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ARTICLE TYPE

Fluorenone Based Low Band Gap Solution Processable Copolymer for Air Stable and High Mobility Organic Field Effect Transistors

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Fluorenone based alternating copolymer (PFN-DPPF) with furan based fused aromatic moiety has been designed and synthesized. PFN-DPPF exhibits a small band gap with lower HOMO value. Testing this polymer semiconductor as the active layer in organic thin-film transistors results in hole mobilities as high as 0.15 cm²/Vs in air.

Recently there have been several reports of using polymer semiconductors for high performance unipolar and ambipolar organic field effect transistors (OFETs).¹ Among the reported ones, a majority of the materials are donor-acceptor copolymers incorporating fused aromatic moieties.² Fluorene based polymers are well known light emitting materials and used successfully as an active layer in organic light emitting diodes (OLEDs), organic light emitting transistors (OLETs) and basic OFET applications.³ Ketone substituted at the C9 position of fluorene is called as "fluorenone" is one of the promising fused aromatic acceptor moieties and so far there has been no report of using this block for making novel polymer semiconductors for OFETs. Fluorenone-thiophene based small conjugated molecules have been successfully used for OFET applications and their self assembly or supramolecular behavior has been studied by scanning tunneling microscopy (STM) on graphite substrates.⁴ Fluorenone-based liquid crystalline organic semiconductors were reported by Lincker *et al* and they found that the ordered mesophase is crucial for enhancing the charge carrier mobility.⁵ Lee *et al* reported perfluorohexylcarbonyl substituted fluorenone based electron acceptors and reported electron mobilities of 0.06 cm²/Vs.⁶ Porzio *et al* reported fluorenone end capped coligomers using 3, 4-dialkyl substituted thiophene as central blocks and demonstrated how the alkyl group inhibits the molecular packing.⁷ Additionally, fluorenone derivatives have been used in bulk heterojunction and stable dye sensitized solar cells.⁸ There are several benefits of using fluorenone as a conjugated block for making a new chemical structures such as: i) fluorenone is chemically more stable, ii) they can be easily commercially available with lower cost, iii) carbonyl group can assist for better solid state interaction/packing and iv) can provide better air stability for polymer semiconductors. Lately, there is a growing interest of using 3,6-Di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DBF) [where furan units on diketopyrrolopyrrole (DPP) have been used instead of thiophene] block for making polymer semiconductors for both p-channel and ambipolar OTFTs.⁹ Some of the polymers developed using DBF block exhibited the hole mobility around 1.54 cm²/Vs.^{9d}

In this communication, we report for the first time, the design and synthesis of fluorenone based solution processable alternating semiconducting polymer combined with another novel DBF block (Scheme 1). Our interest in designing this polymer structure arises from the possibility of using carbonyl substituted two planar fused aromatic blocks (fluorenone and furan flanked DPP) within the conjugated backbone for enhancing the degree of coplanarity intramolecular interactions via a large overlapping area and strong O–H interactions among adjacent molecules. Moreover, insertion of fluorenone as a weak extended linear π -conjugated acceptor block combined with DBF could enhance donor-acceptor interaction between furan-fluorenone blocks which is desirable for better charge carrier transport. Fluorenone and furan flanked DPP are promising units that can alter the optical, electronic (energy levels of the frontier orbitals and band gap) and electrical transport properties. Higher air stability of this polymer is expected due to the lowering of highly occupied molecular orbital (HOMO) arising from the electron withdrawing carbonyl group on fluorenone. It has been previously found that the co-polymerization of fluorenone (electron deficient unit) with thiophene (electron rich unit) lowers the band gap and improves the stability of the resulting copolymers.¹⁰

Scheme 1 Reagents and conditions: i) Bis(pinacolatodiboron), potassium acetate, PdCl₂(dppf), 1,4-dioxane, 80°C for 20h, 62%; (ii) K₂CO₃, 2-decyl-1-tetradecyl bromide, anhydrous DMF, 120-130°C, overnight; (iii) Bromine, chloroform, room temp., overnight, 78%; (iv) Pd(PPh₃)₄, aliquat 336, 2M K₂CO₃, toluene, 80°C for 72h, phenylboronic acid, bromobenzene, 87%.

