Triphenylamine-based amorphous polymers for bulk-heterojunction photovoltaic cells

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Abstract. In this paper, the recent research progress on triphenylamine (TPA)-based donor-acceptor (D-A) amorphous polymers including our developed polymers is reviewed. TPA has three-dimensional branched structures and can provide D-A polymers containing D and A units in the main chain or side chain. The use of TPA-based amorphous polymers in the fabrication of organic photovoltaics (OPVs) offers great advantages over the use of a polycrystalline film in terms of high reproducibility of the OPV performance. The amorphous polymer design using TPA, therefore, indicates a promising direction for the development of new donor materials in OPVs.

1. Introduction
Organic photovoltaics (OPVs) based on solution-processed bulk-heterojunctions (BHJs), where π-conjugated polymer (donor) and fullerene derivative (acceptor) phases are separated during solution coating to form nanoscale donor/acceptor interfaces, have garnered considerable research interest because of their significant advantages such as their low cost, low weight, and mechanical flexibility [1-3]. Interdisciplinary research into BHJ OPV has resulted in a rapid enhancement in the power conversion efficiency (PCE) values by more than 8% under standard illumination conditions (AM 1.5) [4,5]. The development of novel conjugated polymers for BHJ OPV cells has contributed to the significant improvements in PCEs. In recent years, efforts have mainly been focused on varying the molecular structure of π-conjugated polymer backbones. For example, low-bandgap polymers are obtained with an alternating electronic donor-acceptor (D-A) structure along the backbone [6-8]. The presence of D and A units on one chain creates a push-pull charge-transfer (CT) effect that can be excited by lower-energy photons, leading to a red-shifted onset of absorption. This approach has been used to develop efficient, low-bandgap photovoltaic materials. Due to successful applications in organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs), fluorene, carbazole, thiophene and their analogue heterocycles have become the first choice as donors in BHJ OPVs.

Recent years have seen the emergence of a new approach based on the use of triphenylamine (TPA) units in the design of amorphous materials that are used as donors in BHJ solar cells. These TPA-based amorphous polymers present a number of specific advantages, due to their excellent thermal and electrochemical stability, electron donating ability, hole transport properties, and high absorption coefficients. They are now known to be important hole transport layer (HTL) materials in the commercial production of OLEDs [9]. Ultrathin films composed of a pinhole-free homogeneous layer

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with a thickness of less than 100 nm are suitable for HTL for OLEDs as well as for OPVs. Moreover, the incorporation of TPA units into π-conjugated polymers is known to be quite effective for the control of HOMO-LUMO levels and absorption spectra, as well as of their hole transport capability [10]. Thus, the use of TPA units in the design of polymer skeletons for not only OLEDs but also OPVs is an attractive option.

In this paper, the recent research progress on TPA-based D-A amorphous polymers including our developed polymers is reviewed. This review is organized as follows: an overview of TPA-based polymers containing D and A units in the main chain or side chain in the section 2. In the subsequent section 3, an advantage of using TPA-based amorphous polymers in the fabrication of OPVs is described.

2. Designs and OPV properties of triphenylamine-based D-A polymers
As mentioned in the introduction, to obtain low-bandgap polymers, one feasible approach is to design alternating D-A copolymers. TPA has three-dimensional branched structures and can provide D-A polymers containing D and A units in the main chain (Figure 1) or side chain (Figure 2). So, I introduce TPA-based D-A polymers divided into the two structures.

