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 anthracenebased organic small molecules

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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 optoelectrical and photovoltaic properties of the molecules. The maximum absorptions of the anthracenebased 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**:PC₇₁BM (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). © 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The bulk heterojunction solar cells (BHI) containing the photoactive layer made up with the bi-continuous network of electron donating π -conjugated material and electron accepting [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) 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 PC₇₁BM 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 PSCs²⁻⁷ 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,

* 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). 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







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^{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 molecules³¹ 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 anthracenebased molecules, such as **TCV-TpaA_{9,10}T**, **TpaA_{9,10}T-TCV**, **TCV-Tpa-TA_{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 anthracenebased molecules namely TpaA9.10T-TCV and TpaTA9.10T-TCV containing the TCV group at the thiophene unit of the molecules were obtained. The color of TpaA9,10T-TCV and TpaTA9,10T-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



TpaTA_{9,10}T-TCV

group into compound **6** is not expected. Indeed, we found that the reaction did not happen under this condition. Instead, when we treated compound **6** with *n*-BuLi followed by TCNE, we were able to obtain **MTpaA_{9,10}T-TCV** as a brown color solid. These results support that the direct reaction between compound **4** or **5** with TCNE in DMF leads the TCV group incorporation on the *para*-position of the phenyl group of the triphenylamine unit, while the reaction between compounds **4**, **5** or **6** with *n*-BuLi followed by TCNE leads the TCV group incorporation on the end thiophene unit of the molecules. The synthetic route to the synthesis of **MTpaA_{9,10}T-TCV** is displayed in Scheme 2.

compound **9** with *n*-BuLi followed by TCNE. All the synthesized compounds were characterized by NMR and high resolution mass spectroscopy.

2.2. Optical properties

The UV–Visible absorption spectra of the synthesized molecules in 1.00×10^{-5} M chloroform solution and as thin film on glass are presented in Fig. 1. **TCV-TpaA_{9,10}T** and **TCV-TpaTA_{9,10}T** showed relatively weak absorption bands in the range of 300 nm–450 nm and very intense absorption bands in the range of 450 nm–700 nm with



Scheme 2. Synthetic route for the synthesis of MTpaA9,10T-TCV.

To study the linkage position influences of the anthracene chromophore, we also prepared 2,6-linked anthracene-based molecules containing the TCV group at the phenyl group of the triphenylamine unit or at the thiophene unit of the molecules. The synthetic pathway for 2,6-linked anthracene-based molecules TCV-TpaA_{2.6}T and TpaA_{2.6}T-TCV is presented in Scheme 3. The key intermediate 7 was synthesized by using the known literature procedure.³⁶ Compound **7** was subjected to the Stille coupling reaction with 2-(tributylstannyl)thiophene to give compound 8, but dicoupled product was also obtained. After the column separation, pure compound **8** was obtained. Then, the Suzuki coupling reaction between compound 8 and 4-(diphenvlamino)phenvlboronic acid afforded compound 9. The reaction between compound 9 and TCNE in DMF yielded TCV-TpaA₂₆T containing the TCV group at the phenyl group of the triphenylamine unit. **TpaA_{2.6}T-TCV** containing the TCV group at the thiophene unit was obtained by treating maximum absorption at 537 nm and 553 nm, respectively, in solution and at 532 nm and 553 nm, respectively, as film. On the other hand TpaA9,10T-TCV and TpaTA9,10T-TCV showed their strong absorption bands in the range of 300 nm-450 nm with maximum absorption at 413 nm and 410 nm, respectively, in solution and at 386 nm and 370 nm, respectively, as film and guite weak absorption bands in the range of 450 nm-700 nm with maximum absorption at 562 nm and 555 nm, respectively, in solution and at 573 nm and 549 nm, respectively, as film. The absorption band of MTpaA910T-TCV was quite similar to that of TpaA910T-TCV or TpaTA_{9.10}T-TCV with the maximum absorption at 412 nm and 562 nm in solution and 402 nm and 564 nm as film. On the other hand, 2,6-linked anthracene-based molecule TpaA₂₆T-TCV displayed its strong absorption bands in the range of 300 nm-520 nm and 520 nm-800 nm with three absorption maximums at 364 nm, 445 nm and 645 nm both in solution and as



Scheme 3. Synthetic route for the synthesis of TCV-TpaA_{2,6}T and TpaA_{2,6}T-TCV.



Fig. 1. Absorption spectra of the molecules in chloroform $(1 \times 10^{-5} \text{ M})$ solution and as thin film on glass.

film, while **TCV-TpaA_{2,6}T** showed its absorption band quite similar to those of **TCV-TpaA_{9,10}T** and **TCV-TpaTA_{9,10}T** both in solution and as film. The absorption bands of the molecules at shorter wavelength region are expected to be originated from the π - π * electronic transitions while the bands at longer wavelength region might be attributed to the internal chare transfer (ICT) between the donor and acceptor units.

The comparison of the absorption spectra of 9,10-linked anthracene-based molecules **TCV-TpaA**_{9,10}**T**, **TpaA**_{9,10}**T-TCV**, **TCV-TpaTA**_{9,10}**T**, and **TpaTA**_{9,10}**T-TCV** revealed that the ICT between the donor and acceptor units quite efficiently occurred for **TCV-TpaA**_{9,10}**T** and **TCV-TpaTA**_{9,10}**T** while the ICT was quite much prohibited for **TpaA**_{9,10}**T-TCV** and **TpaTA**_{9,10}**T-TCV**. To understand those behaviors of the compounds, we optimized structures of all newly synthesized compounds by using Gaussian 03 and their optimized molecular structures are presented in Fig. 2. The planarity between the 9,10-linked anthracene and the aryl groups attached to the

anthracene was found to be poor (almost perpendicular plane) for all four 9,10-linked anthracene-based molecules TCV-TpaA9,10T, TpaA_{9.10}T-TCV, TCV-TpaTA_{9.10}T, and TpaTA_{9.10}T-TCV. Even though the π -conjugation between the donor (electron donating nitrogen) and acceptor groups (TCV group) is quite short for compounds TCV-TpaA_{9.10}T and TCV-TpaTA_{9.10}T compared with their structural isomers TpaA9.10T-TCV and TpaTA9.10T-TCV, the efficient ICT is expected to occur due to the presence of strong electron donating nitrogen atom near to the TCV group. On the other hand, even though the π -conjugation between the donor (triphenylamine unit) and acceptor group (TCV group) is quite long for TpaA_{9.10}T-TCV and TpaTA9.10T-TCV compared with TCV-TpaA9.10T and TCV-**TpaTA_{9.10}T**, the ICT is expected to be quite much prohibited due to the out of planarity of the anthracene moiety. Consequently, TCV-TpaA_{9.10}T and TCV-TpaTA_{9.10}T displayed strong ICT absorption bands from 450 nm to 700 nm while TpaA_{9,10}T-TCV and TpaTA_{9,10}T-TCV showed very weak ICT absorption bands from 450 nm to



Fig. 2. The optimized structures of the molecules.

