Photoinduced processes in functionalized and organized dye systems
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Abstract

A calix[4]arene scaffold has been functionalized with an electron-accepting perylene bisimide as well as an electron donating pyrene unit. Steady state and time resolved spectroscopy indicate a strong charge transfer (CT) interaction between these two units in all investigated solvents. The signatures of the radical anion of the perylene bisimide and the radical cation of the pyrene are observed with femtosecond transient absorption spectroscopy. A preferential \( \pi \)-stacked conformation is inferred.

In tetrahydrofuran (THF) as a solvent \( \sim 25 \% \) of an extended form is invoked. The CT states of these two ground state populations (\( \pi \)-stacked and extended) have different formation and decay kinetics and result in the spectral distinction of a compact and an extended charge transfer state, upon visible excitation. In the extended conformation, upon UV excitation, pyrene acts as an electron acceptor that is reduced through a photoinduced electron transfer process by the calix[4]arene. In this conformation the calixarene scaffold is accordingly not an uninvolved linker unit but participates effectively in the electron transfer processes.
3.1. Introduction

The development of photoactive organized dye systems for directional excitonic and electronic transport is important for generating new organic photonic applications and electro-optical devices.\(^1\) An important step in this direction was taken by Tang et al.\(^2\) who reported the first two-layer organic solar cell containing 3,4:9,10-perylene tetracarboxylic bis(benzimidazole) as n-type material and copper phthalocyanines as p-type counterpart. Recent work on polymer-C\(_{60}\) solar cells has shown that generating a nanoscopic interpenetrating network is essential for good device operation (for e.g. PCBM-PPV).\(^3\) Next to controlling the physics of phase separation, self-organization of electron donor-acceptor systems with supramolecular functionality is a means towards creating nanoscopic networks.\(^4\) Examples of supramolecular recognition and organization applied in material science are represented by hydrogen bonded polymer systems\(^5\) as well as cyclodextrin functionalized fabrics\(^6\) and dyes.\(^7\) The self-organization can in principle be attained by the introduction of a supramolecular unit that can be used to induce a secondary structure.

The energy transfer cascades in calixarene linked dye systems containing orange, red and green colored perylene bisimide chromophores\(^8\) was reported towards this direction. The 3,4:9,10-perylene tetracarboxylic bis(dicarboximides) dyes (PDI) are excellent highly absorbing and photo-stable organic dyes for such purposes for which the absorption spans a large part of the solar spectrum.\(^9\) This class of compounds is also applied as laser-dyes\(^10\) in Xerography\(^11\) and in car-paints.\(^12\) The simplest supramolecular building block of the calixarene-PDI series\(^13\) (the orange colored PDI “Perylene Orange” linked to a calix[4]arene) as well as calixarenes bearing two identical PDIs\(^14\) have been studied. In this chapter, we report on progress towards charge separation in such cascade systems by introducing an electron donating pyrene chromophore into the calixarene-linked system (see Figure 3.1).

The combination of the text-book-chromophore pyrene\(^15\) with the third generation of supramolecular hosts\(^16\) has been applied before. The excimer emission of calixarenes functionalized with two pyrene units\(^17\) has been used in various ion-sensing modalities.
Whereas “bare” perylene and pyrene have been grafted together onto one calix\(^\text{18}\) previously, the combination of PDI dyes and pyrene onto this scaffold is unprecedented.

![Molecular structure of the Py-c-PDI system, containing a carboxamido-pyrene unit (Py) linked to a calix[4]arene (c) functionalized with PDI (“Perylene Orange”). Also shown are the reference compounds Py-c and PDI-c.](image)

**Figure 3.1.** Molecular structure of the Py-c-PDI system, containing a carboxamido-pyrene unit (Py) linked to a calix[4]arene (c) functionalized with PDI (“Perylene Orange”). Also shown are the reference compounds Py-c and PDI-c.

We show that the excited state dynamics of Py-c-PDI are characterized by charge transfer interactions in all solvents (with polarities ranging from cyclohexane to acetonitrile). Charge transfer absorption bands and optical electron transfer are observed. In tetrahydrofuran (and to a minor extent in benzonitrile) two ground state populations are discovered that arise from specific solute-solvent interactions. These populations exhibit different formation and decay kinetics and result in the spectral distinction of a compact and an extended charge transfer state.

The Py-c-PDI system 5 was synthesized (by Felix Schlosser, working in Prof. Würthner’s group in Germany) in three steps according to Scheme 1.\(^\text{19}\)
Scheme 1. Synthesis of the Py-c-PDI system 5. Reagents and conditions: a) Et₃N, toluene, reflux, yield 58%; b) CF₃COOH, CH₂Cl₂, rt; c) 1-pyrenecarboxylic acid, N-methylmorpholine, N,N'-dicyclohexylcarbodiimide, 1-hydroxybenzotriazole, dimethylformamide, CH₃CN, rt, yield 33% over two steps.

3.2. Results and Discussion

3.2.1. Molecular Modeling

From the structure of Py-c-PDI (Figure 3.1) it can be envisaged that this three component system can adopt two conformations attributed to the two possible pinched-cone conformations of the calix[4]arene: the system can adopt a π-stacked form and an extended form.

