



# Merocyanines for vacuum-deposited small-molecule organic solar cells



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## ABSTRACT

We report here synthesis and photovoltaic properties of three merocyanines dyes (**DPPT**, **DTPT**, **1-NPPT**) which are functionalized with electron withdrawing thiazolidenemalonitrile and electron rich diarylamine functionalities. It is found that structural feature of the diarylamino groups has a profound effect on the physical properties such as the absorption spectrum, oxidation potential, and HOMO/LUMO energy levels. The compound **DTPT** containing a better electron-donating ditolyl group, exhibits red-shifted absorption with relatively higher molar extinction coefficient, indicating its better light-harvesting ability. Hole mobility of these compounds is found to be strongly dependent on the various intermolecular interactions. Interestingly, single crystal structures reveal that the crystal packing motifs are rather closely related to the observed hole mobility in a trend of **DPPT** > **DTPT** > **1-NPPT**. Vacuum-processed small-molecule organic solar cells were fabricated using the title merocyanines as p-type materials (donor) in combination with fullerene (C<sub>60</sub> or C<sub>70</sub>) as n-type material (acceptor) with various device configurations. Among them, the **DPPT**-based devices outperform the devices based on **DTPT** and **1-NPPT**. The power conversion efficiency (PCE) of **DPPT**-based device was improved from 1.55% of a BHJ device to 2.63% of a PMHJ device and 3.52% of a PMHJ device without the thin donor layer.

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## 1. Introduction

Among the various solar energy resources, organic photovoltaics (OPVs) have received great research attention owing to their advantageous features such as, cheaper manufacturing cost, light-weight, material diversity and mechanical flexibility [1–7]. In order to improve the device performance, various efforts have been made since the past two decades which include (1) synthesizing highly delocalized donor–acceptor (D–A) copolymers or small molecules with various light-harvesting regions as p-type materials (donor) and pristine fullerene or soluble derivatives like PC<sub>61</sub>BM, PC<sub>71</sub>BM, ICBA, as n-type materials (acceptor) [8–10]; (2) device engineering for improving exciton diffusion and/or charge transport [11–17]. The joined efforts have led to outstanding device efficiency and stability. To date, 10.7% of PCE has been achieved for a single-junction polymer BHJ solar cell [18] using the famous polymer **PTB7-Th** as donor [19], and 11.6% of PCE has

been reached in a vacuum-processed triple-junction tandem solar cell (10.6% of a double-junction tandem solar cell) [20]. However, compared to the polymeric donors, small molecule based donors have several benefits such as simple preparation and purification, unique final product without batch-to-batch problem, easy tuning of the optoelectronic properties etc. Furthermore, device fabrication becomes more flexible as the small molecule organic solar cells (SMOSCs) could be fabricated using both the solution process and/or vacuum-deposition techniques [21–23]. Linear donor materials using in SMOSCs could roughly be divided into two broad categories with symmetric or asymmetric molecular skeleton. The symmetric system comprises of one electron-rich group (D) as core end-capped with two electron-withdrawing units (A), giving the A–D–A configuration. Another symmetric configuration uses the reverse prototype and arranges the D/A functionalities in D–A–D sequence. Both the A–D–A and D–A–D systems have low molecular dipole moment which may facilitate charge transport in the bulk state [24]. Besides, as the symmetric systems usually have relatively larger  $\pi$ -conjugation, they often offer greater light-harvesting capability and thus enhanced photocurrent density in OPV device [25]. To date, the A–D–A systems in BHJ solar

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cells have been reported to reach efficiency up to 9.8% [26] and 10.1% [27] for single-junction and double-junction tandem solar cells respectively. Similarly, the squaraine-centered D–A–D system has achieved a PCE of 6.1% with vacuum-process [28] and 3.61% with solution-process [29]. In contrast to the symmetric system, the asymmetric D–A type molecular donor typically can perform strong intramolecular charge transfer, giving an evident molecular dipole moment which is considered to be beneficial for the long absorption wavelength in conjunction with high extinction coefficient. However, the dipolar character is suspected to lead to energetic disorder in bulk state, interfering the charge transport and thus reducing the efficiency in BHJ solar cells. Several strategies have been developed so far to resolve the problem of impeding charge hopping in dipolar system, one typical example being the centrosymmetric dimer found in merocyanine dyes. Two neighboring merocyanine molecules are arranged in an antiparallel fashion and this stacking is proposed to eliminate the dipole moments in the bulk state [22,24,25,30]. In this line, our previous reports also conform to the importance of antiparallel packing fashion that can lead to fine device performance [31–34]. Merocyanine is a fascinating molecule for SMOSCs. Many interesting electron-withdrawing groups were employed to the merocyanine systems, one very typical example being the thiazolidenemalononitrile which breaks aromaticity of the thiazole ring while the malononitrile group enhances its electron-withdrawing ability. Würthner and co-workers reported a thiazolidenemalononitrile-based merocyanine dye **HB238**, which although exhibits antiparallel stacking and suitable properties, but the solution-processed BHJ device only performed a low PCE of 1.10% [30]. We infer that the low PCE of **HB238** might be due to the presence of alkyl chains (necessary for better solubility) which could impede hole hopping. In addition, the high electron-rich dibutylaminothiophene donor might be too strong to raise the highest occupied molecular orbital (HOMO), leading to a lower open circuit voltage ( $V_{oc}$ ) in BHJ device. Unfortunately, the replacement of dibutylaminothiophene with diphenylaminophenylene reported by Langa and co-workers could not address this problem, while the new molecule only delivered a deteriorated device performance of 0.25% PCE [35]. These reports clearly indicate that other factors must be considered in order to improve merocyanine-based device performance. Interestingly, a recent work from Thompson reported a boosted up PCE of 5.70% with a squaraine-centered D–A–D donor, where the hole mobility was improved by the incorporation of diarylamino groups typically found in hole-transporting materials used in OLEDs [36]. Along this line, we synthesized three merocyanine dyes (**DPPT** [35], **DTPT**, and

