JOC The Journal of Organic Chemistry

Article

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Development of n-Type Semiconductor Based on Cyclopentene- or Cyclohexene-Fused [C_{60}]-Fullerene Derivatives

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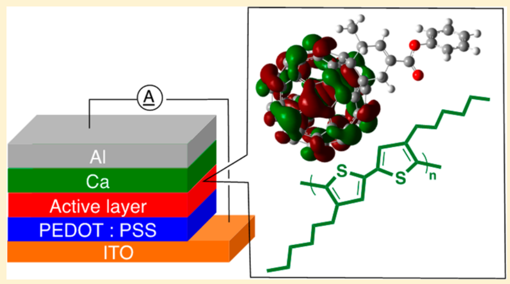
S Supporting Information

ABSTRACT: Properties of cyclopentene- or cyclohexene-fused [C_{60}]-fullerene derivatives as the acceptor in photovoltaic cells have been investigated by use of poly(3-hexylthiophene) (P3HT) as the model donor polymer. Several cyclopentene- or cyclohexene-fused [C_{60}]-fullerene derivatives show high power conversion efficiency (PCE). The highest PCE was obtained for 3′,6′-dihydro-4′-phenoxycarbonyl-6′-methylbenzo[1,9]-[5,6](C_{60}-I_h)fullerene (3.2%); this is superior to that of [C_{60}]-PCBM with the P3HT polymer under the same experimental conditions. PCE of the OPV devices with alkyl-substituted cyclohexene-fused [C_{60}]-fullerenes depended on the alkyl substituent on the cyclohexene ring; compounds with substituents of odd-number alkyl groups showed better PCE than those compounds possessing even-number alkyl groups.



■ INTRODUCTION

Organic photovoltaics (OPV) have been attracting much attention as a next-generation photovoltaic system because of their light weight and shape flexibility, as well as the potential to be produced at low cost.[1] Use of photovoltaic technology is now well-recognized as one of the most important ways to prevent the exhaustion of fossil fuels. Fullerene and its derivatives are widely used as n-type materials in the active layer of OPVs due to their high electron mobility and adequate lowest unoccupied molecular orbital (LUMO) level.[2,3] Recently, a hybrid solar cell based on the mesosuperstructured organometallic halide perovskite has been developed, which had a strong impact on the field of OPV:[4,5] these compounds are now referred to as "a game changer" in photovoltaics.[5a] However, fullerene-based solar cells might be important candidates for green solar cells. Development of stable fullerene derivatives with high power conversion efficiency (PCE) is, therefore, still strongly desired.[6] Methyl [6,6]-phenyl-C_{61}-butyrate ([C_{60}]-PCBM)[7] is known to be the standard blending material among acceptors with poly-3-hexylthiophene (P3HT), which is a donor partner in polymer solar cells.[8] Troshin and co-workers[9] developed various types of methanofullerene derivatives as acceptors for P3HT. Matsuo and co-workers[10] reported OPV devices with silylmethylfullerene (SIMEF) that showed PCE superior to devices with [C_{60}]-PCBM. Recently, Matsuo et al.[11] also reported excellent simple fullerene derivatives such as dihydromethane/indene adducts of [C_{60}] and [C_{70}]-fullerene as acceptor with P3HT.

We found that fulleropyrrolidine derivatives ([C_{60}]-FP)[12,13] worked as a good acceptor with P3HT and the resulting solar cell showed higher PCE compared to that of [C_{60}]-PCBM (Figure 1). However, a weak point was also found that [C_{60}]-FP required a special indium tin oxide (ITO) electrode that lacked the poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT−PSS)[14] layer to display high PCE, because the sulfonic acid group of PSS reacted with the nitrogen atom on the pyrrolidine ring and formed a quarternary ammonium salt that prevented smooth hole transfer.[13] It is known that PEDOT−PSS works as a hole transport layer (HTL), which prevents the leakage of current from the active layer to the ITO electrode, thereby contributing to enhancement of OPV performance, especially fill factor (FF) and open-circuit voltage (V_{oc}).[14] We solved this problem by introducing two aryl groups on the pyrrolidine ring: the resulting *cis*-1,3-diaryl-substituted fulleropyrrolidines, [C_{60}]-Ar_2FP, allowed use of the PEDOT−PSS-coated ITO electrode, due to the protecting effect of the two aryl groups on the nitrogen atom in the pyrrolidine moiety.[15]

Recently, Yang et al.[16] reported the syntheses of cyclopentene- and cyclohexene-fused [C_{60}]-fullerene derivatives through [3 + 2] and [4 + 2] cycloaddition reactions of Morita−Baylis−Hillman adducts with [C_{60}]-fullerene. We are intrigued by these compounds and decided to investigate their potential as resources for OPV materials, because these fullerene derivatives might be free from the influence of PEDOT−PSS. Herein we report the properties of OPV devices with cyclopentene- and cyclohexene-fused [C_{60}]-fullerenes, **1** and **2**, as n-type materials with P3HT (Figure 1). As expected, we have established that some cyclopentene- and cyclohexene-

Received: March 9, 2015
Published: April 9, 2015

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

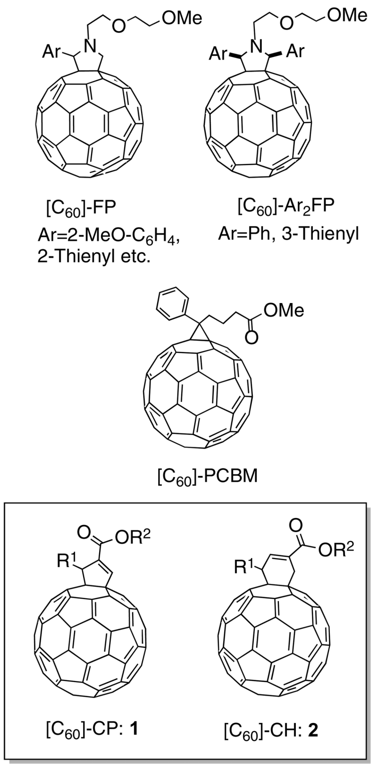


Figure 1. $[C_{60}]$-fullerene derivatives as source of OPVs.

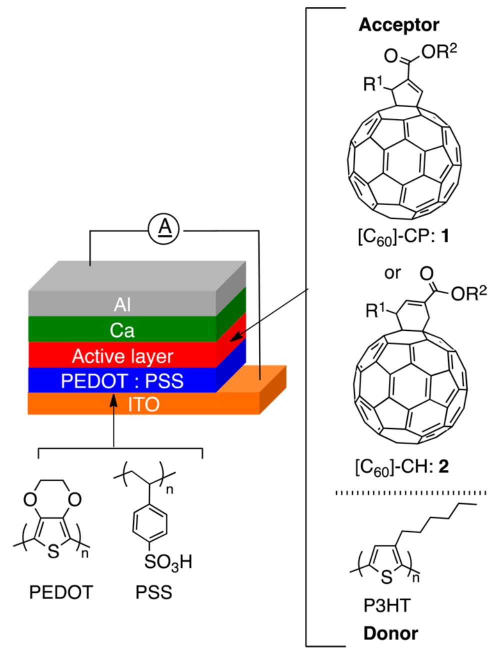


Figure 2. Typical solar cell designed to evaluate cyclopentene- or cyclohexene-fused $[C_{60}]$-fullerene derivatives.

fused $[C_{60}]$-fullerene derivatives showed superior or similar ability to that of $[C_{60}]$-PCBM.

■ RESULTS AND DISCUSSION

Design of Cyclopentene-Fused $[C_{60}]$-Fullerene. Synthesis of cyclopentene-fused $[C_{60}]$-fullerene ($[C_{60}]$-CP) and cyclohexene-fused $[C_{60}]$-fullerene derivatives ($[C_{60}]$-CH) has been accomplished according to the method reported by Yang and co-workers.[16] Using these fullerene derivatives, we prepared model solar cells (Figure 2) and evaluated their efficiency. Cyclopentene- or cyclohexene-fused $[C_{60}]$-fullerene derivatives were mixed with P3HT (1/1 w/w) in chlorobenzene, and the resulting solution was spin-coated onto ITO with PEDOT−PSS[14] as a positive electrode to make an active layer of organic photovoltaic cells. Calcium and aluminum were used as negative electrode.

It is reported that the V_{oc} of an OPV device is determined by the difference between the LUMO level of the n-type conductor and the highest occupied molecular orbital (HOMO) level of the p-type semiconductor.[17] Since it was expected that LUMO level of the cyclopentene ring might be modified by introduction of a π-conjugated group,[13] we initially prepared 13 types of aryl-, alkyl, and thiophene-substituted cyclopentene-fused fullerene derivatives **1a**−**1m** (Figure 3), and the results of evaluation of corresponding OPV devices are summarized in Table 1.

Although the levels of PCE of all $[C_{60}]$-CP were inferior to that of $[C_{60}]$-PCBM (entry 14), the OPV prepared with **1a** showed a similar level to that of $[C_{60}]$-PCBM (entry 1). This device displayed the high short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF), and in particular, the J_{sc} of **1a** was higher than that of $[C_{60}]$-PCBM. However, due to lower V_{oc} and FF values, the resulting PCE was slightly inferior to that of $[C_{60}]$-PCBM. The methoxyphenyl-substituted **1b** showed inferior results (entry 2) to the simple phenyl-substituted **1a**, though introduction of the methoxy group on the phenyl substituent effectively enhanced PCE for fulleropyrrolidine derivatives.[12] Introduction of an electron-withdrawing bromine atom on the phenyl group also significantly reduced both J_{sc} and V_{oc} and afforded poor PCE (entry 3). We next investigated the influence of the ester group on the cyclopentene ring toward efficiency of the OPVs.

Introduction of methoxyethoxyethyl (MEM) moiety on the nitrogen atom of the fulleropyrrolidine ring significantly increased solubility in chlorobenzene, and this not only allowed easy preparation of the devices but also contributed to improved PCE.[12] Comparing the results of **1a** and **1g**, which have the same aromatic group on the CP ring, **1g** showed better solubility in chlorobenzene than **1a**; however, the PCE value of **1g** was inferior to that of **1a** due to poor FF (entry 7). Upon switching the ester carbonyl group to the hydroxylmethyl group, a significant drop in PCE, mainly due to a poor J_{sc} value (entry 8), was obtained for **1h**.

It is reported that the V_{oc} of an OPV device is determined by the difference between the n-type conductor and the HOMO level of the p-type semiconductor.[17] We previously reported that introduction of π-conjugated thiophene group on the fulleropyrrolidine effectively modified the LUMO level of the compound and contributed to the enhancement of PCE of the corresponding OPVs.[13] Therefore, we expected that higher PCE might be obtained for thiophene-substituted cyclopentene-fused $[C_{60}]$-fullerenes. Unfortunately, PCE values of thiophene-substituted compounds were inferior to those of $[C_{60}]$-PCBM and **1a** (entries 9−13). Among methyl, *t*-butyl, and MEM esters of thiophene derivatives (**1i**, **1j**, and **1k**), the best PCE was attained for MEM ester **1k** (entry 11). On the other hand, a better result in PCE was obtained for the simple methyl ester **1l** (entry 12) upon comparing the results obtained by bithiophene-substituted derivatives **1l** and **1m** (entries 12 and 13); this was assumed to be from the poor FF value of **1m**, while J_{sc} was superior to that of **1l**.