2.1. Main-chain D-A polymers
A variety of electro-accepting units such as benzothiadiazole (BTD), dithienylbenzothiadiazole (TBT), and diketopyrrolopyrrole (DPP), have been employed as the counterpart in designing D-A polymers. The author’s group reported a comparative study of the properties of BHJ OPVs using a BTD-TPA small molecule [11] and its polymerized molecule (P1) [12]. OPVs using BTD-TPA or P1:PC_{60}BM at a 1:2 mixing weight ratio were fabricated. The PCE of the P1-based OPV was twice that of the BTD-TPA-based OPV. The field-effect hole mobility of P1 (3.1×10^{-4} cm^2V^{-1}s^{-1}) is two orders of magnitude higher than that of BTD-TPA (5.4×10^{-6} cm^2V^{-1}s^{-1}) and the absorption peak of P1 (494 nm) is at a longer wavelength than that of BTD-TPA (477 nm). Accordingly, the improved hole mobility and enhanced absorption of AM 1.5 solar-simulated light led to a high short-circuit current (J_{sc}) and PCE in OPVs based on P1. By optimizing OPVs with P1:PC_{70}BM (1:4), the device performance exhibited a J_{sc} value of 7.45 mAcm^{-2}, an open-circuit voltage (V_{oc}) of 0.92 V, a PCE of 2.65%, and incident photon to current conversion efficiencies (IPCEs) of around 50% at wavelengths ranging from 360 to 560 nm.

![Figure 1. Chemical structures of TPA-based polymers with main-chain D-A.](image-url)
Blankenburg et al. reported the synthesis of P2 in which BTD and TPA are connected together with rigid acetylenic linkages and the investigation of their optical, electrochemical, and photovoltaic properties [13]. The copolymer was synthesized by the standard Sonogashira-reaction of selected dihalogen BTD with diethynyl TPAs. The controlled polymers in which thiophene or 3-alkylthiophene or alkoxy phenylene was connected with diethynyl TPAs show a prominent absorption at 408-411 nm. Compared with these polymers, the integration of BTD (P2) led to the expected red shift of approximately 100 nm. PCE of 1.85% could be reached without any optimization of concentration of the solutions, the ratio of the polymer to PCBM, the spin coating process itself or annealing.

The steric hindrance between the acceptor BTD unit and the donor benzene-based aromatic units has previously been reported [14], and the conjugated backbone in P1 is also twisted at the BTD-TPA linkage, leading to the possibility of reduced effective conjugation. So, some BTD-TPA-based polymers with a more red-shifted onset of absorption by introducing flanking thienyl groups between BTD and TPA to reduce the amount of steric hindrance between them have been developed [15]. The TBT-TPA polymers, P3, P4 and P5 differ only by the presence and position of the side chains on the thiényl groups, as shown in Figure 1. P3 has no side chains on the flanking thiényl groups, P4 has hexyl side chains on the three-positions of the thiényl groups (pointing toward the BTD unit), and P5 has hexyl side chains on four-positions of the thiényl group (pointing outward from the BTD unit).

The obtained P4 and P5 are soluble in common organic solvents including chloroform (CHCl3) and o-dichlorobenzene (o-DCB). However, P3 was produced as an insoluble material during the polymerization, so the additional thiophene rings could result in a low weight average molecular weight (Mw = 3400) for P3 because of its low solubility. The additional thiophene rings with hexyl side-chains between the BTD-TPA backbones, on the other hand, were attached to engender good solubility and led to an increase in Mw to 21,900. By the addition of alkoxy groups to BTD and two phenyl amines, other TBT-based polymers, P6 and P7, have good solubility in common organic solvents [16,17].

The UV–vis absorption maxima in the CT absorption spectra for the P4 and P5 films appeared at 501 and 538 nm, respectively. The UV–vis absorption maxima for the P1 film appeared at 494 nm. Therefore, BTD-TPA based polymers with a more red-shifted onset of absorption by introducing the flanking thiényl groups between the BTD and TPA have been developed. A comparison of spectra for the P4 and P5 films reveals that the former has a slightly blue-shifted and weakened CT absorption. The spectral position and relative intensity of these peaks varied strongly with the change in the side-chains of the thiényl groups.

