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Synthesis and Properties of Soluble Organic p-Type Semiconductor based on TIPS-anthracene Moiety

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New multi-branched molecules have been synthesized through Horner-Emmons reactions using 10-((triisopropylsilyl)ethynyl) anthracene-9-carbaldehyde as dendrons and octaethyl benzene-1,2,4,5-tetrayltetrakis(methylene) tetraphosphonate as a reactive core unit; these molecules have been fully characterized. Two anthracene-based star-shaped molecules exhibit good solubility in common organic solvents and good self-film forming properties. The four-armed molecule, **4(TIPS-ant)-benzene** *is intrinsically crystalline as they exhibit well-defined X-ray diffraction patterns from relatively uniform orientations of molecules. According to the AFM analysis,* **4(TIPS-ant)-benzene** *helps in attaining good network interconnection of the carrier transport channel, which is responsible for the charge carrier mobility in solution-processed organic semiconductors for organic thin film transistor (OTFT).*

Keywords: multi-branched molecule; organic thin film transistor; soluble semiconductor

INTRODUCTION

Organic materials as electroactive components possess several advantages such as ease of preparation, low processing cost, and a

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flexible molecular architecture and synthesis. For developing flexible organic transistors, many promising conjugated synthetic oligomers and polymers have been demonstrated rather than small molecules such as pentacene, perylene, and rubrene, which can only be processed by the vacuum evaporation method under vacuum [1–4]. Compared with linear organic conjugated oligomers and polymers used in organic thin film transistor (OTFT), star-shaped molecules have a number of advantages including the ability to spatially control the active components. The synthesis of π-conjugated multi-branched molecules raise the possibility of creating thiophene derivatives that are fully tethered to the planar core. Furthermore, the solubility problem in conjugated oligothiophene is totally overcome under a dendritic architecture. Recently, dendritic molecules have been adopted as an interesting class of semiconducting materials and hence, thus far, there are only a few reports about their application in thin film transistors [5–8]. In this study, we prepared crystallizable multi-branched molecules using 10-((triisopropylsilyl)ethynyl) anthracene-9-carbaldehyde as dendritic wedges. We employed the Horner-Emmons method to tether the dendritic wedges to the core which is free from transition metal catalyst. Hexaethyl benzene-1,3,5-triyltris(methylene)triphosphonate and octaethyl benzene-1,2,4,5-tetrayltetrakis(methylene) tetraphosphonate were used as the core unit for the new semiconducting dendritic molecules. We investigated the optical properties, thermal properties, electrochemical properties, and photophysical properties of the new multi-branched conjugated molecules.

EXPERIMENTAL

Instrumental Analysis

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 and 400 MHz spectrometer using deuterated chloroform ($CDCl_3$-*d*) purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. Time-of flight mass spectrometry (MALDI-TOF) was performed using a Voyager-DESTR MALDI-TOF (matrix; DHB) mass spectrometer.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10°C/min. The redox properties of multi-branched molecules were examined by 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 (Bu_4NPF_6) in a freshly dried acetonitrile. 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.

We investigated the carrier transport phenomenon after fabricating OTFT devices using these molecules. Bottom-contact OTFT devices were fabricated using the gold source and drain electrodes which were thermally evaporated using the conventional method. A p-doped polycrystalline silicon was used as a gate electrode with its 250 nm bare SiO_2 surface layer used as a gate dielectric insulator. The deposition of a self-assembled monolayer (SAM) with OTS on the SiO_2 gate dielectric was performed by following the method described in the literature. The gold was deposited onto the untreated and OTS-treated SiO_2 surface via thermal evaporation. A 400 nm thick film of the semiconductor layer was deposited at 25°C by spin coating a 2 wt% solution of multi-branched molecule in monochlorobenzene. Then, it was dried and annealed at a certain temperature for $1 \sim 0.5$ h. The device characteristics of the OTFTs were measured with Keithley 237 source-meters, with the samples in an ambient atmosphere.

