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Recent advances on polymer phototransistors

Pengcheng Gu,a,b† Yifan Yao,b† Linlin Feng,a,b Shujie Niu,a,b Huanli Dong,a,b,*

Phototransistor, a kind of optoelectronic devices that realizes the functionality of light detection and signal magnification in a single device, is an important component of optoelectronic integration. Polymer phototransistors, compared to traditional inorganic phototransistors, demonstrate attractive advantages of light-weight, low-cost, easy solution processing and flexibility, and are the best candidates for Plastic Optoelectronics. Over the past years, significant advances have been achieved for polymer phototransistors with the development of new polymer semiconductor materials and the optimization of device fabrication techniques. In this review, we will give an overview of recent advances on polymer phototransistors, from a brief introduction of the device geometry, working mechanism, performance parameters to the development of device performance and the exploration of their flexible optoelectronic devices. Finally, a perspective and conclusion is also briefly addressed.

1 Introduction

Organic semiconductors have attracted considerable attention over the past decades due to their attractive advantages such as light weight, low cost and easy processing, which make them demonstrate potential applications in large-area flexible organic devices/circuits.1–3 Among them, organic field-effect transistors (OFETs), a key component of organic electronics, have received remarkable progress4–6 with the field-effect mobility significantly increased from the initial value7 of \(10^{-6}\) to the state-of-art value of 43 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for small-molecule semiconductors8 and 36.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for polymer semiconductors.9 Under the development of high performance OFETs, recently, bi/multi-functional OFETs, where two or more types of physical properties are combined together in a single device, have also received increasing interest due to their scientific and technological significance in organic electronic integration, for example organic phototransistors (OPTs).10–14 The concept of phototransistors was first proposed by William Shockley in 1951.15 Compared to photodiodes, phototransistors can exhibit much higher sensitivity and lower noise due to the unique working mechanism of field-effect transistors. Moreover, phototransistors combine light detection and signal amplification together in a single device, and can be easily integrated into various optoelectronic devices/circuits, such as light switches, light memories and light detectors, etc., as shown in Figure 1.10

OPTs are generally divided into two types, such as small-molecule OPTs (SOPTs) and polymer OPTs (PPTs) depending on the types of active layers. Recently, the photoresponsivity of SOPTs has already reached up to 12000 A W\(^{-1}\), which is comparable to that of inorganic phototransistors.13 Over the past several years, great achievements have also been obtained in PPTs under the considerable efforts of chemical scientists for the development of polymer semiconductors and device physicists for the improvement of device fabrication techniques.14,16 In comparison with small molecules, polymer semiconductors exhibit much better solution-processing ability, and compatibility with plastic substrates. Moreover, from molecule perspective, conjugated polymers have much larger conjugation length and broader optical absorption, which enable them more beneficial for optoelectronic devices.13,14 In this MiniRev, we attempt to present a systematic summary of these significant advances on PPTs. In section 2, we will first give a brief introduction with the purpose of offering an intuitive understanding of OPTs including typical structure geometry, working mechanism and basic performance parameters. In section 3, we will focus on the specific research progress of PPTs including the development of material systems and the improvement of device physics. Finally, the exploration of flexible devices and circuits based on PPTs and concise perspectives and conclusion are also briefly demonstrated.
Figure 1. Demonstration of the potential applications of phototransistors. G: gate, D: drain electrode, S: source electrode. (a) optoisolators: the optoisolator is similar to a transformer in that the output is electronically isolated from the input; (b) highly sensitive optical switches: an object is detected when it enters the gap of the optical switch and blocks the light path between the emitter and detector; (c) retro sensors: the retro sensor detects the presence of an object by generating light and then looking for its reflectance off of the object to be sensed; (d-e) basic circuits; and (f) a circuit with greater voltage-switching capability. Copyright with permission from ref. [10] Copyright 2007, John Wiley & Sons.

2 A brief illustration of OPTs

In order to give a comprehensive understanding of OPTs, in this section, we will first briefly outline the fundamentals of device structures, working principles and basic performance parameters for OPTs.

2.1 Device structures of OPTs

The device structures of OPTs are mainly derived from that of OFETs, and also consist of four typical structures: bottom-gate/top-contact (BGTC), bottom-gate/bottom-contact (BGBC), top-gate/top-contact (TGTC) and top-gate/bottom-contact (TGBC), according to the relative positions of dielectric layer, active organic layer and source/drain electrodes. The only difference for OPTs from OFETs is the fourth terminal, light illumination incorporated in the device geometry. According to the position of light illumination, the structures can be further divided into top-light illumination (TL-) and bottom-light illumination (BL-), as shown in Figure 2. It should be stated that whether for TL- or BL-geometries, the gate dielectric layer used in these structures, such as TL-TGBC, TL-TGTC, BL-BGTC and BL-BGBC should be transparent enough in order to guarantee the light efficiently arriving on the active organic semiconductor layer for high device performance.

