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Thiophene-fused carbazole derivative dyes for high-performance dyesensitized solar cells



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ABSTRACT

Two novel dyes that are similar in chemical structure, except for different donor units, **AJ301** and **AJ303** were synthesized, characterized and applied as sensitizers in dye-sensitized solar cells (DSSCs). Both dyes exhibited a wide absorption of visible sunlight. The introduction of fused rings on the donor unit of **AJ303** presented an appropriate energy level, less recombination and longer electron lifetime to achieve a power conversion efficiency (PCE) of 10.2%, far above that achieved for **AJ301** of 6.2% with a $[Co(bpy)_3]^{2+/3+}$ -based electrolyte under standard AM1.5G solar irradiation (100 mW cm⁻²). The DSSCs based on **AJ303** and **AJ301** with $[Cu(tmby)_2]^{2+/+}$ -based electrolyte showed a lower PCE of 8.2% and 5.4%, respectively. Therefore, the results indicated that the introduction of a fused-ring in the donor group is a meaningful synthetic strategy to improve the photovoltaic performance.

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1. Introduction

Dye-sensitized solar cells (DSSCs), a third-generation photovoltaic technology, have attracted much attention, owing to lowcost fabrication and stability under operating conditions, to delay the exhaustion of fossil fuels. The DSSCs mainly consist of a photosensitizer, electrolyte and counter electrode (CE) [1-3]. Since the first report by Grätzel and co-workers of a power conversion efficiency (PCE) of 7.1% [4], various types of dyes have emerged and been applied as photosensitizers for dye-sensitized solar cells, which have boosted the PCE to 14.2% on account of its extremely vital role [5–9]. Metal complex dyes, which contain ruthenium polypyridyl and zinc porphyrin complexes. The Ru-dye use of precious metal is one of the biggest weaknesses, although zinc porphyrin complexes present a high molar extinction coefficient (ε) within their specific feature IR absorption region, they have in common is a lower synthetic yield [10–13]. Yella et al. reported a well-designed dye **YD2-o-C8** to achieve an efficiency exceeding

12%, which delays the rate for back electron transfer occurring at the TiO₂/electrolyte interface and leads to a high voltage approaching 1.0 V [14,15]. Meanwhile, metal-free organic dyes have gradually attracted more attention owing to the high cost and low yield of metal complexes, which normally give a donor (D)– π -bridge (π)-accepter (A) structure. Wang et al. synthesized a series of dyes, where N-annulated perylene was employed as a donor group. These were applied as sensitizers in DSSCs with a $[Co(bpy)_3]^{2+/3+}$ redox couple to achieve a high PCE of 10%–13% [16-18]. Yang et al. reported that for a sensitizer based on triazatruxene (TAT), named ZL003, the devices sensitized by ZL003 with a $[Co(bpy)_3]^{2+}/^{3+}$ redox couple exhibited the highest PCE for a single dye reported to date of 13.6% [19]. Grätzel and co-workers designed and synthesized a series of dyes based on indacenodithiophene (IDT), including named L350. The DSSCs based on L350 achieved a PCE of 11.2% with a high open-circuit voltage (>1.1 V) in conjunction with a copper redox shuttle [20]. Recent work reported by Anders Hagfeldt showed that a higher PCE performance can be attributed to the copper redox shuttle considering the more positive redox potential compared with the traditional Co (II/III) (~0.56 vs NHE) and I^{-}/I_{3}^{-} (~0.4 vs NHE) electrolytes [21–24]. Therefore,



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Fig. 1. Molecular structure of AJ301 and AJ303.

more innovative work on the development of new photosensitizers by adjustment to a suitable energy level (tuning mainly the HOMO values) to further enhance the power conversion efficiency is required.

