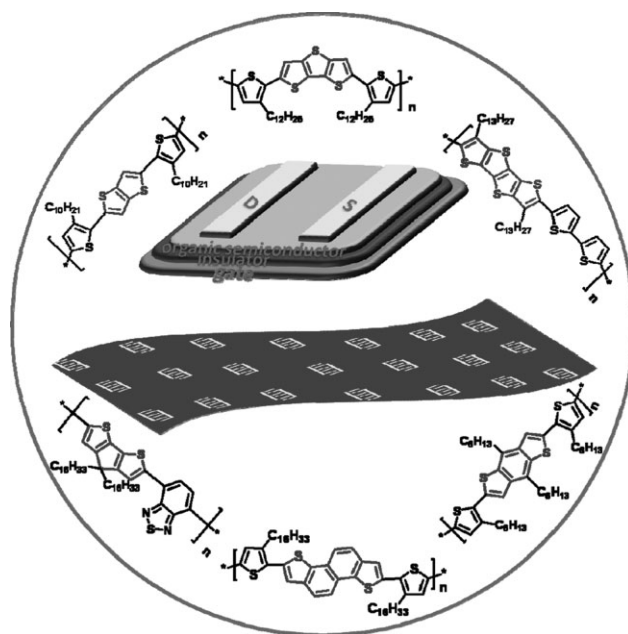


High-Mobility Conjugated Polymers Based on Fused-Thiophene Building Blocks

Yao Liu, Yunqi Liu,* Xiaowei Zhan*

Organic field-effect transistors (OFETs) are a promising cost-effective alternative to silicon-based field-effect transistors, and possess low-cost, light-weight, and flexibility advantages. Conjugated polymers based on fused-thiophene building blocks have received considerable attention in the emerging field of organic electronics. In this review the most recent developments in conjugated polymers based on fused-thiophene rings for high-performance OFETs are summarized. The focus is on correlations of polymer chemical structures with properties, such as energy levels, film-forming property, film morphology, and OFET performance. This structure–property relationship analysis may guide rational structural design and evaluation of organic semiconductors.



Introduction

Metal-insulator-semiconductor field-effect transistors (MISFETs) play an important role in modern microelectronics because they are the key electronic devices, forming virtually the backbone of all microprocessors, active-matrix displays, integrated circuits, and the elements of other electronic products. Nowadays, the technology of silicon-based MISFETs reaches a high level. However, with the scope of applications envisioned for easy fabrication and

cost-effective electronics expanding dramatically, silicon-based transistors, which typically require high process temperature, become incompatible with the concepts mentioned above.^[1]

Organic field-effect transistors (OFETs) utilizing typical MISFETs structure are a promising easy-fabrication and cost-effective alternative to silicon-based transistors, and possess unique advantages compared to their inorganic counterparts, such as low cost, light weight, and large-area device fabrication onto flexible plastic substrates.^[2] Since the first report on field effect of polythiophene in 1986,^[3] there have been extensive studies on OFETs using numerous kinds of conjugated polymers and organic small molecules.^[1,2,4] Recently, the emergence of substantial high-performance organic semiconductors has greatly promoted the progress of OFETs.^[2b,5] Previous limitations, such as ambient stability, electrical performance and so on, are being overcome to some extent.^[6] The hole and electron

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mobilities of a range of organic semiconductors reach or even exceed $0.5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$,^[7] which are proximately equivalent to that of amorphous silicon.^[8] Among those organic semiconductors, materials based on fused-thiophene rings are considerably attractive due to their excellent optoelectronic properties resulting from aromatic-coupled structures with extending π -conjugated length, which form rigid and coplanar conformation, facilitating the achievement of closely packed conjugated backbones and consequently more effective charge intermolecular hopping and transport.^[9] Additionally, relatively strong π stacking is also enhanced by S–S interaction. Recently, Wu et al. have reviewed conjugated organic materials based on fused-thiophenes and other fused-ring building blocks, while they mainly focused on small molecules.^[5a] In the present review, we summarize the representative conjugated polymers based on fused-thiophene units for high-performance OFETs. For a better understanding of the influence of molecular structure, electronic structure, and materials microstructure on charge-carrier transport, we will survey and analyze what is currently known concerning structure/property relationships of these polymer semiconductors.

Fused-Thiophene Polymers for p-Channel Field-Effect Transistors

Polymers Based on Thienothiophene

Attempts to design and synthesize high-performance conjugated polymers based on thiophene units mainly focus on two aspects: improving chain packing in the solid state and lowering the highest occupied molecular orbital (HOMO) level. The former is viewed as the strategy to achieve higher mobility, while the latter concerns better (photo)oxidative stability. The incorporation of building block that consists of fused-thiophenes is a reasonable solution for the aforementioned requests.^[10]

To reduce π electron delocalization while preserve the close π - π intermolecular interaction necessary for high charge carrier mobility, Heeney et al. incorporated a simplest fused-thiophene, less conjugated thieno[2,3-b]thiophene, into the polythiophene backbone (**1a**, Figure 1). **1a** exhibited liquid crystalline phase as revealed by the reversible high-temperature endo- and exotherms process. Wide-angle X-ray scattering measurements of spin coated thin films of **1a** indicate lamellar films with an interlayer spacing of 17 \AA and a π - π stacking distance of 3.7 \AA . **1a** exhibited blue-shifted absorption maximum (470 nm) in film and lower HOMO (-5.3 eV) relative to regioregular head-to-tail poly(3-hexylthiophene) (P3HT), suggesting better oxidation stability. This polymer exhibited a hole mobility up to $0.15 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and on/off ratio of 10^5



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with little degradation observed in the electrical characteristics over time upon storage in ambient atmosphere and light.^[11]

In contrast to polymer **1a**, the thieno[3,2-b]thiophene unit in polymer **1b** (Figure 1) allows conjugation between adjacent thiophenes coupled at 2 and 5 positions, as the sulfur atoms within the fused ring switch from the “syn” to “anti” positioning, leading to different arrangement of double bonds.^[10] Therefore, **1b** has extended π -orbital delocalization. As a result, **1b** exhibits 77 nm red shift of absorption maximum in film and higher HOMO (-5.1 eV) compared to its thieno[2,3-b]thiophene analog **1a** (Table 1).^[12] **1b** exhibits a higher hole mobility ($0.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and higher on/off ratio (10^6) than **1a**, while even higher mobilities ($0.63 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and higher on/off ratio (10^7) were found for the C14 analog of **1b**.^[12] However, further increasing the length of alkyl substituent on thiophene to C16 leads to a lower mobility of $0.44 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ after thermal annealing.^[13] The introduction of unsubstituted thieno[3,2-b]thiophene along the backbone, elimination of the presence of regioisomers in the polymer backbone, relatively large crystalline domain, and highly organized morphology from processing in the mesophase are responsible for the high charge carrier mobility.

