

Cruciform Thiophene-based Molecules as Organic Semiconductors for Field Effect Transistor Applications

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Abstract

Cruciform conjugated molecule, 4(DP3T)-benzene bearing terthiophene moieties has been synthesized through Horner-Emmons Reaction using 5-dodecyl-5''-aldehyde-[2,2',5',2''] terthiophene as dendrons and octaethyl benzene-1,2,4,5-tetrayltetrakis(methylene)tetrakisphosphonate as the core unit; this molecule has been fully characterized. The terthiophene-based molecule exhibits good solubility in common organic solvents and good self-film forming property. They are intrinsically crystalline as they exhibit well-defined X-ray diffraction patterns from uniform orientations of molecules. Thus, intermolecular interaction can be enhanced to affect the carrier transport phenomena after annealing at 148°C. The semiconducting property of 4(DP3T)-benzene have been evaluated in organic field-effect transistors. 4(DP3T)-benzene exhibit carrier mobility as high as $(6.6 \pm 0.5) \times 10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

1. 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 In the exploration of the application of organic semiconductors, organic field-effect transistor (OFET) is an essential component for developing future flexible displays accompanied with organic light emitting materials.³⁻⁵

For developing a flexible field-effect transistor (FET), many soluble poly- and oligothiophenes have been suggested.⁶ In particular, α, α' -dialkylsexithiophene and its derivatives have been intensively employed as an active layer material in OFET.^{7,8} However,

incomplete planarity may decrease intermolecular conjugative effect in α, α' -dialkyloligothiophenes through torsion about single bonds. The solubility of oligothiophene is so poor that it cannot be utilized to solution processing technique for a large scale device application. In comparison with oligomers or polymers, a low generation dendritic or star-shaped molecule has distinct dual characteristics.

Recently, dendritic molecules have been adopted as interesting semiconducting materials and hence, thus far, the reports about their application in field effect transistors (FETs) are few.⁹⁻¹¹ We have designed the π -conjugated cruciform molecule bearing dodecyl substituted terthiophenyl peripheral groups, which exhibit the extended 2-dimensional geometry for ease in crystallization.

We report herein the synthesis and spectroscopic characterization of a new fully conjugated cruciform molecule bearing 5-dodecyl-[2,2',5',2'']terthiophenyl groups as peripheral groups. Preliminary result on field-effect hole mobility of the π -conjugated cruciform molecule were obtained. This result may provide a useful way for the design of new organic semiconducting materials applicable to the solution processable OFET application.

2. Results and Discussion

We display here the unique structure of the new p-type terthiophene-labeled cruciform molecule. Figure 1 illustrates the structure of the cruciform molecule. The four-armed crystalline molecule, 4(DP3T)-benzene contains terthiophene as the dendritic wedge. 4(DP3T)-benzene was synthesized through Horner-Emmons Reaction of 5-dodecyl-5''-aldehyde-[2,2',5',2''] terthiophene and octaethyl benzene-1,2,4,5-tetrayltetrakis

(methylene)tetrakisphosphonate. 5-dodecyl-2,2'-terthiophenyl were synthesized according to the known procedures.^{12,13} In order to attach the reactive group at 5 position of thiophene, a low temperature kinetic formylation reaction was performed to produce the corresponding aldehyde **1**. The reaction yield was around 38 %. This route affords the cruciform star-shaped molecule, 4(DP3T)-benzene in a high purity.

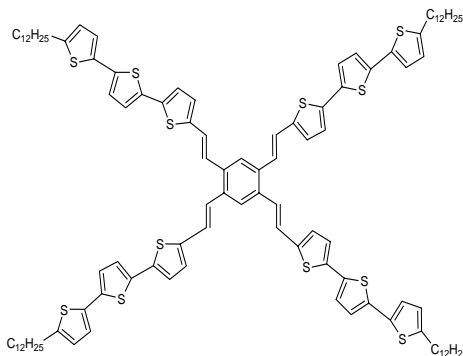


Figure 1. Structure of 4(DP3T)-benzene.

It was found to have good self-film forming property and is well soluble in various organic solvents such as chloroform, xylene, MC, chlorobenzene, and THF. In particular, in comparison to the solubility (about <1 mg/mL) of α,α' -dihexyl sexithiophene (DH-6T) in monochlorobenzene, their solubility proved to be considerably better. More than 10 mg of 4(DP3T)-benzene is soluble in 1 mL monochlorobenzene at an ambient condition.

