Tetrahedron 70 (2014) 1176–1186

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Linkage position influences of anthracene and tricyanovinyl groups on the opto-electrical and photovoltaic properties of anthracene-based organic small molecules

Vellaiappillai Tamilavan [a,†], Myungkwan Song [b,†], Rajalingam Agneeswari [a], Myung Ho Hyun [a,*]

[a] *Department of Chemistry, Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Republic of Korea*
[b] *Advanced Functional Thin Films Department, Korea Institute of Materials Science, Changwon 641-831, Republic of Korea*

ARTICLE INFO

Article history:
Received 25 November 2013
Received in revised form 24 December 2013
Accepted 25 December 2013
Available online 3 January 2014

Keywords:
Bulk heterojunction solar cell
Small molecule organic solar cell
Anthracene
Tricyanovinyl
Triphenylamine

ABSTRACT

Anthracene-based small molecules incorporating an electron accepting tricyanovinyl (TCV) group was prepared to investigate the linkage position influences of the anthracene and TCV groups on the opto-electrical and photovoltaic properties of the molecules. The maximum absorptions of the anthracene-based molecules incorporating the TCV group at the phenyl group of the triphenylamine unit (**TCV-TpaA$_{9,10}$T**, **TCV-TpaTA$_{9,10}$T**, and **TCV-TpaA$_{2,6}$T**) or at the thiophene unit (**TpaA$_{9,10}$T-TCV**, **TpaTA$_{9,10}$T-TCV**, and **TpaA$_{2,6}$T-TCV**) were found to be dependent on the linkage position of the anthracene unit. The HOMO energy levels of the molecules containing TCV group at the phenyl group of the triphenylamine unit were deeper than those of the molecules containing TCV group at the thiophene unit. The solution processed small molecule organic solar cells (SMOSCs) prepared with the structure of ITO/PEDOT:PSS/**TCV-TpaA$_{9,10}$T** or **TCV-TpaA$_{2,6}$T** or **TpaA$_{2,6}$T-TCV**:PC$_{71}$BM (2:1 wt %)/LiF/Al exhibited a maximum energy conversion efficiency of 1.04%, 1.67%, and 1.95%, respectively, under AM 1.5 irradiation (100 mW cm^{-2}).

1. Introduction

The bulk heterojunction solar cells (BHJ) containing the photoactive layer made up with the bi-continuous network of electron donating π-conjugated material and electron accepting [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) derivative are considered as a promising renewable energy production techniques due to their advantages, such as light weight, flexible large-area device fabrication at low cost via solution processability.[1,2] The BHJ solar cells prepared with the π-conjugated polymer as an electron donor and PC$_{71}$BM as an electron acceptor (polymer-based BHJ solar cells, PSCs) gave the maximum solar to electrical energy conversion efficiency of up to 9.2% for single layer PSCs[2–7] and 10.6% for tandem structured PSCs.[8–10] The high power conversion efficiency (*PCE*) of the PSCs induced researcher to evaluate the potential of π-conjugated organic small molecules in BHJ solar cells application. Organic small molecules are believed to be a superior candidate over polymeric donor materials due to their crucial advantages, such as facile synthesis and purification at low cost, reproducibility of the purity and easy structural modification of molecules to tune their absorption and energy levels for optimizing the photovoltaic device performances, while polymeric donor materials have some difficulty in the reproducibility of the synthetic characteristics, such as purity, molecular weight, regioregularity and polydispersity of each batch of the polymerization.[11] In this instance, the electron donating polymers were replaced with organic small molecules in BHJ solar cells and the maximum *PCE* of the small molecule-based BHJ solar cells (Small Molecule Organic Solar Cells, SMOSCs) was rapidly improved up to 8.6%.[12–23] The high *PCE* of the SMOSCs inspired us to develop new low band gap organic small molecules for SMOSCs application.