700 nm. The optimized structure of 2,6-linked anthracene-based molecules, such as TCV-TpaA2.6T and TpaA2.6T-TCV shown in Fig. 2 clearly indicates that the planarity between the 2,6-linked anthracene unit and the neighboring aryl groups is considerably increased compared to that of 9,10-linked anthracene-based molecules. The enhanced planarity of 2,6-linked anthracene-based molecule TpaA_{2.6}T-TCV allows the efficient ICT between the donor and acceptor groups, and consequently, the companied electronic transitions, such as π - π^* and ICT shifted their absorption band up to 800 nm. On the other hand, even though the planarity of TCV-TpaA_{2.6}T is quite much improved compared to that of TCV-TpaA_{9.10}T or TCV-TpaTA_{9.10}T, TCV-TpaA_{2.6}T shows the absorption band similar to that of TCV-TpaA9.10T or TCV-TpaTA9.10T because the effective π -conjugation is extended only from the nitrogen atom of the triphenylamine unit to the TCV group in all three molecules.

To gain more insight on the relatively very weak ICT peaks for 9,10-linked anthracene-based molecules, such as TpaA_{9.10}T-TCV, TpaTA9,10T-TCV, MTpaA9,10T-TCV and the strong ICT peak for 2,6linked anthracene-based molecule TpaA_{2.6}T-TCV, the electron densities at the HOMO and LUMO energy levels of the molecules were calculated from their optimized structures and presented in Fig. 3. The electron densities at the HOMO energy levels of TpaA_{9.10}T-TCV, TpaTA_{9.10}T-TCV, and MTpaA_{9.10}T-TCV were found to be strongly distributed on the donor units, such as triphenylamine and thiophene units and very weakly distributed on the 9,10-linked anthracene unit while the electron densities at the LUMO energy levels of the molecules were found to be strongly distributed on the thiophene and TCV groups. The lack of significant electronic overlap in the HOMO and LUMO levels of TpaA_{9.10}T-TCV, TpaTA_{9.10}T-TCV, and MTpaA_{9.10}T-TCV due to the out of planarity of 9,10-linked anthracene indicates that the ICT between the donor and acceptor units is quite much difficult or very week. In contrast, the electron density was found to be nicely distributed throughout the electron donor groups, such as triphenylamine and 2,6-linked anthracene at the HOMO energy level of **TpaA_{2.6}T-TCV** and the electron density was found to be distributed partly on 2,6-linked anthracene and fully on the thiophene and TCV groups at the LUMO energy level of the molecule. The electronic distribution over the 2,6-linked anthracene unit in both HOMO and LUMO suggests that an effective ICT occurs from the donor to acceptor through the 2,6-linked anthracene unit for TpaA_{2.6}T-TCV.



Fig. 3. The frontier molecular orbitals of molecules TpaA_{9,10}T-TCV, TpaTA_{9,10}T-TCV, MTpaA_{9,10}T-TCV, and TpaA_{2,6}T-TCV.

The optical band gaps (E_g) of **TCV-TpaA_{9,10}T**, **TCV-TpaTA_{9,10}T**, and **TCV-TpaA_{2,6}T** were calculated to be 1.89 eV, 1.74 eV, and 1.74 eV, respectively, from the onset wavelength (656 nm, 712 nm and 712 nm, respectively) of the film state absorption spectra. The band gap values of compounds **TpaA_{9,10}T-TCV**, **TpaTA_{9,10}T-TCV**, **MTpaA_{9,10}T-TCV**, and **TpaA_{2,6}T-TCV** were also calculated to be 1.77 eV, 1.82 eV, 1.72 eV, and 1.52 eV, respectively, from the onset wavelength (700 nm, 681 nm, 720 nm, and 815 nm, respectively) of the film state absorption maximum, molar absorptivity and optical band gap of molecules are summarized in Table 1.

Table	1

Optical and electrochemical	properties of anthracene-based small molecules
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Molecule	$\lambda_{max,solution}$ $(nm)^a$	$\substack{\epsilon \times 10^4 \\ (M^{-1} \text{ cm}^{-1})^b}$	λ _{max,film} (nm) ^c	Eg (eV) ^d	HOMO (eV) ^e	LUMO (eV) ^f
TCV-TpaA _{9,10} T	537	3.1	532	1.89	-5.23	-3.34
TCV-TpaTA _{9,10} T	553	2.8	553	1.74	-5.15	-3.41
TCV-TpaA _{2,6} T	548	3.3	551	1.74	-5.23	-3.49
TpaA _{9,10} T-TCV	413, 562	3.3, 0.3	386, 573	1.77	-5.10	-3.33
TpaTA _{9,10} T-TCV	410, 555	3.5, 0.3	370, 549	1.82	-5.06	-3.24
MTpaA _{9,10} T-TCV	412, 562	3.5, 0.3	402, 564	1.72	-5.02	-3.30
TpaA _{2,6} T-TCV	445, 645	3.1, 2.1	445, 645	1.52	-5.09	-3.57

^a Absorption maximum measurements in chloroform $(1 \times 10^{-5} \text{ M})$.

^b Molar absorptivity measured from $(1 \times 10^{-5} \text{ M})$ chloroform solution.

^c Absorption maximum measurements in thin film on glass.

^d The optical band gap estimated from the onset wavelength of the optical absorption.

^e The HOMO energy level was determined from cyclic voltammetry analysis.

^f The LUMO energy level was calculated using the equation of LUMO=HOMO+ E_{g} .

2.3. Electrochemical properties

In order to evaluate the electrochemical properties of the synthesized compounds, we performed the cyclic voltammetry (CV) analysis for all seven compounds. Each of the seven compounds coated as thin film on platinum working electrode was used to determine the electrochemical properties with the use of Ag/AgCl as reference electrode and platinum as counter electrode in acetonitrile (ACN) containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte. The cyclic voltammograms of the molecules are shown in Fig. 4. From the CV spectra, the onset oxidation potential $(E_{ox,onset})$ values of the molecules were estimated and the highest occupied molecular orbital (HOMO) energy levels were calculated from the $E_{ox,onset}$ values by using the following equation of E_{HOMO} (eV)=-[($E_{ox,onset vs Ag}$ / AgCl)–($E_{ox,ferrocene vs Ag/AgCl}$)]–4.8, where 4.8 eV is the energy level of ferrocene below the vacuum level and $E_{\text{onset}(\text{Fe}/\text{Fe}+\text{ vs Ag/AgCl})}=0.51 \text{ V}.$ The E_{ox,onset} values of TCV-TpaA_{9,10}T, TCV-TpaTA_{9,10}T, and TCV-TpaA_{2.6}T were estimated to be 0.94 V, 0.86 V, and 0.94 V, while those of TpaA9,10T-TCV, TpaTA9,10T-TCV, MTpaA9,10T-TCV, and TpaA_{2.6}T-TCV were determined to be 0.81 V, 0.77 V, 0.73 V, and 0.80 V, respectively. The HOMO energy levels of TCV-TpaA_{9.10}T, TCV-TpaTA_{9,10}T, and TCV-TpaA_{2,6}T were located in between -5.15 eV to -5.23 eV and those of **TpaA_{9.10}T-TCV**, **TpaTA_{9.10}T-TCV**, MTpaA_{9.10}T-TCV, and TpaA_{2.6}T-TCV were positioned in between -5.02 eV to -5.10 eV. The HOMO energy levels of TCV-TpaA_{9.10}T, TCV-TpaTA_{9.10}T, and TCV-TpaA_{2.6}T were found to be slightly deeper than those of TpaA_{9.10}T-TCV, TpaTA_{9.10}T-TCV, MTpaA_{9.10}T-TCV, and TpaA_{2,6}T-TCV (see Table 1), which suggest that the incorporation of TCV group on the phenyl group of the triphenylamine unit lowered the HOMO level more effectively than the incorporation of TCV group on the thiophene unit of the anthracene-based molecules. Interestingly, the HOMO energy levels of 9,10-linked anthracenebased molecule TCV-TpaA9,10T and 2,6-linked anthracene-based molecule TCV-TpaA_{2.6}T containing the TCV group on the phenyl



Fig. 4. Cyclic voltammograms of the molecules films cast on platinum working electrode in 0.1 M Bu₄NBF₄/acetonitrile at 100 mV s⁻¹, potential versus Ag/AgCl.

group of triphenylamine unit were found to be identical with each other (-5.23 eV).