Figure 2. Typical device geometries used for OPTs, specifically including six types (a-f) according to the relative positions of active semiconductor layer, source/drain electrode, dielectric layer and light illumination.

2.2 Photoelectrical characteristics of OPTs

Similar with OFET measurement, transfer and output curves measured under dark and light illumination are two typical characteristics of OPTs, as shown in Figure 3a and 3b (an PPT constructed based on a donor-acceptor copolymer of HXS-1, detailed molecular structure is shown in Scheme 1). Under light illumination, an obvious increase of source-drain current compared to that in dark condition is observed in the corresponding transfer and output curves due to the contribution of photocurrent. Moreover, in OPTs, the incident light can be used as an independent variation to tune the transistor operation, like the function of gate bias in OFETs, working as a typical light and electric bi-functional device (as shown in Figure 3b).

2.3 Working principles of OPTs

There are generally two typical operation models in OPTs reflected by the relationship of photocurrent ($I_{ph}$) and incident optical power ($P_{opt}$): photovoltaic mode and photoconductive mode, which will be discussed in detail below.
Photovoltaic mode. When photovoltaic effect is dominant in OPTs, the shift of threshold voltage ($V_{th}$) is towards more positive (negative) values for p-channel (n-channel) devices when under light irradiation. The photo-generated excitons in the semiconductor dissociate into free charge carriers (electrons and holes) under extra illumination. These photo-generated electrons and holes accumulate under drain and source electrode, respectively. As a result, the large number of trapped photo-generated electrons effectively lowers the potential injection barrier between the source electrode and organic semiconductor surface. Moreover, contact resistance is significantly decreased under the effect of light irradiation. Thereby, the lowered injection barrier and contact resistance result in a positive shift of threshold voltage ($V_{th}$) and a significant increase in the drain current ($I_D$). The photocurrent caused by photovoltaic effect can be described in Figure 3c,$^{19}$ which can be derived according to the following equation (1):$^{19}$

$$I_{ph,pv}=G_0 \Delta V_{th} = A K \eta (1 + \eta q P_{opt}/\mu c-hc)/q$$  (1)

Where $\eta$ is the photo-generation quantum efficiency, $P_{opt}$ is the incident optical power, $I_{pd}$ is the dark current for minority charges, $h$ is the photon energy, $G_0$ is the trans-conductance, $\Delta V_{th}$ is the threshold voltage shift, and $A$ is a proportionality parameter.

Photoconductive mode. When the transistor operates in the depletion region ($V_{GS} \gg V_{th}$), photo-generated $I_p$ appears a linear increase with optical power, also called photoconductive effect. It is similar to the two-terminal devices without the effect of gate voltage. The transverse electric field induced by the extra gate voltage will contribute to the enhancement of photo-generated carriers. Typical characteristic of photocurrent as a function of the incident optical power under photoconductive effects is shown in Figure 3d.$^{19}$ The current can be calculated according to equation (2):

$$I_{ph,pc}=\mu cP_{opt}E_D = B P_{opt}$$  (2)

Where $\mu_c$ is charge carrier mobility, $P$ is charge carrier concentration; $E$ is the electric field in the conducting channel, and $W$ is the gate width, $D$ is the depth of absorption region, and $B$ is a proportionality factor.

2.4 Performance parameters of OPTs

Except for the basic characteristic parameters of OFETs, such as charge carrier mobility ($\mu$), threshold voltage ($V_{th}$) and on/off ratio, photoresponsivity (R) and photosensitivity (that is photocurrent on/off ratio) (P) are another two basic parameters for evaluating the phototransistor performance. The R and P values can be calculated through the following equations (3) and (4) based on their corresponding transfer curves:

$$R = \frac{I_{DS}}{I_{DS}}/I_{DS}$$  (3)

$$P = (1 + \eta q P_{opt}/\mu c-hc)/q$$  (4)

Where $I_{DS}$ and $I_{DS}$ are the drain current in dark and under illumination, respectively. $S$ is the effective area of devices and $P$ is the power of incident optical unit area.

