Unique Aggregate Structure of Fluoroperylene Diimide Thin Film

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A perfluorinated perylene diimide, *N*,*N*′-diperfluorophenyl-3,4,9,10-perylenetetracarboxylic diimide (DFPP), and its nonfluorinated analogue, *N*,*N*′-diphenyl-3,4,9,10-perylenetetracarboxylic diimide (DPP), showed similar UV−vis absorption and fluorescence spectra when they existed as monomeric dyes in solutions, whereas in solid films they exhibited great differences. Absorption band splitting was observed for DPP film; however, for DFPP film, the fine structure of absorptions similar to that in solution still remained in addition to the absorption peaks becoming broader and shifting to longer wavelength regions. Furthermore, it was found that DFPP molecules aggregated to form a crystalline film when the temperature of the substrate was elevated to 200 °C. Through the simulation of the molecular conformation, the theoretical examinations of molecular interactions, the measurement of electron affinity, the observation of the film morphology by AFM and SEM, and the crystalline structure characterization by XRD, the unique aggregate structure of the crystalline DFPP thin film was suggested: DFPP molecules stacked with the perfluorinated phenyl groups straight over or below the perylene cores of the adjacent DFPP molecules.

1. Introduction

Perylene diimides, as organic n-type semiconductors with high optical and thermal stability, have attracted much attention due to their potential applications in organic solar cells,[1−4] organic light-emitting diodes (OLEDs),[5,6] and organic field-effect transistors (OFETs),[7,8] where an electron mobility as high as 0.6 cm^2/(V·s) for the vapor deposited perylene diimide film was detected.

The substituents attached on the periphery of the perylene chromophore in perylene diimides have a crucial effect on their optical and electronic properties induced by the changes of the molecular packing (aggregate structures) in the solid states via the influences of intermolecular interactions. Many efforts have been made to reveal the relationship between molecular stack and optical spectra, ultimately, the electronic structure of perylene diimide.[9−13] Graser et al. proposed that the degree of "area overlap" of successive π-conjugated perylene moieties determined simply the shift of the absorption maximum.[9,10] Kazmaier et al. suggested that the perylene diimides, which showed the larger valence and conduction band broadened by aggregation (the bigger absorption widths), were also those with the higher photosensitivities.[11] Alternatively, Mizuguchi et al. pointed out that the resonance interactions of transition dipoles were responsible for the band splitting of the absorptions that appeared in perylene diimide films.[12,13]

Organic semiconducting materials with strong electron-withdrawing F substituents exhibited unique behaviors. For example, both perfluorinated copper phthalocyanine[14] and perfluorinated naphthalene diimide[15,16] possessed high electron mobilities of over 0.01 cm^2/(V·s) and were stable in air because of their lower LUMO energy levels caused by fluorination. Similarly, we have recently designed and prepared a novel perfluorinated perylene diimide, *N*,*N*′-diperfluorophenyl-3,4,9,-10-perylenetetracarboxylic diimide (DFPP), which was dem-

onstrated to be an organic air-stable electron acceptor with good solubility in common solvents.[17] In the present work, the UV−vis absorption, fluorescence spectra, electron affinities, morphologies, topographies, and XRD patterns of evaporated DFPP films were examined and compared to those of DFPP's nonfluorinated analogue, *N*,*N*′-diphenyl-3,4,9,10-perylenetetra-carboxylic diimide (DPP) film, aiming to clarify the effect of fluorination on the aggregate structure of perylene diimide thin films. On the basis of the results, possible DFPP molecular stack in the film was proposed.

2. Experimental Section

Materials. The molecular structures of DFPP and DPP were depicted in Figure 1. DFPP was synthesized by condensation of 3,4,9,10-perylenetetracarboxylic dianhydride with 2,3,4,5,6-pentafluoroaniline according to the reported procedure[16] and was purified by temperature gradient sublimation. Anal. Calcd for C$_{36}$H$_8$F$_{10}$N$_2$O$_4$: C, 59.85; H, 1.12; N, 3.88. Found: C, 59.74; H, 0.99; N, 3.82. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.82$ (d, $J = 8$ Hz, 4H), 8.76 (d, $J = 8$ Hz, 4H). FTIR (KBr, pellet): $\nu = 1721$, 1685 cm^{-1} (C=O). DPP was prepared in a similar way. Anal. Calcd for C$_{36}$H$_{18}$N$_2$O$_4$: C, 79.70; H, 3.34; N, 5.16. Found: C, 78.88; H, 2.95; N, 5.12. FTIR (KBr, pellet): $\nu = 1703$, 1665 cm^{-1} (C=O). DFPP and DPP films were vacuum evaporated at a pressure below 1×10^{-5} Torr onto quartz, glass, or ITO substrates with different temperatures, and the deposition rate was 1−2 Å/s. All of these thin films were about 40 nm thick, monitored with a quartz crystal oscillator.

