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ARTICLE

Modulating Carrier Transfer Ability—Linker Effect on Thieno[3,4-c]pyrrole-4,6-dione Based Conjugated Polymers

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Three conjugated copolymers Q1, Q2 and Q3 were developed based on thieno[3,4-c]pyrrole-4,6-dione(TPD) and two thiophene units. While Q1 was synthesized through direct linkage, Q2 and Q3 were constructed via introduction of vinylene and ethynylene π-spacer between two thiophene groups. Electrochemical and UV-vis absorption studies as well as theoretical calculation show that LUMO energy of Q3 is lower than Q1, Q2 while Q2 possesses the narrowest bandgap. OFET devices based on thin-films of Q1 and Q2 can be easily fabricated through solution-process with conventional techniques, while OFET devices based on thin-films of Q3 are fabricated by drop-casting. Q1 and Q2 showed maximum hole mobilities of 2.2×10^{-3} cm^2 V^{-1} s^{-1} and 0.01 cm^2 V^{-1} s^{-1}, respectively. Owing to the electron-withdrawing effect by ethynylene group, Q3 based OFET devices exhibit clear ambipolar semiconducting property in air condition, with maximum hole and electron mobility of 1.2×10^{-6} cm^2 V^{-1} s^{-1} and 0.6×10^{-6} cm^2 V^{-1} s^{-1}, respectively.

Introduction

For electron donor (D)-acceptor (A) conjugated polymers, modulation of linkers between the composition groups inside a repeat unit could effectively alter polymer properties such as the planarity, bandgap (E_g) and energy migration etc. However, to date, only a few reports on such 'linker effects' study have been made.[1-4] For instance, three soluble dithienothiophene homopolymers constructing with a single C–C bond, a vinylene group, or an ethynylene group as the linkers were synthesized by Zhang et al. and the linker effect on thermal, UV-vis absorption, photo luminescent and electrochemical properties of the polymers were studied.[3] Conjugated polymers with dioctylfluorene and bipyridine linked by the same three groups mentioned above also have been reported by Liu et al.[4] Furthermore, Sun et al. reported a donor-bridge–acceptor-bridge (DBAB) type of block copolymers in which the linkers were optimized to enhance the photovoltaic performance.[5]

In our previous study, we found that the linkers exerted significant effect on the properties of the benzothiadiazole based D-A conjugated polymers in which the use of the vinyl linkage lowered the polymer E_g and enhanced its coplanarity.[6] With this knowledge in mind, we intended to study the influence of such linker effects on performance of D-A conjugated polymer based organic field effect transistors (OFETs).

To construct such polymers, thieno[3,4-c]pyrrole-4,6-dione (TPD) unit is chosen as an electron acceptor.TPD as one of the imide functional organic electron acceptors has been studied intensively during the last few years.[7-10] Due to its outstanding geometry and electronic properties, TPD-based electron Donor (D)-Acceptor (A) conjugated polymers have shown promising device performance in both OFETs and organic solar cells (OSCs). For instance, copolymerized TPD with oligothiophenes have been reported exhibiting carrier mobilities up to 1.29 cm^2 V^{-1} s^{-1};[9] when copolymerized with dithienosilole, the TPD based polymers exhibit PCEs > 8% and fill factors approaching 80%.[10] However, till now, efforts have been made to improve performance of TPD polymer based devices mostly through modifications on side chains and variations of electron donors. Variations of linkers between the functional units in such polymers have not yet been reported.

In this paper, D-A polymers Q1, Q2 and Q3 with TPD as acceptor and C-C single bond-, vinyl- and ethynylene-linked dithiophene as donors, respectively, were synthesized and their bottom contact OFET devices were fabricated and examined. The results manifest that Q2-based devices exhibit much higher hole mobility up to 0.01 cm^2 V^{-1} s^{-1} as compared to Q1-based devices with hole mobilities of only around 10^{-3} cm^2 V^{-1} s^{-1}. This result is most likely due to the enhanced planarity and conjugation provided by vinyl linkage as described in previous studies.[6,11-14] Interestingly, Q3 with an ethynylene group as linker exhibits detectable ambilpolar properties in air of mobilities up to $\mu_h = 1.2 \times 10^{-6}$cm^2 V^{-1}s^{-1}and $\mu_e = 0.6 \times 10^{-6}$cm^2 V^{-1}s^{-1}, possibly due to the electron-withdrawing effect by triple bond that stabilize the electron