Figure 3.2 shows calculated equilibrium geometries of the π - stacked conformation in which two aromatic chromophores are in face-to-face position and the extended conformer of Py-c-PDI in which the two substituents are farther away from each other.
Figure 3.2. The two possible conformers of Py-c-PDI (π-stacked and extended). Hydrogen atoms are omitted for clarity.

3.2.2. Electronic properties

The absorption and emission spectra of Py-c-PDI in tetrahydrofuran (THF), as shown in Figure 3.3, are characterized by the typical PDI absorption (525, 490, and 461 nm) and emission (530, 580 and 640 nm) peaks of the PDI chromophore in the visible region.

Figure 3.3. Absorption (solid line) and fluorescence spectra (dotted line) of Py-c-PDI in THF together with the sum spectrum (dash-dot line) of the two separate reference chromophores DBPI and Py-c.

A good mirror image can be observed with very small Stokes shift indicating only a small geometrical reorganization of the chromophore in excited state. In the UV region
the peaks of the pyrene at 347 and 333 nm can be clearly discerned.\textsuperscript{20} It can be noted that the amide functionality modulates the fine structure and the intensity of the absorption to the pyrene singlet states. Similar effects have been described before.\textsuperscript{21}

Comparison with the sum spectrum of the two separate chromophores shows a strong perturbation due to interaction between the pyrene- and PDI-units in the ground state. A clear broadening of the PDI absorption peaks is accompanied by a reduction in the molar absorption coefficients for the peak maxima, as compared to reference systems\textsuperscript{13, 22} indicating ground-state interaction. A charge-transfer absorption band is present in the visible range (between 500 - 600 nm); however it strongly overlaps with the PDI absorption bands, preventing deduction of (the maximum of) a structureless charge-transfer absorption band. Absorption and emission data of \textit{Py-c-PDI} in other solvents are presented in Table 3.1.

\textbf{Table 3.1. Absorption and fluorescence properties of \textit{Py-c-PDI} in seven solvents}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption</th>
<th>Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ (nm); $\varepsilon$, M$^{-1}$cm$^{-1}$</td>
<td>$\lambda_{PDI}$\textsuperscript{(a)} (nm)</td>
</tr>
<tr>
<td>CHX</td>
<td>278, 333, 347 (25200) 459, 489, 525 (64700)</td>
<td>525</td>
</tr>
<tr>
<td>TOL</td>
<td>334, 350 (27500) 466, 496, 533 (63900)</td>
<td>538</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>279, 335, 350 (23600) 466, 497, 534 (64600)</td>
<td>538</td>
</tr>
<tr>
<td>THF</td>
<td>278, 333, 347 (28600) 460, 490, 525 (64500)</td>
<td>531</td>
</tr>
<tr>
<td>DCM</td>
<td>279, 334, 349 (23300) 466, 496, 533 (62900)</td>
<td>536</td>
</tr>
<tr>
<td>PhCN</td>
<td>336, 351 (26100) 468, 499, 536 (62400)</td>
<td>539</td>
</tr>
<tr>
<td>ACN</td>
<td>278, 333, 348 (21700) 465, 494, 531 (60650)</td>
<td>531</td>
</tr>
</tbody>
</table>

$\lambda_{exc} = 470$ nm, $\lambda_{exc} = 320$ nm; CHX: cyclohexane, TOL: toluene, CHCl$_3$: chloroform, THF: tetrahydrofuran, DCM: dichloromethane, PhCN: benzonitrile, ACN: acetonitrile.
Strong indications for excited state interactions are provided by the fluorescence quantum yields ($\Phi_F$) for Py-c-PDI (Figure 3.4, Table 3.1). The $\Phi_F$ values indicate a very strong quenching of the perylene unit in Py-c-PDI ($\Phi_F$ ranges from $4 \times 10^{-4}$ to $2.6 \times 10^{-3}$) in comparison with the perylene bisimide chromophore itself ($\Phi_F$ is near unity). These quantum yields are also substantially smaller than those of the calix[4]arene functionalized PDI$^{13}$ (quantum yields of $\approx 0.02$ to 0.03 for PDI-c). By taking Py-c-PDI in CHCl$_3$ as a reference point, it can be seen that the fluorescence quantum yields of Py-c-PDI in PhCN, THF and TOL are up to six times higher than in the other solvents.

![Fluorescence spectra](image)

**Figure 3.4.** Fluorescence spectra of Py-c-PDI (solid line, multiplied by 500) together with reference (DBPI) compound (dotted line) in CHCl$_3$. In the determination of the emission ratios of DBPI and Py-c-PDI, a neutral density filter (ND 1.0) was employed in the excitation pathway for the reference compound, but not for the sample (see experimental).

In all seven solvents the fluorescence quantum yields of the pyrene moiety of Py-c-PDI are less than $10^{-4}$ and, thus, at the detection limit. By contrast, the quantum yield of pyrene in cyclohexane$^{20}$ is 0.65; that of amide-functionalized pyrene$^{21}$ is 0.64. For calix[4]arene–pyrene (Py-c), however, $\Phi_F$ is $\approx 1 \times 10^{-3}$ (see Supporting Information of reference 19)
The steady state spectroscopy of Py-c-PDI shows that the molar absorption coefficients and the luminescence quantum yields are strongly affected by the interaction of the pyrene with the PDI unit, in low and high polarity solvents. It appears that both in the ground state and in the excited state interaction occurs, the former being indicated by the changed absorption properties. As charge separation is envisaged to occur in these molecules, with pyrene as the donor and PDI as the acceptor, time resolved spectroscopy was applied to provide more information on this process.