| Polymer | HOMO (eV) | Absorption in film (nm) | BHJ layer | Jsc (mAcm⁻²) | V oc (V) | FF | PCE (%) | Ref. |
|---------|-----------|------------------------|-----------|--------------|---------|----|--------|-----|
| P0      | 5.33ᵃ     | 379                    |           |              |         |    |        | 10  |
| P1      | 5.47ᵃ     | 494                    | P1:PC70BM (1:4) | 7.45      | 0.92    | 0.39 | 2.65  | 12  |
| P2      | 5.42ᵇ     | 503ᶜ                   | P2:PC70BM (1:4) | 5.22      | 0.89    | 0.40 | 1.85  | 13  |
| P4      | 5.36ᵃ     | 501                    | P4:PC70BM (1:4) | 6.50      | 0.83    | 0.39 | 2.12  | 15  |
| P5      | 5.26ᵃ     | 538                    | P5:PC70BM (1:4) | 6.48      | 0.86    | 0.38 | 2.10  | 15  |
| P6      | 5.29ᵇ     | 558                    | P6:PC70BM (1:3) | 6.9       | 0.77    | 0.43 | 2.3   | 16  |
| P7      | 4.8ᵇ      | 577                    | P7:PC70BM (1:3) | 3.8       | 0.62    | 0.48 | 1.0   | 17  |
| P8      | 5.30ᵇ     | 548                    | P8:PC70BM (1:4) | 7.00      | 0.84    | 0.42 | 2.44  | 18  |
| P9      | 5.32ᵇ     | 554                    | P9:PC70BM (1:4) | 7.4       | 0.93    | 0.44 | 3.1   | 19  |
| P10     | 5.38ᵇ     | 518                    | P10:PC70BM (1:3) | 9.40      | 0.86    | 0.39 | 3.09  | 20  |
| P11     | 5.22ᵇ     | 653                    | P11:PC70BM (1:3) | 10.77     | 0.80    | 0.35 | 2.95  | 20  |

ᵃ The values were estimated by photoelectron yield spectroscopy.
b The values were obtained from cyclic voltammograms.
c Absorption in a solution state.
chain position on the thiophene unit. When the hexyl chains on thiophene rings face toward the BTD, severe steric hindrance is introduced between the flanking thienyl groups and the central BTD unit. In such a case, the conjugated backbone is thereby twisted at the D-A linkage. This leads to a blue-shifted and weakened CT absorption. IPCEs in the region from 550 to 650 nm for the OPV cells prepared using P5 were higher than those for the OPV cells prepared using P4 because the absorption spectrum for the P5 has a slightly red-shifted absorption. The photovoltaic properties of P1-P7 are summarized in Table 1.

2.2. Side-chain D-A polymers
Recent studies have developed a new family of conjugated polymers with conjugated side chains (Figure 2). This type of polymers features high hole mobility thanks to the overlapping of the side chain interactions with the conjugated main chains, and broad absorptions deriving from both the main chains and the conjugated side chains.

As successful examples, Zhang et al. reported copolymers of carbazole and TPA with thiénylenevinylene conjugated side chain containing a dicyano acceptor end group (P8) [18]. BHJ OPV based on P8:PC70BM (1:4) demonstrated OPV performance with Jsc of 7.0 mAcm⁻², FF of 0.42, Voc of 0.84 V, corresponding to a PCE of 2.44%. Duan et al. also reported copolymers of indenofluorene and TPA with the same side chain (P9) and the OPV performance with Jsc of 7.4 mAcm⁻², FF of 0.44, Voc of 0.93 V, corresponding to a PCE of 3.1% [19].

Nie et al. developed two side-chain D-A conjugated copolymers (P10 and P11), in which an alternating binary donor units of benzodithiophene and TPA conjugately formed the main chain, and TBT or DPP acceptor units were pended onto the TPA units to build the side chain [20]. The choice of alternating binary donor units and pending acceptor unit was expected to broaden the absorption area.

Figure 2. Chemical structures of TPA-based polymers with side-chain D-A.
for their resulting copolymers, which was critical to improve device performance. The absorption peaks at 518 nm for P10 and at 653 nm for P11 were observed in their films, respectively. It indicated that attaching the DPP unit instead of TBT unit into the side chain can effectively tune the absorption properties. Compared to the P10-based OPVs, the P11-based OPVs presented an increasing J_{sc} of 10.77 mA cm^{-2}. The photovoltaic properties of P8-P11 are summarized in Table 1.