The starting compound 2, 7-bis (4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9H-fluorene-9-one (2) was synthesized from commercially available 2, 7-dibromo-9H-fluorene-9-one (1) using bis(pinacolato)diboron, PdCl₂(dppf) and KOAc in 1,4-dioxane. Afterwards compound 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3) was easily synthesized using reported procedure, which was then converted to 3,6-bis-(5-bromo-furan-2-yl)-N,N'-bis(2-decyltetradecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (5) via alkylation and bromination. Suzuki coupling polymerization of compounds 2 and 5 results in polymer poly{fluorenone-alt-3,6-difuran-2-yl-2,5-di(2-decyltetradecyl)-

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pyrrolo[3,4-c]pyrrole-1,4-dione} (**PFN-DPPF**) in 76% yield (Scheme 1). **PFN-DPPF** was sequentially purified using methanol, acetone and hexane by Soxhlet extraction in order to remove the oligomer fractions and catalytic impurities from the bulk polymer sample. Finally the polymer was obtained by dissolving in chloroform, followed by precipitation from methanol. The number average (M_n) and weight average molecular weight (M_w) of **PFN-DPPF** are 28380 and 83360 g/mol, respectively measured by gel permeation chromatography (GPC), at a column temperature of 40 °C with THF as eluent and polymethylmethacrylate (PMMA) as standards. The thermal properties of **PFN-DPPF** were examined by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques respectively. TGA showed a decomposition temperature of 410 °C under nitrogen, indicating the high thermal stability of this polymer. **PFN-DPPF** exhibits an endothermic peak at 314 °C and an exothermic peak at 278 °C during the second heating-cooling cycles respectively. These peaks are related to the melting and crystallization temperatures of this polymer (see Supplementary Information).

Fig. 1 (a) UV-vis absorption spectra of **PFN-DPPF** in chloroform solution and in thin film. (b) Photoelectron Spectroscopy in Air (PESA) measurement of **PFN-DPPF** thin film spin coated on glass substrate using chloroform solution.

The solution and solid state optical properties of **PFN-DPPF** was studied by UV-vis absorption spectroscopy using chloroform and spin coated thin film (from chloroform solution). The absorption maximums (λ_{max}) in chloroform and in solid state are almost identical with λ_{max} peak at 711 nm (Figure 1a). This λ_{max} value is almost 169 nm blue shifted compared to our earlier reported PDPP-FBF polymer in which we used benzothiadiazole as a strong electron acceptor comonomer. This observation clearly indicates how the electron affinity of the conjugated comonomer block (fluorenone vs benzothiadiazole) tunes the optical properties. The absorption cut-off value measured in solid state is at 764 nm whereas in solution it is 745 nm. The optical band gap calculated for **PFN-DPPF** from solid state absorption cut-off is 1.62 eV. The HOMO energy level of the **PFN-DPPF** polymer was determined using photoelectron spectroscopy in air (PESA) measurement using spin coated thin film of **PFN-DPPF** on the glass substrate as shown in Figure 1(b). The HOMO energy level

was determined from the onset energy value to be 5.45 eV which is suitable for fabricating oxidative stable organic electronic devices. The LUMO value was expected to be 3.83 eV calculated from the optical band gap and the HOMO level. Solid state ordering and molecular organization of **PFN-DPPF** was studied by 2-D XRD measurements via x-ray irradiation parallel to the polymer flakes. As shown in Figure 2, the primary diffraction peak at $2\theta = 4.64^\circ$ which corresponds to a d-spacing of $\sim 19.02 \text{ \AA}$, whereas the broad peak positioned from $2\theta = 15^\circ$ to 27° is assigned for the π - π stacking distance. The broad peak for π - π stacking distance suggests that not all the **PFN-DPPF** backbones are well aligned perpendicular to the SiO_2/Si substrate.

Fig. 2 2-D XRD pattern intensity graphs and 2-D XRD image (left) obtained with the incident X-ray parallel to the thin film stack of **PFN-DPPF** copolymer (right).

