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# Effect of Fluorination on Aggregate Structure of Perylene Diimide

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**Abstract:** The effect of fluorination on the aggregate structure of a novel fluorinated perylene diimide, N, N'-diperfluorophenyl-3, 4, 9, 10-perylenetetracarboxylic diimide **1**, was investigated by UV-Vis absorptions and the conformation simulations from AM1 semi-empirical quantum mechanics modeling. The results showed that in the solid film **1** molecules stacked with the perfluorinated phenyl groups straightly over or below the perylene cores of the adjacent **1** molecules.

**Keywords:** Fluorination, perylene diimide, aggregate structure, absorption.

Fluorinated π-conjugated organic semiconductors have received much attention due to their excellent electronic performances. For example, both perfluorinated copper phthalocyanine[1] and perfluorinated naphthalene diimide[2,3] possessed high electron mobilities over 0.01 $cm^2/(V·s)$ and good stability in air. However, with similar molecular structures as naphthalene dimides, perfluorinated perylene diimides, which are expected to show the same outstanding properties as naphthalene diimides, have not been reported so far. Before the n-type conductivity of perfluorinated perylene diimide is exploited, it is necessary to investigate the effect of fluorination on the aggregate structure of perylene diimide, which will surely influence its optical and electronic characteristics greatly. In this letter, a novel fluorinated perylene diimide, N, N'-diperfluorophenyl-3, 4, 9, 10-perylenetetracarboxylic diimide **1**, was designed and synthesized[3]. For a comparison, its non-fluorinated analog, N, N'-diphenyl-3, 4, 9, 10-perylenetetracarboxylic diimide **2**, was also prepared. Their absorptions in both solutions and solid films were studied, and their possible aggregate structures were presented as well.

The molecular structures of compounds **1** and **2** are given in the insets of **Figure 1**. Their structures were confirmed by IR, NMR data and elemental analysis[4]. **Figure 1** depicted the UV-Vis spectra of compounds **1** and **2** in DMF solutions. Both of them had three absorption peaks identical to a progression of $\pi$-$\pi^*$ transitions of perylene ring, which were designated as 0-0, 0-1 and 0-2. However, it was found that the absorption peaks of **1** (529, 493, and 461 nm) were red-shifted about 5 nm relative to those of **2** (524, 488, and 457 nm), suggesting the solvation of **1** was stronger than that of **2** due to the

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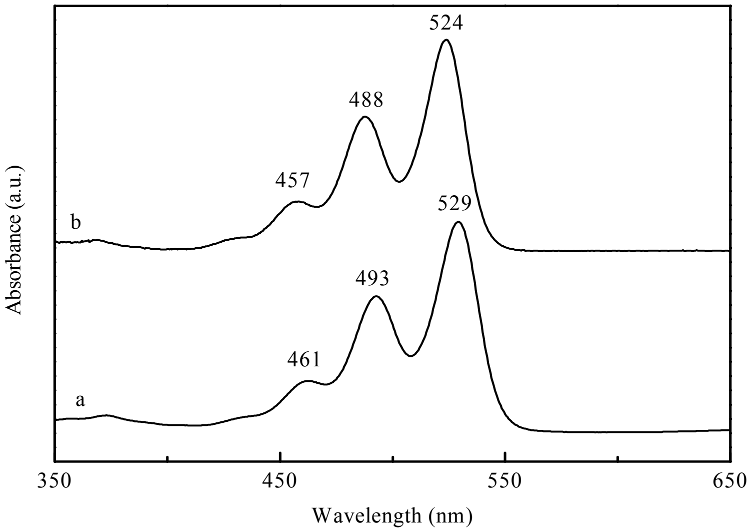
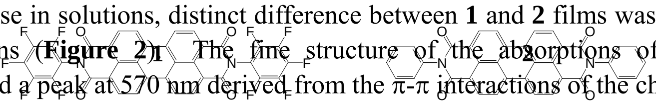
introduction of strong electronegative F atoms into **1**.

**Figure 1** The UV-Vis spectra of compounds (a) **1** and (b) **2** in DMF solutions. The insets are the molecular structures of compounds **1** and **2**



Unlike those in solutions, distinct difference between **1** and **2** films was observed in their absorptions (**Figure 2**). The fine structure of the absorptions of solution **2** disappeared, and a peak at 570 nm derived from the π-π interactions of the chromophores in the solid state appeared[5]. For the film **1**, three clearly resolved bands similar as those of the solution remained but the peaks became broader and red-shifted. Three absorption peaks were located at 560 nm (0-0), 514 nm (0-1) and 476 nm (0-2), from which the gaps of vibrational levels for compound **1** were calculated as 0.198 and 0.193 eV, in exact agreement with the wavenumber of the stretching vibration of perylene ring: 1594 $cm^{-1}$ (0.198 eV)[6]. That is to say, film **1** showed the molecular or monomeric absorptions, implying that the π-π coupling did not exist.

