Communication

Enhanced Open-Circuit Voltage in Perovskite Solar Cells with Open-Cage [60]Fullerene Derivatives as Electron-Transporting Materials

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Received: 25 March 2019; Accepted: 18 April 2019; Published: 23 April 2019

Abstract: The synthesis, characterization, and incorporation of open-cage [60]fullerene derivatives as electron-transporting materials (ETMs) in perovskite solar cells (PSCs) with an inverted planar (p-i-n) structure is reported. Following optical and electrochemical characterization of the open-cage fullerenes 2a–c, p-i-n PSCs with an indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS)/perovskite/fullerene/Ag structure were prepared. The devices obtained from 2a–b exhibit competitive power conversion efficiencies (PCEs) and improved open-circuit voltage ($V_{oc}$) values (>1.0 V) in comparison to a reference cell based on phenyl-C$_{61}$-butyric-acid methyl-ester (PC$_{61}$BM). These results are rationalized in terms of a) the higher passivation ability of the open-cage fullerenes with respect to the other fullerenes, and b) a good overlap between the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) levels of 2a–b and the conduction band of the perovskite.

Keywords: open-cage fullerenes; perovskite solar cells; improving open circuit voltage

1. Introduction

Perovskite solar cells (PSCs) are an emerging class of photovoltaic devices, which promise to rival the performance of state-of-the-art cells, with current record power conversion efficiencies (PCEs) recently reaching 24.2% [1]. A major advantage of PSCs is their facile manufacturing process, which is mostly based on solution processing. However, a number of challenges need to be addressed before a marketable technology is available, including (a) cell performance, (b) cell stability, and (c) upscaling beyond laboratory scale toward the industrial production of commercially viable photovoltaic devices [2–7]. Another desirable yet unmet objective is the replacement of Pb by less toxic metals in the perovskite structure [8].

A PSC consists of a sandwiched structure containing a transparent conductive oxide, a hole transport layer (HTL), a perovskite photo-absorber layer, an electron-transport layer (ETL), and a back-contact electrode [9–15]. Among the various cell configurations available for PSCs, the inverted planar structure (p-i-n) (Figure 1) is the most attractive in terms of manufacturing, because the ETL, which is typically a fullerene derivative, is solution-processed [16], as opposed to the metal oxides employed in the regular planar and mesoscopic configurations, which require high-temperature annealing.
Importantly, p-i-n PSCs can be easily integrated in flexible devices [20]. A downside of the p-i-n configuration is that high open circuit voltage ($V_{oc}$) values are difficult to achieve. Successful strategies to overcome this limitation rely on the incorporation of dopant materials [21–23], interfacial engineering [24–26], morphology control [27,28], or the replacement of the HTL [29,30].

On the other hand, the replacement of phenyl-C$_6$$_1$-butyric-acid methyl-ester (PC$_{61}$BM) by other fullerenes as the ETL has found limited success, with only a few reports of $V_{oc}$ values beyond the 1.0 V threshold [31,32]. For the specific case of poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS)-based devices, examples are even scarcer [11,33,34]. The development of PSCs with PC$_{61}$BM surrogates relies mostly on the incorporation of highly crystalline ETLs. The resulting cells benefit from reduced energy disorder and improved charge trap passivation [35,36]. While this approach has been implemented with a variety of fullerenes, the vast majority of them consist of [3+2], [4+2], or cyclopropane adducts [15]. Thus, the introduction of structurally novel fullerene scaffolds that can expand the ETL repertoire is highly desirable.

Overall, the highest certified PCE value reported for PSCs with p-i-n configurations is 20.9% [37]. The development of efficient ETLs that can increase the efficiency of PSCs without the need of additives or complex manufacturing techniques is a major challenge in the field of inverted planar PSCs.

Open-cage fullerenes are a family of synthetic derivatives in which the three-dimensional backbone of the fullerene cage is distorted by the scission of one or more C–C bonds. Open-cage fullerenes have been successfully used as electron-accepting materials or as additives in bulk-heterojunction solar cells [38–40]. However, their use as ETLs in PSCs remains unexplored. Some of us recently reported a straightforward methodology for the synthesis of open-cage fullerene derivatives (Scheme 1) [41,42]. The promising electrochemical properties and remarkable stability of these compounds, together with the fact that fullerene derivatives are so far the materials of choice as the ETL for p-i-n PSCs, prompted us to study the use of these compounds for PSCs.

