Photoinduced Excimer Generation in Perylene Diimide Dimer: Effects of Solvent Polarity

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Abstract. The aggregation and photoinduced excited state dynamic of organic π-conjugated molecules play a vital role in solar energy conversion and applications. This work investigated how solvent polarity affects the aggregation behavior and the photophysical process of perylene diimide dimer (PDI-II). The results showed that the aggregations between PDI intramolecular chromophores are more likely to generate excimer, and the conjugations between PDI intermolecular chromophores are more likely to experience symmetry-breaking charge separation. Our study can provide a reference for the design of high-efficiency solar energy conversion materials.

Keywords: Excimer, Perylene diimide, Dimer, Solvent effect, Transient absorption spectroscopy
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Introduction. Functional organic materials play a vital role in solar energy conversion and applications. The organic π-conjugated molecules are the most used functional organic materials which mainly refer to molecules containing many benzene rings, such as boron dipyrromethene, porphyrin, perylene, and perylene diimide (PDI), etc.[1] These organic π-conjugated molecules have been widely used in photovoltaics, photosynthesis, photoelectricity, photocatalysis, etc.[2-7] Understanding the microscopic dynamic behavior of organic π-conjugated molecules is crucial for further understanding the photophysical processes to help better applications.[8, 9] Previous studies have shown that this conjugate molecule has many complex and exciting dynamic processes, such as excimer state, singlet fission (SF), symmetry-breaking charge separation (SB-CS), etc.[10-12] Various structures and complex dynamics interest researchers. Excimer state is often considered a mixture of locally excited (LE) state and charge transport (CT) state, which belongs to a trap state.[13, 14] However, in some studies, excimer is also believed to be beneficial to charge separation, and SF.[15] SF is a process in which a singlet state splits into two triplet states. In organic photovoltaics, singlet splitting is generally considered to increase the theoretical limit of OPV beyond the Shockley-Queisser limit.[16] SB-CS process refers to forming radical cations and anions in π-conjugated molecules after photoexcitation, which is conducive to charge separation.

PDI is a typical organic π-conjugated molecule, applied in many fields due to its diverse structure and abundant dynamic processes. Our group previously reported the aggregation behavior of PDI monomers under hydrophobic effect and the SB-CS process after aggregation.[11] Here, we used the identical PDI monomers (PDI-C5) as the basic unit to synthesize a dimer molecule (PDI-II), whose structure is shown in Figure 1. This work studied PDI-II's aggregation behavior and dynamics in different solvents. Unlike the aggregation of PDI-C5, we find excimer formation instead of SB-CS when PDI-II is dissolved in the high polar solvent. This finding is of great significance. Since the generation of SB-CS and excimer states is inseparable from electronic coupling, we suspect that the difference in products is because the aggregation of PDI-C5 in solution belongs to intermolecular aggregation. The electronic coupling between PDI-C5 chromophores is weak. However, when the two chromophores are connected by conjugated bridge structures and are in a highly polar solvent, the electronic coupling is further enhanced, and formation excimer. Our study demonstrates that the excited state dynamics of molecules can be controlled by molecular design and solvation.

Experimental and Methods.
Synthesis. The details of molecular structures, design, and synthesis methods of PDI-II can be seen in the literature.[17] All the essential materials and organic solvents were bought from certified commercial resources and used as received.

Steady-state and Femtosecond transient absorption spectroscopy
For solution experiments, ultraviolet-visible (UV-Vis), and fluorescence and femtosecond transient absorption (Fs-TA) spectroscopy were recorded with Agilent Technologies Cary 60 UV-visible spectrophotometer, FLS980 spectrometer (Edinburgh) and Fs-TA spectrometer (Harpia-TA, Light Conversion), respectively. Details of the instrument have been described in a previous article.[18] The Fs-TA experiment is done several times on different spots of the sample, and when measurement completion, no sample degradation is detected. For UV-Vis and Fs-TA, the concentration was 10^-5 mol/L; for fluorescence, the concentration was 10^-6 mol/L. The fluorescence quantum yield was measured by the comparative method of Williams et al.[19] and the yield of Rhodamine 6G in ethanol was taken as the standard yield.