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

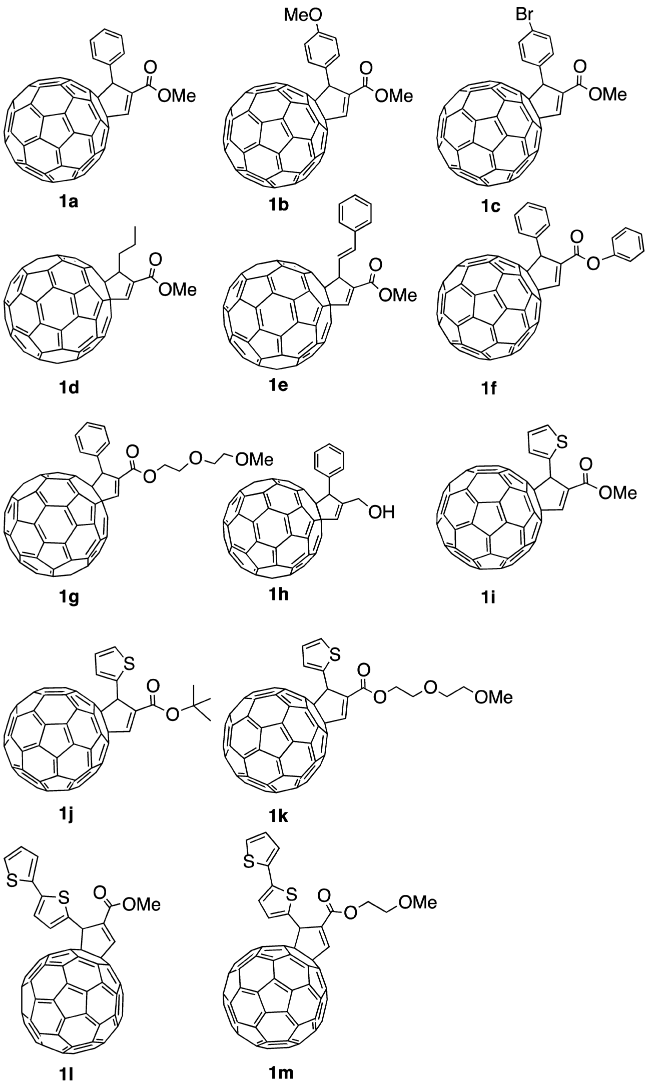


Figure 3. Molecular structures of cyclopentene-fused [C_{60}]-fullerene derivatives.

Table 1. Photovoltaic Performance of P3HT-Based Organic Photovoltaic Devices with Various Types of Cyclopentene-Fused [C_{60}]-Fullerene Derivatives 1[a]

entry	fullerene derivative	PCE (%)	J_{sc} (mA·cm^{-1})	V_{oc} (V)	FF
1	**1a**	2.57	6.76	0.605	0.628
2	**1b**	2.05	5.87	0.604	0.578
3	**1c**	1.60	5.50	0.532	0.548
4	**1d**	1.78	6.88	0.544	0.475
5	**1e**	1.84	6.36	0.541	0.535
6	**1f**	2.15	6.05	0.577	0.617
7	**1g**	1.57	6.38	0.592	0.416
8	**1h**	1.40	3.93	0.592	0.599
9	**1i**	1.97	6.41	0.552	0.556
10	**1j**	1.68	4.71	0.588	0.605
11	**1k**	2.13	6.78	0.544	0.577
12	**1l**	1.88	5.24	0.576	0.623
13	**1m**	1.76	6.16	0.566	0.505
14	[C_{60}]-PCBM	2.59	6.91	0.601	0.625

[a]Under the illumination of AM 1.5G, 100 mW/cm^2. J_{sc}, short-circuit current; V_{oc}, open-circuit voltage; FF, fill factor.

Design of Cyclohexene-Fused [C_{60}]-Fullerene. We next prepared 12 types of cyclohexene-fused [C_{60}]-fullerene derivatives **2a**−**2l** (Figure 4) and evaluated properties of the corresponding OPV devices (Table 2). To our delight, three devices with **2b**, **2g**, and **2l** gave better PCE than the control device derived from [C_{60}]-PCBM. In particular, the highest

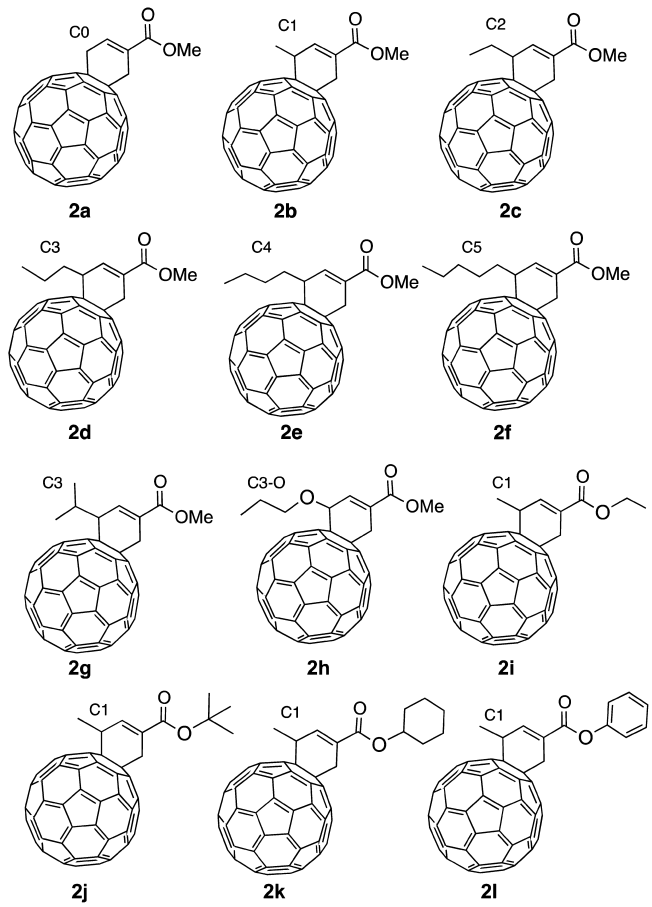


Figure 4. Molecular structures of cyclohexene-fused [C_{60}]-fullerene derivatives.

Table 2. Photovoltaic Performance of P3HT-Based Organic Photovoltaic Devices with Various Types of Cyclohexene-Fused [C_{60}]-Fullerene Derivatives 2[a]

entry	fullerene derivative	PCE (%)	J_{sc} (mA·cm^{-1})	V_{oc} (V)	FF
1	**2a**	0.61	2.00	0.522	0.588
2	**2b**	2.71	6.96	0.619	0.629
3	**2c**	1.14	3.51	0.528	0.616
4	**2d**	2.57	6.46	0.627	0.634
5	**2e**	0.51	2.43	0.544	0.387
6	**2f**	2.26	6.16	0.625	0.587
7	**2g**	2.83	7.71	0.625	0.586
8	**2h**	1.58	5.64	0.615	0.454
9	**2i**	1.47	4.31	0.608	0.561
10	**2j**	1.41	5.26	0.652	0.412
11	**2k**	1.89	5.24	0.672	0.536
12	**2l**	3.20	8.13	0.642	0.614
13	[C_{60}]-PCBM	2.59	6.91	0.601	0.625

[a]Under the illumination of AM 1.5G, 100 mW/cm^2. J_{sc}, short-circuit current; V_{oc}, open-circuit voltage; FF, fill factor.

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

PCE (3.20%) was attained for methyl-substituted phenyl ester **2l** (entry 12): J_{sc} of **2l** reached 8.13 mA·cm^{-1}, and this is the highest value among 26 types of devices tested in the present study. On the contrary, the worst PCE value was obtained for the simple cyclohexene-fused compound **2a** due to very poor J_{sc} (entry 1).

Furthermore, we discovered the very interesting facts that PCE depended on the alkyl substituent on the cyclohexene ring: compounds that have substituents with an odd number of alkyl groups (**2b**, **2d**, **2f**, and **2g**) showed better PCE (entries 2, 4, 6, and 7) than those of compounds with an even number of alkyl groups (**2c** and **2e**) (entries 3 and 5). As shown in Table 2, [C_{60}]-CH with an odd number of alkyl groups generally showed high J_{sc}, while compounds with an even number of alkyl groups showed lower values in J_{sc}.

We also found that all compounds showed good solubility in chlorobenzene; hence it was very easy to prepare OPV films. However, the preparation of fine films sometimes failed when **2c** or **2e** was used due to the formation of very small particles during the baking process. It is speculated that alkyl substituents on the cyclohexene ring significantly influenced the aggregation state of the fullerene derivatives. Since our OPVs are bulk heterojunction-type solar cells, the aggregation state influenced the interaction state with P3HT and this may have reflected on the results of the OPV properties.

Figure 5 shows current density versus V_{oc} for OPVs derived from P3HT with typical fullerene derivatives, **1a**, **1k**, **2b**, **2l**, and

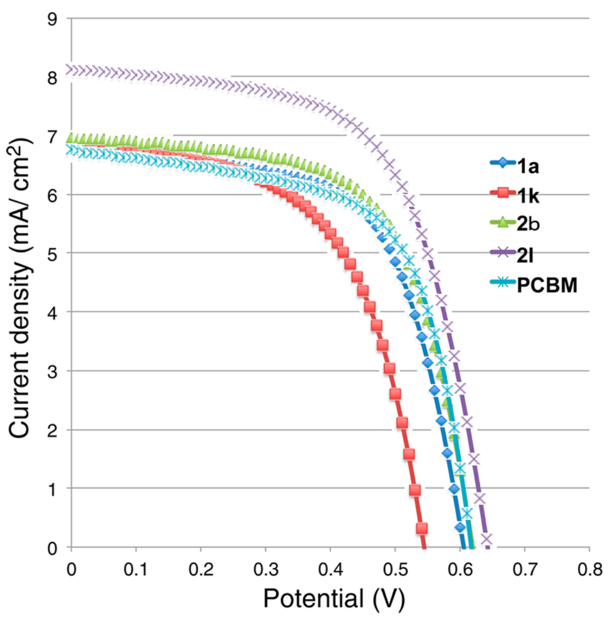


Figure 5. Current density−potential characteristics of P3HT/[C_{60}]-CP (**1a** and **1k**) and P3HT/[C_{60}]-CH (**2b** and **2l**) solar cell devices under illumination by an AM 1.5G solar simulated light (100 mW/cm^2).

control [C_{60}]-PCBM: the **2l** cell shows the highest PCE of 3.20% and J_{sc} of 8.13 mA/cm^2. As clearly shown in this $I-V$ profile, **2l** cell displays superior properties to those of [C_{60}]-PCBM.

Since high PCEs were obtained for cyclohexene-fused [C_{60}]-fullerene, we investigated more detailed properties of OPV devices with three derivatives, **2b**, **2k**, and **2l**, by cyclic voltammogram (CV) analysis, and the results are shown in Figure 6 and Table 3.

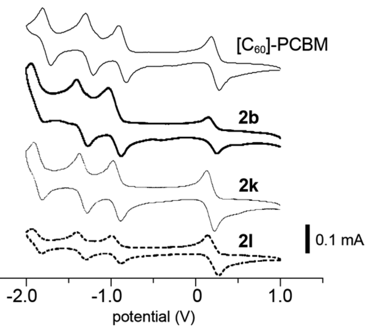


Figure 6. Cyclic voltammograms of [C_{60}]-PCBM, **2b**, **2k**, and **2l** devices in *o*-dichlorobenzene/CH_3CN (4:1 v/v) (0.1 mM) with 0.1 M *n*-Bu_4NPF_6 at a scan rate of 10 mV/s.

Table 3. Reduction Potentials and LUMO Levels for Fullerene Derivatives[a]

entry	fullerene derivative	E^0_1 (V)	E^0_2 (V)	E^0_3 (V)	LUMO (eV)
1	[C_{60}]-PCBM	−1.09	−1.49	−2.00	−3.71
2	**2b**	−1.15	−1.54	−2.06	−3.65
3	**2k**	−1.11	−1.50	−2.04	−3.69
4	**2l**	−1.14	−1.55	−2.08	−3.66

[a]Potential values in this table are versus Fc/Fc$^+$.

