



Effect of acceptor strength in new acceptor–donor–acceptor-type molecules on their miscibility with donor polymers for bulk-heterojunction fullerene-free solar cells



Seo Yeon Park, Gi Eun Park, Suna Choi, Ji Hyung Lee, Dae Hee Lee, Min Ju Cho^{**}, Dong Hoon Choi^{*}

Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, 136-701 Seoul, South Korea

ARTICLE INFO

Article history:

Received 26 April 2017

Received in revised form

6 July 2017

Accepted 6 July 2017

Available online 8 July 2017

Keywords:

Fullerene-free solar cells

Spirobifluorene

Accepting units

Polarity

Miscibility

ABSTRACT

We designed and synthesized two kinds of spirobifluorene (SP)-based acceptor–donor–acceptor (A–D–A)-type acceptor materials, denoted by SP-IC and SP-TCF, which have an A–D–A structure consisting of a 3D tetrathienospirobifluorene donor core and 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC) or 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile (TCF) acceptors as terminal units, respectively. Their LUMO levels (−3.91 eV for SP-IC and −3.97 eV for SP-TCF) are suitable as n-type molecules for PTB7-Th-based polymer solar cells. However, their morphologies in blend films with a conjugated donor polymer, Poly([2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-*b*:3,3-*b*]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}) (PTB7-Th), exhibited considerable differences. The PTB7-Th:SP-IC blend film exhibited a better-defined nanophase-separated morphology than PTB7-Th:SP-TCF blend film. The corresponding bulk heterojunction polymer solar cell based on PTB7-Th:SP-IC showed four times higher power conversion efficiency (PCE = 4.50%) than that of PTB7-Th:SP-TCF. The higher PCE was well explained by investigating the morphology, which was affected by the surface energy of the acceptor molecules at the donor–acceptor interface.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have been widely studied due to merits such as their flexibility, low cost, and light weight [1–6]. In addition, PSCs have exhibited power conversion efficiencies (PCE) of up to 12% thus far [7–10]. While electron-donor materials have been developed over the past few decades for PSCs, studies on their electron-accepting materials have been relatively lacking. Although fullerene derivatives such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are primarily used as electron acceptors in PSCs, they exhibit shortcomings, including high production costs, difficult purification, weak light absorption in the visible wavelength range, and poor morphological miscibility with common conjugated donor polymers [11–13]. Therefore, a

great deal of attention has recently been paid to the development of non-fullerene acceptors, which are very attractive due to their advantages of easily tunable molecular energy levels, absorption spectral broadening, good thermal/photochemical stability, flexibility of the molecular structure, easy purification, and low production costs [14–16].

Among non-fullerene accepting materials, acceptor–donor–acceptor (A–D–A)-type materials have been intensively investigated due to the above-mentioned advantages [17,18]. Recently, many researchers have employed new structural units for constructing A–D–A structures to tune certain properties [10,19,20].

Various A–D–A-type molecules with linear or 3D geometries have been developed [21,22]. Although linear A–D–A molecules have led to high device performance, some problems have arisen, such as solubility, film forming property, and crystallinity inducing molecular aggregates [23–25]. On the other hand, non-fullerene small molecules with a 3D architecture consisting of a spirobifluorene (SP) building block as the core enable tuning the geometrical structure of the final acceptor molecules [26]. Ma et al.

* Corresponding author.

** Corresponding author.

E-mail addresses: chominju@korea.ac.kr (M.J. Cho), dhchoi8803@korea.ac.kr (D.H. Choi).

reported a SP-cored perylene diimide derivative as an electron acceptor, which exhibited a quasi-3D structure to reach a PCE of 5.26% [27]. Li and Chen et al. also reported a SP-cored diketopyrrolopyrrole (DPP) as an accepting unit, which led to a PCE of 5.16% [28]. As shown in these previous reports, it is feasible to tune the properties of SP-cored acceptor molecules by considering the miscibility and proper morphology in blend films with a donor polymer.

In order to obtain a high PCE through good miscibility with a p-type donor polymer and the desired internal morphology in donor–acceptor blend film, it is also important to develop more effective acceptor moieties such as 2-(benzo[*c*][1,2,5]thiadiazol-4-ylmethylene)malononitrile, 1,1-dicyanomethylene-3-indanone (IC) and 2,5-dimethyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (TCF) [29,30].

In this work, we designed and successfully synthesized two fullerene-free A–D–A-type accepting molecules denoted by SP-IC and SP-TCF using SP as a 3D core unit and either IC or 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile (TCF) as terminal moieties. Although IC and TCF are well-known traditional

strong electron-withdrawing groups, they have different polarities in corresponding A–D–A-type acceptor molecules, as shown in Fig. 1. Compared to TCF, IC unit is shorter conjugation length, and its acidic carbon is located on the side of the molecular body. Both SP-IC and SP-TCF showed very similar optical properties (λ_{max} values of 548 and 531 nm, respectively) but they have very different permanent dipole moments and surface energies in the thin film. Possibly due to strong dipole-dipole interaction, it critically influenced the internal morphology in PTB7-Th:A–D–A blend films and the corresponding photovoltaic performances containing it as the active layer.

