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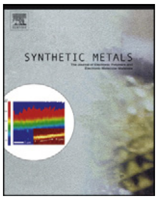

Organic field-effect transistors based on two phenylene–thiophene oligomer derivatives with a biphenyl or fluorene core

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ABSTRACT

The synthesis and full characterization are described of two phenylene–thiophene oligomer derivatives, 2,7-bis[5-(4-*n*-hexylphenyl)-2-thienyl]fluorene (HPTFTPH) and 4,4′-bis[5-(4-*n*-hexylphenyl)-2-thienyl]biphenyl (HPTPPTPH), which are based on a structural combination of a fluorene or biphenyl core, thienyl units, and end-cap hexylphenyl groups. Remarkable shifts in the UV–vis and photoluminescence spectra of thin films relative to their solutions indicate the existence of strong intermolecular π–π interactions in the solid state of the two oligomers. In addition, relatively large energy gaps and low highest occupied molecular orbital energy levels imply that the two oligomers are promising and durable semiconducting materials. Thin-film organic field-effect transistor devices based on the two oligomers show good p-type performances with high hole mobilities. The highest mobility (0.20 $cm^2/V\,s$) was obtained for the HPTPPTPH oligomer with biphenyl core.

1. Introduction

Conjugated oligomers have been widely used in organic electronics, including in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs), taking advantage of their high purity, high charge-carrier mobility, and facile synthesis to tune energy levels [1]. OFETs are expected to be applicable as large-area, low cost, and flexible electronics for applications in displays, sensors, and memories. The mobilities of the best semiconducting oligomer materials have already approached and even surpassed that of amorphous silicon (~0.1 $cm^2/V\,s$) [2]. Among all investigated organic semiconductors, oligothiophene and pentacene, as well-known homoaromatic oligomers, have shown the most outstanding performance. Unfortunately, these two kinds of p-type semiconductor material are easily oxidized because of their relatively high highest occupied molecular orbital energy (HOMO) energy levels and/or low energy band gaps, resulting in poor device stability and making them unsuitable for practical electronic circuit applications without careful encapsulation [1,2].

Thiophene-containing heteroaromatic oligomers derived from arene and thiophene represent another p-type semiconductor material heavily studied, and these usually exhibit unique photoelectronic properties and the possibility of chemical modification, as well as good stability against photodegradation and oxidation. Recently, many units, such as divinyl-benzene, phenylene, naphthalene, anthracene, tetracene, and fluorene, have been successfully introduced into the oligothiophene framework via co-oligomerization. They have been extensively used as stable semiconductor materials with relatively large energy band gaps and low HOMO energy levels [1,2]. Biphenyl, an important unit, is usually introduced into the framework of thiophene-containing heteroaromatic oligomers and acts as an end-cap group. A biphenyl end-capped fused bithiophene oligomer has been used as an active component in OFETs that show relatively high mobility (0.09 $cm^2/V\,s$) [3]. OFETs made of epitaxially grown crystals of another biphenyl-capped thiophene co-oligomer have shown excellent performance, with a variation in mobility of 0.29–0.66 $cm^2/V\,s$ [4], while the mobilities of the thin-film OFETs based on this biphenyl-capped thiophene co-oligomer and its derivatives were no higher than 0.01 $cm^2/V\,s$ [5,6]. The fluorene group is another important unit which is used as a building block in thiophene-containing heteroaromatic oligomers for OLEDs, OSCs, and OFETs due to its high thermal stability and fluorescence

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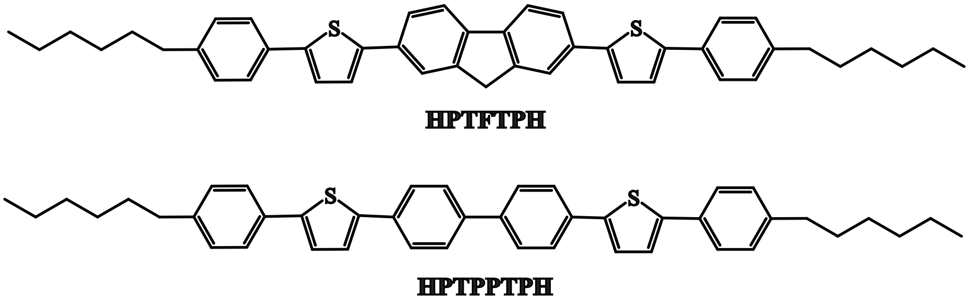


Scheme 1. Chemical structures of HPTFTPH and HPTPPTPH.

