Photocrosslinkable $\pi$-conjugated cruciform molecules for electronic/optoelectronic applications

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Abstract

The development of organic field-effect transistors (OFETs) and organic photovoltaic cells (OPV) has seen much progress using solution-processable organic semiconductors, which can combine high charge transport mobility, stability and patternability. In this work, we report on the design and synthesis of a new type of photopatterning $\pi$-conjugated cruciform molecule. These molecules are capable of photopatterning by virtue of photopolymerization of the reactive end-groups (pentadien or acrylate). Their solubility is very good for solution processing. Transistor devices using these molecules provided a maximum field-effect mobility of $3.7 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ as well as a high current on/off ratio. Remarkably, it was found that their charge carrier mobilities were well-maintained, even after the photocrosslinking process.

Keywords: photocrosslinkable, organic field-effect transistor, cruciform molecule

Classification numbers: 4.10, 6.01, 6.03

1. Introduction

The development of organic field-effect transistors (OFETs) has generated a great deal of interest in solution-processable organic semiconductors, which can combine high charge transport mobility, stability, and patternability. There are several reports describing the photochemical or thermal crosslinking of organic side chain polymers to form insoluble polymer networks as charge-transport and/or emission layers [1–4]. However, the photochemical crosslinking process often caused a substantial degree of photochemical degradation and a reduction of charge-carrier mobility. Liquid crystalline polymer networks formed from reactive mesogens, which contain a polymerizable end-group, have also been developed as an alternative approach to charge-transporting semiconductor material in OFETs and light-emitting polymer networks in organic light-emitting diodes (OLEDs) [5–9]. Polymerization and crosslinking occur either by the thermal or photoinduced generation of free radicals or by ionic photoinitiation [5]. Polymer networks formed from reactive mesogens provide a unique and advantageous combination of properties compared to other approaches: they are monodisperse after standard purification procedures; they form insoluble, intractable polymer films by spin-coating and subsequent polymerization; their films are photopatternable and some exhibit higher photoluminescence (PL) efficiency and improved current–voltage characteristics in prototype OLEDs than the monomers themselves before crosslinking [2,7], and the charge-carrier mobility can also exhibit a low field dependence [9]. However, the carrier mobility of the linear thiophene-based liquid crystalline molecule was observed to decrease after the photocrosslinking reaction due to disruption of the preferred anisotropic molecular packing (figure 1) [10–12].

Recently, Fréchet and co-workers have developed novel photocrosslinkable materials, bromine-functionalized
poly(3-hexylthiophene) copolymers (P3HT-Br), to stabilize the bulk heterojunction (BHJ) film morphology with minimal disturbance in the packing of conjugated polymers, thus enabling a high performing and thermally stable bilayer as well as BHJ photovoltaics [13].

Photopolymerization is preferred to thermal polymerization because of the pixelation capability and also because high temperatures can reduce the order parameter of uniformly oriented reactive mesogens and lead to photodegradation. A very limited number of reactive mesogens with acrylate, methacrylate, oxetane or nonconjugated diene polymerizable end-groups have been used so far as charge-transporting semiconductor material in OFET and light-emitting polymer networks in multilayer OLEDs [2–12]. The polymerizable end-groups should preferentially be polymerized by a radical mechanism to avoid the presence of ionic initiator and reaction products within the resultant crosslinked polymer network. It is suspected that these charged ionic contaminants may act as traps and potentially contribute to device failure. A potential advantage of nonconjugated diene end-groups compared to acrylates or methacrylates is the low tendency of such nonconjugated dienes to polymerize thermally [14]. This means that unreacted monomers should not polymerize spontaneously during the fabrication and operation of a device. Acrylates and methacrylates may also show a greater tendency to photochemical degradation during crosslinking process [2, 14]. The reaction pathways of 1,4-pentadiene monomer to form poly(1,4-pentadienes) and acrylate monomer to form a relatively flexible polyacrylate backbone are as follows:

In this work we report the design of a new class of hole-transporting semiconductor materials incorporating photoreactive end-groups. In this instance, the core of the molecule is designed to have conjugative connecting properties, which will be discussed later. The photopolymerizable 1,4-pentadien-3-yl group at the periphery was used because of its ability to undergo photopolymerization without a photoinitiator [6, 7]. Ultraviolet (UV) radiation (λ = 254–270 nm) at room temperature is effective to induce photocrosslink, forming crosslinks between the reactive units, which results in the formation of insoluble 2D or 3D polymer networks.
2. Experimental

$^1$H nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury NMR 400Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. $^{13}$C NMR spectra were recorded using a Varian Inova-500 spectrometer. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. Mass analysis was performed on a JMS-AX505WA (JEOL) mass spectrometer. MALDI-TOF analysis was performed on a Voyager-DE STR MALDI-TOF (matrix; DHB) mass spectrometer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821e and Mettler TGA 50.