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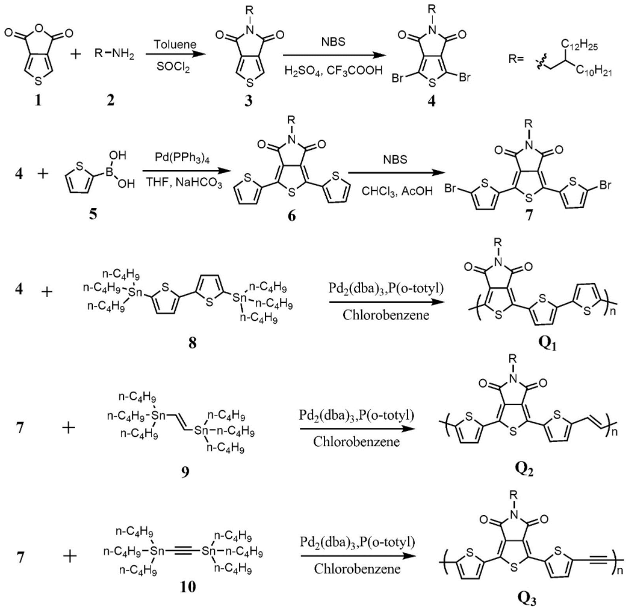
†Electronic Supplementary Information (ESI) available: TGA analysis, detail synthesize, DFT calculation data, XRD, ^{1}H-NMR and ^{13}C-NMR. See DOI: 10.1039/x0xx00000x

transfer abilities and ethynylene group have been reported to be beneficial in constructing n-type and ambipolar semiconducting materials.[15-18] To our best knowledge, few TPD based polymers have been reported exhibiting ambipolar OFET performances[19] and yet none has been reported in air conditions.

Results and Discussion

Synthesis and characterization

As is depicted in scheme 1, Q1, Q2 and Q3 were prepared by Stille reaction and purified by Soxhlet extraction. The large N-alkyl chain was introduced to enhance the polymer solubility while no substituted group was introduced in thiophene units. Q1 and Q2 show good solubility in common solvents such as $CHCl_3$, THF and o-dichlorobenzene with concentrations as high as 10 mg/mL. In contrast, Q3 exhibits rather low solubilityin $CHCl_3$ and o-dichlorobenzene, presumably due to the large rigidity provided by the triple bond. Based on TGA analysis (Figure S1), the decomposition temperatures of Q1, Q2 and Q3 were all above 400 ^{o}C, respectively.



Scheme 1. Synthetic approaches for polymer Q1, Q2 and Q3

Figure 1 shows the Cyclic voltammograms of Q1, Q2 and Q3 in which both reduction and oxidation peaks can be clearly observed. According to the previous studies,[20,21] LUMO of Q1, Q2 and Q3 were estimated to be -3.58eV, -3.65eV and -3.70eV (LUMO = – (E_{onset}^{red1} + 4.44) eV) while HOMO were estimated to be -5.08eV, -4.97eV and -5.12eV (HOMO = – E_{onset}^{ox1} - 4.44 eV), respectively. Among these three polymers, Q3 has the lowest LUMO possibly due to the presence of the electron-withdrawing triple bond;[15,16] all E_g^{CV} of three polymers are rather close. E_g^{CV} of Q2 (1.32 eV) is slightly lower than those of Q1 and Q3. Notably, the narrow band gap of Q1 (1.50 eV), Q2 (1.32 eV) and Q3 (1.42 eV) is much lower than 1.8 eV, indicating that both hole and electron charge carriers for electrode injection are feasible. Therefore, all three polymers possess the potential for the ambipolar semiconducting properties.[22]