3.2.3. Femtosecond Transient Absorption

The transient absorption spectra of Py-c-PDI in THF probed in the visible region and excited at 530 nm (PDI excitation) or at 350 nm (pyrene excitation) (see Figure 3.5A and 3.5B) are rather similar: the spectra show the characteristic features of the PDI unit with strong ground-state bleaching at ca. 492 and 527 nm, the absorption of PDI radical anion at the band centered at 710 nm,\textsuperscript{13, 23} which overlaps with PDI singlet excited state.\textsuperscript{13, 24} Also, the pyrene radical cation absorption band at around 400 - 450 nm can be identified.\textsuperscript{25} Spectra with these two characteristic features were observed in five other solvents of different polarity.

The transient absorption spectra (Figure 3.5A) observed in THF (the solvent with the highest emission quantum yield, $\Phi_{PDI}$) indicate the existence of an extended conformation of Py-c-PDI that shows a slightly slower charge separation process (see later). The spectra observed in all other solvents (see Supporting Information of reference 19) show even less emission irrespective of solvent polarity and are all characteristic for charge separation.

When we compare transient absorption spectra upon visible excitation (Figure 3.5A) with those of PDI-c,\textsuperscript{13} it is noticed that the stimulated emission (the band at of the PDI is much less pronounced in Py-c-PDI. This illustrates the ultrafast charge separation that occurs upon visible excitation. As discussed before, the emission quantum yields
show that very strong quenching of the PDI unit of **Py-c-PDI** is prominent in all solvents (Table 3.1), but relatively weaker in THF, PhCN and TOL.

**Figure 3.5. Femtosecond transient absorption spectroscopy of Py-c-PDI in THF**  
A) $\lambda_{\text{exc}} = 530 \text{ nm}$; B) $\lambda_{\text{exc}} = 350 \text{ nm}$, visible detection; C) $\lambda_{\text{exc}} = 530 \text{ nm}$, NIR detection; D) $\lambda_{\text{exc}} = 350 \text{ nm}$, NIR detection.

Closer inspection of the data obtained with 350 nm excitation (as compared to 530 nm) in THF (Figure 3.5B) indicates some remarkable distinctions that are in agreement with pyrene excitation as well as a small amount of energy transfer from the pyrene unit to the PDI unit. At 2 ps it is clear that the negative PDI bleach is superimposed onto a broader positive absorption centered at ~500 nm. The ~500 nm band is assigned to excited state absorption of pyrene$^{25, 26}$ as well as the pyrene radial anion (490 - 520 nm).
nm).\textsuperscript{27} Also, features of the S\textsubscript{2} – S\textsubscript{n} pyrene absorption (500 - 580 nm)\textsuperscript{25, 28, 29} can be extracted from the data (see next section). The observation of some PDI emission (around 580 nm) upon pyrene excitation provides evidence for some energy transfer from the pyrene singlet excited state to PDI chromophore on a (sub)picosecond time scale in the extended conformer.

The transient absorption spectra of Py-c-PDI in THF with NIR detection (Figure 3.5C and 3.5D, see above) are characterized by the second PDI radical anion band\textsuperscript{13, 23} that is centered at 958 nm. This is in agreement with the formation of a charge-separated state. Upon 530 nm excitation, the singlet PDI absorption with the broad band at 900-1000 nm\textsuperscript{30} is also present at very early times (see also Global analysis section). The spectra of Py-c-PDI in THF with NIR detection confirm that ultrafast electron transfer takes place at both 350 nm and 530 nm excitation. For Py-c-PDI in the other solvents\textsuperscript{19} similar events can be observed.

3.2.4. Global and target analysis of visible excitation

The combined femtosecond transient absorption data matrices of Py-c-PDI obtained with visible or NIR detection (530 nm excitation) were analyzed with spectrotemporal parameterization\textsuperscript{31} in five solvents. A target model that implies ultrafast charge separation followed by fast solvation (with some minor competing charge recombination) and subsequent charge recombination appropriately describes the data in all solvents (model A in Figure 3.6), except in THF. In the latter solvent, in which the highest steady-state luminescence intensity was observed also, another model was applied (model B in Figure 3.6). In THF the presence of two coexisting conformations was invoked, an extended (25 \%) and a π-stacked (75 \%) conformation. In the extended conformation charge separation and charge recombination are slower. The applied models are represented in Figure 3.6.
Figure 3.6. The two models used in target analysis upon 530 nm excitation.

Figure 3.7 exemplifies the Species Associated Difference Spectra (SADS) that are attributed to the first excited singlet state of the PDI and the different charge-transfer states (e.g., CT₁ and CT₂). The first excited singlet state of the PDI is characterized by ground-state bleaching and emission (with a typical negative pattern with peaks at 490, 527 and 574 nm), an absorption band at around 700 nm and a broad absorption band in the NIR region at ~910 nm both attributed to the $S_1 \rightarrow S_n$ absorption. The charge transfer state described by the reduced PDI and the oxidized pyrene unit is characterized by a strong ground-state bleaching (490 and 527 nm), the total absence of PDI-based emission, the radical anion absorption features at 720 nm (broad) and 955 nm (sharp), and weak radical cation features of the pyrene at ~ 400 - 450 nm.
Figure 3.7. Species Associated Difference Spectra (SADS) with decay times of A) the first excited singlet state of PDI and of B) the charge transfer state of the stacked (s) and extended (e) conformation of Py-c-PDI in THF at 530 nm excitation (visible and NIR detection) obtained with target analysis.

