

# Deuterium Isotope Effect on Bulk Heterojunction Solar Cells. Enhancement of Organic Photovoltaic Performances Using Monobenzyl Substituted Deuteriofullerene Acceptors

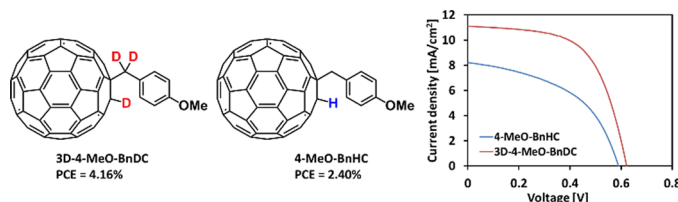
Shirong Lu,<sup>†</sup> Tienan Jin,<sup>\*,†</sup> Takeshi Yasuda,<sup>‡</sup> Weili Si,<sup>†</sup> Kazuaki Oniwa,<sup>†</sup> Khalid A. Alamry,<sup>§</sup> Samia A. Kosa,<sup>§</sup> Abdullah Mohamed Asiri,<sup>§</sup> Liyuan Han,<sup>‡</sup> and Yoshinori Yamamoto<sup>\*,†,§</sup>

WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan, Photovoltaic Materials Unit, National Institute for Materials Science, Tsukuba 305-0047, Japan, and Chemistry Department, Faculty of Science, and Center of Excellence for Advanced Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah, Saudi Arabia

yoshi@m.tohoku.ac.jp; tjin@m.tohoku.ac.jp

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## ABSTRACT



A series of novel monobenzyl-substituted deuteriofullerenes (BnDCs) were synthesized efficiently through Co-catalyzed selective monofunctionalization of C<sub>60</sub>. Bulk heterojunction solar cells, based on poly(3-hexylthiophene) as the donor and BnDCs as the acceptors, exhibited higher photovoltaic performances as compared to the corresponding protonated BnHCs devices.

Functional fullerenes are used as a unique electronic acceptor for bulk heterojunction (BHJ) polymer solar cells (PSCs), because they not only maintain the properties of C<sub>60</sub> such as high electron affinity and electron mobility but also exhibit tunable solubility in organic solvents and a tunable energy level, as well as the superior packing arrangement in the solid state by introducing various functional groups on C<sub>60</sub> core.<sup>1,2</sup> Many efforts on development

of new functional fullerenes have been devoted to improve the photon-to-current conversion efficiencies. The commercially available [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) and its C<sub>70</sub> analogue PC<sub>71</sub>BM exhibit high solubility and high electron transport ability, which are used as the most well-studied benchmark acceptors for testing new donor materials.<sup>3</sup> Recently, bisfunctionalized 56 $\pi$ -electron fullerene acceptors with an up-shifted lowest unoccupied molecular orbital (LUMO), which is favorable for increasing the open circuit voltages ( $V_{oc}$ ) of PSCs, have been developed to show higher power conversion efficiencies (PCEs) than that of PCBM for the PSCs based on poly(3-hexylthiophene) (P3HT) donor.<sup>4</sup> So far, the PSCs

<sup>†</sup> Tohoku University.

<sup>‡</sup> National Institute for Materials Science.

<sup>§</sup> King Abdulaziz University.

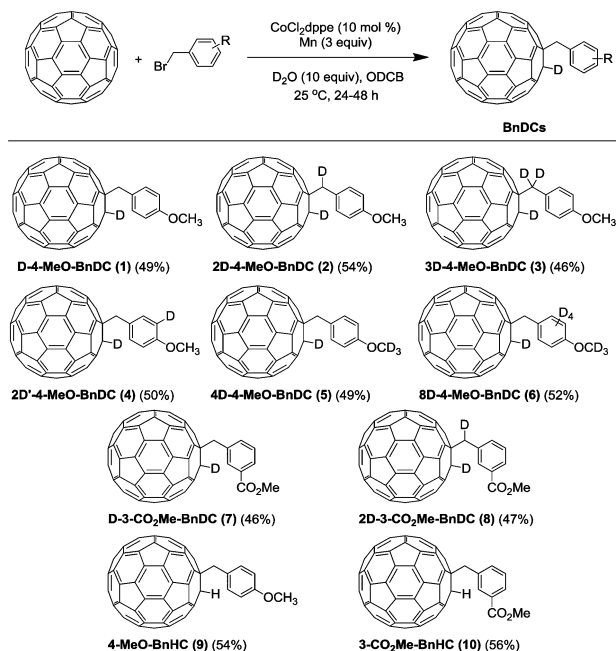
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based on blending the newly developed low band gap donors and PCBM acceptor increased the PCEs up to 7–8%.<sup>5</sup> The development of new fullerene acceptors toward increasing the PCEs through the combination with the innovative polymer donors is still highly desirable.

