



## Tricyanofuran-based donor–acceptor type chromophores for bulk heterojunction organic solar cells

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### ABSTRACT

Tricyanofuran-based small molecules were synthesized through Knoevenagel reaction with formyl heteroaromatic donating moieties and 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) as a strong acceptor. UV–vis absorption demonstrated that the combination of TCF with donating units resulted in an enhanced intra-molecular charge transfer (ICT) transition, which led to long wavelength absorption in the chromophores. The absorption coefficients and the molecular energy levels of the chromophores can be tuned effectively by employing different donating groups. The chromophores were used in conjunction with [6,6]-phenyl C61 butyric acid methyl ester (PC<sub>61</sub>BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC<sub>71</sub>BM) to fabricate organic heterojunction photovoltaic cells. This solution-processed bulk heterojunction (BHJ) solar cells exhibited a power conversion efficiency (PCE) of 2.44%, a short-circuit current density ( $J_{SC}$ ) of 8.74 mA/cm<sup>2</sup>, and an open-circuit voltage ( $V_{OC}$ ) of 0.93 V under simulated air mass 1.5 global irradiation (100 mW/cm<sup>2</sup>).

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### 1. Introduction

Organic semiconductors that are soluble in organic solvents facilitate the use of conventional low-cost spin-coating, drop-casting, and ink-jet techniques for photovoltaic (PV) devices [1–3]. Recently, organic photovoltaic (OPV) devices employing conjugated polymers based heterojunctions have been shown to have a power conversion efficiency (PCE) approaching 5.0–7.4% [4–8]. To achieve high PCE, solution-processed bulk heterojunction (BHJ) devices containing polymeric donors and fullerene-based soluble acceptors have been used; they represent the most efficient BHJ organic solar cell [9–11]. The device performance of these types of devices is varied according to many factors related to the synthetic characteristic of polymers as well as the device parameters such as composition ratio, film thickness, and annealing temperature etc. The performance is particularly affected by their purity, molecular weight, regioregularity, and polydispersity of the p-type polymeric host [12,13]. The polymer-based BHJ usually suffers from the poor reproducibility of internal morphology, which should be overcome for practical applications.

Alternatively, small organic molecules have also been intensively investigated for solar cells due to a number of advantages

including the reproducibility of synthesis and purity, which give rise to consistent device performance, although those molecules still have the chemical/physical stability problems against water and oxygen in photovoltaic applications [14,15]. Further, molecules offer flexibility of design to tune their molecular energy levels for optimizing OPV performances. In the past, a series of  $\pi$ -conjugated linear donor–acceptor (D–A) molecules (PCE=2.67%) [16], star-shaped D–A–D molecules (1.33–2.39%) [17,18], linear D–A–D molecules (2.33–4.4%) [19–21] have been synthesized to provide new electroactive small molecules for application in BHJ solar cells. In most of them, weak acceptors such as malononitrile and benzothiadiazole units have been commonly utilized at the center or peripheral position of their  $\pi$ -conjugated molecular structures, rather than strong electron acceptors such as 2-(3-oxo-indan-1-ylidene)-malononitrile [22], 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) [23], and 2-oxo-5-dicyanomethylene-pyrrolidine (TCP) [24] that had been widely investigated in the push–pull molecular structures of the second-order nonlinear optical chromophores. Therefore, these acceptors are connected to the electron-donor through a sufficiently longer conjugation bridge like thiophene, fused-thiophene, and oligothiophene derivatives, resulting in an extension of the absorption towards the red and NIR wavelengths as well as in an increase of the absorption coefficients due to strong intramolecular interaction. However, this kind of molecular design approach still requires complicated multi-step synthetic methodology.