Herein, we report for the first time the incorporation of open-cage fullerenes in p-i-n PSCs. The cells have been thoroughly characterized, and their photovoltaic performance has been studied. We demonstrate that open-cage fullerenes exhibit improved performances with respect to PC$_{61}$BM-based devices.

2. Results

The open-cage derivatives used in this study, 2a–c, were prepared by the photochemical oxidation of bis(fulleroids) 1a–c, which can be obtained from [60]fullerene in one step using our Rh(I)-catalyzed cycloaddition protocol (Scheme 1) [41]. Importantly, unlike precursors 1a–c, open-cage derivatives 2a–c do not suffer further degradation upon exposure to light and air. In addition to the parent open-cage derivative 2a, we selected compounds possessing desirable features for PSC manufacturing, such as the improved solubility of 2b or the light-harvesting ability of 2c. With 2a–c in hand, we first assessed their optical and electrochemical properties. In solution, 2a–c display remarkable absorption maxima in the visible region ($\lambda_{\text{max}} = 705–710$ nm, Figure S12). The electrochemical properties of 2a–c (Figure S13) and
PC61BM (3) were determined by cyclic voltammetry (CV) in ortho-dichlorobenzene (o-DCB) (see the Supporting Information).

Compounds 2a–c exhibit three fully reversible cathodic electrochemical behaviors between −0.8 and −2.3 V at a scan rate of 100 mV s⁻¹. The highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) values were estimated from the ultraviolet (UV) and CV measurements [43].

The optical properties of compounds 2a–c are summarized in Table 1. Overall, the photophysical and electrochemical properties of the open-cage fullerenes 2a–c are very similar to those of PC61BM, even though the C₆₀ cage skeleton is significantly altered with respect to the latter. These results encouraged us to incorporate 2a–c as the electron-transporting materials (ETMs) in PSCs.

| Comp     | λ_max (nm) | E_g (ev) | E_red (V) | LUMO (ev) | HOMO (ev) |
|----------|------------|----------|-----------|-----------|-----------|
| 2a       | 709        | 1.75     | 0.94      | −3.86     | −5.61     |
| 2b       | 705        | 1.76     | 0.99      | −3.81     | −5.57     |
| 2c       | 705        | 1.76     | 0.85      | −3.95     | −5.71     |
| PC61BM   | 718        | 1.73     | 0.87      | −3.93     | −5.66     |

**Figure 2a** shows the energy level diagram estimated from the onset potential of the first reductions and the maximum onset absorption from UV-vis spectra for all the compounds [44]. The electrical conductivities for PC61BM and compounds 2a–c films were compared by recording current–voltage (J–V) curves for electron-only devices with a structure of ITO/Al/ETM/Al. All the ETls showed similar electron conductivities (4.8, 3.5, 2.8 and 3.7 × 10⁻⁴ cm² s⁻¹ for 2a, 2b, 2c, and PC61BM, respectively).

To probe the passivation ability of compounds 2a–c, we studied the photoluminescence (PL) and time-resolved (TR) PL of the photoactive layer (perovskite) with and without 2a–c, using PC61BM as the control (Figure 2b and Figure S14). A significant PL quenching effect was observed for the perovskite layer coated with the open-cage fullerenes 2a, 2b, and PC61BM (Figure 2b). Meanwhile, the PL intensity of the perovskite increases when using 2c, which is an effect that can be attributed to the lower solubility of 2c in chlorobenzene (CB) (Figure S15). Compound 2a exhibits a higher passivation ability than the other fullerenes, resulting in a more pronounced inhibition of the electron–hole recombination processes [45].
Figure S14 shows the TR-PL decay measurements, monitoring the emission peak of PC$_{61}$BM and 2a–c coated perovskite layers as a function of time. The pristine perovskite layer exhibits a PL lifetime of about 25.6 ns, whereas perovskite/2a, perovskite/2b, perovskite/2c, and perovskite/PC$_{61}$BM exhibit PL lifetimes of 3.8 ns, 4.7 ns, 9.2 ns, and 14.1 ns, respectively. Faster decays are measured for the samples coated with 2a and 2b, indicating that the charge transfer processes are faster than the charge recombination in the perovskite layer [46].