The LUMO energy levels of the fullerene derivatives were estimated from their first half-wave potentials (E^0_1) indicated in the cyclic voltammograms (Figure 6), and the results are summarized in Table 3. The E^0_1 values of [C_{60}]-PCBM, **2b**, **2k**, and **2l** devices were −1.09, −1.15, −1.11, and −1.14 V vs Fc/Fc$^+$, respectively. The LUMO energy levels of the fullerene derivatives from the onset reduction potentials were calculated by use of the following equation: LUMO (eV) = $-(E^0_1 + 4.80)$.[18] Therefore, the LUMO energy levels of [C_{60}]-PCBM, **2b**, **2k**, and **2l** calculated by this method are −3.71, −3.65, −3.69, and −3.66 eV, respectively. The LUMO level of **2l** is raised by 0.05 eV in comparison with that of [C_{60}]-PCBM. The higher LUMO level of **2l** is desirable for its application as an acceptor in the active layer to obtain V_{oc}. It has been reported that the LUMO level corresponded to V_{oc} value. However, the highest LUMO level was observed for **2b**, while the highest V_{oc} was recorded for **2k** (see Table 2, entries 2 and 11). Furthermore, the best PCE was attained for the OPV device with **2l** (see Table 2, entry 12).

Therefore, we further investigated LUMO levels of all cyclopentene- and cyclohexene-fused fullerenes using cyclic voltammograms and found that almost all compounds, except **1e** and **1f**, showed slightly higher LUMO levels than that of [C_{60}]-PCBM (see Experimental Section and Table S1 in Supporting Information). Although it has been reported that the LUMO level corresponded to V_{oc} value, only 48% of OPV cells (11 cells) gave higher V_{oc} than that of [C_{60}]-PCBM, while acceptor materials possess higher LUMO levels than [C_{60}]-PCBM (Table S1, Supporting Information). FF values of most cells are inferior to that of [C_{60}]-PCBM cell except for **1a**, **2b**, and **2d**.

All films showed a broad $\pi-\pi^*$ absorption from 300 to 700 nm, and the λ_{max} of these films is around 500 nm. Similar UV−vis spectra were obtained from films including P3HT with **1a**, **2b**, **2l**, and [C_{60}]-PCBM, though P3HT/**1k** has distinctive broad absorption between 350 and 400 nm and strong absorption around 550 nm, which were assumed to be caused

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

by the thiophene moiety on the cyclopentene molecule (see Figure S1, Supporting Information). UV−vis spectra of OPV film prepared by **2k** shows a lower level of absorption around 500 nm (see Figure S1, Supporting Information); this also suggests poor matching of the cyclohexyl ester with P3HT. These results clearly indicate that PCE levels of these OPVs are not determined only by LUMO level of the n-type materials with P3HT.

■ CONCLUSION

In summary, we have carried out the rational design of cyclopentene- and cyclohexene-fused [C_{60}]-fullerene derivatives as acceptors with poly-3-hexylthiophene (P3HT) and established that these fullerenes worked as good n-type materials. High power conversion efficiency was attained for cyclohexene-fused [C_{60}]-fullerene derivatives, in particular, 3′,6′-dihydro-4′-phenoxycarbonyl-6′-methylbenzo[1,9][5,6](C_{60}-I_h)fullerene (**2l**), which was superior to that of the P3HT-based devices including [C_{60}]-PCBM. A very interesting effect of alkyl substituents attached to cyclohexene ring was observed: an odd number of alkyl group substituents gave better results on PCEs, while compounds with an even number of alkyl groups at the cyclohexene ring gave very poor PCE. These results indicate that both the appropriate band gap level between LUMO level of the acceptor compounds and HOMO level of the donor polymer and sufficiently mixed state of both components determine the total PCE of the OPV devices. Further investigation into the development of novel donor polymers as a partner of cyclopentene- and cyclohexene-fused [C_{60}]-fullerene derivatives will allow the creation of even more efficient solar cells in the near future.

■ EXPERIMENTAL SECTION

Materials. [C_{60}]-fullerene was purchased from Frontier Carbon (nanom purple ST-A), and P3HT was from Aldrich. Silica gel was purchased from Wako Pure Chemical Industry, Ltd. (Wakogel C-300E, 45−75 mm, and silica gel 60N).

Procedure for Synthesis of Cyclopentene-Fused [C_{60}]-Fullerenes: 1a.[16] A solution of [C_{60}]-fullerene (216 mg, 0.30 mmol), methyl 2-[hydroxy(phenyl)methyl]acrylate (**S3a**)[19] (172 mg, 0.90 mmol), and *N*,*N*-dimethylaminopyridine (110 mg, 0.90 mmol) in dry toluene (96 mL) was irradiated under ultrasonic conditions for several minutes to afford a violet solution; then the solution was added to acetic anhydride (91 mg, 0.90 mmol) and the mixture was stirred for 20 h at 120 °C. After being allowed to cool at room temperature, the mixture was evaporated under reduced pressure and the residue was added to methanol. This formed a brown solid, which was collected by an ultramembrane filter, dissolved in carbon disulfide (CS_2), and purified by silica gel (60N) flash chromatography [CS_2/toluene = 1:0, 10:1, and 4:1 (v/v)], affording product **1a** (75.0 mg, 0.074 mmol) as a dark brown amorphous solid in 27% yield; the unreacted fullerene (30 mg) was recovered in 14% yield. **1a** showed no clear melting point and only caused decomposition: ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.74 (br s, 1H), 7.62 (br s, 1H), 7.50 (br s, 1H), 7.39 (br s, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ 163.41, 156.09, 153.57, 150.75, 150.55, 147.22, 147.12, 146.20, 146.13, 145.92, 145.91, 145.87, 145.86, 145.83, 145.80, 145.62, 145.53, 145.47, 145.45, 145.37, 145.35, 145.23, 145.18, 145.10, 144.99, 144.90, 144.83, 144.73, 144.32, 144.23, 144.19, 144.01, 142.95, 142.92, 142.52, 142.44, 142.39, 142.35, 142.27, 142.01, 142.00, 141.97, 141.88, 141.77, 141.60, 141.59, 141.57, 141.45, 140.66, 140.42, 140.19, 139.98, 139.23, 138.40, 136.65, 135.90, 135.34, 133.97, 127.74, 76.71, 74.32, 62.94, 51.75; FT-IR (neat, cm^{-1}) 3020, 2943, 1722, 1646, 1428, 1243, 1095, 767, 694; MALDI-TOF-MS (matrix SA) found 894.0696 (calcd for $C_{71}H_{10}O_2$ exact mass 894.0681); $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1b. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and methyl 2-[hydroxy(4-methoxyphenyl)methyl]acrylate (**S3b**)[19] (172 mg, 0.90 mmol), product **1b** was obtained in 34% yield (162 mg, 0.17 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.04 (d, *J* = 2.0 Hz, 1H), 7.64 (br s, 1H), 7.55 (br s, 1H), 7.00 (br s, 1H), 6.90 (br s, 1H), 6.16 (d, *J* = 1.5 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H); 13C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ163.82, 158.92, 156.31, 153.95, 151.03, 150.71, 147.30, 147.21, 146.27, 146.21, 146.00, 145.98, 145.93, 145.91, 145.87, 145.75, 145.62, 145.55, 145.46, 145.45, 145.41, 145.32, 145.26, 145.17, 145.03, 144.98, 144.93, 144.86, 144.42, 144.32, 144.28, 144.25, 144.09, 143.03, 142.99, 142.59, 142.50, 142.47, 142.42, 142.38, 142.10, 142.07, 142.05, 141.96, 141.85, 141.71, 141.67, 141.65, 141.51, 140.48, 140.22, 140.04, 139.39, 138.66, 136.77, 136.01, 135.33, 133.99, 132.91, 76.68, 74.68, 62.33, 54.82, 51.89; FT-IR (neat, cm^{-1}) 2943, 1723, 1608, 1430, 1244, 1094, 824, 765, 690; MALDI-TOF-MS (matrix SA) found 924.0812 (calcd for $C_{72}H_{12}O_3$ exact mass 924.0786); $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1c. From [C_{60}]-fullerene (359 mg, 0.50 mmol) and methyl 2-[hydroxy(4-bromophenyl)methyl]acrylate (**S3c**)[19] (418 mg, 1.50 mmol), product **1c** was obtained in 33% yield (146 mg, 0.15 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.09 (dd, *J* = 1.0, 1.8 Hz, 1H), 7.62 (br s, 2H), 7.52 (br s, 2H), 6.17 (dd, *J* = 1.8, 1.1 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$-1,2-dichlorobenzene) δ 164.09, 155.83, 153.26, 150.64, 150.32, 147.26, 147.15, 146.20, 146.13, 145.94, 145.88, 145.86, 145.85, 145.81, 145.61, 145.59, 145.52, 145.48, 145.34, 145.32, 145.24, 145.20, 145.20, 145.14, 144.99, 144.93, 144.87, 144.58, 144.21, 144.20, 144.00, 142.90, 142.89, 142.47, 142.43, 142.38, 142.33, 142.21, 141.97, 141.87, 141.78, 141.58, 141.56, 141.53, 141.45, 140.39, 140.30, 140.22, 139.98, 139.32, 137.89, 136.53, 135.94, 135.42, 134.10, 121.93, 76.95, 74.19, 62.53, 52.18; FT-IR (neat, cm^{-1}) 2946, 1720, 1646, 1484, 1430, 1340, 1245, 1186, 1131, 1095, 1011, 889, 819, 765, 691; MALDI-TOF-MS (matrix: SA) found 971.9761 (calcd for $C_{71}H_9O_2Br$ exact mass 971.9786); $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1d. From [C_{60}]-fullerene (362 mg, 0.50 mmol) and methyl 3-hydroxy-2-methylenehexanoate (**S3d**)[19] (243 mg, 1.54 mmol), product **1d** was obtained in 18% yield (79 mg, 0.17 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.78 (d, *J* = 1.8 Hz, 1H), 5.01−5.03 (m, 1H), 4.04 (s, 3H), 2.55−2.62 (m, 1H), 2.38−2.45 (m, 1H), 1.94−2.03 (m, 1H), 1.79−1.87 (m, 1H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 164.69, 156.83, 152.78, 151.28, 151.26, 147.39, 147.26, 146.47, 146.35, 146.30, 146.27, 146.10, 146.08, 146.05, 146.03, 146.00, 145.74, 145.67, 145.55, 145.48, 145.42, 145.40, 145.38, 145.35, 145.26, 145.11, 145.09, 144.81, 144.54, 144.41, 144.27, 143.19, 143.12, 143.05, 142.75, 142.63, 142.54, 142.47, 142.25, 142.23, 142.18, 142.07, 141.97, 141.88, 141.83, 141.70, 141.69, 141.67, 140.51, 140.49, 140.06, 139.98, 139.25, 136.68, 136.43, 135.78, 133.98, 77.46, 73.38, 56.54, 52.04, 36.59, 21.26, 14.68; FT-IR (neat, cm^{-1}) 2950, 2864, 1718, 1511, 1430, 1342, 1241, 1130, 890, 765, 744; MALDI-TOF-MS (matrix SA) found 860.0819 (calcd for $C_{68}H_{12}O_2$ exact mass 860.0837); $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1e. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and (*E*)-methyl 3-hydroxy-2-methylene-5-phenylpent-4-enoate (**S3e**)[19] (327 mg, 1.5 mmol), product **1e** was obtained in 32% yield (155 mg, 0.16 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, CS_2−$CDCl_3$) δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 4.5 Hz, 1H), 6.94 (d, *J* = 15.5 Hz, 1H), 6.76 (dd, *J* = 10.0, 15.5 Hz, 1H), 5.70 (dd, *J* = 1.8, 9.7 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ 164.40, 156.07, 153.18, 150.99, 150.74, 147.52, 147.42, 146.45, 146.42, 146.31, 146.23, 146.22, 146.20, 146.18, 146.15, 146.11, 145.90, 145.87, 145.82, 145.76, 145.62, 145.51, 145.35, 145.25, 145.23, 144.62, 144.55, 144.42, 144.31, 144.26, 143.25, 143.18, 142.76, 142.75, 142.70, 142.63, 142.44, 142.32, 142.28, 142.14, 142.11, 142.08, 142.05, 141.95, 141.79, 141.74, 140.60, 140.49, 140.23, 139.95, 138.49, 136.69, 136.66, 136.14, 135.59, 134.24, 134.19, 129.21, 128.70, 128.06, 126.90, 77.02, 73.85, 60.79, 52.24; FT-IR (neat, cm^{-1}) 3019, 2943, 1724, 1642, 1431, 1225, 1135, 1093, 958,

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

744, 690, 575; MALDI-TOF-MS (matrix SA) found 920.0837 (calcd for $C_{73}H_{12}O_2$ exact mass 920.0833); $E_{1/2}^{red1}$ −1.08, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.72 eV.

