

Diketopyrrolopyrrole-based Conjugated Polymers as Representative Semiconductors for High-Performance Organic Thin-Film Transistors and Circuits

Kai-Qing Liu^{a,†}, Yuan-He Gu^{b,†}, Zheng-Ran Yi^{a,*}, and Yun-Qi Liu^{a,c*}

^a Zhuhai Fudan Innovation Institution, Zhuhai 518057, China

^b Department of Environmental Science and Engineering, Faculty of Innovation Engineering, Macau University of Science and Technology, Macau 999078, China

^c Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract Since the first report of diketopyrrolopyrrole (DPP)-based conjugated polymers for organic thin-film transistors (OTFTs), these polymers have attracted great attention as representative semiconductors in high-performance OTFTs. Through unremitting efforts in molecular-structure regulation and device optimization, significant mobilities exceeding $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ have been achieved in OTFTs, greatly promoting the applied development of organic circuits. In this review, we summarize our progress in molecular design, synthesis and solution-processing of DPP-based conjugated polymers for OTFT devices and circuits, focusing on the roles of design strategies, synthesis methods and processing techniques. Furthermore, the remaining issues and future outlook in the field are briefly discussed.

Keywords Diketopyrrolopyrrole; Polymer semiconductors; Organic thin-film transistor; Organic circuits

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INTRODUCTION

Owing to low cost, mechanical flexibility, solution processability, and tunable electronic properties, polymer semiconductors are considered as promising candidates in organic thin-film transistors (OTFTs) and electronic devices, such as switches, amplifiers, drivers and sensors.^[1–3] The key parameters to evaluate the OTFT performance include mobility (μ), threshold voltage (V_T), current on/off ratio ($I_{\text{ON}}/I_{\text{OFF}}$), open voltage (V_{ON}), and subthreshold swing (SS), among which μ is the most crucial material parameter to benchmark their electrical properties and hence evaluate the application of electronic devices.^[4,5] In recent years, great progress has been acquired in this field through developing novel materials and processing techniques.^[6–8] For instance, some reported conjugated polymers exhibited high mobilities over $1.0 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which have surpassed the performance of amorphous silicon.^[9–17] Among all the conjugated polymers, DPP-based conjugated polymers have gathered much attention due to their excellent semiconductor performance applied in OTFTs and circuits. In the system of DPP-based polymers, the high rigidity and strong

electron deficiency of the DPP unit can greatly enhance interchain π - π interactions of the polymeric backbone, facilitating charge transport.^[18,19]

It has been unambiguously demonstrated that the molecular structures of conjugated polymers, which involve both the backbone and side chain, can greatly influence on the molecular packing, energy levels, and crystallinity of the polymers, thereby affecting their device performance.^[20] Rational molecular design of conjugated polymers can effectively optimize their properties, which has become one of the most effective ways for acquiring excellent OTFT performance. Besides, synthetic methods of the polymers play a crucial role in their molecular weight, structure regularity, and then the OTFT performance.^[21,22] Therefore, synthetic method is another important factor for high-performance polymers. Moreover, solution-processing techniques can effectively control the microstructure of polymer films and thereby optimize the device performance, but also have great potentials in industrial production of large-scale and low-cost organic circuits.

In this review, we summarize recent progress from the following aspects: (1) Molecular engineering of DPP-based conjugated polymers. Strategies of backbone and side-chain engineering were introduced, highlighting the structure-property relationship of the polymers. (2) Synthesis of DPP-based conjugated polymers. Some synthesis methods were summarized and the influences of polymerization condition were also discussed. (3) Solution-processing of DPP-based conjugated polymers. Solution-processing techniques for DPP-based

* Corresponding authors, E-mail: yzr@whu.edu.cn (Z.R.Y.)

E-mail: liuyq@iccas.ac.cn (Y.Q.L.)

† These authors contributed equally to this work.

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polymers were outlined. (4) Organic circuits with DPP-based conjugated polymers. Some circuits based on DPP conjugated polymers, including inverter, oscillator and integrated circuit, were presented. At last, the remaining issues and future outlook in this field are proposed.

MOLECULAR ENGINEERING OF DPP-BASED CONJUGATED POLYMERS

In general, charge transport in polymeric thin film has two pathways: (1) intramolecular transport along the backbones; (2) intermolecular transport *via* π - π stacking. To enhance intramolecular transport, extending the effective π -conjugation of polymers is crucial, which is mainly influenced by the coplanarity and rigidity of the backbone.^[23] For the intermolecular transport, molecular packing and crystallinity of the polymers are the main influential factors.^[24] Moreover, in order to realize stable charge transport, the HOMO/LUMO (highest occupied molecular orbital/lowest unoccupied molecular orbital) energy levels of the polymers should approach the function of Au electrode, facilitating efficient charge injection. All these key factors for achieving high-performance DPP-based conjugated polymers are determined by backbone and side-chain structures. Firstly, the backbone structure could influence the coplanarity, rigidity, energy levels, molecular packing, and crystallinity of the polymers.^[25,26] Moreover, the structure of side chains has very important impacts on the molecular weight, coplanarity, molecular packing of the polymers, and their thin-film morphologies.^[27] Therefore, molecular engineering of DPP-based polymers, including backbone engineering and side-chain engineering, has been one of the most common used methods to acquire high-performance DPP-based polymer semiconductors.

Backbone Engineering of DPP-based Conjugated Polymers

To date, “acceptor architecture” strategy for backbone engineering plays an important part not only in enhancing the mobility of polymer semiconductors, but also in affecting

their charge transport characteristics, greatly promoting the development of polymer semiconductors in OTFTs. In this section, we introduce recent progress in backbone engineering of DPP-based conjugated polymers by using the strategies, including “single-acceptor architecture”, “double-acceptor architecture” and “triple-acceptor architecture” strategy.

Single-Acceptor Architecture

The utilization of “single-acceptor architecture” strategy to build donor-acceptor (D-A) structure in polymeric backbone, can greatly strengthen interchain D-A interactions and hence facilitate effective charge transport.^[28,29] The most prominent example is DPP-based polymers with D-A structure, in which DPP unit is introduced into the polymeric backbone as an acceptor. The high rigidity and strong electron deficiency of the DPP unit contribute to the enhancement of interchain π - π interactions, facilitating effective charge transport.^[20]

In early period, thiophene-based conjugated polymers with thiophene as donor aroused great concern, such as (poly(3-hexylthiophene) (P3HT), poly(3,3'-dialkyl-quatertiophene) (PQT-12), and so forth. Great progress was made in the improvement of OTFT performance, which is largely attributed to the highly ordered packing of the thiophene-based polymers.^[30,31] Also, considering the regioregularity and coplanarity of the polymeric backbone, we introduced a long β -unsubstituted oligothiophene unit (5T) as donor into DPP-based backbone to afford PDPP5T (P1, Fig. 1).^[32] In the backbone of PDPP5T, incorporation of the long 5T unit can extend the distance between two side chains attached to the DPP unit and hence reduce their steric hindrance effect, resulting in good coplanarity of the backbone and thereby inducing strong π - π interactions. The thin-film microstructure demonstrated a well-ordered lamellar structure with close π -stacking (3.65 Å) and high crystallinity. P1-based OTFT device showed high hole mobility (μ_h) and on-to-off current ratio (I_{on}/I_{off}) of 3.46 cm²·V⁻¹·s⁻¹ and 10⁸, respectively. Notably, μ_h of P1 without annealing can reach 1.05 cm²·V⁻¹·s⁻¹, indicating that P1 possesses good capability of molecular ordering at