![Diagram](image)

Figure 2. (a) Schematic illustration of the estimated HOMO and LUMO energy levels, estimated from cyclic voltammetry (CV) and UV-vis. (b) Steady-state photoluminescence (PL) spectra of the perovskite and perovskite/ETM films.

Compounds 2a–c were incorporated in PSCs with an ITO/PEDOT:PSS/perovskite/fullerene/Ag structure (Figure 1, see Supporting Information for details). The 2a (1.01 V) and 2b (0.97 V)-based devices showed a significant enhancement of $V_{oc}$ values compared to the PC$_{61}$BM (0.92 V)-based devices.

On the other hand, the lower solubility of 2c led to low-quality films, resulting in lower photovoltaic performances for the 2c-based devices (Figure 3). Table 2 summarizes the performances of the PSC devices incorporating PC$_{61}$BM and compounds 2a–c. The work functions of the charge transport materials affect the $V_{oc}$ of PSCs significantly, so the higher $V_{oc}$ values obtained from 2a and 2b-based devices can be attributed to their higher LUMO values, when compared with PC$_{61}$BM [25,26,46,47]. Commonly, the $V_{oc}$ values are improved by inserting a work-function interlayer between the perovskite and the ETL [26].

PSCs based on all the fullerene derivatives showed negligible hysteretic behavior (Figure S16). Device performance reproducibilities were calculated from the PCE distributions measured for 25 independent cells (Figure 3b). Figure S17 shows the external quantum efficiency (EQE) of the PSCs based on PC$_{61}$BM and 2a–c; the devices based on 2a show higher photoresponse around 600 nm and 750 nm. The integrated photocurrent densities based on EQE measurements (Figure S17) are consistent with those from $J$–$V$ measurements (Table 2). PC$_{61}$BM devices exhibited a PCE value of 16.22% with a $V_{oc}$ value of 0.92 V, a short circuit current ($J_{sc}$) value of 21.77 mA·cm$^{-2}$, and a fill factor (FF) value of
0.80. In contrast, 2a devices exhibited a PCE value of 16.92% with a $V_{oc}$ value of 1.01 V, a $J_{sc}$ value of 21.21 mA cm$^{-2}$, and a FF value of 0.79. The improved device performance was attributed to the better passivation ability of compounds 2a and 2b, because of their higher work function, which matches well with the conduction band of the perovskite [25,26,46,47].

The stabilities of PSCs fabricated with PC$_{61}$BM, 2a, and 2b were monitored under ca. 25% humidity in air at room temperature without encapsulation for 10 days. The normalized PCEs against time are shown in Figure S18. PC$_{61}$BM-based devices lost 67% of their initial PCE; this was similar to the PC$_{61}$BM-based devices 2a and 2b-based devices, which lost 65% and 63% of their initial PCE, respectively. Meanwhile, the devices based on 2c lost 71% of their initial PCE. Thus, the open-cage compounds are comparable to PC$_{61}$BM in terms of cell stability.

![Figure 3.](image)

**Figure 3.** (a) Current–voltage ($I$–$V$) curves under 1 sun of illumination (100 mW/cm$^2$) in forward voltage scans. (b) The power conversion efficiency (PCE) histograms measured for 25 independent cells.

Table 2. Summary of device performance. The calculated short circuit current ($J_{sc}$) values were obtained from the external quantum efficiency (EQE) curves. Values in parentheses represent the best values measured, * are the average values, and # are the calculated values. PC$_{61}$BM: phenyl-C$_{61}$-butyric-acid methyl-ester.

| Compound | $J_{sc}$* (mA cm$^{-2}$) | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|----------|--------------------------|--------------------------|-------------|--------|---------|
| 2a       | 21.05                    | 21.17 ± 0.24 (21.21)     | 0.99 ± 0.01 (1.01) | 0.79   | 16.30 ± 0.62 (16.92) |
| 2b       | 21.11                    | 20.98 ± 0.20 (21.37)     | 0.96 ± 0.01 (0.97)  | 0.79   | 15.77 ± 0.60 (16.37) |
| 2c       | 14.87                    | 15.01 ± 0.30 (15.20)     | 0.53 ± 0.01 (0.60)  | 0.41   | 3.07 ± 0.67 (3.74)   |
| PC$_{61}$BM | 21.22                    | 21.56 ± 0.23 (21.77)     | 0.88 ± 0.01 (0.92)  | 0.80   | 15.66 ± 0.56 (16.22) |