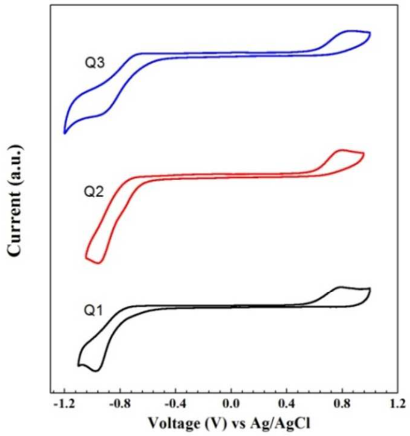


Figure 1. Cyclic voltammograms of polymer Q1, Q2 and Q3 by drop casting thin film on GC working electrode at a scan rate of 100 mV s^{-1}, Pt as counter electrode, Ag/AgCl as counter electrode (saturated KCl) and the reference electrode, and n-Bu_4NPF_6 (0.1 M)/acetonitrile as supporting electrolyte.

Optical absorption spectra of solution and thin film of the three polymers are shown in Figure 2. The maximal absorption peak (λ_{max}) of Q1, Q2 and Q3 in solution are 464 nm, 498 nm and 455 nm, respectively which were assigned as an intramolecular charge transfer (ICT) band caused by its donor-acceptor structures. Interestingly, thin film absorptions of both Q1 and Q2 exhibit distinct intensity increase at around 700 nm presumably because of the occurrence of the well-ordered intermolecular interactions. Comparatively, such increase observed for Q2 is relatively stronger than Q1 due to the contribution of the vinyl group in extending the conjugated length, improving the molecular rigidity and thus enhancing the coplanarity.[14]

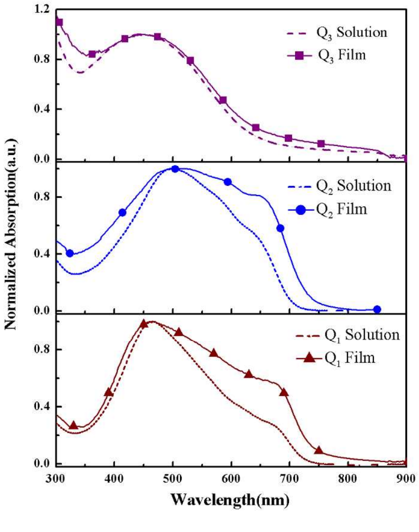


Figure 2. The absorption spectra of solutions (diluted in $CHCl_3$) and thin films of Q1, Q2 and Q3

Table 1. Physical properties of Q1, Q2 and Q3

Pol.	M_n (g/mol)/PDI	λ_{max}(nm) /E_g^{opt} Sol^a	$Film^b$	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g^{CV} (eV)
Q_1	7.08k/1.95	464	470/1.60	-3.58	-5.08	1.50
Q_2	9.06k/1.66	498	516/1.59	-3.65	-4.97	1.32
Q_3	5.74k/2.23	450	455^c/1.65	-3.70	-5.12	1.42

a) Dilute chloroform solution; b) Spin-coated from chloroform solution (5 mg/mL); c) Thin film by drop casting in o-DCB solution.

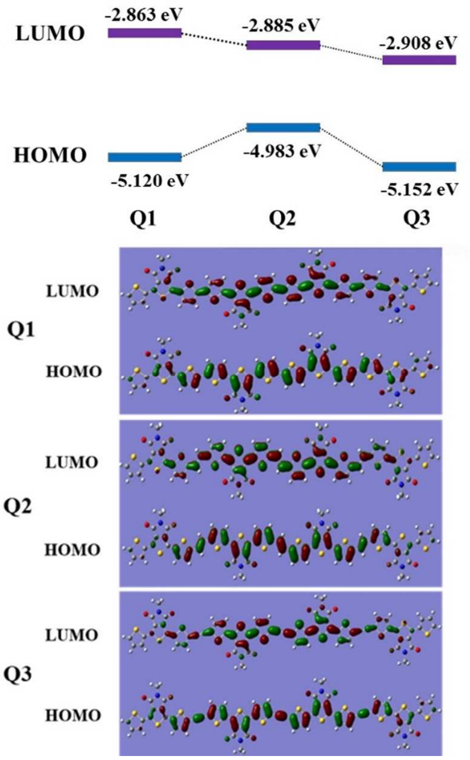


Figure 3. LUMO/HOMO energy level and orbitals of oligomers (n=4) of Q1, Q2 and Q3 obtained by DFT calculations

