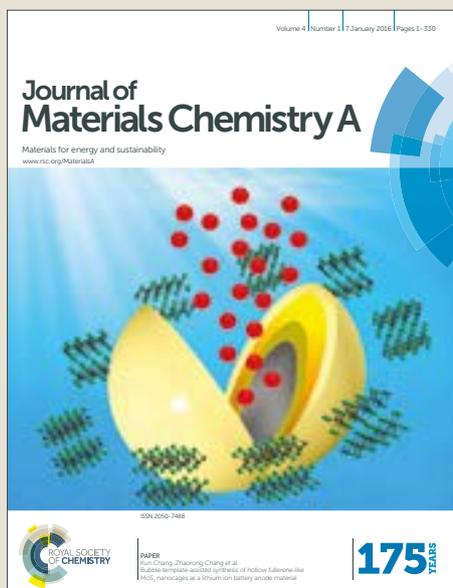


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A dimeric fullerene derivative for efficient inverted planar perovskite solar cells with improved stability

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Abstract

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, 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,^{1,2} long carrier diffusion lengths,³⁻⁵ high electron/hole mobilities,⁶ simple device architectures, low-temperature fabrication processes,⁷ compatibility with flexible substrates,^{8,9} negligible hysteric behavior,¹⁰ and efficiencies comparable to those of commercial standards,¹¹ 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.^{1,12}

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,^{8,13} is connected to the anode, ITO or FTO, while the ETL is typically a fullerene derivative that is 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.^{14,15}

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.¹⁶ 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.²⁰⁻²⁷ 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.^{28,29} Due to the excellent performance of PC₆₁BM-based PSCs,³⁰ 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 16.6%. This value was higher than that for the analogous PC₆₁BM based PSCs, 14.7%. Meanwhile, the higher hydrophobicity of D-C₆₀ compared to that of PC₆₁BM resulted in better device stability.

2. Experimental and methods

Materials Synthesis

[6,6]-phenyl- C_{61} -butyric acid ($PC_{61}BA$) was synthesized by following previously reported procedures.³¹ The synthetic procedure followed to prepare ($D-C_{60}$) is presented in Scheme 1. EDC (25.6 mg, 0.13 mmol) was added slowly to a pre-cooled solution of 2,2-diethyl-1,3-propanediol (6.6 mg, 0.05 mmol), $PC_{61}BA$ (100.0 mg, 0.11 mmol), and a small amount of DMAP in 40 mL of dry dichloromethane. The mixture was stirred for 36 h at room temperature. After drying under vacuum, the residual mixture was purified by silica gel column chromatography (toluene as eluent). $D-C_{60}$ was precipitated from methanol as a dark-brown solid. 1H NMR ($CDCl_3$, 400 MHz) (**Figure S1**): δ (ppm) 0.88 (6H, t, $J=5.16$ Hz), 1.42 (4H, m), 2.19 (4H, m), 2.53 (4H, t, $J=7.52$ Hz), 2.91 (4H, m), 3.68 (4H, s), 7.47 (2H, t, $J=7.32$ Hz), 7.55 (4H, t, $J=7.46$ Hz), 7.93 (4H, d, $J=7.52$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) (**Figure S2**): δ (ppm) 173.48, 148.80, 147.81, 145.85, 145.19, 145.15, 145.08, 145.03, 144.79, 144.66, 144.50, 144.42, 144.01, 143.76, 143.12, 143.03, 142.99, 142.93, 142.23, 142.18, 142.13, 142.11, 140.99, 140.75, 138.03, 137.57, 136.73, 132.09, 128.44, 128.24, 79.86, 51.85, 51.68, 33.88, 33.67, 29.70, 22.37. MALDI-TOF-MS m/z : calcd 1888.3, found 1888.6.