Synthesis

Synthesis of 10-((Triisopropylsilyl)ethynyl)anthracene-9-carbaldehyde (2)

An oven dried, mag.-stirred, 500 mL RBF was charged with a solution of **1** (6.00 g, 21.0 mmol), copper (I) iodide (0.32 g, 1.68 mmol), *trans*-dichlorobis(triphenyl phosphine)palladium(II) (0.59 g, 0.84 mmol), and ethynyltriisopropylsilane (4.60 g, 25.2 mmol) in 100 mL freshly distilled THF and triethylamine (1:1). The reaction was allowed to stir for 16 h at 70°C. After completing the reaction, the reaction was quenched by adding a small amount of water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (eluent: chloroform) and the solvent was distilled off. After dissolving the crude solid in a minimum amount of THF, the solution was poured into ethanol to collect the precipitates. Yield 5.27 g (64.9%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.15 (s, 1H), 8.96 (d, $J = 8.0$ Hz, 2H), 8.76 (d, $J = 8.0$ Hz, 2H), 7.72–7.63 (m, 4H), 1.34–1.25 (m, 21H).

Anal. Calcd for $C_{26}H_{30}OSi$ C, 80.78; H, 7.82, Found: C, 80.86; H, 7.83.

Synthesis of 1,3,5-Tris((E)-2-(10-((triisopropylsilyl)-ethynyl)anthracen-9-yl)vinyl)benzene (3)

Hexaethyl benzene-1,3,5-triyltris(methylene)triphosphonate (0.62 g, 1.17 mmol) and 10-((triisopropylsilyl)ethynyl)anthracene-9-carbaldehyde (1.5 g, 3.88 mmol) were dissolved in 100 mL freshly distilled THF under a nitrogen atmosphere. The reaction was allowed to stir for 0.5 h followed by addition of potassium *tert*-butoxide (0.435 g, 3.88 mmole). After completing the reaction, the solution was poured into ethanol to collect the precipitates. Yield 1.03 g (71.5%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.73 (d, $J = 9.0$ Hz, 6H), 8.49 (d, $J = 8.0$ Hz, 6H), 8.17 (d, $J = 18.0$ Hz, 3H), 8.00 (s, 3H), 7.66–7.53 (m, 12H), 7.15 (d, $J = 18.0$ Hz, 3H), 1.36–1.27 (m, 63H) Anal. Calcd for $C_{87}H_{96}Si_3$ C, 85.23; H, 7.89, Found: C, 85.24; H, 7.75.

MALDI-TOF MS m/z calcd $C_{87}H_{96}Si_3$ $(M)^+$ 1224.6820, Found 1224.6496.

Synthesis of 1,2,4,5-Tetrakis((E)-2-(10-((triisopropylsilyl)-ethynyl)anthracen-9-yl)vinyl)benzene (4)

Octaethyl benzene-1,2,4,5-tetrayltetrakis(methylene) tetraphosphonate (0.62 g, 0.92 mmol) and 10-((triisopropylsilyl)ethynyl)-anthracene-9-carbaldehyde (1.5 g, 3.88 mmol) were dissolved in 100 mL freshly distilled THF. The reaction was allowed to stir for 0.5 h followed by addition of potassium *tert*-butoxide (0.435 g, 3.88 mmole). After completing the reaction, the solution was poured into ethanol to collect the precipitates. Yield 0.94 g (63.5%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, $J = 9.0$ Hz, 8H), 8.53 (s, 2H), 8.49 (d, $J = 9.0$ Hz, 8H), 8.15 (d, $J = 15.0$ Hz, 4H), 7.57–7.50 (m, 10H), 7.45–7.37 (m, 10H), 1.30–1.25 (m, 84H) Anal. Calcd for $C_{114}H_{126}Si_4$ C, 85.12; H, 7.90; Found: C, 85.25; H, 7.72.

MALDI-TOF MS m/z calcd $C_{114}H_{126}Si_4$ $(M)^+$ 1606.8937, Found 1605.1460.

