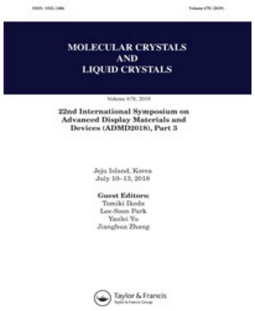

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Synthesis of Poly[N-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] Copolymer and Its Potential as Hole-Transporting Material to Solid-State Dye-Sensitized Solar Cells

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ABSTRACT

In this study, thermally stable and solution-processable conjugated poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer containing alternating carbazole and triarylamine moieties in the polymer backbone was synthesized in a good yield by Pd-catalyzed polycondensation. The polymer exhibited maximum UV-vis absorption peak at 309 nm and maximum photoluminescence peak at 452 nm. From the optical and electrochemical characterization, the band gap, HOMO, and LUMO energy levels of the polymer were measured to be 2.91 eV, -5.19 eV, and -2.28 eV, respectively. The polymer was used to examine the hole-transporting performance to a solid-state dye-sensitized solar cell (ssDSSC). The ssDSSC fabricated with poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer showed a PCE of 1.50% with $J_{sc} = 3.76$ mA/cm^2, $V_{oc} = 538$ mV, and FF = 74.3%, implying the potential of the synthesized polymer as a hole-transport material (HTM) to ssDSSC.

KEY WORDS
carbazole; hole transport; ssDSSC; triarylamine

1. Introduction

Dye-sensitized solar cells (DSSCs), generally composed of a photoelectrode, a liquid electrolyte, and a Pt counter electrode, are considered to be a promising candidate as a large-area and low-cost renewable energy source, due to their various advantages, such as reasonable photovoltaic efficiency, low production cost, brief fabrication process, semi-transparency, and flexibility [1–5]. Power conversion efficiency (PCE) of 14.3% has been obtained with a cobalt (II/III) complex redox liquid electrolyte [6]. Despite the fact that considerable progress has been made in the field of DSSCs, the risk of leakage of volatile liquid electrolyte limit significantly the commercialization of DSSCs.

Significant efforts have been made on solid-state dye-sensitized solar cells (ssDSSCs) to replace former liquid electrolyte system, as well as the development of new HTMs with low cost, facile synthesis and high charge-carrier mobility has been of high priority [7]. Many organic HTMs were originally developed for use in xerography and then in organic light-emitting diodes (OLEDs). One of the most common classes of materials was arylamines, such as *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) and *N*,*N*′-diphenyl-*N*,*N*′-bis(α-naphthyl)benzidine (NPB) [8, 9].

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Moreover, spiro-type arylamines showed higher PCE of 7.2% when employed as HTMs in ssDSSC [10]. Carbazole-based materials have attracted much attention as another type of HTMs. Up to now, many different types of carbazole-structured materials have been intensively utilized in OLEDs because of their good hole-transporting function [11]. The versatile chemical modification of carbazole derivatives was also exploited in the molecular design of new types of HTMs in OLEDs.

Herein, we report on the synthesis of a solution-processable conjugated copolymer composed of alternating carbazole and triarylamine moieties, because both of carbazole and triarylamine groups are known to have hole-transporting performance as mentioned previously. And then, the synthesized copolymer is applied on the preliminary investigation of its potential as a HTM to ssDSSCs.

2. Experiment

Materials

2-Ethylhexylbromide (97%), 3,6-dibromocarbazole (97%), aniline (99.5%), sodium-*tert*-butoxide (NaO-*t*-Bu, 97%), tris(dibenzylidene-acetone)dipalladium(0) ($Pd_2(dba)_3$), $TiCl_4$, and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$, 90%) were purchased from Sigma-Aldrich Chemical Co. Fluorine-doped tin oxide (FTO; sheet resistance ~ 7 Ω/square) glass (TCO22-7), TiO_2 paste for the photoelectrode (Ti-nanooxide T/SP), TiO_2 paste for the scattering layer (Ti-nanooxide R/SP), N719 dye (Ruthenizer 535-bisTBA), and hot-melt adhesive (SX1170-60PF, Surlyn) were obtained from Solaronix. Platinum paste (PT-1, Dyesol-Timo) was selected as the source for the Pt counter-electrode. Lithium bistrifluoro methane sulfonamide (LiTFSI), 1-methyl-3-propylimidazolium iodide (MPII), and 4-tert-butylpyridine (TBP) used as dopants were brought from Sigma-Aldrich Chemical Co. All other chemicals used in the study were reagent grade and used as received.