Carbazole ramification is an excellent method to obtain a rigid conjugated electron-rich aromatic ring, which can then be used in organic thin-film transistors (OTFT), organic-light-emitting diodes (OLEDs) and hole-transport materials (HTM) [25–28]. However, carbazole-ramified photosensitizers have been applied in DSSCs, but there are only a few reports where the PCE is high with a classical redox electrolyte [29–32]. The traditional I⁻/I₃ electrolyte can perfectly and widely match a number of dyes to regenerate the oxidized dyes, owing to the low redox potential, but this results in a limit to obtain a high photovoltage. Until now, very few dyes with carbazole ramification have been applied to DSSCs devices with two different redox shuttles, $Co(bpy)_3^{2+/3+}$ and $Cu(tmby)_2^{1/2+}$. Fortunately, carbazole ramification dyes can successfully solve this problem to be ready for commercialization in the future.

Recently, the introduction of aromatic-fused structures was applied to achieve higher PCE values for DSSCs [33-36] and perovskite solar cells [37–39] owing to the synthesis being simple and easy. To the best of our knowledge, the incorporation of substituted thiophene-fused carbazole cores is still rare. Herein, two novel organic dyes, 2,2'-(thiophene-2,3-diyl) bis(9-(2ethylhexyl)-9H-carbazole) (TPC), employed as a donor unit and named AJ301 with a twisty skeleton, and 11-((R)-2-ethylhexyl)-5-(2-ethylhexyl)-8-(4-hexylphenyl)-5,11-dihydrothieno [2'.3':5.6] benzo[1,2-b:4,3-b'] dicarbazole (DBD), employed as a donor unit and named AJ303 with a coplanar and rigid skeleton, are investigated. 4,7-bis(4-hexylthiophen-2-yl) benzo[c] [1,2,5] thiadiazole (BTBT) as a π -bridge, used to better harvest visible sunlight, and benzoic acid as an accepter unit, were both appointed to the two dyes. We also introduced alkyl chains into the donor unit and π -bridge to increase the solubility in solvents and reduce intermolecular packing. The effect on the optical and electrochemical properties as well as the application as a sensitizer in devices, with the two dyes as different donor units, were investigated. The ideal match of the HOMO energy level with a cobalt electrolyte was the perfect combination for the electron-donating ability of carbazole with a cobalt redox shuttle, which achieved a PCE of 10.2% and 6.2% for AJ303 and AJ301 in Fig. 1, respectively, and, combined with a copper redox shuttle, achieved a PCE of 8.2% and 5.4%, respectively. Additionally, the fusion of thiophene used in the donor units may boost the photovoltaic performances.

2. Experimental

2.1. Basic synthesis process

The synthetic routes towards AJ301 and AJ303 are illustrated in Figure 1, 2, 3, 4, 5, 6, 7 and 8 (see Fig. 1). The two dyes included a donor moiety, a π -bridge and an accepter moiety, which were linked by using Suzuki cross-coupling reactions. The acceptor-side was synthesized according to the process given in a previous report [40]. Cost-effective and readily available 2-bromo-9H-carbazole (1) and 3-(bromomethyl) heptane with a branched alkyl chain were used as starting materials to synthesize 2-bromo-9-octyl-9Hcarbazole (3) in a yield that reached approximately 90%. 9-Octyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (4) was prepared by *n*-butyllithium and isopropoxyboronic acid pinacol ester at -78 °C. 2,3-dibromothiophene was combined with (4) to generate 2,2'-(thiophene-2,3-diyl)bis(9-octyl-9H-carbazole) by using Suzuki cross-coupling reactions. Thereafter, electron-rich (5) carried out a lithium-halogen exchange with *n*-butyllithium at -20 °C and was converted into its corresponding boric acid ester (6). The main roles of 1-bromo-4-hexylbenzene in the central core were to eliminate the thiophene active site and decrease the $\pi - \pi$ stacking. The subsequent anhydrous iron (III) chloride oxidative cyclization formed a π -extended electron-rich donor intermediate 8-(4-hexylphenyl)-5,11-dioctyl-5,11-dihydrothieno[2',3':5,6]benzo [1,2-b:4,3-b']dicarbazole (9) at mild synthetic conditions. The N atom at the para-position of the fused carbazole was brominated with N-bromosuccinimide (NBS), and the para bromo group of (10) was converted to a para boryl group by a palladium-catalyzed reaction. The electron-donating moiety (6 or 11) was further coupled to the π -bridge–accepter to afford the esterified dyes by the Suzuki coupling reaction. The two novel dyes were then successfully obtained with high yields through basic hydrolysis. Detailed synthetic procedures are given in the Supporting Information.