In addition, the HOMO energy levels of molecules TpaA_{9.10}T-TCV and TpaA_{2.6}T-TCV containing the TCV group on the thiophene moiety were found to be almost identical (-5.10 eV and -5.09 eV)respectively). These results revealed that the shift in the HOMO energy levels of the anthracene-based molecules is mainly originated from the linkage position of TCV group, not from the linkage position of anthracene chromophore. In other words, the linkage position influence of anthracene chromophore on the HOMO energy level of the anthracene-based molecules is nil. The lowest unoccupied molecular orbital (LUMO) energy levels of the compounds were calculated by using the following equation LUMO=HOMO+ E_g , where E_g is the optical band gap values obtained from the absorption spectra of the molecules. The LUMO energy levels of the compounds were positioned in between -3.24 eV to -3.57 eV. The HOMO and LUMO energy levels of the molecules are presented in Table 1. The LUMO energy levels of the newly synthesized molecules were found to be higher than that of the LUMO level of PC₇₁BM, which suggests that they can be utilized as electron donor materials in the fabrication of SMOSCs with PC₇₁BM as an electron acceptor material.

2.4. Photovoltaic properties

To investigate the solar to electrical energy conversion efficiency of the 9,10- and 2,6-linked anthracene-based molecules, we prepared SMOSCs with each of the selected compounds, such as TCV-TpaA_{9,10}T, TCV-TpaA_{2,6}T, and TpaA_{2,6}T-TCV as an electron donor and PC71BM as an electron acceptor. It is well known that utilizing the donor molecules showing broad absorption band or the molecules showing their absorption band in the region of 500 nm-800 nm is crucial because the current density of the SMOSCs is directly proportional to the light harvesting ability of the photoactive layer and the light harvesting ability is significantly influenced by the absorption ability of the donor molecule. In this compounds **TpaA**_{9.10}**T-TCV**, **TpaTA**_{9.10}**T-TCV**, instance. and MTpaA_{9.10}T-TCV were omitted for the preparation of SMOSCs due to their poor absorption. Compound TCV-TpaTA_{9.10}T was also omitted because its opto-electrical property was quite similar to that of compound **TCV-TpaA_{9.10}T**, and consequently its photovoltaic property was expected to be similar to that of TCV-TpaA_{9.10}T. In our attempt, we prepared SMOSCs with each of three compounds TCV-TpaA_{9,10}T, TCV-TpaA_{2,6}T, and TpaA_{2,6}T-TCV and PC₇₁BM at three different donor-acceptor ratio, such as 2:1 wt %, 1:1 wt %, and 1:2 wt % with the aim of understanding the linkage position influences on the photovoltaic properties. The SMOSCs were fabricated with the device structure of ITO/PEDOT:PSS/TCV-TpaA_{9.10}T or TCV-TpaA2.6T or TpaA2.6T-TCV:PC71BM (2:1 wt %, 1:1 wt %, and

1:2 wt %)/LiF/Al. The J-V characteristics of the SMOSC devices measured under the illumination of AM 1.5 G (100 mW cm^{-2}) are shown in Fig. 5 and their corresponding photovoltaic parameters, such as power conversion efficiency (PCE), open circuit voltage (V_{oc}) , current density (J_{sc}) and fill factor (FF) are presented in Table 2. All three molecules showed highest photovoltaic performances for the devices constructed with the active layer made up with the donor-acceptor ratio of 2:1 wt %. The SMOSCs fabricated from TCV-TpaA_{9.10}T:PC₇₁BM (2:1 wt %) as an active layer shows the PCE of 1.04% with an $V_{\rm oc}$ of 0.56 V, a $J_{\rm sc}$ of 5.08 mA cm⁻², and FF of 36.03%, while the device fabricated from TCV-TpaA2.6T:PC71BM (2:1 wt %) and TpaA26T-TCV:PC71BM (2:1 wt %) as an active layer shows improved PCE of 1.67% with V_{oc} of 0.61 V, a I_{sc} of 6.26 mA cm⁻², and a FF of 43.85% and PCE of 1.95% with $V_{\rm oc}$ of 0.63 V, a $J_{\rm sc}$ of 6.83 mA cm^{-2} , and a FF of 44.63%, respectively. On the other hand, the SMOSCs constructed by using the donor-acceptor blend ratio of 1:1 wt % or 1:2 wt % displayed decreased PCE compared to that of the blend ratio of 2:1 wt % and their corresponding photovoltaic parameters are presented in Table 2. Interestingly, the shunt resistance was found to be relatively higher and at the same time the series resistance was found to be lower for the device prepared with the 2:1 wt % blends than the devices prepared with 1:1 wt % and 1:2 wt % blends and those values are presented in Table 2. Those results indicate that the presence of higher content of electron donating anthracene-based molecules in active layer produces higher conversion efficiency than the presence of higher content of electron accepting PC71BM. This result is expected to be more favorable for SMOSCs application since PC₇₁BM is quite expensive.

The preliminary photovoltaic studies for the 9,10- and 2,6linked anthracene-based molecules show reasonable energy conversion efficiencies. In this instance, the device optimization is expected to improve the photovoltaic performances. The comparison of the photovoltaic properties of **TCV-TpaA**_{9,10}**T** and **TCV-TpaA**_{2,6}**T** suggests that 2,6-linked anthracene-based molecule is superior to 9,10-linked anthracene-based molecule in terms of energy conversion efficiency. Interestingly, the photovoltaic properties of **TCV-TpaA**_{2,6}**T** and **TpaA**_{2,6}**T-TCV** suggest that the J_{sc} and FF are slightly improved when the TCV group was attached at the thiophene unit of the final molecules, and consequently, the photovoltaic performances are enhanced.

The external quantum efficiency (EQE) spectra of the SMOSC devices were studied to verify the photoresponse further. The EQE spectra for the SMOSCs prepared with the configuration of ITO/PEDOT:PSS/**TCV-TpaA_{9,10}T** or **TCV-TpaA_{2,6}T** or **TpaA_{2,6}T**. **TCV**:PC₇₁BM (2:1 wt %)/LiF/Al are represented in Fig. 6. The EQE response of **TCV-TpaA_{9,10}T**:PC₇₁BM (2:1 wt %)-based SMOSC was found to be in the range of 300–680 nm with maximum EQE of 45% at 511 nm while **TCV-TpaA_{2,6}T**:PC₇₁BM (2:1 wt %)-based SMOSC showed its EQE curve up to 730 nm with EQE maximum of



Fig. 5. J–V characteristics of SMOSCs prepared from ITO/PEDOT:PSS/TCV-TpaA_{9.10}T or TCV-TpaA_{2.6}T or TpaA_{2.6}T. TCV:PC₇₁BM/LiF/Al under AM 1.5 irradiation (100 mW cm⁻²).