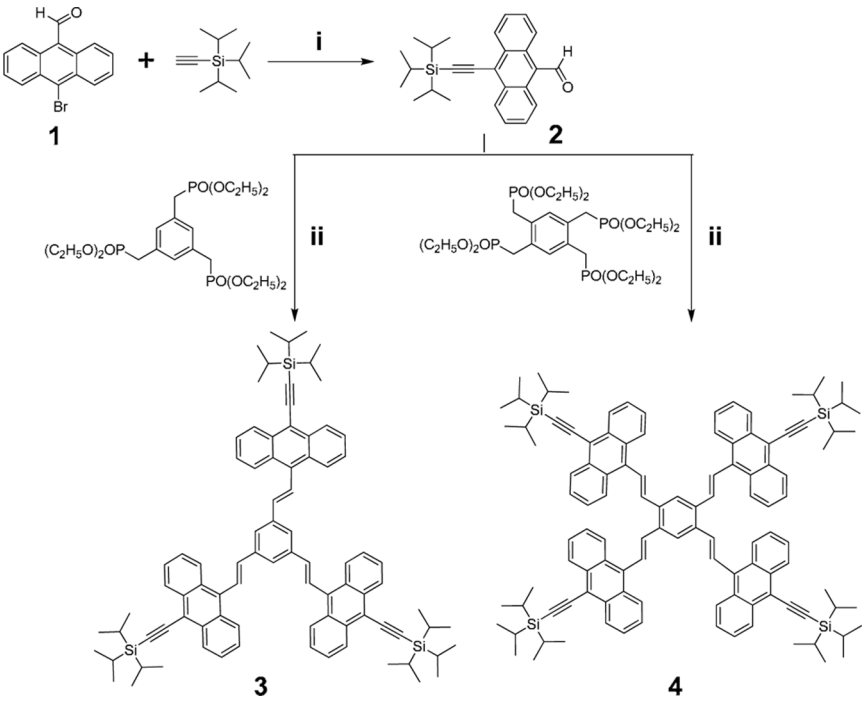
Absorption and Photoluminescence Spectroscopy

Studying absorption and PL spectral behavior, thin films of multi-branched molecules were fabricated on quartz substrates as follows. The solution (2 wt%) of each molecule in chloroform was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 80°C for 24 hours under vacuum. Absorption spectra of film samples and chloroform solution (conc. 1.5×10^{-6} mol/L) were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm. PL spectra were recorded with an AMINCO-Bowman series-2 luminescence spectrometer.

RESULTS AND DISCUSSION

We herein report the synthesis and photophysical characterization of two new π-conjugated multi-branched molecules bearing (anthracen-9-ylethynyl) triisopropylsilane (TIPS-anthracene) as peripheral groups. In order to prepare 3(TIPS-ant)-benzene (**3**) and 4(TIPS-ant)-benzene (**4**), 10-((triisopropylsilyl)ethynyl) anthracene-9-carbaldehyde (**2**) was prepared by the Sonogashira coupling reaction of 10-bromoanthracene-9-carbaldehyde (**1**) and ethynyltriisopropylsilane [9,10].

The convergent syntheses of the two multi-branched molecules were conducted based on the typical Horner-Emmons condensation of **2** and hexaethyl benzene-1,3,5-triyltris(methylene)triphosphonate/octaethylbenzene-1,2,4,5-tetrayltetrakis(methylene)tetraphosphonate core (Scheme 1). The reaction yield of this coupling reaction is fairly high to be around 64–65%.



SCHEME 1 Synthetic route for 3(TIPS-ant)-benzene, 3 and 4(TIPS-ant)-benzene, 4. (i) copper(I) iodide, *trans*-dichlorobis(triphenylphosphine)palladium (II), THF/triethylamine (1:1), 70°C (ii) potassium *tert*-butoxide, THF, room temperature.

