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### COMMUNICATION

# Highly reproducible organic field-effect transistor from pseudo 3-dimensional triphenylamine-based amorphous conjugated copolymer<sup>†</sup>

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An easily accessible 3D donor–acceptor polymer based on triphenylamine (PTPA-*co*-DTDPP) is synthesized by a simple and efficient route. Owing to its non-fibrillar structure, PTPA-*co*-DTDPP features highly reproducible charge carrier mobility of up to  $3.3 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at various fabrication conditions.

Since the initial report of organic field-effect transistors (OFETs) based entirely on organic materials in 1998 at the Philips Research Laboratories,1 their performance has seen a remarkable improvement, because of advances in material development as well as device optimization. In particular, solution-processable  $\pi$ -conjugated polymers for OFETs offer the prospects of low-cost radiofrequency identification (RFID) tags, flexible and large area displays, etc.<sup>2-10</sup> Until now, regioregular poly(3-hexylthiophene) (rr-P3HT) as a prototype microcrystalline polymer is the most widely investigated and exhibits a high hole mobility of 0.1-0.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the devices.<sup>7,11</sup> However, the mobility of rr-P3HT depends very sensitively on the degree of head-to-tail regioregularity7,11 and deposition conditions.<sup>11-13</sup> Such vulnerabilities in the morphology are not only difficult to truly reproduce the high charge mobilities but also rr-P3HT has poor photostability when exposed to ultraviolet sunlight in the presence of oxygen.14 These detrimental features bring out major obstacles to realize the commercial OFETs.

In this regards, we directed our attention toward an amorphous microstructural polymer to provide a uniform path for charge transport, along which carries experience a minimum degree of siteenergy fluctuations. Owing to the noncoplanarity of the three aryl substituents, electron-rich triphenylamine (TPA) with excellent hole transporting ability can be viewed as 3D propeller structure, resulting in the amorphous character of the molecules containing it. When working with these materials, morphology effects can largely be neglected, most likely generating consistency in carrier mobilities. Besides, we believed that the intramolecular charge transfer (ICT) through donor (D)–accepter (A) interaction in D–A building blocks would facilitate the charge carrier transport. Thereby, to create D–A

architecture, diketopyrrolopyrrole (DPP) is chosen as a strong electron-withdrawing building block because of its obvious advantages: extremely light, weather and heat stability, very strong light harvesting covering a wide spectrum of the sunlight, and cost effect synthesis.<sup>15</sup> Especially, the fused DPP ring units for coplanarity and a closer  $\pi$ -stacking distance would be postulated to compensate for the expected loss of charge transport pathway from amorphous materials bearing TPA segments, probably enhancing the charge mobilities with reproducibility. Here, we present a new D-A copolpoly[triphenylamine-4,4'-diyl-co-3,6-dithien-2-yl-2,5-di(2ymer, decyltetradecanyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5',5"-diyl] (PTPAco-DTDPP) that has TPA and DPP moieties in the repeating unit, as shown in Scheme 1. PTPA-co-DTDPP that forms non-fibrillar structure features highly reproducible charge carrier mobility up to  $3.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with an extended optical absorption toward the whole visible region and narrow band gap (1.65 eV).

The synthesis of **PTPA-***co***-DTDPP** is illustrated in Scheme 1. Firstly, 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4dione (**DTDPP**) was synthesized according to a previously reported method.<sup>16,17</sup> To keep good solubility and nonmicrocrystalline structure of **DTDPP**-based copolymer, bulky branched side chains [*i.e.*, 2-decyltetradecyl]<sup>17,18</sup> were introduced at the lactam of NH groups. Dibromination of **DTDPP** in chloroform afforded 3,6-di(2-bromothien-5-yl)-2,5-di(2-decyltetradecyl)-pyrrolo [3,4-*c*]pyrrole-1,4-dione (1). The alternating copolymer, poly[triphenylamine-4,4'-diyl-*co*-3,6-dithien-2-yl-2,5-di(2-decyltetradecanyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-5',5''-diyl] (**PTPA-***co*-**DTDPP**), was



Scheme 1 Synthetic route of PTPA-co-DPP: (i) toluene/2 M aq.  $K_2CO_3$ , Pd(PPh<sub>3</sub>)<sub>4</sub>, 95 °C, 72 h, 75%.

