Photoinduced processes in functionalized and organized dye systems
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Chapter 2

Fullerene C₆₀ – Perylene-3,4:9,10-bis(dicarboximide) Light-Harvesting Dyads:

Spacer Length and Bay-Substituent Effects on Intramolecular Singlet and Triplet Energy Transfer

Energy Transfer

1: R = Cl, n = 2
2: R = Cl, n = 5
3: R = OPh/Ph, n = 2
4: R = OPh/Ph, n = 5

Abstract

In this chapter, the electrochemical and photophysical properties of novel covalent fullerene $C_{60}$-perylene-3,4:9,10-bis(dicarboximide) ($C_{60}$-PDI) dyads (1-4) are presented. Electrochemical studies showed that the reduction potential of PDI can be tuned relative to $C_{60}$ by molecular engineering through altering the substituents on the PDI bay region. It was demonstrated using steady-state and time-resolved spectroscopy that a quantitative, photoinduced energy transfer takes place from the PDI moiety, acting as a light-harvesting antenna, to the $C_{60}$ unit, playing the role of energy acceptor. The bay-substitution (tetrachloro [1 and 2] or tetra-tert-butylphenoxy [3 and 4]) of the PDI antenna and the linkage length (C$_2$ [1 and 3] or C$_5$ [2 and 4]) to the $C_{60}$ acceptor are important parameters in the kinetics of energy transfer. Femtosecond transient absorption spectroscopy indicates singlet-singlet energy-transfer times (from the PDI to the $C_{60}$ unit) of 0.4 and 5 ps (1), 4.5 and 27 ps (2), 0.8 and 12 ps (3), and 7 and 50 ps (4), these values being ascribed to two different conformers for each $C_{60}$-PDI system. Subsequent triplet-triplet energy-transfer times (from the $C_{60}$ unit to the PDI) are slower and in the order of 0.8 ns (1), 6.2 ns (2), 2.7 ns (3), and 9 ns (4). Nanosecond transient absorption spectroscopy of final PDI triplet states show a marked influence of the bay substitution (tetrachloro- or tetra-tert-butylphenoxy), and triplet-state lifetimes and the PDI triplet quantum yields were estimated. The spectroscopy showed no substantial solvent effect upon comparing toluene (non-polar) to benzonitrile (polar), indicating that no electron transfer is occurring in these systems.
2.1. Introduction

Photoinduced energy- and electron-transfer processes are crucial phenomena occurring in natural photosynthesis\(^1\) and the development of artificial photosynthetic systems is still of considerable interest for the elucidation of the mechanisms which convert sunlight into chemical energy.\(^2\)

Several strategies have been employed to mimic the natural photosynthetic system.\(^3\) Among these, artificial light-harvesting antennas incorporated into molecular electron donor-acceptor systems are prone to convert excitation energy into an electrochemical potential or chemical energy in the form of a long-lived charge separation state. Fullerene \(C_{60}\) is now recognized to be a superior electron acceptor with regard to its inherent redox properties, low reorganization energy\(^4\) and highly symmetrical 3-D structure.\(^5\) Porphyrins are the most frequently used as electron donors in photosynthetic model systems.\(^6\) In these molecular donor-acceptor dyads, intramolecular electronic interactions almost always dominate generating (long- or short-lived) charge separated states. Moreover, porphyrins present the advantage to be excellent light-harvesting antennas.\(^7\) It was recently shown that such architectures can be tailored to construct molecular photonic devices as well as artificial photosynthetic systems. This kind of photoinduced electron transfer was recently extended to the production of photovoltaic cells that convert light into electric energy.\(^8\) Attractive systems are now developed for the construction of organic solar cells especially incorporating fullerene \(C_{60}\) in the photoactive layer.\(^9\) In this area, the direct covalent bonding of various \(\pi\)-donors to \(C_{60}\) has emerged as an active field of research.\(^10\) However, for such application, fast back electron transfer and energy transfer from the donor to \(C_{60}\) are events to be minimized to increase the quantum yield and lifetime of charge separation.\(^11\) Consequently, competition between energy- and electron-transfer in a functionalized electron donor-fullerene dyad has to be carefully considered in designing new systems for photovoltaic applications. In many examples, it was shown that efficient photoinduced electron transfer from a donor such as
oligophenylenevinylene,\textsuperscript{12} oligothiophene\textsuperscript{13} or perylene\textsuperscript{14} to fullerene C\textsubscript{60} was the main pathway whereas energy transfer could appear as a competitive process.\textsuperscript{15}

Following the observation of the very fast photoinduced electron transfer occurring on the subpicosecond time scale from conducting polymers to C\textsubscript{60},\textsuperscript{16} a major breakthrough towards efficient organic photovoltaic devices was realized with the development of the bulk-heterojunction concept.\textsuperscript{17} This approach consists of generating an interpenetrating network by blending the p-type electron donating conjugated polymer and C\textsubscript{60} or another fullerene derivative as n-type acceptor material.\textsuperscript{18} In this field, intensive efforts on organic solar cells are still focused on interpenetrating networks using the soluble acceptor [60]PCBM.\textsuperscript{19}

However, the disadvantage of this fullerene derivative is its small molar absorption coefficient in the visible region. Consequently one of the biggest challenges is now the access to materials that present the optimal absorption range, matching as well as possible the solar irradiation spectrum. This can be achieved with the development of p-type low band-gap polymers\textsuperscript{20} which should increase the absorption in the visible and near infrared (NIR) region of the solar spectrum. Another strategy concerns dendrimer-based light-harvesting structures which have attracted attention in the past decade.\textsuperscript{21} The functionalization of C\textsubscript{60} with oligomeric dendrons has given interesting light-harvesting systems in which peripheral chromophores are able to transfer the collected energy to the central core of the dendrimer.\textsuperscript{22} Considering the n-type material incorporated in the blend, the improvement of the light absorption of fullerene derivatives and its relationship with the efficiency of photovoltaic cells was demonstrated with the replacement of the C\textsubscript{60} derivative by the C\textsubscript{70} analogue.\textsuperscript{23}

We are interested in the concept of linking a dye molecule to fullerene C\textsubscript{60} as a potential system presenting efficient light-harvesting properties. The idea behind this is that the dye could act as an antenna by absorbing sunlight, thereby inducing an intramolecular energy transfer towards the fullerene. Perylene-3,4:9,10-

\textit{bis(dicarboximide)} (PDI) dyes were chosen as potential antennas because of their high chemical stability, high photoluminescence quantum yield and the possibility for
tuning the absorption range by variation of the substitution pattern on the perylene core. During the last few years, PDI derivatives have been developed as one of the most useful classes of chromophores. One of the most active areas of research involving PDI systems is related to their utilization in photoinduced electron and/or energy transfer processes. In this regard, electroactive units such as fluorenone and anthraquinone, tetra thiafulvalene, pyrene, oligothiophene, zinc phthalocyanine, 3,4-ethylenedioxy thiophene, zinc porphyrin, hexaazatriphenylenes, anthracene dendrimers, perylenemonoimide, tetraboron-dipyrrin, poly(fluorene-alt-phenylene), were connected to the PDI dye to reach molecular ensembles in which an electron and/or energy transfer event occurs. In the search of such electronic interaction involving PDI, supramolecular architectures were also recently described involving an oligo(p-phenylenevinylene), a bis(ruthenium phthalocyanine) moiety or zeolite crystals.

In the last three years, new electroactive PDI-based systems involving the attractive fullerene C_{60} electron acceptor were considered and the syntheses of many C_{60}-PDI dyad or triad systems have now been reported. Nevertheless, the spectral and kinetic characterizations of the photoinduced processes that are inherent to the combination of these electroactive units have received little attention. It was only recently shown that an efficient photoinduced electron transfer occurs in the C_{60}-PDI dyad in which electron-donating pyrrolidino groups are introduced on the bay region of the PDI moiety. The consequence of such substitution is the corresponding low oxidation potential of the PDI moiety, thus facilitating the electron transfer from PDI to C_{60}.