2.2. Solar cell fabrication

For the preparation of the TiO_2 photoanode, the glass substrates of fluorine-doped tin oxide (FTO) were rinsed with water and sonicated, and then were cleaned sequentially in a dishwashing liquid solution, distilled water, ethanol and acetone for 20 min. Finally, the FTO glass underwent UV-ozone treatment for 30 min to remove the residual organics. The clean FTO glass was treated two times by a TiCl₄ solution (40 mM) at 70 °C for 35 min, which formed



Fig. 2. Synthetic routes towards organic dyes AJ301 and AJ303.

a homogeneous and tight thin TiO_2 film underlayer to reduce the backward electron transfer in the device. Each of the formed TiO_2 films were then sintered at 500 °C for 40 min. On the cooled sintered TiO_2 glass was printed three layers of 18NR-T as the adsorption layer and one layer of TPP200 as the light-scattering layer. Every layer was solidified with the TiO_2 paste before printing the next layer, which was heated at 135 °C for 5 min in a dryer, followed

by sintering the complete TiO₂ layer again at 500 °C for 40 min. The complete working electrode was prepared by immersion in a TiCl₄ (40 mM) deionized water solution at 70 °C for 40 min, which increased the surface area of the TiO₂ particles and tuned the conduction band (CB) of TiO₂. The electrodes were washed with water, followed by sintering at 500 °C for 40 min. After cooling to 70 °C, the TiO₂ photoanode was immersed in a solution of the dye



Fig. 3. Uv-vis spectra of AJ301 and AJ303 measured (a) in dichloromethane and (b) on a TiO₂ film.

Table 1Optical and electrochemical parameters of AJ301 and AJ303.

Dyes	λ_{max}^{a} (nm)	$\epsilon^{a} \left(M^{-1} cm^{-1} \right)$	$\lambda_{max}^{b}(nm)$	HOMO ^c (V)	$E^{opt}_{g}^{d}$ (eV)	LUMO ^e (V)	E _g (DFT) ^f (eV)	HOMO (DFT) ^f (eV)	LUMO (DFT) ^f (eV)
AJ301	504	27,600	518	1.09	1.94	-0.85	2.36	0.80	-1.56
AJ303	502	22,300	511	1.03	1.93	-0.93	2.33	0.65	-1.68

 $^{a}\,$ The UV–vis absorption spectra were measured in dichloromethane (1 \times 10 $^{-5}$ M).

^b The dyes were absorbed on TiO₂ film.

^c Oxidation potentials of dyes were measured at a scan rate of 40 mV/s (calibrated with Fc/Fc⁺ as an external reference and converted to NHE by addition of 0.63 V). ^d The band gap (E^{opt}_{g}) was obtained using equation 1240/ λ , where λ is the tangent line of the TiO₂ film in the UV–vis absorption spectra with the X-axis.

^e The LUMO energy level was calculated with the equation LUMO = HOMO – E_{g} .

^f The computational parameters by DFT.



Fig. 4. Energy level diagram of AJ301 and AJ303.