When we employ the cruciform molecule for OFET applications, its thermal stability and dynamic behavior are emphasized for device fabrication. The thermal properties of 4(DP3T)-benzene were characterized by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). DSC measurement was performed under nitrogen with the highest temperature limited to below the decomposition temperature. In contrast to DH-6T ($T_m=298^\circ\text{C}$), 4(DP3T)-benzene exhibits distinct crystalline-isotropic transition at 198°C . TGA measurements at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen revealed that 4(DP3T)-benzene had good thermal stability. Compared to the onset decomposition temperature of DH-6T, which is at around 309°C ,

4(DP3T)-benzene has enhanced onset decomposition temperatures ($\sim 375^\circ\text{C}$).

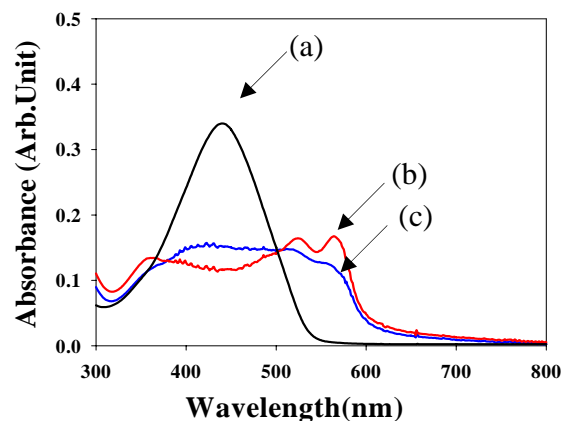


Figure 2. Optical absorption spectra of 4(DP3T)-benzene. *(a) solution, (b) pristine film, (c) annealed film.

The absorption spectra of the sample in chloroform (conc. 1×10^{-5} mole/L) and thin films were obtained (see Figure 2) Compared to DH-6T ($\lambda_{\text{abs}}^{\text{max}} = 438$ nm), the absorption maxima of 4(DP3T)-benzene in a solution state exhibits a red-shift of 3 nm and are located at 441 nm, respectively. It exhibits a lower λ_{max} due to its longer intramolecular conjugation length than DH-6T.

We observe a drastic spectral change in the film state, which is attributed to a high degree of intermolecular interaction. In the thin film after annealing at 148°C , the absorption spectrum is significantly red-shifted and broadened with a featureless structure. Although the lowest bandgap energies (E_g s) in the crystalline films were not accurately determined by absorption spectroscopy, the difference between the bandgap energies ($\Delta E_g = E_g^{\text{solution}} - E_g^{\text{film}}$) in solution and film states provides useful information in understanding the intermolecular interactions.

The optical bandgap energy was determined to be around 2.3 eV in a solution state. In the thin film of 4(DP3T)-benzene after annealing at 148°C a baseline became floated due to severe optical scattering through crystallization of 4(DP3T)-benzene and the absorption spectrum of the annealed film was significantly red-shifted to show fairly large decrease of a bandgap energy

(~ 2.0 eV). It is mainly attributed to a formation of ordered structure with an intermolecular π - π stacking.¹³

The large difference (ΔE_g) ($=0.3$ eV) between the solution and annealed film of 4(DP3T)-benzene implies the existence of a high degree of intermolecular interaction due to easy crystallization.

In order to study the crystallinity and preferred orientations of the cruciform molecule, X-ray diffraction (XRD) was performed. (see Figure 3) The cruciform molecular layers could be associated with the layered stacking properties brought about by the terminal alkyl groups, which are already known to induce long-range ordering. X-ray diffraction pattern of film of 4(DP3T)-benzene annealed at 148°C reveal the high crystalline order and uniform molecular orientation. The orientation of the molecule is inferred through the high reflection intensity of the peaks at 47.0 Å and the presence of peaks in the 3 - 4 Å region, as seen in our X-ray diffractograms. The inset diffractogram was obtained by small angle X-ray scattering (SAXS). The former spacing corresponds to the edge-to-edge transverse packing of the peripheral arms, and the latter to a π - π stacked distance having a π -electron cloud overlap.

We assumed that orientation of the 4(DP3T)-benzene molecule to the substrate is relatively disordered although an intermolecular layered structure and a π - π stacked structure can coexist in crystalline thin films.