3 Recent advances on PPTs

The first PPT in literatures was demonstrated by Narayan’s group in 2001, which was constructed based on BL-BGTC geometry with poly(3-octylthiophene-2,5-diyl) (P3OT) as the active layer and polyvinylalcohol (PVA) as the transparent gate dielectric layer.$^{21}$ This P3OT-based PPT demonstrated a R value of 1 A W$^{-1}$, which was higher than that of its corresponding planar two-terminal photodetectors, however, it was still obviously lower than that of inorganic phototransistors and SOPTs,$^{10,18}$ probably due to the slow relaxation process in polythiophene layer.$^{22}$ So, in following, how to further improve the device performance of PPTs has been the research focus in this field. With the development of polymer semiconductors$^4$ and device fabrication techniques of OFETs,$^5$ significant improvement has also been achieved for PPTs. A timeline of literature publication numbers and device performance of PPTs as a function of years are simply depicted in Figure 4. Obviously, over the past 14 years, the PPT device performance, with P and R as parameter references has undergone remarkable increase with tens and even more than two orders of magnitude, and the highest P and R value of PPTs is approaching $10^{12}$ and $10^{14}$ A W$^{-1}$, respectively.

The basic requirements for polymer semiconductors used in PPTs are high carrier mobility and wide absorption, in order to facilitate the whole process of effective light absorption, exciton dissociation and charge carrier transport like that in polymer solar cells.$^{23}$ Scheme 1 shows the chemical structures of typical polymer semiconductors recently used in PPTs. It can be seen that the polymer material systems are becoming more and more rich, including not only the classical semiconductor polymers,

![Figure 3. Photoelectrical characteristics of OPTs: (a) transfer and (b) output curves under dark and light illumination for a PPTs based on HXS-1 polymer semiconductor. [17] Copyright 2011, John Wiley & Sons. Two classical working modes: (c) photovoltaic effect and (d) photoconductive effect in phototransistors. [19] Copyright 2004, American Institute of Physics.](image-url)
such as P3HT, P3OT, TA-PPE, etc., but also the recently investigated field-effect donor-acceptor (D-A) copolymers. Besides polymer semiconductor themselves, device fabrication techniques and device structures are also crucial for the resulting device performance. In following, we will give more detailed discussions for the development strategies of high performance PPTs according to the types of active layers used.

**Scheme 1.** Chemical structures of polymer semiconductors recently used in PPTs.
spin-coated 100 nm P3OT film used as the active layer. PPTs were constructed based on such a device structure, where the active layer is composed of only one kind of polymer semiconductor, and are usually used as molecular wires in nano/molecular devices. In 2004, Xu et al., constructed PPTs based on single component film of a cross-conjugated polymer, poly(2,5-bis(dibutylaminostyryl)-1,4-phenylene-b-alkyne-b-1,4-bis(2-ethylhexyl)benzeneterpolymer (BAS-PPE) with a BL-BGBC geometry. Typical photoelectrical characteristics were observed for BAS-PPE based PPTs, giving a high P value of $6 \times 10^4$ and a R value of 5 mA W$^{-1}$. In following, Nakashima et al., fabricated another novel rigid-rod PPE derivative with thioacetylen-functionalized groups (TA-PPE). Hu et al., first fabricated polymer nanoscale photoswitches and phototransistors based on the self-assembled TA-PPE molecules and planar nanogap electrodes. With light illumination switching on and off, these devices exhibited typical on and off states, with a fast switching rate of 400 Hz and high P ratio of $3.3 \times 10^3$ at $V_{GS}=0$ V. Moreover, the optoelectronic properties for polymer thin films is significantly affected by the molecular orientation in solid state, and the higher orders of polymer chains are, the higher the device performance is. Additionally, different from P3AT-based devices, PPE-based phototransistors and photoswitches both exhibit relatively fast on and off switching rate under the effect of light illumination on and off. Two effects, photoconductive and photovoltaic effects, were both characterized in the same transistors, depending on the gate bias. With gatebias, the polymer phototransistors were dominated by photovoltaic effect, while without gate bias, they were dominated by photoconductive effect.