 $(2 \times 10^{-4} \text{ M in CH}_2\text{Cl}_2)$ and chenodeoxycholic acid (CDCA, 2 mM) for 12 h to absorb the dye. A 25-µm-thick Surlyn film was used to encapsulate the platinum (Pt) counter electrode and the TiO₂ photoanode with the adsorbed dyes at 125 °C for 30s. The electrolyte was injected from predrilled holes in the counter electrodes under a negative pressure by using a water pump. The devices were measured use a mask area of 0.16 cm². The electrolyte composition was 0.25 M [Co(II) (bpy)₃] (TFSI)₂, 0.05 M [Co(III) (bpy)₃] (TFSI)₃, 0.1 M LiTFSI and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile. The concentrations of the copper electrolytes used were 0.2 M Cu(I) (tmby)₂(TFSI)₂, 0.04 M Cu(II) (tmby)₂TFSI, 0.1 M LiTFSI and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile.

3. Results and discussion

3.1. Optical properties

Uv–vis absorption spectra of **AJ301** and **AJ303** measured in CH_2Cl_2 solution and absorbed on TiO_2 film are shown in Fig. 3 (a, b).

The corresponding data are found in Table 1, 2, 3 and 4. As shown in Fig. 3a, AJ301 and AJ303 exhibited their maximum absorption at $\lambda_{max} = 504$ nm ($\varepsilon = 27,600$ mol L⁻¹ cm⁻¹) and $\lambda_{max} = 502$ ($\varepsilon = 22,300$ mol L⁻¹ cm⁻¹) in dichloromethane, respectively. The high ε values and appropriate band gap energies (E^{opt} g) will be a great benefit to obtain sufficiently light capture capacity. The two dyes shared a similar absorption tendency when dissolved in CH₂Cl₂, owing to the similar chemical structure except their different donor unit, which indicated that the incorporation of the TPC and DBD donors into the dye backbone did not impact the light capture. Both dyes exhibited an intense absorption between 300 and 400 nm, as well as between 450 and 600 nm. A slight red-shift of 14 nm for AJ301 and 9 nm for AJ303 of the maximum absorption is shown in Fig. 3b when the dyes were attached to the TiO₂ film.

3.1.1. Electrochemical properties

Differential pulse voltammetry (DPV) was performed with 0.1 M TBAPF₆ as a support electrolyte dissolved in CH₂Cl₂, Ag/AgNO₃ as reference electrode with ferrocene as an external standard, glassy carbon as a working electrode and Pt wire as a counter electrode. The oxidation potential of ferrocene, AJ301 and AJ303 were 0.16 V, 0.62 V and 0.56 V, respectively. The results are shown in Fig. S1. AJ301 (1.09 V vs normal hydrogen electrode, NHE) exhibited a more positive highest occupied molecular orbital (HOMO) energy level compared with AJ303 (1.03 V vs NHE), which implied a weaker donor-ability of TPC than DBD. An ample potential gap was obtained between the HOMO energy level for both dyes with $Co(bpy)_3^{2+/3+}$ (0.56 vs NHE) and $Cu(tmby)_2^{+/2+}$ (0.87 V vs NHE), which ensured efficient dye regeneration in the DSSCs. E^{opt}_g was calculated using the equation $\vec{E^{opt}}_g = 1240/\lambda$, where λ is the intersection of the tangent of the absorption on the TiO₂ film with the xaxis, which was 1.94 V for AJ301 and 1.93 V for AJ303. The minor difference for E^{opt}_{g} was attributed to the influence of the donor units TPC and DBD, which is normally negligible since E^{opt}_{g} is largely dominated by the same π -bridge–accepter unit. The lowest

Table 2

Frontier molecular orbitals of the HOMO and LUMO for	the dyes AJ301 and AJ303 that were	calculated using DFI
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unoccupied molecular orbital (LUMO) energy levels of **AJ301** and **AJ303** were -0.85 V and -0.93 V vs NHE, calculated by LUMO = HOMO - E^{opt}_{g} , which meant sufficient driving force for electron injection from the excited sensitizers to the CB of TiO₂. The calculated HOMO values are 0.80 V and 0.65 V, the calculated LUMO values are -1.56 V and -1.68 V. The calculated energy level accord with the variation trend of the measured values. The energy level diagram for the two dyes is shown in Fig. 4 and the corresponding data can be found in Table 1.