Device Fabrication

Methylammonium iodide (CH_3NH_3I) was prepared using a previously reported procedure.³² PSCs with a configuration of FTO/PEDOT:PSS/ $CH_3NH_3PbI_3/PC_{61}BM$ (or $D-C_{60}$)/Al were fabricated on FTO-coated glass substrates with a resistivity of $10 \Omega/cm^2$. The patterned FTO glass substrates were cleaned sequentially with detergent, deionized water, and ethanol, each step for 15 min dried with nitrogen gas and finally treated in a UV-ozone oven for 20 min. After passing through a $0.45 \mu m$ PVDF filter, the PEDOT:PSS solution (Baytron P VP AI 4083) was 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 CH₃NH₃PbI₃ by means of a vapor-assisted gas–solid crystallization process following previously reported methods.^{27,33} After the CH₃NH₃PbI₃ films were formed and then cooled to room temperature, 2 wt% PC₆₁BM (or D-C₆₀) dissolved in chlorobenzene was spin-coated onto the CH₃NH₃PbI₃ 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).

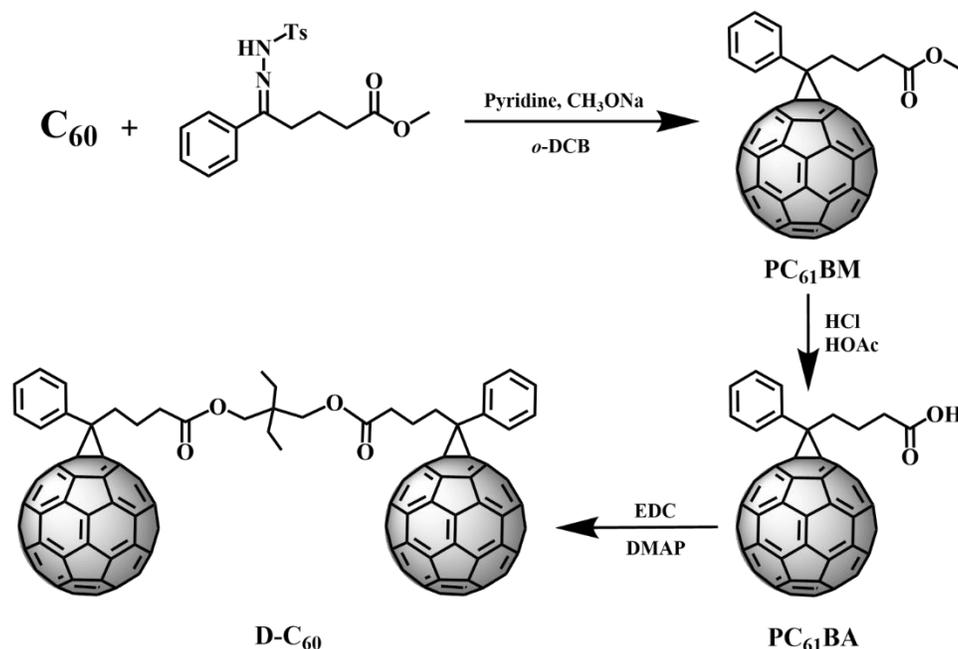
Device characterization

J–V characteristics of photovoltaic cells were tested using a Keithley 2420 source measure unit under a Photo Emission Tech SS100 Solar Simulator, and the light intensity was calibrated by a standard Si solar cell. The external quantum efficiencies (EQEs) were measured using a Bentham (from Bentham Instruments Ltd) measurement system. The light intensity was calibrated using a single-crystal Si photovoltaic cell as the reference. The *J-V* and EQE measurements were carried out in air. The SEM images were collected using a ZEISS Sigma FE-SEM, where the electron beam was accelerated in the range of 500 V to 30 kV. Film thicknesses were measured using a KLA Tencor profilometer. The contact angles of water were determined using a Ramé-Hart model 250 goniometer using pure deionized water at room temperature at a constant volume of 5 μL. A total of ten static measurements were analyzed and averaged for each ETM layer. The steady photoluminescence (PL) spectra were obtained using an Edinburgh instruments FLS980 fluorescence spectrometer.

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 PC₆₁BM. D-C₆₀ exhibits a slightly higher lowest unoccupied molecular orbital (LUMO) energy level than the mono-adduct fullerene derivatives,³⁰ 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 and to result in a homogeneous and compact film, with high hydrophobicity to improve water inclusion and enhance the device stability.

PC₆₁BM (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 supporting information). 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.



Scheme 1. The synthetic route for the synthesis of D-C₆₀.

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 **Figure 1a** and **Figure 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_{red}^{on}) using the equation; LUMO energy level = $-e(E_{red}^{on} + 4.80)$ (eV).³⁴ 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 **Figure 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.