The recent progress of anthracene-based PSCs,[24,25] dye sensitized solar cells (DSSCs)[26,27] and organic thin film transistor (OTFTs)[28–30] displayed impressive carrier mobility and high energy conversion efficiency. The planar structured and highly crystalline anthracene chromophore might be the important factors for the impressive carrier mobility and high energy conversion efficiency. In this instance, we expect that the insertion of anthracene chromophore as a π-conjugation linker in organic small molecules might induce broad absorption and high carrier mobility, and consequently, offer high *PCE* in SMOSCs. To the best of our knowledge anthracene-based small molecules have not yet been applied

---

* Corresponding author. Department of Chemistry, Pusan National University, Busan 609-735, Korea. Tel.: +82 51 510 2245; fax: +82 51 516 7421; e-mail address: mhhyun@pusan.ac.kr (M.H. Hyun).

[†] V. Tamilavan and M. Song made equal contribution to this work.

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.12.079

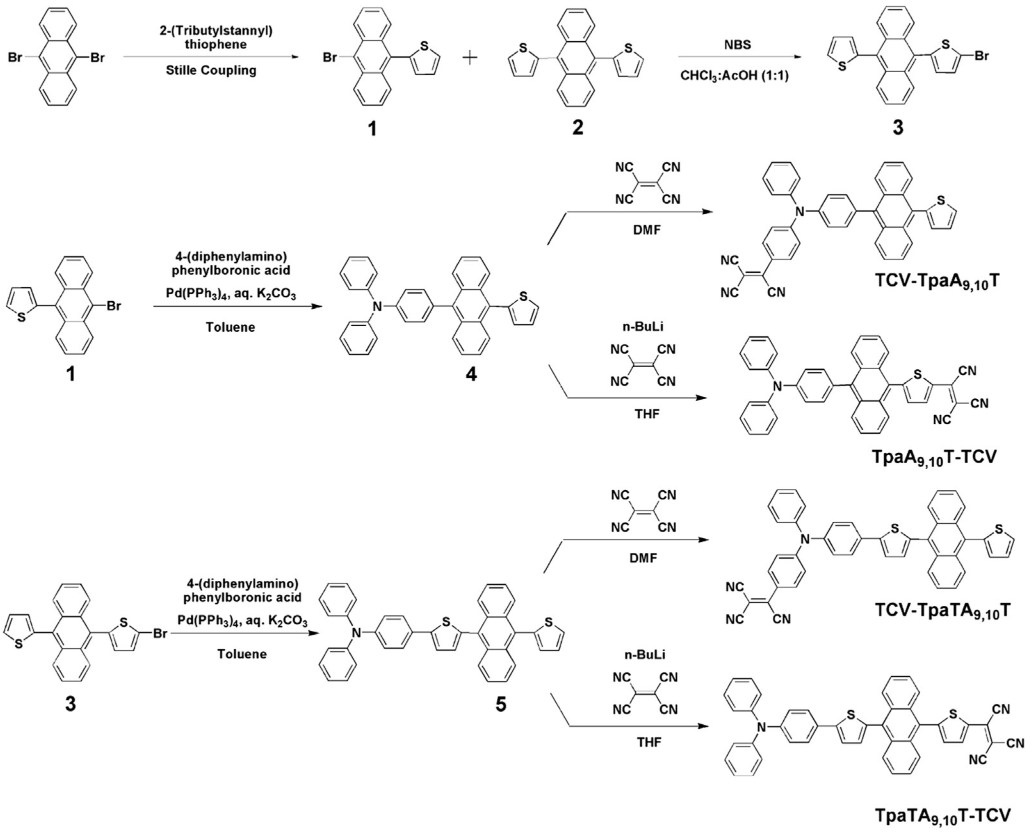
to SMOSCs. In this anticipation, we liked anthracene moiety with strong electron donating triphenylamine and thiophene units via 9,10- and 2,6-positions of anthracene. To extend the absorptions of final molecules towards longer wavelength region of the solar spectrum or to lower their optical band gaps, we have been interested in incorporating cyano functional group on their back bone. Among the reported cyano functional groups, tricyanovinyl (TCV, $-C(CN){=}C(CN)_2$) group was found to be quite efficient to lower the band gap of the organic molecules[31] compared with monocyano ($-CH{=}CHCN$), dicyano ($-CH{=}C(CN)_2$ and DCBP) and tricyanofuran (TCF) groups.[32–34] In addition, our recent study evidently supports that the band gaps of the relatively less π-conjugated molecules are also significantly lowered with the use of TCV group.[35] To investigate the linkage position influences, we attached the TCV group at the phenyl group of triphenylamine unit or at the thiophene unit of 9,10- and 2,6-linked anthracene-bridged molecules. Here, we wish to report the synthesis, optical, electrochemical and photovoltaic properties of 9,10- and 2,6-linked anthracene-based small molecules bearing TCV at two different positions.