3.2. Theoretical model calculations

To gain a clear understanding of the influence of TBP and DBD donors on the geometric configuration and electron distribution, density functional theory (DFT) was applied for calculations at the B3LYP/6-31G*(d, p) level. The calculated transition energies are shown in Table 2. For the HOMO orbitals of the two dyes in the ground state, the electron density was mainly focused on the TPC and DBD donors. The LUMO orbitals were mainly distributed on the π -bridge groups. The LUMO+1 orbitals were predominantly



Fig. 6. (a) J - V curves of the corresponding DSSCs measured under AM 1.5 G illumination (100 mW cm⁻²). (b) IPCE spectra for DSSCs based on dyes Aj301 and Aj303 with a $[Co(bpy)_3]^{2+/3+}$ redox shuttle.

 Table 3

 Photovoltaic performance parameters of the AJ301 and AJ303 dyes measured under AM1.5 G irradiation.

Dyes	Electrolyte	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}({ m mV})$	FF (%)	PCE (%)
AJ301 AJ303 AJ301	Co ²⁺ /Co ³⁺ Co ²⁺ /Co ³⁺ Cu ⁺ /Cu ²⁺	10.3 (±0.59) 15.8 (±0.49) 7.3 (±0.28)	807 (±9.2) 914 (±4.7) 951(±5.7)	74.6 (±0.62) 70.4 (±0.61) 77.8 (±0.63)	$6.2(\pm 0.26)$ 10.2(± 0.25) 5.4(± 0.17)
AJ303	Cu^+/Cu^{2+}	11.3 (±0.31)	1007(±4.9)	71.9 (±0.64)	8.2(±0.36)

distributed on the accepter and slightly distributed on the π -bridge framework. The result indicates that the excited state dye was effective for intramolecular charge transfer from the donor to acceptor group.

For the two dyes, a significant difference of the twisted dihedral angles was clearly observed between the two donor units and the neighboring π -bridge-acceptors in Fig. 5. Compared with **AJ301**, the DBD donor of **AJ303** exhibited a larger dihedral angle of 54.1° between the conjugated carbazole unit and the hexylthiophene of the π -bridge group, because the backbone coplanarity of the donor group of **AJ301** was introduced in the dye. However, for **AJ301**, owing to the strong steric effect between adjacent flexible carbazole groups on the thiophene with large twisted dihedral angles of 48.1° and 41.1°, the dihedral angle between the strong electrondonating ability of thiophene and adjacent hexylthiophene of the π -bridge group exhibited excellent backbone coplanarity with the smallest twisted dihedral angles of 47.5°. This result explains the small difference between the UV–vis absorption spectra.

3.3. Device performance

The photocurrent density–voltage (*J* - V) curves measured under standard AM1.5G solar irradiation (100 mW cm⁻²) of the devices based on **AJ301** and **AJ303** are shown in Fig. 6a. The corresponding photovoltaic parameters in Table 3. The devices based on **AJ301** showed a lower PCE of 6.2% with a short-circuit photocurrent density (J_{sc}) of 10.3 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 870 mV and a fill factor (*FF*) of 74.6%, in conjunction with a cobalt redox shuttle. The DSSCs based on **AJ303** exhibited a better PCE of 10.2%, ($J_{sc} = 15.8 \text{ mA cm}^{-2}$, $V_{oc} = 914 \text{ mV}$, *FF* = 70.4%). **AJ301** and **AJ303** were also used to fabricate DSSC devices with a copper redox shuttle. For the excellent **AJ303**, a PCE of 8.2% was obtained, with a J_{sc} of 11.3 mA cm⁻², V_{oc} of 1007 mV and *FF* of 71.9%, which was 5.4% higher than for **AJ301**. A lower V_{oc} was obtained owing to the more negative potential for Co (bpy)^{2+/3+}₃ compared with Cu(tmby)^{+/2+}₂.