DFT calculations

Density functional theory (DFT) calculation was also carried out to investigate the energy levels of Q1, Q2 and Q3. To simplify the calculation results, an oligomer with 4 repeat units was chosen for all the three polymers and the large N-alkyl chains were replaced by N-methyl group. As shown in figure 3, LUMO of Q1, Q2 and Q3 oligomers are calculated to be -2.863 eV, -2.885 eV and -2.908 eV, respectively, and their corresponding HOMO values are -5.120 eV, -4.983 eV and -5.152 eV. Note that the solvent effects were not included in the theoretical calculation and the number of the repeat units were limited. Thus, there are differences between the calculated LUMO and HOMO energies and their experimental values. However, this tendency of the calculated values for three polymers is consistent with the experimental results from CV. It is widely accepted that lower LUMO energy can beneficially stabilize electron charge carriers therefore enhancing the n-type performance. Since electron carriers are highly quenchable by O_2 and H_2O in air conditions,[23] Q3 with the lowered LUMO exhibits its electron charge carrier ability in air condition and facilitates ambipolar semiconducting properties as compared to the rest ones. Moreover, Q2 exhibits significant lower E_g of 1.998 eV compared to Q1 (2.257 eV) and Q3 (2.244 eV) and such tendency is also consistent with the results estimated from CV. As suggested inprevious studies, this phenomenon can be attributed to the extended conjugation length, higher planarity and reduced torsional defects provided by vinyl linkage.[6,14] Interestingly, in our case, all three polymers exhibit quite good coplanarity and their dihedral angles are relatively small. In fact, previous reports showed that geometry of TPD should impose reduced steric hindrance on neighboring arenes, and intramolecular thienyl(S)···carbonyl(O) interactions are likely to enforce backbone coplanarity.[24]

OFETs based on thin films of Q1, Q2 and Q3

Thin-films of Q1 and Q2 can be prepared by spin-coating with the corresponding $CHCl_3$ solutions while due to its low solubility, thin films of Q3 were obtained by drop casting with ODCB solutions. The field-effect transistors were fabricated in air with conventional techniques using doped n-type Si as the gate electrode, Au as both source and drain electrodes and OTS-modified SiO_2 as the dielectric layer. The OFET devices were examined in air, and the corresponding output characteristics and transfer characteristics were measured.

As depicted in Figure 4, both Q1 and Q2 exhibit p-type OFET performances. Both devices of Q1 and Q2 exhibit the highest performance after annealing at 180 °C.[§] The OFET device of Q1 showed the following performance: $\mu_h = 2.2 \times 10^{-3}$ cm^2 V^{-1} s^{-1}, $I_{on/off} = 10^6$ and V_T = -2 V. On the other hand, the vinyl-containing Q2 exhibits relatively higher performance of μ_h = 0.01 cm^2 V^{-1} s^{-1}, $I_{on/off} = 10^6$ and V_T = -5 V. Previous report suggested that incorporating vinyl groups would extend the conjugation length and improve the molecular rigidity, there by preventing the adjacent thiophene rings from rotating and in turn, increase the degree of coplanarity of the polymer backbone thus enhancing the conjugation of D-A structure.[11-14] Such effects should be useful for polymer charge carrier transporting ability in thin films, thus promoting the higher mobility of OFET devices of Q2.

Table 2. Fundamental parameters of Q1, Q2 and Q3 based bottom contact OFET devices. (Au electrode, W/L = 10-50 μm/1440 μm)

polymer	$^a\mu_h$ (cm^2 V^{-1} s^{-1})	$I_{on/off}$	V_T(V)
Q1	2.2×10^{-3} (1.5×10^{-3})	10^6	-5
Q2	0.01 (6×10^{-3})	10^6	-7
Q3	$^h1.2\times 10^{-6}$(6×10^{-7})	10^3	-15
	$^e0.6 \times 10^{-6}$(2×10^{-7})	10^3	10

[a] The mobilities data are based on more than 10 different OFET devices and presented in highest (average) style; h and e superscript refers to hole and electron mobility, respectively.