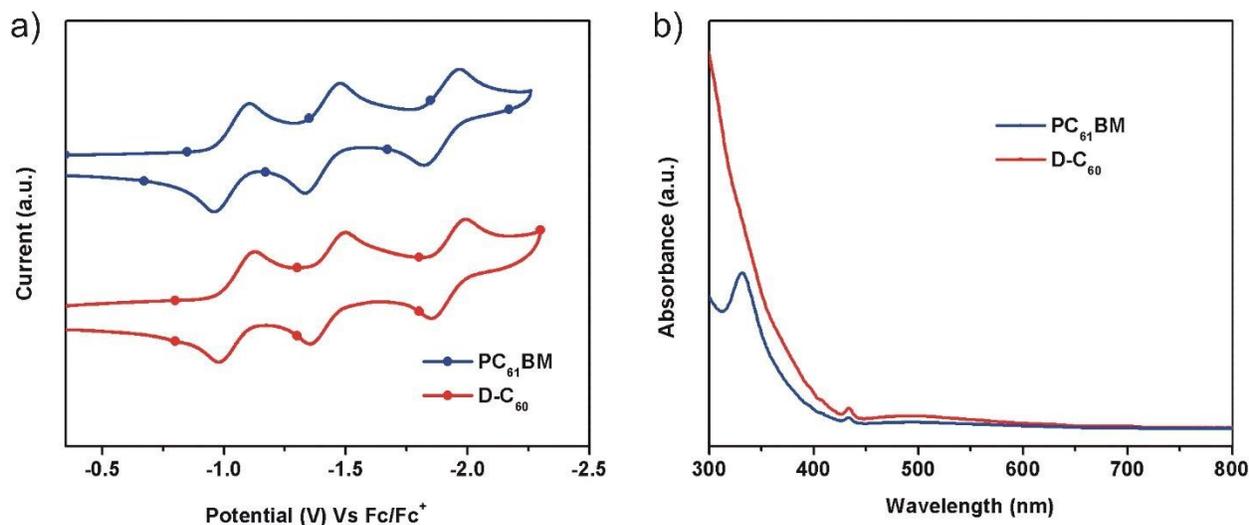


Figure 1. a) Cyclic voltammetric scans for D-C₆₀ and PC₆₁BM at a scan rate of 100 mV/s. b) UV-Vis absorption spectra of D-C₆₀ and PC₆₁BM in toluene solution.

Table 1. Electrochemical and photo-physical data of D-C₆₀ and PC₆₁BM

Compound	λ_{abs} (nm)	E_g (eV)	$E_{\text{red}}^{\text{on}}$ (V)	LUMO (eV)	HOMO (eV)
D-C ₆₀	717	1.73	0.92	-3.88	-5.61
PC ₆₁ BM	718	1.73	0.90	-3.90	-5.63

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 (**Figure S4**) and the Mott–Gurney law,³⁵ based on electron-only devices with the structure ITO/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 **Figure 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 **Figure 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 **Figure 2c**, exhibits homogeneous and well packed grains with no pinholes. As shown in the cross-section of the device (**Figure 2d**), excellent contact results between the perovskite and the fullerene layers. The thickness of each layer was measured using a profilometer, showing that the PEDOT:PSS layer, perovskite layer and fullerene derivative layer are around 40 nm, 350 nm and 60 nm, respectively.

