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A dimeric fullerene derivative for efficient inverted planar perovskite solar cells with improved stability

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A dimeric fullerene derivative for efficient inverted planar perovskite solar cells with improved stability†

Chengbo Tian, Kevin Kochiss, Edison Castro, German Betancourt-Solis, Hongwei Han and Luis Echegoyen*

Fullerene derivatives can efficiently passivate the interfacial defects of perovskite layers to improve the performance of perovskite solar cells. In this work, a new dimeric fullerene derivative (D-C60) with two [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) units was designed, synthesized and applied as the electron transporting material (ETM) in perovskite solar cells (PSCs) taking advantage of its appropriate energy levels, relatively fast electron mobility, and easy solution processability compared to the widely used PC61BM. D-C60 can efficiently passivate the trap states between the perovskite and fullerene layers, leading to improved electron extraction and overall photovoltaic performance. Devices based on D-C60 as the ETM achieved power conversion efficiencies (PCEs) of 16.6%, which is significantly higher than that observed with PC61BM (14.7%). In addition, the more hydrophobic and compact D-C60 layer resulted in higher device stability than that with PC61BM. These results show that covalently linked dimeric fullerene derivative can act as efficient electron transporting materials (ETMs) for high performance PSCs.

1. Introduction

The unique properties of organic–inorganic hybrid perovskite materials (typically CH3NH3PbI3), such as high light absorption coefficients, long carrier diffusion lengths, high electron/hole mobilities, simple device architectures, low-temperature fabrication processes, compatibility with flexible substrates, negligible hysteric behavior, and efficiencies comparable to those of commercial standards, make them promising candidates for the development of the next-generation photovoltaic solar cells for commercial applications. Currently, PSCs are the most rapidly developing class, with certified efficiencies rising from 3.8% in 2009 to 22.1% in 2016.1-11

In inverted planar PSCs, the perovskite layer is surrounded by an electron transporting layer (ETL) and a hole transporting layer (HTL). The HTL, PEDOT:PSS or NiOx, is connected to the anode, ITO or FTO, while the ETL is typically a fullerene derivative that is in direct contact with the metal cathode, Al.

PC61BM is the most widely used fullerene derivative in photovoltaic applications, and has become the standard in the field, due to its efficient electron transporting and solution processable properties.12-15

In 2013, Jeng and co-workers reported a PCE of 3.9% for inverted planar PSCs using PC61BM as the ETM. The reasonable efficiency of this type of devices demonstrated that fullerene derivatives were promising ETMs in PSCs.20-22 Recently, Nie and Im’s group reported a device with an efficiency of 18% by developing a new perovskite deposition technique.17,18 Huang’s group recently obtained a remarkable efficiency, as high as 19.4%, which is comparable to those of mesoporous perovskite solar cells, by means of a simple solvent annealing process to improve the surface of the perovskite, resulting in a better electron extraction into the fullerene layer.19

To explore the effect of functional groups on the performance of fullerene-based PSCs, double fullerene layers or fullerene derivatives with different functional groups have been studied. However, up to now, all of the fullerene derivatives reported in PSCs are monomeric derivatives and to the best of our knowledge, dimeric fullerene derivatives as ETMs in PSCs have never been explored. There is a limited number of dimeric fullerene derivatives that were investigated in polymer solar cells.20,21 Due to the excellent performance of PC61BM-based PSCs, a dimeric fullerene with two PC61BM units was expected to show improved performance in PSCs.

Herein, we report the synthesis, characterization and photovoltaic properties of a fullerene dimer derivative (D-C60), the structure of which is shown in Scheme 1. Due to suitable energy levels and adequate electron mobility of D-C60, the best efficiency obtained from a device based on this compound was

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta00362e
spin-coated onto the treated FTO substrates at 5000 rpm for 30 s, and heated at 150 °C for 15 min in air. Then a solution of 1 M PbI₂ in DMF was spin-coated at 3000 rpm for 30 s on top of the PEDOT:PSS coated substrates, and dried on a hot plate at 70 °C for 10 min. The FTO/PEDOT:PSS/PbI₂ substrates were then transferred to a vacuum oven to be converted to CH₃NH₂PbI₃ by means of a vapor-assisted gas–solid crystallization process following previously reported methods. After the CH₃NH₂PbI₃ films were formed and then cooled to room temperature, 2 wt% PC₆₁BM (or D-C₆₀) dissolved in chlorobenzene was spin-coated onto the CH₃NH₂PbI₃ layer at 1200 rpm for 30 s. To complete the devices, aluminum electrodes (100 nm) were deposited by thermal evaporation under a pressure of 2 × 10⁻⁶ Torr through a shadow mask. The active area of the devices was determined by a mask with an aperture in the middle (7 mm²).