1f. From [C_{60}]-fullerene (216 mg, 0.30 mmol) and phenyl 2-[hydroxy(phenyl)methyl]acrylate (**S3f**)[23] (305 mg, 1.20 mmol), product **1f** was obtained in 37% yield (111 mg, 0.12 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, CS_2−$CDCl_3$) δ 8.30 (d, *J* = 2.0 Hz, 1H), 7.88 (br s, 1H), 7.66 (br s, 1H), 7.55 (br s, 1H), 7.31−7.41 (m, 5H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.33 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (126 MHz, ppm, $CDCl_3$) δ 162.30, 156.25, 153.72, 150.85, 150.48, 147.54, 147.44, 146.63, 146.52, 146.44, 146.23, 146.18, 146.16, 146.14, 146.10, 145.98, 145.82, 145.80, 145.70, 145.68, 145.63, 145.55, 145.50, 145.41, 145.27, 145.21, 145.15, 145.01, 144.56, 144.53, 144.47, 144.31, 143.23, 143.20, 142.80, 142.73, 142.68, 142.64, 142.51, 142.30, 142.29, 142.21, 142.17, 142.08, 142.04, 141.91, 141.89, 141.87, 141.85, 141.74, 140.93, 140.70, 140.48, 140.25, 139.54, 138.41, 136.98, 136.32, 135.61, 134.27, 129.54, 128.07, 126.14, 121.47, 74.66, 65.98, 63.22; FT-IR (neat, cm^{-1}) 3028, 2913, 1736, 1490, 1217, 1188, 1077, 894, 744, 697, 573; MALDI-TOF-MS (matrix SA) found 956.0821 (calcd for $C_{76}H_{12}O_2$ exact mass 956.0837); $E_{1/2}^{red1}$ −1.07, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.73 eV.

1g. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and 2-(2-methoxyethoxy)ethyl 2-[hydroxy(phenyl)methyl]acrylate (**S3g**) (420 mg, 1.50 mmol), product **1g** was obtained in 32% yield (158 mg, 0.16 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.77 (br s, 1H), 7.63 (br s, 1H), 7.50 (br s, 1H), 7.37 (br s, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.22 (d, *J* = 1.8 Hz, 1H), 4.46−4.51 (m, 1H), 4.38−4.42 (m, 1H), 3.74−3.78 (m, 1H), 3.67−3.71 (m, 1H), 3.61−3.63 (m, 2H), 3.56−3.58 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ 163.59, 156.27, 153.76, 150.96, 150.73, 147.41, 147.31, 146.38, 146.30, 146.10, 146.05, 146.03, 146.01, 145.97, 145.84, 145.72, 145.69, 145.63, 145.57, 145.54, 145.50, 145.41, 145.37, 145.29, 145.18, 145.13, 145.08, 145.00, 144.91, 144.46, 144.41, 144.37, 144.20, 143.11, 143.08, 142.67, 142.61, 142.56, 142.53, 142.42, 142.18, 142.17, 142.13, 142.06, 141.96, 141.95, 141.77, 141.75, 141.73, 141.62, 140.95, 140.57, 140.35, 140.12, 139.37, 138.45, 136.78, 136.11, 135.50, 134.16, 127.81, 77.41, 77.16, 76.95, 76.91, 74.54, 70.56, 69.12, 64.23, 63.04, 59.04; FT-IR (neat, cm^{-1}) 3109, 2945, 1727, 1645, 1429, 1225, 1094, 801, 765, 697, 575; MALDI-TOF-MS (matrix SA) found 982.1205 (calcd for $C_{75}H_{18}O_2$ exact mass 982.1212); $E_{1/2}^{red1}$ −1.10, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.70 eV.

1h. A mixture of **1a** (57.2 mg, 0.064 mmol) in dry toluene (60 mL) was irradiated under ultrasonic conditions for several minutes to afford a clear solution, and then this solution was cooled at −78 °C. To this was added diisobutylaluminium hydride (DIBAL-H; 0.32 mL, 0.1 M hexane) at the same temperature, and the mixture was stirred for 19 h and allowed to warm to room temperature. To this solution was added 20 mL of potassium sodium tartrate tetrahydrate (Rochelle salt) saturated aqueous solution; the mixture was stirred for 1 h and the resulting organic layer was collected. The aqueous layer was extracted with toluene (30 mL, 3 times). The combined organic layers were washed with brine, dried, and evaporated to dryness. The residue was dissolved in toluene and purified by silica gel (60N) flash chromatography [toluene/ethyl acetate = 1:0 and 5:1 (v/v)], affording **1h** (39.2 mg, 0.0457 mmol) as a dark brown amorphous solid in 71% yield: ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.58 (br s, 2H), 7.32−7.38 (m, 2H), 7.17 (d, *J* = 1.7 Hz, 1H), 5.96 (s, 1H), 4.84 (dq, *J* = 4.3, 10.5 Hz, 2H), 1.82 (t, *J* = 5.3 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−1,2-dichlorobenzene) δ 157.39, 154.49, 153.39, 152.70, 152.31, 147.12, 146.98, 146.57, 145.97, 145.90, 145.82, 145.79, 145.75, 145.69, 145.66, 145.61, 145.57, 145.52, 145.40, 145.08, 145.02, 145.00, 144.98, 144.89, 144.80, 144.77, 144.63, 144.17, 144.08, 144.07, 142.81, 142.79, 142.29, 142.26, 142.20, 142.17, 142.09, 141.83, 141.74, 141.69, 141.48, 141.45, 141.41, 141.34, 140.18, 140.14, 140.05, 139.74, 139.01, 135.89, 135.82, 135.49, 134.29, 77.19, 75.38, 64.34, 60.79; FT-IR (neat, cm^{-1}) 3583, 3024, 2857, 1599, 1491, 1426, 1182, 1026, 864, 698, 573; MALDI-TOF-MS (matrix SA) found 866.0719 (calcd for $C_{70}H_{10}O$ exact mass 866.0732); $E_{1/2}^{red1}$ −1.14, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.66 eV.

1i. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and methyl 2-[hydroxy(thiophen-2-yl)methyl]acrylate (**S3h**)[24] (297 mg, 1.50 mmol), product **1i** was obtained in 52% yield (230 mg, 0.26 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.01 (d, *J* = 1.5 Hz, 1H), 7.28 (t, *J* = 5.0 Hz, 2H), 7.04 (dd, *J* = 3.5, 5.0 Hz, 1H), 6.43 (d, *J* = 1.5 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ 163.91, 155.52, 152.98, 150.95, 150.58, 147.44, 147.33, 146.38, 146.33, 146.15, 146.10, 146.07, 146.06, 146.02, 145.99, 145.94, 145.73, 145.69, 145.61, 145.57, 145.55, 145.53, 145.43, 145.37, 145.28, 145.25, 145.14, 145.10, 144.97, 144.88, 144.54, 144.47, 144.39, 144.37, 144.18, 143.09, 143.05, 142.73, 142.62, 142.56, 142.53, 142.39, 142.22, 142.19, 142.07, 141.95, 141.85, 141.81, 141.81, 141.77, 141.69, 141.58, 140.58, 140.32, 140.12, 139.29, 138.09, 137.05, 135.97, 135.69, 134.33, 127.73, 126.69, 125.72, 76.54, 74.71, 57.87, 52.24; FT-IR (neat, cm^{-1}) 3069, 2843, 1723, 1645, 1430, 1225, 1131, 1095, 894, 698; MALDI-TOF-MS (matrix SA) found 900.0233 (calcd for $C_{69}H_8O_2S$ exact mass 900.0245); $E_{1/2}^{red1}$ −1.10, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.70 eV.

1j. From [C_{60}]-fullerene (370 mg, 0.51 mmol) and *tert*-butyl 2-[hydroxy(thiophen-2-yl)methyl]acrylate (**S3i**) (365 mg, 1.52 mmol), product **1j** was obtained in 46% yield (219 mg, 0.23 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.96 (d, *J* = 1.9 Hz, 1H), 7.32−7.30 (m, 2H), 7.07 (dd, *J* = 3.7, 5.5 Hz, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 162.66, 155.81, 153.22, 151.20, 150.87, 147.45, 147.33, 146.38, 146.33, 146.16, 146.11, 146.08, 146.06, 146.03, 146.01, 145.99, 145.82, 145.74, 145.65, 145.62, 145.53, 145.44, 145.37, 145.28, 145.23, 145.14, 145.11, 145.01, 144.96, 144.54, 144.41, 144.24, 143.75, 143.11, 143.07, 142.72, 142.62, 142.57, 142.54, 142.41, 142.22, 142.09, 141.98, 141.95, 141.82, 141.81, 141.78, 141.77, 141.60, 140.60, 140.34, 140.11, 140.00, 139.34, 136.90, 135.99, 135.75, 134.35, 127.52, 126.54, 125.46, 81.63, 76.49, 74.78, 58.05, 27.98; FT-IR (neat, cm^{-1}) 3070, 2972, 2926, 1709, 1646, 1365, 1248, 1132, 845, 765, 691; MALDI-TOF-MS (matrix SA) found 942.0670 ($C_{72}H_{14}O_2S$ exact mass 942.0715) ; $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1k. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and 2-(2-methoxyethoxy)ethyl 2-[hydroxy(thiophen-2-yl)methyl]acrylate (**S3j**) (430 mg, 1.50 mmol), product **1k** was obtained in 40% yield (200 mg, 0.20 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$−CS_2) δ 8.10 (d, *J* = 1.7 Hz, 1H), 7.34 (dd, *J* = 1.0, 3.6 Hz, 1H), 7.31 (dd, *J* = 1.0, 4.9 Hz, 1H), 7.07 (dd, *J* = 3.6, 4.9 Hz, 1H), 6.48 (d, *J* = 1.8 Hz, 1H), 4.52−4.56 (m, 1H), 4.45−4.49 (m, 1H), 3.80−3.84 (m, 1H), 3.74−3.78 (m, 1H), 3.66−3.68 (m, 2H), 3.59−3.61 (m, 2H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 163.29, 155.47, 152.94, 150.91, 150.51, 147.38, 147.27, 146.33, 146.27, 146.10, 146.04, 146.02, 146.00, 145.96, 145.93, 145.89, 145.67, 145.56, 145.51, 145.49, 145.48, 145.38, 145.32, 145.22, 145.19, 145.07, 145.05, 144.91, 144.47, 144.34, 144.32, 144.14, 143.04, 143.00, 142.67, 142.56, 142.51, 142.48, 142.34, 142.16, 142.13, 142.02, 141.91, 141.81, 141.75, 141.72, 141.65, 141.53, 140.54, 140.27, 140.07, 139.24, 138.02, 138.01, 136.95, 135.95, 135.64, 134.29, 127.63, 126.65, 125.60, 76.50, 74.66, 71.98, 70.56, 69.12, 64.29, 58.99, 57.79; FT-IR (KBr, cm^{-1}) 3075, 2887, 2727, 2328, 1726, 1658, 1438, 1255, 1094, 855, 709, 530; MALDI-TOF-MS (matrix SA) found 988.0806 (calcd for $C_{73}H_{16}O_4S$ exact mass 988.0769); $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

1l. From [C_{60}]-fullerene (360 mg, 0.50 mmol) and methyl 2-[(2,2′-bithiophen)-5-yl(hydroxyl)methyl]acrylate (**S3k**) (420 mg, 1.50 mmol), product **1l** was obtained in 42% yield (210 mg, 0.21 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.05 (d, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.00 (dd, *J* = 3.7, 5.1 Hz, 1H), 6.41 (d, *J* = 1.8 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2−$CDCl_3$) δ 164.02, 155.50, 152.87, 150.88, 150.53, 147.49, 147.39, 146.44, 146.39, 146.20, 146.15, 146.12, 146.08, 146.05, 145.96, 145.75, 145.73, 145.64, 145.60, 145.58, 145.50, 145.42, 145.33, 145.30, 145.25, 145.22, 145.20, 144.96, 144.58, 144.44, 144.42, 144.23, 143.43, 143.13, 143.10, 142.77, 142.67, 142.62, 142.58, 142.41, 142.29, 142.26, 142.13, 142.00, 141.90, 141.89, 141.87, 141.83, 141.62, 140.63, 140.37, 140.17, 139.51, 137.92, 137.90, 137.33, 137.13, 136.00,

DOI: 10.1021/acs.joc.5b00530
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135.89, 134.35, 127.87, 127.57, 124.58, 124.10, 123.87, 77.41, 77.16, 76.91, 76.63, 74.74, 58.14, 52.43; FT-IR (neat, cm^{-1}) 3109, 3063,2945, 1727, 1645, 1429, 1225, 1131, 1094, 765, 697, 575; MALDI-TOF-MS (matrix 9-NA) found 982.0142 (calcd for $C_{73}H_{10}O_2S_2$ exact mass 982.0122); $E_{1/2}^{red1}$ −1.12, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.68 eV.