The redox properties of the molecules were examined using cyclic voltammetry (model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{NPF}_6$) in a freshly dried dichloromethane (DCM). The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV s$^{-1}$. Fourier transformed-infrared (FT-IR) spectra were recorded using a Nicolet 380 infrared spectrophotometer.

Absorption spectra of chloroform solutions were obtained using a UV-vis spectrometer (HP 8453, PDA type) in a wavelength range of 190–1100 nm. PL spectra were recorded with a Hitachi’s F-7000 FL spectrophotometer.

Atomic force microscopy (AFM) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The film samples were fabricated by spin-coating (1500 rpm) on silicon wafer followed by drying under a vacuum (solvent: chloroform, solution concentration: 10 mg ml$^{-1}$).

The field-effect transistors consisted of heavily doped (100) silicon that we used as the gate electrode, with 300 nm thermally-grown SiO$_2$ used as gate insulator. The source and drain electrodes (120 nm Au) were deposited by thermal evaporation through a shadow mask. We washed the wafers with acetone, isopropanol, followed by UV-ozone exposure to clean the wafers. The silicon oxide was treated with octyltrichlorosilane (OTS) by immersing freshly cleaned wafers in an 8 mmol l$^{-1}$ solution of OTS in anhydrous toluene for 30 min, followed by sonication in toluene and isopropanol, consecutively. The film devices were fabricated by directly spin-coating a 1% solution of semiconductor materials onto the dielectric substrate at 1600 rpm.

3. Result and discussion

3.1. Identity and structure of the synthetic materials

We successfully synthesized new photopolymerizable p-type thiophene-based cruciform semiconducting molecules: PT1, PT3, and PT4 bearing pentadienyl reactive groups while PT2 bearing acrylate reactive groups at the periphery (figure 2). In the case of PT1 and PT2, thiophene groups were attached to the benzene ring directly. By contrast, in the case of PT3 and PT4, thiophene groups were attached to the benzene ring via double bonds.

The identity and purity of the synthetic materials were confirmed by $^1$H NMR, $^{13}$C NMR, MALDI-TOF mass spectrometry and elemental analysis. They were found to have good self-film-forming properties and to be soluble in various organic solvents such as chloroform, DCM, ethyl acetate, chlorobenzene and tetrahydrofuran.

Furthermore, computer calculations using the AM1 theoretical model incorporated into the Spartan program (‘06) were performed to determine the minimum energy conformations for four molecules [15]. Such calculations have
been found to be reliable for the determination of geometrical shapes in cruciform molecules. The optimized geometrical structures of the four molecules are illustrated in figure 3. The shapes of two molecules PT1 and PT2 are expected to be quite similar. Four bithiophene groups are twisted with a benzene ring. This is the reason why PT1 and PT2 showed weak intermolecular interaction as well as low crystallinity. By contrast, PT3 and PT4 showed quite a planar structure due to four bithiophene groups that were attached to the benzene ring via double bonds. PT3 is likely to have randomly oriented photoreactive peripheral moieties. In particular, PT4 has two hexyl peripheral groups with zigzag extended conformation, which can be interdigitated through molecular interaction.

The thermal properties of the molecules were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurement was performed at a heating (cooling) scan rate of 5 °C min⁻¹ under nitrogen with the highest temperature limited to below 400 °C. The thermal analysis revealed that PT3 showed a melting point at 110 °C, while PT2 exhibited a melting point at 120 °C. The TGA analysis showed that PT3 and PT2 had a weight loss of about 5% at 200 °C, indicating a good thermal stability.

Figure 3. Optimized geometries of four molecules. (A) PT1, (B) PT2, (C) PT3 and (D) PT4.

