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Perylenetetracarboxylic Diimide Derivatives Linked with Spirobifluorene

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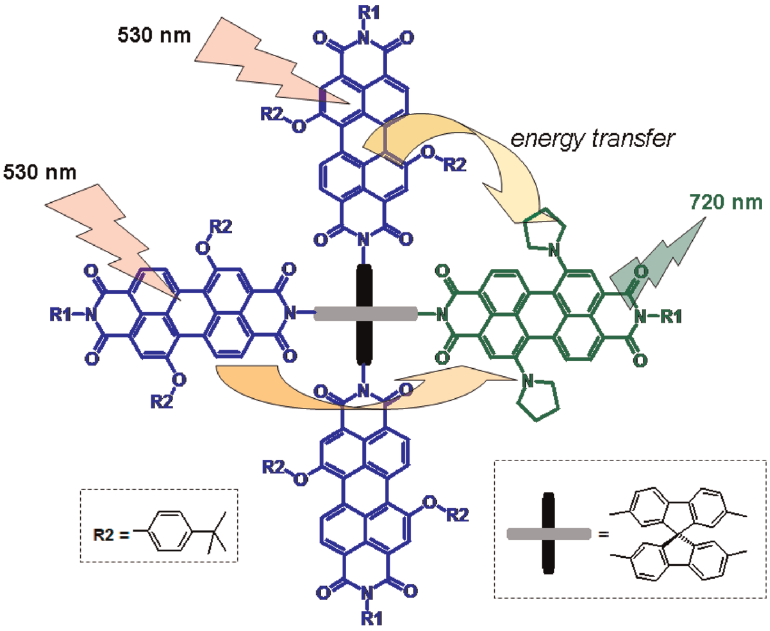
ABSTRACT



A series of perylenetetracarboxylic diimide (PDI) compounds linked with spirobifluorene have been prepared. The orthogonal configuration of the PDI subunits efficiently hindered their molecular aggregation in solution. Energy transfer from a 1,7-diphenoxyl group substituted PDI (PO-PDI) to a 1,7-dipyrrolidinyl group substituted PDI (PY-PDI) occurred with a large efficiency when PO-PDI was selectively excited, despite the orthogonal orientation of the two units. This observation was in direct conflict with predictions derived from the Förster theory. More interestingly, this efficient energy transfer also occurred in the solid state.

Significant effort has recently been devoted to the synthesis of highly ordered organic materials based on perylenetetracarboxylic diimide (PDI) by utilizing weak intermolecular forces.[1] The photophysical properties of individual molecular components in the molecular assembly were, however, found to be dramatically varied because of the strong intermolecular interactions. More importantly, changes in the photophysical properties were sometimes unpredictable. The development of covalently connected PDI oligomers with rigid conformations between the PDI units, with the aim of revealing the relationship between the structure and photophysical properties of the PDI assembly, is therefore necessary.[2] PDI molecules arranged in a parallel manner have been reported by

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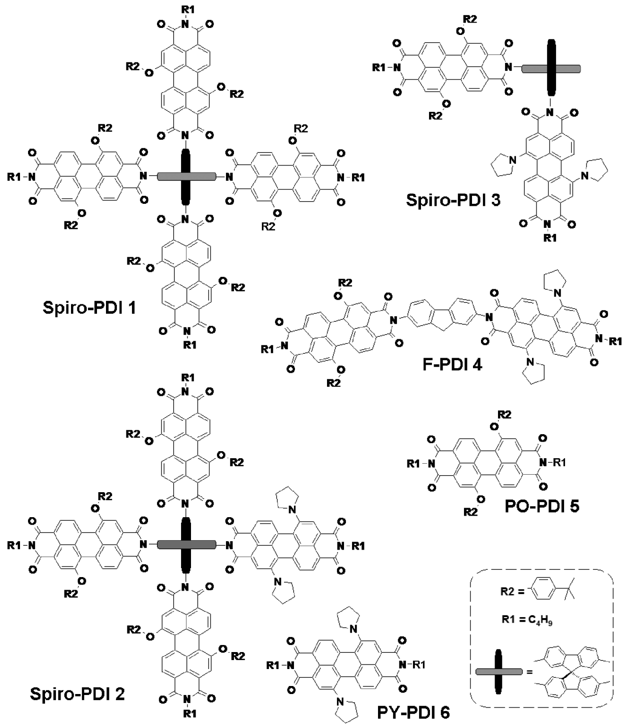
several groups in the literature.[3] PDIs aggregated with relative orthogonal orientations, however, have rarely been reported.[4] Therefore, further investigation of the effects of the orthogonal orientation between neighboring PDI units on the photophysical properties is required.