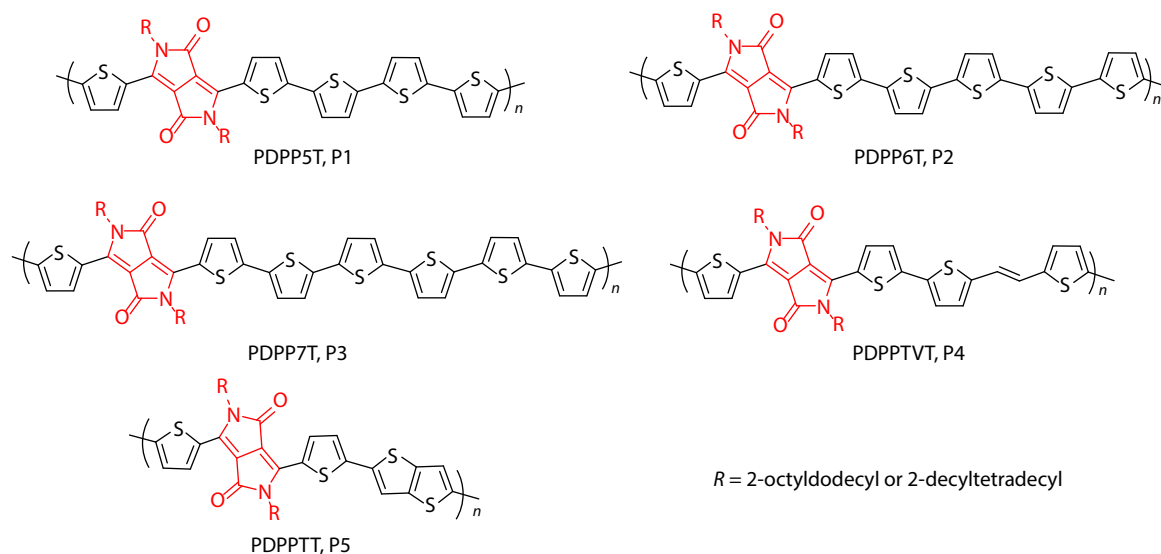


Fig. 1 Molecular structures of typical DPP-based conjugated polymers with single-acceptor architecture.

room temperature. To further investigate the influence of the space length of donor unit on OTFT performances of DPP-based conjugated polymers, PDPP6T and PDPP7T with β -unsubstituted sextetthiophene and heptetthiophene (6T and 7T) (P2 and P3, Fig. 1), respectively, were well-designed and synthesized.^[33] Remarkably high mobility of 3.94 and 2.82 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ were achieved for P2 and P3, respectively. Grazing incidence X-ray diffraction (GIXRD) characterization demonstrated that increasing the space length of donor unit enabled the polymers to construct more highly-ordered lamellar structure with short π - π stacking distance (3.69 and 3.63 Å for P2 and P3 thin films annealed at 200 and 180 °C, respectively). However, the improvement of the DPP backbone rigidity resulted in decreased solubility and low molecular weight of the polymer, which affected its solution processability, efficient charge transport, and thereby the OTFT performance. Therefore, to achieve optimal OTFT performance, it is crucial to regulate the balance among solution processability, interchain π - π stacking, and molecular weight in the molecular engineering of D-A polymers.

The incorporation of vinylene groups into the DPP backbone can effectively improve co-planarity and strengthen π - π intermolecular interactions. PDPPTVT (P4, Fig. 1) containing highly π -extended (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT) and thiophene-flanked DPP units, showed good OTFT performance with μ_h and $I_{\text{on}}/I_{\text{off}}$ up to 8.2 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and 10⁷, respectively.^[34] P4 thin film exhibited well-connected morphology and tight molecular packing with short π - π stacking distance of 3.72 Å, which is beneficial for acquiring high mobility.

Besides non-fused rings, fused aromatic ring is also a promising type of building block for molecular engineering of DPP-based conjugated polymers. The fused aromatic rings facilitate the formation of π - π stacks with wide area of overlap and the induction of high-ordered molecular packing, leading to high crystallinity and effective charge transport *via* intermolecular hopping.^[35] In 2012, we designed and prepared a high-molecular-weight DPP-based conjugated polymer P5, in which fused ring of thieno[3,2-*b*]thiophene (TT) was combined with dithienyl-DPP aromatic moieties.^[22] Theoretical calculations showed that P5 with TT moiety possessed smaller reorganization energy and higher coupling strength in comparison to DPP-based conjugated polymers with other donor components (thiophene or furan), implying tighter molecular packing and more efficient charge transport for P5. GIXRD characterization (Fig. 2) indicated a short π - π stacking distance of 3.43 Å and high crystallinity for this polymer. High-resolution transmission electron microscopy (TEM) analysis (Fig. 2) further demonstrated the close π - π stacking (0.334–0.349 nm for π - π stacking distance) in highly crystalline areas of thin film. OTFT devices based on P5 a remarkably high μ_h up to 10.5 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, with $I_{\text{on}}/I_{\text{off}}$ over 10⁶ and milli-ampere-order drain current. Note that it is the first to achieve high mobility over 10 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ in polymer-based OTFTs.

Double-Acceptors Architecture

Besides the electron-donor building blocks, the introduction of an additional electron-acceptor building block (benzothiadiazole, DPP or thiazolothiazole, etc.) into the DPP backbone to construct double-acceptors architecture is also an

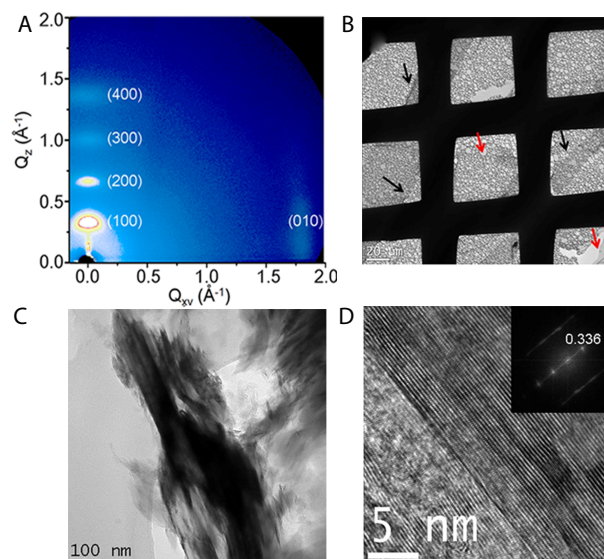


Fig. 2 GIXRD pattern (A) and TEM images (B, C and D) of P5 thin films. (Reproduced with permission from Ref. [17]; Copyright (2012) Springer Nature).