Interestingly, the radical anion features of the extended form are sharper than of the π-stacked form. This implies spectral differentiation between an extended charge-transfer state and a compact charge-transfer state\textsuperscript{32} by transient absorption spectroscopy.

Table 3.2 summarizes the outcome of the target analysis in the five solvents. Only for DCM as a solvent is a structural reorganization of the CT\textsubscript{2} state, leading to the CT\textsubscript{3} state invoked.
Table 3.2. The time constants of the processes occurring in Py-c-PDI extracted from global and target analysis (excitation at 530 nm)\(^{(a)}\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\tau_{CS}) (ps)</th>
<th>(\tau_{cr1}) (ps)</th>
<th>(\tau_{cr2}) (ps)</th>
<th>(\tau_{cr3}) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHX</td>
<td>0.10</td>
<td>4</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>TOL</td>
<td>0.20</td>
<td>10</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>THF (s)</td>
<td>0.17</td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF (e)</td>
<td>11.0</td>
<td>373</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>0.10</td>
<td>1.6</td>
<td>16</td>
<td>50</td>
</tr>
<tr>
<td>ACN</td>
<td>0.10</td>
<td>1.4</td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) In THF data is given for the stacked (s) and the extended (e) conformation. Due to the limitation of the analysis (the maximum number of unknown species is five), the less important processes such as fast solvation were omitted. In all other solvents only the stacked conformation is present. CHX: cyclohexane; TOL: toluene; THF: tetrahydrofuran; DCM: dichloromethane; ACN: acetonitrile.

It is important to notice that a photoinduced charge separation has also been observed in the model system PDI-c.\(^{13}\) Compared to Py-c-PDI, charge separation in PDI-c occurs much slower (\(\tau_{CS}\) ranges from 25 to 64 ps for PDI-c). In another study on calix[4]arenes bearing two identical PDI chromophores the coexistence of two conformations in non-polar solvents could be proven by fast spectroscopy and confirmed by force field calculations.\(^{14}\)

**Excited state properties of Pyrene-calix Py-c**

In order to clarify the excited-state properties of Py-c-PDI that play a role upon UV excitation it is needed to expand on the properties of Py-c. As stated before, the emission of Py-c is strongly quenched (relative to, e.g., amide functionalized pyrene) and this must be due to the presence of the electron donating calix[4]arene.

The femtosecond transient absorption spectra (Figure 3.8) of Py-c excited at the S\(_0\) \(\rightarrow\) S\(_2\) transition of pyrene moiety (350 nm) display the evidence of the electron-transfer process in which the calixarene acts as the electron donor. The absorption band at a
delay time 2 ps with a maximum at 550 nm is known as the $S_1 \rightarrow S_n$ absorption of pyrene unit. The band peaking in region 490 – 520 nm after 4 ps can be assigned to the pyrene radical anion.\(^27\)

![Figure 3.8](image.png)

**Figure 3.8.** *Femtosecond transient absorption spectroscopy of Py-c in THF at 350 nm excitation. Different delay times (in ps) are indicated.*

The global and target analysis (Figure 3.9) of the whole data-matrix associated with Figure 3.8 indicates the presence of four species: the second and the first excited singlet state of pyrene ($S_2$ and $S_1$) and the two charge-transfer states ($CT_1$ and $CT_2$). The $S_2$ state is created within the laser pulse and then decays via two possible channels. One is ultrafast internal conversion from $S_2$ into $S_1$ of pyrene,\(^{26,28}\) the other is electron transfer from calixarene to pyrene. Part of the newly formed charge-transfer state ($CT_1$) undergoes a solvation process to the $CT_2$ state. These two charge-transfer states then decay to ground state via a fast charge recombination process.

In summary, the excited-state behaviour of Py-c is characterized by very fast charge separation from the calixarene to the pyrene, followed by fast charge recombination.
3.2.5. Energetic considerations

The Gibbs energy of photoinduced electron transfer ($\Delta_{ET} G^0$) in a solvent with relative permittivity $\varepsilon_s$ can be estimated by equation Eq.2.1 (written here for neutral starting species).33

$$
\Delta_{ET} G^0 = e\left[ E_{D^{**}/D}^0 + E_{A/A^+}^0 \right] - \Delta E_{0,0} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_C} + \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \left( \frac{1}{\varepsilon_{EC}} - \frac{1}{\varepsilon_s} \right)
$$

Eq.2.1

For the Py-c-PDI system, the standard electrode potentials ($E^{0}(D^{**}/D)$ and $E^{0}(A/A^+)$) of the donor (D) and the acceptor (A) are +0.90 V (Py/Py⁺) and −1.09V vs Fc/Fc⁺ (PDI/PDI⁻), respectively, in the reference solvent dichloromethane with a relative permittivity $\varepsilon_{EC}$ of 8.93 (for cyclic voltammetry, see reference 19). The zero – zero transition energy $E_{0,0}$ of the chromophore slightly varies with solvent. The center-to-center distance $R_c$ between the donor and the acceptor was determined from geometries of Py-c-PDI optimized by using a semi-empirical AM1 method giving a value of 5.6 Å for stacked conformer and 17.7 Å for extended conformer. The