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In 2010, Meerholz et al. reported a new series of low band gap merocyanine (MC) dye based D–A small molecules containing 2-(3-oxo-indan-1-ylidene)-malononitrile (1.4–2.6%) [25] or 2-oxo-5-dicyanomethylene-pyrrolidine (1%) [26] as strong acceptors. Even though they have a relatively shorter  $\pi$ -conjugation length than for the molecules previously used for solar cells, these dyes show the comparable absorption coefficients and lower band gap, as compare to conjugated dyes with longer conjugated length bearing relatively weak acceptor. Very recently, Tian et al. have fabricated BHJ photovoltaic devices by introducing analogs of a well-known red-emitting dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) that has a strong electron acceptor, 2-pyran-4-ylidenemalononitrile (PM). The resulting photovoltaic devices with PC<sub>71</sub>BM exhibit a PCE value reaching up to 2.47%, but the spectral response was limited to < 650 nm [27]. Therefore, it is a reasonable approach to incorporate a conventional class of powerful electron-withdrawing moieties into small molecules for solar cell device to extend the absorption spectrum efficiently on the principle of strong intramolecular charge transfer (ICT) to achieve broad light harvesting in solar spectrum. As a consequence, these new challenges showed that small molecules containing a strong acceptor have potential for photovoltaic application.

Herein, we designed and synthesized four new kinds of D–A type low band gap chromophores containing 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) group as the strong acceptor. TCF-based chromophores have provided potential advantages for nonlinear optics [28] and photorefractive devices [29], because they have high absorption coefficients, high dipole moments, polarizabilities, and facile tenability of molecular energy levels using various donating groups and  $\pi$ -conjugated bridges. To compare the photophysical, electrochemical, and photovoltaic properties, these chromophores were designed to contain well-known donating groups such as carbazole, phenothiazine, and triphenylamine derivatives. The molecular energy levels of the chromophores could be tuned effectively by employing different donating groups. The result of DFT calculation provided the conformational geometry variation of those donors that can affect the quality of blend film and the device performance. Especially, triphenylamine (TPA) donor-based molecules showed the better film-forming ability with PC<sub>71</sub>BM due to the intrinsic peripheral 3D structure of TPA preventing self-aggregation. The resulting best device exhibited a PCE of 2.44%, a short-circuit current density ( $J_{sc}$ ) of 8.74 mA/cm<sup>2</sup>, and an open-circuit voltage ( $V_{oc}$ ) of 0.93 V under simulated AM 1.5 illumination (100 mW/cm<sup>2</sup>). A broad spectral response was also found, which covered in the entire visible wavelength from 350 nm to 700 nm.

## 2. Experimental

### 2.1. Materials

All reagents were purchased from Sigma-Aldrich Co. and used without further purification unless stated otherwise. Reagent grade solvents used in this study were freshly dried under standard distillation methods.

### 2.2. Synthesis of chromophores

2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF, **2**), 10-ethyl-10H-phenothiazine-3-carbaldehyde (**1b**) and 4-(bis(4-*tert*-butylphenyl)amino)benzaldehyde (**4b**) were prepared according to published procedures [30–32]. 9-Ethyl-9H-carbazole-3-carbaldehyde (**1a**) and 4-(diphenylamino)benzaldehyde (**4a**) were purchased from Sigma-Aldrich Co.

*General synthetic procedure of 3a, 3b, 5a, and 5b by Knoevenagel reaction.*

The TCF-based chromophores were prepared by a similar procedure of condensation with 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (**2**) and aldehydes of **1a**, **1b**, **4a**, and **4b**, respectively. In a dried 250 mL round bottom flask, aldehyde (10 mmol), the TCF acceptor (12 mmol) and a trace amount of ammonium acetate were dissolved in ethanol (50 mL). The mixture was refluxed under nitrogen atmosphere for 5 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on a silica gel (ethylacetate:chloroform=1:20 v/v%). The yield, <sup>1</sup>H NMR, elemental analysis (EA), and Mass of chromophores are described below.