effective strategy for achieving high mobility, especially ambipolar mobility.^[36] In this architecture, two introduced acceptors can greatly improve interchain interactions through heteroatom contacts or π - π stacking and hence induce well-ordered packing.^[37] Moreover, it endows the polymers with the low-lying HOMO/LUMO energy levels, leading to improved oxidative stability and efficient electron injection.^[38]

Based on this architecture, we developed PDPPTzBT (P6, Fig. 3) with thiazolothiazole (Tz) and DPP acceptor moieties, exhibiting high μ_h exceeding 3.4 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ under gentle annealing condition.^[39] The optical property showed that P6 thin film had a distinct absorption shoulder at 718 nm, indicating the formation of an ordered structure. Atomic force microscope (AFM) and GIXRD characterizations revealed highly ordered molecular packing with short π - π stacking distance (3.52 Å) and strong-crystallinity structure in P6 thin film, suggesting that incorporating the Tz acceptor moiety into DPP-based polymer enables to form tight π - π stacking with large-area overlap. Afterwards, a novel DPP-based polymer PDBPy-DT2FBT was reported (P7, Fig. 2), in which 5,6-difluorobenzo-*c*[1,2,5]thiadiazole (2FBT) and DPP building blocks were used as two acceptors in thiophene backbone.^[40] Due to high electron-affinity of two acceptor units and then the induction of strong D-A interactions, P7 exhibited low LUMO energy level and short π - π stacking distance up to -4.02 eV and 3.52 Å, respectively, facilitating effective electron injection and transport in OTFT devices. It was also demonstrated that the introduction of the two acceptors endows the polymer with good capability of ordered packing and high crystallinity at low temperatures, likely due to the extended π -conjugation and large co-planarity in the backbone. The above factors led to distinct ambipolar characteristics for P7-based OTFTs under gentle annealing conditions (80 and 100 °C), with high hole and electron mobilities (μ_e) of 0.24 and 0.65 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, respectively.

Incorporating one additional DPP acceptor moiety into DPP

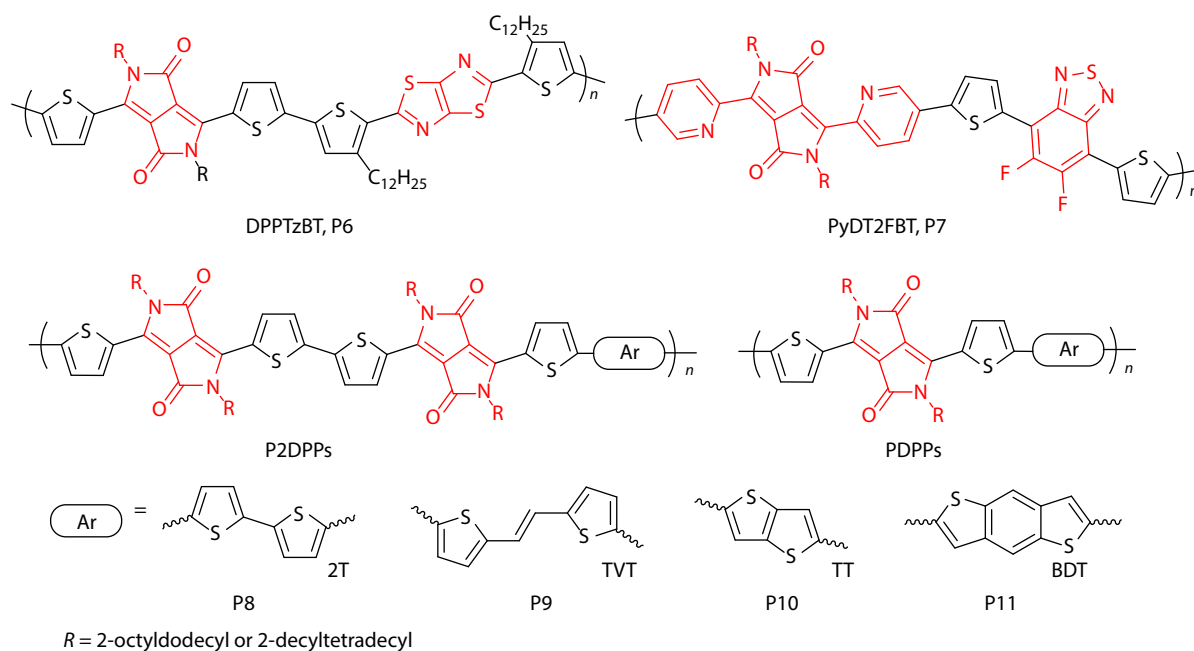


Fig. 3 Molecular structures of typical DPP-based conjugated polymers with double-acceptor architecture.

backbone to construct double-DPP (2DPP) architecture is a facile strategy for high ambipolar polymers. Recently, we designed a series of 2DPP-based polymers (P2DPPs, P8–P11).^[41] In the synthetic procedure, 2DPP monomer was prepared through dimerizing DPP, and followed by the coupling polymerization of 2DPP and thiophene-based monomers (2T, TVT, TT or BDT) to afford the target polymers. The optical property revealed that P2DPPs exhibited a remarkable red shift of optical absorption relative to the polymers with one DPP acceptor moiety (PDPPs), implying the enhanced intra- and intermolecular interactions for P2DPPs. Also, incorporation of additional DPP building block endows P2DPPs with about those of PDPPs, which is favourable for effective electron injection. P2DPPs-OTFT devices with plastic substrates exhibited excellent ambipolar transport behaviors, of which P9 showed well-balanced ambipolar characteristics with μ_h/μ_e up to 4.16/3.01 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Triple-Acceptors Architecture

We first proposed “triple-acceptors architecture” strategy for designing high-performance ambipolar polymers, in which three electron-deficient acceptors and appropriate electron-rich donors are introduced.^[42] On one hand, the use of this architecture can further induce more D-A interaction between polymer chains and more charge coupling relative to the single-acceptor or double-acceptors architectures, resulting in more effective intra- and intermolecular charge transports. On the other hand, more donor/acceptor building blocks can be selected in molecular engineering of the backbone, facilitating the fine-tuning of the energy levels for efficient hole/electron injections.