The morphology and microstructure of thin films of the **1b** series polymers play an important role in their OFET

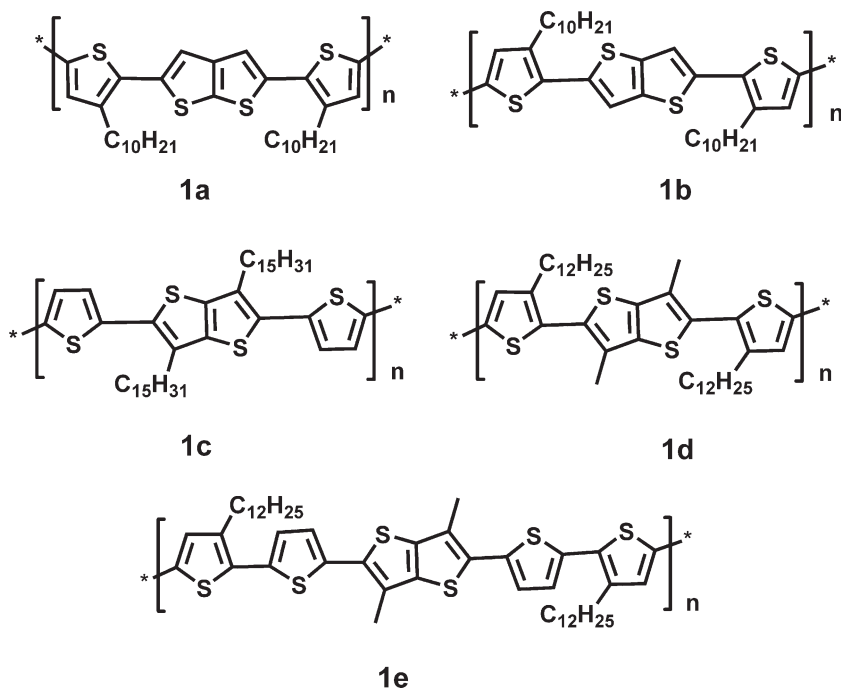


Figure 1. Chemical structure of some polymers based on thienothiophene.

device performance. Kline et al. found that the C12 analog of **1b** has a significant dependence of morphology and charge carrier mobility on substrate surface chemistry upon heating into its liquid crystalline phase.^[14] The functionalization on silicon oxide with octyltrichlorosilane (OTS) leads to substantial increases in the lateral dimensions of molecular terraces from nanometers to micrometers, increased orientational order, and higher charge carrier mobility of the polymer films relative to that on the bare silicon oxide surfaces. These results were further validated by Chabinyk et al. using synchrotron X-ray diffraction and atomic force microscopy (AFM) to investigate the microstructure of the thin films of this polymer on different substrates.^[15] Although the X-ray scattering is nearly identical on both SiO₂ and OTS/SiO₂ surfaces, AFM shows

that the domain size of the crystalline regions depends on the substrate surface. Lucas et al. investigated the effects of temperature on the microstructure and mobility of thin films of this polymer using a combinatorial temperature gradient technique.^[16] An increase in crystal domain size and orientation, all of which occur abruptly at a temperature closely corresponding to a bulk liquid crystal phase transition, played an important role in mobility enhancement.

Poly(3,6-dipentadecylthieno[3,2-b]thiophene-co-bithiophene) (**1c**, Figure 1) has the same fully delocalized π electron backbone as **1b**, but differs in the attachment location of the side chains, which are at 3 and 6 positions of thieno[3,2-b]thiophene in **1c**. **1c** exhibits 50 nm blue shift of absorption maximum in film and lower HOMO (−5.23 eV) compared to **1b** (Table 1).^[17] This may be due to the rotational torsion of the bithiophene unit, leading to reduced π orbital overlap, or

possibly the reduced impact of the electron donating alkyl groups into the more resonantly stabilized thieno[3,2-b]thiophene.^[18] **1c** exhibits a hole mobility of 0.25 cm² · V^{−1} · s^{−1} and an on/off ratio of 10⁷. The thiophene number (2) in repeated unit of **1c** is reduced to 1 to give poly(3,6-dialkylthieno[3,2-b]thiophene-co-thiophene); the mobilities achieved are similar.^[10] However, if the thiophene number (2) in repeated unit of **1c** is reduced to 0 to give poly(3,6-dialkylthieno[3,2-b]thiophene), the mobilities are decreased to 10^{−6} cm² · V^{−1} · s^{−1}, due to the limited π – π stacking among the polymer chains caused by the highly twisted structure of the main chain.^[19] The introduction of vinylene into poly(3,6-dialkylthieno[3,2-b]thiophene) backbone to form poly(3,6-dialkylthieno[3,2-b]thiophene vinylene) leads to more coplanar backbones, stronger π – π

Table 1. Electronic properties and OFET device data for polymers based on thienothiophene.

	$\lambda_{\max}^{\text{abs a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\max}^{\text{d)}$ cm ² · V ^{−1} · s ^{−1}	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
1a	470	−5.3	3.7	0.15	−3	10 ⁵	[11]
1b	547	−5.1	3.72	0.3	–	10 ⁶	[12]
1c	496	−5.23	3.93	0.25	−8	10 ⁷	[17]
1d	394	−5.5	–	8.1×10^{-7}	−39	10	[21]
1e	552	−5.0	–	0.03	−7	10 ⁶	[21]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π – π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

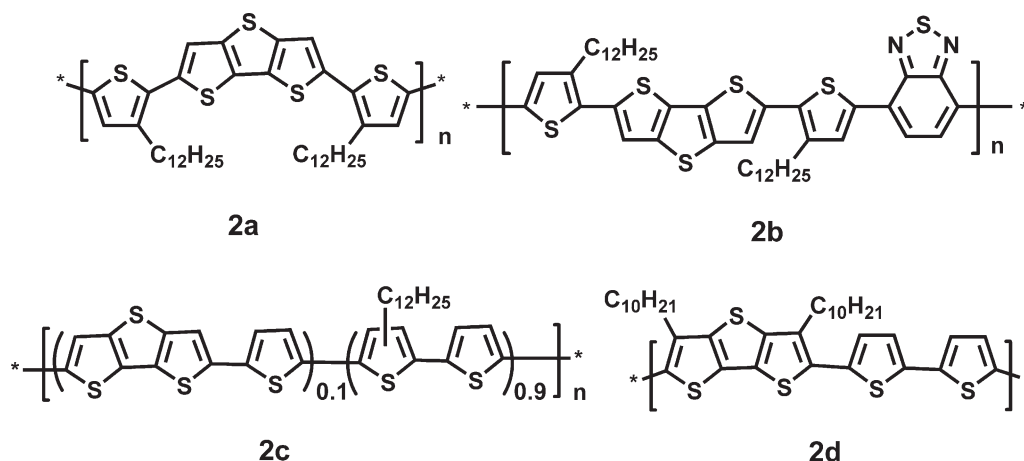


Figure 2. Chemical structure of some polymers based on dithienothiophene.

stacking, and much higher hole mobility ($0.032 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).^[20] On the other hand, attachment of alkyl side chains to the bithiophene unit in poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene) also causes steric hindrance, reduces backbone coplanarity and inter-chain interaction, and finally disfavor charge transport. For example, poly(3,6-dimethylthieno[3,2-b]thiophene-co-bi-3-dodecylthiophene) (**1d**, Figure 1) exhibits 100–150 nm blue shift of absorption maximum in film, 0.3–0.4 eV lower HOMO and six orders of magnitude lower mobility compared to **1b** and **1c** (Table 1).^[21] Insertion of unsubstituted thiophene ring between 3,6-dimethylthieno[3,2-b]thiophene and 3-dodecylthiophene in **1d** diminishes the distortion of the core units (**1e**, Figure 1) and enhances hole mobility.^[21]

Polymers Based on Dithienothiophene

To extend effective conjugated length and enhance coplanarity of the molecules, larger fused-thiophene rings were incorporated into the polymer main chains. Dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) is sulfur rich (three S atoms) and electron rich species, and serves as an

important building block of a number of materials for electronic and photonic applications, such as electroluminescence, two-photon absorption, nonlinear optics, photochromism, OFETs, and organic solar cells.^[22] Holmes and co-workers pioneered the use of DTT as a very promising building block for semiconductor materials in OFETs.^[23] Recently, we fabricated high-performance OFET devices using DTT derivatives.^[24]

Li et al. synthesized a solution-processable copolymer, poly(DTT-co-bi-3-dodecylthiophene) (**2a**, Figure 2).^[25] **2a** exhibits 10 nm red shift of absorption maximum in film relative to its thieno[3,2-b]thiophene counterpart **1b** due to the larger fused ring of DTT (Table 2). OFETs based on **2a** exhibit a high mobility ($0.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and a high on/off ratio (10^7) after annealing at 160°C . Incorporation of benzo[1,2,5]thiadiazole into this copolymer backbone (**2b**, Figure 2) leads to 70 nm red shift of absorption maximum in film and four orders of magnitude decrease in mobility.^[26] Liu and co-workers reported the synthesis of a series of air-stable copolymers based on rigid DTT moieties and single thiophene units.^[27] **2c** (Figure 2) exhibits 14 nm blue shift of absorption maximum in film and one order of magnitude decrease in mobility relative to **2a** probably due to increase

Table 2. Electronic properties and OFET device data for polymers based on dithienothiophene.