In this chapter we describe the electrochemical and photophysical properties of C_{60}-PDI dyads 1-4 (Scheme 2.1) in the search of an efficient energy transfer from PDI to C_{60}. In designing these systems, it was assumed that the distance between PDI and C_{60} moieties and their mutual orientation could be crucial parameters for the rate of energy transfer and could play an important role in the electronic interaction between both partners. Another objective was to demonstrate that the nature of the substituents on the PDI bay region strongly influence the electronic properties of these dyads for their
further utilization in photovoltaic devices. In the design of these solar cells it is considered that inside the photoactive layer the following events occur: 1) self assembly into an interpenetrating nanoscopic network, 2) an energy transfer from PDI towards fullerene $C_{60}$ with the dye acting exclusively as a light-harvesting antenna, 3) a selective electron transfer between the p-type polymer donor such as poly(3-hexylthiophene) (P3HT) to the $C_{60}$ unit (Scheme 2.1). We report here on the second point that is energy transfer phenomena occurring from the PDI-unit towards fullerene $C_{60}$ and on the influence of the spacer length and bay-substitution of the PDI on the kinetics and spectral features.

**Scheme 2.1.** *Representation of the photoactive layer of an organic solar cell incorporating the p-type P3HT polymer donor and the $C_{60}$-PDI dyad.*

### 2.2. Results and Discussion

Electrochemical and optical properties were performed by the group of Prof. Hudhomme in France and were also published on reference 42.

#### 2.2.1 Electrochemical properties:
Cyclic voltammetry was used to electrochemically characterize dyads 1-4 (Table 2.1). Compounds 5, 6 and 7 were used
as references (scheme 2.2) allowing the determination of the nature of reduced species.

![Diagram](image_url)

Scheme 2.2. The reference compounds

Dyad 1 showed three reversible reduction waves and the first one-electron process at $E^\circ_{\text{red1}} = -0.84 \text{ V (vs Fc}^+/\text{Fc})$ was assigned to the formation of the anion radical of the PDI moiety ($C_{60}$-PDI$^\text{-}$). The following two one-electron reduction process at $E^\circ_{\text{red2}} = -1.08 \text{ V}$ corresponding to the generation of the $C_{60}$-PDI$^{2-}$ species suggested that the first reduction wave of fullerene and the second reduction wave of PDI were overlapping. The third one-electron wave appearing at $E^\circ_{\text{red3}} = -1.47 \text{ V}$ resulted from the formation of $C_{60}^{2-}$-PDI$^{2-}$ species. One irreversible oxidation process was observed at $E^\circ_{\text{ox1}} = +1.24 \text{ V}$.

The cyclic voltammogram of dyad 3 showed four reversible one-electron reduction waves. The first process arising at $E^\circ_{\text{red1}} = -1.10 \text{ V (vs Fc}^+/\text{Fc})$ was assigned to the formation of the anion radical of the $C_{60}$ moiety ($C_{60}$-PDI$^\text{-}$). This was followed by both one-electron reduction processes of the PDI moiety leading successively to $C_{60}$-PDI$^\text{-}$ ($E^\circ_{\text{red2}} = -1.24 \text{ V}$) then $C_{60}$-PDI$^{2-}$ species ($E^\circ_{\text{red3}} = -1.35 \text{ V}$). The fourth one-electron reduction wave was corresponding to the generation of the $C_{60}^{2-}$-PDI$^{2-}$ species at $E^\circ_{\text{red4}} = -1.46 \text{ V}$. A first reversible one-electron oxidation process arising at $E^\circ_{\text{ox1}} = +0.83 \text{ V}$ was followed by an irreversible wave appearing at $E^\circ_{\text{ox2}} = +1.23 \text{ V}$.

Considering the cyclic voltammogram of dyads 2 and 4, it should be noted that the influence of the length for the alkyl chain on the imide position is not characteristic.
The reason is that the imide nitrogen atoms correspond to nodes in the LUMO of PDI derivatives, thus indicating that substituents at those positions do not really influence the corresponding energy levels.\textsuperscript{43}

### Table 2.1. Redox-potential values (vs Fe\textsuperscript{3+}/Fe\textsuperscript{2+}) of dyads 1-4 and reference compounds 5, 6, and 7 recorded in a CH\textsubscript{2}Cl\textsubscript{2} solution using Bu\textsubscript{4}NPF\textsubscript{6} (0.1 M) as the supporting electrolyte, Ag wire as the reference, Pt wires as counter and working electrodes. Scan rate: 100 mV s\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{\text{red}4}^{0}[V])</th>
<th>(E_{\text{red}3}^{0}[V])</th>
<th>(E_{\text{red}2}^{0}[V])</th>
<th>(E_{\text{red}1}^{0}[V])</th>
<th>(E_{\text{ox}1}^{0}[V])</th>
<th>(E_{\text{ox}2}^{0}[V])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-1.47</td>
<td>-1.08\textsuperscript{(a)}</td>
<td>-0.84</td>
<td>+1.24\textsuperscript{(b)}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-1.87\textsuperscript{(b)}</td>
<td>-1.45</td>
<td>-1.07\textsuperscript{(a)}</td>
<td>-0.86</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-1.46</td>
<td>-1.35</td>
<td>-1.24</td>
<td>-1.10</td>
<td>+0.83</td>
<td>+1.23\textsuperscript{(b)}</td>
</tr>
<tr>
<td>4</td>
<td>-1.44</td>
<td>-1.37</td>
<td>-1.23</td>
<td>-1.09</td>
<td>+0.82</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-1.06</td>
<td>-0.87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-1.37</td>
<td>-1.21</td>
<td>+0.80</td>
<td>+1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-1.47</td>
<td>-1.08</td>
<td>+1.22\textsuperscript{(b)}</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\textsuperscript{(a)}\) Two one-electron process; \(\textsuperscript{(b)}\) Irreversible process.

It was reported in the case of C\textsubscript{60}-PDI dyads with PDI bearing only hydrogen atoms at the bay region,\textsuperscript{40d} that the first reduction potential corresponds to a reversible two one-electron process leading directly to the C\textsubscript{60}\textsuperscript{-}-PDI\textsuperscript{-} species. In the case of dyads 1 and 2 with the PDI substituted by four chlorine atoms at the bay region, the first reduction occurs on the PDI moiety. The enhancement of the electron affinity is explained by the electron-withdrawing inductive effect of the chlorine atoms stabilizing the anion radical PDI\textsuperscript{-}. For dyads 3 and 4 with the PDI bearing tert-butylphenoxo groups at the bay region, the C\textsubscript{60} moiety appears to be the favoured electron acceptor. This demonstrates that electronic properties of C\textsubscript{60}-PDI dyads can be perfectly tuned thanks to a well-defined substitution of the PDI bay region.
2.2.2. Steady-state UV-Vis Absorption and Emission

2.2.2.1. UV-Vis absorption spectra of dyads 1-4 (scheme 2.1) and reference compounds 5, 6, 7 (scheme 2.2) were recorded in toluene and dichloromethane at room temperature (Figure 2.1 and Table 2.2).

![Absorption spectra of dyads 1 and 3 and reference compounds 5, 6 and 7 in toluene at 298 K (c < 10^-6 M).](image)

No significant solvent effect was observed, but further insight into solvatochromism was prevented by the lack of solubility of the dyads. All compounds containing the PDI unit exhibit the three typical absorption peaks at ca. 430, 485 and 520 nm for 1, 2 and 5 or 450, 540 and 580 nm for 3, 4 and 6. The values reported for a PDI derivative bearing hydrogen atoms at the bay region are intermediate (434, 460, 491 and 528 nm). The hypsochromic effect observed for 1, 2 and 5 could be ascribed to the bay substitution pattern of the PDI moiety and more precisely of the electron-withdrawing inductive effect of chlorine atoms. On the other hand, the bathochromic effect for 3, 4 and 6 could be related to the electron-donating mesomeric effect of phenoxy groups. It appears clearly that electronic effects are predominant. The expected hypsochromic effect due to the decrease of conjugation because of the torsion induced by the bay substitution is less important.

