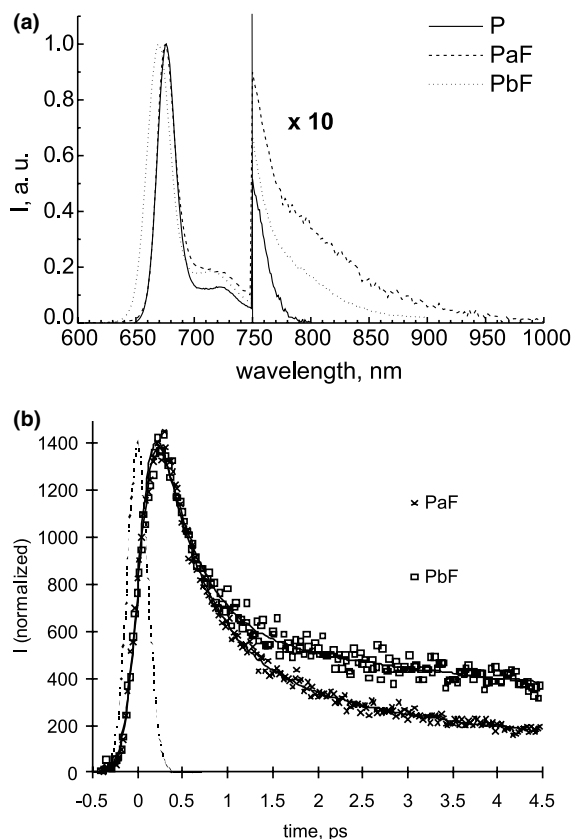

Fig. 3. (a) Normalized fluorescence emission spectra of the reference compound $3^1,3^2$-didehydrophytochlorin (P), and phytochlorin–[60]fullerene dyads PaF and PbF in toluene. (b) Fluorescence decays of PaF and PbF in benzonitrile at 670 nm. Solid lines represent the fittings and the dotted line is the instrumental response function.

phytochlorin moiety of the dyads relaxes rapidly to its first excited singlet state. The fluorescence of both dyads decays very fast even in non-polar toluene and the decays are practically identical. The fitted lifetimes are 0.59 ps (75% relative amplitude) and 8.5 ps (25%) for PaF, and 0.53 ps (75%) and 8.0 ps (25%) for PbF. In polar benzonitrile, there is a minor difference in the lifetimes and relative amplitudes of the components: 0.54 ps (80%) and 4.4 ps (20%) for PaF, and 0.53 ps (70%) and 9.8 ps (30%) for PbF (Fig. 3b).

Transient-absorption spectra of the dyads were recorded using the pump–probe technique in two wavelength domains. The Q-band region

Fig. 2. Absorption spectra of P, PaF, PbF, and C_{60} in toluene. Sample concentrations are 10 μM.

(550–770 nm) gives information about the photo-processes of the phytochlorin part, whereas the signal in the NIR (850–1070 nm) is mainly due to the transients of the fullerene moiety. In each spectral region, the measurements were carried out, one dyad immediately after another, keeping the experimental conditions constant. Multiexponential global fittings were applied to transient-absorption decay curves at different wavelengths [8]. In toluene, three-exponential fittings gave reasonable results for both dyads.

The most essential difference in the photochemistry of the dyads was observed in polar benzonitrile, as presented in Fig. 4. A three-exponential fit of the pump–probe results gives a reasonably good approximation for PbF 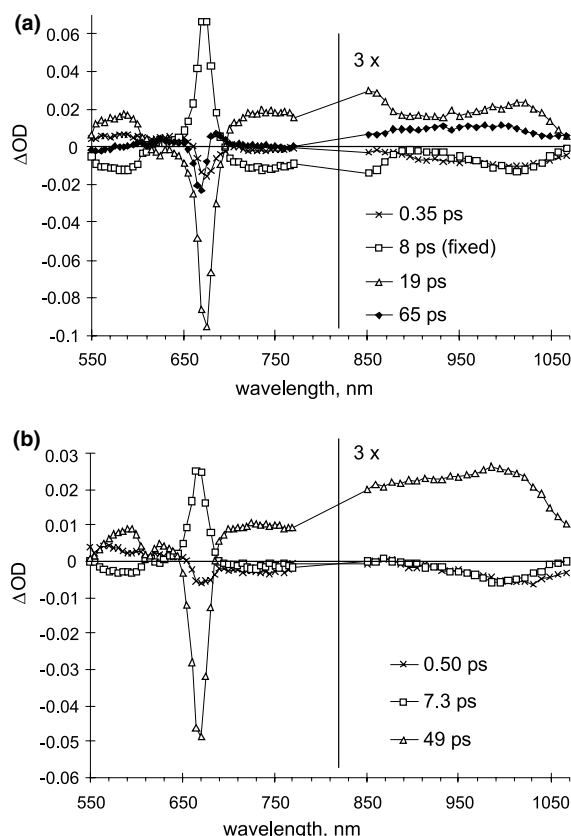and the application of a four-exponential model does not improve the goodness of the fit (σ^2-value decreased only by 4.5%). However, for PaF in benzonitrile, a four-exponential model has to be used, as reported earlier [8]. The four meta-stable states resulting after photoexcitation of PaF are: the first excited singlet state of the phytochlorin chromophore, P^*F, the first excited singlet state of the fullerene chromophore, PF^*, the intramolecular exciplex, $(PF)^*$, and the charge transfer state, P^+F^- [8], as shown in Fig. 5. Noticeably, the exciplex was observed in both polar and non-polar solvents, i.e. benzonitrile and toluene, whereas charge transfer (CT) is observed only in polar solvents.