More flexible alkyl chains and fused rings were introduced to DBD to decrease the intermolecular packing and recombination for a higher photovoltaic performance. The incident photo-to-electron

conversion efficiency (IPCE) was also measured to further investigate the performance difference of the devices based on the two dyes. As shown in Fig. 6b (the copper electrolyte based on device for IPCE in Fig. S2), AJ303 maintained a relatively high conversion efficiency over all of the visible region compared with AJ301, which corresponded to the order of the photocurrent, where AJ303 $(15.8 \text{ mA cm}^{-2}) > \text{AJ301} (10.3 \text{ mA cm}^{-2})$. This was attributed to the different energy gaps between LUMO and the CB level of the TiO₂ semiconductor sensitized by dyes. The integrated photocurrent, 10.6 mA cm⁻² for AJ301 and 14.5 mA cm⁻² for AJ303, was calculated and agreed-well with the J - V measurements. The efficiency distribution of repeatable devices shown in Fig. S3a. The best performing dye of AJ303 exhibited IPCE values above 70% in the range of 400–680 nm, which revealed a higher intensity IPCE response compared with the AJ301 dye, and resulted in an improved photocurrent and photovoltaic efficiency.

Therefore, it should be noted that the surface coverage of dyes on the TiO₂ film is also an important factor for the IPCE values. The higher IPCE values can be ascribed to the increased dye loading to obtain a better light-harvesting capacity. We measured the absorbance of dye loading on a TiO₂ electrode, which was immersed into a THF/H₂O (V/V = 1:1) solution containing 0.1 M NaOH. The dye loading amount of **AJ303** (2.32×10^{-7} mol cm⁻²) was higher than that of **AJ301** (9.91×10^{-8} mol cm⁻²), as shown in Fig. S4. The higher dye loading values were attributed to the presence of a smaller steric hindrance of the thiophene-fused electron-donating group in the **AJ303** dye[41,42].[]The relatively high J_{sc} of **AJ303** compared with that of the **AJ301**-based DSSC device was not surprising because the two dyes had a similar absorption range in the visible region and ε , so the major factor was a higher light capture ability to increase the light-harvesting ability.

3.4. Electrochemical impedance spectroscopy

To better research the different donor structure with performance relationships, electrochemical impedance spectroscopy (EIS) was performed to understand the interfacial charge-transfer mechanisms in the devices. The devices were operated at different bias voltages in the range of 0.75-0.95 V with an interval of 50 mV in a dark room. The parameters of the frequency were the set range of 0.1 Hz–100 kHz and the amplitude applied at 10 mV. The chemical capacitance was directly related to the V_{oc} values, which can present the electronic storage ability to effect the shift of CB of TiO₂. The electron recombination resistance (R_{rec}) and transport resistance (R_{tr}) were present at the TiO₂/dye/electrolyte interface and electrolyte/Pt interface. The Bode plots are shown and Nyquist plots of the devices with a forward bias of -0.90 V are shown in Fig. 7a and Fig. S5. Two semicircles were visible, where



Fig. 7. EIS analysis data with a $[Co(bpy)_3]^{2+/3+}$ redox shuttle. (a) Bode phase plots of the dyes. (b) Chemical capacitance C_{μ} . (c) Recombination resistance R_{rec} . (d) Electron lifetime τ .

Table 4 EIS parameters a with a $[Co(bpy)_3]^{2+/3+}$ redox shuttle for DSSCs sensitized by AJ301 and AJ303.