3. Results and discussion

The synthetic approach to prepare D-C₆₀ is presented in Scheme 1. In this approach the two fullerenes are linked by an alkyl bridge between the ester functional groups on the PC₆₁BMs. D-C₆₀ exhibits a slightly higher lowest unoccupied molecular orbital (LUMO) energy level than the mono-adduct fullerene derivatives, making it a good candidate to act as the ETM in PSCs. 2,2-Diethyl-1,3-propanediol was used to connect the two PC₆₁BM units in order to increase the solubility of the dimer derivatives, modifying it a good candidate to act as the ETM in PSCs. 2,2-Diethyl-1,3-propanediol was used to connect the two PC₆₁BM units in order to increase the solubility of the dimer derivatives, making it a good candidate to act as the ETM in PSCs. PC₆₁BA (99%) was bought from Nano-C. PC₆₁BA was synthesized heating PC₆₁BM and hydrochloric acid under reflux in toluene for 12 h. D-C₆₀ was obtained from the reaction of PC₆₁BA with 2,2-diethyl-1,3-propanediol in anhydrous dichloromethane. The final product was characterized by MALDI-TOF mass spectrometry, ¹H and ¹³C NMR (see ESIL).
Due to the flexible connecting group, D-C60 exhibits excellent solubility in normal organic solvents such as dichloromethane, chloroform, and chlorobenzene, which makes it suitable for solution-processed PSCs.

The energy levels of fullerene derivatives are important to assess their electron extraction and hole blocking properties in PSCs. The electrochemical properties of PC61BM and D-C60 were studied via cyclic voltammetry (CV) in the range of 0 to −2.0 V vs. Fc/Fc⁺. Both exhibit three independent well-defined reversible reduction waves (see Fig. 1a and S3†). The half-wave potentials for the reduction processes are listed in Table S1.† The LUMO energy levels of the compounds were calculated from their onset reduction potentials (E_on red) using the equation:

\[
\text{LUMO energy level} = -e(E_{\text{on red}} + 4.80) \text{ (eV)}.
\]

These values are listed in Table 1. The LUMO energy levels were estimated at −3.88 and −3.90 eV for D-C60 and PC61BM respectively, which are similar to previous reports.29 These values indicate that both compounds can be used as efficient ETMs in PSCs.

Based on their maximum absorption onsets, as shown in Fig. 1b and Table 1, and the values of the LUMO energy levels, D-C60 and PC61BM were estimated to have HOMO values of −5.61 and −5.63 eV, respectively, deep enough to block holes.

For PSC devices, photovoltaic performance is heavily influenced by the carrier mobilities of the charge transporting layers. High electron mobility of the fullerene derivatives improves the short-circuit current density (J_sc) and thus the PCEs. The electron mobility of D-C60 and PC61BM were measured by the space-charge limited current (SCLC) method (Fig. S4†) and the Mott-Gurney law,35 based on electron-only devices with the structure FTO/Cs₂CO₃/fullerene derivative/Ca/Al, and found to be 9.83 × 10⁻⁴ and 6.85 × 10⁻⁴ cm² V⁻¹ s⁻¹, respectively. The higher electron mobility of D-C60 suggests that the fullerene cages are better packed for D-C60 than for PC61BM. The higher electron mobility of D-C60 leads to a higher short-circuit current density and PCE than that of PC61BM-based PSC devices.

To test the performance of D-C60 as the ETM in PSCs, planar structure devices were prepared, as shown in Fig. 2a, with a configuration: FTO/PEDOT:PSS/CH₃NH₃PbI₃/PC61BM (or D-C60)/Al. The energy-level alignment of all materials involved in the device is shown in Fig. 2b. The perovskite layer of the device was prepared by a vapor-assisted gas-solid crystallization process, previously reported.33 After this process, the perovskite layer on PEDOT:PSS, as shown in Fig. 2c, exhibits homogeneous and well packed grains with no pinholes. As shown in the cross-section of the device (Fig. 2d), excellent contact results between the perovskite and the fullerene layers. The thickness of each layer was measured using a profilometer, showing that the