According to the literature, these bands could be attributed to the transitions 3-0, 1-0, 0-0, with a weak transition 2-0 which could be only barely distinguished around...
460 nm for 5 and 500 nm for 6. The extinction coefficient values found are in agreement with those reported in literature and are within the range 30000-40000 M⁻¹ cm⁻¹ for these compounds.²⁶b,46 The strong absorption band at 330 nm observed for 1-4 and 7 was ascribed to fullerene C₆₀ absorption. The sharp peak at 430 nm observed for 7 is characteristic of [6,6]-methanofullerene derivatives, as well as the peak at 689 nm which corresponds to the S₁→S₀ transition.⁴⁷ Rather similar spectral features are also observed for pyrrolidine C₆₀ derivatives⁴⁷b and for C₆₀ Diels-Alder adducts.⁴⁷c Moreover, the UV-visible absorption spectra of dyads 1-4 match the profile obtained by superposition of the spectra of corresponding reference compounds 5 or 6 and 7. Independently, of the bay substitution pattern or spacer length between PDI and C₆₀ moieties, this characterizes the absence of significant interaction in the ground state between these two partners.

Table 2.2. Electronic absorption data for dyads 1-4 and reference compounds 5, 6, 7.

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th></th>
<th>Dichloromethane</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>𝜆ₘₐₓ [nm]</td>
<td>𝜖ₘₐₓ [M⁻¹cm⁻¹]</td>
<td>𝜆ₘₐₓ [nm]</td>
<td>𝜖ₘₐₓ [M⁻¹cm⁻¹]</td>
</tr>
<tr>
<td>1</td>
<td>524</td>
<td>29 800</td>
<td>522</td>
<td>32 800</td>
</tr>
<tr>
<td>2</td>
<td>522</td>
<td>31 350</td>
<td>520</td>
<td>32 800</td>
</tr>
<tr>
<td>3</td>
<td>579</td>
<td>36 800</td>
<td>586</td>
<td>38 500</td>
</tr>
<tr>
<td>4</td>
<td>576</td>
<td>37 300</td>
<td>582</td>
<td>38 500</td>
</tr>
<tr>
<td>5</td>
<td>522</td>
<td>33 900</td>
<td>518</td>
<td>40 300</td>
</tr>
<tr>
<td>6</td>
<td>575</td>
<td>42 000</td>
<td>582</td>
<td>42 700</td>
</tr>
<tr>
<td>7(a)</td>
<td>689 (490, 428)</td>
<td>250 (1700, 3000)</td>
<td>693 (496, 430)</td>
<td>105 (1400, 2500)</td>
</tr>
</tbody>
</table>

(a) Other absorption bands of compound 7 and their respective molar absorption coefficients.

2.2.2.2. Fluorescence emission spectra of reference compounds 5, 6 and 7 were recorded in toluene and dichloromethane and were found to be independent on the excitation wavelength (Figure 2.2A and Table 2.3).

Fluorescence emission spectra matched the absorption profile over the entire wavelength range. As expected, PDI-based compounds 5 and 6 are strongly emissive
in the visible range with fluorescence quantum yields being close to unity at room temperature. On the other hand, compound 7 presented a typical weak emission centered at 697 nm with a fluorescence quantum yield at of $5 \times 10^{-4}$ at room temperature, characteristic of [6,6]-methanofullerene derivatives.\(^{47,48,49}\) All the fluorescence emission spectra of dyads 1-4 are composed of two bands, one characteristic of the PDI moiety in the 500-650 nm range, the second corresponding to the methanofullerene in the 670-750 nm region (Figure 2.2B and Table 2.3). For dyads 3 and 4 bearing \textit{tert}-butylphenoxy groups at the bay area, a bathochromic shift of the emission maxima was noticed in agreement with the absorption spectrum. The consequence is an overlapping of emissions centered on the PDI and C\textsubscript{60} moieties.

**Table 2.3. Photophysical properties of dyads 1 - 4 and reference compounds 5, 6, 7**

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th>Dichloromethane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ [nm]</td>
<td>$\Delta \bar{\nu}$ [cm\textsuperscript{-1}]</td>
</tr>
<tr>
<td>1</td>
<td>549 (696)</td>
<td>869</td>
</tr>
<tr>
<td>2</td>
<td>548 (696)</td>
<td>909</td>
</tr>
<tr>
<td>3</td>
<td>602 (698)</td>
<td>660</td>
</tr>
<tr>
<td>4</td>
<td>600 (697)</td>
<td>694</td>
</tr>
<tr>
<td>5</td>
<td>548</td>
<td>909</td>
</tr>
<tr>
<td>6</td>
<td>601</td>
<td>752</td>
</tr>
<tr>
<td>7</td>
<td>697</td>
<td>167</td>
</tr>
</tbody>
</table>

The values in the rounded parentheses present the emission maximum of C\textsubscript{60} moiety, \textsuperscript{(a)} from single photon counting (SPC) measurements (see below), \textsuperscript{(b)} in good agreement with reference 47a. $\Phi _f$: fluorescence quantum yield; $\tau$: fluorescence lifetime; $k_{\text{EnT}}$: rate constant of energy transfer calculated from $\tau$. $\Delta \bar{\nu}$: Stokes’ shift. Experiments were measured at 298 K.

The Stokes’ shift values in both toluene and dichloromethane are in the 600-900 cm\textsuperscript{-1} range, except for 7 for which the Stokes’ shift value is smaller (Table 2.3), all these
values being coherent with a weak geometrical reorganization of the considered fluorophore at the excited state (PDI for 1-4, 5, 6 and C_{60} for 7).

Figure 2.2. Emission spectra of A) reference compounds 5 (\(\lambda_{\text{exc}} = 485\,\text{nm}\)), 6 (\(\lambda_{\text{exc}} = 550\,\text{nm}\)) and 7 (\(\lambda_{\text{exc}} = 450\,\text{nm}\)) and B) dyads 1 (\(\lambda_{\text{exc}} = 520\,\text{nm}\)) and 3 (\(\lambda_{\text{exc}} = 550\,\text{nm}\)) in toluene at 298 K (c < 10^{-6} M).

Moreover, there is a dramatic quenching of the PDI fluorescence emission for all the dyads. At room temperature, the fluorescence quantum yields are in the range 2 – 3 \times 10^{-3}, this being also dependent on the spacer length. Considering identical bay substitution, the shorter is the alkyl chain between PDI and C_{60} units, the stronger is the quenching of fluorescence. This strong quenching (up to 99.8\%, depending on the dyad) should result from an intramolecular interaction between PDI and C_{60} in the excited state. In a control experiment with the two separate chromophores at similar concentration, no quenching was observed.

To get further insights into the nature of this new process, fluorescence emission spectrum of 1 was recorded by selectively exciting the PDI unit in the dyad (Figure 2.2B). The C_{60} emission features are still observed, evidencing a singlet-singlet energy transfer between PDI and C_{60}. This process is in agreement with the energy levels of the PDI and C_{60} units, 2.32 eV for 5 and 1.79 for 7 in toluene, respectively. This was confirmed by the excitation spectrum recorded at 695 nm in dichloromethane. Indeed,
the characteristic absorption bands of PDI are still present on this spectrum (Figure 2.3).

![Excitation spectra of dyad 1 at \( \lambda_{\text{obs}} = 570 \text{ nm} \) and at \( \lambda_{\text{obs}} = 695 \text{ nm} \), in dichloromethane at 298 K (\( c < 10^{-6} \text{ M} \)).](image)

**Figure 2.3.** Excitation spectra of dyad 1 at \( \lambda_{\text{obs}} = 570 \text{ nm} \) and at \( \lambda_{\text{obs}} = 695 \text{ nm} \), in dichloromethane at 298 K (\( c < 10^{-6} \text{ M} \)).