Synthesis of N-(2-Ethylhexyl)-3,6-dibromocarbazole

A mixture of 3,6-dibromocarbazole (18.46 mmol) and K_2CO_3 (37 mmol) in DMF (20 ml) was refluxed in N_2 atmosphere and heated to 80 °C. 2-Ethylhexylbromide (28 mmol) was added dropwise. After complete addition, the reaction was continued for 16 hrs. The product was isolated by diethylether/water extraction. The organic layer was dried with $MgSO_4$, then filtered and concentrated. The viscous liquid *N*-(2-ethylhexyl)-3,6-dibromocarbazole was obtained by column chromatography (eluent: hexane). Yield 56%. Figure 1 shows ^1H and ^{13}C NMR spectra of *N*-2-ethylhexyl-3,6-dibromocarbazole. ^1H NMR (300 MHz in $CDCl_3$, δ): 8.11 (d, 2H, Ar-H), 7.48 (d, 2H, Ar-H), 7.22 (d, 2H, Ar-H), 4.18 (m, 2H, $-N-CH_2-$), 1.23 ~ 1.44 (m, 9H, -CH-, $-CH_2-$), 0.91 (m, 6H, $-CH_3$). ^{13}C NMR (60 MHz in $CDCl_3$, δ): 139.7, 129.0, 123.4, 123.2, 112.1, 110.7, 47.6, 39.5, 31.1, 29.0, 24.6, 23.3, 14.3, 11.1.

Polymerization of poly[N-(2-ethylhexyl)-3,6-carbazole-alt-aniline] copolymer

The polymerization was carried out via Pd-catalyzed polycondensation reaction. A mixture of *N*-(2-ethylhexyl)-3,6-dibromocarbazole (2.58 mmol) and aniline (2.58 mmol) was

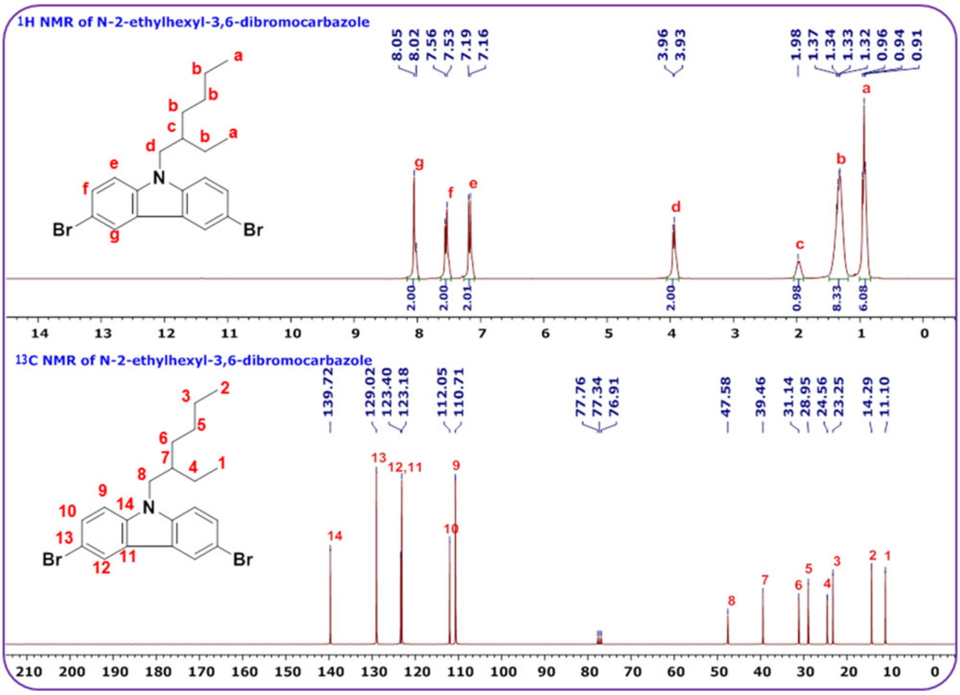

Figure 1. ^{1}H and ^{13}C NMR spectra of *N*-2-ethylhexyl-3,6-dibromocarbazole.