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synthesized by Suzuki polycondensation in toluene using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst from dibromo-monomer **1** and diboronated triphenylamine (TPA) monomer.<sup>19</sup> **PTPA-***co***-DTDPP** has good solubility in common organic solvents such as chloroform, toluene, and chlorobenzene owing to its long branched side chains. Molecular weight and polydispersity index (PDI) of **PTPA-***co***-DTDPP** are determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. **PTPA-***co***-DTDPP** has a high number-averaged molecular weight ( $M_n$ ) of 14.9 kg mol<sup>-1</sup> with a PDI of 1.39.

The UV-Vis spectra of the copolymer in dilute chloroform solution and thin film are shown in Fig. 1a. In the solution, PTPA-co-DTDPP exhibits two absorption bands. The first peak is in the wavelength range of 300-400 nm and the second is in the range of 500-700 nm. The low energy band is due to ICT between the electron-donating TPA and electron-withdrawing DPP blocks. The absorption maximum  $(\lambda_{max})$  of the **PTPA-co-DTDPP** in solution is observed between 600 and 640 nm with a somewhat vibronic feature, indicating the rigid-rod nature of the polymer main backbone, as a result of the coplanar structure and strong polarity of the DPP units. In contrast, the absorption of PTPA-co-DTDPP keeps almost unchanged from the solution to the film, suggesting that the  $\pi$ - $\pi$ stacking along the polymer chains is limited due to the presence of 3D propeller-like TPA units and two bulky side substituents on the DPP units. The optical band gap  $(E_{g}^{opt})$ , estimated from the absorption edge of the thin film absorption spectrum, is 1.66 eV, much smaller than that (1.9 eV) of widely used rr-P3HT.

To estimate HOMO and LUMO energy levels of **PTPA-***co***-DTDPP**, we have studied electrochemical properties using cyclic voltammetry of films drop cast onto a platinum carbon working electrode with a platinum-wire auxiliary electrode, a Ag wire pseudo-reference electrode, and Fc/Fc<sup>+</sup> as the external standard (Fig. 1b). **PTPA-***co***-DTDPP** shows one quasi-reversible oxidation peak and one quasi-reversible reduction peak. According to the empirical equation  $E_{(HOMO)/(LUMO)} = [(E_{(ox)/(red)} - E_{(ferrocene)}) + 4.8]$  eV, the HOMO and LUMO energy levels were estimated as -5.07 and -3.42 eV for **PTPA-***co***-DTDPP**. An excellent agreement is found for the optical band gap (1.66 eV) and the electrochemical band gap (1.65 eV from CV).

Fig. 2 shows the OFET characteristics fabricated using **PTPA**-*co*-**DTDPP** as an active semiconductor. **PTPA**-*co*-**DTDPP** reveals a typical p-type semiconductor characteristic operating in accumulation mode. Importantly, a markedly high on/off current ratio of approximately  $10^5$  is not only obtained from the drain-source current ( $I_{ds}$ ) versus the gate voltage ( $V_G$ ) graph, but also the output characteristics indicate highly stable device performance with reliable



**Fig. 1** (a) UV-Vis absorption spectra of **PTPA***-co***-DTDPP** in dilute CHCl<sub>3</sub> solution and thin film on quartz plate. (b) Cyclic voltammogram of **PTPA***-co***-DTDPP** thin film on the Pt electrode in 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at room temperature.



Fig. 2 (a) Chemical structure of **PTPA-***co***-DTDPP**. (b) Schematic representation of OFETs. (c) Transfer and (d) output characteristics of OFET device with **PTPA-***co***-DTDPP** ( $L = 50 \mu m$ , W = 1.5 mm).

saturation. The OFET mobilities are calculated in the saturation regime using the following equation:  $I_{\rm ds} = (W/2L)\mu C_{\rm i} (V_{\rm gs} - V_{\rm th})^2$ , where W and L are the channel width and length, respectively,  $C_{\rm i}$  is the capacitance per unit area of the insulation layer. Linear plots of  $I_{\rm ds}^{1/2}$  vs.  $V_{\rm gs}$ , deduced from the  $I_{\rm ds}$  vs.  $V_{\rm gs}$  measurements, yielded a hole mobility of  $\mu = 3.3 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