Measurements. Elemental analyses data were determined on a Perkin-Elmer 240C elemental analyzer. The NMR spectrum was obtained on a Bruker AVANCE DMX500 nuclear resonance spectroscope. FTIR spectra were obtained on a Vector 22 Fourier transform infrared spectroscope. UV−vis spectra were taken on a Varian CARY 100 Bio spectrometer. Fluorescence spectra were recorded at an excitation wavelength of 470 nm on a Hitachi 4500 fluorescence spectrophotometer. Cyclic

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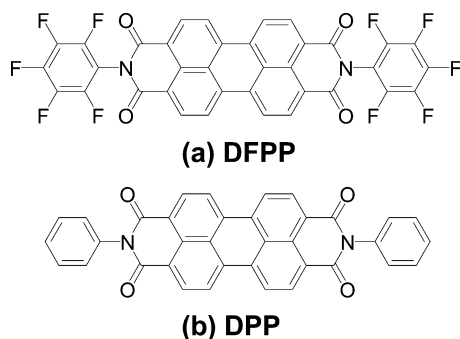
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(a) DFPP

(b) DPP

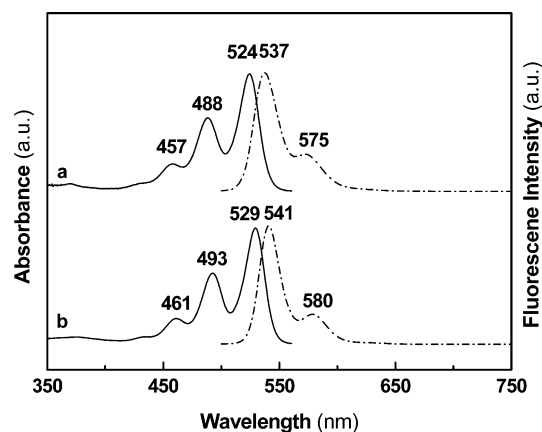**Figure 1.** The molecular structures of (a) DFPP and (b) DPP.

Figure 2. UV−vis absorption (−) and photoluminescence (− · − · −) spectra of (a) DPP and (b) DFPP solutions in CHCl₃. The excitation wavelength was 470 nm.

Figure 3. UV−vis absorption (−) and photoluminescence (− · − · −) spectra of perylene diimide thin films evaporated on various temperature substrates: (a) DPP on the substrate at room temperature, (b) DFPP on the substrate at room temperature, and (c) DFPP on the substrate at 200 °C. The excitation wavelength was 470 nm.

voltammetry (CV) measurements of DFPP films vapor deposited on ITO substrates were carried out on a CHI600A electrochemical workstation, with solutions in CH₃CN containing 0.1 M supporting electrolyte of tetrabutylammonium perchlorate, in a three electrode cell, where ITO was the working electrode, Pt wire was the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. The morphologies of the films were observed on a Skeio SPI3800N atomic force microscope (AFM) and a JEOL JSM5510 scanning electron microscope (SEM). The crystalline structures of the DFPP films deposited on glass substrates with different temperatures were investigated with a Bede D1 system high-solution X-ray diffractometer (XRD).

3. Results and Discussion

Shown in Figure 2 are the UV−vis absorption and fluorescence spectra of DFPP and DPP solutions in CHCl₃, respectively. It is found that the absorption and fluorescence spectra in solutions were almost not affected by the fluorination of perylene diimide. Both DFPP and DPP had absorption and emission peaks identical to those of a progression of $\pi-\pi^*$ transitions of the perylene ring, designated as 0−0, 0−1, and 0−2, in addition to the absorption and emission peaks of DFPP (absorptions, 529, 493, and 461 nm; emissions, 541 and 580 nm) being red-shifted about 5 nm relative to those of DPP (absorptions, 524, 488, and 457 nm; emissions, 537 and 575 nm). These observations suggested that the solvation of DFPP was stronger than that of DPP due to the introduction of strong electronegative F atoms into DFPP.