Results and Discussion. The PDI-C5’s molecular structure is shown in Figure 1a. The molecule contains two aliphatic branches or “swallow-tail” side chains in the imide position, improving the solubility.[20] The molecular structure of PDI-II is shown in Figure 1b. We modify the bay position of the PDI-C5 and then connect the two PDI-C5 to the central benzene core by an acetylene spacer to form a dimer (PDI-II).[17] The flexibility of the alkyne bond makes it possible for the solvent to regulate the strength of the electronic coupling between the two chromophores. The absorption and fluorescence spectra of PDI-C5 in dichloromethane (DCM), tetrahydrofuran (THF), and acetone are...
shown in Figure 1c. As shown in Figure 1c, PDI-C5 shows three absorption peaks with apparent fine structure in solution, corresponding to the vibrational transition of S$_0$-S$_1$.[21] The vibrational transition intensity progression follows the order $\Delta \varepsilon_{01}$ (502-550 nm)$>\Delta \varepsilon_{02}$ (485-466 nm)$>\Delta \varepsilon_{03}$ (435-466 nm) is PDI monomer absorption characteristics.[22] At the same time, with increasing solvent polarity, the profile of the absorption spectrum remains consistent. Still, it appears to have a slight blue shift because of different energy levels of the excited states of the perylene moieties.[23] The fluorescence spectrum of PDI-C5 showed a mirror image symmetric configuration with the absorption spectrum, proving that PDI-C5 has a monomeric feature in these three solvents.[24] The absorption and fluorescence spectra of PDI-II in the three solvents are shown in Figure 1d. PDI-II showed three characteristic absorption peaks with prominent fine structures in DCM and THF and followed the order $\Delta \varepsilon_{00}$ (527-595 nm)$>\Delta \varepsilon_{01}$ (488-527 nm)$>\Delta \varepsilon_{02}$ (440-488 nm). Different from Figure 1c, the three absorption peaks are redshift and broader, which is caused by the link of the conjugated bridge structure and increases the electronic coupling of the PDI-II chromophore.[25] The absorption spectrum of PDI-II in acetone appears strange, possibly due to the aggregation of PDI-II in high polar solvents.[22, 26] The fluorescence spectra in Figure 1d become broader and less structured. Especially for PDI-II in acetone, the 650-750 nm fluorescence becomes obvious, indicating the excimer formation.[27] We measured the fluorescence lifetime ($\tau$) and corresponding fluorescence quantum yield ($\Phi$) in solution, and the results are shown in Table 1. With increasing solvent polarity, the lifetime of both molecules changes slightly. However, the PDI-II's quantum yield decreases sharply with increasing solvent polarity and is almost quenched in the high polar solvent. This phenomenon implies that PDI-II relaxes to a nonradiative state in high polarity solvents.[25, 28]

Table 1. Fluorescence quantum yields and corresponding fluorescence lifetime of PDI-C5 and PDI-II in different solvent.

<table>
<thead>
<tr>
<th>molecular</th>
<th>Solvent</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI-C5</td>
<td>DCM</td>
<td>3.4</td>
<td>&gt;0.95</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>4.2</td>
<td>&gt;0.95</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>5.4</td>
<td>&gt;0.95</td>
</tr>
</tbody>
</table>

Fs-TA spectroscopy was used to study PDI-II molecular excited-state energy transfer mechanism in solutions. For comparison, the excited-state dynamics process of PDI-C5 is measured and shown in Figure 2. As shown in Figure 2ac, three consecutive negative peaks and a broad positive signal appears. Compared with the absorption and fluorescence spectrum label in the figures, we conclude the negative peak near 530, and 620 nm is the stimulated radiation (SE), and the sharp and high-intensity signal in 500-550 nm belongs to the superposition of the ground state bleaching (GSB) and SE. This mountain-like signal is in good agreement with the absorption and fluorescence spectra, consistent with the high fluorescence quantum yield of PDI-C5 in the three solvents (Table 1). The sharp positive signal between 670 and 760 nm belongs to the locally excited (LE) state or excited singlet state.[29] After photoexcitation, the positive signal in the 630-910 nm appeared and increased together with the GSB signal. According to the literature, this prolonged signal growth is caused by vibrational relaxation of the hot singlet state or the charge transfer (CT) process.[25] By comparing the various dynamic processes in Figure 2, PDI-C5 showed almost the same dynamics process in the three solvents, which means that the solvent polarity has little influence on the dynamics process of simple PDI monomer molecular.

Figure 2. The TA spectra at select delay time of PDI-C5 in (a, d) DCM, (b, e) THF and (c, f) Acetone. (a-c) is short time decay range. (d-f) is long time decay range. Excited at 480 nm.
Figure 3. The TA spectra at select delay time of PDI-II in (a, d) DCM, (b, e) THF and (c, f) Acetone. (a-c) is short time decay range. (d-f) is long time decay range. Excited at 480 nm.