	$\lambda_{\text{max}}^{\text{abs a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
2a	558	−5.14	3.8	0.3	−14.2	10^7	[25]
2b	626	−5.12	—	8×10^{-5}	−10	6×10^3	[26]
2c	554	−5.08	—	0.028	−18.9	2×10^4	[27]
2d	534	−5.15	—	1.7×10^{-3}	−11	10^3	[28]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

in rotational freedom of the main chain and/or presence of regioisomers. Poly(3,6-didecanyl-dithienothiophene-co-bithiophene) (**2d**, Figure 2) has the same delocalized π electron backbone as **2a**, but differs in the attachment location of the side chains, which are at 3 and 6 positions of DTT in **2d**. **2d** exhibits 24 nm blue shift of absorption maximum in film and two orders of magnitude decrease in mobility relative to **2a** (Table 2).^[28] This may be due to the rotational torsion of the bithiophene unit, leading to reduced π orbital overlap and weaker intermolecular interaction.

Effect of Fused-Thiophene Ring Size

He et al. designed and synthesized a family of conjugated polymers with fused aromatic structures consisting of three to five thiophene rings (**2d**, **3a**, and **3b**, Figure 3).^[28] All three polymers with different fused-thiophene ring size showed well-extended conjugation through the polymer backbone with similar absorption maxima and similar HOMO levels (Table 3). They drew the following conclusions: (i) The polymer with the even number of fused-thiophene rings forms a tight crystalline structure due to its tilted side chain arrangement, while the polymer with the odd number of fused-thiophene rings packs more loosely. As a result, the mobility of the polymer with the even number of rings is one order of magnitude higher than its odd-numbered counterparts. (ii) A regioregular structure with side chains pointing in opposite directions favor to yield high mobility. (iii) Larger conjugated units tend to form self-assembled structures.^[28] (iv) Repeat unit that possesses a C_2 -axis

perpendicular to the conjugation plane tends to minimize the lamellar spacing of these polymer films and enhance charge carrier mobility.^[29] It is interesting that replacing C10 side chain in **3a** with C13 (**3c**, Figure 3) leads to four times enhancement of mobility.^[30]

Polymers Based on Benzodithiophene

The large planar benzodithiophene (BDT) unit has emerged as an attractive building block for conjugated polymers. Recently, polymer solar cells based on blends of BDT-based copolymers and soluble fullerene derivatives PC₆₁BM or PC₇₁BM afforded high power conversion efficiencies (4.7–7.7%).^[31] Two conventional isomers of BDT have been extensively investigated. From a standpoint of structure, benzo[1,2-*b*:4,5-*b'*]dithiophene with a linear structure allows conjugation between adjacent aromatic ring units coupled at 2 and 6 positions. Consequently, copolymers containing benzo[1,2-*b*:4,5-*b'*]dithiophene unit exhibit extended π -orbital delocalization with relatively lower bandgap.^[32] On the other hand, benzo[2,1-*b*:3,4-*b'*]dithiophene with a curved structure prevents a fully conjugated pathway between substituents at 2 and 6 positions. Hence, delocalization of the conjugated π electron system along the copolymer backbone is disfavored by the incorporation of this unit. This increases the ionization potential of the polymer and is thus expected to improve air stability under operation.^[33] Additionally, compared to a single thiophene ring, it must be pointed out that due to the large resonance stabilization energy of BDT, the delocalization of electrons from the BDT unit into the backbone is less

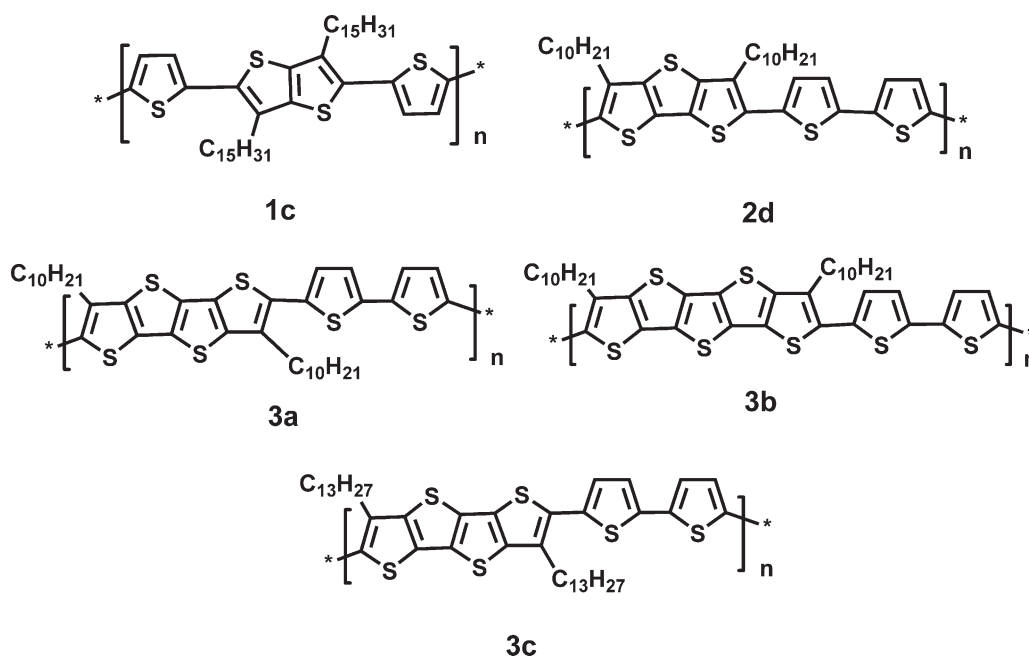


Figure 3. Chemical structure of some polymers based on different size fused-thiophenes.

Table 3. Electronic properties and OFET device data for polymers based on different size fused-thiophenes.

	$\lambda_{\max}^{\text{abs a)}$	HOMO ^{b)}	$d_{\pi-\pi}^{\text{c)}$	$\mu_{\max}^{\text{d)}$	$V_{\text{th}}^{\text{e)}$	$I_{\text{on}}/I_{\text{off}}$	Ref.
	nm	eV	Å	$\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	V		
1c	496	-5.23	3.93	0.25	-8	10^7	[17]
2d	534	-5.15	–	1.7×10^{-3}	-11	10^3	[28]
3a	545	-5.20	3.65	8.7×10^{-2}	-4	10^6	[28]
3b	523	-5.21	–	2.3×10^{-3}	-9	10^3 - 10^4	[28]
3c	546	–	3.76	0.33	-10	10^5	[30]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

favorable than from the thiophene ring. As a result, a more soluble copolymer with high performance can be obtained by using BDT as the core unit.