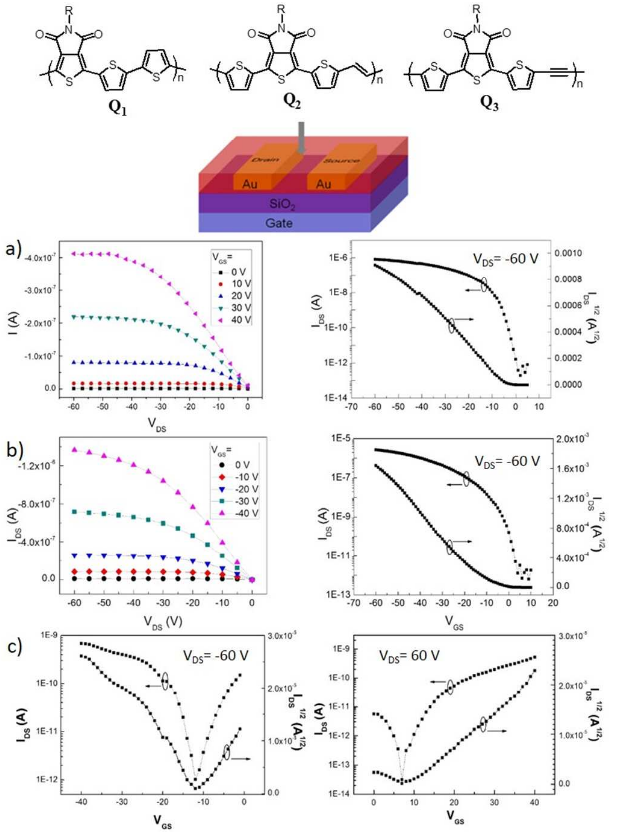


Figure 4. Device structure, output characteristics and transfer characteristics for OFET devices of Q1 (a), Q2 (b) annealed at 180 °C, the channel width (*W*) and length (*L*) were 30 nm and 1440 nm, respectively; transfer characteristics of for OFET device of Q3 (c) with channel *W*=10 nm and *L*= 1440 nm.

Due to its low solubility, the morphology of Q3 thin films by drop casting were not satisfying as evidenced by the absence of a strong contact between the electrode and film layer. Thus resulted in relatively low device performances so that the transfer curves obtained seemed rough and the output characteristics are not fully obtained. In addition, thermal annealing shows little effect on device performances of Q3. Despite that, interestingly, OFET device of Q3 exhibits clear ambipolar semiconducting property with p-type performance of μ_h = 1.2× 10^{-6} cm^2 V^{-1} s^{-1}, $I_{on/off}$ = 10^4 and V_T = -12 V while n-type performance up to μ_e = 0.6 × 10^{-6}cm^2 V^{-1} s^{-1}, $I_{on/off}$ = 10^4 and V_T = 10 V. Evidently, the introduction of ethynylene lowered the LUMO level of Q3 relative to Q1 and Q2. Accordingly, lower LUMO is beneficial to stabilizethe electron charge carrier which is easily quenched in air and usually hard to observe in such conditions.[23] This, even though all three polymers have relatively low band gaps, only devices based on Q3 showed n-type performance with the detectable ambipolar OFET properties in air condition.

AFM and XRD

The as prepared and annealed thin films of Q1, Q2 and Q3 were invesigated by X-ray diffraction (XRD) and atomic force microscopy (AFM).[§§] Compared to the as prepared thin film, AFM image showed that after annealing at 180 °C, the grain size in thin films of Q1 was only slightly enhanced. Comparatively, the grain size increasing phenomenon in thin films of Q2 seemed more obvious and the film continuity improved as seen from the annealed thin film morphology. Such morphology changes are most likely due to an improved molecular arrangement in solid state and the charge carrier mobilities. However, no obvious diffraction peaks were observed for the films before or after the annealing process for all three polymers in XRD (see Figure S3 in ESI for details), indicating the polymers are not orderly packed within the thin film which agrees with the observation that all mobilities obtained from OFET devices are not very high. Thus, in our case, the annealing process showed limited effects in improving device perfomances.

