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Semiconducting 2,3,6,7,10,11-Hexakis{[4-(5-dodecylthiophen-2-yl)phenyl]ethynyl}triphenylene and Its Discotic Liquid Crystalline Properties

Mai Ha Hoang, Min Ju Cho, Kyung Hwan Kim, Tae Wan Lee, Jung-Il Jin, and Dong Hoon Choi*
Department of Chemistry, Advanced Materials Chemistry Research Center, Korea University, Seoul 136-701, Korea

(Received January 21, 2010; CL-100066; E-mail: dhchoi8803@korea.ac.kr)

We report on the design and synthesis of a new discotic liquid crystalline (LC) semiconducting material based on a triphenylene core. The molecule is readily soluble in common organic solvents to exhibit self-organizing long fiber structures with supramolecularly ordered columnar stacks that lie parallel to the substrate. Compared to all the previously reported triphenylene derivatives, this molecule has a relatively lower band gap energy ($E_g = 2.53$ eV), which makes it suitable for electronic and optoelectronic applications.

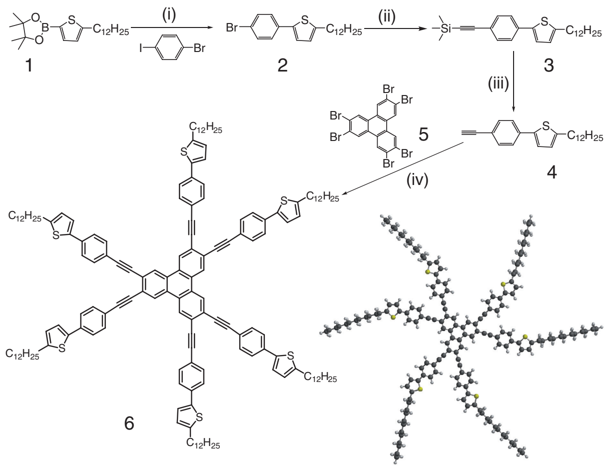
Columnar discotics is an interesting class of materials that can be potentially used as organic semiconductors in electronic devices. The corresponding mesogens consist of an aromatic or fused aromatic core, which can be chemically modified by peripheral substitution and self-assemble into one-dimensional columnar superstructures that then arrange in a two-dimensional lattice. The overlapping of the π-orbitals of adjacent molecules within the columns ensures that one-dimensional intra-columnar charge-carrier transport occurs. While charge carrier mobilities that are more than sufficient for thin film transistor applications have been reported, utilization of the discotic liquid crystalline molecule will be realized only when the pathways for transport can be uniaxially aligned parallel to the surfaces in thin film geometries that have length scales of at least 100 nm.[1,2]

Triphenylenes and their derivatives have been intensively synthesized and investigated in recent decades. Such molecules have attracted attention mainly because of their unique tendency to aggregate into geometrically confined one-dimension columnar arrays that can display LC properties. Hexaalkoxytriphenylenes, hexakis(alkylsulfanyl)triphenylenes, hexaphenyltriphenylenes, and hexakis(phenylethynyl)triphenylenes[3,4] have been synthesized as its derivatives. However, these derivatives show high band gap energies that would weaken their potential in electronic applications.

In a previous study, in an effort to reduce the band gap energy, we reported semiconducting multibranched conjugated molecules based on a π-extended triphenylene core and bearing six bithiophene groups. Their band gap energies were so low that they can be used for organic thin film transistor fabrication. However, the previous triphenylene-based molecules did not clearly show liquid crystalline properties.[5]

In this paper, we report the design and synthesis of a new semiconducting molecule based on a triphenylene core. This molecule showed a relatively low band gap energy ($E_g = 2.53$ eV) and an interesting LC properties.

Compound **5** was prepared according to a procedure described in literature.[6] Compound **2** was prepared by the Suzuki coupling reaction of compound **1** with 1-bromo-4-iodobenzene. Through the Sonogashira coupling with trimethylsilyl acetylene, compound **2** was converted to compound **3** before deprotecting the trimethylsilyl group to yield compound **4**. 2,3,6,7,10,11-Hexabromotriphenylene (**5**) was used as the core moiety in the Sonogashira coupling with compound **4** to efficiently yield compound **6** (HDTPT) (yield, ca. 60%)[7] (Scheme 1). Computer calculations using the density functional theory (DFT) model incorporated with the Spartan program ('06) showed that the π-extended core had an absolutely planar structure, which is a prerequisite for the uniaxial orientation of columnar discotic liquid crystals.



Scheme 1. Synthetic route and optimized geometry of compound **6** (HDTPT). (i) $Pd(PPh_3)_4/Ba(OH)_2/H_2O$/Dimethoxyethane, 80 °C; (ii) trimethylsilyl acetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt; (iii) K_2CO_3, CH_2Cl_2, MeOH, rt; (iv) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 90 °C.

Figure 1 shows the absorption and emission spectra in solutions and thin films of this molecule. The absorption of HDTPT in a dilute chloroform solution showed an absorption maximum at 382 nm. A drastic spectral change was observed in the film state of this molecule, which is attributed to a high degree of intermolecular interaction. Compared to the molecules of previously reported triphenylene derivatives, molecule **6** showed red-shifted absorption spectral behavior arising from lower band gap energy in the solid state. HDTPT exhibited photoluminescence (PL) spectral behaviors with an emission maximum at 438 nm in the solution state and 501 nm in the film state. The PL spectrum in the film state is significantly red-shifted and the color emission was totally changed to green.

The thermal properties of HDTPT were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (scan rate of 5 °C min^{-1} under nitrogen). HDTPT displayed an endothermic peak at 67 °C and a clear crystalline transition at 22 °C in the cooling cycle (inset of Figure 2).