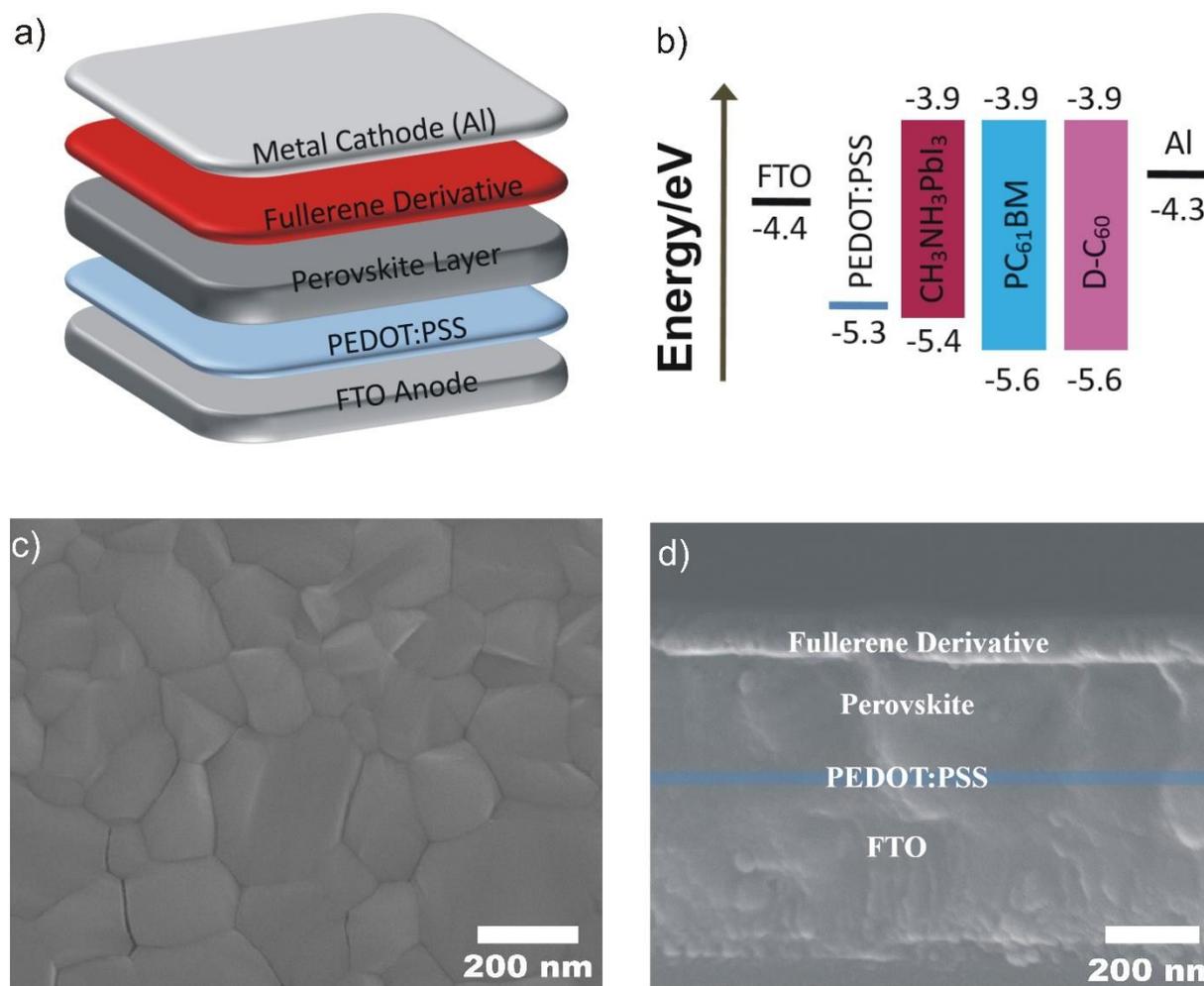


Figure 2. (a) Configuration scheme of the inverted structure planar perovskite solar cells, (b) Energy level diagram of the materials used in PSCs, (c) Top-view SEM image of the perovskite film, and (d) Cross-sectional SEM image of the device FTO/PEDOT:PSS/perovskite/fullerene derivative film.

The current-voltage (J - V) curves of PSCs with PC₆₁BM and D-C₆₀ 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 **Figure 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-C₆₀ as ETM yielded a PCE of 16.6%. The efficiencies

are significantly higher than those of devices based on PC₆₁BM 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 PC₆₁BM and D-C₆₀ as the ETMs are shown in **Figure 3c**. The average efficiencies for D-C₆₀ and PC₆₁BM based devices are 16.1±0.5% and 13.9±0.7%, respectively. The narrower distribution of the key photovoltaic parameters illustrate that D-C₆₀ is an excellent ETM for inverted planar structure PSCs.

The higher J_{sc} values of the D-C₆₀ based devices were verified by the incident photon-to-electron conversion efficiency (IPCE) spectrum, as shown in **Figure 3b**. The integrated current densities from the IPCE curve for devices involving D-C₆₀ and PC₆₁BM 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-C₆₀ based devices can be related to the higher electron mobility and electron extraction ability.