1m. From [C_{60}]-fullerene (187 mg, 0.26 mmol) and 2-methoxyethyl 2-[(2,2′-bithiophen)-5-yl(hydroxyl)methyl]acrylate (**S3l**) (259 mg, 0.80 mmol), product **1m** was obtained in 33% yield (99 mg, 0.087 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 8.08 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.19 (dd, *J* = 1.0, 5.0 Hz, 1H), 7.15 (d, *J* = 4.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 4.0, 5.5 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 4.50−4.54 (m, 1H), 4.42−4.46 (m, 1H), 3.64−3.72 (m, 2H), 3.41 (s, 3H); ^{13}C NMR (125 MHz, ppm, CS_2-CDCl_3) δ 163.52, 155.50, 152.88, 150.89, 150.50, 147.48, 147.38, 146.43, 146.38, 146.19, 146.14, 146.11, 146.10, 146.07, 146.04, 145.96, 145.76, 145.73, 145.65, 145.64, 145.58, 145.49, 145.42, 145.33, 145.29, 145.24, 145.19, 144.95, 144.56, 144.42, 144.23, 143.46, 143.11, 143.09, 142.75, 142.66, 142.60, 142.57, 142.39, 142.28, 142.24, 142.24, 142.12, 142.00, 141.89, 141.85, 141.83, 141.82, 141.62, 140.62, 140.37, 140.16, 139.51, 137.85, 137.83, 137.35, 137.06, 136.04, 135.87, 134.36, 127.88, 127.60, 124.54, 124.04, 123.81, 76.66, 74.70, 70.47, 64.38, 59.03, 58.09; FT-IR (neat, cm^{-1}) 3066, 2873, 1719, 1646, 1426, 1223, 1127, 1090, 801, 764, 689, 574; MALDI-TOF-MS (matrix 9-NA) found 1026.0351 (calcd for $C_{75}H_{14}O_3S_2$ exact mass 1026.0384); $E_{1/2}^{red1}$ −1.12, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.68 eV.

Procedure for Synthesis of Cyclohexene-Fused [C_{60}]-Fullerenes: 2b. A solution of [C_{60}]-fullerene (359 mg, 0.50 mmol), methyl 3-hydroxy-2-methylenepentanoate (**S3n**)[19] (232 mg, 1.55 mmol), and *N*,*N*-dimethylaminopyridine (184 mg, 1.51 mmol) in dry toluene (160 mL) was irradiated under ultrasonic conditions for several minutes to afford violet solution; then the solution was added to acetic anhydride (0.14 mL, 1.48 mol) and the mixture was stirred for 2.5 h at 120 °C. After the mixture was allowed to cool at room temperature, the solvent was evaporated under reduced pressure and the residue was added to methanol. This formed a brown solid, which was collected on an ultramembrane filter, dissolved in carbon disulfide (CS_2), and purified by silica gel (60N) flash chromatography [CS_2/toluene =1:0, 5:1, and 3:1 (v/v)], affording product **2b** (211 mg, 0.249 mmol) as a brown amorphous solid in 50% yield; the unreacted fullerene (62 mg) was recovered in 18% yield. **2b** showed no clear melting point and only caused decomposition: ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 7.76 (s, 1H), 4.69 (d, *J* = 14.3 Hz, 1H), 4.21−4.13 (m, 2H), 3.97 (s, 3H), 2.15 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3-CS_2$) δ 165.15, 156.88, 156.70, 153.15, 147.77, 147.62, 147.51, 146.67, 146.61, 146.56, 146.55, 146.46, 146.21, 146.18, 146.16, 145.77, 145.76, 145.53, 145.51, 145.50, 145.41, 145.39, 145.36, 145.35, 145.34, 145.12, 144.72, 144.68, 144.55, 144.53, 143.08, 143.07, 142.66, 142.63, 142.61, 142.59, 142.19, 142.17, 142.07, 142.02, 142.00, 141.84, 141.73, 141.57, 141.45, 141.36, 140.30, 140.28, 139.11, 138.94, 136.50, 135.71, 135.66, 134.99, 133.82, 70.02, 66.92, 52.13, 42.38, 39.17, 18.45; FT-IR (neat, cm^{-1}) 2980, 2564, 1714, 1640, 1431, 1364, 1258, 1208, 1127, 746, 575; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{67}H_{10}O_2Na$ 869.0578, found 869.0579; $E_{1/2}^{red1}$ −1.15, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.65 eV.

2a. From [C_{60}]-fullerene (363 mg, 0.50 mmol) and methyl 3-hydroxy-2-methylenebutanoate (**S3m**)[19] (222 mg, 1.63 mmol), product **2a** was obtained in 48% yield (201 mg, 0.24 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 8.06 (t, *J* = 5.8 Hz, 1H), 4.39 (s, 2H), 4.22 (d, *J* = 5.8 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3-CS_2$) δ 164.84, 156.16, 156.10, 147.57, 147.52, 146.45, 146.41, 146.16, 146.13, 145.68, 145.47, 145.35, 145.19, 144.99, 144.62, 144.52, 143.03, 142.52, 142.49, 142.09, 142.07, 142.02, 141.92, 141.58, 141.54, 141.44, 140.16, 140.08, 135.73, 135.64, 135.49, 65.48, 64.97, 51.97, 41.10, 38.76; FT-IR (neat, cm^{-1}) 2940, 2836, 1713, 1638, 1511, 1429, 1366, 1262, 1211, 1124, 746; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{66}H_8O_2Na$ 855.0422, found 855.0418; $E_{1/2}^{red1}$ −1.14, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.66 eV.

2c. From [C_{60}]-fullerene (362 mg, 0.50 mmol) and methyl 3-hydroxy-2-methylenehexanoate (**S3d**)[19] (230 mg, 1.45 mmol), product **2c** was obtained in 47% yield (200 mg, 0.23 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 7.88 (s, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.18 (d, *J* = 13.9 Hz, 1H), 3.97 (s, 3H), 3.88 (br s, 1H), 2.84−2.90 (m, 1H), 2.30 (br s, 1H), 1.48 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3-CS_2$) δ 164.48, 156.75, 156.52, 153.59, 147.46, 147.32, 146.63, 146.40, 146.30, 146.16, 146.04, 145.87, 145.63, 145.38, 145.30, 145.22, 145.15, 145.01, 144.58, 144.53, 144.38, 142.93, 142.50, 142.46, 142.02, 141.94, 141.87, 141.69, 141.60, 141.45, 141.29, 141.20, 140.19, 138.88, 138.75, 136.12, 135.60, 134.86, 134.42, 69.80, 67.21, 51.81, 49.52, 39.19, 26.04, 13.71; FT-IR (neat, cm^{-1}) 2958, 2868, 1713, 1639, 1511, 1430, 1266, 1131, 1080, 759, 575; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{68}H_{12}O_2Na$ 883.0735, found 883.0726; $E_{1/2}^{red1}$ −1.15, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.65 eV.

2d. From [C_{60}]-fullerene (357 mg, 0.50 mmol) and methyl 3-hydroxy-2-methyleneheptanoate (**S3o**)[25] (251 mg, 1.46 mmol), product **2d** was obtained in 48% yield (210 mg, 0.24 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 7.86 (s, 1H), 4.68 (d, *J* = 13.3 Hz, 1H), 4.18 (d, *J* = 13.3 Hz, 1H), 3.96 (s, 4H), 2.72−2.80 (m, 1H), 2.29 (br s, 1H), 1.99−2.07 (m, 1H), 1.74−1.81 (m, 1H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−1,2-dichlorobenzene) δ 165.27, 156.81, 153.84, 147.38, 147.26, 146.48, 146.30, 146.26, 146.20, 146.17, 145.94, 145.57, 145.48, 145.24, 145.19, 145.14, 144.96, 144.92, 144.43, 144.32, 142.81, 142.76, 142.37, 142.33, 141.94, 141.90, 141.85, 141.81, 141.68, 141.39, 141.34, 141.18, 141.12, 140.02, 140.01, 138.81, 138.67, 136.02, 135.61, 135.50, 134.92, 134.33, 69.91, 66.10, 51.97, 47.66, 39.28, 34.65, 22.24, 14.28; IR (neat, cm^{-1}) 2955, 2927, 2855, 1707, 1639, 1513, 1433, 1372, 1269, 1205, 1132, 1086, 958, 748, 573; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{69}H_{14}O_2Na$ 897.0891, found 897.0883; $E_{1/2}^{red1}$ −1.16, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.64 eV.

2e. From [C_{60}]-fullerene (367 mg, 0.51 mmol) and methyl 3-hydroxy-2-methyleneoctanoate (**S3p**)[25] (272 mg, 1.46 mmol), product **2e** was obtained in 41% yield (187 mg, 0.21 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 7.85 (br s, 1H), 4.68 (d, *J* = 13.8 Hz, 1H), 4.15 (d, *J* = 14.2 Hz, 1H), 3.98 (m, 4H), 2.75−2.81 (m, 1H), 2.29 (br s, 1H), 1.96 (br s, 1H), 1.69−1.78 (m, 1H), 1.54−1.68 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); FT-IR (neat, cm^{-1}) 2947, 2915, 2851, 1708, 1640, 1512, 1430, 1373, 1263, 1210, 1128, 1086, 748, 573; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{70}H_{16}O_2Na$ 911.1048, found 911.1039 ; $E_{1/2}^{red1}$ −1.11, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.69 eV. Due to very poor solubility of **2e** in all solvents tested, such as $CDCl_3$ and CS_2, we were unable to obtain reliable ^{13}C NMR spectra.