Recently, D-A copolymers have also been applied into PPTs due to their attractive advantages of high charge carrier mobility and broad absorption region. Poly(9,9-dioctylfluorene-co-bithiophene (F8T2) is the first copolymer used in PPTs. Hamilton et al., systematically studied the photoelectrical properties of F8T2-PPTs based on a BL-BGBC structure, which demonstrated a significant increase of current in the off-state, while a small change in the on-state under light illumination, attributed to the different effect of photoconductive and photovoltaic. A R value of 0.7 mA W$^{-1}$ in
the strong accumulation region and a P value of \(10^3\) in the off-state were obtained for F8T2-PPTs. Further, the authors examined the effect of light wavelength on the device performance of F8T2-based PPTs. It was found that high photo-energy photons produced by short wavelength were easier to be absorbed by the polymers, thus giving high density of charges in the active layer and high device performance of PPTs. Later, a higher R value of 18.5 A W\(^{-1}\) was further obtained for F8T2-PPTs by Wang et al.\(^{39}\)

Inspired by previous works, more recently, a variety of narrow-band gap D-A copolymers have been used as the active layer in PPTs. For example, the large planar benzo[1,2-b:4,5-b']dithiophene (BDT) unit is an attractive building block for design of novel D-A conjugated polymers. In 2009, Qin et al., designed and synthesized a novel BDT-based copolymer (HXS-1), which demonstrated very high photovoltaic performance with a power conversion efficiency (PCE) of over 5%, due to its close molecular packing in the solid state and a wide range of visible absorption.\(^{40}\) Subsequently, Dong et al., fabricated PPTs based on the thin films of HXS-1 polymer and obtained a high charge carrier mobility of 0.06 cm\(^2\) V\(^{-1}\) s\(^{-1}\), on/off ratio of over 10\(^3\) as well as high photoelectric property with a P value of \(4.6 \times 10^4\), which is also the highest P value in its reported time.\(^{17}\) Huang et al., fabricated PPTs based on another BDT-based copolymer, poly[4,8-bis(2'-ethylhexylthiophene)benzo[1,2-b:3,4-b']difuran-alt-5,5-(4',7'-di-2-thienyl-5',6'-dioctyloxy-2',1',3'-benzothia diazole (PBDFTDTBT), and achieved a P value of \(1.2 \times 10^5\) and R value of 360 mA W\(^{-1}\) under white light illumination.\(^{41}\) Li et al., constructed PPTs based on the self-assembled ultrathin crystalline copolymer films of P3AT copolymer,\(^{42}\) which showed a R value of 970 A W\(^{-1}\), and a P value of \(1.36 \times 10^4\) under a very low white light irradiation (43 mW cm\(^{-2}\)).

Diketopyrrolopyrrole (DPP)-based semiconductors are another type of promising building block for copolymer materials, due to their easily tuned structures, solubility and high crystallinity in solid state. In 2013, Yang et al., designed and synthesized two novel DPP-based copolymers, P(DTDPP-alt-(1,6)PY and P(DTDPP-alt-(2,7)PY (with the different anchoring positions in the pyrene).\(^{45}\) These two polymers exhibit not only good charge transport performance with carrier mobility of 0.23 cm\(^2\) V\(^{-1}\) s\(^{-1}\) but also high photoelectrical property with a high P value of \(1.2 \times 10^5\) and R value of 360 mA W\(^{-1}\) in

![Figure 5](image-url)
PPTs. Recently, Zhan et al. designed and synthesized a novel DPP-based copolymer, P(DPP4T-co-BDT) by the polymerization of 3,6-bis(5'-bromo-[2,2']-bithiophen]-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo-[3,4-c]-pyrrole-1,4(2H,5H)-dione and 2,6-bis(trimethyltin)-4,8-dimethoxybenzo[1,2-b:3,4-b']dithiophene. The copolymer P(DPP4T-co-BDT)-based thin film PPTs showed excellent photo-response property with R up to $4 \times 10^4$ A W$^{-1}$ (the highest value to date) and P up to $6.8 \times 10^3$ under a low intensity of light illumination, which was much higher than that of inorganic single crystal silicon phototransistor. Nam and co-workers demonstrated OPTs based on a novel dense and conformal surface PDA thin film, which was produced using self-polymerization of a homogenous PDA solution under oxygen bubbling instead of a conventional air stream. Device measurement results showed that the PDA thin film device performance could be tailored by adjusting the incident light intensity and gate voltage (with the highest R value of A W$^{-1}$ at $V_D$=12 V and P value of $6.9 \times 10^3$ at $V_G$=-2 V) and a prompt reproducible photo-switching property was obtained for this novel PDA-based OPTs with a fast response rate (rise and decay time: ~0.5 s and 1.2 s, respectively). Li et al., fabricated PPTs based on anode ambipolar D-Acopolymer (PPhTQ), and achieved a maximum photo-responsivity of 400 A W$^{-1}$ and a balanced hole (0.09 cm$^2$ V$^{-1}$ s$^{-1}$) and electron (0.06 cm$^2$ V$^{-1}$ s$^{-1}$) charge transport mobility. Except for the development of polymeric materials, the advances of device fabrication techniques, such as adopting short-channel geometry in devices, also could enable high performance of PPTs. More recently, Wang et al., successfully constructed an ultrasensitive and high performance PPT based on a short-channel device geometry with a BGTC structure and diketopyrrolopyrrole-thiazolothiazole copolymer (PDPPTzBT) as the active layer. A series of short conducting channel arrays were constructed through a simple and effective ‘coffee ring lithography’ inkjet printing technique via a 50 μm orifice nozzle, giving the channel lengths from several micrometers down to 700 nm (Figure 5b-i). A high carrier mobility of 1.2 cm$^2$ V$^{-1}$ s$^{-1}$, and photo-responsivity with an extremely high R of $10^6$ A W$^{-1}$ were obtained for PDPPTzBT-based PPTs with 700 nm channel length. Moreover, it is found that the onset gate voltage ($\Delta V_{on}$).