**Scheme 1.** Co-Catalyzed Monobenzoylation of C<sub>60</sub> for Synthesis of BnDCs and Structure of Various BnDCs and Their Corresponding Protonated BnHCs<sup>a</sup>



<sup>a</sup> 4-MeO-BnHC (9) and 3-CO<sub>2</sub>Me-BnHC (10) were prepared by using H<sub>2</sub>O (10 equiv) instead of D<sub>2</sub>O.

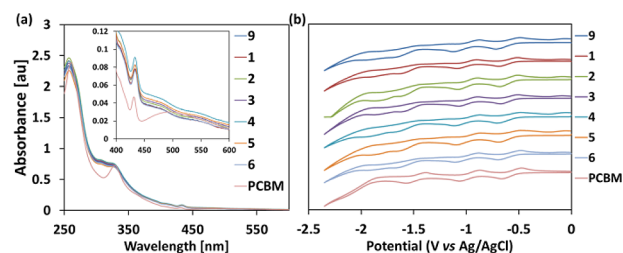
Recently, we reported an efficient Co-catalyzed selective monofunctionalization of C<sub>60</sub> with benzyl bromides, producing various 2-benzyl-1,2-dihydro[60]fullerenes (BnHCs)

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in high yields.<sup>6</sup> We also reported that PSCs based on those BnHCs as acceptors including 4-MeO-BnHC (9) and 3-CO<sub>2</sub>Me-BnHC (10) exhibited high PCEs by blending with P3HT as the donor (Scheme 1).<sup>7</sup> Surprisingly, during our investigation of photovoltaic performances of BnHCs, we found that PSCs based on the deuterated fullerenes (BnDCs) bearing deuterium atoms on the fullerene core and the benzyl moiety displayed a noticeable PCE improvement compared to the corresponding protonated BnHCs-devices. It was noted that the deuterium isotope effect has been used in organic light-emitting diodes (OLED) to increase the excited state lifetime of organic molecules, resulting in the increased external quantum efficiency as compared to the corresponding protonated devices, due to the vibronic coupling induced reduction of the nonradiative decay rate.<sup>8</sup> However, to the best of our knowledge, the deuterium isotope effect on photovoltaic performance has never been investigated. Herein, we report the facile synthesis of various novel BnDCs, characterization of photophysical and electrochemical properties, and their distinguished PSC performances by blending with P3HT as the donor (Scheme 1). The deuterated BnDCs exhibited higher PCEs compared to their corresponding protonated BnHCs. Among them, the PSC based on the blend of 3D-4-MeO-BnDC (3)/P3HT showed the highest PCE of 4.16% which is higher than the PC<sub>61</sub>BM-based PSC.

BnDCs 1–8 were prepared in one step following our previously reported Co-catalyzed selective monobenzoylation method in 46–56% yields (Scheme 1).<sup>6</sup> The reaction of pristine C<sub>60</sub> with various substituted benzyl bromides (1.5 equiv) was carried out in the presence of CoCl<sub>2</sub>dppe (10 mol %), a Mn reductant (3 equiv), and D<sub>2</sub>O (10 equiv) in 1,2-dichlorobenzene (ODCB) under an argon atmosphere at rt. The corresponding protonated BnHCs 9 and 10 were prepared under the standard conditions by using H<sub>2</sub>O instead of D<sub>2</sub>O.<sup>6</sup> All the products were simply purified by silica gel chromatography using toluene and hexane as the eluents. It was noted that BnDCs showed solubility comparable with BnHCs and PC<sub>61</sub>BM in chloroform, toluene, and ODCB.