2f. From [C_{60}]-fullerene (361 mg, 0.50 mmol) and methyl 3-hydroxy-2-methylenenonanoate (**S3q**)[24] (290 mg, 1.5 mmol), product **2f** was obtained in 34% yield (155 mg, 0.17 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 7.86 (s, 1H), 4.67 (d, *J* = 14.0 Hz, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 3.97 (m, 4H), 2.71−2.80 (m, 1H), 2.28 (br s, 1H), 1.92−2.01 (m, 1H), 1.67−1.78 (m, 1H), 1.44−1.56 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3-CS_2$) δ 164.62, 156.82, 156.57, 153.68, 147.52, 147.37, 146.70, 146.41, 146.32, 146.09, 146.06, 145.68, 145.40, 145.24, 145.07, 144.59, 144.42, 142.98, 142.52, 142.04, 141.95, 141.75, 141.71, 141.61, 141.53, 141.46, 141.30, 141.22, 140.22, 140.19, 138.97, 138.91, 138.84, 138.79, 136.18, 136.16, 136.12, 135.64, 134.98, 134.93, 134.33, 134.27, 69.83, 67.25, 51.89, 51.85, 47.85, 39.20, 32.84, 32.36, 29.11, 23.24, 14.46; FT-IR (neat, cm^{-1}) 2918, 2852, 1710, 1641, 1432, 1374, 1267, 1210, 1128, 1088, 748, 574; HRMS (ESI-TOF) *m*/*z* [M + Na^+] calcd for $C_{71}H_{18}O_2Na$ 925.1204, found 925.1199; $E_{1/2}^{red1}$ −1.16, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.64 eV.

2g. From [C_{60}]-fullerene (363 mg, 0.50 mmol) and methyl 3-hydroxy-5-methyl-2-methylenehexanoate (**S3r**)[19] (278 mg, 1.5 mmol), product **2g** was obtained in 32% yield (139 mg, 0.16 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3-CS_2$) δ 8.05 (s, 1H), 4.70 (d, *J* = 14.1 Hz, 1H), 4.13 (d, *J* = 12.9 Hz, 1H), 3.98 (s, 4H), 3.32 (ddt, *J* = 3.3, 6.8, 13.5 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−1,2-

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

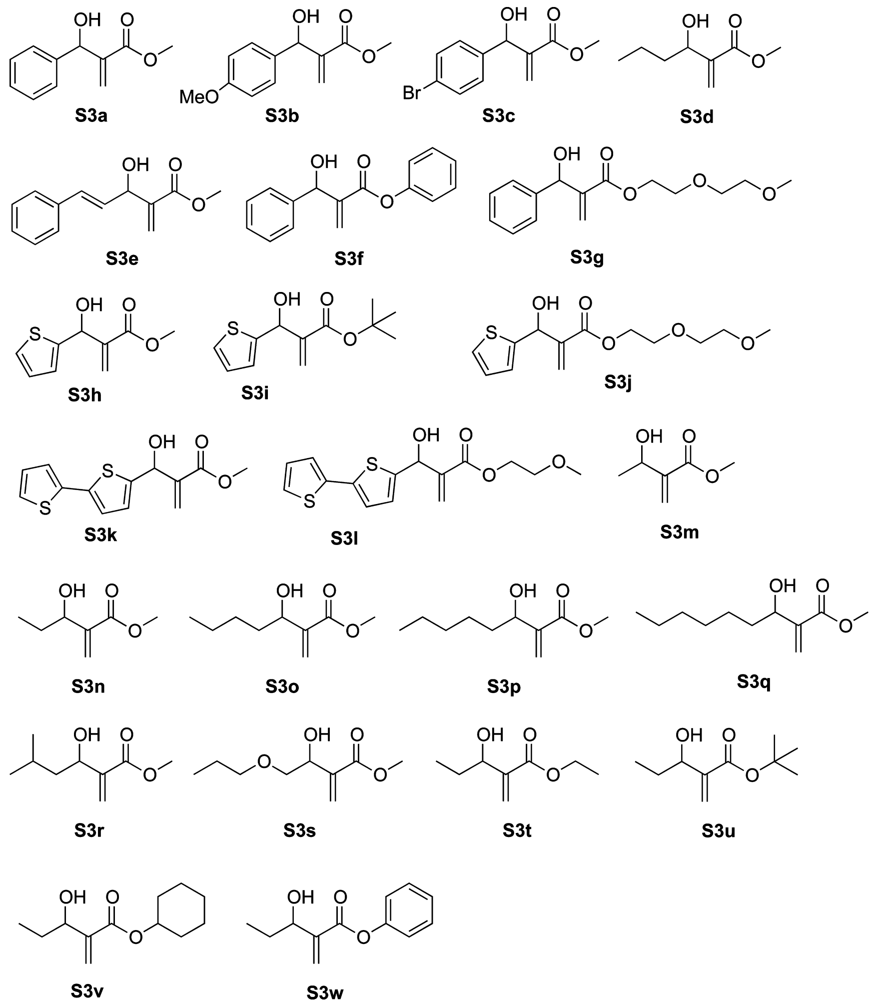

Figure 7. Starting materials for preparing [C_{60}]-CP and [C_{60}]-CH.

dichlorobenzene) δ 165.46, 157.73, 156.69, 154.21, 147.45, 147.30, 146.59, 146.39, 146.33, 146.22, 146.05, 146.01, 145.96, 145.84, 145.68, 145.57, 145.37, 145.27, 145.23, 145.15, 145.09, 145.02, 144.85, 144.50, 144.45, 144.35, 144.31, 143.07, 142.86, 142.48, 142.40, 142.05, 142.01, 141.96, 141.87, 141.74, 141.54, 141.50, 141.36, 141.24, 140.23, 140.07, 138.71, 135.86, 135.61, 134.87, 134.55, 69.93, 67.45, 54.13, 52.17, 39.70, 27.35, 25.35, 19.86; FT-IR (neat, cm^{-1}) 2952, 1709, 1646, 1432, 1237, 1208, 1122, 1088, 748, 574; HRMS (ESI-TOF) m/z [M + Na^+] calcd for $C_{69}H_{14}O_2Na$ 897.0891, found 897.0886; $E_{1/2}^{red1}$ −1.16, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.64 eV.

2h. From [C_{60}]-fullerene (329 mg, 0.46 mmol) and methyl 3-hydroxy-2-methylene-4-propoxybutanoate (**S3s**) (247 mg, 1.31 mmol), product **2h** was obtained in 37% yield (153 mg, 0.17 mmol) as a brown amorphous solid. ^1H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.96 (s, 1H), 5.56 (s, 1H), 4.72 (d, J = 14.5 Hz, 1H), 4.10 (br s, 2H), 3.99 (s, 3H), 3.87−3.94 (m, 1H), 1.80 (sextet, J = 7.3 Hz, 2H), 1.01 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 165.18, 156.44, 153.56, 147.64, 146.62, 146.59, 146.59, 146.56, 146.32, 146.26, 146.23, 146.21, 145.86, 145.86, 145.86, 145.81, 145.70, 145.61, 145.48, 145.44, 145.42, 145.42, 145.14, 144.75, 144.68, 144.64, 143.10, 143.07, 142.68, 142.66, 142.66, 142.61, 142.28, 142.25, 142.16, 142.11, 142.11, 142.00, 141.84, 141.64, 141.63, 141.43, 140.32, 140.29, 139.41, 136.04, 135.21, 81.76, 74.31, 70.39, 65.43, 52.52, 38.21, 23.48, 11.11; FT-IR (neat, cm^{-1}) 2946, 22867, 1716, 1511, 1430, 1364, 1234, 1090, 965, 745, 573; HRMS (ESI-TOF) m/z [M + Na^+] calcd for $C_{69}H_{14}O_3Na$ 913.0841, found 913.0828; $E_{1/2}^{red1}$ −1.11, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.69 eV.

2i. From [C_{60}]-fullerene (359 mg, 0.50 mmol) and ethyl 3-hydroxy-2-methylenepentanoate (**S3t**)[26] (237 mg, 1.50 mmol), product **2i** was obtained in 34% yield (146 mg, 0.17 mmol) as a brown amorphous solid. ^1H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.74 (s, 1H), 4.68 (d, J = 13.3 Hz, 1H), 4.69 (d, J = 14.3 Hz, 1H), 4.37−4.45 (m, 2H), 4.13−4.20 (m, 2H), 2.16 (d, J = 7.2 Hz, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 164.39, 156.85, 156.66, 153.06, 147.52, 147.41, 147.10, 146.59, 146.53, 146.47, 146.46, 146.36, 146.12, 146.09, 146.07, 145.68, 145.45, 145.43, 145.32, 145.30, 145.27, 145.26, 145.03, 144.64, 144.60, 144.46, 144.44, 143.00, 142.98, 142.57, 142.54, 142.52, 142.51, 142.10, 142.09, 141.99, 141.93, 141.77, 141.65, 141.49, 141.37, 141.27, 140.23, 140.21, 139.04, 138.86, 136.46, 135.61, 135.59, 134.90, 134.08, 69.96, 66.85, 61.06, 42.33, 39.10, 18.42, 14.54; IR (neat, cm^{-1}) 2970, 2849, 1705, 1637, 1511, 1428, 1369, 1246, 1205, 1125, 1060, 1020, 860, 745, 575; HRMS (ESI-TOF) m/z [M + Na^+] calcd for $C_{68}H_{12}O_2Na$ 883.0735, found 883.0728; $E_{1/2}^{red1}$ −1.15, LUMO = $-(4.8 + E_{1/2}^{red1})$ = −3.65 eV.

2j. From [C_{60}]-fullerene (356 mg, 0.49 mmol) and *tert*-butyl 3-hydroxy-2-methylenepetanoate (**S3u**)[27] (282 mg, 1.52 mmol), product **2j** was obtained in 31% yield (134 mg, 0.15 mmol) as a brown amorphous solid. ^1H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.61 (s, 1H), 4.64 (d, J = 14.0 Hz, 1H), 4.12−4.17 (m, 1H), 4.08 (dd, J = 2.1, 14.3 Hz, 1H), 2.14 (d, J = 7.0 Hz, 3H), 1.64 (s, 9H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 164.01, 157.25, 156.89, 153.25, 147.59, 147.47, 146.74, 146.68, 146.53, 146.51, 146.43, 146.41, 146.21, 146.17, 146.15, 146.13, 145.77, 145.76, 145.49, 145.46, 145.41, 145.38, 145.36, 145.33, 145.32, 145.27, 145.09, 144.71, 144.67, 144.54, 144.51, 143.06, 143.04, 142.63, 142.60, 142.56, 142.21, 142.16, 142.15, 142.05, 142.00, 141.84, 141.68, 141.56, 141.42, 141.33, 140.30, 140.23, 139.07, 138.87, 136.56, 135.67, 135.51, 135.48, 134.95, 80.94, 70.10, 67.04, 42.32, 39.22, 28.20,18.49; FT-IR (neat, cm^{-1}) 2969, 2927, 1705, 1640, 1450,

DOI: 10.1021/acs.joc.5b00530
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1364, 1279, 1127, 1079, 847, 745; HRMS (ESI-TOF) m/z [M + Na$^+$] calcd for $C_{70}H_{16}O_2Na$ 911.1048, found 911.1054; $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.69 eV.

2k. From [C_{60}]-fullerene (370 mg, 0.51 mmol) and cyclohexyl 3-hydroxy-2-methylenepentanoate (**S3v**) (319 mg, 1.50 mmol), product **2k** was obtained in 31% yield (146 mg, 0.16 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 7.72 (s, 1H), 5.04 (septet, J = 4.1 Hz, 1H), 4.69 (d, J = 14.2 Hz, 1H), 4.12−4.19 (m, 2H), 2.15 (d, J = 7.2 Hz, 3H), 1.98 (br s, 2H), 1.75−1.85 (m, 2H), 1.58−1.70 (m, 3H), 1.44−1.50 (m, 2H), 1.34−1.39 (m, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 164.48, 157.24, 156.90, 154.63, 153.34, 147.67, 147.56, 147.16, 146.82, 146.77, 146.60, 146.51, 146.49, 146.28, 146.25, 146.23, 146.20, 145.85, 145.83, 145.57, 145.53, 145.51, 145.46, 145.44, 145.42, 145.41, 145.32, 145.14, 144.78, 144.61, 143.13, 143.12, 142.70, 142.67, 142.64, 142.28, 142.24, 142.22, 142.13, 142.11, 142.09, 142.07, 141.91, 141.76, 141.62, 141.50, 141.40, 140.34, 140.29, 139.13, 138.94, 136.57, 135.77, 135.62, 135.07, 134.65, 73.31, 70.23, 67.15, 42.36, 39.39, 31.76, 31.68, 25.67, 23.85, 23.75, 18.47; FT-IR (neat, cm^{-1}) 2926, 2851, 1706, 1641, 1446, 1379, 1248, 1207, 1118, 1012, 746, 574; HRMS (ESI-TOF) m/z [M + Na$^+$] calcd for $C_{72}H_{18}O_2Na$ 937.1204, found 937.1199; $E_{1/2}^{red1}$ −1.11, LUMO = −(4.8+ $E_{1/2}^{red1}$) = −3.69 eV.