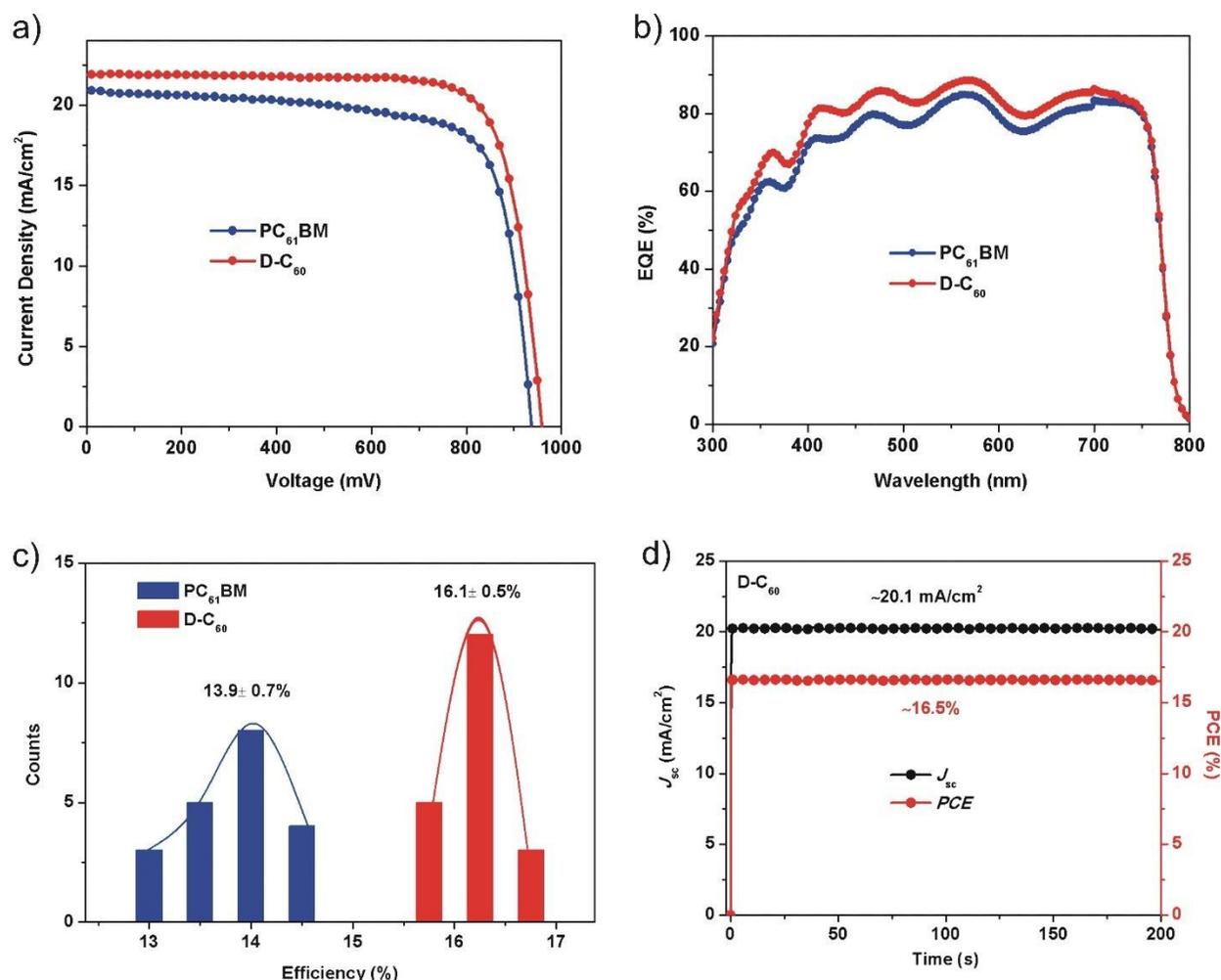


Figure 3. Device performance and reproducibility of perovskite solar cells fabricated by using D-C₆₀ and PC₆₁BM as ETMs. a) $J-V$ curves of devices using D-C₆₀ and PC₆₁BM. (b) EQE spectra for perovskite solar cells fabricated by using D-C₆₀ and PC₆₁BM as ETMs. (c) Histograms of device PCE measured for 20 individual devices based on PC₆₁BM and D-C₆₀ ETMs. d) Maximal steady-state photocurrent output at the maximum power point for D-C₆₀ based device at 0.82 V and its corresponding power output.