<table>
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<th>Compound</th>
<th>λ_abs (nm)</th>
<th>E_g (eV)</th>
<th>E_on red (V)</th>
<th>LUMO (eV)</th>
<th>HOMO (eV)</th>
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<tr>
<td>D-C60</td>
<td>717</td>
<td>1.73</td>
<td>0.92</td>
<td>−3.88</td>
<td>−5.61</td>
</tr>
<tr>
<td>PC61BM</td>
<td>718</td>
<td>1.73</td>
<td>0.90</td>
<td>−3.90</td>
<td>−5.63</td>
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Fig. 1 (a) Cyclic voltammetric scans for D-C60 and PC61BM at a scan rate of 100 mV s⁻¹. (b) UV-vis absorption spectra of D-C60 and PC61BM in toluene solution.

Fig. 2 (a) Configuration scheme of the inverted structure planar perovskite solar cells, (b) energy level diagram of the materials used in PSCs, (c) top-view SEM image of the perovskite film, and (d) cross-sectional SEM image of the device FTO/PEDOT:PSS/perovskite/fullerene derivative film.
PEDOT:PSS layer, perovskite layer and fullerene derivative layer are around 40 nm, 350 nm and 60 nm, respectively.

The $J-V$ curves of PSCs with PC$_61$BM and D-C$_{60}$ as the ETMs were obtained under AM 1.5G irradiation (100 mW cm$^{-2}$) in air. The $J-V$ curves of the devices are shown in Fig. 3a and the key photovoltaic performance parameters $V_{oc}$, $J_{sc}$, FF, and PCE are listed in Table 2. The most efficient device using D-C$_{60}$ as ETM yielded a PCE of 16.6%. The efficiencies are significantly higher than those of devices based on PC$_61$BM as ETM, which resulted in an optimal PCE of 14.7%.

In order to better compare the device performances, a statistical histogram of the efficiencies of 20 individual devices using PC$_61$BM and D-C$_{60}$ as ETMs are shown in Fig. 3c. The average efficiencies for D-C$_{60}$ and PC$_61$BM based devices are 16.1 ± 0.5% and 13.9 ± 0.7%, respectively. The narrower distribution of the key photovoltaic parameters illustrate that D-C$_{60}$ is an excellent ETM for inverted planar structure PSCs.

The higher $J_{sc}$ values of the D-C$_{60}$ based devices were verified by the incident photon-to-electron conversion efficiency (IPCE) spectrum, as shown in Fig. 3b. The integrated current densities from the IPCE curve for devices involving D-C$_{60}$ and PC$_61$BM as the ETMs are 21.5 and 20.4 mA cm$^{-2}$, respectively, which are consistent with the values from the $J-V$ curves. Furthermore, the higher $J_{sc}$ and FF of D-C$_{60}$ based devices can be related to the higher electron mobility and electron extraction ability.

The maximal steady-state power and photocurrent outputs were used to further verify device efficiencies. As shown in Fig. 3d, D-C$_{60}$ based devices resulting in 20.1 mA cm$^{-2}$ at 0.82 V had PCEs of 16.5%. PC$_61$BM based devices resulting in 18.2 mA cm$^{-2}$ at 0.80 V, had PCEs of 14.5% (Fig. S5†). Both efficiencies are very similar to the values determined from the $J-V$ data.

It is worth noting that the D-C$_{60}$ based devices exhibited a slightly higher $V_{oc}$ than those of PC$_61$BM based devices, which can be reasonably attributed to the slightly higher LUMO energy.

\[ \text{Table 2 } \text{Summary of device performance analysis in Fig. 3. The calculated } J_{sc} \text{ values are obtained from the EQE curves} \]

<table>
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<tr>
<th>Type</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Calculated $J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tr>
<td>PC$_61$BM</td>
<td>0.94</td>
<td>20.96</td>
<td>20.4</td>
<td>74.4</td>
<td>14.7</td>
</tr>
<tr>
<td>D-C$_{60}$</td>
<td>0.96</td>
<td>21.89</td>
<td>21.5</td>
<td>78.8</td>
<td>16.6</td>
</tr>
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</table>