The homopolymer of benzo[1,2-*b*:4,5-*b'*]dithiophene (**4b**, Figure 4) displayed a hole mobility of $\approx 0.01 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ after annealing at 140°C .^[34] Compared with **4b**, thin films based on the homopolymer of benzo[2,1-*b*:3,4-*b'*]dithiophene (**4a**, Figure 4) exhibited a low degree of ordering with a large value of π - π stacking distance (4.3 Å), which reduced charge carrier mobility by two orders of magnitude.^[33] The linear polymer **4d** (Figure 4) exhibits charge-carrier mobilities of one order of magnitude lower than the curved counterpart **4c** (Figure 4).^[33] This is surprising if comparing the almost identical X-ray scattering patterns of both polymers. The curvature of **4c** guarantees an optimum compromise between solubility and aggregation tendency to drive quick formation of highly ordered spin-coated polymer films. The very low solubility of **4d** seems to be the reason for low charge carrier mobility. Furthermore, FETs based on **4c** manufactured on flexible substrate exhibited even higher charge carrier mobility of $0.5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ when the source-gate voltage is increased to 60 V, demonstrating its great potential for industrial application.^[33]

Incorporation of bi-3-methylthiophene into backbone of **4b** leads to 100 nm red shift of absorption maximum of the room-temperature solution of **4b** (Table 4), suggesting a greater π -conjugation and substantially more ordered structure in **4e**.^[34] The distance between the neighboring dodecyl chains in **4e** is about 16 Å,

much larger than that of **4b** (8.5 Å), thus permitting a closer intermolecular chain packing. Indeed, the interlayer distance of **4e** (17.7 Å) is much smaller than that of **4b** (23.9 Å). As an as-prepared thin-film semiconductor without thermal annealing, copolymer **4e** exhibited excellent FET properties with a mobility of $\approx 0.15 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, one

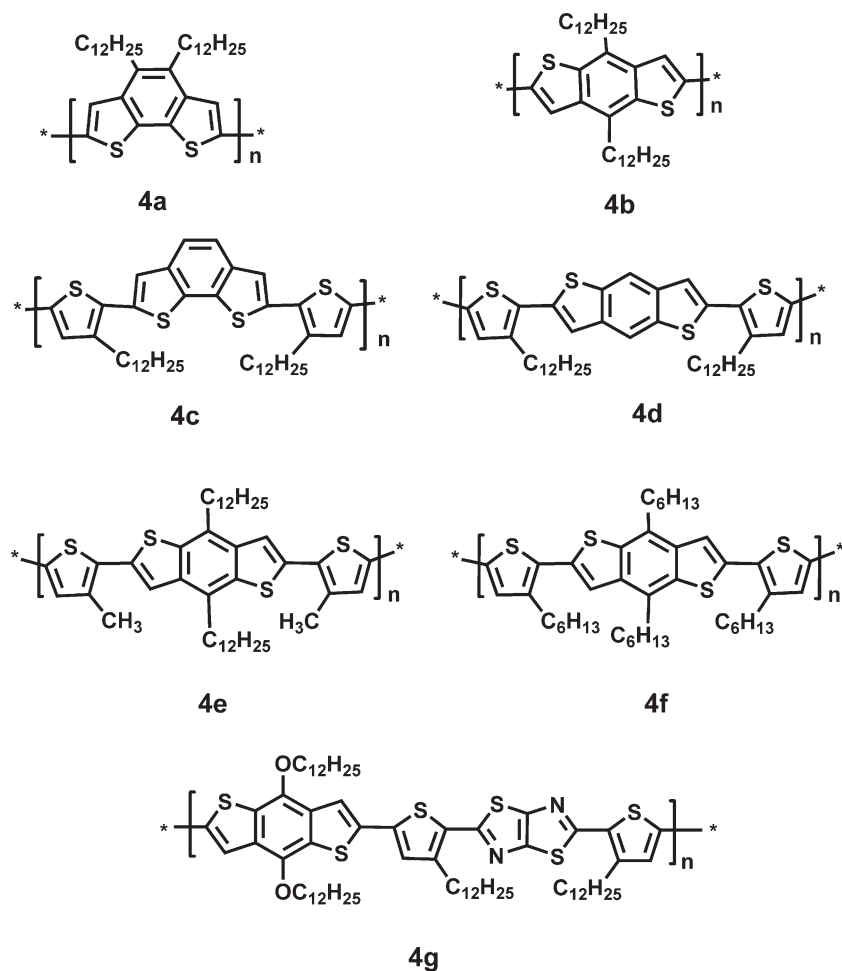


Figure 4. Chemical structure of some polymers based on benzodithiophene.

Table 4. Electronic properties and OFET device data for polymers based on benzodithiophene.

	$\lambda_{\text{max}}^{\text{abs a)}$	HOMO ^{b)}	$d_{\pi-\pi}^{\text{c)}$	$\mu_{\text{max}}^{\text{d)}$	$V_{\text{th}}^{\text{e)}$	$I_{\text{on}}/I_{\text{off}}$	Ref.
	nm	eV	Å	$\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	V		
4a	–	–	4.3	1.3×10^{-4}	–	2.4×10^2	[33]
4b	481	–	–	0.01	–	–	[34]
4c	–	–	3.7	0.134	–	1.9×10^5	[33]
4d	–	–	3.7	1.5×10^{-2}	–	9.1×10^4	[33]
4e	580	–5.05	4.1	0.15	–11	10^6	[34]
4f	581	–5.12	3.9	0.25	–5.9	10^5 – 10^6	[35]
4g	582	–5.3	–	2.8×10^{-3}	–19	10^3	[36]

^{a)}Absorption maxima in solution; ^{b)}Highest occupied molecular orbital; ^{c)} π – π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

order of magnitude higher than that of **4b**. The tendency of **4e** to exhibit strong backbone interactions in the as-cast film rendered it highly crystalline, leading to high mobility even without thermal annealing.^[34] Ong and co-workers reported a regioregular polymer (**4f**, Figure 4) using a monomer of two 3-hexylthiophene units coupled at the 2 and 6 positions of BDT as building block.^[35] **4f** exhibited a similar absorption maximum, similar HOMO level, but shorter π – π stacking distance relative to **4e**. Solution-processed FET device based on **4f** showed a high mobility of 0.15 – $0.25 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, an on/off ratio of 10^5 – 10^6 , a small threshold voltage of -5.9 V , and a sub-threshold slope of ca. $2 \text{ V} \cdot \text{decade}^{-1}$ in ambient conditions without postdeposition thermal annealing, which resulted from a relatively lower HOMO and a highly ordered structure of the polymer film formed at room temperature.^[35] The mobility of the test device decreased slightly from 0.20 to about

$0.16 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ over a period of 30 d in an ambient environment at 20% relative humidity. Zhan and co-workers reported a D-A copolymer based on BDT and thiazolothiazole units (**4g**, Figure 4).^[36] **4g** exhibited a lower HOMO and lower mobility relative to **4f** (Table 4).

