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p-Type Semiconducting Dendrimers Bearing Thiophenyl Peripheral Moieties: Effect of Alkyl Chains on Molecular Packing Geometry

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Summary: First generation thiophene-labeled conjugated dendrimers have been synthesized through the Heck coupling reaction between the 5-vinyl-[2,2′]bithiophenyl derivative and 1,2,4,5-tetrabromo-benzene as a core. One dendrimer has hexyl groups at the periphery and the other does not have it. They display a considerably better solubility than the linear conjugated oligothiophene. We observe drastic spectral change in a film state of dendrimer due to crystallization and a high extent of intermolecular interaction. Effect of peripheral alkyl groups on the intermolecular interaction and lamella orderness was investigated using two dendrimers.

Keywords: conjugated dendrimer; intermolecular interaction; intramolecular conjugation; semiconductor

Introduction

Organic semiconductor materials based on extended linear π-conjugated systems have been very intriguing and significant development has been achieved in these materials over the last several years[1,2] A number of research has been made to synthesize π-conjugated small molecules, dendrimers, oligomer, and polymers because of their strong potential to electronics and optoelectronics such as organic light-emitting diodes (OLEDs),[3–5] organic field effect transistors,[6,7] and photovoltaic cells.[8–10] In the exploration of the application of organic semiconductors in electronic devices, organic field effect transistor (OFET) is an important component for developing future flexible displays accompanied by organic light emitting materials.[11–13]

For developing a flexible field effect transistor, many soluble poly- and oligothiophenes have been suggested.[14] In particular, α,α′-dialkylsexithiophene and its derivatives have been intensively employed as an active layer material in OFET.[15,16] In comparison with oligomers or polymers, low generation dendrimers have distinct dual characteristics. It is easier to cast them in solution and to thermally evaporate them under vacuum.

We also have designed π-conjugated dendrimers bearing bithiophenyl peripheral groups, which exhibit 2-dimensional planar geometry for ease in crystallization. The solubility problem in linear conjugated oligothiophenes was completely overcome using the dendrimers.[17–19] Although poorer carrier mobility and low on/off ratio in the dendrimer and polymers are observed in a field effect transistor, wet processability and patternability will be advantages than the other small polyacene molecules. When we fabricate the thin film by spin coating technique, molecular disorderness cannot be improved significantly. Annealing process at a proper temperature can improve it to some extent. Intermolecular π-stacking

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structure is essential to improve the molecular orderness and inter-layer charge carrier hopping between the adjacent phenyl or thiophene units.

We report herein the structural properties of fully conjugated dendrimers bearing 5-hexyl-[2,2′]bithiophenyl or [2,2′]bithiophenyl group as peripheral groups. In order to limit the freely rotating conformation in a linear molecules, we prepared planar four-armed dendrimers. When we measure the carrier mobilities of the devices fabricated with 4(HPBT)-benzene and 4(PBT)-benzene, the former showed a higher mobility than the latter. In the light of ease of crystallization and lamella packing, 4(PBT)-benzene should have shown a comparable or higher value. This is why we tried to investigate the reason using absorption spectroscopy, X-ray diffractometry, and atomic force microscopy in detail. We suggested a possible mechanism to explain this phenomenon.

Experimental Part

Detailed synthetic procedures for the dendrimers will be reported elsewhere. DSC measurements (Mettler, DSC821^{e} temperature rate 5 °C under N_2) were carried out in a heating (cooling) cycle. Absorption spectra of film samples and chloroform solutions (conc. 1×10^{-5} mol/L) were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm.

In order to study the crystallinity of the synthesized dendrimers, X-ray diffraction (XRD) was performed using Rigaku D/MAX 2000 or using the synchrotron radiation (1.542 Å) of the 3C2 beam line at the Pohang Synchrotron Laboratory, Korea. For AFM measurements, we used a AFM instrument (CP-II SPM, PSI Inc.) operating in the tapping mode.