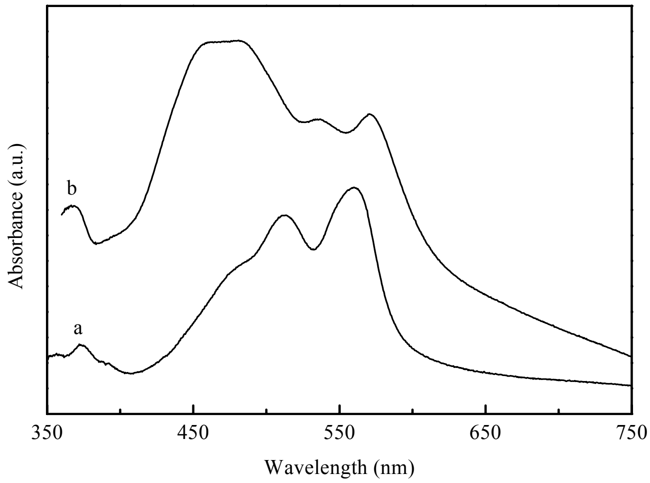


According to the model of transition dipole interaction, the energy of an ordered multilayer thin film is given by[7]:

$$\Delta E_{CR} = \Delta E_S + D - S + e \qquad (1)$$

where $\Delta E_{CR}$ is the transition energy for the molecule in solid film, $\Delta E_S$ is the transition energy for the molecule in solution, $D$–$S$ is the difference between the van der Walls intermolecular energies in the excited and the ground states as compared between the solid state and the solution, and $e$ is the sum of the coupling energies of the transition dipoles in the film. For film **1**, $e$ was zero due to no band splitting observed in the UV-Vis spectrum, thus $D$–$S$ was obtained as $\Delta E_{CR}$ (560 nm) - $\Delta E_S$ (529 nm) = 31 nm (-0.130 eV). Such big value was surprising when compared to that of N, N'-di(2, 6-xylyl)-3, 4, 9, 10-perylenetetracarboxylic diimide **3**: 3 nm (-0.013eV)[8]. **3** also showed monomeric absorptions because the large substituent, 2,6-xylyl group, was perpendicular to the flat π-electron-system of perylene, and sterically hindered **3** from forming crystal. Due to this argument, the following hypothesis was put forward to explain why the *D–S* value for compound **1** was so big. In the film, **1** molecules stacked with the perfluorinated phenyl groups straightly over or below the perylene cores of the adjacent molecules to achieve the most favorable energetic state, and the π electrons of perylene received great van der Walls forces at the same time (**Figure 3**).

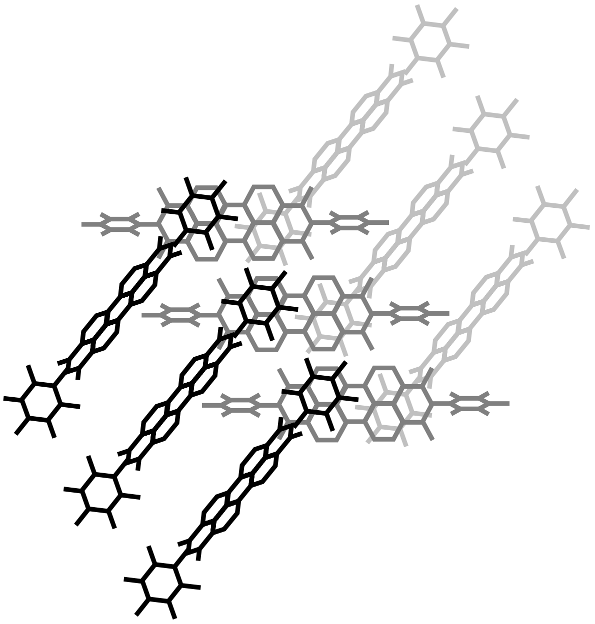
**Figure 2** The UV-Vis spectra of (a) **1** and (b) **2** films by evaporation



The simulations of the molecular conformations of **1** and **2** were performed by AM1 semi-empirical quantum mechanics modeling. It was found that the angle between the perylene moiety and the terminal substituent (perfluorinated phenyl group) of **1** was ~70°, whereas that of **2** was ~50°. The larger angle of **1** disrupted the planarity of perylene diimide molecules. Moreover, the strong electronegative F atoms in near end groups were electrostatic repulsive from each other, preventing compound **1** from aggregating through π-π interactions of successive perylene rings. On the contrary, the molecular stacking of the perfluorinated phenyl groups being straightly over or below the perylene cores of the adjacent molecules was allowed. This simulation result also supported the mentioned hypothesis.

In conclusion, a novel perfluorinated perylene diimide, N, N'-diperfluorophenyl-3, 4, 9, 10-perylene-tetracarboxylic diimide **1**, was designed and synthesized for the first time. Fluorination showed a great influence on the UV-Vis absorptions and aggregate structure of compound **1**. It was found that in the solid film **1** molecules stacked with the perfluorinated phenyl groups straightly over or below the perylene cores of the adjacent **1** molecules.

**Figure 3** The possible molecular stacking of compound **1** in the solid film



## Acknowledgments

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4. Selected data for **1**: FTIR (KBr, pellet): $\nu$=1721, 1685 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): $\delta$ 8.82 (d, 4H, *J*=8 Hz), 8.76 (d, 4H, *J*=8 Hz); Anal. Calcd. for $C_{36}H_8F_{10}N_2O_4$: C, 59.85; H, 1.12; N, 3.88. Found: C, 59.74; H, 0.99; N, 3.82. For **2**: FTIR (KBr, pellet): $\nu$=1703, 1665 $cm^{-1}$ (C=O); Anal. Calcd for $C_{36}H_{18}N_2O_4$: C, 79.70; H, 3.34; N, 5.16. Found: C, 78.88; H, 2.95; N, 5.12.
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