The identity and purity of the synthetic materials were confirmed by ^{1}H NMR, MALDI-TOF mass spectrometry, and elemental analysis. These synthetic materials were found to have a good self-film-forming property and showed good solubility in various organic solvents such as chloroform, xylene, chlorobenzene, and tetrahydrofuran (THF).

The thermal properties of the two multi-branched conjugated molecules were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). **3(TIPS-ant)-benzene** (**3**) exhibits no discernible crystalline-isotropic transitions observed in DSC thermograms (see Table 1). The glass transition temperatures (T_gs) of the two molecules are 134 and 175°C for **3** and **4**, respectively. This indicates that three armed molecule exhibits an amorphous morphology in solid films. When comparing two glass transition temperatures, we found the fact that the molecular rigidity of **4** is attributed to higher molecular weight as well as crystalline nature. Non-polar van der Waals interaction between **4** molecules is a important molecular specific interaction which can affect the physical properties significantly. TGA measurements at a heating rate of 10°C/min under nitrogen revealed good thermal stability. Two multi-branched molecules are thermally stable up to 418−428°C. (see Table 1)

Figure 1 displays the absorption and PL spectra of the synthesized compounds such as **3** and **4** in dilute chloroform solutions and films. The absorption λ_{max} of **3** and **4** appeared 424 and 430 nm in solution, respectively. The absorption maxima of thin films are almost consistent with those of solutions, which is attributed to less intermolecular interaction between the molecules. The PL spectra of two molecules in chloroform solutions are featureless and are almost a mirror-image of the low-energy absorption band (Fig. 1).

Electrochemical characterization of these molecules as films evidenced that their oxidation is reversible, which is a necessary condition for an electroactive material. Unfortunately, the reduction

TABLE 1 Measured and Calculated Parameters for the Synthesized Compounds

				Absorption			Energy level	
	T_g (°C)	T_m (°C)	T_d (°C)	λ_{max} (nm) Solution	λ_{max} (nm) Film	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)[b]
3	133.9	–	428.1	424	427(426)[a]	2.56[a]	−5.30	−2.74
4	175.4	252.6	418.7	430	431(441)[a]	2.44 (2.42)[a]	−5.25	−2.81 (−2.83)[a]

[a]After annealing.

[b]E_{LUMO} (eV) = E_{HOMO} (eV) + E_g^{opt}(eV).

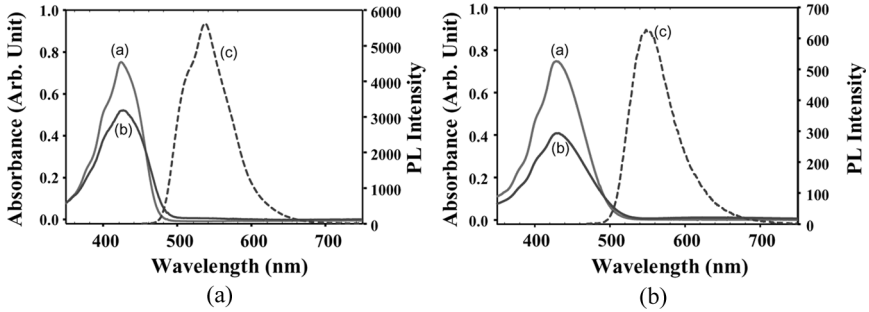


FIGURE 1 Absorption and PL spectra of the multi-branched molecules. A: 3(TIPS-ant)benzene, B: 4(TIPS-ant)benzene. (a) Solution in chloroform (1.5×10^{-6} M), (b) Film (thickness: 80 nm). (c) PL spectrum of the solution.

potentials were irreversible; therefore, we were unable to accurately estimate their HOMO and LUMO energies. In order to determine the LUMO levels, we combined the oxidation potential in CV with the optical energy bandgap (E_g^{opt}) resulting from the absorption edge in the absorption spectrum. Voltammograms of **3** and **4** in the film state show that their lowest oxidative waves are at + 0.90 and +0.85 V, respectively. As shown in Table 1, the compounds 3 and 4 have HOMO levels of − 5.30 and −5.25 eV, respectively. The relatively higher HOMO levels should endow the material with better environmental stability. In addition, **3** and **4** have LUMO energy levels of −2.74 and −2.83 eV, respectively.