The primary steps of the relaxation of the excited singlet states of the dyads are similar according to the good matching between the emission decay curves (Fig. 3b) and between the two shortest-lived components of transient-absorption decay (Fig. 4). Thus, from the point of the energy transfer ($P^*F \rightarrow PF^*$), PaF and PbF are very alike.

The exciplex is formed via two pathways [8]. For both dyads, the time-resolved process is $PF^* \rightarrow (PF)^*$ and the other pathway is relaxation directly from the second excited singlet state of the phytochlorin, $P^{2S}F \rightarrow (PF)^*$, which takes place in less than 100 fs and cannot be time-resolved with the available instruments. Both pathways are equally probable as it follows from the ratio of the component amplitudes with lifetimes of 8 and 19 ps

Fig. 4. Component spectra of transient-absorption decay for: (a) PaF and (b) PbF in benzonitrile. Lifetimes of the components are indicated.
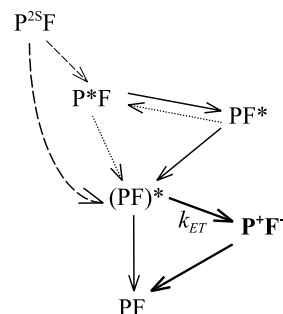

Fig. 5. Transient states and photochemical pathways of the PaF and PbF dyads. Experimentally proven paths are indicated with solid arrows. Processes that are not resolved in time are represented with dashed arrows, and possible, but experimentally not proven reactions with dotted arrows.

for PaF, and 7.3 and 49 ps for PbF in the Q-band region in benzonitrile (Fig. 4). Thus, the formation of the exciplex is an unavoidable step in the relaxation of the dyads.

It is worth noticing that in toluene, the spectra of the transient-absorption decay components are almost identical for both dyads. The formation time-constants of the exciplex $(PF^* \rightarrow (PF)^*)$ are, however, different, 47 ps for PaF and 230 ps for PbF. This is a surprising result, since the formation of the exciplex in benzonitrile takes place in 8 ps for both dyads.

A comparison of the decay component spectra in benzonitrile (Fig. 4) reveals that the component having the 65 ps lifetime in the case of PaF is missing in the relaxation of PbF. This component was previously attributed to the charge transfer state, P^+F^- [8]. Therefore, PbF does not form a CT state, not even in polar solvents.

In PaF, the fullerene-spacer is attached to the position 3, which belongs to the aromatic 18-π-electron [18]-diazaannulene delocalization pathway, whereas, in the PbF dyad, the fullerene-spacer is linked to position 7, which lies outside of the aromatic delocalization pathway of the phytochlorin ring. An indication of the non-equivalence of the attachment position can be seen in the ^{1}H NMR data. The 2′-CH proton of the pyrrolidine ring of PaF is clearly less shielded ($\delta_H = 6.35$–6.77 for the four different isomers of PaF) [13] than the 2′-CH proton in PbF ($\delta_H = 6.02$, for the chromatographically purified PbF there was no experimental evidence for the presence of more than one isomer). This indicates that the electronic properties of the linking bridge are changed by altering the attachment position. The stronger deshielding effect observed for the 2′-CH proton of PaF can be attributed to a stronger ring current effect due to a shorter distance between this proton and the aromatic π-system of the phytochlorin ring.

In the diabatic limit of the Fermi golden rule, the rate of the electron transfer depends on the electronic coupling between the reactant and the product, H_{RP}, and on the Franck–Condon density (FC) of the states [21],

$$k_{ET} = (2\pi/\hbar)H_{RP}^2(FC). \qquad (1)$$

The density of the states should be about the same for both dyads as they are composed of a similar donor–acceptor pair linked by a similar bridge. Therefore, the difference between the ET rates of the dyads should arise from the difference in the electronic coupling, H_{RP}. The presence of a vinyl group in a conjugated position to the aromatic π-system of the phytochlorin ring could influence the electronic coupling in PbF and thus, it could affect the formation of the CT state. However, a more likely reason for the difference in electronic coupling is the attachment position of the fullerene-spacer to the phytochlorin macrocycle (Fig. 1). Determination of the electronic coupling, H_{RP} requires quantum mechanical computations [22], which are beyond the scope of this Letter.

4. Conclusions

The complete electron transfer takes place in PaF, but is not observed for PbF. The difference may arise from the fact that, in the PaF, the fullerene-spacer moiety is attached to position 3, which belongs to the aromatic delocalization pathway of the phytochlorin ring, whereas, in the PbF dyad, fullerene-spacer is linked to position 7, which lies outside of the aromatic delocalization pathway. The comparison of the PaF and PbF dyads shows that the ET properties of the DA compounds can be tuned by a proper selection of the attachment position of the bridge.

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