Organic Electronics 27 (2015) 72–83

Contents lists available at ScienceDirect

Organic Electronics

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

Donor–acceptor–acceptor–donor small molecules for solution processed bulk heterojunction solar cells

P. Gautam [a], Rajnessh Misra [a, **], Emmanuel N. Koukaras [b, c], Abhishek Sharma [d], Ganesh D. Sharma [e, *]

[a] Department of Chemistry, Indian Institute of Technology Indore, Madhya Pradesh, 452017, India
[b] Molecular Engineering Laboratory, Department of Physics, University of Patras, Patras, 26500, GR, Greece
[c] Institute of Chemical Engineering Sciences, Foundation for Research & Technology, Hellas (FORTH/ICE-HT), Stadiou Str., Platani, Patras, 26504, Greece
[d] Department of Electronics and Communication Engineering, LNMIIT, Jaipur, 302031, India
[e] R and D Center for Science and Engineering, JEC Group of Colleges, Jaipur Engineering College Campus, Kukas, Jaipur, 303101, Rajasthan, India

ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form
17 August 2015
Accepted 6 September 2015
Available online xxx

Keywords:
Donor–acceptor–acceptor–donor
benzothiadiazole small molecule
Bulk heterojunction organic solar cells
Power conversion efficiency
Solvent additives

ABSTRACT

We report on the optical and electrochemical characterization (experimental and theoretical) of two donor substituted benzothiadiazole with different cyano based acceptor π-linkers, tetracyanobutadiene (TCBD) **SM1** and dicyanoquinomethane (DCNQ) **SM2**, and explore them as the donor component for solution processed bulk heterojunction organic solar cells, along with $PC_{71}BM$ as the electron acceptor. The solution bulk heterojunction (BHJ) solar cells based on dichloromethane (DCM) processed active layer with **SM1** and **SM2** as donor and $PC_{71}BM$ as acceptor achieve power conversion efficiency (PCE) of 2.76% and 3.61%, respectively. The solar cells based on these two small molecules exhibit good Voc, which is attributed to their deep HOMO energy level. The higher PCE of the device based on **SM2** compared to **SM1** is attributed to the its small bandgap, broader absorption profile and enhanced hole mobility. Additionally, the PCE of the **SM2**:$PC_{71}BM$ based solar cells processed with 1-chloronaphthalene CN (3 v%)/DCM is further improved reaching upto 4.86%. This increase in PCE has been attributed to the improved nanoscale morphology and more balanced charge transport in the device, due to the solvent additive.

1. Introduction

Research on bulk heterojunction (BHJ) organic solar cells based on solution processed small molecules has rapidly grown in the past few years due to their advantages over polymeric counterpart such as well defined molecular structures, mono-dispersive nature, high absorption coefficient and charge carrier mobility [1–12]. A power conversion efficiency (PCE) higher than 8% has been recently reported due to the excellent solubility in organic solvents, broadband light absorption and good charge transport property of the solution-processed SM donor [13,14]. Chen and co-workers have developed a series of small molecules, used as donors, with a benzodithiophene core, a terthiophene spacer, and a rhodamine end-group and have achieved a PCE of 8.12% [15]. An organic solar cell (OSC) based on the small molecule donor of *p*-DTS(FBTTh$_2$)$_2$ was recently reported by Bazan et al. and they found that the fill factor (FF) of the device can be significantly enhanced by barium cathode layer by increasing the charge collection at the cathode [10,11,16]. Finally the PCE for the SMOSCs was improved to the record value of 9.02% and thus making solution processed SMOSCs strong competitors to polymeric solar cells. More recently, the PCE in the range of 9–10% has been reported of D-A conjugated small molecules BHJ organic solar cells [17–20].

In the field of organic solar cells, the most efficient organic semiconductors investigated so far are with donor-acceptor (-D-A-) backbone where D is electron rich (D) moiety and A electron deficient (A) moiety. In recent years, the search for new small molecules based donor systems resulted in the development of a large variety of organic small molecules with different D-A moiety combinations [21] Large number of symmetrical acceptor-donor-acceptor (A-D-A) [22–26], donor-acceptor-donor (D-A-D) [27–29], A-D-A-D-A [30] and D-A-D-A-D [11,31,32], as well as unsymmetrical D-A [33,34] and D-A-A [35,36] small molecules have been developed. The reported PCE values of OSCs based on these SM donors are quickly approaching the best values for polymeric solar cells [37–40].

* Corresponding author.
** Corresponding author.
E-mail addresses: rajneeshmisra@iiti.ac.in (R. Misra), sharmagd_in@yahoo.com, gdsharma273@gmail.com (G.D. Sharma).

http://dx.doi.org/10.1016/j.orgel.2015.09.006
1566-1199/

In this contribution we report benzothiadiazole-based small molecules as donor for solution BHJ solar cells. The design of this molecule is based upon the following consideration: (i) The incorporation of triphenylamine (TPA) moiety, which has a three dimensional propeller structure can effectively impede molecular aggregation, increase solution processability and function as a donor unit [41–43]; (ii)The incorporation of carbazole donor unit as a building block to synthesize organic/polymer donor materials results in low HOMO levels which leads to high open circuit voltage for their OSCs [44–48]; (iii) Incorporation of strong acceptor benzothiadiazole results in low HOMO–LUMO gap; and (iv) Incorporation of TCNE/TCNQ units results in strong intramolecular charge transfer chromophores.