2l. From [C_{60}]-fullerene (358 mg, 0.50 mmol) and phenyl 3-hydroxy-2-methylenepentanoate (**S3w**) (200 mg, 0.97 mmol), product **2l** was obtained in 38% yield (173 mg, 0.19 mmol) as a brown amorphous solid. ^{1}H NMR (500 MHz, ppm, $CDCl_3$−CS_2) δ 8.01 (s, 1H), 7.43−7.47 (m, 2H), 7.26−7.30 (m, 3H), 4.80 (d, J = 14.3 Hz, 1H), 4.24−4.30 (m, 2H), 2.22 (d, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$−CS_2) δ 163.17, 156.82, 156.52, 153.02, 150.74, 149.59, 147.62, 147.50, 146.65, 146.59, 146.56, 146.55, 146.45, 146.20, 146.17, 146.16, 145.76, 145.75, 145.54, 145.52, 145.40, 145.39, 145.37, 145.35, 145.32, 145.06, 144.71, 144.67, 144.53, 144.52, 143.08, 143.07, 142.66, 142.61, 142.60, 142.59, 142.19, 142.16, 142.07, 142.02, 141.98, 141.82, 141.73, 141.58, 141.45, 141.36, 140.34, 140.28, 139.12, 138.96, 136.48, 135.71, 135.61, 135.01, 133.51, 129.49, 125.90, 121.62, 70.01, 66.91, 42.61, 39.20, 18.46; FT-IR (neat, cm^{-1}) 3061, 2960, 1725, 1639, 11589, 1489, 1428, 1245, 1188, 1160, 1115, 1051, 903, 738, 684; HRMS (ESI-TOF) m/z [M + Na$^+$] calcd for $C_{72}H_{12}O_2Na$ 931.0735, found 931.0728; $E_{1/2}^{red1}$ −1.14, LUMO = −(4.8 + $E_{1/2}^{red1}$) = −3.66 eV.

Preparation of Organic Photovoltaic Device. Photovoltaic devices were prepared by spin-coating the cyclopentene- or cyclohexene-fused [C_{60}]-fullerene blends from chlorobenzene onto an indium tin oxide (ITO) glass electrode as follows: To a P3HT (1.0 wt %) solution of chlorobenzene were added cyclopentene-fused [C_{60}]-fullerene **1a** (equal weight as P3HT) and silica gel (1.0 wt % versus P3HT solution), and then the mixture was stirred for 12 h at ambient temperature. It was then filtered through a Teflon (0.2 mm) filter. The resulting solution was applied to the surface of an ITO plate [with PEDOT−PSS (AI4083 (pH = 1.8)] by the spin-coating method at a thickness of ca. 100 nm, and the surface was washed with acetone and irradiated under UV light and ozone gas for 20 min to decompose the impurities. After being dried under vacuum for 20 min, the resulting plate was placed in a vacuum chamber and the surface was coated with the electrode layers of calcium (4 nm) and aluminum (100 nm) by evaporation at 10^{-4} Pa at room temperature. We placed the glass plate on the resulting film, and the plate was firmly fixed by use of a bonding agent under an argon atmosphere to produce the solar cell. The PCE values were obtained with the solar simulator Otento-Sun II (AM1.5G, 100 mW/cm^2). Cyclic voltammograms were obtained in acetonitrile with 0.1 mM tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte with glassy carbon (1 mm diameter) as a working electrode, a Pt counter electrode, and Ag/AgCl reference electrode.

Preparation of Starting Materials for [C_{60}]-CP and [C_{60}]-CH. [C_{60}]-CP and [C_{60}]-CH were synthesized by use of 23 types of α-methylene-β-hydroxy esters as starting materials (Figure 7). These esters were prepared following the method developed by González and co-workers[19] through Morita-Baylis-Hillmann reaction.[20]

*2-(2-Methoxyethoxy)ethyl 2-[Hydroxy(phenyl)methyl]acrylate (**S3g**)*. To a mixture of 2-(2-methoxyethoxy)ethyl acrylate (1.5 g, 8.6 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (193 mg, 1.72 mmol) was added benzaldehyde (1.10 g, 10.3 mmol), and the mixture was stirred for 62 h at room temperature. Then this was diluted with ethyl acetate (20 mL) and washed with brine (10 mL, three times). The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60 N, hexane/ethyl acetate = 5:1, 2:1, then 1:1 v/v) to afford **S3g** (1.67 g, 5.96 mmol) in 69% yield as a colorless liquid: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.33−7.39 (m, 4H), 7.26−7.30 (m, 1H), 6.38 (s, 1H), 6.00 (s, 1H), 5.80 (t, J = 1.2 Hz, 1H), 5.57 (d, J = 4.8 Hz, 1H), 4.29 (ddd, J = 1.0, 3.8, 5.8 Hz, 2H), 3.66−3.70 (m, 2H), 3.58−3.62 (m, 2H), 3.50−3.54 (m, 2H), 3.37 (s, 3H), 3.15 (d, J = 5.6 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.1, 142.1, 141.4, 128.4, 127.7, 126.7, 72.9, 70.6, 69.8, 68.9, 66.7, 63.9, 15.2; ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.14, 142.12, 141.38, 128.35, 127.73, 126.68, 72.91, 70.57, 69.76, 68.85, 66.72, 63.89; IR (neat, cm^{-1}) 3417, 2881, 1714, 1634, 1453, 1266, 1135, 1105, 1042, 1024, 957, 840, 765, 699; HRMS (ESI-TOF) m/z calcd for [M + Na]$^+$ $C_{15}H_{20}O_5Na$, 303.1208; found, 303.1203.

*tert-Butyl 2-[Hydroxy(thiophen-2-yl)methyl]acrylate (**S3i**)*. To a mixture of thiophene-2-carbaldehyde (0.92 mL, 10 mmol) and DABCO (1.12 g, 10 mmol) in 1.0 mL of mixed solvent (1,4-dioxane/H_2O = 1.0 mL, 1:1 v/v) was added *tert*-butyl acrylate (4.4 mL, 30 mmol), and the mixture was stirred for 48 h at room temperature. Then this was diluted with water (20 mL) and extracted with ether (20 mL, 3 times). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60N, hexane/ethyl acetate = 15:1, 10:1, then 3:1 v/v) to afford **S3i** (0.595 g, 2.48 mmol) in 25% yield as a light yellow oil: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.25 (dd, J = 1.2, 4.0 Hz, 1H), 6.94−6,98 (m, 2H), 6.27 (s, 1H), 5.82 (s, 1H), 5.69 (d, J = 7.1 Hz, 1H), 3.45 (d, J = 7.1 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 165.5, 148.3, 142.7, 128.8, 125.1, 124.5, 92.0, 70.0, 29.0; IR (neat, cm^{-1}) 3423, 2978, 2933, 1699, 1630, 1393, 1368, 1288, 1255, 1146, 1025, 957, 848, 762, 697; HRMS (ESI-TOF) m/z [M + Na$^+$] calcd for $C_{12}H_{16}O_3SNa$, 263.0718; found, 263.0712.

*2-(2-Methoxyethoxy)ethyl 2-[Hydroxy(thiophen-2-yl)methyl]-acrylate (**S3j**)*. To a mixture of 2-(2-methoxyethoxy)ethyl acrylate (1.15 g, 6.6 mmol) and DABCO (0.148 g, 1.32 mmol) was added thiophene-2-carbaldehyde (0.710 g, 6.6 mmol), and the mixture was stirred for 72 h at room temperature. Then this was diluted with ethyl acetate (20 mL) and washed with brine (10 mL, three times). The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60N, hexane/ethyl acetate = 5:1, 2:1, then 1:1 v/v) to afford **S3j** (1.44 g, 5.03 mmol) in 76% yield as a light yellow oil: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.25−7.26 (m, 1H), 6.93−6.98 (m, 2H), 6.40 (s, 1H), 5.92 (s, 1H), 5.77 (d, J = 6.8 Hz, 1H), 4.32 (t, J = 4.7 Hz, 2H), 3.67−3.73 (m, 2H), 3.61 (dd, J = 3.3, 5.7 Hz, 2H), 3.53 (dd, J = 3.5, 5.5 Hz, 2H), 3.49 (d, J = 6.9 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 165.9, 145.9, 141.4, 126.8, 126.6, 124.7, 71.8, 70.4, 69.4, 68.9, 64.0, 59.1; IR (neat, cm^{-1}) 3407, 2920, 1713, 1629, 1452, 1397, 1259, 1104, 1026, 853, 841, 771, 700; HRMS (ESI-TOF) m/z calcd for [M + Na]$^+$ $C_{13}H_{18}O_5SNa$, 309.0773; found, 309.0763.

*Methyl 2-[(2,2′-Bithiophen)-5-yl(hydroxy)methyl]acrylate (**S3k**)*. To a mixture of methyl acrylate (0.86 g, 10 mmol) and , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.52 g, 10 mmol) was added 2,2′-bithiophene-5-carboxyaldehyde (1.94 g, 10 mmol), and the mixture was stirred for 5 h at room temperature. Then this was diluted with ethyl acetate (20 mL) and washed with brine (10 mL, three times). The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60N, hexane/ethyl acetate = 10:1

DOI: 10.1021/acs.joc.5b00530
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then 4:1 v/v) to afford **S3k** (1.12 g, 4.0 mmol) in 40% yield as a light yellow oil: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.20 (dd, J = 1.1, 5.1 Hz, 1H), 7.13 (dd, J = 1.1, 31.6 Hz, 1H), 7.02 (d, J = 3.7 Hz, 1H), 7.00 (dd, J = 3.6, 5.1 Hz, 1H), 6.86 (dd, J = 0.9, 3.7 Hz, 1H), 6.39 (s, 1H), 6.00 (s, 1H), 5.72 (d, J = 6.8 Hz, 1H), 3.78 (s, 3H), 3.38 (d, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.5, 144.7, 140.9, 137.4, 137.3, 127.9, 126.5, 125.5, 124.5, 123.7, 123.4, 69.8, 52.2; IR (neat, cm^{-1}) 3254. 2959, 1715, 1634, 1435, 1263, 1200, 1156, 1004, 982, 969, 955, 801, 776, 695; HRMS (ESI-TOF) m/z calcd for [M + Na]$^+$ $C_{13}H_{12}O_3S_2Na$, 303.0126; found, 303.0120.

*2-Methoxyethyl 2-[(2,2′-Bithiophen)-5-yl(hydroxy)methyl]-acrylate (**S3l**).* To a mixture of methyl acrylate (0.52 g, 4.0 mmol) and 2,2′-bithiophene-5-carboxyaldehyde (0.79 g, 4.0 mmol) was added DABCO (0.089 g, 0.8 mmol), and the mixture was stirred for 48 h at roo, temperature. Then this was diluted with diethyl ether (20 mL) and washed with brine (10 mL, three times). The aqueous phase was extracted with ether. The combined organic layers were dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60N, hexane/ethyl acetate = 9:1, 4:1, then 2:1 v/v) to afford **S3l** (0.844 g, 2.6 mmol) in 65% yield as a light yellow oil: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.20 (d, J = 5.0 Hz, 1H), 7.13 (d, J = 3.1 Hz, 1H), 7.02 (d, J = 3.6 Hz, 1H), 7.00 (t, J = 4.5 Hz, 1H), 6.86 (d, J = 3.3 Hz, 1H), 6.43 (s, 1H), 5.99 (s, 1H), 5.73 (s, 1H), 4.32 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.5 Hz, 2H), 3.47 (d, J = 6.8 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.0, 144.8, 141.0, 137.4, 137.3, 127.9, 127.0, 125.5, 124.5, 123.7, 123.4, 70.2, 69.8, 64.1, 59.1; IR (neat, cm^{-1}) 3403, 3101, 2890, 1712, 1638, 1403, 1259, 1200, 1152, 1123, 1028, 960, 838, 801, 695; HRMS (ESI-TOF) m/z calcd for [M + Na]$^+$ $C_{15}H_{16}O_4S_2Na$, 347.0388; found, 347.0383.