2. Results and discussion

2.1. Synthesis and characterization

The general synthetic strategies for the 9,10-linked anthracene-based molecules, such as **TCV-TpaA$_{9,10}$T**, **TpaA$_{9,10}$T-TCV**, **TCV-TpaTA$_{9,10}$T**, and **TpaTA$_{9,10}$T-TCV** are outlined in Scheme 1. The Stille coupling reaction between 9,10-dibromoanthracene and 2-(tributylstannyl)thiophene afforded a mixture of compounds **1** and **2**. After the careful separation, compound **2** was subjected to bromination by using NBS. This bromination afforded mono-brominated compound **3** and di-brominated compound along with unreacted compound **2**. The mixture was separated by using column chromatography to afford compound **3**. Then, the Suzuki coupling reaction between 4-(diphenylamino)phenylboronic acid and each of compounds **1** and **3** afforded compounds **4** and **5**, respectively. Finally, the 9,10-linked anthracene-based molecules namely **TCV-TpaA$_{9,10}$T** and **TCV-TpaTA$_{9,10}$T** containing the TCV group at the phenyl group of the triphenylamine unit of the molecules were obtained by treating each of compounds **4** and **5** with tetracyanoethylene (TCNE) in DMF. Notably, the reaction rate between compound **4** or **5** and TCNE was very slow and to increase the reaction rate and yield at least 10 equiv of TCNE were used. Even though 10 equiv of TCNE were used, only one TCV group was found to be introduced on one phenyl ring of the triphenylamine unit possibly because the TCV group introduced first is expected to decrease the electron density of the other phenyl ring and, consequently, inhibit the reaction between TCNE and the second phenyl ring. The color of **TCV-TpaA$_{9,10}$T**, **TCV-TpaTA$_{9,10}$T** was intense blue. The NMR and high resolution mass analysis evidenced that the molecules obtained from the above reaction contain only one TCV group attached on the phenyl group of the triphenylamine unit. On the contrary, when we treated each of compounds **4** and **5** with *n*-BuLi and then TCNE by using the similar reported procedure,[31] 9,10-linked anthracene-based molecules namely **TpaA$_{9,10}$T-TCV** and **TpaTA$_{9,10}$T-TCV** containing the TCV group at the thiophene unit of the molecules were obtained. The color of **TpaA$_{9,10}$T-TCV** and **TpaTA$_{9,10}$T-TCV** was brown.

To confirm the TCV group position on **TCV-TpaA$_{9,10}$T** and **TCV-TpaTA$_{9,10}$T**, we treated compound **6** with 10 equiv of TCNE in DMF at 150 °C for 48 h. The two *para*-positions of the phenyl groups of the triphenylamine unit of compound **6** are already occupied by the methoxy groups. In this instance, the incorporation of the TCV



Scheme 1. Synthetic route for the synthesis of **TCV-TpaA$_{9,10}$T**, **TpaA$_{9,10}$T-TCV**, **TCV-TpaTA$_{9,10}$T**, and **TpaTA$_{9,10}$T-TCV**.