dissolved in toluene (25 ml). NaO-*t*-Bu (7.74 mmol), $Pd_2(dba)_3$ (0.065 mmol), and P(*t*-Bu)$_3$ (0.39 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 48 hrs. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (50 ml) and the product was extracted with $CHCl_3$. The organic fraction was concentrated and reprecipitated from $CHCl_3$/methanol several times.

ssDSSC fabrication

The FTO glasses were cleaned in a detergent solution using a sonication for 20 min, and then thoroughly rinsed with deionized water and ethanol. After the ultrasonic cleaning, the FTO glasses were immersed in a 40-mM $TiCl_4$ solution at 70 °C for 30 min, and then washed with deionized water and ethanol. One active TiO_2 layer, which formed on the FTO glass, was prepared via doctor-blade coating with the TiO_2 paste. An additional TiO_2 layer consisting of particles with around 400 nm diameter was deposited on the active TiO_2 layer and then calcinated at 500 °C for 60 hr to produce the scattering layer. The TiO_2 films were again treated with a 40 mM $TiCl_4$ solution and annealed at 500 °C for 60 hr; thus, TiO_2/FTO electrodes with the scattering layer were prepared. Finally, the TiO_2/FTO photoelectrodes were immersed into 0.5 mM of N719 dye solution (acetonitrile/tert-butyl alcohol = 1/1, v/v) for 12 hrs to obtain working electrodes.

To prepare the counter-electrode, two holes were formed in the FTO glass with a drill, and then cleaned with the method described above. A Pt layer was formed on the FTO glass via the doctor-blade method using Pt paste, followed by a calcination process at 400 °C for 30 min. The thermally treated Pt counter-electrodes were placed on the photoelectrodes and sealed with a 25-μm-thick sealing material. The solution of the polymer:dopant (3:1 v:v) was introduced into the cells through one of the two small holes drilled on the counter-electrodes to produce ssDSSCs with a 25 mm^2 active area, and dried under vacuum at 50 °C for 1 hr. This process was repeated 3 times. Hole-only device [12] was fabricated with a configuration of ITO/PEDOT:PSS (30 nm)/HTM (100 nm)/Au (70 nm), where Au with a high work function was used as the cathode to keep the injection of electrons away from the cathode.

Instruments

^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity Plus 300 spectrometer, and chemical shifts were recorded in ppm. Number and weight average molecular weights were measured by Waters gel permeation chromatography (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at 40 °C. Thermal gravimetric analysis (TGA) was performed under N_2 atmosphere at a heating rate of 20 °C/min with a TG/DTA320 thermal analyzer. The decomposition temperature (T_d) was taken as the temperature at which a 5% weight loss occurred. UV-visible absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer, and the photoluminescence (PL) spectra were made on a Shimadzu RF-5301PC fluorimeter. The ionization potential (I_p) was measured by photoelectron spectroscopy (Riken Keiki AC-2). The photocurrent-voltage measurement was performed using a CompactStat (Ivium Technologies B.V.) potensiostat and a PEC-L01 solar simulator system equipped with a 150 W xenon arc lamp (Peccell Technologies, Inc.). The light intensity was adjusted to 1 sun (100 mW/cm^2) with a silicon photodiode (model PEC-SI01, Peccell Technologies, Inc.). The active area of the dye-adsorbed TiO_2 films was estimated using a digital microscope camera (OLYMPUS SZ61) with image analysis software.