Dyes	$\mathbf{R}_{tr}\left(\Omega ight)$	$\mathbf{R}_{rec}\left(\Omega ight)$	C_{μ} (mF)	τ (ms)	$\eta_{cc}(\%)$
AJ301	4.68	31.38	0.165	5.19	87.0
AJ303	5.01	50.33	0.143	7.21	90.9

^a Calculated value from EIS data measured at a forward bias of -0.90 V under dark conditions. R_{tr}, transport resistance; R_{rec}, charge recombination resistance; C_µ, chemical capacitance; τ , electron lifetime; η_{cc} , charge-collection efficiency.

the small semicircle was attributed to R_{tr} corresponding to a high frequency in the Bode plots and the large semicircles depicted the impedances of R_{rec} at the middle frequency. The R_{tr} represent the FTO/Pt interface, which have similar resistance for Pt counter electrode [43]. A larger semicircle in theory means a larger R_{rec}, which indicates a slower electron recombination rate. Comparing AJ301 with AJ303, the large semicircle radius increased in the order of **AJ303** (50.33 Ω) > **AJ301** (31.38 Ω) under dark room, which was in good agreement with the V_{oc} tendencies of AJ303 > AJ301 in Table 4. The electron lifetime (τ) was calculated by using R_{rec} $(\tau = R_{rec} \times C_{\mu})$, as shown in Fig. 7d. As a result, the τ values showed increase tendencies of AJ303 > AJ301, which indicted a longer electron lifetime and meant that a lower charge recombination rate led to the TiO₂ CB shifting-up, thereby resulting in enhanced V_{oc} and PCE values. A longer τ and larger R_{rec} provided a reasonable explanation for AJ303 having a higher V_{oc} . The charge-collection efficiency (η_{cc}) of the dye-based devices was calculated by $\eta_{cc}=$ $(1+R_{tr}/R_{rec})^{-1}$. The η_{cc} values of **AJ301** and **AJ303** were 87.0% and 90.9%, respectively, where AJ303 clearly reflected that the injected electrons rate was more efficient than that of AI301 to obtain a good photovoltaic performance. Although, the DBD donor showed a better planarity of the conjugated skeleton, the higher V_{oc} values of **AJ303** than **AJ301** dyes using the Co^{2+/3+} redox mediator suggested more effective suppression of electron recombination owing to the bulky hexylphenyl moieties. Photovoltaic devices based on copper electrolyte have similar charge transfer mechanism, as shown in Fig. S6.

3.5. The stability of devices

The stability of devices are important for practical application. We measured the **AJ303** devices based on $[Co(bpy)_3]^{2+/3+}$ redox shuttle at LED light for 360 h. The parameters of change rule of device were depicted in Fig. 8. The PCE values have fallen by roughly 16% compared with initial value, which shows a relatively stable property under the 1 sun illumination.

4. Conclusion

We designed and synthesized two carbazole sensitizers containing a thiophene group with the use of different redox couples to improve the photovoltaic efficiency of DSSC. The dye of the TPC donor and the dye of the DBD donor using a cobalt-based electrolyte exhibited PCE of 6.2% and 10.2%, and a copper-based electrolyte exhibited PCE of 5.4% and 8.2%. The higher J_{sc} values of AJ303 than AJ301 dyes were ascribed to more dye loading and a higher chargecollection efficiency. The DBD donor showed a better rigidity and planarity of the conjugated skeleton to reduce steric hindrance. Therefore, the fused carbazole concept was applied to the introduction of a thiophene-fused structure on the donor to improve high-performance DSSCs. The sensitizer AJ303 exhibited a blocking effect of hexylbenzene group in the donor, which effectively suppressed the recombination process with an electrolyte, as shown by EIS and photovoltage transient studies. The results indicated the enhanced $V_{\rm oc}$ values were attributed to the longer electron lifetimes by introducing the bulkiness of an alkyl chain around the thiophene-fused donor side. These results provide an enlightened



Fig. 8. The stability of **AJ303** with a $[Co(bpy)_3]^{2+/3+}$ redox shuttle by normalization.

strategy for designing the fusion of substituted new efficient organic dyes for high-performance DSSCs.

Notes

The authors declare no competing financial interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132124.

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