Polymers Based on Cyclopentadithiophene

Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDT) derivatives have attracted considerable attention due to its fully coplanar structure, low bandgap, and strong intermolecular interactions. Particularly, the rigid fused-ring structure of CDT lowers the reorganization energy, a factor that has been shown to strongly affect the rate of intermolecular hopping and hence the charge carrier mobility in organic semiconductor, making it a promising core unit for conjugated polymers.^[37] Recently, CDT-based polymers were used in

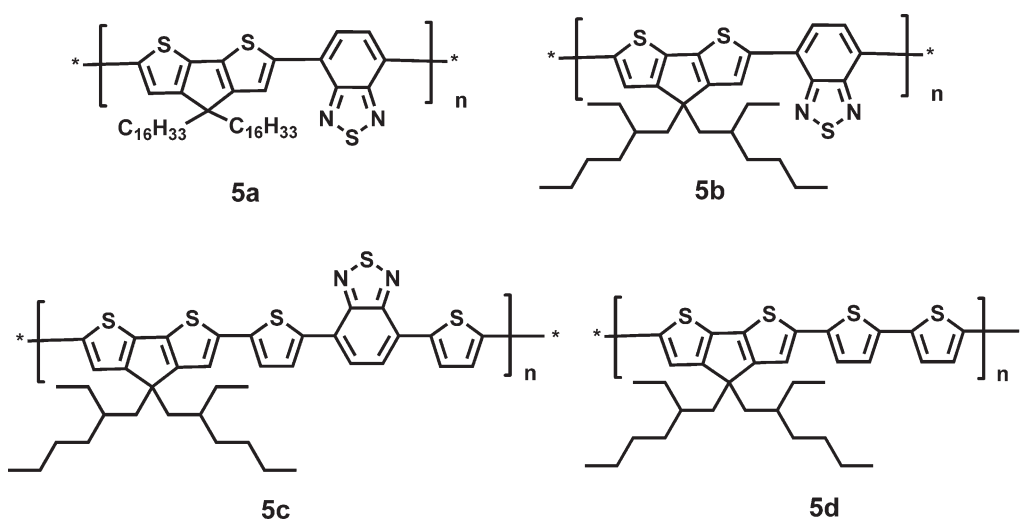


Figure 5. Chemical structure of some polymers based on cyclopentadithiophene.

polymer solar cells and exhibited power conversion efficiencies over 6%.^[38]

Müllen and co-workers reported a copolymer (**5a**, Figure 5) using 4,4-dihexyldecyl-substituted CDT and benzothiadiazole as building blocks. Molecular weight of the copolymer is a crucial factor that affects the structural order of the polymer films.^[39] Under low molecular weight ($\bar{M}_n = 1.01 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$), the macroscopic order of the polymer films was extremely poor even after annealing as confirmed by wide-angle X-ray scattering. Fortunately, due to the small π - π stacking distance (3.7 Å), this conjugated polymer shows functionally desirable FET performance with a hole mobility up to $0.17 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.^[39a] While under high molecular weight ($\bar{M}_n = 5 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$), improved structural order and an elevated hole mobility were obtained for solution-deposited polymer films. After a further optimization by directionally aligning the polymer via dip-coating, inducing a tendency of long-range molecular orientation, a hole mobility up to $1.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was obtained, among the highest values reported so far for polymer-based OFETs (Table 5).^[39b]

Replacement of hexyldecyl at 4 position of CDT in **5a** with 2-ethylhexyl (**5b**, Figure 5) leads to three orders of magnitude decrease in mobility possibly as 2-ethylhexyl substituents are not favorable for molecular ordering.^[40] Incorporation of 2 thiophene units into the main chain of **5b** to give **5c** induced 64 nm blue shift of absorption maximum and one order of magnitude decrease in mobility.^[41] Adding benzothiadiazole between 2 thiophene units in **5d** lead to 142 nm red shift of absorption maximum due to intermolecular charge transfer in **5c**, but reduced mobility by one order of magnitude.^[40]

Polymers Based on Dithienopyrrole

Dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP), having a pyrrole ring condensed with dithiophene, has attracted considerable attention as a useful unit in conjugated polymers owing to its strong electron-donating and charge-transporting properties. Additionally, the N-H bond of DTP unit can be easily

substituted by functional groups without damaging its good molecular planarity. Thus, the solubility and ordering of conjugated polymers based on DTP unit become more adjustable through the N-substituents without disrupting the polymer backbone. Rasmussen and co-workers developed a simple and efficient synthetic route to N-functionalized DTP and pioneered the use of N-alkyl substituted DTP as a promising fused aromatic building block for electronic materials.^[42] Koeckelberghs et al. synthesized several chiral polymers containing DTP units and investigated their chiroptical properties.^[43] Polymer solar cells based on blends of DTP-based polymers and PCBM exhibited power conversion efficiencies up to 2.8%.^[44]

McCullough et al. incorporated alkyl-substituted thiophene units into poly-DTP backbone and then synthesized a series of copolymers with excellent solubility and high molecular weights.^[45] They found that hole mobility ($0.026 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) of as-cast, less ordered samples of **6a** (Figure 6) is much higher than that observed after annealing ($0.0058 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). This abnormal phenomenon suggests that the presence of highly ordered microcrystalline structures in polymer thin films is not necessary for excellent performance of organic transistors. Hence, amorphous π -conjugated polymers that possess long-range π -connectivity on the microscopic scale could also achieve high mobility. Unfortunately, polymer **6a** applied in FETs exhibited extremely poor on/off ratio (4). It may be ascribed to its low oxidation potential resulting from the electron-rich character of DTP units in the polymer backbone.^[45]

Another independent work reported by Li and co-workers gave an insight into the effect of alkyl chain at the N atom on the structural order of the polymer films and subsequently the device performance.^[46] OFETs based on **6b** (Figure 6) exhibit a mobility of $0.11 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and an on/off ratio close to 10^4 , which are higher than that of **6b**'s counterpart with methyl at N-position. The long alkyl chain at the N atom facilitates the ordered aggregation in polymer films and then enhance charge carrier mobility. In

Table 5. Electronic properties and OFET device data for polymers based on cyclopentadithiophene.

	$\lambda_{\text{max}}^{\text{abs a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
5a	750	–	3.7	1.4	–	10^4 – 10^5	[39]
5b	760	–5.3	–	1×10^{-3}	–	–	[40]
5c	696	–	–	2×10^{-4}	–	–	[41]
5d	554	–5.35	–	2×10^{-3}	–	–	[40]

a) Absorption maxima in films; b) Highest occupied molecular orbital; c) π - π stacking distance; d) Maximum hole mobility; e) Threshold voltage.

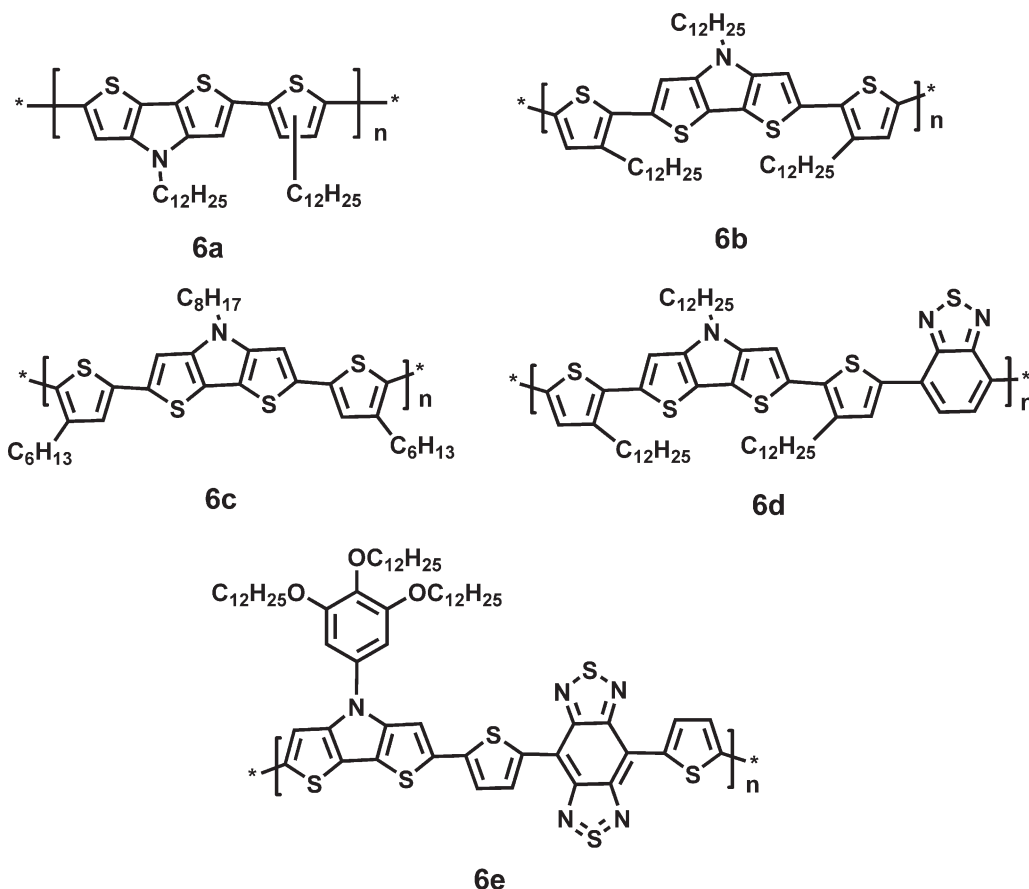


Figure 6. Chemical structure of some polymers based on dithienopyrrole.