**Figure 3.9.** The Evolution Associated Different Spectra (EADS) of Py-c in THF from global analysis of fs-TA spectroscopy.
effective radii of the donor ($r^+$) and acceptor ($r^-$) are estimated using a spherical approach\textsuperscript{34}. These values are 3.98 Å for pyrene\textsuperscript{35} (density 1.271 g/cm\textsuperscript{3}) and 4.78 Å for PDI\textsuperscript{36} (density 1.407 g/cm\textsuperscript{3}). The results are shown in Table 3.3. The rates of the charge separation (CS) of Py-c-PDI in different solvents were determined theoretically by applying the Arrhenius equation.

\[
k_{\text{ET}} = A \exp(-\Delta G^\# / k_B T)
\]

Eq.2.2

in which $k_B$ is the Boltzmann constant, $T$ is temperature and $\Delta G^\#$ is the Gibbs activation energy of the charge separation process. The pre-exponential factor $A$ in Eq 2.2 depends on the nature of the process (e.g., intermolecular or intramolecular electron transfer). We assume that for the system Py-c-PDI, $A$ is constant with a value of $10^{13}$ s\textsuperscript{-1} in all solvents.\textsuperscript{37} The Gibbs energy of activation ($\Delta G^\#$) and the driving force ($\Delta G = \Delta_{\text{ET}} G^0$) of the charge separation process are correlated using the Eq 2.3\textsuperscript{38}

\[
\Delta G^\# = \frac{(\lambda + \Delta G)^2}{4\lambda}
\]

Eq.2.3

where $\lambda$ is the reorganization energy consisting of solvent reorganization ($\lambda_s$) and internal reorganization ($\lambda_i$) energies, $\lambda = \lambda_i + \lambda_s$; The internal reorganization energy was assumed to be $\lambda_i = 0.2$ eV.\textsuperscript{39} Using the Born–Hush approach,\textsuperscript{34} the solvent reorganization energy ($\lambda_s$) is expressed as

\[
\lambda_s = e^2/(4\pi\varepsilon_o)(1/r - 1/R_e)(1/\varepsilon_{op} - 1/\varepsilon_S)
\]

Eq.2.4

In this equation, $\varepsilon_{op} (= n^2$, $n$ is the solvent refractive index) and $\varepsilon_S$ are the optical and static dielectric constants of the medium, $r = (r^+ + r^-)/2$. With these parameters, the barrier as well as the rate constants of the charge separation process taking place in Py-c-PDI system in several solvents were estimated and shown in the Tables 3.3 and 3.4.
Table 3.3. The driving force for charge separation ($\Delta G_{CS}$), the Gibbs energy of activation ($\Delta G^\#$) of the Py-c-PDI system at PDI (A) excitation in different solvents.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\varepsilon^{(a)}$</th>
<th>$n^{(b)}$</th>
<th>$E_{0,0}^{(c)}$ [PDI] (eV)</th>
<th>$\pi$-stacked conformer</th>
<th>extended conformer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\Delta G_{CS}$ (eV)</td>
<td>$\lambda$ (eV)</td>
</tr>
<tr>
<td>CHX</td>
<td>2.02</td>
<td>1.43</td>
<td>2.36</td>
<td>-0.39</td>
<td>0.20</td>
</tr>
<tr>
<td>TOL</td>
<td>2.38</td>
<td>1.49</td>
<td>2.31</td>
<td>-0.38</td>
<td>0.22</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>4.86</td>
<td>1.44</td>
<td>2.31</td>
<td>-0.54</td>
<td>0.39</td>
</tr>
<tr>
<td>THF</td>
<td>7.58</td>
<td>1.41</td>
<td>2.35</td>
<td>-0.63</td>
<td>0.47</td>
</tr>
<tr>
<td>DCM</td>
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<td>1.42</td>
<td>2.32</td>
<td>-0.61</td>
<td>0.47</td>
</tr>
<tr>
<td>PhCN</td>
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<td>1.53</td>
<td>2.30</td>
<td>-0.66</td>
<td>0.48</td>
</tr>
<tr>
<td>ACN</td>
<td>35.94</td>
<td>1.34</td>
<td>2.33</td>
<td>-0.70</td>
<td>0.58</td>
</tr>
</tbody>
</table>

(a) At 25°C$^{20}$, (b) At 20°C$^{20}$, (c) Estimated from intersection between absorption and emission spectra of perylene moiety in Py-c-PDI; $E_{o_d}(D) = +0.9$ V, $E_{o_d}(A) = -1.09$ V (in CH$_2$Cl$_2$ vs Fc/Fc$^+$); $r^+ = 3.98$, $r^- = 4.78$, $R_C = 5.6$ Å and 17.7 Å corresponding to the stacked and extended conformations, respectively, $\lambda_i = 0.2$ eV.