Similar experiments could not be conducted for dyads 3 or 4 as fluorescence emissions of PDI and \( C_{60} \) are overlapping. Nevertheless, by subtracting the contribution of PDI from the emission spectrum of 3 or 4, the fullerene emission is still observed, even when the PDI is selectively excited at a wavelength above 550 nm.\(^{40}\) This result associated with the strong fluorescence quenching of PDI emission corroborate the hypothesis of an energy transfer from PDI to \( C_{60} \) for these dyads. Energy levels are still in agreement as the first excited state of 6 is at 2.11 eV, *i.e.* 0.32 eV higher than the first excited state of compound 7 in toluene (Table 2.4).

**Table 2.4.** Energy level of the charge separated state for dyads 1 - 4 with parameters used for the calculation obtained from \( \Delta G = e(E_{\text{ox}} - E_{\text{red}}) - E_{0-0} \)

<table>
<thead>
<tr>
<th>Dyad</th>
<th>( E_{\text{ox}} ) (eV)</th>
<th>( E_{\text{red}} ) (eV)</th>
<th>( E_{0-0} ) (eV)</th>
<th>( \Delta G ) (eV)</th>
<th>( E_{\text{PDI}} )</th>
<th>( E_{\text{CS}} )</th>
<th>( E_{C_{60}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>+1.24</td>
<td>-0.84</td>
<td>2.32</td>
<td>-0.24</td>
<td>2.33</td>
<td>2.09</td>
<td>1.79</td>
</tr>
<tr>
<td>3, 4</td>
<td>+0.83</td>
<td>-1.10</td>
<td>2.11</td>
<td>-0.18</td>
<td>2.11</td>
<td>1.93</td>
<td>1.79</td>
</tr>
</tbody>
</table>
Altogether these results underline the dependency of the efficiency of this process as a function of bay area substitution and spacer length. Indeed, the quenching of fluorescence appears higher for chlorine substituted dyad 1 in comparison with tert-butylphenoxy substituted dyad 3 (Table 2.3). This phenomenon is confirmed by the emission spectra of dyads 1-4 recorded in rigid solvent glass (methylcyclohexane/toluene 7:3) at low temperature (77 K) (Figure 2.4).

**Figure 2.4.** Normalized fluorescence emission spectra at 77 K in methylcyclohexane/toluene (7:3) matrix: (A) for dyads 1 and 2 ($\lambda_{exc} = 490$ nm); (B) for dyads 3 and 4 ($\lambda_{exc} = 450$ nm).

A slight bathochromic shift with decreasing temperature for fluorescence emission of dyads 1 and 2 was remarked ($\Delta\lambda_{max} = 11$ nm between 77 K and room temperature). These spectra showed well-structured vibronic bands in agreement with the lack of solvent relaxation in rigid medium. Consequently, at 77 K a better comparison of the intensity ratio between the PDI emission band (550 nm for dyads 1-2 and 600 nm for dyads 3-4) and the C$_{60}$ emission band (ca. 700 nm) could be performed. Considering
the same bay substitution and PDI fluorescence emission intensity being normalized, it was clearly displayed from these spectra that C\textsubscript{60} centered emission is more important for dyads presenting the shortest spacer, thus confirming the real influence of the spacer length on the efficiency of energy transfer between PDI and C\textsubscript{60}.

The intramolecular energy transfer from PDI to C\textsubscript{60} could be discussed in terms of Coulombic interactions (Förster)\textsuperscript{50} or exchange interactions (Dexter).\textsuperscript{51} In order to know if this energy transfer could be due to Coulombic interaction, Förster radii R\textsubscript{o} were calculated for each dyad (Table 2.5), according to equation 1:\textsuperscript{50}

\[
R_o = 0.2108 \left[ \kappa^2 \phi_D^0 n^{-4} \int_0^\infty I_D(\lambda) \kappa_A(\lambda) \lambda^4 d\lambda \right]^{1/6}
\]

where \(\kappa\) is the orientation factor, \(\phi_D^0\) is the emission quantum yield of the reference donor chromophore, \(I_D(\lambda)\) is the corrected fluorescence intensity of the donor with the total intensity normalized to unity and \(n\) is the refractive index of the solvent. For dyads 1 – 4, \(\phi_D^0\) is equal to one and \(\kappa^2\) to 2/3 because of the random orientation of the dipole between molecules. All the values obtained for \(R_o\) in both toluene and dichloromethane exceed the distance calculated by molecular structure optimization between PDI and C\textsubscript{60} for each dyads.\textsuperscript{49} According to this result, the nature of the energy transfer to dyads 1 - 4 should be of Förster type. Using these \(R_o\) values and the experimental rates, center-to-center distances could be estimated (see appendix 2).

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th>Dichloromethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.3</td>
<td>31.5</td>
</tr>
<tr>
<td>2</td>
<td>32.3</td>
<td>31.5</td>
</tr>
<tr>
<td>3</td>
<td>28.1</td>
<td>30.0</td>
</tr>
<tr>
<td>4</td>
<td>28.1</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table 2.5. Calculated Förster radii \(R_o\) (in Å) for dyads 1 - 4
To study the possibility of a competitive reductive (for dyads 1 and 2) or oxidative (for dyads 3 and 4) electron transfer process, the Gibbs energy of photoinduced electron transfer dyad was estimated for each dyad.\(^5^2\) For all the dyads, the corresponding charge separated state lies at an intermediate energy level between the fullerene and PDI singlet excited states (Table 2.4). If the Coulomb and solvent correction terms are taken into account, the energy level will be lowered, making it energetically more accessible in dichloromethane and benzonitrile. In toluene however, charge separation would be an endergonic process (using ‘average’ center-to-center distances from Table A2.2 in appendix 2 and average ionic radii of 4 Å). Apparently the excited state processes in polar solvents are governed by kinetic factors: charge separation is energetically possible, but it is not observed (see below).

### 2.2.3. Time-resolved Spectroscopy

In order to get more information on the effects of the bay substitution and the spacer length on the interaction between the fullerene unit and the PDI chromophore, various types of time resolved spectroscopy were applied. The photophysical properties of the systems (1 - 4) containing fullerene C\(_{60}\) covalently linked to the perylenediimide as well as those of the reference compounds 5, 6 and 7 in toluene were investigated. Benzonitrile as a solvent was in some femto- and nano-second transient absorption experiments, showing no sign of electron transfer (some results are presented in the appendix 2, Figure A2.1-A2.3).

**2.2.3.1. Single Photon Counting** (SPC) was used to determine the emission decays of the dyads 1-4 and the reference systems 5, 6 and 7 in toluene. The decay curves recorded for dyads 1-2 (at 550 nm) and dyads 3-4 (at 610 nm) monitoring the PDI emission gave bi-exponential decays. The major (95 - 99%) short components (9 - 54 ps) as well as the energy transfer rates (\(k_{\text{ET}}\)) derived from there are given in Table 2.3.