Based on this strategy, a triple-acceptors polymer P2DPP-BT was designed and synthesized (P12, Fig. 4), in which each of three acceptors, including two DPP and one benzothiadiazole (BT), is flanked by thiophene donors to balance hole/electron transports and diminish steric hindrance of side

chains.^[24] Strong electron deficiency of the triple-acceptors moieties can effectively strengthen interchain interactions with shorter π - π stacking distance of 3.70 Å (versus 3.73 Å for double-acceptors polymer DPP-TBT), and also achieve lower HOMO/LUMO energy levels of $-5.38/-4.19$ eV (versus $-5.20/-4.00$ eV for DPP-TBT), facilitating effective charge injection and interchain hopping *via* π -stacking. OTFT devices based on P2DPP-BT displayed balanced ambipolar transport performance, with high μ_h/μ_e of up to 3.01/3.84 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Recently, the strategy was also utilized to develop a series of triple-acceptors polymers, including P2FDPP-BT, P2FDPP-BO and P2FDPP-BSe (P13–P15).^[42] In this system, two DPP and one benzo-fused ring (BT, BO or BSe) were used as acceptor building blocks to construct a triple-acceptors architecture, in which fluorothiophene (FT) unit is flanked by dithienyl-DPP unit. Photophysical properties revealed that the introduction of F atoms enabled the corresponding polymers to have a tendency of H-aggregation of the molecules (face-to-face packing), facilitating the formation of π - π stacks with large area of overlap. Microstructure characterization further demonstrated that the polymers with FT units exhibited highly ordered molecular packing with face-on orientation and tight π - π stacking. All these triple-acceptors polymers exhibited typical ambipolar transport performance, in which P2FDPP-BT displayed high and well-balanced hole/electron mobilities of up to 3.56/3.7 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Side-chain Engineering of DPP-based Conjugated Polymers

The introduction of suitable side chains is crucial to the solubility and solution-processability of the target polymer, thereby influencing its device performance. Additionally, side-chain structure has very important impact on the molecular weight, co-planarity of the polymer, and hence molecular packing and morphology of polymer thin film.^[15] Therefore, side-chain engineering, involving alterations in shape, position, length and

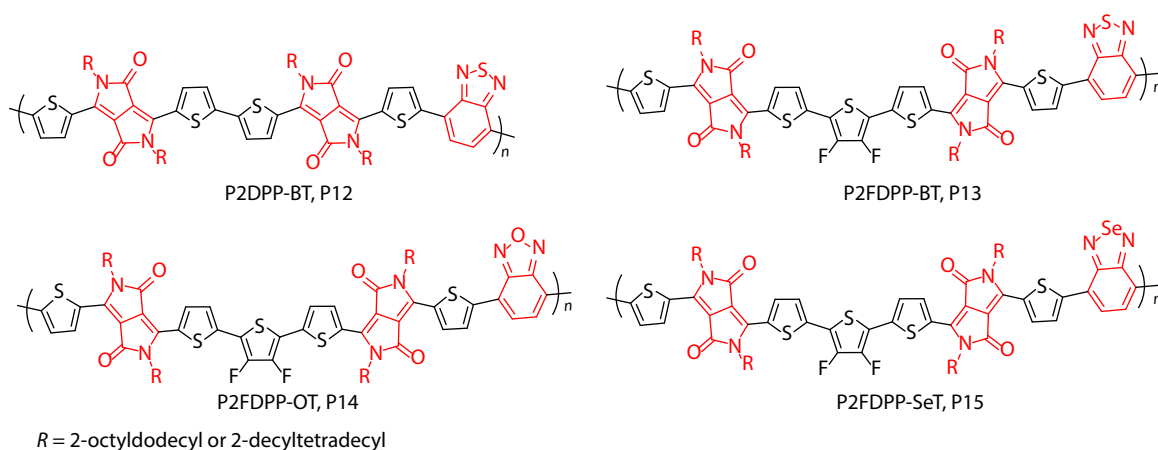


Fig. 4 Molecular structures of typical DPP-based conjugated polymers with triple-acceptors architecture.

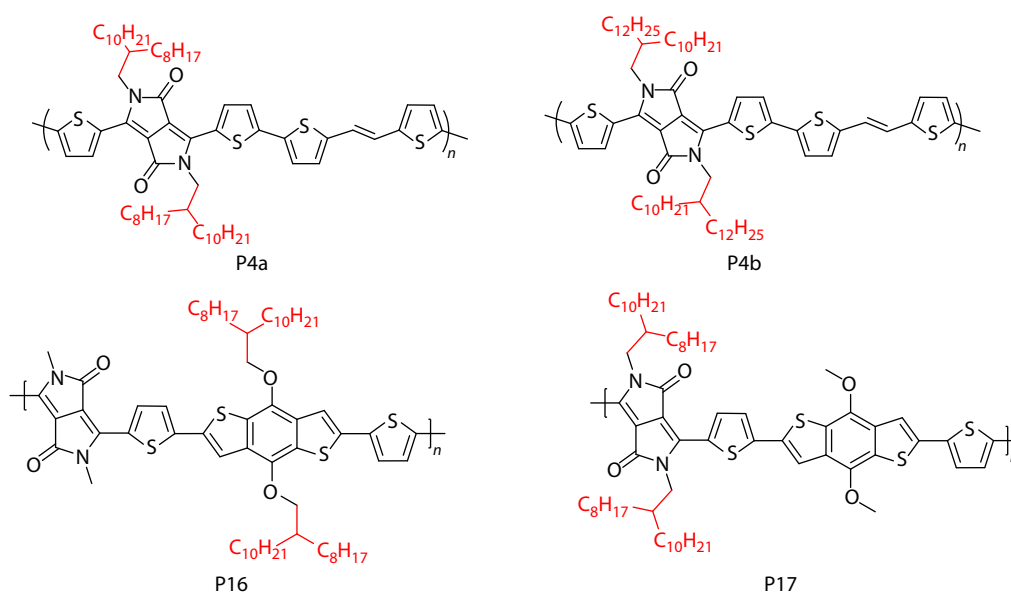


Fig. 5 Investigation of the side-chain length and position in DPP-based polymers.

so on, has been considered as a feasible strategy to obtain high-performance polymers. This section focuses on the side-chain engineering of DPP-based polymers from the aspects of side-chain length and position.

The length of side chain can greatly influence molecular packing and hence charge transport properties of conjugated polymers.^[43] A classic example is the side-chain engineering of poly(3-alkylthiophene). In thiophene-based polymer system, adopting hexyl groups as side chains enables P3HT to have an edge-on packing orientation, leading to higher mobility relative to the counterparts with other alkyl chains.^[30] To investigate the effect of side-chain length on the OTFT performance of DPP-based conjugated polymers, we designed and synthesized two DPPTVT-based polymers with different-length side chains (2-octyldodecyl and 2-decyltetradecyl side chains for P4a and P4b, respectively).^[34] GIXRD characterization revealed that P4b with longer alkyl chains had a shorter π - π stacking distance than P4a (3.66 versus 3.72 Å), implying stronger interchain interaction in P4b film. Furthermore, the AFM images of polymer thin films manifested

higher crystallinity with large-size grains in P4b film. The tighter molecular packing and better morphology contributed to excellent charge transport properties of P4b, with higher μ_h of 8.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (versus 4.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for P4a).