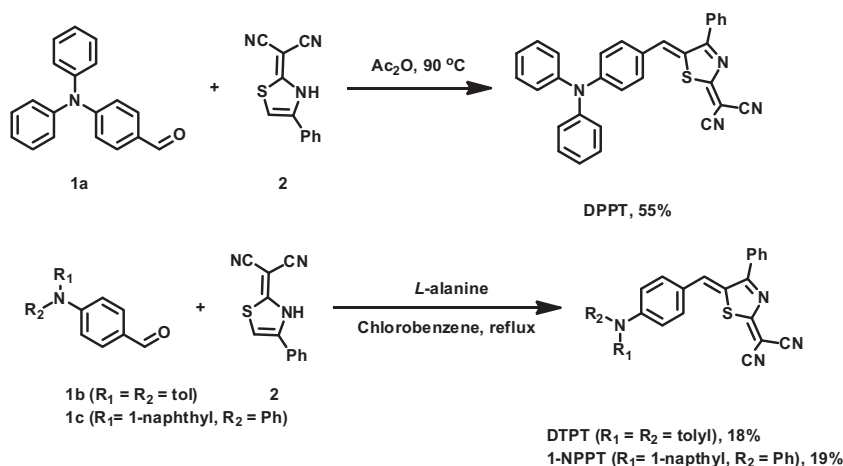
**1-NPPT**, **Scheme 1**) based on thiazolidenemalononitrile as the electron-poor block while three diarylamino phenylenes are the electron-rich blocks. Instead of previously reported solution-process, we fabricated the OPV devices with vacuum deposition. Among these three D–A type molecular donors, device based on **DPPT** together with  $C_{70}$  gave the best device performance with a short circuit current density ( $J_{sc}$ ) of  $9.05 \text{ mA cm}^{-2}$ ,  $V_{oc}$  of 0.98 V, fill factor ( $FF$ ) of 0.40, and PCE up to 3.52%. The device characteristics finely correlate to the hole mobilities, which are governed by the subtle intermolecular interactions found in X-ray crystal structures.

## 2. Experimental section

### 2.1. Synthesis

**Synthesis of DPPT** [35]. A mixture of **1a** (1.57 g, 5.75 mmol), and **2** (1.13 g, 5 mmol) in  $Ac_2O$  (50 mL) was stirred and heated at  $90^\circ C$  under argon for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting sticky mixture was purified by column chromatography on silica gel with dichloromethane/hexane (2:1) as eluent to afford **DPPT** as a purple solid (1.33 g, 55%).  $^1H$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  7.90 (t,  $J = 4.2$  Hz, 3H), 7.73 (dd,  $J = 12.0, 8.2$  Hz, 3H), 7.65 (t,  $J = 7.4$  Hz, 2H), 7.50–7.44 (m, 4H), 7.34–7.27 (m, 6H), 7.03 (d,  $J = 9.0$  Hz, 2H).  $^{13}C$  NMR (100 MHz,  $d_6$ -acetone)  $\delta$  183.4, 182.1, 153.6, 146.4, 143.9, 135.2, 133.2, 132.9, 132.5, 131.5, 131.0, 130.0, 127.9, 127.2, 126.1, 119.8, 115.8, 114.0; HRMS ( $m/z$ ,  $FAB^+$ ) Calcd for  $C_{31}H_{20}N_4S$  480.1409 [M] $^+$ , found 480.1410.

**Synthesis of DTPT**. A mixture of **1b** (5.65 g, 18.74 mmol), **2** (3.84 g, 17.0 mmol) and L-alanine (0.75 g, 8.52 mmol) in chlorobenzene (34 mL) was stirred and heated at  $140^\circ C$  under argon for 2.5 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was purified by column chromatography on silica gel with dichloromethane/hexane (2:1) as eluent to afford **DTPT** as a purple solid (1.55 g, 18%), mp:  $271$ – $273^\circ C$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.90–7.70 (m, 2H), 7.63 (s, 1H), 7.57 (d,  $J = 6.1$  Hz, 3H), 7.44 (d,  $J = 9.0$  Hz, 2H), 7.18 (d,  $J = 8.0$  Hz, 4H), 7.09 (d,  $J = 8.4$  Hz, 4H), 6.95 (d,  $J = 9.0$  Hz, 2H), 2.37 (s, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  182.4, 180.3, 152.7, 142.5, 141.8, 136.2, 133.8, 132.1, 131.9, 131.5, 130.6, 130.5, 129.0, 126.5, 124.3, 118.5, 115.2, 113.3, 21.0. IR (KBr)  $\nu$  3060, 3021, 2921, 2852, 2214, 1601, 1561, 1507, 1463, 1090, 820, 796, 715,  $629 \text{ cm}^{-1}$ . HRMS ( $m/z$ ,  $ESI^+$ ) calcd for  $C_{33}H_{24}N_4NaS$ , 531.1614 [M+Na] $^+$ , found 531.1622.



**Scheme 1.** Synthetic route of these merocyanine dyes.

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