Figure 2.5 shows the decay traces of the four C\(_{60}\)-PDI systems. Interestingly, a minor long component (0.2 - 4%, 3 - 5 ns) is observed in the time resolved emission.\(^{5^3}\) Table 2.3 shows the mono-exponential fluorescence lifetimes of the reference compounds 5,
6 and 7. The lifetimes are virtually independent of de-aerating and are in accordance with reported lifetimes for similar systems.\textsuperscript{27, 45, 47, 49, 54}

By using the quenched lifetimes and applying $k_{\text{EnT}} = 1/\tau - 1/\tau_0$, singlet energy transfer rates of $1.1 \times 10^{10}$ s$^{-1}$ (for 1), $3.3 \times 10^{10}$ s$^{-1}$ (for 2), $3.9 \times 10^{10}$ s$^{-1}$ (for 3) and $1.8 \times 10^{10}$ s$^{-1}$ (for 4) were obtained (Table 2.3). From these data, it is already clear that the rate of energy transfer is modulated both by the bay substituent and by the spacer length. The shortest spacers display the faster rates. Considering the same spacer length, energy transfer is more efficient for the chlorinated than for the tert-butylphenoxy substituted dyads. It can be noted that the energy transfer rates obtained for dyads 1-4 are higher than those reported in the literature for other C$_{60}$ fullerene based dyads.\textsuperscript{14, 15, 40, 55}

**Figure 2.5.** Emission decay traces obtained with SPC of compounds 1 to 4 in toluene. Pulse is also shown ($\lambda_{\text{ex}} = 324$ nm, 17 ps FWHM, detection wavelength is indicated in the legend).

2.2.3.2. Femtosecond transient absorption\textsuperscript{56} (fs-TA) was used to get more accurate information on the singlet and triplet energy transfer processes in the dyads. fs-TA of compound 1 was published in a separate work.\textsuperscript{57} The spectral data obtained for 2 in toluene are shown in Figure 2.6.

The typical bands of the PDI moiety such as the ground state bleaching (at 500 and 525 nm), the singlet state emission (at ca. 600 nm), the singlet excited-state absorption
(at ca. 800 nm) and the triplet–excited state absorption (at ca. 560 nm) are observed, similar to those reported before for 1.\textsuperscript{57} The kinetics of 2, however, is different showing a slower decay of the PDI excited singlet state and a slower rise of the 560 nm band. For all dyads (1 to 4) the singlet excited state of the fullerene adduct is observed as an intermediate state (see reference 57). Its absorption is rather weak and covers the whole visible range, with a minimum around 600 nm.\textsuperscript{57,58}

**Figure 2.6.** A) Femtosecond transient absorption (fs-TA) spectra of compound 2 in toluene (λ\textsubscript{ex} = 530 nm, 150 fs FWHM); B) kinetic traces at 600 nm (on a 100 ps timescale) and at 560 nm; C) on the full timescale with tri-exponential fit (τ\textsubscript{1} = 4.5 ps; τ\textsubscript{2} = 27 ps and τ\textsubscript{3} = 6.2 ns). Time delays are indicated in the legend in A).

Overall, the phenoxy substituted compounds 3 and 4 display similar behaviour as 1 and 2, but the spectral features of the PDI singlet and triplet excited states are different (Figure 2.7), especially the modulation by the strong ground state bleaching at 580 nm for 3 and 4.
Figure 2.7. A) 3D surface plot of fs-TA data obtained for 3 in toluene (λ<sub>ex</sub> = 530 nm, 150 fs FWHM). Signal intensity is also projected on the x-y plane. The incremental time delay is short (0.04 ps) at the start and longer (50 ps) at later times (total timescale -10 to 3600 ps). Note that the time increases to the front and the wavelength increases to the left. B) fs-TA spectra of compound 3. Time delays are indicated in the legend of (B). Kinetic traces at 600 nm (C) and at 500 nm (D) together with tri-exponential fit. (τ<sub>1</sub> = 0.8 ps; τ<sub>2</sub> = 12 ps and τ<sub>3</sub> = 2.7 ns)
The phenoxy substituted PDI moiety shows ground state bleaching (at 540 and 580 nm), the singlet state emission (at ca. 600 and 650 nm) and weak singlet excited-state absorption (at ~ 700 nm). The final state populated (the triplet of PDI) is characterized by maxima at 510, 550 and by the strong bleach at 580 nm and an almost flat absorption band between 600 and 800 nm. Again, the dyad with the longer spacer (4) shows slower singlet and triplet energy transfer. Table 2.6 summarizes the characteristic times observed with femtosecond transient absorption for the dyads 1 to 4 in toluene.

**Table 2.6. Decay and rise times observed for the dyads 1-4 in toluene with femtosecond transient absorption spectroscopy, corresponding to singlet-singlet energy transfer ($\tau_1$, $\tau_2$) and triplet-triplet energy transfer ($\tau_3$).**

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ [ps]</th>
<th>$\tau_2$ [ps]</th>
<th>$\tau_3$ [ns]</th>
</tr>
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<tr>
<td>1</td>
<td>0.4</td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>27</td>
<td>6.2</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>12</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>50</td>
<td>9&lt;sup&gt;(b)&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> these value were published in reference 57.

<sup>(b)</sup> from nanosecond transient absorption measurement (see below).

It is interesting to notice that the ultrafast component observed in the femtosecond transient absorption spectroscopy is not detected with SPC, due to its lower time resolution. The slower components ($\tau_2$) are in reasonable agreement with the fluorescence emission lifetimes (Table 2.3).

Femtosecond transient absorption spectroscopy was also performed in benzonitrile for compounds 1 and 3 in order to assess solvent dependent photophysical behaviour (*i.e.* the occurrence of electron transfer). Very similar spectral features were observed as well as slightly different kinetics, the latter being attributed to small differences in solvent-dependent conformations resulting in slightly altered interchromophoric distances in the two solvents for the extended and folded forms. This clearly indicates
that a charge transfer state is not formed (or has no population build-up). Furthermore, the singlet energy transfer from the PDI to the C$_{60}$ unit and subsequent triplet energy transfer from the fullerene triplet state to the perylene-based triplet are relatively insensitive to the solvent polarity.

The femtosecond spectroscopy confirms that light energy harvested by the PDI antenna is transferred very efficiently to the C$_{60}$ moiety on a (sub)picosecond (for 1) to tens of picosecond time scale and that no electron transfer occurred between PDI and C$_{60}$ moieties. No spectral features attributable to either the PDI radical anion or cation$^{59}$ or the C$_{60}$ radical cation$^{60}$ or anion$^{61}$ were observed. Using NIR detection, compounds 1 and 3 show only singlet-singlet absorption in toluene$^{41h}$ at 990 nm for 1 and at 960 and 1040 nm for 3 (see Figure A2.4 in appendix 2 for the spectra and decay) with kinetics similar to the singlet excited state kinetics observed with the femtosecond transient absorption data using VIS detection. Moreover, the final excited state is a low-energy (1.2 eV) triplet state localized on the PDI,$^{45}$ normally rarely observed in perylene dyes. Two rates of fast singlet energy transfer are observed, which were attributed to the co-existence of a folded and an extended conformer. The two faster rates observed with transient absorption show that the interchromophoric distance in the folded conformer of 2 and 4 is longer than for 1 and 3, in agreement with DFT and HF calculations performed in reference 62.

2.2.3.3. Nanosecond transient absorption: The ultrafast spectroscopy described in the previous section clearly shows the formation of a longer-lived triplet state that is localized on the PDI unit in all four dyads. The triplet-triplet absorption spectra of the PDI chromophores observed with nanosecond transient absorption spectroscopy are given in Figure 2.8. The similarity to the final femtosecond transients (at $\sim$ 3.0 ns) is perfect. Tetrachloro-substituted PDI (1 and 2) are characterized by a very strong triplet–excited state absorption at 560 nm. Ground-state bleaching features are observed at 490 and 525 nm. Tetra-tert-butylphenoxy substituted PDI (3 and 4) show a markedly different spectrum, due to the strong ground-state bleaching at 580 nm, characterized by maxima at 510, 550 nm.
Figure 2.8. Nanosecond transient absorption spectra (ns-TA) of the triplet state in toluene of A) compound 2, incremental time delay 2500 ns (argon degassed); B) compound 3, incremental time delay 120 ns (non-degassed); C) compound 4, incremental time delay 1 ns, \( \lambda_{\text{ex}} = 580 \) nm. The first spectrum is dotted in A) and B) (time increases from grey to black). A) and B) present the decay of the PDI triplets. In A) the last trace (~ 3 ns) in fs-TA was added for comparison. In B) some triplet C\text{60} is observed at 710 nm which shows a different decay behavior in C), where also the rise of the PDI triplet can be observed. For C) the time zero was chosen slightly before the laser pulse (2 ns).
The observed triplet-state lifetimes in air and under de-aerated conductions are given in Table 2.7. Notably, the lifetimes under degassed conditions are very sensitive to traces of oxygen left in solution and influenced by triplet–triplet annihilation (and can thus be considered lower limits). The effects of de-oxygenation and comparison of the spectral shape with literature data\textsuperscript{45, 63} clearly show the nature of the PDI localized triple state.\textsuperscript{64}

**Table 2.7.** The triplet state lifetimes of the compounds 1 to 4 in toluene (TOL) and benzonitrile (PhCN) under aerated conditions (air) and under de-aerated conditions (Ar) as observed with nanosecond transient absorption spectroscopy.