![Figure 6](image)

**Figure 6.** Logic circuits based on ambipolar OPTs and unipolar OFETs. (a) Circuity of the electro-optical NOT gate together with its symbolic representation and the truth table. (b) Circuity of the electro-optical OR gate together with its symbolic representation and the truth table. The circuit combines two inputs, one electrical (A IN) and one optical (B IN ). Copyright with redraw permission from ref. [51] Copyright 2007, American Institute of Physics.

is strongly dependent on the channel length, that is, the reduction of channel lengths is accompanied by an increasing trend of $\Delta V_{on}$, due to modulation of the gate voltage (Figure 5b-i). A gigantic shift of onset voltage ($V_{on}$) was observed in the sub-micron channel transistors, which was mounting to 90 V under the illumination of 40 μW cm$^{-2}$. Additionally, PDPPTzBT-based PPTs demonstrated relatively long recovery time and exhibited an unique characteristic of persistent photoconductivity with a stable intermediate current state after switching off the light illumination. Such characteristic combining its gate controllable property enables these devices to function as reproducible light-triggered memory devices (Figure 5b-ii), where by applying appropriate light illumination and pulse gate voltage, the writing process, different memory states and erase process could be realized in a single device.

### 3.2 PPTs based on blend films of polymer semiconductors

The combination of bulk hetero-junction effect, where donor and acceptor materials are combined together in the active layer, are widely used in organic photovoltaic devices, due to the ultrafast long-range charge separation at the donor-acceptor interface. Such a concept has also been used in PPTs. Anthopoulos et al., reported light-sensing PPTs based on donor and acceptor blend films of ‘6,6’-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) and poly-2-methoxy-5,7-dimethoxyctyloxy-p-phenylene vinylene (OC$_{5}$(C$_{7}$)PPV), which demonstrated not only ambipolar charge transport characteristic but also much faster response time than unipolar OPTs devices. Interestingly, by carefully tuning the ambipolar transport property, their photo-responsivity can be further controlled and improved. The fast response and controlled photo-responsivity property of blend film based PPTs demonstrated their potential applications in electro-optical switchers and logic circuits (Figure 6). Yasnet al., further fabricated organic bulk-hetero-junction based on blend films of P3HT and PCBM and obtained a R value of 3 A W$^{-1}$ at $V_{DS}$=-8 V. In addition, except for polymer/small molecule blends, polymer/inorganic nanoparticles are also used as the blends in PPTs. In 2008, Mok et al. successfully introduced photo-sensitive composite films of P3HT and TiO$_2$ nanoparticles in PPTs. These devices based on P3HT:TiO$_2$ active blend films demonstrated a rapid change in channel current under illumination due to the electrons trapped by TiO$_2$ nanoparticles, showing fast response time and high stability. Based on this result, they further deeply investigated the photo-responsive characteristics of P3HT:TiO$_2$-based devices, and found that their photo-response property was extremely sensitive to weak light due to an integration effect. Moreover, the photo induced mechanism was investigated clearly that photons first absorbed by P3HT and then excitons effectively separated into free charge at the
3.3 PPTs based on Micro/nano-crystals of polymer semiconductors