The CS rate constant ($k_{CS}$) also can be evaluated from the fluorescence quantum yield $\Phi_f$ as follows: the processes occurring in the parent chromophore (i.e., pyrene itself or DBPI in the case of the Py-c-PDI system) after excitation are fluorescence, relaxation to the ground state (internal conversion) and intersystem crossing to the triplet state with the rate constants $k_f$, $k_{IC}$, and $k_{ISC}$, respectively. Then, the fluorescence quantum yield of the parent chromophore ($\Phi_f^{ref}$) and its fluorescence lifetime ($\tau_f^{ref}$) are determined by expressions:

$$\Phi_f^{ref} = \frac{k_f}{k_f + k_{IC} + k_{ISC}} \quad \text{Eq. 2.5}$$

$$\tau_f^{ref} = \frac{1}{k_f + k_{IC} + k_{ISC}} \quad \text{Eq. 2.6}$$
If the electron transfer in an electron donor-acceptor system occurs, the fluorescence quantum yield is lowered to $\Phi_f$ and the time constant is decreased to $\tau_f$:

$$\Phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC} + k_{CS}}$$  \hspace{1cm} \text{Eq.2.7}

$$\tau_f = \frac{1}{k_f + k_{IC} + k_{ISC} + k_{CS}}$$  \hspace{1cm} \text{Eq.2.8}

Thus, we can determine the charge separation rates ($k_{CS}$) by using the equations:

$$k_{CS} = \frac{1}{\tau_f} - \frac{1}{\tau_f^{\text{ref}}}$$  \hspace{1cm} \text{Eq.2.9}

$$k_{CS} = (\Phi_f^{\text{ref}} / \Phi_f - 1) / \tau_f^{\text{ref}}$$  \hspace{1cm} \text{Eq.2.10}

For the PDI chromophore, the fluorescence quantum yields in various solvents are almost unity, $\Phi_f \approx 1$ and the fluorescence lifetime is also unchanged, $\tau_f \approx 4$ ns.\textsuperscript{22} The charge-transfer rates estimated via the fluorescence quantum yield of PDI in several solvents are collected in Table 3.4. These rates are smaller than those obtained from the global analysis results because the “real” emission quantum yields are most likely smaller (they are at the edge of the detection limit in the fluorescence measurements and less accurate than the global analysis results). By combining the outcome of the spectroscopy upon visible excitation with the driving force calculations in Table 3.3 we can create a coherent representation of the excited state processes occurring in Py-c-PDI.

For the $\pi$-stacked conformer there is a driving force for charge separation in all solvents ($\Delta G = -0.39$ to -0.70 eV), ranging from cyclohexane to acetonitrile, with a small barrier to CS ($\Delta G^\neq = 0.04$ to 0.006 eV). For the extended conformation the CS is endergonic in non-polar solvents such as CHX and TOL (see Table 3.3). On the basis of the steady-state emission quenching and the FTA measurements, we concluded that a $\pi$-stacked conformation prevails in these two solvents, since e.g., all
PDI emission is quenched. In the $\pi$-stacked conformation, pyrene acts as the donor and PDI as the acceptor.

**Table 3.4.** The rate constants of charge separation (CS) and charge recombination (CR) processes obtained from theoretical estimates and experimental results (corresponding to 530 nm excitation) for Py-c-PBI.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi_f$ [exp]</th>
<th>$k_{CS}$ (s$^{-1}$) [exp]$^a$</th>
<th>$k_{ET}$ (s$^{-1}$) [calc]$^b$</th>
<th>$k_{CS}$ (s$^{-1}$) [exp]$^c$</th>
<th>$k_{CR}$ (s$^{-1}$) [exp]$^c$</th>
<th>$k_{CR}'$ (s$^{-1}$) [exp]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHX</td>
<td>$5 \times 10^{-4}$</td>
<td>$0.5 \times 10^{12}$</td>
<td>$2.0 \times 10^{12}$</td>
<td>$10 \times 10^{12}$</td>
<td>$25 \times 10^{10}$</td>
<td>$5.2 \times 10^{10}$</td>
</tr>
<tr>
<td>TOL</td>
<td>$12 \times 10^{-4}$</td>
<td>$0.2 \times 10^{12}$</td>
<td>$3.2 \times 10^{12}$</td>
<td>$5 \times 10^{12}$</td>
<td>$10 \times 10^{10}$</td>
<td>$8.0 \times 10^{10}$</td>
</tr>
<tr>
<td>THF(s)</td>
<td>$5.7 \times 10^{12}$</td>
<td>$6 \times 10^{12}$</td>
<td>$1.9 \times 10^{10}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF(e)</td>
<td>$26 \times 10^{-4}$</td>
<td>$0.9 \times 10^{11}$</td>
<td>$1.0 \times 10^{11}$</td>
<td>$0.93 \times 10^{11}$</td>
<td>$0.26 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>$4 \times 10^{-4}$</td>
<td>$0.6 \times 10^{12}$</td>
<td>$6.4 \times 10^{12}$</td>
<td>$10 \times 10^{12}$</td>
<td>$62 \times 10^{10}$</td>
<td>$6.4 \times 10^{10}$</td>
</tr>
<tr>
<td>CAN</td>
<td>$5 \times 10^{-4}$</td>
<td>$0.5 \times 10^{12}$</td>
<td>$7.0 \times 10^{12}$</td>
<td>$10 \times 10^{12}$</td>
<td>$71 \times 10^{10}$</td>
<td>$1.1 \times 10^{10}$</td>
</tr>
</tbody>
</table>

$^a$ Calculated from fluorescence quantum yield of PDI unit, using Eq. 2.10; $^b$ estimated by using Marcus theory for $\pi$-stacked conformer (s) and extended (e) (Eq. 2.1 – Eq. 2.4); $^c$ from the global and target analysis (see above).