<table>
<thead>
<tr>
<th></th>
<th>(\tau) [ns, TOL, air]</th>
<th>(\tau) [s, TOL, Ar]</th>
<th>(\tau) [ns, PhCN, air]</th>
<th>(\tau) [ns, PhCN, Ar]</th>
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</thead>
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<tr>
<td>1</td>
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<td>(1.2 \times 10^4)</td>
<td>640</td>
<td>(1.5 \times 10^4)</td>
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<tr>
<td>2</td>
<td>400</td>
<td>(1.0 \times 10^4)</td>
<td>590</td>
<td>(1.4 \times 10^4)</td>
</tr>
<tr>
<td>3</td>
<td>330</td>
<td>(1.4 \times 10^4)</td>
<td>680</td>
<td>(1.4 \times 10^4)</td>
</tr>
<tr>
<td>4</td>
<td>310</td>
<td>(1.5 \times 10^4)</td>
<td>590</td>
<td>(2.0 \times 10^4)</td>
</tr>
</tbody>
</table>

The spectroscopy of compound 1 does not reveal any indication of \(C_{60}\) triplet state formation in the femtosecond and nanosecond transient absorption, and its intermediacy is inferred from the intrinsic fullerene properties. This is different for, however, compound 4. Figure 2.8C shows the clear kinetic difference for the 500 and 710 nm bands in the first 50 ns (see Figure A2.6, appendix 2 for spectra of 1 and 2). From these data, an initial rise time of 9 ns is deduced (at 500 nm) which corresponds to the triplet energy transfer from \(C_{60}\) to the PDI. Now, a second slower triplet-energy transfer (in 33 ns) is inferred from the decay at 710 nm. A rise time at 500 nm is not observed due to overlapping bands and the small yield of this slower process. However, in a large part of the population of excited-state molecules, the fullerene triplet does not transfer its energy and decays with a lifetime very similar to that of the PDI triplet (Table 2.7). Clearly, the two conformations deduced from two singlet energy-transfer rates in the femtosecond transient now also give two different triplet-energy transfer rates.
Similar observations are made for compound 3, where the 710 nm band is clear in the nanosecond transient. Closer inspection of Figure 2.6 also reveals a spectroscopic sign for $C_{60}^*$ formation in compound 2, by the small hump at 710 nm in the last trace (at 2988 ps). In the nanosecond transient however, this appears to be masked by the strong and more red-shifted $PDI^*$ absorption (Figure 2.8). The feature at 710 nm is also not observed for compound 1.$^5^7$

For comparison and completeness the triplet-triplet absorption spectra$^6^5$ of the methanofullerene adduct 7 and pristine C$_{60}$ are given in Figure A2.5, appendix 2. The singlet-singlet absorption of 5 was reported previously.$^5^7$

Quantum yields of triplet PDI formation were estimated using the comparative method$^{[6^6]}$ and molar absorption coefficients.$^{4^5, 5^8}$ From this analysis we estimate that $\Phi_T (1) = 0.75$, $\Phi_T (2) = 0.70$ and $\Phi_T (3) = 0.60$, $\Phi_T (4) = 0.52$. The molar absorption coefficients of the transient triplet species were estimated by using the iso-absorptive points$^{4^5}$ (see appendix 2 for the detailed description.). The observed triplet absorption spectrum has maximum at 560 nm ($\varepsilon_{(T1-Tn)} = 29000 \text{ M}^{-1}\text{cm}^{-1}$) and at 710 nm ($\varepsilon_{(T1-Tn)} = 9400 \text{ M}^{-1}\text{cm}^{-1}$) for compound 3 and 4. The observed triplet absorption spectra of 1 and 2 have a maximum at 560 nm ($\varepsilon_{(T1-Tn)} = 51600 \text{ M}^{-1}\text{cm}^{-1}$).

We can now assess the energetic scheme reported in Figure 2.9 for dyad 1. Excitation at 520 nm, where the PDI moiety selectively absorbs, leads to the population of the singlet state centered on PDI. $1PDI^* - C_{60}$ decays by very fast energy transfer to form $PDI - 1C_{60}^*$ for which two rates are observed, attributed to a folded and an extended conformation. Fluorescence emission is more than 99 % quenched. A charge separated state $PDI^* - C_{60}^+$ is not populated, although its energy level is below that of $1PDI^*$ (Table 2.4). Clearly singlet energy transfer is much faster. The final triplet state $3PDI^* - C_{60}$ is populated in high yield. Although the triplet state PDI$^* - C_{60}$ is not observed for dyad 1, it is clearly observed for dyads 2-4. Thus it is clear that intersystem crossing from PDI$ - 1C_{60}^*$ to PDI$ - 3C_{60}^*$ precedes the energy transfer to the final PDI triplet state. Indeed, intersystem crossing is known to be very efficient for most mono-
functionalized C₆₀ derivatives (Φᵣ close to unity, τᵣ ~ 1.5 ns and Φᵣ ~ 5 × 10⁻⁴) such as 7 and other compounds described in the literature.⁴⁷, ⁴⁹, ⁶⁵, ⁶⁷

Figure 2.9. Energy level diagram (in eV) showing the processes that take place in the two conformations of dyad 1 upon selective excitation of PDI moiety (toluene, room temperature). Lifetimes and efficiencies are also indicated.

2.3. Conclusion:

Novel [60]fullerene-perylenebisimide (C₆₀-PDI) dyads were developed as efficient light-harvesting systems designed for directional energy transfer. The PDI was introduced to play the role of a visible-light antenna and after excitation of this PDI moiety in the dyads, we could prove a quantitative intramolecular energy transfer (> 99%) from the PDI donor to the C₆₀ acceptor. A Förster-type mechanism is suggested to explain this singlet-singlet energy transfer and it was demonstrated that the final populated excited state is a low-energy triplet state localized on the PDI moiety.

Interestingly, various intramolecular energy transfer rates⁴¹h, ⁵⁷ between C₆₀ and different PDI containing chloro-, phenoxy- and pyrrolidino-substituents at the bay position (the orange, red and green PDI family⁶⁸) at different molecular configurations
are now available making an extensive comparison of factors influencing the rates possible (see appendix 2 for table with all rates reported there). It can already be noted that the combination of the green PDI with C\textsubscript{60} through a pyrrolidine bridge results in much slower singlet and triplet energy transfer\textsuperscript{41h} (in toluene), not only due to the restricted conformational freedom, but also to the much less favorable Förster overlap. This would imply that these types of NIR-absorbing imide dyes (that can harvest more of the sunlight) should be designed to display Dexter-type energy transfer.