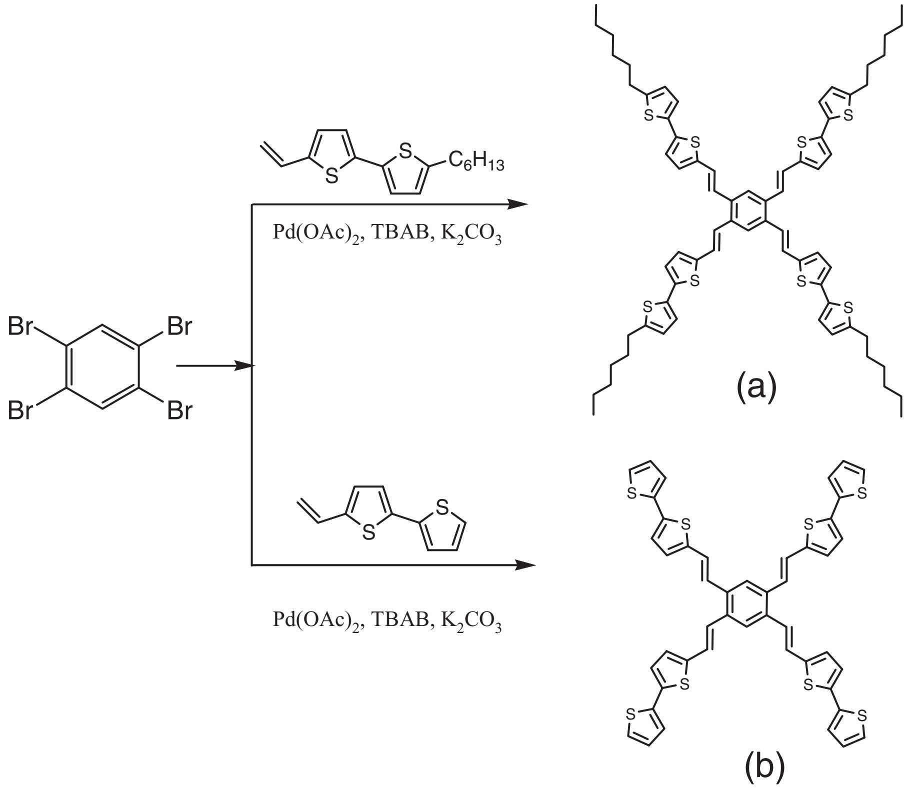
Results and Discussion

General Properties of Dendrimer

The synthetic route to prepare two dendrimers can be found in Scheme 1. We prepared four-armed crystalline dendrimers containing 5-hexyl-5-propenyl-[2,2′] bithiophenyl or the 5-propenyl-[2,2′]bithiophenyl group as a dendritic wedge. In this report, the dendrimers bearing 5-hexyl-5-propenyl-[2,2′]bithiophenyl and 5-propenyl-[2,2′]bithiophenyl are denoted to be 4(HPBT)-benzene and 4(PBT)-benzene, respectively. First, 5′-hexyl-[2,2′]bithiophenyl-5-carbaldehyde was prepared by Vilsmeier reaction of 5-hexyl-[2,2′]bithiophenyl. 5-Hexyl-5′-vinyl-[2,2′]bithiophenyl was synthesized by the Wittig reaction between 5′-hexyl-[2,2′]bithiophenyl-5-carbaldehyde and methyltriphenyl phosphonium iodide. Same methods were utilized for synthesizing the intermediates for 4(PBT)-benzene. Two dendrimers were synthesized by a Pd$^{(0)}$-catalyzed Heck coupling reaction of the 1,2,4,5-tetrabromobenzene and the 5-hexyl-5-propenyl-[2,2′] bithiophenyl or 2-hexyl-5-propenyl-thieno [3,2-*b*]thiophene peripheral group in a yield of 30–45%. Only difference between two dendrimers is the existence of a hexyl group at the periphery. They have a good self-film forming property and are well soluble in various organic solvents such as chloroform, xylene, dichloromethane, chlorobenzene, and tetrahydrofuran.

In contrast to DH-6T ($T_m = 310\,°C$), 4(HPBT)-benzene and 4(PBT)-benzene exhibit a distinct crystalline-isotropic transition at 172 and 252 °C, respectively. (Figure 1A) 4(PBT)-benzene showed a glass transition behavior at 137 °C. This indicates that some amorphous region coexists with a crystalline region due to molecular disorderness to some extent. In TGA thermograms, we can find that the onset temperature of decomposition is quite similar around 370 °C. (See Figure 1B) The residual weight at a higher temperature is much larger in 4(PBT)-benzene due to absence of a hexyl group.

The geometries of two dendrimers were optimized by means of the MOPAC 2002 (CAChe version 5.04, PM3-Hamiltonian). In Figure 2, the outermost thiophene unit showed slightly distorted compared to the structure of the planar core structure in



Scheme 1.
Synthetic procedure of two thiophene-labeled 1st generation dendrimers. (a) 4(HPBT)-benzene, (b) 4(PBT)-benzene.