Side-chain position also plays an important role in molecular engineering of high-performance DPP-based polymers. We first investigated the effect of bulky side chains attached to acceptor or donor unit on the properties of the polymers. In this molecular engineering, DPP and BDT were used as acceptor and donor moieties, respectively, to construct D-A polymers (P16 and P17, Fig. 5), in which the bulky side chains were attached at BDT units for P16 and at DPP units for P17.^[44] GIXRD analysis revealed a larger π - π stacking distance of 3.88 Å for P17 relative to P16 (3.55 Å), whereas P17 displayed much higher μ_h than P16 by almost two orders of magnitude (0.29 versus 0.004 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). We proposed that packing regularity of the polymers played an important part in charge transport. Compared with P16, P17 exhibited approximate 100 nm red-shift of absorption maxima in solution and two distinct maximum absorption peaks in thin film, in-

dicating that the higher coplanarity of the P17 backbone in solution and hence the formation of more well-ordered structure after coating. Additionally, AFM images showed many observed voids in P16 film and good-connectivity structure in P17 film, which is also important evidence to explain the higher performance in P17-based OTFTs. This work unambiguously demonstrated that side-chain position greatly influenced the molecular packing, film morphology and charge transport behavior of DPP-based polymers, which is crucial to the achievement of excellent OTFT performance.

SYNTHESIS OF DPP-BASED CONJUGATED POLYMERS

Synthetic methods of polymer semiconductors play a crucial role in determining the structural integrity, molecular weight and polydispersity, greatly influencing their OTFT performance. Generally, DPP-based conjugated polymers are prepared through Suzuki or Stille coupling polymerization of halide monomer with boronic ester (Suzuki) or trialkyltin (Stille) monomer, in which Pd(0) or Pd(II) catalysts is used as catalysis. Despite some advantages in low toxicity and good stability of boronic ester monomer, Suzuki coupling polymerization is mainly restricted to moderate electron-rich moieties, such as carbazoles, fluorenes and so forth, likely due to the tendency of the hydrolysis in the moieties.^[45] Additionally, in order to realize effective coupling and achieve high molecular weight, the selection of suitable base is required for optimizing the hydrolysis.^[46,47] For the Suzuki-polymerization preparation of DPP-based polymers, achieving high molecular weight is still a challenge. For example, P2DPP-BT, which was synthesized through Suzuki polymerization of brominated DPP and boronic-ester BT moieties (Fig. 6), exhibited low number-average molecular weights (M_n) of 11.6 kDa.^[24] Unlike Suzuki polymerization, Stille polymerization has relatively simple for lack of the hydrolysis process, facilitating the achievement of high molecular weight. As a result, Stille polymerization is the most common method for the preparation of polymer semiconductor in OTFTs, especially DPP-based polymers. In the process of Stille polymerization, polymerization time, polymerization temperature and catalyst system are the key factors for achieving high molecular weight. For the synthesis of PDPPTT, the prolongation of polymerization time from 48 h to 60 h, can increase the M_n of the polymer from 27.8 kDa to 44.0 kDa, leading to improved μ_h value up to $3.46 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (versus $1.24 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).^[32] Fig. 5 shows the synthesis route of

PDPPTT.^[17] Results showed that the use of $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tol})_3$ as catalyst system and the employing high reaction temperature of $130 \text{ }^\circ\text{C}$, contributed to achieving high M_n (11.0 kDa) for PDPPTT, and hence excellent OTFT performance with μ_h of up to $10.5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.

Although Stille polymerization is an effective method for achieving high molecular weight, the monomers always suffer from tedious synthesis and high toxicity of the raw materials and byproducts, such as trialkyltin halides, probably hindering the applied development of polymer semiconductors.^[48] Since the first report of direct C—H activation polymerization (or called direct arylation) applied in the synthesis of polymer semiconductors,^[49] the method has gained much attention because of the simple preparation of monomers. However, low reactivity and poor selectivity of C—H bonds are particularly two challenging issues for C—H activation polymerization, resulting low molecular weight and high structure defects.^[50] In recent years, some progresses have been made in this field. It has been demonstrated that optimizing polymerization conditions is an effective way for high-regularity polymer semiconductors.^[51] Recently, a series of DPP-based conjugated polymers (P13–P15, Fig. 7) were successfully synthesized through C—H activation polymerization.^[42] The synthetic route is illustrated in Fig. 7. It was found that the solvent polarity and catalyst system had an outstanding effect on the reactivity for C—H activation polymerization. For instance, the utilization of $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tol})_3$ and DMAc/toluene mixtures in appropriate stoichiometry (1:1) as catalyst system and reaction solvent, respectively, can effectively shorten C—H activation polymerization time to 1 h, affording a higher- M_n polymer P13b than “Suzuki-version” polymer (25 versus 16 kDa for M_n). OTFT characterization revealed the higher M_n of the polymer led to its better OTFT performance ($2.03/1.64$ versus $1.36/1.22 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for μ_h/μ_e).

Recently, a “chain-extending polymerization” strategy was proposed to prepare DPP-based conjugated polymer.^[52] In the polymerization procedure (Fig. 8), prepolymer PDPPTT-a was prepared by Stille polymerization of the TT and DPP monomers, and followed by secondary polymerization with the vinylene monomer to afford PDPPTT-vinylene (P18). By comparing with PDPPTT (P5), it was demonstrated that incorporating the vinylene linkers into the backbone in secondary polymerization process, played an importance role in not only expanding π -conjugation system, but also strengthening interchain π - π interactions and fine-tuning the energy level of the polymers, leading to excellent OTFT performance for P18

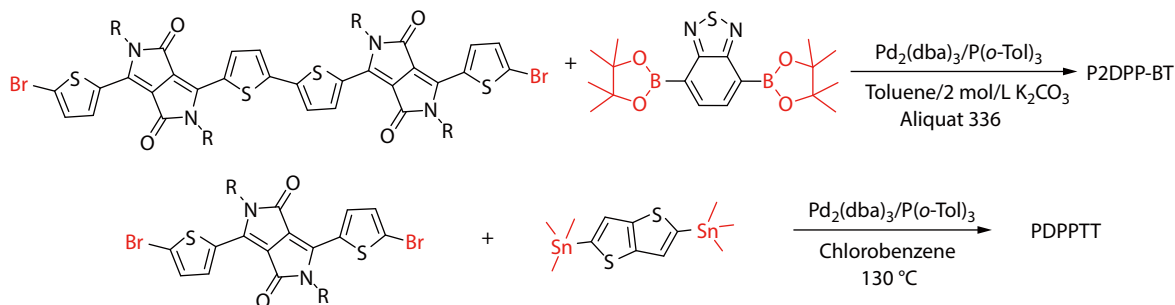


Fig. 6 Typical examples of Suzuki and Stille polymerization for the synthesis of DPP-based polymers.

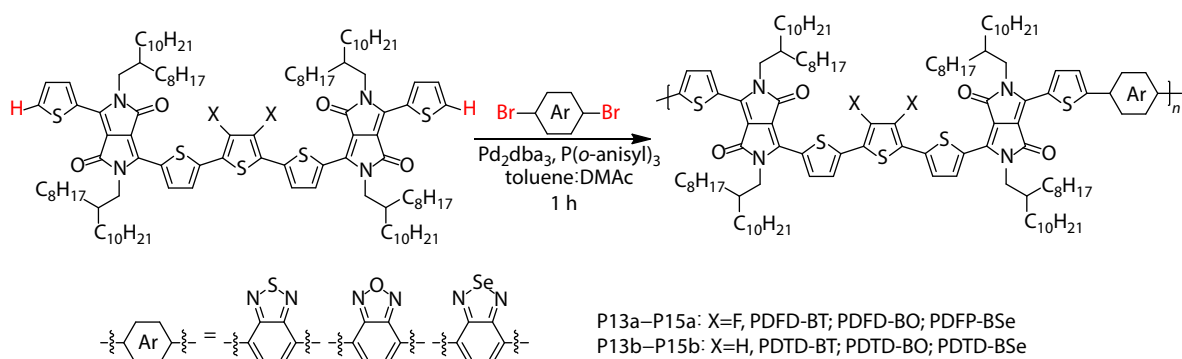


Fig. 7 Typical example of C–H polymerization for the synthesis of DPP-based polymers.