In contrast, the absorption and fluorescence spectra of DFPP and DPP films vapor deposited on various temperature quartz substrates (Figure 3) showed obvious F substituent effects. For
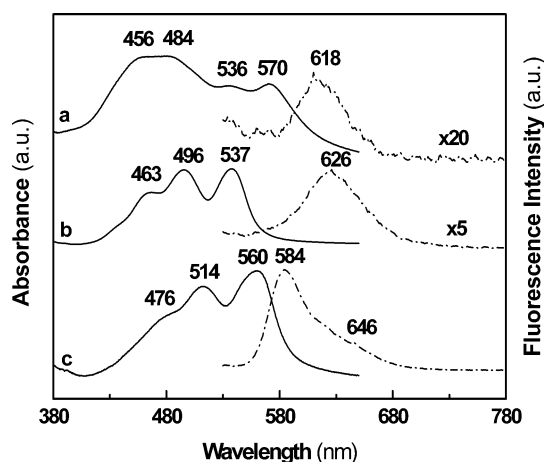
DPP film deposited on the substrate at room temperature (Figure 3a), the fine structure of the DPP absorptions in solution disappeared, and a new peak at 570 nm derived from $\pi-\pi$ interactions of the chromophores in the solid state appeared,[18] indicating that a crystalline thin film was formed by overlapping neighboring perylene moieties.[12] For DFPP film evaporated on the substrate at either room temperature (DFPP-1 film, Figure 3b) or 200 °C (DFPP-2 film, Figure 3c), the same three clearly resolved absorption bands as those in solution still existed; nevertheless, they became broader and red-shifted. The higher the substrate temperature was, the greater the red-shift was. That is to say, DFPP film showed molecular or monomeric absorptions, implying the absence of $\pi-\pi$ coupling. According to the model of transition dipole interaction, the energy of an ordered multilayer thin film is given by:[19]

$$\Delta E_{CR} = \Delta E_S + D - S + e \tag{1}$$

where ΔE_{CR} is the transition energy, ΔE_S is the energy of the transition for the molecule in solution, $D - S$ is the difference between the van der Waals intermolecular energies in the excited and the ground state as compared to that between the solid state and the solution, and e is the sum of the coupling energies of the transition dipoles in the film. For both the DFPP-1 and the DFPP-2 films, the e value was zero because no band splitting was observed in their UV−vis absorption spectra; thus $D - S$ of DFPP-1 film was obtained as ΔE_{CR} (537 nm) − ΔE_S (529 nm) = 8 nm (−0.035 eV), and that of the DFPP-2 film was ΔE_{CR} (560 nm) − ΔE_S (529 nm) = 31 nm (−0.130 eV). Such a great gap of van der Waals forces between DFPP-1 and DFPP-2 films was interesting, but what caused it?

To find the answer to the mentioned question, the simulations of the molecular conformations of DFPP and DPP molecules were performed by AM1 semiempirical quantum mechanics modeling. It was found that the angle between the perylene moiety and the terminal substituent, the perfluorinated or nonfluorinated phenyl group, is ∼70° for the DFPP molecule, whereas it is ∼50° for the DPP molecule. The larger angle in DFPP molecule can disrupt the planarity of the perylene diimide molecule, and the strong electronegative F atoms in near end groups are electrostatic repulsive from each other. As a result, DFPP molecules were prevented from stacking through $\pi-\pi$ interactions of successive perylene rings. So, the reasonable interpreting was that, on the substrate at room temperature,
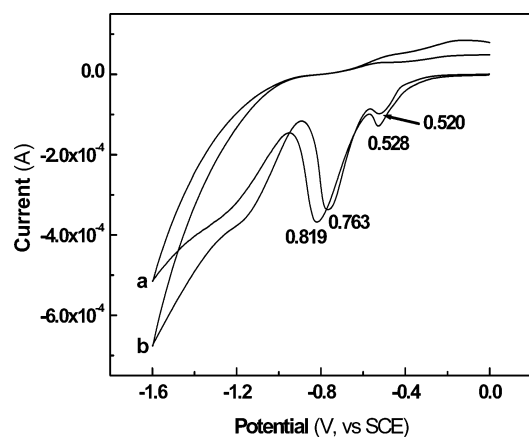
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Figure 4. The cyclic voltammograms of DFPP films formed on various temperature substrates: (a) at room temperature and (b) at 200 °C. The scanning rate was 50 mV/s.