Table 2. Summary of device performance analysis in **Figure 3**. The calculated J_{sc} values are obtained from the EQE curves.

Type	V_{oc} (V)	J_{sc} (mA/cm ²)	Calculated J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PC ₆₁ BM	0.94	20.96	20.4	74.4	14.7
D-C ₆₀	0.96	21.89	21.5	78.8	16.6

The maximal steady-state power and photocurrent outputs were used to further verify device efficiencies. As shown in **Figure 3d**, D-C₆₀ based devices resulting in 20.1 mA cm⁻² at 0.82 V had PCEs of 16.5%. PC₆₁BM based devices resulting in 18.2 mA cm⁻² at 0.80 V, had PCEs of 14.5% (**Figure S5**). Both efficiencies are very similar to the values determined from the J - V data.

It is worth noting that the D-C₆₀ based devices exhibited a slightly higher V_{oc} than those of PC₆₁BM based devices, which can be reasonably attributed to the slightly higher LUMO energy level of D-C₆₀.³⁶⁻³⁸ The hysteresis effects of the devices were also studied. As shown in **Figure 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. **Figure 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 more efficiently inhibits electron-hole recombination.⁹

Additionally, TRPL, was measured by monitoring the emission peak of the perovskite layer as a function of time as shown in **Figure 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 J_{sc} 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 (**Figure S7** and **Table S2**) consisting of a contact resistance between the fullerene/perovskite or perovskite/PEDOT:PSS interface and the recombination resistance (R_{rec}).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 efficient 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.

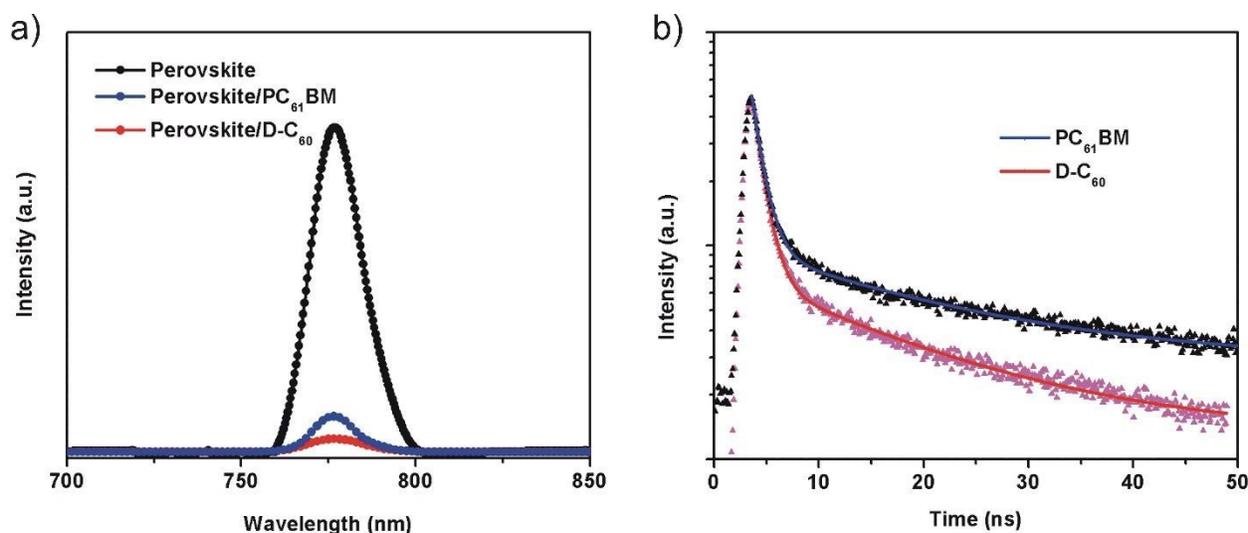


Figure 4. (a) steady-state photoluminescence spectra, and (b) TRPL decay transient spectra of FTO/perovskite/PC₆₁BM and FTO/perovskite/D-C₆₀.