comparison with **6b**, having alkyl at 3-position of thiophene, **6c**, having alkyl at 4-position of thiophene, exhibits 93 nm blue shift of absorption maximum and two orders of magnitude lower mobility (Table 6), probably due to highly twisted structure and limited conjugation of the polymer chain caused by the steric hindrance of bi-4-hexylthiophene in **6c**.^[45]

Introduction of benzothiadiazole into the main chain of **6b** lead to 152 nm red shift of absorption maximum due to intermolecular charge transfer in **6d**, lower HOMO level, and lower mobility.^[26] Reynolds and co-workers developed a low-bandgap copolymer (**6e**, Figure 6) using N-(3,4,5-tris(dodecyloxy)phenyl)-DTP as a strong donor and benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole as a strong acceptor.

Table 6. Electronic properties and OFET device data for polymers based on dithienopyrrole.

	$\lambda_{\max}^{\text{abs a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\max}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
6a	575	-4.68	3.6	0.026	60	4	[45]
6b	570	-4.93	4.0	0.11	-8.1	10 ⁴	[46]
6c	477	-4.96	—	3.5×10^{-3}	-23	140	[45]
6d	722	-5.07	—	0.03	-16	10 ³	[26]
6e	—	-5.1	—	1.2×10^{-3}	—	—	[47]

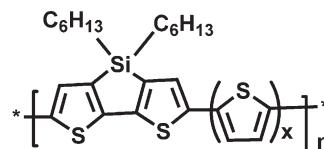
^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

Field-effect mobilities of 1.2×10^{-3} and 5.8×10^{-4} $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ were measured for p-channel and n-channel devices based on **6e**, respectively.^[47]

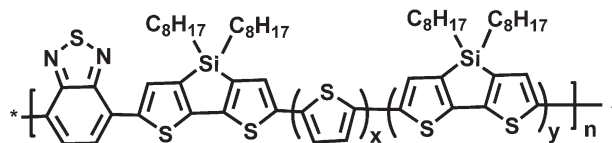
Polymers Based on Dithienosilole

Siloles (silacyclopentadienes) have recently attracted attention as semiconductor materials for organic electronics since they may exhibit relatively large electron affinities, relatively high electron mobilities and high photoluminescence quantum yields due to $\pi^*-\sigma^*$ conjugation.^[48,49] Among various π -conjugated silole systems, dithienosilole (DTS) unit has emerged as a useful building block for synthesis of organic semiconductors.^[50] Mixing of the π^* orbital of the butadiene fragment with relatively low-lying set of σ^* orbitals of the out of plane substituents on the silicon atom creates an orbital that has $\pi^*-\sigma^*$ conjugation. This $\pi^*-\sigma^*$ conjugation leads to a low-lying lowest unoccupied molecular orbital (LUMO) and a relatively small bandgap. Additionally, alkyl-substituted silicon is known to stabilize adjacent carbanionic centers due to the effective hyper-conjugation between negatively charged carbon centers and the adjacent silyl groups.^[51] The good ring planarity and the aforementioned considerations renders DTS unit an excellent monomer that might induce π -electron overlap along the polymer backbone without compromising their ambient stability.^[51]

In order to explore architecture-electronic structure relationship of silole-based conjugated polymers, Marks and co-workers coupled alkyl-substituted DTS unit with thiophene unit in different proportions (**7a–c**, Figure 7).^[51] Theoretical calculations and optical characterization suggested a high degree of π -delocalization in the silole-based polymers with increased ionization potentials and electron affinities relative to their carbon counterparts, making the silole-based copolymers less susceptible to oxygen. Due to



7a $x = 0$
7b $x = 1$
7c $x = 2$



7d $x = 0, y = 0$
7e $x = 0, y = 1$
7f $x = 1, y = 1$
7g $x = 2, y = 1$

Figure 7. Chemical structure of some polymers based on dithienosilole.

the poor or no crystallinity of DTS-based homopolymer, **7a** did not exhibit FET behavior. Copolymers based on DTS and thiophene units (**7b–c**) exhibited high crystallinity in films after thermal annealing. **7b** and **7c** exhibited hole mobilities of $0.05\text{--}0.08 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and on/off ratios of $10^4\text{--}10^5$ (Table 7). An impressive stability of **7c** can be confirmed by its ability of subject to repeated on/off cycle test under ambient conditions at different gate voltage with negligible degradation of output characteristics. These results indicated that the FETs performance of DTS-based polymers primarily depend on crystallinity and morphology of the thin films.

Inspired by the work mentioned above, Reynolds and co-workers synthesized donor–acceptor copolymers based on

Table 7. Electronic properties and OFET device data for polymers based on dithienosilole.

	$\lambda_{\text{max}}^{\text{abs a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
7a	535	−5.6	–	–	–	–	[51]
7b	574	−5.3	–	0.05	–	1×10^5	[51]
7c	545	−5.2	–	0.08	–	5×10^4	[51]
7d	–	–	–	2×10^{-6}	–	1×10^2	[52]
7e	–	–	3.6	3×10^{-4}	–	6×10^3	[52]
7f	–	–	–	3×10^{-3}	–	2×10^4	[52]
7g	–	–	3.6	2×10^{-2}	–	1×10^3	[52]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π – π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

electron-rich DTS and electron-deficient benzothiadiazole, which absorb across the entire visible spectrum (**7d–g**, Figure 7).^[52] Though all copolymers were able to self-assemble into lamellar superstructures, only **7e** and **7g** showed a propensity to π -stacking. Although both **7d** and **7f** exhibited less ordered polymer films without π -stacking, **7f** displayed three orders of magnitude higher mobility than **7d** due to the extended π -conjugated length of **7f** (Table 7). The highest hole mobility of $0.02 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was achieved by **7g** owing to the presence of unsubstituted bithiophene spacers, which create effective charge hopping sites, reduce the concentration of solubilizing groups, and increase the coplanarity of the backbone.^[52] It is interesting that replacement of octyl on silicon atom of DTS in **7d** with 2-ethylhexyl leads to three orders of magnitude enhancement in mobility.^[53]

Polymers Based on Thienopyrazine

Thienopyrazine (TP) is attractive as an acceptor unit,^[54] which allows readily modification of the pyrazine ring without introducing steric effects directly into the polymer backbone,^[55] facilitating fine-tuning of the copolymer bandgap.^[56] Thus, various substituents such as alkyl and aryl groups can be added at 2 and 3 positions to tune structural and electronic properties of TP.^[57] In addition, the introduction of TP moiety into the conjugated polymers can provide a planar backbone, allowing the enhancement of π - π stacking among polymeric chains.^[58] Particularly, the fused aromatic TP monomers contain a flat π -electron rich face, which intend to maximize the π -orbital overlap and

possibly to induce face-to-face π -stacking, facilitating charge intermolecular hopping and transport.^[59]

Bao and co-workers reported a series of copolymers based on TP fused by BDT (**8a–d**, Figure 8).^[60] TP-CDT copolymers **8c–d** exhibit red-shifted absorption, higher HOMO, and higher mobilities relative to their fluorene counterparts (**8a–b**) (Table 8). On the other hand, copolymers based on TP fused by benzo[2,1-*b*:3,4-*b'*]dithiophene (**8b** and **8d**) exhibit higher mobilities than their isomers (**8a** and **8c**).