**Figure 1.** (a) UV–vis absorption in chloroform. (b) Cyclic voltammograms in ODCB solution with Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte (vs Ag/AgCl).

The UV–vis absorption of BnDCs and BnHCs as well as the reference PC<sub>61</sub>BM were measured in chloroform (Figure 1a and Figure S1 in the Supporting Information (SI)).

**Table 1.** Electrochemical Reduction Potentials and LUMO Energy Levels of BnDCs, BnHCs and PC<sub>61</sub>BM<sup>a,b</sup>

compd	$E_{1/2}^1/V$	$E_{1/2}^2/V$	$E_{1/2}^3/V$	LUMO/eV
<b>1</b>	−0.60	−0.99	−1.56	−3.56
<b>2</b>	−0.59	−0.99	−1.54	−3.57
<b>3</b>	−0.58	−0.98	−1.53	−3.58
<b>4</b>	−0.59	−0.98	−1.52	−3.57
<b>5</b>	−0.59	−0.98	−1.55	−3.57
<b>6</b>	−0.59	−0.99	−1.55	−3.57
<b>7</b>	−0.60	−0.99	−1.45	−3.56
<b>8</b>	−0.60	−0.99	−1.54	−3.56
<b>9</b>	−0.60	−0.99	−1.56	−3.56
<b>10</b>	−0.61	−0.99	−1.46	−3.55
PC <sub>61</sub> BM	−0.58	−0.98	−1.48	−3.58

<sup>a</sup> Potential values are versus Ag/AgCl reference electrode; reduction potential of ferrocene (0.64 V) is versus Ag/AgCl. <sup>b</sup> The LUMO energy levels were estimated using the following equation: LUMO =  $-(4.80 + E_{1/2}^1 - 0.64)$  eV.

BnDCs and their corresponding BnHCs show similar absorption spectra despite the different functional groups on the phenyl ring, and the different position and number of deuterium atoms, while they exhibit slightly enhanced absorption compared to that of PC<sub>61</sub>BM in the regions 280–330 nm and 400–500 nm. The reduction potentials were measured by cyclic voltammetry (CV) in ODCB, and the LUMO energy levels were estimated by the first reduction potentials ( $E_{1/2}^1$ ) (Figure 1b, Table 1, and Figure S1, SI). Both BnDCs and BnHCs having an electron-donating (**1–6** and **9**) and an electron-withdrawing group (**7**, **8**, and **10**) showed similar potentials to PC<sub>61</sub>BM. The LUMO energy levels are estimated to be in the range −3.56 eV to −3.58 eV, comparable with PC<sub>61</sub>BM (−3.58 eV), which are expected to be applicable to acceptors in PSCs. We concluded that the introduction of deuterium atoms does not affect the absorption and energy levels of BnDCs compared to the protonated BnHCs.

PSCs based on blending new BnDCs acceptors and the P3HT donor were fabricated with a thickness of about 200 nm. The photovoltaic characterizations for ITO/PEDOT: PSS (40 nm)/P3HT:D-BnDCs (w/w = 1/1)/LiF (1 nm)/Al (80 nm) under illumination with 100 mW cm<sup>2</sup> of AM 1.5 are shown in Table 2. Previously, we reported that the PSC device based on the protonated 4-MeO-BnHC (**9**) blended with P3HT exhibited a moderate PCE of 2.40% ( $J_{sc}$  = 8.24 mA cm<sup>−2</sup>,  $V_{oc}$  = 0.60 V, and FF = 48%).<sup>7</sup> It was interesting that when the D-4-MeO-BnDC (**1**) having a deuterium atom on the C<sub>60</sub> cage was employed as the acceptor under the same device conditions, a much higher PCE of 3.63% ( $J_{sc}$  = 10.08 mA cm<sup>−2</sup>,  $V_{oc}$  = 0.62 V, and FF = 57%) was achieved. In order to further investigate the deuterium effect on PSC performances, a series of