#### 2.2.1. Synthesis of (E)-2-(3-cyano-4-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)-malononitrile (**3a**)

Compound **3a** was synthesized following the general synthetic procedure as a dark green powder in a yield of 84%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =8.37 (s, 1H), 8.16 (d,  $J$ =8.0 Hz, 1H), 7.90 (d,  $J$ =16.5 Hz, 1H), 7.79 (d,  $J$ =8.5 Hz, 1H), 7.56 (t,  $J$ =8.0 Hz, 1H), 7.48 (d,  $J$ =8.5 Hz, 1H), 7.47 (d,  $J$ =8.5 Hz, 1H), 7.35 (t,  $J$ =8.0 Hz, 1H), 7.07 (d,  $J$ =16.0 Hz, 1H), 4.42 (q, 2H), 1.84 (s, 6H), 1.49 (t, 3H). Anal. calcd for C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>O: C, 77.21; H, 4.98; N, 13.85. Found: C, 77.18; H, 4.99; N, 13.68. HRMS (m/z) calcd for C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>O (M+H) 405.1715; found, 405.1706.

#### 2.2.2. Synthesis of (E)-2-(3-cyano-4-(2-(10-ethyl-10H-phenothiazin-3-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**3b**)

Compound **3b** was synthesized following the general synthetic procedure as a black powder in a yield of 71%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.52 (d,  $J$ =16.5 Hz, 1H), 7.40 (d,  $J$ =9.0 Hz, 1H), 7.33 (s, 1H), 7.17 (t,  $J$ =9.0 Hz, 1H), 7.00 (d,  $J$ =7.5 Hz, 1H), 6.97 (t,  $J$ =8.5 Hz, 1H), 6.91 (d,  $J$ =8.0 Hz, 1H), 6.86 (d,  $J$ =9.0 Hz, 1H), 6.82 (d,  $J$ =16.0 Hz, 1H), 3.99 (q, 2H), 1.76 (s, 6H), 1.46 (t, 3H). Anal. calcd for C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>OS: C, 71.54; H, 4.62; N, 12.83. Found: C, 71.56; H, 4.63; N, 12.78. HRMS (m/z) calcd for C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>OS (M+H) 437.1436; found, 437.1425.

#### 2.2.3. Synthesis of (E)-2-(3-cyano-4-(4-(diphenylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**5a**)

Compound **5a** was synthesized following the general synthetic procedure as a green powder in a yield of 87%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.58 (d,  $J$ =16.0 Hz, 1H), 7.46 (d,  $J$ =8.5 Hz, 2H), 7.36 (t,  $J$ =7.5 Hz, 4H), 7.20 (t,  $J$ =7.5 Hz, 2H), 7.18 (d,  $J$ =7.5 Hz, 4H), 6.98 (d,  $J$ =9.5 Hz, 2H), 6.82 (d,  $J$ =16.0 Hz, 1H), 1.76 (s, 6H). Anal. calcd for C<sub>30</sub>H<sub>22</sub>N<sub>4</sub>O: C, 79.27; H, 4.88; N, 12.33. Found: C, 79.21; H, 4.82; N, 12.31. HRMS (m/z) calcd for C<sub>30</sub>H<sub>22</sub>N<sub>4</sub>O (M+H) 455.1872; found, 455.1863.

#### 2.2.4. Synthesis of (E)-2-(4-(4-(bis(4-*tert*-butylphenyl)amino)styryl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**5b**)

Compound **5b** was synthesized following the general synthetic procedure as a dark purple powder in a yield of 63%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.57 (d,  $J$ =16.0 Hz, 1H), 7.44 (d,  $J$ =8.5 Hz, 2H), 7.36 (d,  $J$ =8.0 Hz, 4H), 7.10 (d,  $J$ =8.0 Hz, 4H), 6.94 (d,  $J$ =8.5 Hz, 2H), 6.79 (d,  $J$ =16.0 Hz, 1H), 1.75 (s, 6H), 1.33 (s, 18H). Anal. calcd for C<sub>38</sub>H<sub>38</sub>N<sub>4</sub>O: C, 80.53; H, 6.76; N, 9.89. Found: C, 80.49; H, 6.78; N, 9.85. HRMS (m/z) calcd for C<sub>38</sub>H<sub>38</sub>N<sub>4</sub>O (M+H) 567.3124; found, 567.3115.

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