Polymers Based on Pentacyclic Fused-Thiophene-Phenylene-Thiophene

In order to enhance the π - π stacking and then extend the conjugation length, it is necessary to avoid the twisting between adjacent thiophene rings by fusing the thiophene rings at the end of the heteroacene structure.^[61] Ko and co-workers synthesized copolymers of pentacyclic fused-thiophene-phenylene-thiophene (TPT) unit with thiophene in different proportions (**9a–c**, Figure 9).^[62] This rigid planar structure facilitates effective π -conjugation and strong intermolecular interactions. With increasing thiophene number per repeat unit, the absorption maximum and HOMO level keep almost unchanged, but the hole mobility increases steadily (Table 9). Introduction of benzothiadiazole into the main chain of **9c** leads to red shift of absorption and lower HOMO, but the mobilities are similar.^[63]

Osaka et al. reported novel semiconducting polymers that incorporate naphtha [1,2-*b*:5,6-*b'*]dithiophene (NDT) into a regiosymmetric polythiophene system.^[64] NDT is

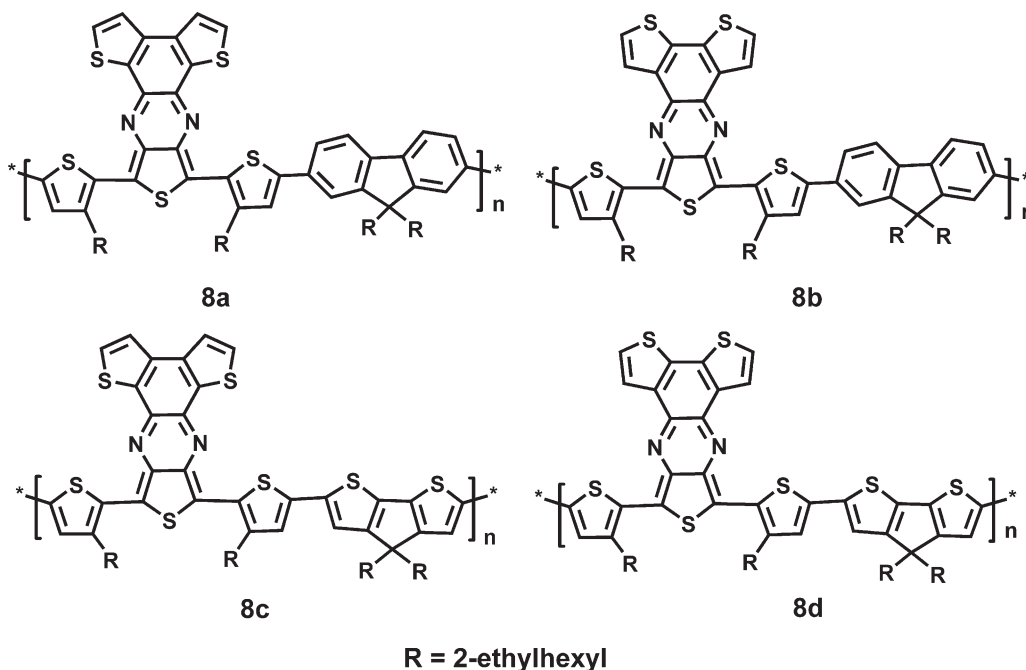


Figure 8. Chemical structure of some polymers based on thienopyrazine.

Table 8. Electronic properties and OFET device data for polymers based on thienopyrazine.

	$\lambda_{\text{max}}^{\text{a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
8a	777	-4.85	4.39	6.8×10^{-6}	17	64	[60]
8b	779	-4.84	3.85	1.8×10^{-3}	-25	3×10^3	[60]
8c	904	-4.60	4.05	1.6×10^{-4}	-4	2×10^3	[60]
8d	870	-4.60	4.01	3.8×10^{-3}	-13	1×10^3	[60]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

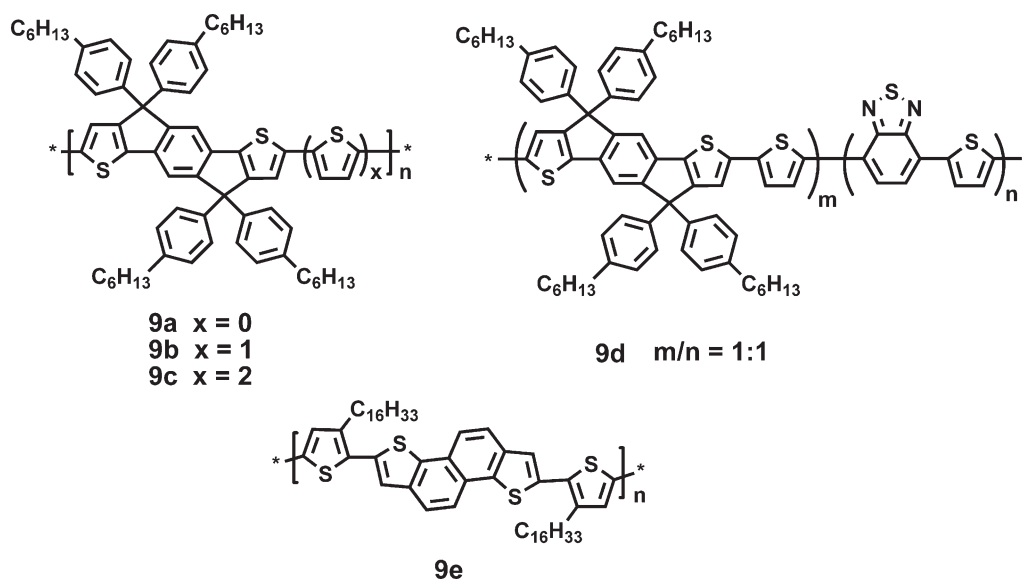


Figure 9. Chemical structure of some polymers based on pentacyclic fused-thiophene-phenylene-thiophene.

expected to provide a highly rigid planar backbone in the polythiophene system, enhancing the intermolecular π -orbital overlap. Furthermore, its zigzag motif induces curvature in the unit structure and thus offers sufficient

solubility. A striking structure of these polymers is the highly crystalline π stacking of the facing polymeric chains with a close distance of 3.6 Å. Thus, **9e** (Figure 9) with a moderate length of alkyl attached to thiophene units

Table 9. Electronic properties and OFET device data for polymers based on pentacyclic fused-thiophene-phenylene-thiophene.

	$\lambda_{\text{max}}^{\text{a)}$ nm	HOMO ^{b)} eV	$d_{\pi-\pi}^{\text{c)}$ Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
9a	510	-5.18	—	1.5×10^{-4}	—	1.4×10^4	[62]
9b	510	-5.1	—	8.3×10^{-4}	—	9.1×10^4	[62]
9c	508	-5.18	—	3.0×10^{-3}	—	1.3×10^6	[62]
9d	590	-5.43	—	3.4×10^{-3}	—	5.6×10^6	[63]
9e	540	-5.0	3.6	0.54	—	10^7	[64]

^{a)}Absorption maxima in films; ^{b)}Highest occupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum hole mobility; ^{e)}Threshold voltage.