3. Result and discussion

Synthesis and characterization of poly[N-(2-ethylhexyl)-3,6-carbazole-alt-aniline] copolymer

Synthetic route to the carbazole/triarylamine-based alternating poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer prepared by Pd-catalyzed polycondensation is presented in Figure 2. The alternating copolymer was synthesized in high yields. According to its structure, poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer possessed basic structure of alternating carbazole/triarylamine polymers, in which triarylamine moiety was linked to 3,6-disubstituted carbazole groups. *N*-2-Ethylhexyl group on the carbazole in the main chain of the alternating copolymer was introduced to impart high solubility in common organic solvent, which was required for a solution process. Therefore, the copolymer exhibited excellent solubility in common organic solvents such as toluene, benzene, chloroform, TCE, and THF. In addition, the polymer showed good film forming quality from a spin coating process.

Results on physical properties of the synthesized alternating copolymer such as molecular weight, molecular weight distribution, and decomposition temperature are

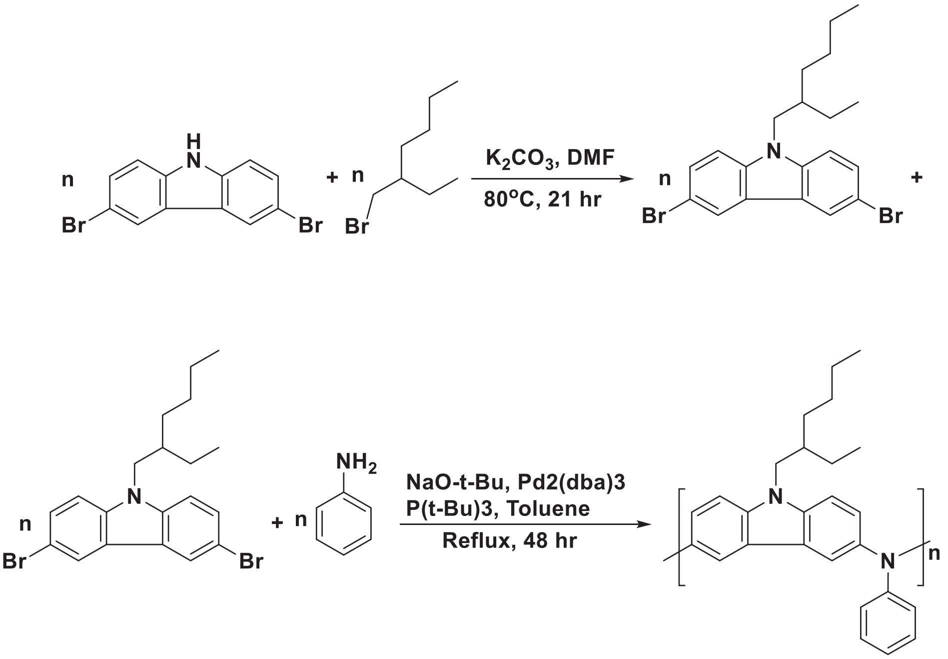

Figure 2. Reaction scheme to poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer.

Table 1. Physical and Optical Properties of Poly[N-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer

			$\lambda_{max,UV}$ (nm)		$\lambda_{max,PL}$ (nm)		Bandgap energy (eV)[b]	HOMO (eV)[c]	LUMO (eV)[d]
M_w (g/mole)	M_w/M_n	T_d (°C)[a]	solution	film	solution	film			
1,790	1.40	442	309	310	452	453	2.91	−5.19	−2.28

[a] temperature at 5 wt% loss based on the initial weight
[b] calculated from the crosspoint of UV-Vis and PL spectra
[c] measured by a RIKEN Keiki AC-2
[d] estimated from the HOMO and band gap

summarized in Table 1. As shown in Figure 3, the polymer showed molecular weight (M_w) of 1,790 g/mole with a molecular weight distribution of 1.40. Thermal properties of the copolymer were determined by using TGA and DSC measurements. The polymer showed good thermal stability with decomposition temperature (T_d) of 442 °C at 5 wt% loss under a nitrogen atmosphere, as presented in Figure 4. Over the decomposition temperature, the weight loss curves of the polymer fell rapidly, indicating the decomposition of the backbone of the polymer. In DSC measurement, no melting temperature and obvious glass transition temperature could be observed below 400 °C, suggesting the polymer was virtually amorphous polymeric material.