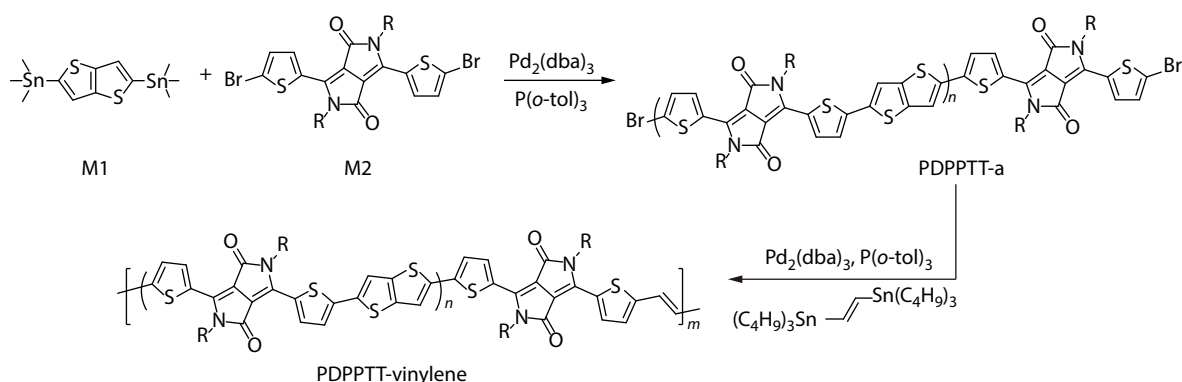


Fig. 8 Typical example of chain-extending polymerization for the synthesis of DPP-based polymers. (Molar ratio of M2 to M1 is 1.1.)

with μ_h/μ_e of 3.70/2.96 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (versus 2.71/0.63 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for P5). This work provided a new synthesis strategy for preparing high-performance DPP-based conjugated polymers.

SOLUTION PROCESSING OF DPP-BASED CONJUGATED POLYMERS

The development of polymer-based OTFTs is greatly dependent on advances in not only rational molecular-engineering of polymer semiconductors, but also their processing methods. Owing to high solubility and good film-forming ability, polymer semiconductors are ideal candidates for solution-processing in the fabrication of OTFT devices, facilitating industrial production of large-scale and low-cost organic circuits. Common solution-processing methods includes spin coating, bar coating, solution shearing, drop casting, and printing (Fig. 9). This section focuses on the methods in the fabrication of OTFT devices with DPP-based polymers as semiconducting layer.

Due to its simplicity and high-efficiency, spin coating is the most frequently-used solution-processing method to fabricate OTFTs with DPP-based polymers. Through the spin-coating method, well-ordered and high-crystallinity PDPPTVT films were successfully prepared. In the fabrication procedure, source-drain electrodes were prepared through photolithography. Subsequently, a PDPPTVT solution was deposited onto the substrate through spin-coating to form the polymer film, and followed by the encapsulation of polymethyl methacrylate. OTFT characterization revealed the spin-coated PDPPTVT film exhibited high μ_h value of 8.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.^[34]

Through this method, remarkably high mobility of 10.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ was also achieved for PDPPTT-based OTFTs.^[22]

Bar coating method has great potentials in the production of large-area film, in which three main steps are involved: depositing polymer solution onto the substrate, wet-coating the solution by coating bar, and drying the film. In addition, the crystallinity and packing orientation of polymer semiconductors can be effectively controlled by using bar-coating method.^[58] Noh *et al.* found that bar-coated PDPPTT film showed stronger crystallinity and better morphology compared with spin-coated one, leading to improved μ_h (2.73 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) and excellent performance in organic circuits. Recently, Geng *et al.* utilized bar coating method for successful preparation of PDPPTT (DPP-tripletiophene-based polymer) film with aligned microstructure, exhibiting high μ_h and reliability factor of 9.24 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and 87%.

Drop casting method involves the dropping of a polymer solution onto a substrate, and the subsequent formation of polymer thin films after solvent evaporation. The challenge for this method is to effectively control the uniformity of polymer films, which is not beneficial for charge transport. Han *et al.* reported an improved drop-casting method, named solvent vapor enhanced drop-casting (SVE DC), to prepare PDPPTT thin film. In the process, a substrate with polymer solution was placed in lidded Petri dishes to reduce the rate of solvent evaporation.^[59] As a result, polymer chains were sheared by the receded contact line and rearranged to form aligned structure. Transmission electron microscopy (TEM) and GIXRD characterization revealed highly uniform morphology and well-ordered packing with edge-on orientation.

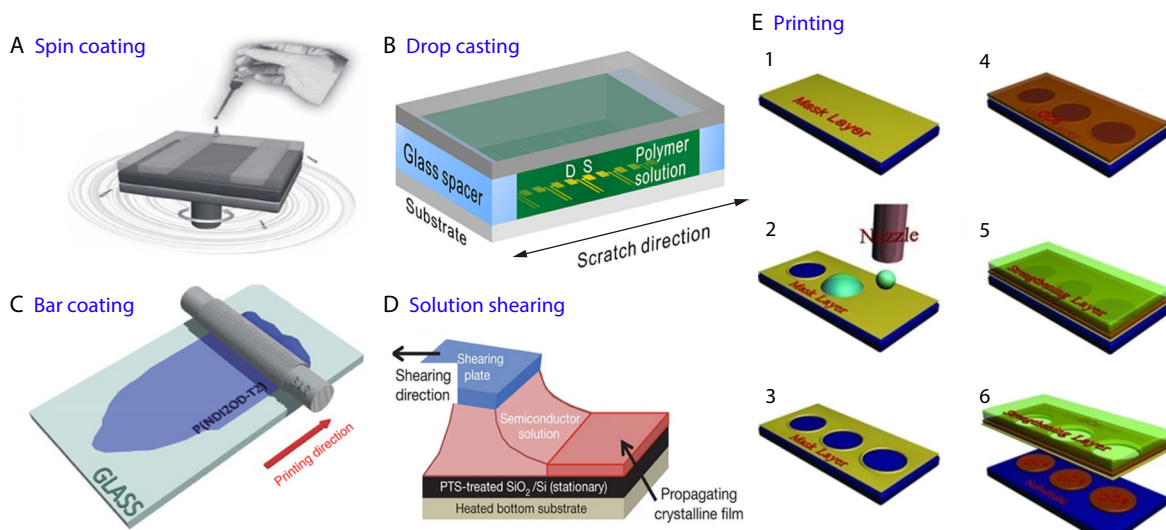


Fig. 9 (A) Schematic illustration of the spin coating process. (Reproduced with permission from Ref. [53]; Copyright (2013) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (B) Schematic illustration of the drop-coating process. (Reproduced with permission from Ref. [54]; Copyright (2014) American Chemical Society). (C) Illustration of the bar-coating process. (Reproduced with permission from Ref. [55]; Copyright (2015) Springer Nature). (D) Schematic illustration of solution shearing. (Reproduced with permission from Ref. [56]; Copyright (2011) Springer Nature). (E) Schematic illustration of inkjet-printing. (Reproduced with permission from Ref. [57]; Copyright (2012) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