As well known, the performance of devices is highly sensitive to solid state crystallinity, crystal grain size and molecular packing of organic semiconductors. However, the inevitable large amounts of defects and grain boundaries in thin films play a negative impact in improvement of device performance. So, obtaining highly ordered microstructures is another effective approach to further realize the enhancement of device performance, and also beneficial for the integration of micro/nano-optoelectronic devices and circuits. In 2004, Pal et al., reported PPTs based on regular P3HT fibers, which were prepared through high-boiling point solvent of p-xylene. The high crystallinity of P3HT nanowires contributed to the high photoelectrical property of its PPTs with a R value of 250 A W⁻¹ and P value of 3.8 × 10⁻³. Dierckx et al., also fabricated PPTs based on the P3HT fibers and obtained a much higher P value of 6.8 × 10⁻³ due to the further improvement of its crystallinity by optimizing the self-assembly process. Liu et al., prepared large-area nanowire arrays of poly[(9,9-dihexyfluorene-2,7-diyl)-alt-[4,7-bis(3-dodecylthiophen-5-yl)-2,1,3-benzothiadiazole-2,2'-diyl)](PFTBT) through traditional anodic aluminium oxide (AAO) template methods by elaborately tuning and controlling the self-assembly of molecules into the AAO pores. PPTs based on PFTBTNanowires exhibited a R value of as high as 1700 mAW⁻¹ and switch P ratio of 2000. Obviously, incorporating polymer microstructures in PPTs is a good way to improve the device performance because of the reduced defects compared to thin films, however, the crystallinity of these previously reported polymer nanostructures is still not high enough, or even some of them are still in amorphous state. So, in this case, how to prepare high crystalline polymer micro/nanostructures is crucial not only for construction of high polymer optoelectronic devices but also establishing an accurate platform for repeated probing charge transport and photoelectrical property of polymersemiconductors.

Since 2000s, small-molecule organic single crystals have been widely investigated and remarkable progresses have been achieved in this field, including the growth of high quality organic single crystals, the development of feasible fabrication techniques and the construction of high performance devices, which indeed greatly contributed to the development of organic electronics. However, how about are crystalline or single crystals of polymer micro/nanostructures? Actually, it has been a challenging task in polymer science to grow large-size and high-quality polymer crystals, especially for the electron-rich conjugated polymers. In 2006, Kim et al., first reported the single crystal microwires of P3HT polymer, which were prepared through a self-seeding method from a dilute chloroform solution. The authors found that in the P3HT microcrystals, P3HT were arranged with their π-π stacking direction along the long axis of microwires. In 2009, Dong et al., reported single crystal micro/nanowires of TA-PPE through a modified solvent assisted self-assembly method, where a different polymer molecular packing from that of P3HT microwires was observed, i.e., the conjugated polymer backbones of TA-PPE were aligned along the long axis of nanowires. The obtainment of high-quality crystals of P3HT and TA-PPE opens up a new area for the investigation of other conjugated polymer crystals as well as corresponding optoelectronic devices. To date, various conjugated polymers have been proved to form crystal microstructures, leading to the significant improvement of charge transport compared to their corresponding thin films, and the highest mobility value for conjugated polymer crystals obtained recently was up to 24.0 cm² V⁻¹ s⁻¹. In 2013, Liu et al., first reported PPTs based on crystal microwires of bithiazole-thiazolothiazolecoacopolymer(PTz), which were prepared through the solvent assisted self-assembly method similar with that of TA-PPE nanowires. PPTs based on PTz nanowires exhibited high device performance with hole mobility of 0.46 cm² V⁻¹ s⁻¹ and R of 2531 A W⁻¹ and Pof 1.7 × 10⁻⁴ due to its close π-stacking and unique molecular packing with the conjugated backbones aligned to the long axis of nanowires, (Figure 7). More recently, Umet et al., fabricated PPTs based on single crystals of another D-A conjugated polymer, 1,2-bis[5-(thiophen-2-yl)selenophen-2-yl]ethene (DPPBTSPE),
which also showed high device performance with $R$ of 1920 A W$^{-1}$ and $P$ value of $10^4$. Much higher device performance is expected for conjugated polymer crystals and more deep investigations are still needed in this field. Table 1 summarizes the device performance of PPTs discussed in the manuscript.