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 **Figure 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 **Figure 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.

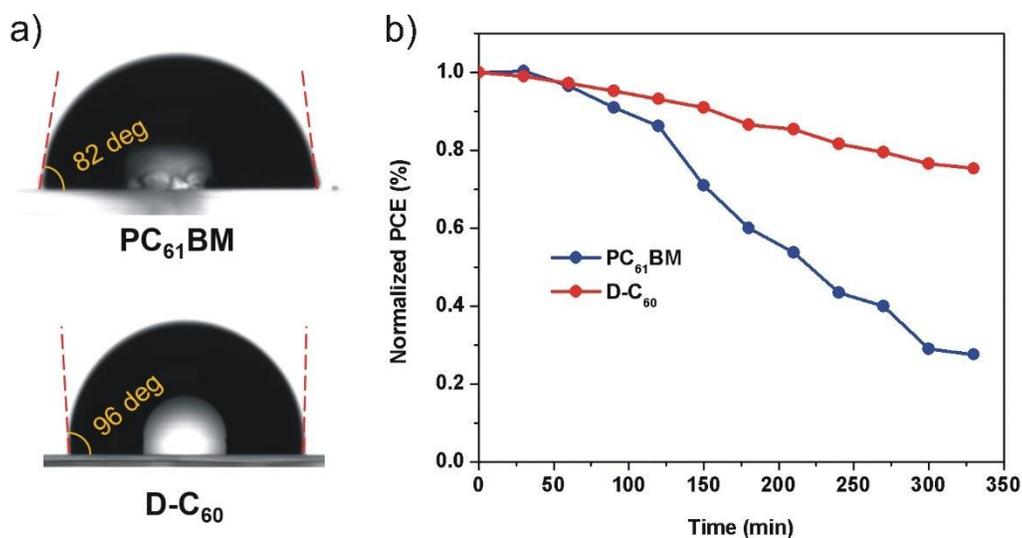


Figure 5. (a) The images of the water droplet contact angles on different surfaces of fullerene derivative film. (b) Normalized PCE of perovskite solar cells employing D-C₆₀ and PC₆₁BM ETMs as a function of storage time in air.

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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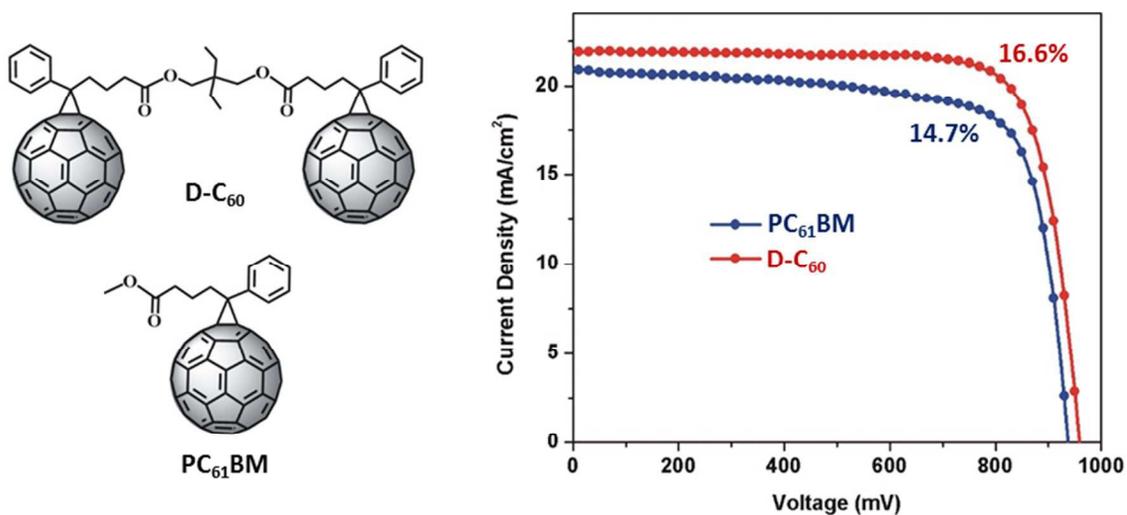
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