Herein, we have investigated the optical and electrochemical (experimental and theoretical) properties of two unsymmetrical novel D1–A1–A2–D2 small molecule **SM1** and **SM2** donors that bear the same benzothiadiazole (BTD) acceptor (A2), carbazole (CA) (D2) and TPA (D1) donor units with different A1, i.e. tetracyanobutadiene (TCBD) and dicyanoquinodimethane (DCNQ) for **SM1** and **SM2**, respectively. We have used them as a donor component along with $PC_{71}BM$ as acceptor for the fabrication of solution processed BHJ small molecule solar cells. The BHJ solar cells based on **SM1**:$PC_{71}BM$ and **SM2**:$PC_{71}BM$ processed with DCM solvent showed PCE of 2.76% and 3.61%, respectively. The PCE of the device based on **SM2**:$PC_{71}BM$ processed with CN/DCM has been improved up to 4.86%. The increase in PCE for the device processed with 1-chloronaphthalene (CN) as additive, could be attributed to the improved nanoscale morphology and balanced charge transport, induced from solvent additive during film formation.

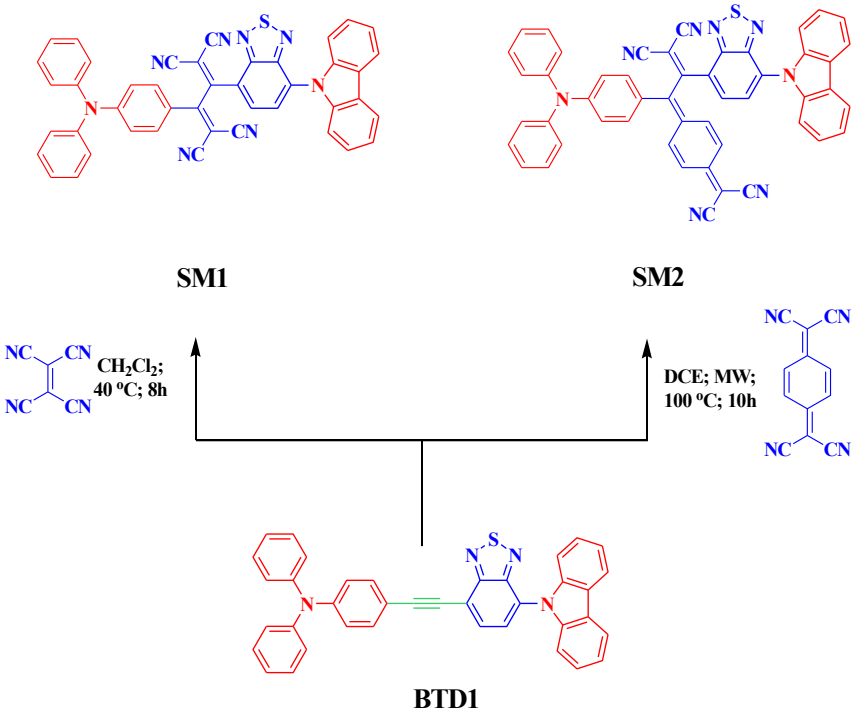
2. Experimental details

2.1. Device fabrication and characterization

The BHJ organic solar cells were prepared using the indium tin oxide (ITO) coated glass substrate as anode, Al as cathode and a blended film of **SM1** or **SM2**:$PC_{71}BM$ between the two electrodes as the photoactive layer as follows: Firstly, ITO coated glass substrates were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried in an oven for 12 h. An aqueous solution of PEDOT:PSS (Heraeus, Clevious P VP, Al 4083) in aqueous solution was spin cast on the ITO substrates obtaining a film of about 40 nm thick. The PEDOT:PSS film was then dried for 10 min at a temperature of 120 °C in ambient conditions. Then, a 20 mg/mL solution of **SM1** or **SM2**/$PC_{71}BM$ blends in different solvents were prepared with different weight ratio and then spun cast on the top of PEDOT:PSS layer and then dried at 80 °C for 10 min. The solvents include dichloromethane (DCM) and DCM containing 1, 2, 3 and 4% (v%) CN. The thickness of the photoactive layer is about 100 ± 10 nm. Finally ~90 nm thick Al electrode was deposited on the top of BHJ film under reduced pressure ($<10^{-6}$ Torr). All the devices were fabricated and tested in ambient atmosphere without encapsulation. The active area of the devices is about 20 mm^2.

The current–voltage characteristics of the devices were measured using a computer controlled Keithley 238 source meter in dark as well as under illumination intensity of 100 mW/cm^2. A xenon light source coupled with AM 1.5 optical filter was used as the light source to illuminate the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured while illuminating the device through the light source and monochromator and the resulting current was measured using Keithley electrometer under short circuit condition.

The charge carrier mobility of the BHJ active layers was measured using space charge limited current (SCLC) method. The hole only and electron only devices ITO/PEODT:PSS/**donor**:$PC_{71}BM$/Au and Al/**donor**:$PC_{71}BM$/Al structures were fabricated to measure the hole and electron mobility, respectively and measured their J–V characteristics in dark. The hole and electron mobilities were extracted by modeling the dark current (J) under forward bias using



Scheme 1. Synthetic route of **SM1** and **SM2**.