It was also shown in these C\textsubscript{60}-PDI dyads that the relative position of the first reduction potential of the PDI moiety in solution relative to this of C\textsubscript{60} can be finely tuned by molecular engineering around the PDI bay region. This electrochemical parameter was correlated with preliminary results obtained from the conception of photovoltaic devices. These were tested by blending P3HT with C\textsubscript{60}-PDI dyad and it was clearly evidenced in agreement with absorption and electrochemical properties that better photovoltaic characteristics were obtained using dyad 3 instead of with dyad 1.\textsuperscript{42} Further investigation concerning the incorporation of these dyads in photovoltaic devices is underway. Firstly, the possibility of using the C\textsubscript{60}-PDI dyad associated in variable amount with [60]PCBM in the photoactive layer and secondly, the design of new light-harvesting dyads in which the first reduction process should be more selective between the two units.

### 2.4. Experimental Section

**Materials and Methods**

The studied compounds 1-4 and the reference compounds 5, 6, 7 were synthesized by Dr. J. Baffreau from the group of Prof. Hudhomme in France. For the detail of synthesis and NMR data, see the reference.\textsuperscript{69}

All solvents were at spectroscopic or HPLC grade from Aldrich or Acros and were used without any further purification.
Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum electrode and a platinum wire counter-electrode. A silver wire served as quasi-reference electrode and its potential was checked against the ferricinium/ferrocene couple (Fe$^{3+}$/Fe) before and after each experiment. The electrolytic media involved CH$_2$Cl$_2$ (HPLC grade), o-dichlorobenzene (Aldrich spectroscopic grade) and 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHP - puriss quality). All experiments were performed in a glove box containing dry, oxygen-free (< 1 ppm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat.

Steady-state absorption spectroscopy was recorded with a Lambda 19 NIR model from Perkin-Elmer. Fluorescence spectra were recorded in non-deoxygenated solvents (spectroscopic grade) at 20°C with a QM-4/QuantaMaster™ fluorometer from PTI® equipped with rapid monochannel detection and continuous excitation source. Quantum yields were determined using cresyl violet as a standard reference ($\Phi_f = 0.54$ at 20°C in MeOH).

For time resolved spectroscopy, samples were dissolved in spectroscopic solvents (toluene and benzonitrile from Aldrich) and filtered (0.4 µm PVDF HPLC-filters) to remove particles and potential aggregates. The samples had an absorbance of ca. 0.7 – 0.9 (1 cm) for nanosecond transient measurements and of ca. 0.3 – 0.7 (2 mm) for femtosecond transient at the excitation wavelength. The UV-Vis absorption spectra of the samples were measured before and after the laser experiments and were found to be virtually identical, thus ruling out any possible degradation or chemical change of the samples. All photophysical data reported here have a 5 to 10 % error limit, unless indicated otherwise. The experiments were performed at room temperature.

Femtosecond transient absorption experiments were performed with a Spectra-Physics Hurricane Titanium:Sapphire regenerative amplifier system. The full spectrum setup was based on an optical parametric amplifier (Spectra-Physics OPA 800C) as the pump. The residual fundamental light, from the pump OPA, was used for white light generation, which was detected with a CCD spectrograph (Ocean Optics). The
polarization of the pump light was controlled by a Berek Polarization Compensator (New Focus). The Berek-Polarizer was always included in the setup to provide the Magic-Angle conditions. The probe light was double-passed over a delay line (Physik Instrumente, M-531DD) that provides an experimental time window of 3.6 ns with a maximal resolution of 0.6 fs/step. The OPA was used to generate excitation pulses at 530 nm. The laser output was typically 3.5-5 μJ pulse\(^{-1}\) (130 fs FWHM) with a repetition rate of 1 kHz. The samples were placed into cells of 2 mm path length (Hellma) and were stirred with a downward projected PTFE shaft, using a direct drive spectro-stir (SPECTRO-CELL). This stir system was also used for the white light generation in a 2 mm water cell. For femtosecond transient absorption in the NIR region a Control Development NIR-256L-1.7T1-USB, optical spectrometer system, InGaAs detector with 512 element arrays responding to wavelengths range from 900-1700 nm, was used. Detection light was generated with a sapphire plate.

Time-resolved fluorescence measurements were performed on a picosecond single photon counting (SPC) setup. The frequency doubled (323 nm, 1 ps, 3.8 MHz) output of a cavity dumped DCM dye laser (Coherent model 700) pumped by a mode-locked Ar-ion laser (Coherent 486 AS Mode Locker, Coherent Innova 200 laser) was used as the excitation source. A (Hamamatsu R3809) micro channel plate photomultiplier was used as detector. The instrument response (~17 ps FWHM) was recorded using the Raman scattering of a doubly de-ionized water sample. Time windows (4000 channels) of 5 ns (1.25 ps/channel) – 50 ns (12.5 ps/channel) could be used, enabling the measurement of lifetimes of 5 ps - 40 ns. The recorded traces were fitted by using the Igor Pro program.

In nanosecond pump-probe experiments, for excitation a (Coherent) Infinity Nd: YAG-XPO laser was used. The laser illuminated a slit of 10 x 2 mm. Perpendicular to this, the probe light provided by an EG&G (FX504) low pressure Xenon lamp, which irradiated the sample through a 1 mm pinhole. The overlap of the two beams falls within the first two millimeters of the cell, after the slit. The probe light from both the signal and the reference channels is then collected in optical fibers which are connected to an Acton SpectraPro-150 spectrograph which is coupled to a Princeton
Instruments ICCD-576-G/RB-EM gated intensified CCD camera. Using a 5 ns gate this camera simultaneously records the spectrally dispersed light from both optical fibers on separate stripes of the CCD. De-aeration was performed by bubbling with Argon for 20 to 30 minutes.

2.5. References


We attribute this to the presence of a PDI derivative impurity in spite of repetitive efforts for the purification of dyads by preparative HPLC. Indeed, taking into account both the relative emission intensity and amplitudes of the long components, the amounts could be estimated to be 0.003 to 0.015 %, implying 99.997 and 99.985 % purity (!) of the dyads. A second hypothesis considers that this long-lived component could be also due to a non active conformation of the dyad.


Appendix 2

This appendix gives detailed background information to the research described in the chapter 2.

The energy transfer rates are given in table A2.1 for compounds 1 – 4 in toluene and benzonitrile. Based on the resonance energy transfer rate and the Förster radii experimentally determined, the center-to-center distance of the two moieties can be estimated. The results are shown in Table A2.2.

In order to show unequivocally that the compounds shows very similar behaviour in non-polar (toluene) and in the polar solvent (benzonitrile), spectra and kinetic traces are given in both solvents for selected compounds. Comparison can be made in figures A.2.1. to A2.3. (see reference 1 for spectra of compound 1). Figure A2.4 indicates that the excited state absorption on a femtosecond timescale in the NIR region is characterized by maxima at 990 nm for 1 and at 960 and 1040 nm for 3, which can be attributed to the singlet-singlet absorption of the perylene bisimide units. The kinetics of these bands is very similar to that observed in the Vis for the PDI singlet states. Similar spectra have been reported for the singlet state of the green perylene (with two pyrrolidine substituents in the bay position).2 As the triplet state of the C₆₀ unit is observed for the compounds 2-4, the triplet-triplet absorption spectra of the Bingel adduct (compound 7) are given in figure A 2.5, together with that of pristine C₆₀. Figure A2.6 shows that upon going from 1 to 4 the amount of triplet C₆₀ that remains as one of the final states, increases. This is clearly visible in the OMA data with 1 ns increment, where the amount of the 710 nm absorption band is indicative. This band is not observed for 1, shows a ns rise and decay for 2 and a slower rise and much slower decay for 4.

In Figure A2.7, information is given on the PDI triplet states. By using a similar method as described by Ford and Kamat3 an estimate is made for the extinction coefficient of the PDI triplet states of 2 and 3. Finally, the estimations of the triplet quantum yields (see also reference 4) are given.
Energy transfer rates and center to center distances.

The table A 2.1 presents the energy transfer rates of compounds 1 – 4 in toluene (non-polar solvent) and benzonitrile (polar solvent).