Figure 3 shows the excited-state dynamics process of PDI-II in three solvents, and the TA results under different solvents have apparent differences. Figure 3a shows the dynamics process of PDI-II in DCM. The results are the same as in Figure 2. Compared with the absorption and fluorescence spectrum, the negative peak at 500nm is GSB, the peak at 600nm is SE, and the middle high-intensity peak is the superposition signal of GSB and SE. The positive signal in the 610-910 nm band appeared and increased together with the GSB, the same as the PDI-C5, caused by the vibrational relaxation of the hot singlet state.[25] Figures 3b and 3e show the TA spectra of PDI-II in THF. Unlike Figure 3a, a clear positive signal appears in the 580-720 nm range and forms an isosbestic point at 712 nm. It has been reported that the excimer state has a strong characteristic absorption signal in the 600-800 nm band.[16, 30] The excimer state usually appears as a trap state, leading to fluorescence quenching.[15, 31] We attribute this new absorption signal to the excimer. In some studies, excimer is also believed beneficial to charge separation and SF.[15, 32] Since no new positive signal emerges in the range of 750-910 nm, which is the absorption range of PDI radical anions,[10-12, 25, 32] we exclude the generation of the symmetry-breaking charge separation process. Since the fluorescence did not appear to have a long lifetime, we excluded the SF process. Figure 3c shows the dynamic process of PDI-II in acetone. PDI-II shows a different dynamic process in acetone than in the previous two solvents. In Figure 3c, only one wide negative signal generation. The one negative peak is attributed to the PDI-II aggregates in acetone, leading to enhanced conjugation, so the absorption spectrum is concentrated near 550 nm, and fluorescence quenching simultaneously causes the SE signal around 600 nm to almost disappear. The positive signal at 0.5 ps is the same as Figure 3a, ascribed to the LE. But a new positive peak in 578-668 nm is the same as Figure 3b and ascribes to excimer.

Table 2. Time Constants Estimated for Different Processes of PDI-C5 and PDI-II in Different Solvents Determined by Fs-TA Measurements

<table>
<thead>
<tr>
<th>molecular</th>
<th>Solution</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
<th>$\tau_4$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI-C5</td>
<td>DCM</td>
<td>129±1</td>
<td>2967±11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>139±1</td>
<td>3417±14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>113±6</td>
<td>3355±31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDI-II</td>
<td>DCM</td>
<td>92±17</td>
<td>4402±54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>7.69±0.71</td>
<td>213±76</td>
<td>2874±56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>6.48±0.72</td>
<td>131±25</td>
<td>3169±117</td>
<td></td>
</tr>
</tbody>
</table>

Combined with the above analysis, the global fitting can well decompose the various excited state components and the corresponding decay time during the decay process. For PDI-C5 in the three solvents and PDI-II in DCM, two continuous processes provide an excellent fit for the dynamic process. However, for PDI-II in THF and acetone, three components are needed to fit the kinetic process because of the generation of excimer. The species-associated difference spectra (SADS) and corresponding concentration is shown in Figure 4 and Figure 5. The time constants of corresponding excited-state processes are presented in Table 2. The global fitting results of PDI-C5 in the three solvents are shown in Figure 4. PDI-C5 presents the same dynamics process in the three solvents: this coincides with the above discussion that PDI-C5 is a monomer state in these solvents. The 480 nm high-energy photon excites the PDI-C5 to the high vibrational level of the lowest singly excited state (LE state) and then undergoes a vibrational relaxation process (~120 ps) to the
lowest vibrational $S_1$ (or CT). The second time constants (~3 ns) are attributed to the relaxed $S_1$ back to the ground state. Figure 5 shows the global fitting results of PDI-II in the three solvents. Since PDI-II exhibits monomer characteristics in DCM, two components are sufficient for fitting, and the result is shown in Figure 5a,d. The results are almost consistent with the PDI-C5, which consists of a fast vibrational relaxation process (~90 ps), and a slow recombine process (~4 ns). However, for PDI-II in THF and acetone, the generation of excimer states makes them present different dynamics processes. The second and third SADSs in Figure 5c show a new absorption peak around 578-720 nm is consistent with the previous analysis. According to the above study, a simple fitted model diagram can illustrate various kinetic processes of PDI-II in solution (Figure 6). For PDI-II in DCM, LE states are generated immediately after photoexcitation, undergo a vibrational relaxation, and return to the ground state through a radiative relaxation process. But due to high polarity interaction enhanced electronic coupling, the excimer states are generated in THF and acetone, then come across a structural relaxation and return to the ground state.

Figure 5: Global target analysis results derived from Fs-TA of PDI-II. SADSs and population of PDI-II in (a, d) DCM, (b, e) THF, and (c, d) Acetone. (Ex. is excimer, Re. Ex. is relaxed excimer.)

Figure 6: Jablonski diagram illustrating the kinetic model used to fit TA from PDI-C5 and PDI-II solutions.

Conclusion. We have studied a PDI dimer's steady-state spectral characteristics and excited state dynamics under different solvents. Steady-state spectral results show that, the UV-Vis spectra show aggregation characteristics with increasing solvent polarity while the fluorescence quantum yield decreases. Transient absorption spectra show that the excited state energy relaxes to the ground state by excimer in a highly polar solvent. Previous studies have shown that when monomer PDI-C5 aggregates under the hydrophobicity effect, it finally produces the SB-CS. However, in this work, we found that the aggregation of dimers under the solvent polarity effect will form the excimer. Since excimer and SB-CS are closely related to the electronic coupling between the chromophore, we believe that this product gap is caused by the conjugated bridge structure in the middle of the dimer, which enhances the electronic coupling. We demonstrated that excimer formation was achieved in dimer molecules through molecular design and solvent regulation. Our research can provide a reference for the design of high-efficiency solar energy conversion materials.

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References.