Table	2				
Solar	cell	performances	of	ITO/PEDOT:PSS/TCV-TpaA9,10T or TCV-TpaA2,6T	or
TpaA ₂	T-T	CV:PC71BM (2:1	wt	% and 1:1 wt % and 1:2 wt %)/LiF/Al devices	

Active layer	V _{oc} (V) ^a	J _{sc} (mA cm ⁻²) ^b	FF (%) ^c	PCE (%) ^d	$R_{\rm sh}$ $(\Omega \ {\rm cm}^2)^{\rm e}$	$\frac{R_{\rm s}}{(\Omega \ {\rm cm}^2)^{\rm f}}$	Integrated J _{sc} (mA cm ⁻²) ^g
TCV-TpaA _{9,10} T:	0.56	5.08	36.03	1.04	3.4×10 ³	19	4.89
(2.1 wt %)							
TCV-TpaA _{9 10} T:	0.56	1.67	26.80	0.25	7.8×10 ²	36	1.52
PC ₇₁ BM							
(1:1 wt %)							
TCV-TpaA _{9,10} T:	0.56	2.51	30.11	0.43	1.0×10^{3}	30	2.21
$PC_{71}BM$							
(1:2 Wt %)	0.61	6.26	12 95	167	5.1×10^{3}	10	6 10
$PC_{71}BM$	0.01	0.20	45.85	1.07	J.1×10	10	0.10
(2:1 wt %)							
TCV-TpaA _{2.6} T:	0.61	2.70	36.16	0.60	1.6×10 ³	25	2.53
PC ₇₁ BM							
(1:1 wt %)					2		
TCV-TpaA _{2,6} T:	0.61	4.78	39.46	1.16	3.8×10 ³	17	4.53
$PC_{71}BM$							
(1.2 WL %)	0.63	6.83	44 63	1 95	6.7×10^{3}	9	6.60
PC ₇₁ BM	0.05	0.05	11.05	1.55	0.7 \ 10	5	0.00
(2:1 wt %)							
TpaA _{2,6} T-TCV:	0.62	3.69	35.70	0.82	2.8×10 ³	20	3.57
PC71BM							
(1:1 wt %)					2		
TpaA _{2,6} T-TCV:	0.61	4.38	41.92	1.13	3.0×10 ³	15	4.21
$PC_{71}BM$							
(1.2 WL %)							

^a Open-circuit voltage.
 ^b Short-circuit current density.

^c Fill factor.

^d Power conversion efficiency.

^e Shunt resistance.

^f Series resistance.

^g Calculated from EQE.



Fig. 6. IPCE spectra for the SMOSCs prepared from TCV-TpaA_{9,10}T, TCV-TpaA_{2,6}T, and TpaA_{2,6}T-TCV (2:1 wt %) as an active layer.

52% at 542 nm. Interestingly, the SMOSC containing the active layer of **TpaA_{2,6}T-TCV**:PC₇₁BM (2:1 wt %) displayed its EQE band in the quite broad range of 300–800 nm with three maximum EQE values of 51% at 340 nm, 50% at 478 nm and 41% at 642 nm. The EQE spectra were found to be red shifted in the order of **TCV-TpaA_{9,10}T**<**TCV-TpaA_{2,6}T**-**TpaA_{2,6}T-TCV** and the maximum EQE values also appeared in the same order mentioned above, and consequently, the J_{sc} values obtained from the J_{-V} curves are expected in the above mentioned order and the same was found to be correlated well with each other. Moreover, the J_{sc} values calculated from integration of the EQE spectra concur well with the J_{sc} obtained from the J-V measurements. The error range between

the measured J_{sc} and integrated photocurrent were ca. 5%, which is usually in the range of 5–10%.³⁷ Comparisons of the integrals of the calculated photocurrent densities with those of photocurrent densities from a solar simulator are summarized in Table 2.

3. Conclusion

In this study, we prepared a series of anthracene-based organic small molecules for SMOSCs application. In order to investigate the linkage position influences of the anthracene and TCV groups on the optical, electrochemical and photovoltaic properties of organic molecules, we linked the planar structured anthracene moiety with two different aryl groups via 9,10- and 2,6-positions and the TCV group was attached at the phenyl group of the triphenylamine unit or at the thiophene unit of the molecules. The 9,10-linked anthracene-based molecules showed red shifted absorption maxima when the TCV group was incorporated at the phenyl group of the triphenylamine unit. On the other hand, 2,6-linked anthracene-based molecules displayed red shifted absorption maxima when the TCV group was incorporated at the thiophene unit. Both of the 9,10- and 2,6-linked anthracene-based molecules containing the TCV group at the phenyl group of the triphenylamine unit showed almost similar absorption band. On the contrary, the 2,6-linked anthracenebased molecule showed very much red shifted and broad absorption band compared to the 9,10-linked anthracene-based molecule when the TCV group was incorporated at the thiophene unit. The planarity of the 2,6-linked anthracene-based compounds was found to be much better than that of 9,10linked anthracene-based compounds, and consequently, the red shifted absorption band was resulted. The HOMO energy levels of the compounds containing TCV group at the phenyl group of the triphenylamine unit were found to be slightly deeper than those of the compounds containing TCV group at the thiophene unit. The preliminary photovoltaic studies of the solution processed SMOSCs afforded maximum conversion efficiency of 1.04% and 1.95%, respectively, for the 9,10- and 2,6-linked anthracene-based molecules. From this study, we concluded the linkage position of the anthracene and TCV units significantly influenced the properties of final compounds and we believe this study would be quite useful for the design of new organic compounds for SMOSCs application.

4. Experimental section

4.1. Materials and general procedure

The necessary reagents were obtained from Aldrich or TCI chemicals and used without further purification unless otherwise noted. The common organic solvents were purified by using standard procedure and handled in a moisture-free atmosphere. Flash column chromatography was performed on silica gel (Merck Kieselgel 60, 70–230 mesh).

4.2. Instruments and measurements

The nuclear magnetic resonance spectra (¹H and ¹³C NMR) were recorded by using 300-MHz Varian Mercury Plus spectrometer in deuterated chloroform as reference. The absorption spectra were recorded by using a JASCO V-570 spectrophotometer in chloroform and as thin films on glass at room temperature. The cyclic voltammetry analyses of the molecules were performed by using a CH Instruments Electrochemical Analyzer made up with the standard three electrode system, such as Ag/AgCl and platinum.

4.3. Fabrication and characterization of solar cell devices

4.3.1. Fabrication. The SMOSCs were constructed as follows. The transparent ITO electrodes (12 Ω /sq sheet resistance) coated on glass were subjected to ultrasonication sequentially in detergent. deionized water, acetone, and isopropyl alcohol to clean the electrode. Then, the substrates were dried and poly(3.4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS. ~50 nm) (CLEVIOUS P:IPA (1:2 v/v)) was spin-coated onto the UVozone treated ITO substrates at 5000 rpm for 40 s. The ITO/ PEDOT:PSS substrates were baked in air at 150 °C for 10 min. Subsequently, the active layer (~95 nm) made up with the TCV-TpaA_{9.10}T or TCV-TpaA_{2.6}T or TpaA_{2.6}T-TCV:PC₇₁BM blend solution in chloroform was spin-coated onto the ITO/PEDOT:PSS substrates at 900 rpm for 40 s. The blend solution was prepared by mixing each of molecules TCV-TpaA_{9.10}T, TCV-TpaA_{2.6}T, and TpaA_{2.6}T-TCV with $PC_{71}BM$ at a weight ratio of 1:1 wt %, 2:1 wt %, and 1:2 wt % in chloroform. Then, the ITO/PEDOT:PSS/Molecule:PC71BM substrates were heated at 80 °C for 30 min in glove box to remove the residual solvent. After drying the solvent, the electron transporting LiF $(\sim 0.7 \text{ nm})$ was spin-coated onto the active layer and subjected to a vacuum $(3 \times 10^{-6} \text{ Torr})$ and then an Al electrode with thickness of around 100 nm was deposited onto the LiF layer. The top metal electrode area, comprising the active area of the solar cells, was found to be 0.38 cm². All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere.