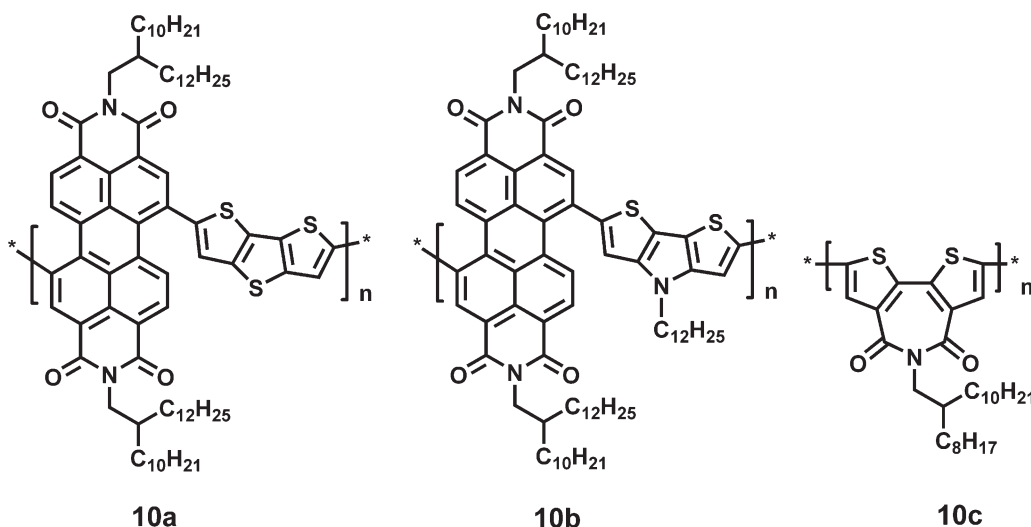


Figure 10. Chemical structure of some n-type polymers based on fused-thiophene.

exhibits a highest hole mobility of $0.54 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and an on/off ratio of 10^7 (Table 9).^[64]

Fused-Thiophene Polymers for n-Channel Field-Effect Transistors

The combination of p-channel and n-channel thin film transistors would permit complementary circuits that show much faster speed, better reliability, and better stability than unipolar circuits.^[65] Inspired by this attractive prospect, the realization of n-channel OFETs showing the equivalent performance to their p-channel counterparts becomes more and more urgent. Recent studies have demonstrated that fused-thiophene units possess the potential as comonomers of conjugated polymers in the application of n-channel OFETs or polymer solar cells as electron acceptors.^[66]

Zhan et al. pioneered the use of DTT as a comonomer coupled with *N,N'*-dialkyl-1,7-dibromo-3,4:9,10-perylene diimide (PDI) (**10a**, Figure 10). **10a** was used in bottom-gate OFETs and exhibited an electron mobility in the saturation

regime as high as $1.3 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in nitrogen.^[67] Interestingly, top-gate OFETs exhibited an electron mobility of $6 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in air (Table 10).^[68] As for **10a**-based bottom-gate device, the typical field-effect behavior can only be observed in nitrogen atmosphere. However, the mobility of top-gate device can maintain at $0.03\text{--}0.05 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for 2–7 d and typical device characteristic can still be observed even after three months in air, with a mobility of $0.005 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and an on/off ratio of 10^4 . These results clearly demonstrated the superior stability of top-gate OFETs based on **10a**.

After replacing the DTT moieties with DTP units, there gave the copolymer **10b**.^[69] The significant red shift in the low-energy absorption band seen on replacing DTT with DTP is consistent with a charge-transfer-type assignment given the more electron-rich character of DTP versus DTT. Relatively lower electron mobility ($1.2 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) was achieved for **10b** possibly due to the dilution of electron-transporting PDI units by the presence of the additional of *N*-substituent of the DTP donors.

Marks and co-workers reported synthesis of homopolymers based on a novel electron-depleted monomer of

Table 10. Electronic properties and OFET device data for n-type polymers based on fused-thiophene.

	$\lambda_{\text{max}}^{\text{abs a)}$ nm	LUMO ^{b)} eV	$d_{\pi-\pi}$ ^{c)} Å	$\mu_{\text{max}}^{\text{d)}$ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$V_{\text{th}}^{\text{e)}$ V	$I_{\text{on}}/I_{\text{off}}$	Ref.
10a	630	−3.9	—	6×10^{-2}	7	10^4	[68]
10b	747	−3.9	—	1.2×10^{-3}	8.6	10^3	[69]
10c	524	−3.47	—	1.1×10^{-2}	75	2×10^7	[70]

^{a)}Absorption maxima in films; ^{b)}Lowest unoccupied molecular orbital; ^{c)} π - π stacking distance; ^{d)}Maximum electron mobility; ^{e)}Threshold voltage.

N-alkyl-2,2'-bithiophene-3,3'-dicarboximide (BTI).^[70] The introduction of the π -electron-deficient imide moiety fused with two thiophene rings significantly increases the electron affinity of BTI. In addition, the combination of bithiophene planarity and efficient π - π stacking with the electron-withdrawing capacity of the imide makes BTI an attractive building block for electron transporting conjugated polymers. **10c** (Figure 10) displayed electron mobility of $0.01 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and on/off ratio of 10^7 under vacuum after the optimization of the device fabrication. However, the device air stability is poor due to small electron affinity of **10c** (3.47 eV).

Conclusion and Outlook

For decades, organic electronics is an emerging technology, driven by the impressive progress in the design, synthesis, and processing of organic semiconductors. Organic thin-film transistors are potentially useful for applications that require large areas distribution on flexible plastic substrate. A key challenge related to OFETs is to control electronic structures, film morphology, and device properties of organic semiconductors by modifying their chemical structures. The basic requirements for an ideal FET conjugated polymer material include: (i) good solubility and ordered-film forming properties; (ii) robust air stability and operation stability; (iii) suitable energy levels matching the available electrodes; (iv) high purity and easy to synthesize.

Among organic semiconductors, polymers based on fused-thiophene rings are considerably attractive due to their rigid and coplanar conformation, high mobility, and good environmental stability. Some fused-thiophene polymers show extremely high charge carrier mobility (0.3 – $1.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), similar to that of amorphous silicon. Since fused-thiophene polymers are among the most promising semiconductors and have received extensive attention, we have systematically reviewed the synthesis of fused-thiophene polymers and their use in high-performance FETs. We expect that some useful inspirations could be provided by our intentionally highlighting the structure–property relationships. To summarize:

- (i) The π -electron aromatic core in fused-thiophenes plays a key role in determining electronic and charge transport properties of the corresponding polymers. Thus, fused-thiophene core size and structure have been found to exhibit significant impact on the absorption, energy level, and mobility of polymers.
- (ii) The solid-state packing and charge-transport properties of fused-thiophene polymers can be tailored by fused-thiophene core or substituents on the aromatic core.
- (iii) Ambient stability of fused-thiophene polymers can be achieved through tuning the energy levels by

controlling the effective conjugation length or regulating the proportion of donor versus acceptor units. It is generally accepted that a HOMO level below -5.0 eV and a LUMO level below -4.0 eV is necessary for an air-stable p-type and n-type operation, respectively.

- (iv) Optimization of film morphology is of essential importance in achieving high charge carrier mobility. Crystalline polymers must be processed into homogeneous micro- or nanocrystalline layers with low roughness.

Acknowledgements: This material is based upon work supported in part by the NSFC (Grants 21025418, 20774104 and 21021091), the MOST (Grant 2011CB808400), and the Chinese Academy of Sciences.

Received: October 29, 2010; Published online: January 19, 2011;
DOI: 10.1002/macp.201000677

Keywords: conjugated polymers; field-effect transistors; fused-thiophenes; mobilities; structure–property relations

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