In more polar solvents, the driving force in the extended conformation is always less than in the $\pi$-stacked one, with a higher barrier, implying a smaller rate of charge separation for the extended form. This slower process, however, is only readily observed in THF solvent, and present to a minor extent in benzonitrile. Apparently, in all other solvents the $\pi - \pi$ stacking between PDI and Py is stronger than the solute – solvent interactions.

Similar to the visible excitation, also in the data obtained with UV excitation, two conformations have to be invoked. In the $\pi$-stacked conformation, ultrafast charge separation occurs, which leads to the formation of a compact charge-transfer state.

In the extended form, however, strongly competitive electron-transfer interaction between the calixarene and the pyrene occurs. These processes are now faster than the
interaction between Py and PDI, as the distance between these two chromophores has now strongly increased. The main process that can be observed in Py-c-PDI upon UV excitation at the early times, in the extended conformation is the photoinduced electron transfer from the calixarene to pyrene unit, a process that is also observed in the reference system Py-c. This process is very fast because of the short distance between donor and acceptor and is energetically allowed as well as characterized by a very small barrier to charge separation (see Supporting Information of reference 19).

In the case of charge separation in the solvent THF, upon visible excitation, the rate constants obtained from estimates (based on Marcus theory) are well correlated to the global analysis results (Table 3.4). It is noticed that the higher fluorescence quantum yield of Py-c-PDI in THF compared with those in other solvents is due to coexistence of the extended conformation, in which the photoinduced electron transfer is taking place much slower. However, it is hard to get more detail of the solvent effects on the electron transfer occurring in Py-c-PDI as the charge separation time constants in all solvents are similar to the instrument response function (IRF; ~ 0.1 ps).

The charge separation process occurring in the dyad Py-c-PDI in THF are presented in the energy scheme (Figure 3.10), with excitation at 350 nm and 530 nm.

Formation of an extended structure is envisaged to occur by a competition of solute–solvent interactions (favorsing the extended conformation) with π–π interactions between pyrene and PDI (favorsing the π-stacked conformation). The high polarizability of a solvent (like toluene or benzonitrile with high refractive indices) will play a role in these competitive interactions as strong polarizability plays a role in π–π interactions. The exact reason why the extended form is most abundant in THF remains unclear. Most likely its H-bond accepting oxygen competes efficiently with the π–π stacking between PDI and Py, i.e. by hydrogen bonding to the amide NH on the Py.

Also, encapsulation of THF in the calix[4]arene cavity has been observed in single crystals which may point at specific host-guest interactions that lead to a conformational change. Apparently the π–π interactions dominate strongly in
solvents such as cyclohexane, dichloromethane and acetonitrile leading to the π-stacked conformation. A distinct upfield shift of the pyrene $^1$H-NMR resonances$^{19}$ (in tetrachloroethane-$d_2$) also indicate the presence of a π-stacked conformer.

Figure 3.10. Schematic representation (A) of the processes occurring in the two conformations, upon pyrene or perylene excitation, and (B) energy level scheme and processes taking place in Py-c-PDI in THF, upon PDI excitation. (s) and (e) refer to the stacked and the extended conformation, respectively.
3.3. Conclusions

The electron donating pyrene and the PDI acceptor have been grafted onto a calixarene scaffold. UV-Vis absorption and steady state emission indicate a strong interaction between the two chromophores, manifested by broadened absorption bands and reduced molar absorption coefficients as well as strongly quenched emission. Femtosecond transient absorption spectroscopy shows charge separation phenomena occurring on the time scale of the instrument response function (0.1 ps) and clear evidence for radical ion pair formation. The radical cation of pyrene is observed around 450 nm and the PDI radical anion is probed in the NIR region (980 nm). The formation of the CT state occurs irrespective of solvent polarity which has to be attributed to the preferential population of Py-c-PDI in a π-stacked conformation which shows charge-transfer absorption and is characterized by optical electron transfer. This contrasts to our previously reported energy-transfer systems based on calixarene-tethered perylene bisimide dyes in which extended conformations prevailed.8

In THF, two excited state decay channels are observed which indicate the presence of two conformations that are attributed to a π-stacked conformation showing fast optical charge transfer (within the 0.1 ps laser pulse excitation) and an extended conformation showing slower photoinduced electron transfer (11 ps). Upon pyrene excitation (350 nm) in THF a fast competitive charge separation process is observed for the extended conformation, in which the pyrene now acts as the electron acceptor. In this conformation the calixarene scaffold is participating in the photoinduced interactions, taking a role as electron donor. Through specific solute-solvent interactions, competing with π−π interactions, the extended conformation can be probed in, e.g., THF and to a minor extent in PhCN. In these solvents, for both conformations a driving force for electron transfer is present.

Molecular modeling and calculations of the driving force are in accordance with the presence of a π-stacked conformation with a small center to center distance and an
extended form with a larger distance and less driving force. In non-polar solvents no driving force for electron transfer is present for the extended conformation.

The charge separation process is in good agreement with the Gibbs energy for electron transfer and the classical Marcus model. Simultaneous target analysis of the femtosecond data matrices obtained in the visible and NIR regions was performed and indicates that in THF a compact and an extended charge transfer states are formed, which can be spectrally distinguished.