DFPP molecules stacked randomly to give an amorphous film, consistent with the *N*,*N*′-di(2,6-xylyl)-3,4,9,10-perylenetetra-carboxylic diimide film, which also showed monomeric absorptions because the large substituent, 2,6-xylyl group, was perpendicular to the flat π-electron-system of perylene and was sterically hindered to form crystals.[20] Instead, on the substrate at 200 °C, the energy of DFPP molecules was high enough to overcome the intermolecular steric actions and the electrostatic repulsions, so that DFPP molecules could arrange with the perfluorinated phenyl group straight over or below the perylene core of the adjacent molecule to achieve the most favorable energetic state; that is, a crystalline DFPP film was obtained. At the same time, π electrons of perylene received great van der Waals forces.

The hypothesis for the aggregation of DFPP molecules was supported by the results from the fluorescence spectra of DPP and DFPP films (Figure 3) and cyclic voltammograms of DFPP films (Figure 4). It was disclosed that DPP film exhibited an excimer emission peak[21] at 618 nm (Figure 3a) because of the short intermolecular distances, although π−π interactions favored fluorescence quenching through photoinduced charge transfer. Because DFPP molecules distributed randomly in DFPP-1 film, the distance between a few of the perylene diimide molecules must be close enough that DFPP-1 film also showed an excimer emission at 626 nm (Figure 3b). However, in DFPP-2 film, the distance between perylene chromophores was remote so that DFPP-2 film only showed monomeric emission peaks at 584 (0−0) and 646 nm (0−1), from which the gap of the vibrational levels was found to be 0.204 eV, in agreement with the wavenumber for the stretching vibration of the perylene ring of 1594 cm^{-1} (0.198 eV).[22] It was also noticeable that the fluorescence intensity of DFPP-2 film was about 5 or 20 times higher, respectively, than that of DFPP-1 or DPP film because there was no dimer formation. In Figure 4, the two reduction peaks of DFPP-2 film were more positive than those of DFPP-1 film; that is, the electron affinity of DFPP-2 film was higher than that of DFPP-1 film. It was believed that the electronic characteristics of π-conjugated perylene rings were significantly influenced by the inductive effects of near strong electronegative perfluorinated phenyl groups in DFPP-2 film, leading to higher electron affinity of DFPP-2 film.

The hypothesis can also be confirmed directly by SEM, AFM (Figure 5), and XRD (Figure 6) characterizations. As AFM and SEM photographs have shown, DPP film consisted of spherical crystalline particles with diameters of about 250 nm, and DFPP-1 film appeared very smooth with a typical root-mean-square roughness (R_q) of 3.7 nm, indicating the characteristic of an amorphous film. Interestingly, in DFPP-2 film, there were many nanowires with diameters of 100−200 nm, implying that an ordered crystalline film was obtained. As demonstrated in
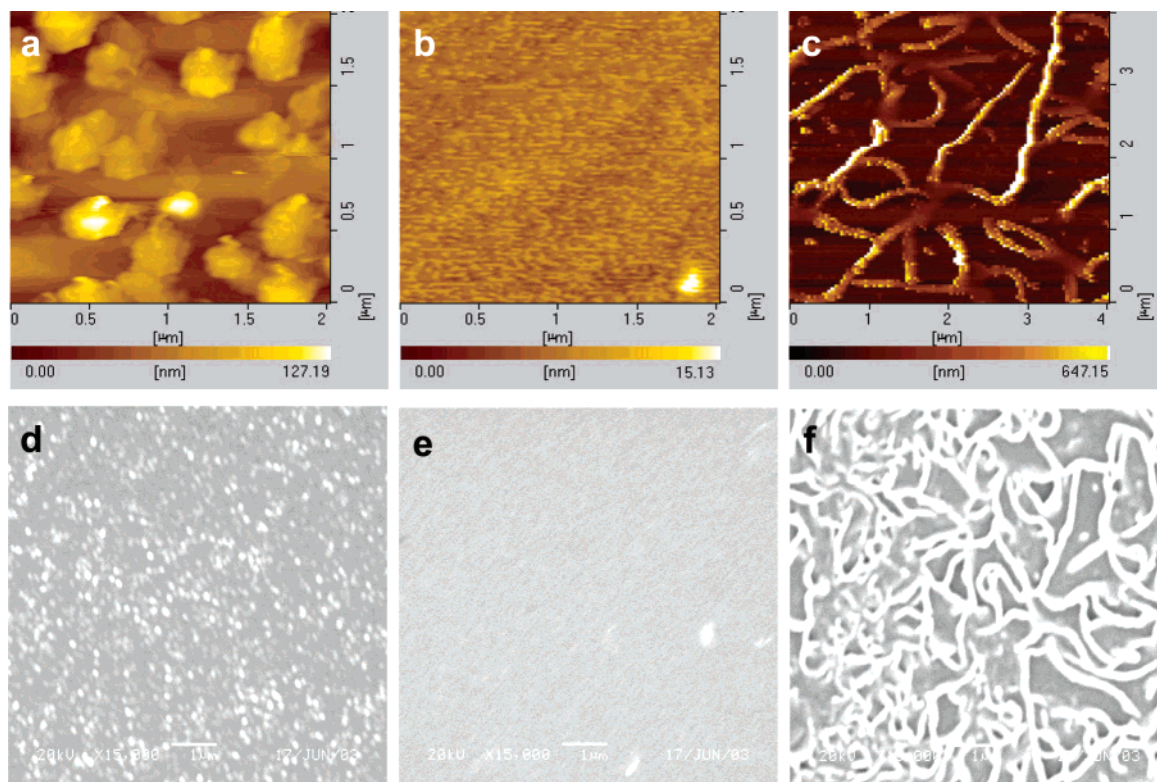