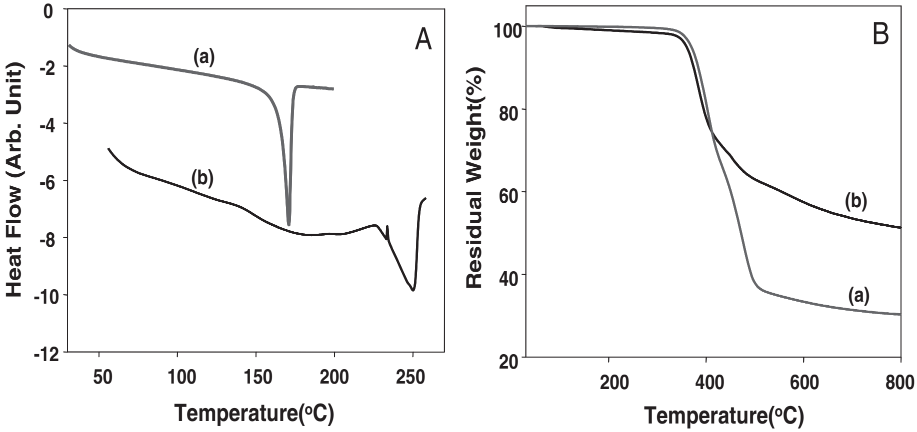


Figure 1.
Thermal analysis results of two denrimers. A: DSC thermogram, B: TGA thermogram. (a) 4(HPBT)-benzene, (b) 4(PBT)-benzene.

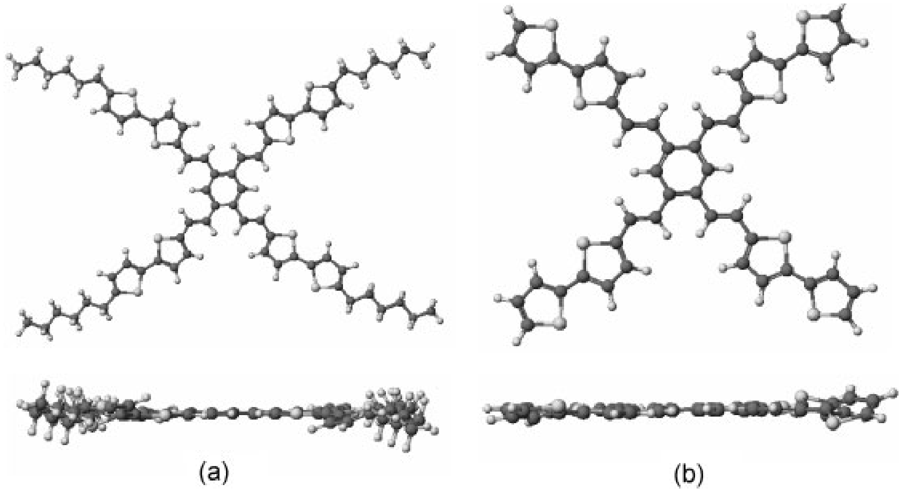


Figure 2.
Optimized geometry of the structures of two dendrimers. (a) 4(HPBT)-benzene, (b) 4(PBT)-benzene.

4(HPBT)-benzene. We found that new dendritic molecule has a larger planar moiety in the center composed of 1,2,4,5-tetravinyl-benzene. Well-defined planar star-shaped molecular arrangement could have induced good lamella ordering. The peripheral hexyl group can affect the inter-lamella spacing and distance of π-stacking between the dendrimers.

The absorption spectra of the dendrimer samples in solution (chloroform, conc. 1×10^{-5} mol/L) and thin films were obtained in the range of 250–800 nm. (see Figure 3) Compared to DH-6T ($\lambda_{abs}^{max} =$ 438 nm), the absorption maxima of 4(HPBT)-benzene and 4(PBT)-benzene in solution states are located at 422 nm identically. In the thin film of 4(HPBT)-benzene before and after annealing at 150 °C, the absorption was significantly read-shifted with clear vibronic transitions at 480 and 516 nm which are attributed to a formation of ordered structure with an intermolecular π-stacking.[20–22] (See Figure 3A, (c)) The baseline was floated due to a severe optical scattering from the crystallite in thin films. In the case of 4(PBT)-benzene, the as-cast film is totally opaque. Crystallization is much facile to occur compared to 4(HPBT)-benzene. It can be found that a significantly large peak