4.3.2. Characterization of solar cell devices. The performances of the SMOSCs were measured under simulated AM 1.5 illumination with an irradiance of 100 mW cm⁻² (PEC-L11, Pecell Technologies Inc.). The irradiance of the sunlight-simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The *J*–*V* curves were recorded automatically using a Keithley 2400 SourceMeter source measurement unit. The series resistance (*R*_s) and shunt resistance (*R*_{sh}) were obtained from the slope of the dark current curves. The quantum efficiency measurements (IPCE) were carried out by using Oriel IQE-200. Oriel IQE-200 is made up by using 250 W quartz tungsten halogen (QTH) lamp, monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm.

4.4. Synthesis

4.4.1. Synthesis of 2-(10-bromoanthracen-9-yl)thiophene (1) and 2-(10-(thiophen-2-yl)anthracen-9-yl)thiophene (2). A solution of 9,10-dibromoanthracene (5.0 g, 15.0 mmol) and 2-(tributylstannyl)thiophene (5.70 mL, 18.0 mmol) in toluene (60 mL) was stirred well under argon atmosphere for 30 min and then Pd(PPh₃)₄ (2 mol %) was added. The solution was refluxed for 15 h under argon atmosphere, and then the solvent was completely removed by using a rotary evaporator. The residue was dissolved in chloroform (100 mL) and washed with brine solution, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane-methylene chloride=90:10, v/v) to afford compounds 1 and 2 as yellow solids. Compound 1: Yield 1.80 g (36%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.18 (dd, 1H), 7.31 (dd, 1H), 7.40-7.50 (m, 2H), 7.56-7.68 (m, 3H), 7.84 (d, 2H), 8.60 (d, 2H); $^{13}\mathrm{C}$ NMR (75 MHz, CDCl₃) δ (ppm) 126.3, 127.2, 127.3, 127.4, 127.5, 128.1, 129.9, 130.4, 132.8, 138.6; HRMS (EI⁺, m/ *z*) [m⁺] calcd for C₁₈H₁₁BrS 337.9765, found 337.9771. Compound **2**: Yield 2.1 g (41%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.22 (dd, 2H), 7.33 (dd, 2H), 7.38-7.46 (m, 4H), 7.64 (dd, 2H), 7.84-7.92 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 125.9, 126.9, 127.1, 127.4, 129.8, 130.5, 131.7, 139.1; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C₂₂H₁₄S₂ 342.0537, found 342.0537.

4.4.2. Synthesis of 2-(10-(5-bromothiophen-2-yl)anthracen-9-yl) thiophene (3). To a stirred solution of compound 2 (2.0 g. 5.85 mmol) in the mixed solvent of chloroform and acetic acid (1:1 v/v. 50 mL) was added *N*-bromosuccinimide (*NBS*, 1.05 g. 5.90 mmol) in one portion at room temperature (RT). The solution was stirred for 12 h at rt. Then, the solution was poured into 100 mL water and extracted with chloroform (3×30 mL). The combined organic layer was washed with 2 N sodium hydroxide (NaOH) solution until the aqueous layer became basic. Then, organic layer was washed once with brine solution, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane-methylene chloride=90:10, v/v) to afford compound **3** as a yellow solid. Yield 1.30 g (53%); ¹H NMR (CDCl₃, 300 MHz, ppm) δ 6.98 (d, 1H), 7.21 (dd, 1H), 7.28 (d, 1H), 7.32 (dd, 1H), 7.38-7.48 (m, 4H), 7.63 (dd, 1H), 7.84–7.96 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 113.2, 126.0, 126.3, 126.6, 127.0, 127.1, 127.5, 129.8, 130.2, 130.4, 131.6, 131.7, 138.9, 141.0; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C₂₂H₁₃BrS₂ 419.9642, found 419.9648.

4.4.3. Synthesis of N-phenyl-N-(4-(10-(thiophen-2-yl)anthracen-9yl)phenyl)benzenamine (4). A solution of compound 1 (1.52 g, 4.50 mmol) and 4-(diphenylamino)phenylboronic acid (1.45 g, 5.00 mmol) in toluene (30 mL) was stirred under argon for 45 min. To this solution were added $Pd(PPh_3)_4$ (2 mol %) and aqueous 2 M K₂CO₃ solution (7 mL). The mixture was heated to reflux under argon atmosphere. After 24 h, the reaction mixture was cooled to rt and the solvent was completely removed by using a rotary evaporator. The remaining residue was dissolved in chloroform (60 mL) and washed with brine solution, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane-methylene chloride=80:20, v/v) to afford compound **4** as a yellow solid. Yield 1.87 g (83%). ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.04–7.12 (m, 2H), 7.22 (dd, 1H), 7.28–7.44 (m, 17H), 7.62 (dd, 1H), 7.80–7.92 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 123.2, 123.4, 125.0, 125.3, 125.8, 126.9, 127.3, 127.4, 128.8, 129.6, 129.7, 130.2, 131.9, 1322, 132.6, 138.7, 139.5, 147.5, 148.0; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C₃₆H₂₅NS 503.1708, found 503.1712.

4.4.4. Synthesis of N-(phenyl-4-ethene-1,2,2-tricarbonitrile)-N-phenyl-4-(10-(thiophen-2-yl)anthracen-9-yl)benzenamine (TCV-**TpaA**_{9.10}**T**). To a stirred solution of compound 4 (0.50 g, 1.00 mmol) in DMF (30 mL) was added tetracyanoethylene (TCNE) (0.26 g, 2.00 mmol) at rt and the solution was slowly heated to 140 °C for 12 h. The thin layer chromatography analysis indicates that the reaction late is very slow. To the stirred solution, TCNE (0.26 g, 2.00 mmol) was added every 2 h four times at 140 °C. After that, the solution was stirred at 140 °C for 12 h. Total 10 equiv of TCNE were added. The reaction mixture was refluxed for 36 h. After that the solution was cooled to rt and the solvent was concentrated by using a rotary evaporator. The residue was dissolved in ethyl acetate (50 mL) and the organic solution was washed with brine and dried over anhydrous Na₂SO₄. The solution was filtered and concentrated by using a rotary evaporator. The blue color residue was purified by column chromatography (silica gel, methylene chloride) to afford $\textbf{TCV-TpaA}_{9,10}\textbf{T}$ as a blue solid. Yield 0.50 g (83%); ^{1}H NMR (300 MHz, CDCl₃) δ (ppm) 7.13 (d, 2H), 7.23 (dd, 1H), 7.34 (dd, 1H), 7.38–7.58 (m, 13H), 7.64 (dd, 1H), 7.66-7.74 (m, 2H), 7.88-7.94 (dd, 2H), 8.07 (d, 2H); 13 C NMR (75 MHz, CDCl₃) δ (ppm) 113.2, 113.4, 114.4, 118.5, 120.7, 125.8, 125.9, 126.7, 126.9, 127.1, 127.2, 127.5, 127.6, 129.6, 129.8,130.0, 130.7, 131.8, 132.6, 133.3, 137.1, 137.9, 138.4, 139.2, 143.9, 144.5, 154.7; HRMS (EI⁺, m/z) [m⁺] calcd for C₄₁H₂₄N₄S 604.1722, found 604.1725.