Scheme 1. Molecular Structures of the Compounds



The linking of conjugated components with a spiro-bridge represents a sophisticated strategy for achieving an orthogonal orientation between two conjugated components.[5] Herein, we present the design and synthesis of a series of novel PDI compounds connected by a spirobifluorene core, **Spiro-PDI 1**, **Spiro-PDI 2**, and **Spiro-PDI 3** (Scheme 1). For the sake of comparison, one other model compound, **F-PDI 4**, containing the same components but with a different linkage, was also prepared. The distances and angles between the PDI units were fixed by the spiro-bridge because of its rigid molecular structure,[6] and these compounds were therefore expected to behave as ideal models for studying the interactions between PDI units with orthogonally arranged orientations. Detailed synthetic procedures and the corresponding structural characterizations are shown in the Supporting Information (SI). All of the new compounds were fully characterized by ^{1}H and ^{13}C NMR and MALDI-TOF mass spectra or elemental analysis.

The absorption spectra of **Spiro-PDI 1**, **Spiro-PDI 2**, and **Spiro-PDI 3** in solution showed two absorption maxima at 545 and 510 nm, which were attributed to the absorption of PO-PDI (Figure 1). Another absorption band that was centered at 688 nm in the absorption spectra of **Spiro-PDI 2** and **Spiro-PDI 3** was assigned to the absorption of PY-PDI. The absorption spectra of the PO-PDI and PY-PDI units in these compounds were identical to those of their monomeric counterparts **PO-PDI 5** and **PY-PDI 6**, suggesting that there are no significant ground state interactions within these compounds between the PO-PDI or PY-PDI subunits. More importantly, the absorption spectra of **Spiro-PDIs** revealed no changes with increasing concentration, suggesting that **Spiro-PDI** compounds do not self-assemble into molecular aggregates within the concentration range tested (1×10^{-6}–1×10^{-4} mol·L^{-1}), The absorption spectra of **F-PDI 4**, however, changed dramatically with increasing concentration, as shown in the SI, indicating directly the formation of molecular aggregates in a concentrated solution. These results clearly revealed the importance of the orthogonal orientation on hindering the formation of molecular aggregates in a concentrated solution.

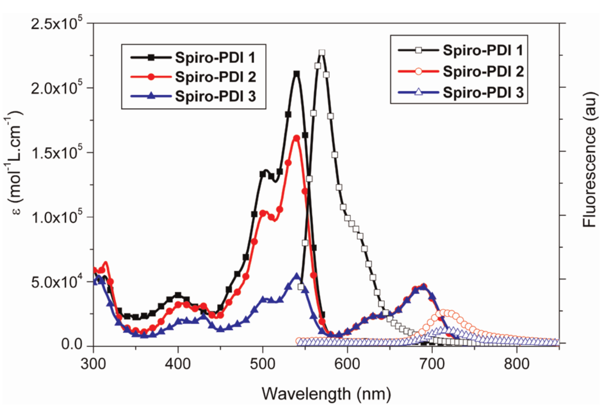


Figure 1. Absoprtion (solid symbol) and fluorescence (open symbol) spectra of **Spiro-PDI 1** (black), **Spiro-PDI 2** (red), and **Spiro-PDI 3** (blue) in toluene.

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The fluorescence spectra of **Spiro-PDI 1** bear a close resemblance to those of monomeric **PO-PDI 5** with a strong emission band at 580 nm and a 96% fluorescence quantum yield (λ_{ex} 530 nm). The fluorescence lifetime was measured to be 4.3 ns, which was also similar to that of standard **PO-PDI 5** (Figure 1, Table 1).[7] Taken together, these results further demonstrate that there is no ground state interaction between the PO-PDI units within compound **Spiro-PDI 1**.

When the PO-PDI units are selectively excited at 530 nm, the fluorescence spectra of **Spiro-PDI 2**, **Spiro-PDI 3**, and **F-PDI 4** show one broad band centered at 720 nm, which was attributed to the fluorescence of PY-PDI.[3d,8] The fluorescence from PO-PDI at 570 nm was too weak to be detected. This result revealed that the fluorescence of PO-PDI was efficiently quenched by PY-PDI in **Spiro-PDI 2**, **Spiro-PDI 3**, and **F-PDI 4**. The fluorescence quenching efficiencies (Φ_q) calculated from the fluorescence quantum yields were close to 100%. The appearance of the fluorescence of PY-PDI when PO-PDI was selectively excited suggested the presence of an energy transfer from PO-PDI to PY-PDI within **Spiro-PDI 2**, **Spiro-PDI 3**, and **F-PDI 4**. Due to no ground state interactions between donor and acceptor as revealed by the absorption spectra, the Förster type energy transfer is expected. The presence of an energy transfer was also supported by the excitation spectra of these three compounds. When the fluorescence intensity of PY-PDI at 720 nm was monitored, the absorption of PO-PDI in the range of 350−580 nm contributed significantly to the fluorescence of PY-PDI (SI, Figure S1).