Fig. 3 Device performance and reproducibility of perovskite solar cells fabricated by using D-C$_{60}$ and PC$_61$BM as ETMs. (a) $J-V$ curves of devices using D-C$_{60}$ and PC$_61$BM. (b) EQE spectra for perovskite solar cells fabricated by using D-C$_{60}$ and PC$_61$BM as ETMs. (c) Histograms of device PCE measured for 20 individual devices based on PC$_61$BM and D-C$_{60}$ ETMs. (d) Maximal steady-state photocurrent output at the maximum power point for D-C$_{60}$ based device at 0.82 V and its corresponding power output.
level of D-C60. The hysteresis effects of the devices were also studied. As shown in Fig. S6,† no obvious J–V curve differences were observed, regardless of the scan direction for the D-C60 based devices. The negligible hysteresis effect in the PSCs with D-C60 as the ETMs further indicate that the fullerene derivatives effectively passivate the charge traps at the fullerene/perovskite interface.10,39

To investigate the electron extraction ability of D-C60 as the ETM in PSCs, steady state and time-resolved photoluminescence (PL, TRPL) spectra were recorded. Fig. 4a shows the steady-state PL spectra of perovskite, perovskite/PC61BM and perovskite/D-C60 thin film substrates. When the perovskite layer forms a contact with PC61BM or D-C60, a significant PL quenching effect was observed. Notably, devices based on D-C60 show more efficient PL quenching than those based on PC61BM, which indicates that D-C60 inhibits electron–hole recombination more efficiently.9 Additionally, TRPL, was measured by monitoring the emission peak of the perovskite layer as a function of time as shown in Fig. 4b. Perovskite/D-C60 devices exhibit a shorter PL decay time (11.1 ns) than that observed for the perovskite/PC61BM (14.0 ns) devices, which implies that electrons are more efficiently transferred to D-C60 than to PC61BM. The faster decay is the result of PL quenching due to electron transfer at the interface, which suppresses electron–hole recombination and increases the Jsc and FF of the device.40

To probe charge transfer processes at the perovskite/D-C60 interface, electrical impedance spectroscopy (EIS) measurements were conducted for both perovskite/D-C60 and perovskite/PC61BM devices. The data were fit to a relatively simple equivalent circuit (Fig. S7 and Table S2†) consisting of a contact resistance between the fullerene/perovskite or perovskite/PEDOT:PSS interface and the recombination resistance (Rrec).41 The Nyquist plots for the perovskite/D-C60 devices show lower contact resistances and larger recombination resistances than those for perovskite/PC61BM devices, thus D-C60 can decrease charge recombination more efficiently than PC61BM at the fullerene/perovskite interface and electron extraction into the ETL is facilitated with D-C60. This must be associated with the differences of charge recombination efficiencies at the perovskite/D-C60 or perovskite/PC61BM interface since the PEDOT:PSS/perovskite interface is identical for both cases.42 This result is totally consistent with the higher PL quenching observed for perovskite/D-C60 devices.

Fig. 4 (a) Steady-state photoluminescence spectra, and (b) TRPL decay transient spectra of FTO/perovskite/PC61BM and FTO/perovskite/D-C60.

Fig. 5 (a) The images of the water droplet contact angles on different surfaces of fullerene derivative film. (b) Normalized PCE of perovskite solar cells employing D-C60 and PC61BM ETMs as a function of storage time in air.
Assessment of the stability of devices with D-C60 and PC61BM as the ETMs was conducted under a 50% humidity in air at room temperature without encapsulation. As shown in Fig. 5b, the devices with D-C60 retained more than 75% of its original performance after 10 days, while devices with PC61BM as the ETM retained only 25% after 10 days. The higher stability of the D-C60-based devices may result from the higher hydrophobicity of D-C60 as well as the more compact self-assembled layer. As shown in Fig. 5a, the hydrophobic properties of the different fullerene derivatives were investigated. Water droplets on perovskite/PC61BM and perovskite/D-C60 layers result in contact angles of 82° and 96°, respectively. These values indicate that the two C60 subunits in D-C60 make the fullerene derivative more hydrophobic than PC61BM.

4. Conclusions

In summary, we synthesized a dimeric fullerene derivative D-C60 and applied it as an ETM for PSCs taking advantage of its appropriate energy levels, relatively fast electron mobility, easy solution processability and device stability. As evidenced by CV, SCLC, EIS, PL and TRPL studies, D-C60 can effectively passivate the surface defects of the perovskite film, as well as efficiently extract and transport electrons. As a result, using D-C60 as ETM, PSC devices reached up to 16.6%, PCEs, higher than those of PC61BM based devices. Due to its higher hydrophobicity D-C60 also enhanced the stability of the devices compared to PC61BM. We believe that dimeric fullerene derivatives have the potential to become high performance alternatives for ETMs in PSCs.

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