In order to observe the surface topography, we employed atomic force microscope (AFM). After complete drying, we took two sets of micrographs as shown in Figure 2. Among two molecules, compound **4** shows

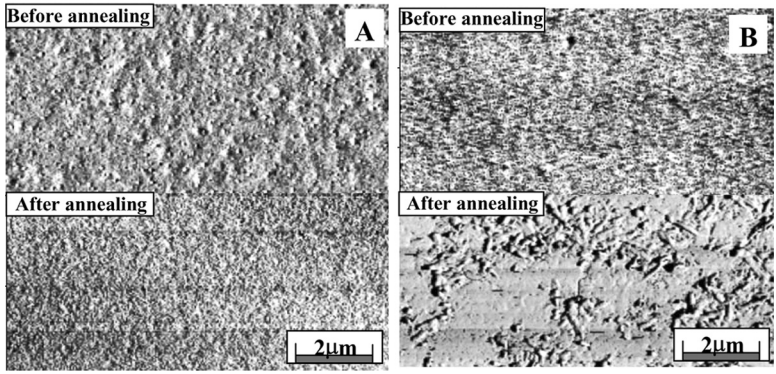


FIGURE 2 AFM topography and phase images (10 μm × 10 μm). A: **3**, annealing temperature = 150°C, 20 min, B: **4**. annealing temperature = 200°C, 20 min.

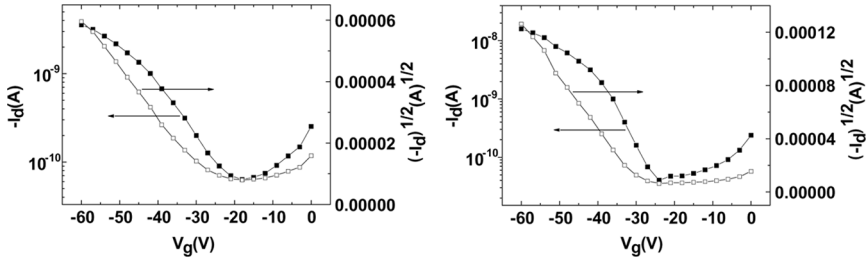


FIGURE 3 I_d-V_g transfer characteristics (bottom contact device) of OTFT devices made of two molecules. (a): **3**, annealing temperature = 150°C, 20 min, (b): **4**. annealing temperature = 200°C, 20 min.

the densest structure on the surface locally and drastic change of the surface topography after annealing, which is attributed to the highly crystalline nature, which can be supported by thermal analysis data.

We could obtain the carrier mobility for OTFT devices with 5 μm channel length and 1.5 mm channel width. The transistor devices made of **3** and **4** provided a carrier mobility of 1.8×10^{-6} and 7.12×10^{-6} $cm^2V^{-1}s^{-1}$ together with a low current on/off ratio and a low threshold voltage ($V_{th} < -15$ V) (Fig. 3). As we expected, TFT with **3** did show very poor transistor behavior due to its amorphous nature. The device performances should be optimized further by varying the channel length and width. In addition, we will employ the surface treated silicon oxide insulating layer for new devices.

CONCLUSION

We have successfully synthesized and characterized new multi-branched conjugated molecules that are well soluble in organic solvents. **4(TIPS-ant)-benzene** not only forms smooth films on large surfaces but also shows better homogeneous layer formation with relatively large crystallites. We fabricated the organic thin film transistor in a bottom contact configuration. The mobility was measured to be around 7.12×10^{-6} $cm^2V^{-1}s^{-1}$, that should be optimized further. The surface treatment of the polymeric dielectric layer is now underway to enhance the field-effect mobility and the other device performances.

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