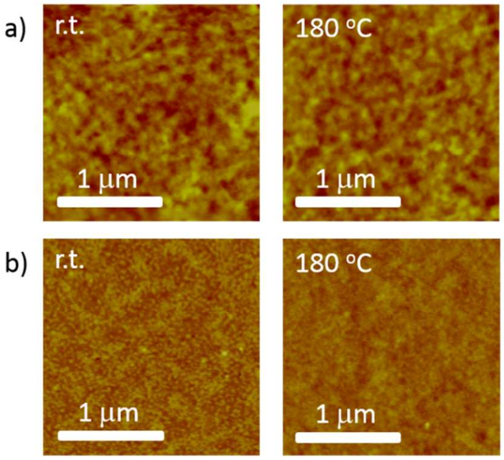


Figure 5. AFM image of thin films of Q1, Q2

Conclusions

In summary, we present three D-A conjugated polymers Q1, Q2 and Q3 in which TPD is used as electron acceptor and di-thiophene units as electron donors are linked with a single bond, a vinyl group and an ethynylene group. DFT calculation and CV studies indicate that all three polymers exhibit narrow band gaps while Q3 exhibit the lowest LUMO energy. OFET devices based on Q1, Q2 and Q3 can be fabricated by conventional solution techniques. Interestingly, devices of Q2 exhibit the best performance of hole mobility up to 0.01 cm^2 V^{-1} s^{-1} possibly because the vinyl groups enhances coplanarity of the polymer backbone and thus is useful for its conjugation and charge carrier mobility. On the other hand, due to the lowered LUMO level of Q3 by the presence of ethynylene group, devices of Q3 exhibit ambipolar OFET performance in air condition of hole and electron mobilities up to μ_h = 1.2 × 10^{-6}cm^2 V^{-1}s^{-1} and 0.6 × 10^{-6}cm^{2}V^{-1}s^{-1}, respectively. In general, accordingly, choosing a vinyl group as linkers can be benifical for p-type semiconducting properties for D-A copolymers while an ethynylene group should be introduced if it is needed to facilitate n-type propoerties. Our present results show promise for modulation of the polymer semiconducting properties by varying the linkers between functional units and further studies along this vein deserve attentions.

Experimental

General

Chemicals were purchased form Alfa-Aesar, Sigma-Aldrich etc. and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker DMX-400&600 NMR Spectrometers using tetramethylsilane as internal standard. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. MALDI-TOF MS were recorded with BEFLEX III spectrometer. Thin films absorption spectra were measured with PE lambda 950 UV-Vis spectrophtometer. TGA-DTA measurements were carried out on a NETZSCH STA 449 F3 Jupiter® instruments under a dry nitrogen flow, heating from room temperature to 550 °C, with a heating rate of 20 °C/min. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using glassy carbon(GC) as working electrodes of 2 mm diameter, a platinum wire as counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI660E instruments at room temperature. X-ray diffraction (XRD) measurements were carried out in the reflection mode at room temperature using a Rigaku-D/max-2500 X-ray diffractometer under reflection mode with the power rate of 40 kV/200 mA and wavelength of 1.54 Å. The molecular structures of the compounds were optimized using the DFT method at the level of B3LYP/6-31G*. All calculations were performed with the programs Gaussian 09.

Fabrication of OFET devices

A bottom contact OFET was fabricated. A heavily doped n-type Si wafer and a layer of dry oxidized SiO_2 (300 nm) were used as a gate electrode and gate dielectric layer, respectively. The source-drain (D-S) gold contacts were fabricated by photo-lithography. The channel length and width are 10-50 µm and 1440 µm, respectively. The substrates were cleaned in water, deionized water, alcohol, and rinsed in acetone. And then, the surface was modified by n-octadecyltrimethoxysilane (OTS). Q1 and Q2 were dissolved in $CHCl_3$ (about 10 mg/mL) and spin-coated on above substrate at 2000 r/m, while Q3 was dissolved in ODCB and drop-casted on above substrate.