Optical properties such as UV-visible absorption maximum ($\lambda_{max,UV}$) and PL emission maximum ($\lambda_{max,PL}$) are also summarized in Table 1. As presented in Figure 5, the polymer presented maximum PL emission peak at 442 nm with narrow bandwidth. From photophysical study, band gap, HOMO, and LUMO energy levels of the polymer were measured as follows; 2.91 eV, -5.19 eV, and -2.28 eV, respectively. In this paper, we preliminary study on the feasibility of the synthesized alternating copolymer for hole-transporting layer in ssDSSC.

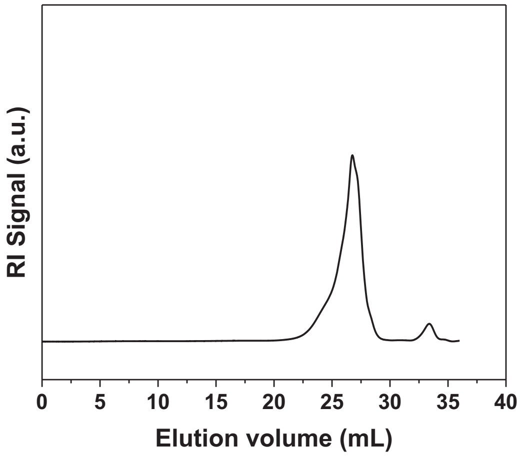

Figure 3. GPC chromatogram of poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer.

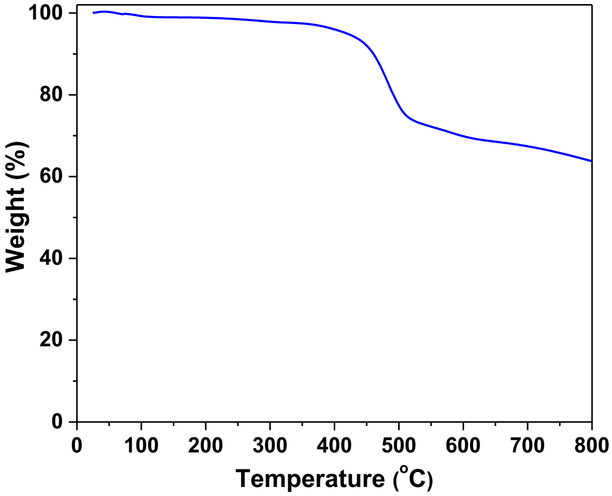

Figure 4. TGA thermogram of poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer.

Performance of ssDSSC with polymers as a HTM

Space charge limited current (SCLC) measurement was used to evaluate charge mobility under steady state conditions of current in organic layers [12–14]. A hole mobility study of the device was conducted using the SCLC method. The current density using the SCLC model is given by Eq. (1)

$$\frac{ln\ J_{SCLC}L^3}{V^2} = \frac{0.89}{\sqrt{E_0}}\sqrt{\frac{V}{L}} + \frac{ln\ 9}{8}\varepsilon_r\varepsilon_0\mu_0 \tag{1}$$

where ε_r is the electric constant (assumed to be 3, which is a typical value for conjugated polymers) of the polymer, ε_0 is the permittivity of free space, μ_{h0} (or μ_{e0}) is the zero-field hole (or electron) mobility, L is the film thickness, E_0 is the characteristic field, and $V = V_{appl} - (V_r + V_{bi})$; where V_{appl} is the applied voltage to the device, V_r is

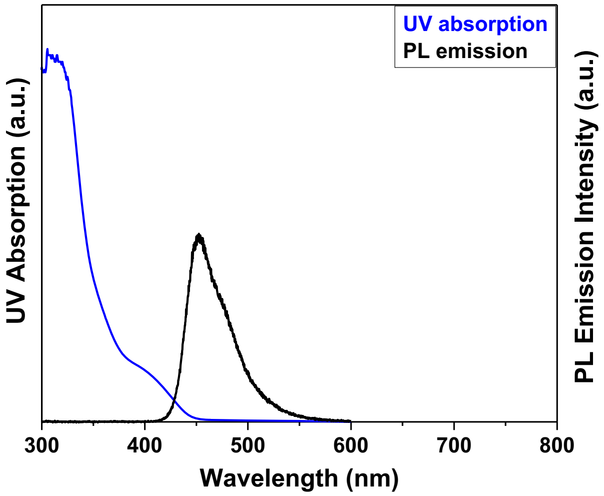

Figure 5. UV-visible absorption and PL emission spectrum of poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer.