Charge carrier mobility of 4(DP3T)-benzene was measured in OFET using a bottom contact device configuration. (channel length of 10 μm and channel width of 1.5 mm) The organic semiconductor layers (400 nm) were deposited by spin coating technique at room temperature. In this device, we employed *bare* SiO_2 (250 nm) without any surface treatment and interlayer at an ambient condition. The device made of DH-6T we synthesized was also characterized with the same configuration under an identical environment. Under an identical device configuration, DH-6T device provide $4.0 \pm 0.5 \times 10^{-4}$ cm^2/Vs ($I_{\text{on}}/I_{\text{off}} \sim 10^3$), that was selected as a reference sample. Electrical

transfer characteristics of an OFET based on 4(DP3T)-benzene are shown in Figure 4.

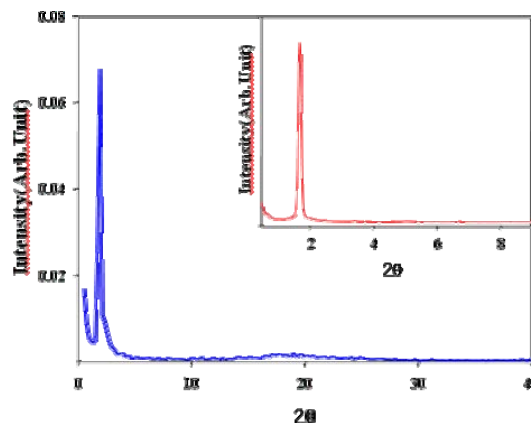


Figure 3. X-ray diffraction pattern of 4(DP3T)-benzene.

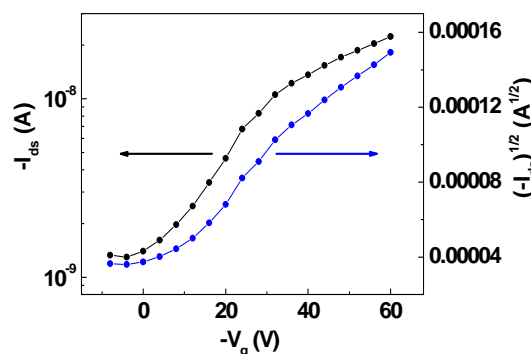


Figure 4. Transfer characteristics of OFET made by spin coating of 4(DP3T)-benzene from chloroform solution, annealed 148°C for 30 min.

The carrier mobility of $(6.6 \pm 0.5) \times 10^{-4}$ cm^2/Vs at the on/off current ratio of about 10 was obtained after averaging the data from ten time experiments. The novel dendritic architecture provides possible candidates for solution processable OFET applications.

In addition to the long-range molecular structural organization confirmed by X-ray study, the AFM micrographs display well-resolved surface structures on the dielectric layer. Therefore, we analyzed the topography and phase image of the semiconducting layer on the SiO_2 layer. We prepared the solution of each molecule,

and then, performed spin coating to cover the dielectric surface with each solution. After complete drying, we took atomic force micrographs as shown in Figure 5. It shows the compact structure on the surface with relatively large crystallites. A high coverage of the substrate is achieved simply by spin coating.

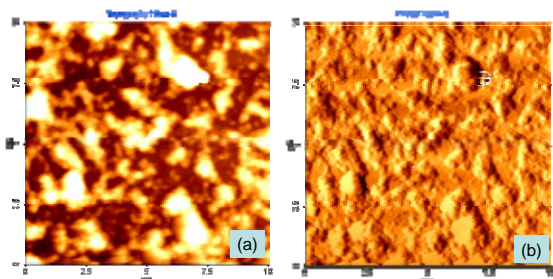


Figure 5. AFM micrographs of 4(DP3T)-benzene. (a) height image; (b) phase image.

Conclusion

We demonstrated the facile synthesis of 4(DP3T)-benzene and easily purified it compared to the conjugated polymers. Uniform symmetric molecular architecture induces high degree of crystallinity after annealing process. After annealing, intermolecular interaction of molecules was significantly enhanced, confirmed by reduction of the lowest bandgap energy. The semiconducting property of the cruciform molecule was evaluated in an organic field-effect transistor. Despite that the molecular arrangement on the substrate is ambiguous to define, the small crystallites of 4(DP3T)-benzene cover the substrate densely and exhibit good network interconnection between the crystallites that is probably responsible for moderately high carrier mobility in a solution processed organic semiconductor for OFET.

4. Acknowledgements

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5. References

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