Figure 4. FT-IR spectra before (a) and after (b) UV exposure of two molecular films: (A) PT3 bearing pentadien groups and (B) PT2 bearing acrylate groups.
the decomposition temperature. PT1, PT2, PT3 and PT4 displayed distinct melting temperatures at 95, 145, 76 and 142 °C in heating cycles and distinct isotropic-to-crystalline transitions at 78, 127, 58 and 116 °C during cooling cycles, respectively. By comparison of the crystalline and melting points of PT3 and PT4, we determined that the hexyl peripheral groups play a key role in increasing the crystallinity due to the presence of 2D lamella ordering.

TGA measurements at a heating rate of 10 °C min⁻¹ under nitrogen revealed that four molecules had good thermal stabilities. These molecules showed the onset decomposition temperature around 300 °C.

3.2. Confirmation of photocrosslinking of photoreactive π-conjugated cruciform molecules

An FT-IR investigation was carried out to confirm that photocopolymerization had occurred between the photoreactive units (dien or acrylate). Figure 4 shows FT-IR spectra of the PT3 (A) and PT2 (B) films before and after UV exposure (λ = 254 nm, I = 40.64 mW cm⁻²). We chose a FT-IR spectrum of PT3 as a representative spectrum of three molecules bearing pentadien groups PT1, PT3 and PT4. The characteristic absorption bands at 932, 993, 1150, 1640 and 1737 cm⁻¹, which can be unambiguously assigned to the diene or acrylate photoreactive groups, are labeled in figure 4. The difference spectrum shows a differential line shape at ∼1737 cm⁻¹, corresponding to a spectral shift of the C=O transition of the diene groups as a result of crosslinking. This shift occurs because the transition is inductively coupled to the double bond, which was decomposed during polymerization. The decrease in intensity of the = CH wag transitions at 993, 932 and 1641 cm⁻¹ further verified crosslinking.

Approximate 100-nm-thick films of PT1, PT2, PT3 and PT4 were spin-coated on the quartz glass and annealed at proper temperatures. The films were exposed to UV light (λ = 254 nm, I = 40.64 mW cm⁻²) for 10 min. It is notable that no photoinitiator was used with PT1, PT3 and PT4. The exposed films were immersed in chloroform for 60 s. The partially polymerized regions of the film were washed away. The thickness decreased by about ∼10% after washing, indicating that only a small amount of the material is removed. This confirms conclusively that crosslinked networks were formed in film of predominantly above four molecules.

3.3. Optical properties of photoreactive π-conjugated cruciform molecules

The absorption and PL spectra of four molecules PT1, PT2, PT3 and PT4 in both dilute chloroform solution (concentration = 1 × 10⁻⁶ M) and thin solid films spin-coated on a quartz substrate are illustrated in figure 5. The UV absorption, PL maxima and energy levels of four molecules
are summarized in Table 1. In solution states, molecules PT1, PT2, PT3 and PT4 exhibited absorption maximum at 355, 355, 415 and 416 nm, respectively. The absorption spectrum of the films of two molecules PT1 and PT2 exhibited insignificant broadening and slightly red shifted by 6 nm compared to that of the solution state. This phenomenon was explained by their distorted structures which led to the low degree of intramolecular interaction. By contrast, a drastic spectral change was observed in the film states of PT3 and PT4, which is attributed to a high degree of intramolecular interaction. By contrast, a drastic spectral change was observed in the film states of PT3 and PT4, which is attributed to a high degree of intermolecular interaction. For instance, in the film state after annealing, the PT4 absorption spectrum is significantly red-shifted with vibronic transitions; this shift may be due to the formation of an ordered structure with intermolecular π-stacking.

Four molecules, PT1, PT2, PT3 and PT4, exhibited PL spectral behaviors with emission maxima at 496, 498, 539 and 557 nm in solution states, respectively; 570 for PT3 and 557 nm for PT4 in film states.

### 3.4. Electrochemical analysis of photoreactive π-conjugated cruciform molecules

Electrochemical characterization of these molecules revealed that their oxidation is reversible, which is a necessary condition for a stable OFET active material. The values of the ionization potential match well with the work function of a gold electrode. Cyclic voltammograms (CV) were recorded on a film sample and the potentials were obtained relative to an internal ferrocene reference (Fc/Fc⁺). These CV scans in the range of −2.0 to +2.0 V (versus Ag/AgCl) show quasi-reversible oxidation peaks. Unfortunately, the reduction behaviors were irreversible; therefore, accurate estimation of HOMO and LUMO energies was not possible. To determine the LUMO levels, the oxidation potential in CV was combined with the optical energy band gap \( E_{opt} \) resulting from the absorption edge in the absorption spectrum. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of four molecules are shown in Table 1.