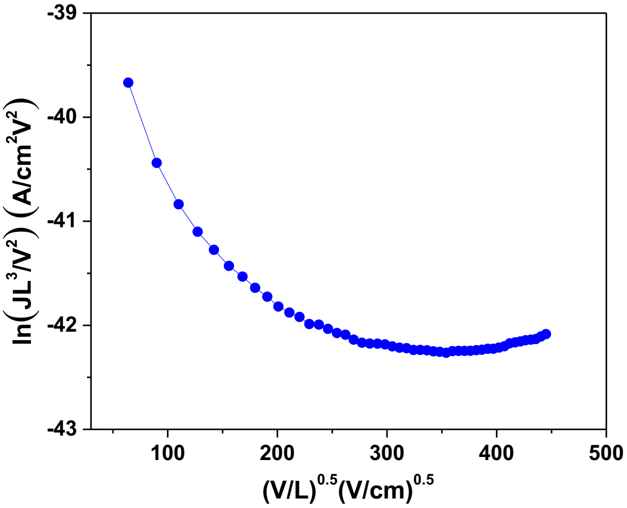

Figure 6. $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$ plot constructed from *J-V* characteristics of hole-only device with a configuration of ITO/PEDOT:PSS (30 nm)/HTM (100 nm)/Au (70 nm).

the voltage drop due to series resistance across the electrodes, and V_{bi} is the built-in voltage.

The hole mobility of the device was calculated from Eq. (1) using the *J-V* curve of the hole-only device with the configuration of ITO/PEDOT:PSS (30 nm)/HTM (100 nm)/Au (70 nm), which could prevent the electron injection from the cathode due to the large mismatch between the LUMO energy level (2.18 eV) of the copolymer and the work function (5.10 eV) of the Au cathode. In the graph (Figure 6) of the logarithm of JL^3/V^2 vs. the square root of V/L, the intercept of the line gives the hole mobility.

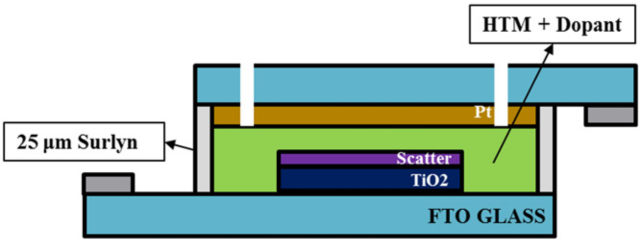

Figure 7. Schematic ssDSSC device structure with a cross-sectional view.

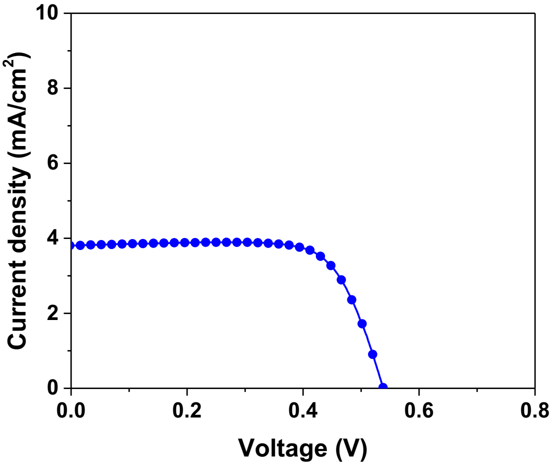

Figure 8. *J-V* characteristics of ssDSSC with poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer as a HTM.