**Table A 2.1. Energy transfer rates of compound 1 – 4 in toluene and benzonitrile**

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
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</thead>
<tbody>
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<td>$k_2$ [s$^{-1}$]</td>
<td>$k_3$ [s$^{-1}$]</td>
</tr>
<tr>
<td>1</td>
<td>$2.5 \times 10^{12}$</td>
<td>$20.0 \times 10^{10}$</td>
<td>$1.25 \times 10^{9}$</td>
</tr>
<tr>
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<td>$3.7 \times 10^{10}$</td>
<td>$0.16 \times 10^{9}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.2 \times 10^{12}$</td>
<td>$8.3 \times 10^{10}$</td>
<td>$0.37 \times 10^{9}$</td>
</tr>
<tr>
<td>4</td>
<td>$0.1 \times 10^{12}$</td>
<td>$2.0 \times 10^{10}$</td>
<td>$0.25 \times 10^{9}$ ($3 \times 10^7$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Benzonitrile (not all rates were determined)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$3.3 \times 10^{12}$</td>
<td>$25 \times 10^{10}$</td>
<td>$1.0 \times 10^{9}$</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>$1.67 \times 10^{12}$</td>
<td>$9.1 \times 10^{10}$</td>
<td>$1.6 \times 10^{9}$</td>
</tr>
<tr>
<td>4</td>
<td>$0.1 \times 10^{12}$</td>
<td>$1.0 \times 10^{10}$</td>
<td></td>
</tr>
</tbody>
</table>

The center to center distances ($R$) of compounds 1 – 4 were estimated using equation:

$$R = (k_{\text{EnT}} \tau_D)^{-6} R_o,$$

in which $R_o$ was calculated according to Eq.2.1 (see the main chapter). Overlap integrals used were: $J = 1.46 \times 10^{14}$ M$^{-1}$cm$^{-1}$nm$^4$ (for 1 and 2 in toluene); $J = 1.03 \times 10^{14}$ M$^{-1}$cm$^{-1}$nm$^4$; $J = 6.33 \times 10^{13}$ M$^{-1}$cm$^{-1}$nm$^4$ (for 3 and 4 in toluene). $\tau_D$ for compounds 1 and 2 is 5580 ps, and that for compound 3 and 4 is 5950 ps. The results are given in Table A 2.2, indicating reasonable distances ranging from 6.4 to 12.6 Å.

**Table A 2.2. Estimated center to center distances ($R$) between C60 and PDI moieties.**

<table>
<thead>
<tr>
<th></th>
<th>$R_{(1)}$ Å</th>
<th>$R_{(2)}$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.6</td>
<td>10.0</td>
</tr>
<tr>
<td>2</td>
<td>9.9</td>
<td>13.3</td>
</tr>
<tr>
<td>3</td>
<td>6.4</td>
<td>10.0</td>
</tr>
<tr>
<td>4</td>
<td>10.5</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Transient absorption spectroscopy

The femtosecond transient absorption of compound 1 and 4 in toluene and benzonitrile shows that there is no significant difference in the cases of polar and non-polar solvents. This indicates the absence of photoinduced electron transfer in the investigated systems.

**Figure A2.1.** Comparison to the kinetic traces at 560 (above), 600 (middle) and 725 nm (below) of 1 in benzonitrile (left) and in toluene (right), together with tri-exponential fit ($\tau_1 = 0.3$ ps; $\tau_2 = 4$ ps and $\tau_3 = 1$ ns for 1 in benzonitrile and $\tau_1 = 0.4$ ps; $\tau_2 = 5$ ps and $\tau_3 = 0.8$ ns for 1 in toluene).
Figure A2.2.A Femtosecond transient absorption spectra of compound 4 in benzonitrile with kinetic traces at 600 nm (left) and at 560 nm (right) ($\tau_1 = 11$ ps; $\tau_2 = 100$ ps).

Figure A2.2B Femtosecond transient absorption spectra of compound 4 in toluene with kinetic traces at 600 nm (left) and at 560 nm (right). $\tau_1 = 7$ ps; $\tau_2 = 50$ ps)
Interestingly the triplet-triplet absorption of 1 and 2 in benzonitrile is substantially sharper than that in toluene, with a higher extinction coefficient. The area under the band, between 530 and 700 nm however, remains the same in agreement with a non-altered total transition probability.

Figure A2.3. Nanosecond transient absorption spectra (A, B) of compound 2 (non-degassed) and (C, D) of compound 3 (argon degassed) in benzonitrile and in toluene.
The femtosecond transient absorption in NIR detection shows the singlet-singlet absorption band of perylene derivatives in both compounds, the chloro-substituent (compound 1) and the phenoxy-substituent (compound 3), supporting the conclusion that the process occurring in the system is energy transfer.

Figure A 2.4. Fs-TA spectra ($\lambda_{ex} = 530$ nm, 150 fs fwhm) with NIR detection of (A): compound 1 in toluene; (B): compound 3 in toluene together with (C) kinetic trace at 990 nm of 1 together with fit ($\tau_1 = 0.4$ ps; $\tau_2 = 5$ ps). (see also reference 2).
The nanosecond transient absorption of C₆₀ and C₆₀ derivative shows the typical triplet absorption band at 710 nm which were also observed in some early tens of nanoseconds in the cases of C₆₀ – PDI systems (see below).

![Nanosecond transient absorption spectra](image)

**Figure A 2.5.** Nanosecond transient absorption spectra (A) of compound 7 (Bingel-adduct reference compound) and (B) of pristine C₆₀ in toluene, incremental time delays is 650 ns (argon degassed), $\lambda_{ex} = 460$ nm.

The nanosecond transient spectroscopy of compound 1, 2 and 4 (figure A2.6) in the first 25 ns indicates different behavior depending either on spacer length (*i.e.* compound 1 and 2) or on bay-area substitution of perylene bisimide moieties (compound 2 in comparison to compound 4).

The increased population of the triplet state of C₆₀ absorbing at 710 nm is clearly visible, when going from 1 to 2 to 4. Time increases from light grey to black. First spectrum is before laser pulse.
Figure A 2.6. Nanosecond transient absorption spectra of compound 1(A), 2(B) and 4(C) in toluene with a 1 ns incremental time delay, $\lambda_{ex} = 580$ nm.
Estimation of PDI triplet-triplet molar absorption coefficient.

A) B)

Figure A 2.7. True triplet-triplet absorption spectrum of 2 (A) and 3 (B) in toluene on an absorption coefficient scale, together with observed transient absorption spectrum and the ground state UV-Vis absorption spectrum. A small contribution of the triplet of C$_{60}$ at 710 nm is present in case of 3.

This method assumes that all molecules that are ground state depleted are in the PDI triplet state. The iso-absorptive points thus indicate equal extinctions of ground state and triplet excited state. Based on these values, the quantum yield of triplet PDI formation could be estimated, using the comparative method.$^4$

Estimation of triplet quantum yields:

The PDI triplet quantum yield of 1 (see reference 1) was previously determined to be (more than) 40 %. With the more accurate (slightly lower) epsilon and the double-passing of the delay line (giving a longer rise time of the 560 nm band) this has been determined to be $\sim$75 %.

The comparative method indicates: $\Phi_T(1) \times 0.95 = \Phi_T(2)$ and $\Phi_T(3) \times 0.87 = \Phi_T(4)$ both in toluene and in benzonitrile. The triplet yield for the longer spacers is slightly lower, assuming equal absorption for 3 and 4 and for 1 and 2, in the same solvent. The triplet yield of 3 is estimated from the molecular absorption coefficients of compound 7 and the PDI triplet of 3, using equal absorption at the two maxima and a quantum yield sum of unity. For 3 at 710 nm ($\varepsilon_{(T1-Tn)} = 9400 \text{ M}^{-1}\text{cm}^{-1}$); for compound 7 at 710 nm ($\varepsilon_{(T1-Tn)} = 14000 \text{ M}^{-1}\text{cm}^{-1}$, see reference 5).
Chapter 2

References for appendix 2