### 3.5. Properties of OFET made from photoreactive π-conjugated cruciform molecules

Bottom-contact OFET devices were fabricated using gold source and drain electrodes which were thermally evaporated using a conventional method. To achieve optimal performance, the OFET devices made of four molecules PT1, PT2, PT3 and PT4 were further annealed at 80, 120, 65 and 115 °C, respectively, for 10 min. The saturated field-effect mobility, \( \mu_{EF} \), can be calculated from the amplification characteristics by using the classical equations describing field-effect transistors. The mobility values obtained by measuring different devices are listed in Table 2. PT1 and PT2 do not show significant charge transport behavior. This may be due to the high bandgap energies and low intermolecular interaction. By contrast, the output characteristics of devices made by PT3 and PT4 showed very good saturation behaviors and clear saturation currents that were quadratic to the gate bias.

The transistor devices of PT3 and PT4 after annealing provided a field-effect mobility of \( 1.3(±0.2) \times 10^{-3} \) to \( 3.7(±0.5) \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) as well as a high current on/off ratio and a low threshold voltage. Compared to PT3, PT4 showed higher mobility due to the more compact structure on the surface with larger crystallites. This molecule exhibited a carrier mobility of \( 3.7(±0.5) \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for a 10 µm channel length device, with a current on/off ratio higher than \( 10^3 \) and a threshold voltage of −16 V (figure 6 and Table 2). It is assumed that the hexyl peripheral groups and lamella ordering induce higher intermolecular interaction and preferred molecular orientation, leading to increased carrier mobility.

In previous reports on photopolymerizable linear organic semiconductors, a reduction in charge transport was observed. The field-effect mobility in crosslinked films was reduced approximately ten-fold [10]. However, in the case of the cruciform conjugated molecule PT4, the field-effect mobility in crosslinked films was well-maintained. A possible
Table 2. Physical properties and OFET device performance of four molecules PT1, PT2, PT3 and PT4. \( T_d \): decomposition temperature; \( T_m \): melting temperature; \( T_c \): crystallization temperature.

| Sample     | \( T_d \) (°C) | \( T_m \) (°C) | \( T_c \) (°C) | \( \mu_{\text{max}} \) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) | \( I_{\text{on}}/I_{\text{off}} \) |
|------------|----------------|---------------|---------------|---------------------------------|--------------|
| PT1        | 295            | 95            | 78            | –                               | –            |
| PT2        | 300            | 145           | 127           | –                               | –            |
| PT3        | 320            | 76            | 58            | 1.3(±0.2) \times 10^{-3}        | 3.4(±0.5) \times 10^{-4} > 10^3 |
| PT4        | 330            | 76            | 58            | 3.7(±0.5) \times 10^{-3}        | 3.6(±0.5) \times 10^{-3} > 10^3 |

An explanation could be related to the strong intermolecular interaction of the cruciform structure, which could arrest the molecular axis under push-pull force during the crosslinking and is accompanied by a high degree of lamella ordering in two directions. Thus, a cruciform structure seems to be a suitable design for photopatterable semiconductor molecules.

4. Conclusion

We have successfully synthesized and characterized novel, solution-processible, photocrosslinkable, cruciform conjugated molecules. The patterning process was carried out by photocrosslink of the reactive end-groups, creating an insoluble network. These molecules bearing pentadiene groups can be photopolymerized without a photoinitiator, which can behave as a charge trap. The maximum field-effect mobility of these molecules was found to be approximately 3.7(±0.5) \times 10^{-3} cm\(^2\) V\(^{-1}\) s\(^{-1}\) with a current on/off ratio higher than 10^3. It was also found that cruciform molecules exhibited great persistency of field-effect mobility even after photocrosslink, which suggests that the patternable process is feasible for the fabrication of OFET array device structures. This result can be applied to the design of photoreactive semiconductor molecules for practical electronic applications.

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