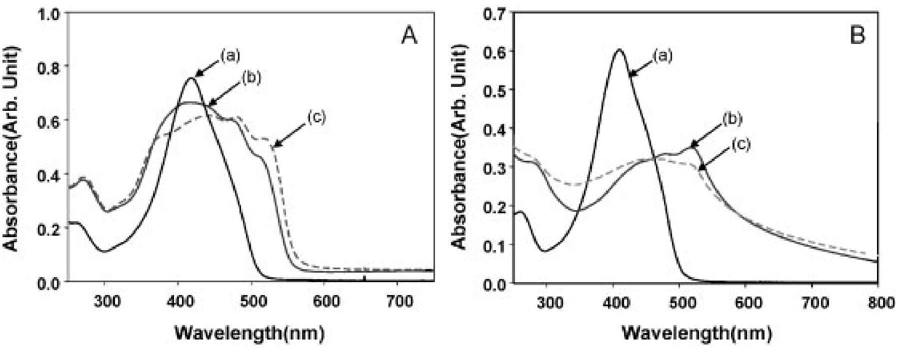


Figure 3.
Optical absorption (UV/Vis) and emission (PL) spectra of 4(HPBT)-benzene and 4(HPTT)-benzene. A: 4(HPBT)-benzene, B: 4(PBT)-benzene, (a) solution, (b) as-cast film, (c) annealed film.

shift was also observed in this sample too. It is hard to determine an accurate optical bend-gap energy in this sample. However, a large reduction of a bandgap could be expected from this spectral behavior. A high degree of intermolecular interaction can be expected in this sample.

In order to study the crystallinity of the synthesized dendrimers, X-ray diffraction (XRD) experiment was performed. In Figure 4(a), the X-ray diffraction pattern of annealed 4(HPBT)-benzene film showed the strong first-order reflections at 2.9°. It corresponds to an interlayer spacing of 29.7 Å of the loosely packed lamellar structure. Another diffraction peak at 19.3° corresponds to a spacing of 4.6 Å although the intensity is relatively small. This can be attributed to the intermolecular π–π stacking distance of successive planar moieties between two dendritic molecules. In Figure 4(b), the interlayer diffraction spacing of 18.0 Å were calculated for 4(PBT)-benzene along with 4.2 Å of a π–π stacking distance that is smaller than that of 4(PBT)-benzene. This implies that the dendrimer without hexyl tails are more facile to be stacked each other. However, the reflection intensity from a lamella order is quite weak and other small peaks can be observed around 4.5°. (19.38 Å) Without a hexyl group at the periphery, the molecular ordering in a longitudinal direction is a little bit random to give several different inter-lamella spacings irrespective of a high degree of ordering into the vertical direction to the long molecular axis. (See Figure 5).

AFM studies allow us to obtain good information of the fine structure of thiophene-labeled dendrimers. Figure 6 shows AMF images of thin films after annealing at their corresponding temperature. The image of 4(HPBT)-benzene reveals the formation of the uniform lamella networks on the silicon oxide. As we discussed in XRD analysis, the lamella ordering was quite uniform so that the regular domain could be built by nonpolar van der Waals interaction. The orthorhombic shaped crystallites exhibited relatively uniform alignment that is perpendicular to the surface.

However, 4(PBT)-benzene did not show uniform arrangement of the crystallites. In XRD results, nonuniformity of lamella ordering was discussed although their interlayer π-stacking was densely formed. In the case of crystallites of 4(PBT)-benzene, the flat molecular plane was randomly overlapped resulting from faster crystallization. Regarding the long-range

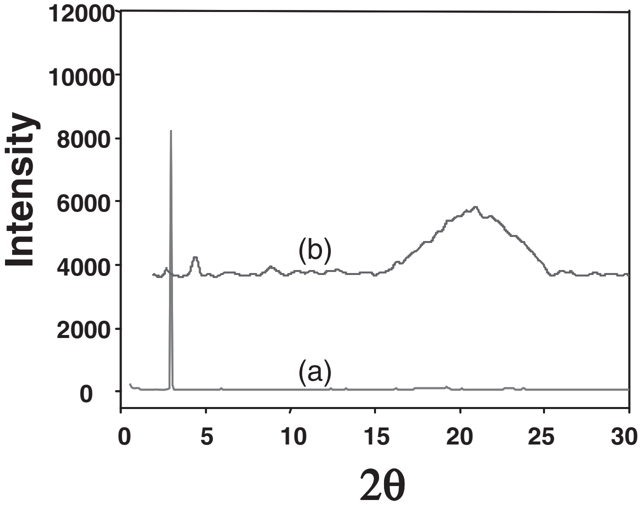


Figure 4.
X-Ray diffraction patterns of the two dendrimers. (a) 4(HPBT)-benzene, (b) 4(PBT)-benzene.