### Table 1. Detailed device performance of PPTs

<table>
<thead>
<tr>
<th>Polymer semiconductor</th>
<th>Structure (dielectric)</th>
<th>Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)</th>
<th>$R$ A W$^{-1}$ (light wavelength, intensity)</th>
<th>$P$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3OT</td>
<td>BL-BGTC (PVA)</td>
<td>$10^{-3}$-$10^{-4}$</td>
<td>1 (532nm, 1mW cm$^{-2}$)</td>
<td>$10^2$-$10^3$</td>
<td>[21]</td>
</tr>
<tr>
<td>P3HT</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.01-0.07</td>
<td>245 (White light, 51mW cm$^{-2}$)</td>
<td>$3.8\times10^3$</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>NA</td>
<td>250 (White light, 0.91mW cm$^{-2}$)</td>
<td>$6.8\times10^3$</td>
<td>[57]</td>
</tr>
<tr>
<td>PQT-12</td>
<td>BL-TGBC (PMMAPVP)</td>
<td>$1.1\times10^{-3}$</td>
<td>6.6 (525nm, 3μW cm$^{-2}$)</td>
<td>$\sim10^2$</td>
<td>[26]</td>
</tr>
<tr>
<td>BAS-PPE</td>
<td>TL-BGTC (Polyimide)</td>
<td>NA</td>
<td>0.005 (White light, 4 μW cm$^{-2}$)</td>
<td>$6\times10^3$</td>
<td>[30]</td>
</tr>
<tr>
<td>TA-PPE</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>NA</td>
<td>0.036 (White light, 5.76 mW cm$^{-2}$)</td>
<td>$3.3\times10^3$</td>
<td>[33]</td>
</tr>
<tr>
<td>F8T2</td>
<td>TL-BGTC (BCB/SiN)</td>
<td>$3\times10^{-3}$</td>
<td>1 (White light, 2.9 mW cm$^{-2}$)</td>
<td>$10^3$</td>
<td>[37,38]</td>
</tr>
<tr>
<td></td>
<td>TL-BGBC ($\text{SiO}_2$)</td>
<td>1.2×10$^{-4}$</td>
<td>18.5 (465nm, 5μW cm$^{-2}$)</td>
<td>$10^3$</td>
<td>[39]</td>
</tr>
<tr>
<td>HXS-1</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.06</td>
<td>NA (White light, 5.76 mW cm$^{-2}$)</td>
<td>$4.6\times10^4$</td>
<td>[17]</td>
</tr>
<tr>
<td>PBDFTDDBT</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.05</td>
<td>0.36 (White light, 1mW cm$^{-2}$)</td>
<td>$1.2\times10^3$</td>
<td>[41]</td>
</tr>
<tr>
<td>PQBOCB</td>
<td>BGTC ($\text{SiO}_2$)</td>
<td>0.13</td>
<td>970 (White light, 0.28mW cm$^{-2}$)</td>
<td>$1.36\times10^3$</td>
<td>[42]</td>
</tr>
<tr>
<td>P(BDPP-alt(1,6)PY)</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.23</td>
<td>0.36 (White light, 1 mW cm$^{-2}$)</td>
<td>$1.2\times10^3$</td>
<td>[43]</td>
</tr>
<tr>
<td>P(DPP4T-co-BDT)</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.047</td>
<td>4000 (White light, 9.7μW cm$^{-2}$)</td>
<td>$6.8\times10^3$</td>
<td>[46]</td>
</tr>
<tr>
<td>PDA</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.96</td>
<td>9 (White light, 19.3 mW cm$^{-2}$)</td>
<td>$6.9\times10^3$</td>
<td>[47]</td>
</tr>
<tr>
<td>PDPPDTBT</td>
<td>BGTC($\text{SiO}_2$ PMMA)</td>
<td>1.8</td>
<td>$10^6$ (White light)</td>
<td>$10^8$</td>
<td>[49]</td>
</tr>
<tr>
<td>PPhTQ</td>
<td>TL-BGTC ($\text{SiO}_2$HMDS)</td>
<td>0.09(hole)</td>
<td>400 (White light)</td>
<td>NA</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06(electron)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3HT/PCBM</td>
<td>TL-TGBC</td>
<td>$1.6\times10^{-4}$</td>
<td>0.047 (White light, 100 mW cm$^{-2}$)</td>
<td>3</td>
<td>[52]</td>
</tr>
<tr>
<td>MDMOPPV:PC$_{61}$BM</td>
<td>BGBC ($\text{SiO}_2$HMDS)</td>
<td>$10^{-4}$-$10^{-5}$</td>
<td>NA (469 nm)</td>
<td>$10^4$</td>
<td>[51]</td>
</tr>
<tr>
<td>P3HT/TiO$_2$</td>
<td>BGBC ($\text{SiO}_2$)</td>
<td>NA</td>
<td>NA (370-590 nm, 0.2 mW cm$^{-2}$)</td>
<td>$\sim10^3$</td>
<td>[53,54]</td>
</tr>
<tr>
<td>PFTBT</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>NA</td>
<td>1.7 (White light, 5.76 mW cm$^{-2}$)</td>
<td>$2\times10^3$</td>
<td>[58]</td>
</tr>
<tr>
<td>PT$_2$</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>0.46</td>
<td>2531 (White light, 0.65 mW cm$^{-2}$)</td>
<td>$1.7\times10^4$</td>
<td>[67]</td>
</tr>
<tr>
<td>DPPBTSE</td>
<td>TL-BGTC ($\text{SiO}_2$)</td>
<td>24</td>
<td>1920 (632nm, 24 mW cm$^{-2}$)</td>
<td>$\sim10^3$</td>
<td>[66]</td>
</tr>
<tr>
<td>PTCID-C13H27</td>
<td>BGBC (C-PVP)</td>
<td>NA</td>
<td>0.41 (532nm, 22.5 mW cm$^{-2}$)</td>
<td>NA</td>
<td>[68]</td>
</tr>
<tr>
<td>PDPP-DLTE</td>
<td>TGBC (PEDOT-PSS)</td>
<td>0.26</td>
<td>NA (White light, 9 mW cm$^{-2}$)</td>
<td>5</td>
<td>[69]</td>
</tr>
</tbody>
</table>