3.4. Experimental Section

3.4.1. Sample preparation.

The molar absorption coefficient ($\varepsilon$) of Py-c-PDI in dichloromethane was determined gravimetrically to be 62900 M$^{-1}$ cm$^{-1}$ at 533 nm. The values of $\varepsilon$ in other solvents were determined by preparing solutions of known concentration from a stock solution of millimolar concentration of Py-c-PDI in dichloromethane of which the concentration was determined spectrophotometrically based on the above value of $\varepsilon$. The fraction of the stock solution is not more than 0.5 % in volume. All the solvents were purchased from Aldrich, Acros or Merck with spectrophotometric or HPLC grade and were used as received. For the absorption and fluorescence measurements, the spectra of solvents were recorded before the samples were prepared, to ensure absence of interference. For femtosecond transient measurements, the samples were filtered (0.4 $\mu$m PVDF filters) to remove particles and had an absorbance of ca. 0.15 – 0.20 at the excitation wavelength using 2 mm cells. 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 a possible degradation or chemical change of the samples.

3.4.2. Steady State Absorption and Fluorescence Measurements

Electronic absorption spectra were measured in a quartz cuvette (1 cm, Hellma) on a Cary 300 spectrophotometer for determining molar absorption coefficients and absorbance of samples for quantum yield measurements. Steady state fluorescence
spectra were recorded on a SPEX Fluorolog 3-22 fluorimeter, equipped with a Xe arc light source, a Hamamatsu R636 - 10 photomultiplier tube detector and double excitation and emission monochromators, using a 475 nm cutoff filter (emission) for perylene emission and a 345 nm cutoff filter (emission) for pyrene emission.

Fluorescence quantum yields\textsuperscript{41} were measured in optically dilute solutions (< 10\textsuperscript{-6}M), using the indicated reference solutions, according to the following equation:

\[
\Phi_u = \frac{(A_r I_u n_u^2)}{(A_u I_r n_r^2)} \Phi_r \tag{Eq.2.10}
\]

where \( u \) and \( r \) denote the unknown and the reference, \( \Phi \) is the quantum yield, \( A \) is the absorbance (0.07~ 0.1 using 10 mm cuvet) at the excitation wavelength, \( I \) is the integrated emission intensity, and \( n \) is the refractive index of the solvent(s). \( N_N'-\text{Bis}(2,5-di-tert-butylphenyl)-3,4:9,10-perylenedicarboximide (DBPI; fluorescence quantum yield is 0.99 in chloroform)\textsuperscript{22} and anthracene (0.27 in ethanol)\textsuperscript{42} were used as standards for perylene emission and pyrene, respectively.

In order to determine the very small quantum yield of the perylene emission of \textbf{Py-c-PDI} with a higher accuracy a Neutral Density filter (ND 1.0, Schott) was used in the excitation pathway for the measurement of the reference (but was taken out for the sample measurement, while using the same system configuration). By using the absorption of the ND filter at the excitation wavelength (\( A_{470 \text{ nm}} = 0.96 \)) the quantum yield of \textbf{Py-c-PDI} was determined. The effect of the ND filter on the emission intensity of the reference was verified first and in good accordance with the ND filter effect (reducing its emission intensity with a factor \( 10^{-A} \)). The estimated error of applying this method for the determination of very low quantum yields is less than 5 \%, (by using this comparison). This method allowed measurements with excitation and emission slits of 12 nm and 2 nm, respectively (these setting would normally overload our detector for this reference compound). Integration times 1s and increments 1 nm were used.
3.4.3. Femtosecond transient absorption (FTA)

FTA 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 PC2000 + slave) for Vis detection. 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 350 or 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 stirring 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.

All photophysical data reported here have a 5 to 10 % error limit. All the experiments were performed at room temperature.

3.4.4. Molecular Modeling

Molecular modeling was performed with the Spartan’04 V1.03 package (Wavefunction Inc.). The molecule was first built in two forms, extended and π-stacked, then equilibrium conformers were calculated using molecular mechanics method at the MMFF level to get the initial structures. Next, geometry optimization was performed using the semi-empirical AM1 method.
3.4.5. Global and target analysis

For the global and target analysis \(^{31}\) all time-gated spectra were collated in a matrix, which was globally fitted using a sequential kinetic scheme with increasing lifetimes. From this the lifetimes and the evolution-associated difference spectra (EADS) were estimated. The instrument response function (IRF) is described by a Gaussian shape, and the white light dispersion over the spectral range is modeled by a third order polynomial. With increasing lifetimes, and thus decreasing rates, the first EADS decays with the first lifetime and corresponds to the difference spectrum at time zero with an ideal infinitely small IRF. The second EADS is formed with the first lifetime and decays with the second lifetime, etc. The final EADS represents the difference spectrum of the longest living species. The error in the lifetimes obtained from the fitting procedure does not exceed 10%. EADS may not represent pure species, except for the final EADS, and they are interpreted as a weighted sum (with only positive contributions) of species-associated difference spectra (SADS). The quality of the fit was judged by inspection of the singular vectors of the matrix of residuals, which had to be structure-less. Next, in target analysis a kinetic scheme was used in combination with spectral assumptions to estimate microscopic rate constants and SADS.

3.5. References


Photoinduced Interactions in a Py-c-PDI Dye System