Table 1. Fluorescence Properties of the Compounds

compound	λ_{em} (nm)	Φ_f (%)[a] PO-PDI	PY-PDI	τ (ns) PY-PDI	Φ_{Ent}[b] (%)	Φ_q[c] (%)
Spiro-PDI 1	569	96	—	—	—	—
Spiro-PDI 2	713	0.14	1.78	2.31	100	99.9
Spiro-PDI 3	715	0.12	2.66	3.35	100	99.9
F-PDI 4	714	0.00	3.61	4.40	100	100

[a] With **PO-PDI 5** in toluene ($\Phi_f = 100\%$) as standard. [b] Calculated from the fluorescence quantum yields (Φ_f). [c] $\Phi_q = 1 - \Phi_f/\Phi_0$.[9]

The energy transfer efficiency (Φ_{Ent}) can be estimated from the excitation and absorption spectra of the compounds. After normalizing the absorption and excitation spectra at the wavelength of the maximum absorption (688 nm), the difference between these two spectra in the range of 350−580 nm, where only PO-PDI absorbs light, reflects the efficiency of the energy transfer. The Φ_{Ent} values calculated in this way for **Spiro-PDI 2** and **Spiro-PDI 3** were ~100%.

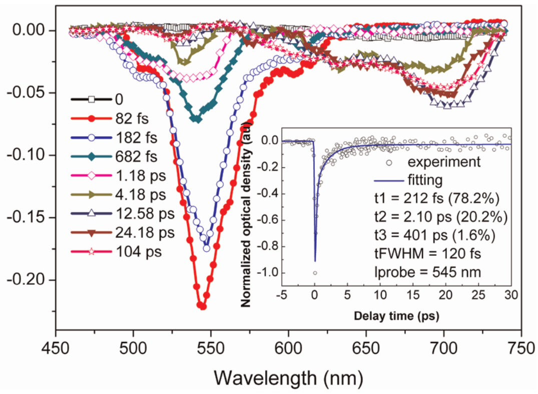

Figure 2. Transient absorption spectra of **Spiro-PDI 2** in toluene after excitation at 530 nm with a 120 fs pulse of laser. The inset shows the dynamic decay of the bleaching at 545 nm and the fitting results.

This efficient energy transfer between PO-PDI and PY-PDI within **Spiro-PDI-2** and **Spiro-PDI-3** was surprising because the Förster theory predicts that the resonance energy transfer between a pair of orthogonally arranged transition dipole moments is a forbidden process. The transition dipole moments of PDIs are oriented parallel to the connection line between the nitrogen atoms of the imides for both absorption and fluorescence.[10] The observed efficient energy transfers between PO-PDI and PY-PDI within **Spiro-PDI 2** and **Spiro-PDI 3** are therefore extraordinary. Only one example can be found in the literature involving an efficient energy transfer between a pair of perpendicularly arranged transition dipoles,[4] in which the energy transfer was attributed to thermally populated ground-state vibrations breaking the orthogonal arrangement.

The kinetics of the energy transfer within **Spiro-PDI 2** were investigated using femtosecond transient absorption measurements by selectively exciting the PO-PDI units at 530 nm (120 fs in pulse width) and probing them with a white light supercontinuum probe (460−750 nm). The transient spectra of **Spiro-PDI 2** in pure toluene taken at different delay times are shown in Figure 2. The major features centered at 460 to 610 nm were attributed to the ground state bleaching of PO-PDI.[11] Excitation at 530 nm generated the immediate bleaching of PO-PDI, with the bleaching of PY-PDI appearing subsequently at 700 nm along with the decay of the PO-PDI bleaching. Kinetic analysis on the bleaching of PO-PDI at 545 nm revealed

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three dynamic decay processes with time constants of $\tau_1 = 212$ fs (78.2%), $\tau_2 = 2.10$ ps (20.2%), and $\tau_3 = 401$ ps (1.6%). The two fastest components of the decay were attributed to the energy transfer from PO-PDI to PY-PDI, whereas the minor slower component was attributed to another fluorescence quenching process, which was assumed to be an electron transfer between PO-PDI and PY-PDI.[12]