Figure 5. AFM (upper) and SEM (bottom) images of perylene diimide thin films evaporated on various temperature substrates: DPP on the substrate at room temperature ((a) AFM, (d) SEM), DFPP on the substrate at room temperature ((b) AFM, (e) SEM), and DFPP on the substrate at 200 °C ((c) AFM, (f) SEM).
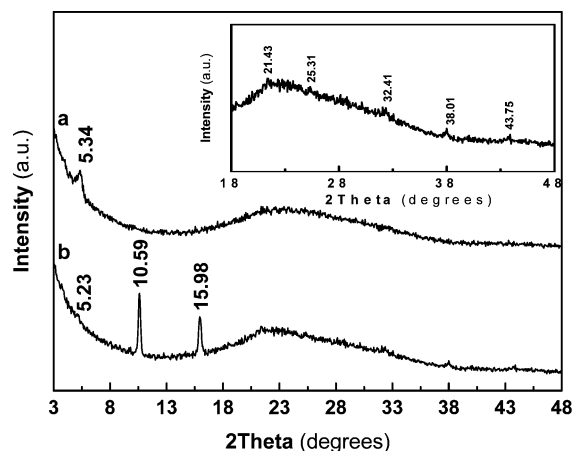
Figure 6. XRD patterns of DFPP films deposited on the glass substrates at (a) room temperature and (b) 200 °C. Inset: the enlarged pattern for (b) from 18° to 48°.

Figure 6, DFPP-1 film only exhibited a weak XRD peak at 2θ = 5.34° (Figure 6a), implying low crystallinity. However, DFPP-2 film showed two strong XRD peaks at 10.59° and 15.98° (Figure 6b), with some small peaks at 5.23°, 21.43°, 25.31°, 32.41°, 38.01°, and 43.75° (inset of Figure 6). From these peaks, the *d* values were determined as 16.88, 8.34, 5.54, 4.14, 3.51, 2.76, 2.36, and 2.07 Å. These *d* values could be divided into two groups: the first group was composed of 16.88, 8.34, 5.54, 4.14, 2.76, and 2.07 Å, and the second group was composed of 3.51 and 2.36 Å. It was easily observed that in the first group the ratios of all *d* values to 16.88 Å were exactly 1, $^{1}/_{2}$, $^{1}/_{3}$, $^{1}/_{4}$, $^{1}/_{6}$, and $^{1}/_{8}$, and in the second group the ratio of 3.51 to 2.36 Å was $^{3}/_{2}$. Therefore, it could be concluded that in DFPP-2 film most DFPP molecules aggregated to form a highly ordered crystalline film with a unique aggregate structure, in addition to that few molecules packed through $\pi-\pi$ interactions of near perylene rings because all known perylene diimides adopted in their crystal structure an interplanar *d* spacing of approximately 3.5 Å.[9,10]

4. Conclusions

In conclusion, a crystalline DFPP thin film, which showed monomeric or molecular absorption and emission spectra, could be prepared by elevating the temperature of the substrate to 200 °C. The film had a unique aggregate structure, where DFPP molecules stacked with the perfluorinated phenyl groups straight over or below the perylene cores of the adjacent DFPP molecules. Knowing how the fluorination influences the aggregate structure of perylene diimide thin films will definitely help us to understand the unique behaviors of fluoroperylene diimides in optoelectronic devices.

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