4.4.5. Synthesis of 1-(5-(10-(4-(diphenylamino)phenyl)anthracen-9*yl*)*thiophen-2-yl*)*ethene-1,2,2-tricarbonitrile* (TpaA_{9.10}T-TCV). To a stirred solution of compound 4 (0.50 g. 1.00 mmol) in dry tetrahvdrofuran (THF. 60 mL) was added *n*-BuLi (2.5 M in hexane. 0.48 mL 1.20 mmol) drop by drop at 0 °C under argon atmosphere. The solution was stirred for 30 min in the same bath and then TCNE (0.15 g, 1.20 mmol) in dry THF (10 mL) was added in one potion at 0 °C. The solution was slowly warmed to room temperature and stirred at rt for overnight. The solution was poured into brine solution (50 mL), and the aqueous solution was extracted with ethyl acetate (3×50 mL). The combined organic layer was dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by silica gel column chromatography (silica gel, methylene chloride) to afford compound TpaA_{9.10}T-TCV as a brown solid. Yield 0.26 g (43%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.06–7.14 (m, 2H), 7.28–7.54 (m, 17H), 7.72 (d, 2H), 7.89 (d, 2H), 8.36 (d, 1H); ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3) \delta$ (ppm) 111.9, 112.1, 113.0, 122.9, 123.6, 124.2, 125.1, 125.4, 125.7, 127.2, 127.9, 129.7, 130.2, 131.0, 131.5, 132.0, 132.8, 135.2, 140.6, 141.2, 147.8, 156.5; HRMS (EI⁺, m/z) [m⁺] calcd for C₄₁H₂₄N₄S 604.1722, found 604.1719.

4.4.6. Synthesis of N-phenyl-N-(4-(5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)phenyl)benzenamine (5). Compound 5 was synthesized by using the similar synthetic procedure for the synthesis of compound **4**. In this reaction, compound **3** (1.00 g, 2.40 mmol) and 4-(diphenylamino)phenylboronic acid (0.80 g, 2.80 mmol) were subjected to Suzuki coupling reaction and the crude product was purified by using column chromatography (silica gel, hexane-methylene chloride=80:20, v/v) to afford compound 5 as a yellow solid. Yield is 1.16 g (83%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.02–7.10 (m, 2H), 7.10–7.20 (m, 8H), 7.23 (d, 1H), 7.28-7.34 (m, 3H), 7.38-7.48 (m, 6H), 7.59 (d, 2H), 7.63 (d, 1H), 7.84-7.92 (m, 2H), 8.00-8.08 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 122.5, 123.3, 124.1, 124.7, 125.9, 126.8, 126.9, 127.1, 127.4, 128.5, 129.6, 129.8, 130.9, 131.6, 131.7, 137.7, 139.1, 145.9, 147.6, 147.7; HRMS (EI⁺, m/z) [m⁺] calcd for C₄₀H₂₇NS₂ 585.1585, found 585.1587.

4.4.7. Synthesis of N-(phenyl-4-ethene-1,2,2-tricarbonitrile)-N-phenyl-4-(5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)benzenamine (**TCV-TpaTA_{9,10}T**). The mixture of compound **5** (0.40 g, 0.68 mmol) and TCNE (0.87 g, 6.80 mmol) in DMF (30 mL) was heated to 140 °C for 24 h. The similar workup and purification procedures were used as described in the synthesis of **TCV-TpaA_{9,10}T**. The product (**TCV-TpaTA_{9,10}T**) was obtained as a blue solid. Yield 0.41 g (87%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.04 (d, 2H), 7.10–7.24 (m, 4H), 7.28–7.36 (m, 4H), 7.40–7.50 (m, 5H), 7.52–7.66 (m, 4H), 7.75 (d, 2H), 7.86–7.92 (m, 2H), 7.96–8.04 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 113.2, 133.4, 114.4, 118.7, 120.8, 123.3, 124.0, 124.7, 126.0, 126.1, 126.7, 127.0, 127.2, 127.4, 127.5, 129.6, 129.8, 130.5, 130.9, 131.1, 131.5, 131.7, 132.5, 133.1, 138.3, 139.0, 139.5, 143.7, 144.4, 144.5, 154.4; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C₄₅H₂₆N₄S₂ 686.1599, found 686.1603.

4.4.8. Synthesis of 1-(5-(10-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)ethene-1,2,2-tricarbonitrile (**Tpa-TA**_{9,10}**T-TCV**). Compound **TpaTA**_{9,10}**T-TCV** was synthesized by using the similar synthetic procedure for the synthesis of compound **TpaA**_{9,10}**T-TCV**. In this reaction, compound **5** (0.59 g, 1.00 mmol) was used instead of compound **4**. The product (**TpaTA**_{9,10}**T-TCV**) was obtained as a brown solid. Yield 0.27 g (39%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.02–7.10 (m, 2H), 7.10–7.20 (m, 8H), 7.26–7.34 (m, 3H), 7.40–7.54 (m, 6H), 7.58 (d, 2H), 7.68–7.74 (m, 2H), 8.04–8.12 (m, 2H), 8.36 (d, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm); 112.0, 112.1, 122.5, 123.4, 124.0, 124.8, 125.4, 125.8, 126.3, 126.8, 127.3, 127.5, 128.2, 129.6, 130.9, 131.1, 131.5, 132.8, 133.1, 133.3, 135.3, 136.5, 140.5, 146.4, 147.7, 147.8, 155.9; HRMS (EI⁺, *m/z*) [m⁺] calcd for C₄₅H₂₆N₄S₂ 686.1599, found 686.1603.

4.4.9. Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(10-(thiophen-2-yl)anthracen-9-yl)phenyl)benzenamine (**6**). The typical Suzuki coupling reaction between 4-(bis(4-methoxyphenyl)amino) phenylboronic acid (0.42 g, 1.20 mmol), which was prepared via the known procedure,³⁸ and compound **1** (0.34 g, 1.00 mmol) as described in the synthesis of compound **4**, followed by the typical workup and purification by column chromatography (silica gel, hexane–methylene chloride=80:20, v/v) afforded compound **6** as a yellow solid. Yield 0.51 g (91%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 3.83 (s, 6H), 6.90 (d, 4H), 7.08–7.24 (m, 9H), 7.31 (dd, 1H), 7.34–7.44 (m, 4H), 7.62 (dd, 1H), 7.80–7.90 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 55.7, 115.1, 119.9, 125.2, 125.7, 126.9, 127.2, 127.3, 127.4, 128.6, 129.7, 130.4, 131.9, 132.0, 139.6, 141.2, 156.3; HRMS (El⁺, *m/z*) [m⁺] calcd for C₃₈H₂₉NO₂S 563.1919, found 563.1921.

4.4.10. Synthesis of 1-(5-(10-(4-(bis(4-methoxyphenyl)amino)phenyl)anthracen-9-yl)thiophen-2-yl)ethene-1,2,2-tricarbonitrile (**MTpaA_{9,10}T-TCV**). Compound **MTpaA_{9,10}T-TCV** was synthesized by using the similar synthetic procedure for the synthesis of compound **TpaA_{9,10}T-TCV**. Compound **6** (0.28 g, 0.50 mmol), 1.2 equiv of *n*-BuLi and TCNE were used for this reaction. The product (**MTpaA_{9,10}T-TCV**) was obtained as a brown solid. Yield 0.13 g (39%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 3.83 (s, 6H), 6.92 (d, 4H), 7.10–7.25 (m, 7H), 7.10–7.25 (m, 6H), 7.71 (d, 2H), 7.91 (d, 2H), 8.35 (d, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 112.0, 112.1, 113.0, 115.1, 119.6, 124.0, 125.4, 125.6, 127.1, 127.3, 128.0, 129.2, 130.2, 131.0, 131.8, 132.8, 133.3, 135.2, 140.6, 140.9, 141.6, 148.7, 156.4, 156.7; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C₄₃H₂₈N₄O₂S 664.1933, found 664.1938.