Solution shearing is an effective method for acquiring highly oriented films. In the process, a semiconductor solution is added between two sheets of the shearing plate and the preheated substrate that slide pass each other. The processing method contributes to effective control of alignment degree, morphology and molecular packing. Based on DPP-based polymer (PDPPTzBT), oriented films were successfully prepared by using the solution-shearing method.^[60] AFM images revealed that the polymer films showed an orientation along the direction of solution shearing. GIXRD analysis further demonstrated that the solution-shearing direction was aligned with the backbone and the films exhibited well-ordered packing with an edge-on lamellar structure. As a result, the highly-oriented films displayed high μ_h up to $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.

Printing technique is well suited to low-cost and large-scale production of OTFT devices and circuits.^[61] In which the prepared films can be readily patterned. Printing technique includes inkjet printing, spray printing, gravure printing, screen printing, transfer printing, and so forth. More details on these techniques are given in some reported reviews.^[2,62] For DPP-based conjugated polymers, some printing techniques have successfully been used to fabricate OTFT devices and circuits. For instance, Caironi *et al.* reported PDPPTVt-based OTFT by using inkjet-printing technique, which exhibited uniform transport property at low operating voltages and thereby enabled complementary logic circuits to operate at a low voltage bias.^[63]

ORGANIC CIRCUITS

With the fast development of material science and processing technology, DPP-based conjugated polymers have become a type of outstanding semiconductor used in high-performance OTFT devices, which enables promising applications in organic

circuits, such as inverters, oscillators, sensors, drivers and so on.^[64,65]

The inverters are the basic units of organic circuits, which are often used as a standard for testing device performance and verifying feasibility in complex organic circuits. In the structure of an inverter, two OTFTs are serially connected to each other. Generally, organic inverters have two architectures: (1) complementary architecture, involving a p-type and an n-type OTFTs, or two ambipolar OTFTs; (2) unipolar architecture, involving two p-type OTFTs or two n-type OTFTs. The architecture selection for the inverter mostly depends on charge transport characteristic in polymer-based OTFTs. To simplify the fabrication process and reduce costs, developing ambipolar polymer semiconductors is a feasible way for the inverters and logic circuits. For instance, on basis of P2DPP-BT, exhibiting balance ambipolar behaviors with high hole/electron mobilities of $3.01/3.84 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, a complementary-like inverter was successfully fabricated.^[24] This inverter showed apparent switching-action responses and a high value of 171, implying a promising application in logic circuits. Odd numbered inverters are integrated to yield a ring oscillator, which is widely applied in voltage-controlled oscillators, decorative lights, audio systems, *etc.* Owing to good p-type transport property of PDPPTT, a unipolar-architecture inverter and a five-state ring oscillator based on this polymer were also reported,^[22] exhibiting a high value and a switching frequency of up to 92 and 1.2 kHz, respectively (Fig. 10).

Besides logic circuits, polymer-based OTFTs can effectively applied in analog circuits, such as sensors. Sensors are a type of election devices that can deliver output from sensing changes in the environment (Fig. 11), in which involves light, pressure, temperature and so on. Due to the function of signal amplification, OTFT-based sensors typically exhibit high sensitivity. For example, a photo sensor based on DPP-based

polymer DPP4T-co-BDT was reported,^[67] exhibiting remarkably high photoresponsivity photocurrent/dark-current ratio of $4.0 \times 10^3 \text{ A} \cdot \text{W}^{-1}$ and 6.8×10^5 , under low-intensity white light. Recently, a near-infrared organic photodetector was built on an inverted structure with a thick active layer of PDPPDTT and PCBM. The device showed a high specific detectivity of 8.28×10^{11} Jones under near-infrared light ($0.53 \mu\text{W} \cdot \text{cm}^{-2}$) (Fig. 11).^[68]

Polymer-based OTFTs can be also applied in complex in-

tegrated circuits. For example, the transistors have a promising application in the drive circuits for active-matrix organic light-emitting diode (AMOLED), facilitating the development of flexible display.^[69] Excellent OTFT performance and good solution-processability for DPP-based polymers would enable the realization of the light-emitting driving. Recently, an OTFT-OLED active circuit ($5 \text{ cm} \times 5 \text{ cm}$) based on PDPTVT (P4) was reported.^[70] Results showed that OTFT devices exhibited a switch-on state at the constant gate voltage of -50

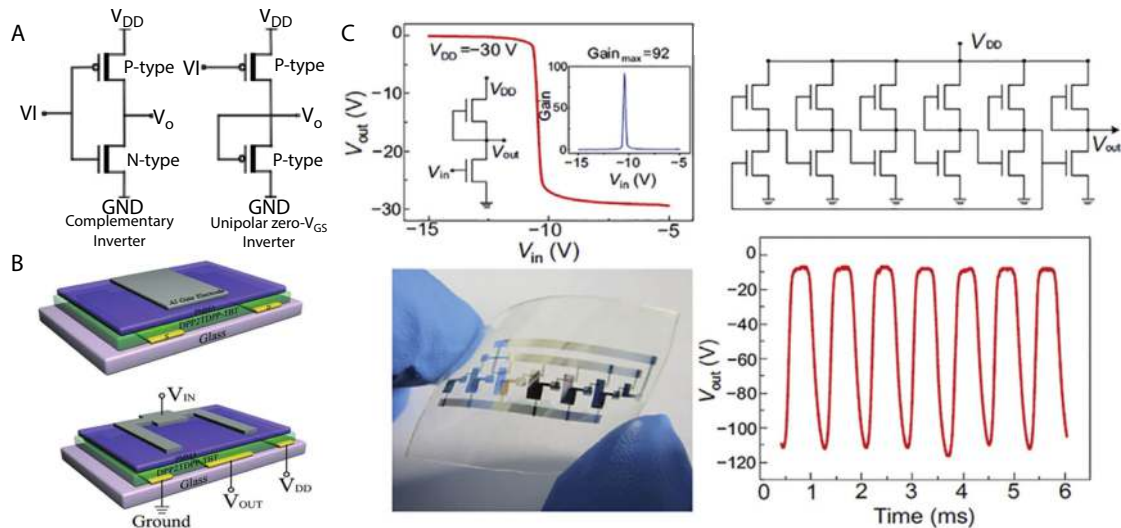


Fig. 10 (A) Circuit diagram of complementary inverter and unipolar-inverter. (B) Schematic diagrams of OTFTs and inverter based on P2DPP-BT. (C) Schematic diagrams and electrical performance of inverter and oscillator circuit based on PDPTT. (Reproduced with permission from Ref. [22]; Copyright (2012) Springer Nature).