3. Conclusions

In conclusion, we have successfully prepared a series of p-i-n type PSCs incorporating dicarboxylic open-cage [60]fullerene derivatives 2a–c as the ETL. For those compounds with appropriate solubility,
the resulting PSCs offer performances rivaling or even superior to those of analogous cells employing the PC$_{61}$BM reference. These results are commensurate with a good overlap between the HOMO/LUMO levels of fulleroids 2a–b and the conduction band of the perovskite. The modularity of our synthetic approach to open-cage fullerene derivatives 2a–c offers a promising opportunity to develop superior PSCs beyond this preliminary account.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/1996-1944/12/8/1314/s1](http://www.mdpi.com/1996-1944/12/8/1314/s1), Figure S-1. 1H NMR (400 MHz, CDCl$_3$) of compound 3a. Figure S-2. 1H NMR (400 MHz, CDCl$_3$) of compound 3b. Figure S-3. 1H NMR (400 MHz, CDCl$_3$) of compound 3c. Figure S-4. 1H NMR (400 MHz, CDCl$_3$) of compound 1a. Figure S-5. 1H NMR (400 MHz, CDCl$_3$) of compound 1b. Figure S-6. 1H NMR (400 MHz, o-DCB$_{24}$/Cs$_2$) of compound S-5. Figure S-7. 1H NMR (400 MHz, CDCl$_3$) of compound 1c. Figure S-8. 1H NMR (400 MHz, CDCl$_3$) of compound 2a. Figure S-9. 1H NMR (400 MHz, CDCl$_3$) of compound 2b. Figure S-10. 13C NMR (100 MHz, CDCl$_3$) of compound 2b. Figure S-11. 1H NMR (400 MHz, CDCl$_3$) of compound 2c. Figure S-12. UV-vis spectra of compounds 2a–c and PC$_{61}$BM. Figure S-13. Cyclic voltammetry of compounds 2a–c. Figure S-14. Time-resolved photoluminescence of perovskite, perovskite/compounds 2a–c and perovskite/PC$_{61}$BM films. Figure S-15. Fullerene derivatives 2a–c and PC$_{61}$BM in o-dichlorobenzene (20 mg/mL). Figure S-16. J–V curves of the inverted PSCs based on PC$_{61}$BM (a) and 2a,b (b and c, respectively) with respect to forward and reverse scan directions (the scanning rate was 100 mV/s). Figure S-17. EQE measurements for 2a–c and PC$_{61}$BM-based devices. Figure S-18. Stability studies of 2a–c and PC$_{61}$BM-based devices. Figure S-19. Top-view SEM image of the perovskite film.

**Author Contributions:** E.C., A.A, F.L. and F.P.: synthesis, characterization, and cells fabrication: E.C., A.A., F.L., F.P.

**Funding:** The authors thank the US National Science Foundation (NSF) for its generous support of this work under the NSF-PREM program (DMR 1205302, and CHE-1801317 to L.E.). The Robert A. Welch Foundation is also gratefully acknowledged for an endowed chair to L. E. (Grant AH-0033). Financial support by the Spanish Ministry of Economy and Competitivity (MINECO), European Social Fund (ESF) (Projects CTQ2017-83587-P, FPI predoctoral grant to A. A., RyC contract RYC2012-11112 to A. L.), and the Generalitat de Catalunya (Project 2017-SGR-39) is gratefully acknowledged. The EU has also funded this research under FEDER grant UNGI10-4E-801. X.-Y.Z thanks the Office of Naval Research for support under award no. N00014-16-1-2921. This research was supported in part by the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Award under the EERE Solar Energy Technologies Office administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by Oak Ridge Associated Universities (ORAU) under DOE contract number DE-SC0014664. All of the opinions expressed in this paper are the authors’ and do not necessarily reflect the policies and views of DOE, ORAU, or ORISE.

**Conflicts of Interest:** There are no conflicts to declare.

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