4.4.11. Synthesis of 2-(2-bromo-9,10-dipropoxyanthracen-6-yl)thiophene (8). A solution of compound 7 (3.00 g, 6.60 mmol), which was prepared via the known procedure,³⁶ and 2-(tributylstannyl) thiophene (2.1 mL, 6.60 mmol) in toluene (50 mL) was stirred well under argon for 30 min. To this solution was added Pd(PPh₃)₄ (2 mol %). The reaction mixture was heated to reflux under argon atmosphere. After 16 h, the reaction mixture was cooled to rt and the solvent was completely removed by using a rotary evaporator. The remaining residue was dissolved in chloroform (60 mL) and washed with brine solution, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane-methylene chloride=60:40, v/v) to afford compound **8** as a yellow solid. Yield 1.23 g (41%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.10–1.30 (m, 6H), 2.00-2.20 (m, 4H), 4.00-4.20 (m, 4H), 7.16 (dd, 1H), 7.36 (dd, 1H), 7.46-7.54 (m, 2H), 7.77 (dd, 1H), 8.14 (d, 1H), 8.28 (d, 1H), 8.41 (s, 1H), 8.47 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 10.9, 11.1, 24.1, 24.2, 78.2, 78.3, 118.8, 120.1, 123.8, 124.0, 124.2, 124.8, 124.9, 125.1, 125.2, 125.6, 125.7, 126.3, 128.5, 129.1, 131.5, 144.8, 146.9, 148.3; HRMS (EI⁺, m/z) [m⁺] calcd for C₂₄H₂₃BrO₂S 454.0602, found 454.0606.

4.4.12. Synthesis of N,N-diphenyl-4-(9,10-dipropoxy-2-(thiophen-2-yl)anthracen-6-yl)benzenamine (**9**). Compound **9** was synthesized by using the similar synthetic procedure for the synthesis of compound **4**. In this reaction, compound **8** (0.90 g, 2.00 mmol) and 4-(diphenylamino)phenylboronic acid (0.58 g, 2.00 mmol) were subjected to Suzuki coupling reaction and the crude product was purified by using column chromatography (silica gel, hexane—methylene chloride=60:40, v/v) to afford compound **9** as a yellow solid. Yield 1.05 g (85%); ¹H NMR (300 MHz, CDCl₃) δ (ppm)

1.20–1.40 (m, 6H), 2.00–2.20 (m, 4H), 4.10–4.30 (m, 4H), 7.06–7.10 (m, 2H), 7.12–7.24 (m, 7H), 7.27–7.38 (m, 5H), 7.51 (d, 1H), 7.68 (d, 2H), 7.76 (d, 2H), 8.31 (t, 2H), 8.44 (s, 1H), 8.51 (s, 1H); 13 C NMR (75 MHz, CDCl₃) δ (ppm) 11.0, 11.1, 24.1, 24.2, 78.0, 78.1, 118.9, 119.5, 123.3, 123.6, 123.7, 123.8, 124.0, 124.3, 124.9, 125.0, 125.3, 125.4, 125.9, 128.1, 128.5, 129.6, 131.0, 135.0, 137.2, 145.1, 147.7, 147.9, 147.9, 148.0; HRMS (EI⁺, *m/z*) [m⁺] calcd for C₄₂H₃₇NO₂S 619.2545, found 619.2549.

4.4.13. Synthesis of N-(phenyl-4-ethene-1,2,2-tricarbonitrile)-Nphenyl-4-(9,10-dipropoxy-2-(thiophen-2-yl)anthracen-6-yl)benzenamine (TCV-TpaA_{2.6}T). The mixture of compound 9 (0.40 g, 0.65 mmol) and TCNE (0.83 g, 6.50 mmol) in DMF (30 mL) was heated to 140 °C for 6 h. The similar workup and purification procedures were used as described in the synthesis of TCV-TpaA_{9.10}T. The product (TCV-TpaA_{2.6}T) was obtained as a blue solid. Yield 0.33 g (71%); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.20–1.40 (m, 6H), 2.00-2.20 (m, 4H), 4.10-4.30 (m, 4H), 7.05 (d, 2H), 7.17 (dd, 1H), 7.27-7.40 (m, 5H), 7.42-7.56 (m, 3H), 7.70-7.86 (m, 4H), 8.00 (d, 2H), 8.31 (d, 1H), 8.36 (d, 1H), 8.49 (d, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 11.0, 11.1, 24.1, 24.2, 78.0, 78.1, 113.2, 113.4, 114.4, 118.6, 118.9, 120.7, 123.9, 124.0, 124.6, 125.0, 125.1, 125.5, 125.7, 125.8, 127.3, 127.5, 128.5, 129.0, 130.5, 131.3, 132.5, 136.3, 139.9, 143.8, 144.5, 145.0, 148.2, 154.5; HRMS (EI⁺, *m*/*z*) [m⁺] calcd for C47H36N4O2S 720.2559, found 720.2557.

4.4.14. Synthesis of 1-(5-(2-(4-(diphenylamino)phenyl)-9,10dipropoxvanthracen-6-vl)thiophen-2-vl)ethene-1.2.2-tricarbonitrile (TpaA26T-TCV). Compound TpaA26T-TCV was synthesized by using the similar synthetic procedure for the synthesis of compound **TpaA**_{9.10}**T-TCV**. Compound **9** (0.40 g, 0.65 mmol), 1.4 equiv of *n*-BuLi and TCNE were used for this reaction. The product (**TpaA_{2.6}T-TCV**) was obtained as a green solid. Yield 0.22 g (47%); ¹H NMR $(300 \text{ MHz, CDCl}_3) \delta$ (ppm) 1.20–1.40 (m, 6H), 2.00–2.20 (m, 4H), 4.20-4.40 (m, 4H), 7.08 (t, 2H), 7.12-7.25 (m, 6H), 7.27-7.38 (m, 4H), 7.64–7.74 (m, 3H), 7.82 (d, 1H), 8.07 (d, 1H), 8.33 (d, 2H), 8.45 (s, 1H), 8.67 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 11.0, 11.2, 24.2, 24.3, 77.4, 112.4, 112.6, 113.0, 119.4, 122.7, 122.9, 123.6, 123.7, 124.0, 124.6, 125.0, 125.3, 125.5, 125.7, 126.2, 127.7, 127.9, 128.2, 129.6, 132.9, 134.2, 138.7, 141.5, 147.1, 148.1, 148.2, 149.5, 160.0; HRMS (EI⁺, m/z) [m⁺] calcd for C₄₇H₃₆N₄O₂S 720.2559, found 720.2562.

Acknowledgements

This study was financially supported by the 2013 Post-Doc. Development Program of Pusan National University.