Thin solid films of compounds **Spiro-PDI 1** and **Spiro-PDI 2** were prepared by simply spreading drops of toluene solution (1×10^{-5} mol L^{-1}) of these compounds onto the surface of a substrate. Following evaporation of the solvents at rt in a closed container, the absorption and fluorescence spectra of the thin solid films were recorded (Figure 3). The absorption spectra of **Spiro-PDI 1** in solid film showed two absorption bands at 512 and 545 nm, respectively, with the one at 512 nm having the maximum intensity. Both of the bands were red-shifted by 5 nm relative to those of monomeric PO-PDI in solution. The fluorescence spectra contained a red-shifted broad band at ~650 nm, which was assigned to an excimer emission.[3c,7b] The results of both absorption and fluorescence spectra revealed effective $\pi-\pi$ interactions between the PO-PDI units in the thin solid films, which might be the result of the sub-branch interactions of different molecules in the solid films.

The absorption spectra of the thin solid film of **Spiro-PDI 2** showed two broad absorption bands, which were similar with those of **Spiro-PDI 1**. But these two absorption bands further red-shifted to 519 and 551 nm in comparison with that of **Spiro-PDI 1**. The band at 551 nm had the largest oscillation strength, suggesting the presence of "*J*-type" $\pi-\pi$ interactions between the PO-PDI units of different molecules in the thin solid films of **Spiro-PDI 2**.[13] The fluorescence spectra (λ_{ex} 530 nm), however, showed only the emission of PY-PDI, which slightly blue-shifted relative to the monomeric **PY-PDI 6**, and no emission of PO-PDI could be detected. This result demonstrated that the energy transfer from PO-PDI to PY-PDI in this thin solid film occurred with a large efficiency. It is worthy of note that the PY-PDI is normally not fluorescent in the aggregated state, as reported in the literatures.[3b,d] The observed emission of PY-PDI in the thin solid films of **Spiro-PDI 2** indicated that the PY-PDI of **Spiro-PDI 2** does not form aggregates in the thin solid films likely because of the spiro-bridge. This result has also been supported by the absorption and fluorescence spectra of the thin solid films of **Spiro-PDI 3** (SI, Figure S5). This finding provided us with a new idea for the design of novel fluorescent solid materials.

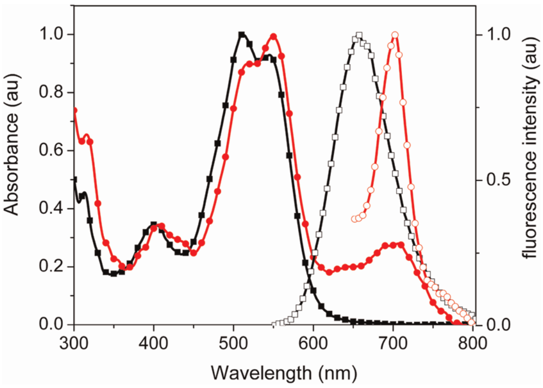

Figure 3. Normalized fluorescence (open symbol) and absorption (solid symbol) spectra of the thin solid films of **Spiro-PDI 1** (black) and **Spiro-PDI 2** (red).

In summary, a series of PDI compounds, **Spiro-PDI 1**, **Spiro-PDI 2**, and **Spiro-PDI 3**, containing PO-PDI and PY-PDI units linked by a spiro-bridge, were designed and prepared. An unexpected efficient and quick photoinduced energy transfer from PO-PDI to a perpendicularly arranged PY-PDI was found in these compounds, which was in direct conflict with the predictions of the Förster theory. Due to Langhal's report of a similar energy transfer in a different system,[4] we suggest that this kind of "unexpected" energy transfer might be a common phenomenon in orthogonally configured systems. More importantly, energy transfer from PO-PDI to PY-PDI was also observed in the thin solid films of **Spiro-PDI 2**. We believe that this finding will be useful for the design of new artificial photosynthetic systems and also helpful in guiding the design of organic fluorescent materials for molecular electronic devices.

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Supporting Information Available. Details of synthesis and characterizations, excitation fluorescence spectra, concentration dependent absorption spectra, time resovled emission traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The estimated free energy changes (ΔG) of the electron transfer between PO-PDI and PY-PDI within **Spior-PDI 2** following the Rehm–Weller equation is –0.16 eV. The electron transfer is a thermal dynamically favorable reaction.

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