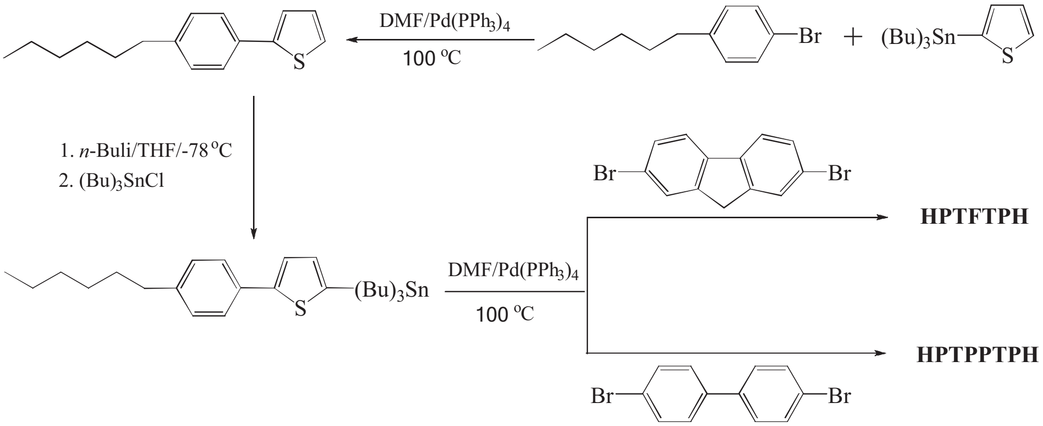
quantum yield, resulting in rigid structures with less conformational freedom [3,7]. A highly ordered polycrystalline thin-film OFET device based on alkyl fluorene end-capped oligomeric fluorene–thiophene has been fabricated, with a reported field-effect mobility of 0.12 $cm^2/V s$ and an on/off ratio up to 10^5 [7]. The alternating variation of thiophene and other arene units usually results in noticeable changes in the energy levels and molecular packing, thus leading to different OFET performance. To the best of our knowledge, previous attention has focused on biphenyl/fluorene end-capped thiophene co-oligomers, with scarce regard for the biphenylyl/fluorene unit acting as the molecular core in thiophene-containing heteroaromatic oligomers. Furthermore, only one paper has reported on the synthesis of a thiophene-containing heteroaromatic oligomer with a fluorene core and no report of its OFET performance has been made [8].

Phenylene–thiophene oligomers are a promising class of semiconductor material and many have been employed in OLEDs [9] and p-channel OFETs [10–12]. Previous works on OFETs fabricated from phenylene–thiophene oligomers suggest that phenylene substituents introduced at the 2-position or within the oligothiophene backbone can result in a lowering of the HOMO energy level, which can lead to a reduction in the off-current and thus an increase in the on/off ratio of OFET devices. Furthermore, the introduction of end-cap phenyl substituents at the 2-position can provide stability against oxidation and polymerization, while minimizing steric interactions that can prohibit coplanarity of the thiophene rings, as observed for oligothiophenes. The synthesis and application of some examples of phenylene–thiophene oligomers for OTFTs were previously presented by Mushrush et al. [11] and Fritz et al. [12]. However, they either used end-cap alkyl phenyl or end-cap biphenylyl, and thienyl rings in the conjugated oligomer, thus obtaining mobilities ranging from 10^{-5} to 0.09 $cm^2/V s$. A relatively small change in the molecular structure of thiophene-containing heteroaromatic oligomers usually results in significant improvement in hole mobility. Herein, we present the facile synthesis, full characterization, and thin-film OFET performance of two thiophene-containing heteroaromatic oligomers (as shown in Scheme 1) that are based on a structural combination of a biphenyl or fluorene core, and thienyl and end-cap hexylphenyl groups. Three types of subunits were incorporated into one molecule with mobility values up to 0.09–0.20 $cm^2/V s$ obtained in the resultant thin-film OFET devices. As expected, the phenylene–thiophene oligomer derivatives with biphenyl or fluorene core are good p-type semiconductor materials and their hole mobilities are higher than those of the most reported phenylene–thiophene and fluorene/biphenyl-capped thiophene-containing heteroaromatic oligomers.

2. Experimental

2.1. Materials and characterization

All commercially available reagents were purchased from Tokyo Kasei Industry or Sigma–Aldrich and used as received. All synthetic procedures were performed under an inert nitrogen atmosphere with oven-dried glassware. ^1H NMR was recorded on a JEOL ECA 600 MHz spectrometer using 1,1,2,2-tetrachloroethane-D_2 as the solvent. All chemical shifts were shown in parts per million (ppm) and referenced to the residual dichloromethane at 5.96 ppm. Mass spectra were measured using a JEOL GCmate mass spectrometer. Elemental analyses were carried out using an elemental analyzer (Choice Analytical Elementar VARIO EL). UV–vis absorption spectra were recorded on a JASCO V-550 spectrophotometer, and photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorospectrophotometer in cuvettes (in tetrachloroethane) or in films fabricated by vacuum evaporation on quartz substrates. Cyclic voltammetry, with a potential scanning rate of 50 mV/s, was performed using a potentiostat (Hokuto Denko HZ-5000) and



Scheme 2. Synthetic pathways to HPTFTPH and HPTPPTPH.