References and notes

- Søndergaard, R.; Hösel, M.; Angmo, D.; Larsen-Olsen, T. T.; Krebs, F. C. Mater. Today 2012, 15, 36.
- 2. Kim, B.; Yeoma, H. R.; Choi, W.-Y.; Kim, J. Y.; Yang, C. Tetrahedron 2012, 68, 6696.
- Cabanetos, C.; Labban, A. E.; Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Frechet, J. M. J.; McGehee, M. D.; Beaujuge, P. M. J. Am. Chem. Soc. 2013, 135, 4656.
- Osaka, I.; Kakara, T.; Takemura, N.; Koganezawa, T.; Takimiya, K. J. Am. Chem. Soc. 2013, 135, 8834.
- 5. He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Nat. Photonics 2012, 6, 591.
- Son, H. J.; Wang, W.; Xu, T.; Liang, Y.; Wu, Y.; Li, G.; Yu, L. J. Am. Chem. Soc. 2011, 133, 1885.
- Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. J. Am. Chem. Soc. 2011, 133, 10062.
- 8. You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. Nat. Commun. **2013**, *4*, 1446.
- 9. You, J.; Chen, C.-C.; Hong, Z.; Yoshimura, K.; Ohya, K.; Xu, R.; Ye, S.; Gao, J.; Li, G.; Yang, Y. Adv. Mater. **2013**, *25*, 3973.
- 10. Dou, L.; You, J.; Yang, J.; Chen, C.-C.; He, Y.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. *Nat. Photonics* **2012**, *6*, 180.
- 11. Zhang, F.; Wu, D.; Xua, Y.; Feng, X. J. Mater. Chem. 2011, 21, 17590.
- 12. Proctor, C. M.; Kim, C.; Neher, D.; Nguyen, T.-Q. Adv. Funct. Mater. 2013, 23, 3584.

- 13. Zhou, J.; Zuo, Y.; Wan, X.; Long, G.; Zhang, Q.; Ni, W.; Liu, Y.; Li, Z.; He, G.; Li, C.; Kan, B.; Li, M.; Chen, Y. J. Am. Chem. Soc. 2013, 135, 8484.
- 14. Love, J. A.; Proctor, C. M.; Liu, J.; Takacs, C. J.; Sharenko, A.; Poll, T. S.; Heeger, A. J.; Bazan, G. C.; Nguyen, T.-Q. Adv. Funct. Mater. 2013, 23, 5019.
- 15. Shen, S.; Jiang, P.; He, C.; Zhang, J.; Shen, P.; Zhang, Y.; Yi, Y.; Zhang, Z.; Li, Z.; Li, Y. Chem. Mater. **2013**, 25, 2274.
- 16. Fitzner, R.; Elschner, C.; Weil, M.; Uhrich, C.; Körner, C.; Riede, M.; Leo, K.; Pfeiffer, M.; Reinold, E.; Mena-Osteritz, E.; Bauerle, P. Adv. Mater. 2012, 24, 675.
- 17. Sun, Y.; Welch, G. C.; Leong, W. L.; Takacs, C. J.; Bazan, G. C.; Heeger, A. J. Nat. Mater. 2012, 11, 44.
- 18. Chen, Y.-H.; Lin, L.-Y.; Lu, C.-W.; Lin, F.; Huang, Z.-Y.; Lin, H.-W.; Wang, P.-H.; Liu, Y.-H.; Wong, K.-T.; Wen, J.; Miller, D. J.; Darling, S. B. J. Am. Chem. Soc. **2012**, 134, 13616.
- Liu, Y.; Wan, X.; Wang, F.; Zhou, J.; Long, G.; Tian, J.; You, J.; Yang, Y.; Chen, Y. Adv. Energy Mater. 2011, 1, 771.
- 20. Zhou, J.; Wan, X.; Liu, Y.; Zuo, Y.; Li, Z.; He, G.; Long, G.; Ni, W.; Li, C.; Su, X.;
- Zhou, J.; Wan, X.; Liu, Y.; Zuo, Y.; Li, Z.; He, G.; Long, G., M, W., E, C., Su, X., Chen, Y. J. Am. Chem. Soc. 2012, 134, 16345.
 Lin, L.-Y.; Chen, Y.-H.; Huang, Z.-Y.; Lin, H.-W.; Chou, S.-H.; Lin, F.; Chen, C.-W.; Liu, Y.-H.; Wong, K.-T. J. Am. Chem. Soc. 2011, 133, 15822.
 Chiu, S.-W.; Lin, L.-Y.; Lin, H.-W.; Chen, Y.-H.; Huang, Z.-Y.; Lin, Y.-T.; Lin, F.; Liu,
- Y.-H.; Wong, K.-T. Chem. Commun. 2012, 1857.
 Lin, H.-Y.; Huang, W.-C.; Chen, Y.-C.; Chou, H.-H.; Hsu, C.-Y.; Lin, J. T.; Lin, H.-W. Chem. Commun. 2012, 8913.

- 24. Almeataq, M. S.; Yi, H.; Al-Faifi, S.; Alghamdi, A. A. B.; Iraqi, A.; Scarratt, N. W.; Wang, T.; Lidzey, D. G. Chem. Commun. 2013, 2252.
- 25. Liu, C.; Cai, W.; Guan, X.; Duan, C.; Xue, Q.; Ying, L.; Huang, F.; Cao, Y. Polym. Chem. 2013, 4, 3949.
- Lin, R. Y.-Y.; Lin, H.-W.; Yen, Y.-S.; Chang, C.-H.; Chou, H.-H.; Chen, P.-W.; Hsu, C.-Y.; Chen, Y.-C.; Lin, J. T.; Ho, K.-C. *Energy Environ. Sci.* 2013, 6, 2477.
- 27. Teng, C.; Yang, X.; Yang, C.; Li, S.; Cheng, M.; Hagfeldt, A.; Sun, L. J. Phys. Chem. C. 2010, 114, 9101.
- Lee, D. H.; Shin, J.; Cho, M. J.; Choi, D. H. *Chem. Commun.* 2013, 3896.
 Park, J.-H.; Chung, D. S.; Park, J.-W.; Ahn, T.; Kong, H.; Jung, Y. K.; Lee, J.; Yi, M.
- H.; Park, C. E.; Kwon, S.-K.; Shim, H.-K. Org. *Lett.* **200**7, 9, 2573.
 Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew.*
- Chem. 2003, 115, 1191. 31. Xia, P. F.; Feng, X. J.; Lu, J.; Movileanu, R.; Tao, Y.; Baribeau, J.-M.; Wong, M. S. J. *Phys. Chem. C.* **2008**, 112, 16714.
- 32. Mishra, A.; Bauerl, P. Angew. Chem. Int. Ed. 2012, 51, 2020.
- 33. Kim, J.; Cho, N.; Ko, H. M.; Kim, C.; Lee, J. K.; Ko, J. Sol. Energy Mater. Sol. 2012,
- 102, 159,
- Cho, N.; Kim, J.; Song, K.; Lee, J. K.; Ko, J. *Tetrahedron* **2012**, *68*, 4029.
 Tamilavan, V.; Song, M.; Kang, J.-W.; Hyun, M. H. Synth. Met. **2013**, *176*, 96.
- Lee, S. K.; Yang, W. J.; Choi, J. J.; Kim, C. H.; Jeon, S.-J.; Cho, B. R. Org. Lett. 2005, 7, 323.
 Varghese, O. K.; Crimes, C. A. Sol. Energy Mater. Sol. 2008, 92, 374.
- 38. Tamilavan, V.; Cho, N.; Kim, C.; Ko, J.; Hyun, M. H. Synth. Met. 2012, 162, 2155.