The variation of mobility values from rr-P3HT OFET performance is very large because of its various degrees of crystallinity as induced by the fabrication conditions. For example, hexamethyldisilazene (HMDS),<sup>7,13</sup> octadecyltrichlorosilane (OTS),<sup>20,21</sup> or other silane or alkyl<sup>20</sup> treatments have been used to provide a well-defined, ordered surface for subsequent semiconductor deposition, which is attributed to significant improvements in the performance of polythiophenes due to the perpendicular orientation of molecules to the substrate.7,13 Our experimental results obtained from rr-P3HT devices also exhibit the massive variation of mobility values upon various modified substrates even on the same fabrication condition, leading to the differences of over two order of magnitude in the OFET performance (see Fig. 3). Notably, in contrast to rr-P3HT, the mobilities of PTPA-co-DTDPP OFETs are almost no change when going from bare SiO<sub>2</sub> to HMDS or OTS treated substrates. In order to obtain further additional evidence on a morphological dependence free in the OFETs, we subsequently decide to study the annealing temperature dependence of the mobilities. Fig. 4 shows the mobility data as a function of annealing temperatures under various modified substrates (SiO<sub>2</sub>, HMDS, and OTS), respectively. It is clearly revealed that various annealing temperatures are sufficient to induce significant morphological changes in the case of rr-P3HT OFETs, resulting in large deviations for the measured mobilities, which is consistent with other literatures.<sup>22,23</sup> However, the contribution from the temperature dependence of the PTPA-co-DTDPP OFETs is slightly negligible in the temperature range studied (Fig. 4b). Therefore, PTPA-co-DTDPP can be ideal to be OFETs with a variety of dielectrics in both top and bottom gate configurations and isolate effects relating to morphology.



**Fig. 3** Variation of mobility values of rr-P3HT (a) and **PTPA***-co***-DTDPP** (b) OFETs as a function of various modified substrates.



Fig. 4 Variation of mobility values of rr-P3HT (a) and PTPA-co-DTDPP (b) OFETs as a function of annealing temperatures under various modified substrates.

Tapping mode atomic force microscopy was employed to study the surface morphology of the polymer films. Fig. 5a shows that an as-cast **PTPA-***co***-DTDPP** film consists of small 'nodules' and is similar to that typically reported for rr-P3HT films.<sup>24,25</sup> Interestingly,



Fig. 5 AFM height images of **PTPA-co-DTDPP** films (a) at room temperature and (b) after annealing at 120 °C. (c) XRD data obtained from spin-coated **PTPA-co-DTDPP** thin films annealed at different temperatures.

the polymer film annealed at 120 °C is still composed of clustered non-fibrillar structures with small grains, whereas annealed rr-P3HT and DPP-based polymers films<sup>26,27</sup> have been revealed highly oriented crystallite domains with isotropic phase. The macroscopically disordered, amorphous morphology of **PTPA-***co***-DTDPP** films in both as-spun and annealed is supported by no scattering patterns by X-ray diffraction (XRD) analysis (Fig. 5b) at the same temperatures employed for AFM study. This is attributed to the harmonized effects of the star-shaped TPA units and sparse side chain placement. From these results, it would be tempting to conclude that **PTPA-***co***-DTDPP** is away from materials that depend on the morphology. This notion is indeed good consistent with OFET data described above. Despite that **PTPA-***co***-DTDPP** does not show the nano-fibrillar morphology, it enables to achieve a high mobility of  $3.3 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with reproducibility.

From judicious molecular design, we have demonstrated the realization of reproducible high-mobility transistor using a common gold electrode and a new donor–acceptor copolymer semiconductor (**PTPA-***co***-DTDPP**) that consists of electron-rich TPA and fused electron deficient DPP building blocks. Cyclic voltammetry measurement shows a narrow band gap of 1.65 eV and clear reversibility in both the p-doping and n-doping processes. Even though an amorphous morphology in the solid state of **PTPA-***co***-DTDPP** at various annealing temperatures forces due to the combination of the 3D propeller-like TPA units and bulky branched side chains, the unusually high mobility of up to  $3.3 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> is observed. It must be enunciated that considering the morphology independency with a high charge transport property and cost effectiveness, **PTPA-***co***-DTDPP** can be a promising material for practical, scalable optoelectronic applications.

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