The electrical characteristics of the OFETs were measured with Keithley 4200 SCS semiconductor parameter analyzer under ambient conditions. The mobility of the OFETs in the saturation region was extracted from the following equation:

$$I_{DS} = \frac{W}{2L}\mu C_i\left(V_{GS} - V_{th}\right)^2$$

where I_{DS} is the drain electrode collected current; L and W are the channel length and width, respectively; μ is the mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer; V_{GS} is the gate voltage, V_T is the threshold voltage, the V_T of the device was determined by extrapolating the $(I_{DS},sat)^{1/2}$ vs. V_{GS} plot to $I_{DS} = 0$.

Synthesis

Compound 3, 4, 6 and 7 are synthesized via method reported previously,[19,25] and the characteristic details are listed in electronic supplementary information.

Preparation of polymer Q1: compound 4 (300 mg, 0.463 mmol) and compound 8 (172 mg, 0.35 mmol) were dissolved in 10 mL chlorobenzene, stirred and purged three times by vacuum/argon cycling. Then $Pd_2(dba)_3$ (3.2 mg, 1.0 mol%) and Tri(o-tolyl)phosphine (15 mg, 14 mol%) were added into the reaction mixture at liquid nitrogen bath and purged three times to remove oxygen of catalyst and ligands. The reaction solution was warmed from ambient temperature to 135 ^{o}C using the oil bath equipment for 48hrs. The crude product was poured into 120 mL methanol. The precipitate was filtered. The solid was extracted by Soxhlet with hexane and acetone and finally the product was extracted with chloroform, the chloroform was removed under reduced pressure provided violet black solid. Yield: 300 mg (95%). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ = 7.73 (br 2H), 6.68 (br 2H), 3.53 (br 2H), 1.49-0.84 (m 47H). Elemental analysis: Calcd. For $[C_{38}H_{53}NO_2S_3]_n$: C 70.00, H 8.19, N 2.15, S 14.75. Found: C 69.72, H 7.68, N 2.06, S 14.38.

Preparation of polymer Q2: The copolymer was synthesized via similar method described from Q1 using compound 7 (569 mg, 0.701 mmol), compound 9 (425 mg, 0.701 mmol), $Pd_2(dba)_3$ (3.2 mg, 1.0 mol%) and Tri(o-tolyl)phosphine (30 mg, 14 mol%) in chlorobenzene (10 mL) at 135 ^{o}C to afford the product as black purple solid. Yield: 465 mg (94%).^{1}H NMR (400MHz, $CDCl_3$, ppm):δ = 7.82 (br 2H), 6.50 (br 4H), 3.49 (br 2H), 1.37-0.86 (m 47H). Elemental analysis: Calcd. For $[C_{40}H_{55}NO_2S_3]_n$: C 70.85, H 8.18, N 2.07, S 14.19. Found: C 69.83, H 7.96, N 1.96, S 13.81.

Preparation of polymer Q3: The copolymer of Q3 was synthesized as described for Q1 using compound 7 (150 mg, 0.185 mmol), compound 10 (112 mg, 0.185 mmol), $Pd_2(dba)_3$ (1.6 mg, 0.5 mol%) and Tri(o-tolyl)phosphine (7.4 mg, 14 mol%) in chlorobenzene (5 mL) at 135 ^{o}C for 48 hrs. The crude product was poured into 120 mL methanol. The precipitate was filtered. The solid was extracted by Soxhlet with hexane, acetone, the residue was dissolved in o-dichlorobenzeneto and heated to 100 ^{o}C over night. Then the solution is filtered while it is hot. After that the solution is reprecipitate to afford the product as dark brownish solid. Yield: 78 mg (60%).^{1}H NMR (400MHz, CDCl3, ppm): δ = 7.54 (br 2H), 6.97 (br 2H), 3.53 (br 2H), 1.28-1.21 (br 41H), 0.86-0.83 (br 6H). Elemental analysis: Calcd. For $[C_{40}H_{53}NO_2S_3]_n$: C 71.06, H 7.90, N 2.07, S 14.23. Found: C 70.48, H 7.24, N 1.98, S 13.92.

Acknowledgements

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Notes and references

§ Thermal annealing only results in about 30% improvement maximum of OFETs performances and is not discussed in detail.

§§ Due to low solubilites of Q3, quality of its thin films by drop casting were not satisfying thus the AFM morphologies were not presented in the main paragraph (see ESI for details).

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