BnDCs devices were fabricated. PSCs utilizing other BnDCs such as **2–6** with deuterium atoms at the benzylic position or on the phenyl ring or on the methoxy group also showed higher PCEs (3.28% to 4.16%) than that of the protonated 4-MeO-BnHC (**9**). Among them, 3D-MeO-BnDC (**3**) showed considerable improvement of the PCEs up to 4.16% with  $J_{sc}$  = 11.10 mA cm<sup>−2</sup>,  $V_{oc}$  = 0.62 V, and FF = 60%, which accounts for 73% improvement compared to the corresponding protonated 4-MeO-BnHC (**9**) device. It should be noted that the devices using 2D-MeO-BnDC (**2**), 3D-MeO-BnDC (**3**), and 8D-MeO-BnDC (**6**) as acceptors, respectively, displayed higher PCEs as compared to the PC<sub>61</sub>BM device.

A similar deuterium effect was also observed for the devices using a series of 3-CO<sub>2</sub>Me-BnDCs. The PCEs of D-3-CO<sub>2</sub>Me-BnDC (**7**) and 2D-CO<sub>2</sub>Me-BnDC (**8**) with an ester group on the phenyl ring are 3.75% and 3.63%, respectively, which are higher than that of the corresponding protonated 3-CO<sub>2</sub>Me-BnHC (**10**) (2.74%) (Table 2 and Figure S2, SI). However, it should be noted that this deuterium effect on photovoltaic performance might not always hold for various fullerene acceptors. For example, we found that the devices using PC<sub>61</sub>BM and 5D-PC<sub>61</sub>BM showed almost similar PCEs of 3.78% and 3.66%, respectively (Table 2 and Figure S3, SI). It was noted that every acceptor combined with the P3HT donor was evaluated at least 3 times using the same fabrication method and the PSCs based on BnDCs showed a much higher average PCE than that of the protonated BnHCs, indicating high reliability of device performances (Table S1, SI).

**Table 2.** PSC Performances Based on BnDCs and BnHCs Acceptors with P3HT Donor (w/w = 1/1)<sup>a</sup>

acceptor	$J_{sc}$ [mA cm <sup>−2</sup> ]	$V_{oc}$ [V]	FF [%]	PCE [%]
<b>1</b>	10.08	0.62	57.4	3.63
<b>2</b>	10.75	0.61	59.5	3.93
<b>3</b>	11.10	0.62	60.3	4.16
<b>4</b>	9.16	0.60	59.5	3.28
<b>5</b>	10.04	0.60	58.3	3.48
<b>6</b>	11.44	0.61	57.6	4.03
<b>7</b>	10.72	0.60	58.2	3.75
<b>8</b>	10.13	0.62	58.2	3.63
<b>9</b>	8.24	0.60	48.4	2.40
<b>10</b>	9.66	0.61	46.6	2.74
PC <sub>61</sub> BM	9.86	0.60	64.0	3.78
5D-PC <sub>61</sub> BM	10.29	0.58	61.5	3.66

<sup>a</sup> Blend film was prepared using P3HT (20 mg) and BnDCs (20 mg) in 1,2-dichlorobenzene (1 mL); annealing temperature is 110 °C (10 min).  $V_{oc}$ : open-circuit voltage;  $J_{sc}$ : short-circuit current density; FF: fill factor.

It can be seen in Table 2 and Figure 2a that similar  $V_{oc}$  values were observed between BnDCs and the protonated BnHCs. These results are in agreement with their LUMO energy levels as shown in Table 1, since it is well-known that the  $V_{oc}$  of PSCs is proportional to the energy gap between the LUMO of the acceptor and the HOMO of the donor.<sup>9</sup> The photovoltaic performances indicated that the

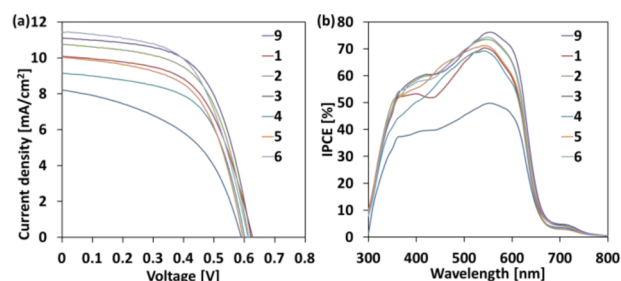
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enhanced PCEs of BnDC devices are attributed to the increased  $J_{sc}$  and FF as compared to the protonated BnHCs devices. The much higher incident photon-to-current conversion efficiency (IPCE) values of the BnDC devices than that of the protonated BnHC devices in the region 350–650 nm correspond to the higher  $J_{sc}$  values of BnDC devices (Figure 2b and Figure S2, SI).