*PVA: polyvinyl alcohol; PMMA: polymethyl methacrylate; PVP: polyvinyl pyrrolidone; BCB: benzocyclobutene; HMDS: hexamethyldisilazane.

NA refers to no related data reported in the literature.

### 4 Flexible organic phototransistors (FOPTs)

The attractive advantages of light weight, low cost, easy solution processing of SOPTs and PPTs have recently advanced the exploration of their flexible and stretchable devices and circuits. For instance, Chou et al. presented flexible in-cell devices by incorporating a phototransistor and a photoswitch together based on a transparent polyethersulfone (PES) substrate with a cross-linked poly(4-vinylphenol) as polymer dielectric layer and N,N’-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (PTCDI-C$_{13}$H$_{27}$) as the active layer. This flexible optoelectronic circuit demonstrated a low operation voltage (3.0 V) and high opto-electrical property with a $R$ value of $0.41$ A W$^{-1}$, indicating its potential application in in-cell touch screens (Figure 8a-e). Kim et al. demonstrated another successful flexible polymer...
phototransistors based on transparent and colourless polyimide plastic substrate through an all-solution process, such as roll-to-plate reverse offset printing (ROP), inkjet printing and bar coating (Figure 8d-e).\(^{69}\) High crystallinity in the active layer poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-di(2,2’-bithiophen-5-yl)ethene] (PDPP-DBTE) was obtained by optimizing the processing conditions, such as high-temperature thermal treatment at 180 °C, which contributed to the resulting excellent electrical switching property with a fast response time of 11.2 s and high photosensitivity with photo-to-dark ratio property of 1.54×10\(^5\) in off-state \((V_{GS} = 11 \text{ V})\). These results provide us hope and confidence for the realization of large-area flexible optoelectronic applications of OPTs.

Figure 8. (a) Schematic process flow for fabrication of OPTs based on a combination of printing methods; (b) Transfer characteristics of this flexible device in the dark and under illumination at different light intensity and at \(V_D = -30 \text{ V}\). (c) Schematic of a flexible in-cell device incorporating a photo-OTFT and a switch-OTFT. (d) Photograph of the flexible testing devices. (e) Drain–source current as a function of time (upper panel) then the photo-OTFT is subjected to light pulses (lower panel). [68] Copyright 2014, Royal Society of Chemistry and ref. [69] Copyright 2014, Elsevier B.V.

5 Perspective and conclusion
In this review, we have systematically summarized the development of polymer phototransistors over the past years under the development of polymer semiconductors and device physics. Despite tremendous progress have been demonstrated for polymer phototransistors, there are still large space to further improve the device performance, such as by further (1) enriching the polymer material systems in PPTs, especially incorporating the recently reported high-mobility, narrow-band D-A copolymers; (2) improving the crystallinity of polymer chains in solid state with appropriate molecular packing; (3) optimizing device structures from the aspects of interface contact and channel sizes; (4) with theoretical calculations to guide the experimental studies. Opportunities and challenges coexist and we believe under the joint efforts of material scientists, physical scientists and theoretical scientists, significant progresses could be further achieved for polymer phototransistors to advance their practical applications, especially in integrated flexible optoelectronic devices/circuits.
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References

The table of contents entry:

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Title: Recent advances on polymer phototransistors

In this MiniRev, we will give a highlight on the recent advances on polymer phototransistors.