The hole mobility of the device with the poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer was calculated to be 0.7×10^{-5} cm^2/Vs.

The ssDSSC device was fabricated with a structure as shown in Figure 7. Figure 8 shows the current density (J) and voltage (V) curve of the ssDSSC fabricated with poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer as a HTM. The ssDSSC showed a PCE of 1.50% with $J_{sc} = 3.76\,\text{mA/cm}^2$, $V_{oc} = 538\,\text{mV}$, and FF = 74.3%, implying the potential of the synthesized polymer as the HTM to ssDSSC.

4. Conclusions

In conclusion, we have succeeded in synthesizing the conjugated poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer by Pd-catalyzed polycondensation reaction. Common structural characteristics of the copolymer were alternating units of a carbazole and a hole-transporting triarylamine in the polymer backbone. The synthesized copolymer was soluble in common organic solvents, and showed good film forming and high thermal stability. From the optical and electrochemical characterization, the polymer exhibited $\lambda_{max,UV}$ at 309 nm and $\lambda_{max,PL}$ at 452 nm with wide band gap (2.91 eV) energy, HOMO (-5.19 eV) and LUMO (-2.28 eV) levels. The synthesized conjugated poly[*N*-(2-ethylhexyl)-3,6-carbazole-*alt*-aniline] copolymer was applied to ssDSSC as the HTM. The ssDSSC device showed a performance with J_{sc} = 3.76 mA/cm^2, V_{oc} = 538 mV, and FF = 74.3%, leading to a PCE of 1.50%.

Acknowledgement

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References

[1] O'Regan, B. & Grätzel, M. (1991). *Nature*, 353, 737.
[2] Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., & Pettersson, H. (2010). *Chem. Rev.*, 110, 6595.
[3] Gong, J., Liang, J., & Sumathy, K. (2012). *Renew. Sust. Energ. Rev.*, 16, 5848.
[4] Hawash, Z., Ono, L. K., & Qi, Y. (2018). *Adv. Mater. Interfaces*, 5, 1700623.
[5] Liu, P., Xu, B., Hua, Y., Cheng, M., Aitola, K., Sveinbjornsson, K., Zhang, J., Boschloo, G., Sun, L., & Kloo, L. (2017). *J. Power Sources*, 344, 11.
[6] Kakiage, K., Aoyama, Y., Yano, T., Oya, K., Fujisawa, J., & Hanaya, M. (2015). *Chem. Commun.*, 51, 15894.
[7] Xu, B., Sheibani, E., Liu, P., Zhang, J., Tian, H., Vlachopoulos, N., Boschloo, G., Kloo, L., Hagfeldt, A., & Sun, L. (2014). *Adv. Mater.*, 26, 6629.
[8] Bellmann, E., Shaheen, S. E., Grubbs, R. H., Marder, S. R., Kippelen, B. N., & Peyghambarian, B. (1999). *Chem. Mater.*, 11, 399.
[9] Redecker, M., Bradley, D. D. C., Inbasekaran, M., Wu, W. W., & Woo, E. P. (1999). *Adv. Mater.*, 11, 241.
[10] Burschka, J., Dualeh, A., Kessler, F., Baranoff, E., Cevey-Ha, N.-L., Yi, C., Nazeeruddin, M. K., & Grätzel, M. (2011). *J. Am. Chem. Soc.*, 133, 18042.
[11] Puckyte, G., Schmaltz, B., Tomkeviciene, A., Degbia, M., Grazulevicius, J. V., Melhem, H., Boucle, J., & Tran-Van, F. (2013). *J. Power Sources*, 233, 86.
[12] Chivase, D., Chiguvare, Z., Knipper, M., Parisi, J., Dyakonov, V., & Hummelen, J. C. (2003). *J. Appl. Phys.*, 93, 3376.
[13] Shrotriya, V., Yao, Y., Li, G., & Yang, Y. (2006). *Appl. Phys. Lett.*, 89, 063505.
[14] Jeong, S., Han, Y. S., Kwon, Y., Choi, M.-S., Cho, G., Kim, K.-S., & Kim, Y. (2010). *Syn. Met.*, 160, 2109.