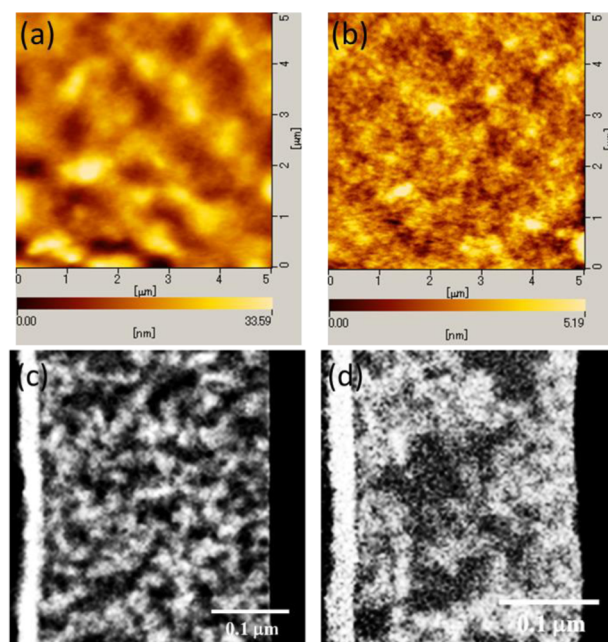


**Figure 2.** (a) Current density–voltage ( $I$ – $V$ ) curves and (b) incident photon-to-current conversion efficiency (IPCE).

The homogeneous active layers and obvious nanoscale phase separation of the BnDCs/P3HT thin films were observed by atomic force microscopy (AFM) (Figure 3a and 3b, and Figure S4, SI). For example, the root mean squares (rms) were 0.78 nm for 3D-4-MeO-BnDC (3) and 5.25 nm for the protonated 4-MeO-BnHC (9), indicating that the introduction of deuterium atoms influences the roughness of the blend films. The transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) mappings of the cross section of BnDC (3) and BnHC (9) devices, obtained by the ion beam, showed that the morphology of the BnDC device has a more clear binary network structure than that of the BnHC device, indicating a better connection of the donor and acceptor across the film (Figure 3c and 3d). Taking into consideration the similar energy levels and absorption between the deuterated BnDCs and the protonated BnHCs, the increase in PCEs and  $J_{sc}$  for the BnDCs devices might be ascribed to the optimal interfacial contact between the polymer donor and fullerene acceptor.

In conclusion, we have synthesized a new series of deuterated monobenzyl-substituted deuteriofullerenes which were successfully applied in bulk heterojunction polymer solar cells. Partial replacement of a proton for a deuterium atom in monobenzyl-substituted hydrofullerenes

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**Figure 3.** AFM images of P3HT donor with 4-MeO-BnHC (9) (a) and 3D-4-MeO-BnDC (3) (b); TEM-EELS mappings of cross section of 4-MeO-BnHC (9) (c) and 3D-4-MeO-BnDC (3) (d) devices. The bright and dark regions represent the P3HT-rich domains and fullerene-acceptor-rich domains, respectively.

obviously improved the photovoltaic performances due to the increased  $J_{sc}$  and FF compared to the protonated BnHCs by using P3HT as the donor. The highest PCE was up to 4.16% for the device based on 3D-4-MeO-BnDC (3) as the acceptor, which is higher than the PC<sub>61</sub>BM device. Although further investigation is needed to clarify the reason for the deuterium effect, it is clear that deuterium labeling provides a new approach to improve the power conversion efficiency of PSCs. Further investigation is in progress.

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**Supporting Information Available.** Experimental procedures, device fabrication, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.