The surface energy of SP-IC was found to be very similar to that of PTB7-Th, whereas that of SP-TCF was very different from that of PTB7-Th. The significantly large difference between the surface energies of the acceptor materials and that of the donor polymer causes the miscibility problem in blend films. Due to its better miscibility, which induced nano-phase segregation, the PTB7-Th:SP-IC-based device exhibited a maximum PCE of 4.50%, which is four-times larger than the PCE (~0.97%) of the SP-TCF-based device.

2. Experimental

2.1. General information and materials

All reagent chemicals were purchased from the Sigma-Aldrich Chemical Company, TCI, or the Alfa Aesar Company and were generally used as received. The polymer, PTB7-Th ($M_n = 48.0$ kDa, PDI = 2.5), were purchased from One Materials. All reactions were conducted under an N_2 atmosphere. Compound **1** was prepared using methods in the literature [31]. The syntheses of SP-IC and SP-TCF are illustrated in Scheme 1.

2.2. Synthesis

2.2.1. 5,5',5'',5'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrakis(3-hexylthiophene-2-carbaldehyde) (**1**)

A mixture of 2,2',7,7'-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (1.0 g, 1.58 mmol), 5-

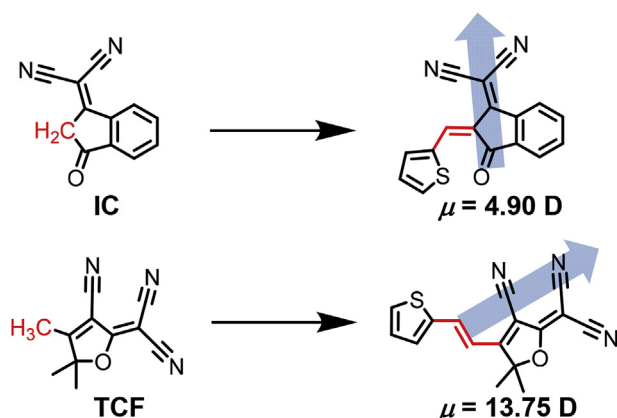
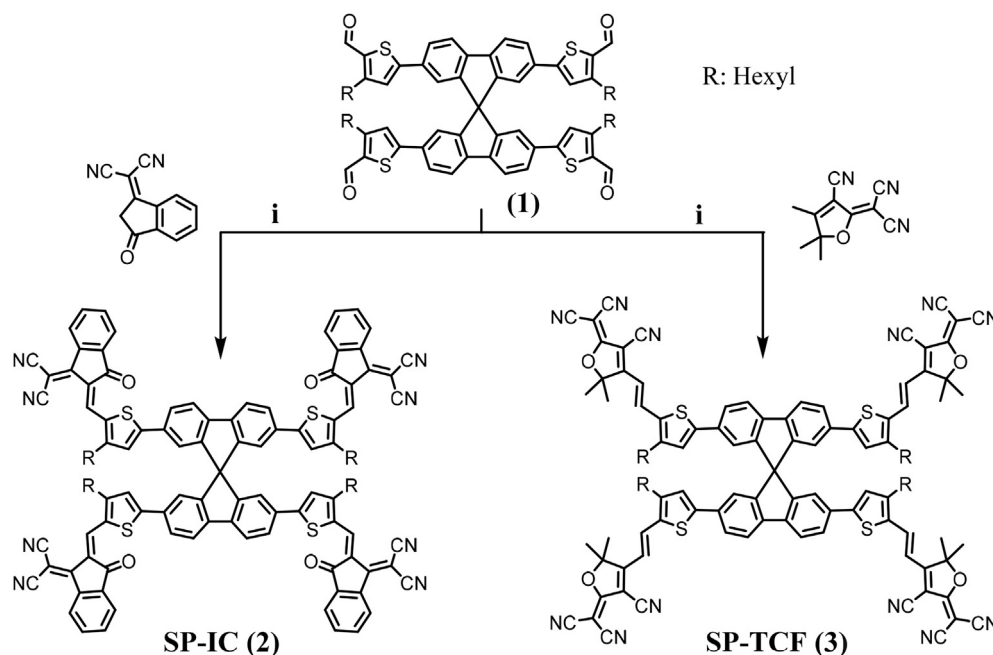


Fig. 1. Molecular structure of the IC and TCF acceptors (left), and the calculated dipole moment (μ) of thienylene-vinylene-connected acceptors (right).



Scheme 1. Synthetic procedure for SP-IC and SP-TCF: i) $AcONH_4$, $CHCl_3$, $80^\circ C$, overnight.

Download English Version:

<https://daneshyari.com/en/article/4765587>

Download Persian Version:

<https://daneshyari.com/article/4765587>

[Daneshyari.com](https://daneshyari.com)