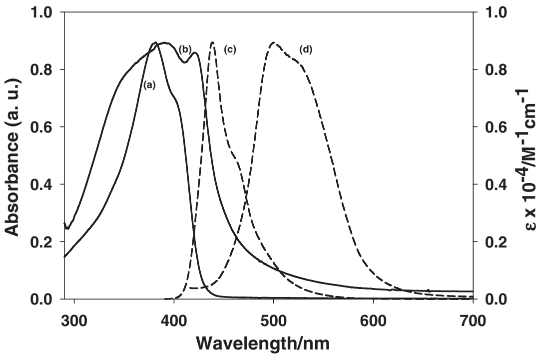


Figure 1. UV–vis absorption and PL emission spectra of HDTPT. (a) Absorption spectrum in solution state, (b) absorption spectrum in film state, (c) PL spectrum in solution state, and (d) PL spectrum in film state.

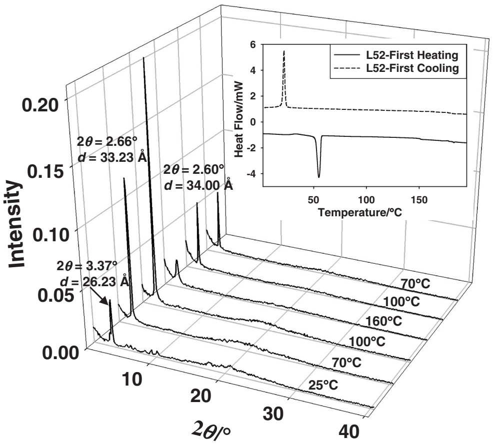


Figure 2. Temperature dependence of X-ray diffraction patterns of HDTPT.

To confirm the crystalline property of this LC molecule, X-ray diffraction (XRD) experiments were performed at varying temperatures using the synchrotron radiation (1.542 Å) of the 3C2 beam line. The X-ray diffraction scans of HDTPT film annealed at different temperatures reveal the temperature at which the highest crystalline order is achieved (Figure 2). From the peaks at $2\theta = 3.37°$, the interlayer spacing is evaluated to be 26.23 Å. The peak shifts to a lower 2θ direction above the melting point (67 °C), reflecting a crystalline–crystalline phase transition. The diffraction intensity increased drastically above this temperature, and the peak position shifted to $2\theta = 2.66°$ ($d = 33.23$ Å), which is the intercolumnar distance of the nematic phase. The liquid crystalline mesogenic phase of discotic LC was maintained in a broad temperature range from 67 to 160 °C. Although the diffraction intensity decreased significantly when the temperature reached 160 °C, an ordered phase was retained upon cooling. The presence of peaks in the 3.8–5.2 Å [(010) reflection] region showed the stacking periodicity of molecules in a nematic columnar phase.

By using a hot-stage optical microscope (Mettler Co.), the LC properties of the molecule were observed under crossed polarizers. Depending on the temperature for annealing, we could observe different LC textures. Figure 3 shows the highly ordered LC columnar phase of HDTPT (×400 times). The molecule can be processed from solution to form self-organizing long fibers with supramolecularly ordered columnar stacks that lie parallel to the substrate and can be oriented uniaxially onto normal glass slides. An optical micrograph of the texture on a rubbed polyimide film clearly displays the uniaxial alignment of the molecules.

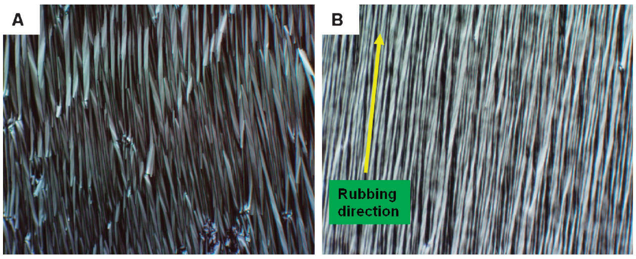


Figure 3. Optical micrographs of HDTPT annealed at 140 °C. (A) Film on normal glass slide and (B) film on rubbed polyimide film.

The intermolecular coupling of π electrons on adjacent molecules along the columnar stack in discotic LCs has been recognized as a promising structure that can allow easy charge movement along the stack. The fabrication of a thin film transistor using highly ordered HDTPT is now in progress.

We have successfully synthesized and characterized a new discotic LC semiconducting material, based on a triphenylene core. The molecule can be oriented uniaxially to form self-organizing long fibers that lie parallel to the substrate. The findings reported in this paper are expected to contribute to the design of new discotic LC semiconductors based on π-extended triphenylene for future electronic and optoelectronic applications.

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7 HDTPT: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.10 (s, 6H), 7.43 (d, $J = 8.2$ Hz, 12H), 7.29 (d, $J = 8.2$ Hz, 12H), 7.01 (d, $J = 3.2$ Hz, 6H), 6.69 (d, $J = 3.2$ Hz, 6H), 2.81 (t, 12H), 1.74 (m, 12H), 1.30 (m, 108H), 0.90 (t, 18H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 146.14, 141.45, 134.40, 132.70, 127.47, 125.26, 125.10, 124.62, 124.35, 122.07, 94.79, 90.06, 32.24, 31.98, 30.67, 30.06, 30.02, 30.00, 29.82, 29.70, 29.66, 22.30, 14.43. MS (MALDI-TOF) m/z: calcd $C_{162}H_{192}S_6$ [M$^+$] 2329.33; found 2329.12 Anal. Calcd for $C_{162}H_{192}S_6$: C, 83.45; H, 8.30; S, 8.25%. Found: C, 83.43; H, 8.30; S, 8.25%.