3. Advantage of using TPA-based amorphous polymers in the fabrication of OPVs

As mentioned in the introduction, remarkable improvements in the performance of BHJ OPVs have been made in recent years. In contrast, it is insufficiently known and inadequately documented that the performance of BHJ OPVs based on polycrystalline polymers such as regioregular poly(3-hexylthiophene) (P3HT) is largely dependent on the fabrication conditions such as the solvents used for dissolving the polymer and PCBM, the film-fabrication methods, and the annealing temperatures used for the BHJ films. Large fluctuations in the PCEs from sample to sample are observed even in BHJ OPVs using the same active layers [21]. To ensure proper industrial application, the PCE deviation of fabricated BHJ OPVs should be as small as possible.

The use of an amorphous film in the fabrication of OPVs offers great advantages over the use of a polycrystalline film in terms of high reproducibility of the OPV performance; TPA-based OPV performances are independent of the casting solvent and the thermal annealing temperature. The OPV based on P1:PC_{70}BM (1:4) that was fabricated using CHCl_{3} (boiling point of 61 °C) and annealed at 60 °C for 10 min exhibited a PCE of 2.81%. On the other hand, the OPV fabricated using o-DCB (boiling point of 181 °C) and annealed at 110 °C for 10 min exhibited a PCE of 2.65%. Almost the same PCEs were obtained in both OPVs [22].

The performance of BHJ-OPV using P5 was also independent of the casting solvent and the thermal annealing temperature. The OPV based on P5:PC_{70}BM (1:4) that was fabricated using the CHCl_{3} solution and annealed at 60 °C for 10 min exhibited a PCE of 2.09%. The OPV fabricated using the o-DCB solution and annealed at 110 °C for 10 min, conversely, exhibited a PCE of 2.10% [15].

Moreover, Wang et al. reported the OPVs of P6:PC_{70}BM (1:3) fabricated from trichlorobenzene (TCB, boiling point of 208 °C) or chlorobenzene (CB, boiling point of 132 °C) solution both showed PCE of 2.1% [16]. The reproducible photovoltaic properties of these polymers are summarized in Table 2.

### Table 2. Processes of fabricating BHJ layers and the photovoltaic parameters under illumination with 100 mWcm^{-2} of AM 1.5.

| Polymer | Solvent | Annealing temperature (°C) | BHJ layer | J_{sc} (mA cm^{-2}) | V_{oc} (V) | FF | PCE (%) | Ref. |
|---------|---------|---------------------------|-----------|---------------------|-----------|-----|---------|------|
| P1      | o-DCB   | 110                       | P1:PC_{70}BM (1:4) | 7.45     | 0.92    | 0.39 | 2.65    | 22   |
| P1      | CHCl_{3} | 60                        | P1:PC_{70}BM (1:4) | 8.48     | 0.93    | 0.39 | 2.81    | 22   |
| P5      | o-DCB   | 110                       | P5:PC_{70}BM (1:4) | 6.48     | 0.86    | 0.38 | 2.10    | 15   |
| P5      | CHCl_{3} | 60                        | P5:PC_{70}BM (1:4) | 6.49     | 0.85    | 0.38 | 2.09    | 15   |
| P6      | TCB     | -                         | P6:PC_{70}BM (1:3) | 5.4      | 0.77    | 0.50 | 2.1     | 16   |
| P6      | CB      | -                         | P6:PC_{70}BM (1:3) | 5.7      | 0.76    | 0.46 | 2.1     | 16   |

4. Concluding remarks

TPA has three-dimensional branched structures and can provide D-A polymers containing D and A units in the main chain or side chain. The use of amorphous TPA-based polymers in the fabrication of OPVs offers great advantages over the use of a polycrystalline film in terms of high reproducibility of the OPV performance. It is striking that the performance of the solar cells are not extremely sensitive to the solvents, which can simplify the preparation of devices and it is unnecessary to select one kind of the solvent strictly. Such insensitivity might be due to three-dimensional branched structures of TPA-based polymers, since the structure can suppress the aggregation of polymer chains. The amorphous TPA-based polymer design, therefore, indicates a promising direction for the development of new donor materials in OPVs.
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