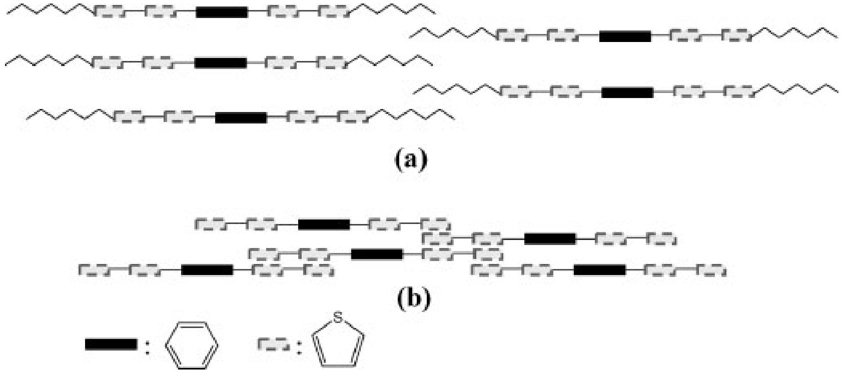


Figure 5.
Hypothetical schematic diagram of molecular arrangement. (a) 4(HPBT)-benzene, (b) 4(PBT)-benzene.

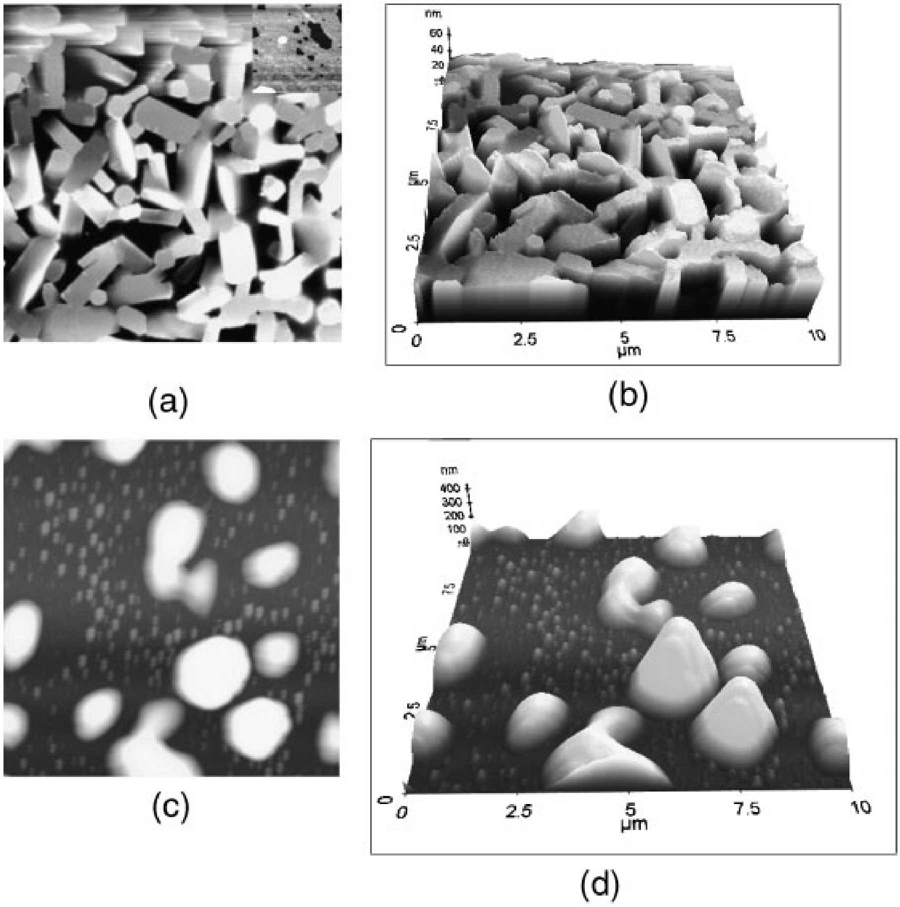


Figure 6.
AFM images of thin films deposited onto silicon oxide by spin coating. Two samples were annealed at 150 and 230 °C for 30 min. (a) Topography of 4(HPBT)-benzene, (b) 3-D surface image of 4(HPBT)-benzene, (c) Topography of 4(PBT)-benzene, (d) 3-D surface image of 4(PBT)-benzene.

orientation of crystallites, hexyl terminal chains played an important role to control the arrangement of dendritic molecules.

Conclusion

Two 1st-generation dendrimers were prepared to investigate the effect of alkyl peripheral group on molecular interaction. In the thin film of 4(HPBT)-benzene after annealing at 150 °C, the absorption was significantly read-shifted with clear vibronic transitions at 480 and 516 nm. The XRD results and AFM image of 4(HPBT)-benzene reveals the formation of the uniform lamella networks on the silicon oxide. 4(HPBT)-benzene having an intermolecular lamella and π–π stacking structure can become a promising candidate for organic field effect transistor.

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