The electrical properties of **PFN-DPPF** as a channel semiconductor in OFET devices were evaluated using a bottom-gate, bottom-contact configuration. Heavily n-doped conductive silicon wafer with a layer of $\sim 200 \text{ nm}$ SiO_2 on the surface was used as the substrate. The SiO_2 functions as the gate insulator and the doped Si as the gate. The source/drain electrodes were defined by photolithography and chrome/gold (2.5 nm/50 nm) bilayers were deposited by thermal evaporation. In order to improve the electric contact with the **PFN-DPPF**, the electrode were treated with pentafluorobenzenethiol (PFBT).^{11, 12} The active polymer thin film ($\sim 40 \text{ nm}$) was spin coated on top of an octadecyltrimethoxysilane (OTMS) modified SiO_2 surface using a polymer solution in chloroform (8 mg/mL) at 1500 rpm for 40 seconds.

Fig. 3 Output (V_{DS} vs. I_{DS}) characteristics of **PFN-DPPF** OFET devices annealed at 140 °C (a) with PFBT and (b) without PFBT treatments. Transfer characteristics (V_{GS} vs. I_{DS}) (c) and field effect mobility vs. gate voltages (d) of **PFN-DPPF** OFET devices annealed at various temperatures. Device dimensions: channel length = 4 μm ; channel width = 80 μm . All devices are measured in air.

The polymer thin films were annealed at 140 °C, 200 °C and 300 °C respectively for 30 min on a hot plate in nitrogen atmosphere. The output characteristics of **PFN-DPPF** based OFET annealed at 300 °C with and without PFBT self assembled monolayer (SAM) exhibits p-channel conductance which are shown in Figure 3a and 3b respectively. The current-voltage (I-V) curves of the **PFN-DPPF** based OFET devices without surface treatment clearly exhibits high contact resistance whereas SAM treated devices exhibits current flow under very low drain bias (V_D). It has been well documented that the SAM treatment lessens the number of traps present in the thin film and improves the ordering of organic semiconductors on the dielectric surface (see Supplementary Information). Transfer characteristics and mobility disparity with respect to different annealing temperatures are shown in Figure 3c and Figure 3d respectively. Device performance parameters are listed in Table 1. It was found that the polymer thin film annealed at 200 °C and 300 °C exhibits almost similar hole mobility of 0.14 cm²/Vs and 0.15 cm²/Vs respectively at $V_D = -60$ V. An on-to-off current ratio (I_{on}/I_{off}) of $\sim 10^4$ is calculated for all of the devices. It is crucial to mention that all the electrical characteristics of these OFET devices were measured in air. The higher stability of these devices is due to the deep HOMO level of the polymer and the inclusion of oxidative stable fluorenone moiety in the backbone. To our knowledge, this is the first report of stable fluorenone based polymer for OFET application with such a high mobility.

Fig. 4 AFM phase images of **PFN-DPPF** thin films annealed at 140°C, 200°C and 300°C on OTMS treated Si/SiO₂ substrates.

Table 1. **PFN-DPPF** based OFET device parameters

Annealing Temp.(°C)	Mobility (cm ² /Vs)	Threshold Voltage (V)	On/off ratio
140	0.097	- 16.2	1.3×10^4
200	0.141	- 4.90	5.1×10^4
300	0.152	- 3.50	7.0×10^4

Atomic force microscopy (AFM) was performed on the samples preannealed at various temperatures in order to study the effect of annealing on the morphological variations. AFM height images of the polymer thin films annealed at 140 °C, 200 °C and 300 °C are shown in Fig 4. **PFN-DPPF** preannealed sample at 140 °C exhibits smaller grain size with large void space nano-morphology whereas samples annealed at 200°C and 300 °C show better connected nano-domains with bigger grain size. Well connected bigger grains are supportive for the efficient charge transport.

Conclusions

For the first time fluorenone based low band gap solution processable polymer semiconductor **PFN-DPPF** has been designed, synthesized and used in OFET application. Incorporation of two condensed aromatic moieties containing carbonyl rings tunes the energy levels which are suitable for making stable OFET devices. **PFN-DPPF** based OFET devices displayed high hole mobility of 0.15 cm²/Vs in air for annealed samples. These results clearly demonstrate that the fluorenone is one of the promising conjugated building block for designing novel high performance and stable organic electronic devices.

Notes and references

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