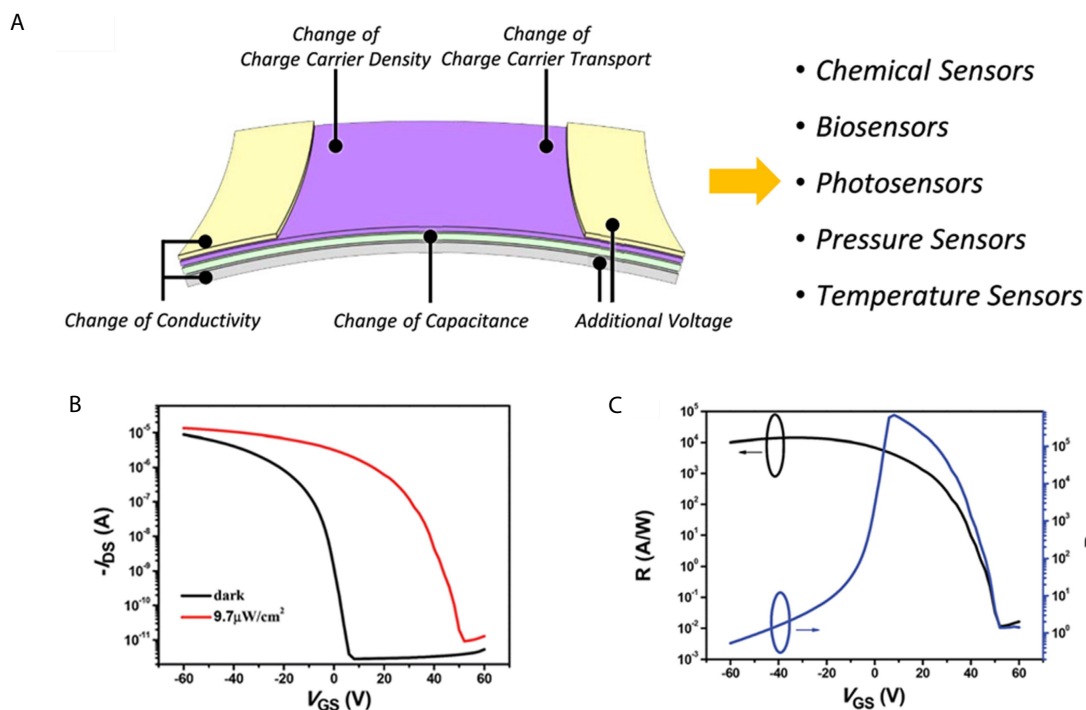


Fig. 11 (A) Schematic diagram of representative OTFT-based sensors. (Reproduced with permission from Ref. [66]; Copyright (2017) Elsevier). (B) Electric performance of sensors based on DPP4T-co-BDT thin films. (Reproduced with permission from Ref. [67]; Copyright (2015) The Royal Society of Chemistry).

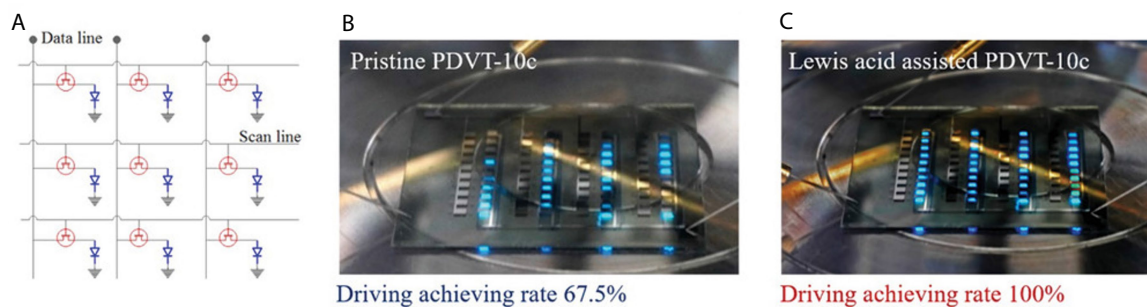


Fig. 12 Circuit diagram (A) and optical images (B, C) of the OTFT-OLED active circuit based on PDPTVT. (Reproduced with permission from Ref. [65], Copyright (2021) Wiley-VCH GmbH).

V and provided an enough current density ($\approx 0.625 \text{ mA}\cdot\text{cm}^{-2}$) to drive the OLED, achieving an electroluminescent brightness over $100 \text{ cd}\cdot\text{cm}^{-2}$ (Fig. 12). Moreover, active circuit showed a driving achieving rate of up to 100% after adding protonic aid. The work also revealed the potential of DPP-based polymers in organic circuits.

SUMMARY AND OUTLOOK

Over the last few decades, DPP-based conjugated polymers have become representative semiconductors to apply in high-performance organic thin-film transistors and circuits, greatly promoting the development of organic electronics. In the review, we firstly outline recent progress in molecular design and synthesis of DPP-based conjugated polymers. The results indicate that backbone and side-chain engineering, polymerization-conditions adjustments are effective strategies for fine-tuning the energy levels, molecular packing, and crystallinity of the polymers, facilitating efficient charge carrier injection and transport. Combining with the development of fabrication technologies, DPP-based polymers have become ideal candidates for solution processing in the fabrication of high-performance OTFT devices with the mobility over $10 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, thereby promoting the applied development of organic circuits.

Although outstanding achievements have been made in OTFT devices and circuits on basis of DPP polymers, some key issues must be addressed to promote their commercialization. Firstly, it still requires achieving higher-performance DPP-based polymers for the purpose of applications, which involve p-type, n-type or ambipolar semiconductors. In order to optimize their properties, the design and synthesis strategies are required to be developed for new DPP-based polymers, including the invention of novel building blocks and side chains, the development of new molecular architectures and catalyst system, for example. Furthermore, solution-processing techniques play a key role in not only guiding the molecular design of DPP-based conjugated polymers, but also fabricating high-performance OTFT devices and circuits. However, current techniques generally suffer from complex multilayer structure of OTFT devices and circuits, which is extremely vulnerable to interface, temperature, etc. Therefore, new solution-processing techniques are desired for achieving uniform and reproducible film, facilitating industrial production of large-scale organic circuits.

BIOGRAPHIES

Zheng-Ran Yi received his PhD degree in organic chemistry from Wuhan University in 2012. After postdoctoral research at Purdue University, he joined Zhuhai Fudan Innovation Institute as a researcher. His research focuses on the design and synthesis of polymer semiconductors for organic field-effect transistors.

Yun-Qi Liu graduated from Nanjing University in 1975, received a doctorate from Tokyo Institute of Technology, Japan, in 1991. Presently, he is a professor at the Institute of Chemistry, an Academician of CAS, and a Member of TWAS. His research interests include molecular materials and devices, the synthesis and applications of carbon nanomaterials, and organic electronics.

NOTES

The authors declare no competing financial interest.

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