*Methyl 3-Hydroxy-2-methylene-4-propoxybutanoate (**S3s**).* A mixture of 1-propanol (4.55 g, 76 mmol), sodium hydroxide (1.95 g, 49 mmol), and 2-bromo-1,1-dimethoxyethane (2.6 g, 15.4 mmol) was stirred at 80 °C. After stirring for 9 h at the same temperature, 1-propanol (1.0 g, 17 mmol) was added and the mixture was further stirred for 6 h. After being allowed to cool at room temperature, the mixture was diluted with water (30 mL) to give the biphasic layer. The organic layer formed was collected and the water layer was extracted with ether (30 mL, five times). The combined organic layers were dried over anhydrous sodium sulfate (Na_2SO_4) and evaporated to dryness. The residue was purified by silica gel flash column chromatography to afford 1-(2,2-dimethoxyethoxy)propane[21] (0.885 g, 5.98 mmol) in 39% yield.

To a solution of 1-(2,2-dimethoxyethoxy)propane in deionized water (25 mL) was added p-toluenesulfonic acid monohydrate (4.0 g, 21 mmol), and the mixture was stirred for 14.5 h at room temperature and then extracted with ether (30 mL, five times). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, and condensed to ca. 0.5 mL (0.497 g), and then this was diluted with 0.4 mL of mixed solvent (1,4-dioxane/water = 1:1 v/v). To this solution were added DABCO (0.549 g, 4.9 mmol) and methyl acrylate (1.3 mL, 14.5 mmol), and the mixture was stirred for 20 h at room temperature. The resulting solution was diluted with water (10 mL) and extracted with ether (20 mL, three times). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and evaporated to dryness. The residue was separated by silica gel flash column chromatography (Wakogel C-300E, hexane/ethyl acetate = 10:1 then 3:1 v/v) to give **S3s** (0.247 g, 1.31 mmol) in 22% yield (two steps) as a colorless liquid: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.36 (t, J = 1.1 Hz, 1H), 6.02 (t, J = 1.3 Hz, 1H), 4.68−4.72 (m, 1H), 3.77 (s, 3H), 3.87 (dd, J = 3.5, 9.7 Hz, 1H), 3.40−3.49 (m, 2H), 3.33 (dd, J = 7.4, 9.7 Hz, 1H), 2.89 (d, J = 4.3 Hz, 1H), 1.60 (sext, J = 7.0 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) 166.5, 139.3, 126.6, 74.1, 73.0, 69.3, 51.9, 22.9, 10.6; IR (neat, cm^{-1}) 3441, 2961, 2876, 1715, 1631, 1439, 1274, 1159, 1080, 939, 819; HRMS (ESI-TOF) m/z [M + H$^+$] calcd for $C_9H_{17}O_4$, 189.1127; found, 189.1127.

*Cyclohexyl 3-Hydroxy-2-methylenepentanoate (**S3v**).* To a mixture of propionaldehyde (0.70 mL, 9.8 mmol) and DABCO (1.15 g, 10 mmol) in 1.0 mL of mixed solvent (1,4-dioxane/water = 1:1 v/v) was added cyclohexyl acrylate (4.8 mL, 30 mmol), and the mixture was stirred for 39 h at room temperature and diluted with water (20 mL) to give the biphasic layer. After collection of the organic layer, the water layer was extracted with ether (20 mL, three times). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, and the filtrate was evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica gel 60N, hexane/ethyl acetate = 10:1 then 8:1 v/v) to give **S3v** (0.495 g, 2.33 mmol) in 24% yield as a colorless liquid: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (d, J = 1.2 Hz, 1H), 5.74 (t, J = 1.2 Hz, 1H), 4.88 (septet, J = 4.4 Hz, 1H), 4.31 (q, J = 6.7 Hz, 1H), 2.65 (d, J = 7.0 Hz, 1H), 1.84−1.90 (m, 2H), 1.64−1.76 (m, 4H), 1.47−1.57 (m, 3H), 1.36−1.44 (m, 2H), 1.27−1.34 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.2, 142.8, 124.7, 73.3, 73.2, 31.5, 29.3, 25.4, 23.7, 10.3; IR (neat, cm^{-1}) 3431, 2935, 2860, 1707, 1628, 1451, 1259, 1167, 1095, 1038, 1014, 982, 950, 819; HRMS (ESI-TOF) m/z [M + H$^+$] calcd for $C_{12}H_{21}O_3$, 213.1491; found, 213.1488.

*Phenyl 3-Hydroxy-2-methylenepentanoate (**S3w**).* Potassium carbonate (14 g, 100 mmol) was dissolved in deionized water (25 mL) and acetone (100 mL) in a 500 mL flask and cooled to 0 °C. To this solution was added acryl chloride (8 mL, 99 mmol) and an acetone (10 mL) solution of phenol (4.79 g, 51 mmol); the mixture was stirred for 4 h at 0 °C to cause precipitation. The white precipitate formed was removed by filtration, the filtrate was evaporated, and the resulting syrup was dissolved in water (50 mL). This was extracted with ether (50 mL, three times) and the combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4, evaporated to dryness, and chromatographed on silica gel flash column (silica gel 60N, hexane/ethyl acetate = 12:1 v/v) to give phenylacrylic acid[22] (6.0 g, 40.6 mmol) in 80% yield.

To a solution of phenylacrylic acid (0.445 g, 3.1 mmol) and DABCO (119 mg, 1.1 mmol) in a mixed solvent of 1,4-dioxane and H_2O (0.1 mL, 1:1 v/v) in a 50 mL flask was added propionaldehyde (0.07 mL, 0.98 mmol), and the mixture was stirred for 113 h at room temperature. Then this was diluted with water (10 mL) and extracted with ether (10 mL, three times). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and evaporated to dryness. The residue was purified by silica gel flash column chromatography (silica fel 60N, hexane/ethyl acetate = 10:1 then 5:1 v/v) to afford **S3w** (0.0663 g, 0.32 mmol) in 33% yield as a colorless liquid: ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.41 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 8.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.52 (s, 1H), 6.01 (s, 1H), 4.44 (q, J = 6.7 Hz, 1H), 2.47 (d, J = 6.8 Hz, 1H), 1.71−1.94 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 165.2, 150.5, 141.9, 129.6, 127.0, 126.1, 121.7, 73.0, 29.3, 10.3; IR (neat, cm^{-1}) 3472, 2968, 2936, 2879, 1728, 1491, 1191, 1162, 1137, 1079, 981, 751, 688; HRMS (ESI-TOF) m/z [M + Na$^+$] calcd for $C_{12}H_{14}O_3Na$, 229.0841; found, 229.0836.

Spectra of Known Compounds. Spectra of known compounds are completely identical with those in the literature cited.

S3b:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.29 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 6.32 (s, 1H), 5.84 (t, J = 1.0 Hz, 1H), 5.53 (d, J = 5.5 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.85 (d, J = 5.5 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.93, 159.30, 142.13, 133.46, 128.00, 125.90, 113.92, 72.94, 55.38, 52.11.

S3c:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 6.34 (s, 1H), 5.83 (t, J = 1.0 Hz, 1H), 5.51 (d, J = 5.7 Hz, 1H), 3.73 (s, 3H), 3.07 (d, J = 5.8 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.8, 141.6, 140.4, 131.7, 128.4, 126.6, 121.9, 72.9, 52.2.

S3d:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (s, 1H), 5.79 (s, 1H), 4.40 (q, J = 7.4 Hz, 1H), 3.78 (s, 3H), 2.52 (d, J = 7.0 Hz, 1H), 1.63 (q, J = 7.4 Hz, 2H), 1.48 (sextet, J = 6.7 Hz, 1H), 1.36 (sextet, J = 7.6 Hz, 1H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.1, 142.7, 124.9, 71.3, 51.9, 38.4, 19.1, 13.9.

S3e:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.39 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 6.31 (d, J = 14.5 Hz, 1H), 6.30 (t, J = 8.0 Hz, 1H), 5.92 (s, 1H), 5.13 (t, J = 6.5 Hz, 1H), 3.80 (s, 3H), 2.89 (d, J = 5.5 Hz,

DOI: 10.1021/acs.joc.5b00530
J. Org. Chem. 2015, 80, 4638−4649

1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.84, 141.23, 136.46, 131.47, 129.23, 128.63, 127.90, 126.66, 126.02, 72.03, 52.14.

S3f:[23] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.30−7.39 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.61 (s, 1H), 6.07 (s, 1H), 5.68 (s, 1H), 2.90 (br s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 164.80, 150.34, 141.80, 141.17, 129.50, 128.59, 128.08, 127.51, 126.83, 126.06, 121.54, 72.99.

S3h:[24] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 7.25−7.26 (m, 1H), 6.96−6.97 (m, 2H), 6.36 (s, 1H), 5.92 (s, 1H), 5.76 (d, *J* = 6.5 Hz, 1H), 3.76 (s, 3H), 3.34 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.56, 145.70, 141.28, 126.85, 126.23, 125.30, 124.81, 69.36, 52.13.

S3m:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (s, 1H), 5.83 (t, *J* = 1.1 Hz, 1H), 4.62 (quintet, *J* = 6.5 Hz, 1H), 3.79 (3H, s), 2.64−2.67 (m, 1H), 1.39 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.2, 143.6, 124.3, 67.1, 52.0, 22.2.

S3n:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.24 (s, 1H), 5.79 (s, 1H), 4.32 (q, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 2.53 (d, *J* = 6.5 Hz, 1H), 1.75−1.63 (sextet, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.1, 142.3, 125.2, 72.9, 51.8, 29.1, 10.1.

S3o:[25] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (d, *J* = 1.0 Hz, 1H), 5.79 (s, 1H), 4.38 (q, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 2.52 (d, *J* = 6.9 Hz, 1H), 1.62−1.70 (m, 2H), 1.27−1.40 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.2, 142.8, 125.1, 71.8, 52.0, 36.0, 28.1, 22.6, 14.1.

S3p:[25] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (d, *J* = 1.0 Hz, 1H), 5.79 (t, *J* = 1.1 Hz, 1H), 4.38 (q, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 2.53 (d, *J* = 6.8 Hz, 1H), 1.81−1.87 (m, 2H), 1.44 (br s, 1H), 1.30 (br s, 5H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.1, 142.7, 124.9, 71.7, 51.9, 36.3, 31.7, 25.6, 22.7, 14.1.

S3q:[24] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.22 (s, 1H), 5.79 (d, *J* = 0.8 Hz, 1H), 4.38 (q, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 2.53 (d, *J* = 6.9 Hz, 1H), 1.58−1.69 (m, 2H), 1.39−1.47 (m, 1H), 1.23−1.35 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.1, 142.7, 124.9, 71.7, 51.9, 36.4, 31.9, 29.2, 25.9, 22.7, 14.1.

S3r:[19] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.21 (s, 1H), 5.80 (s, 1H), 4.45−4.47 (m, 1H), 3.78 (s, 3H), 2.51 (d, *J* = 6.9 Hz, 1H), 1.76−1.84 (m, 1H), 1.55−1.61 (m, 1H), 1.40−1.46 (m, 1H), 0.94 (t, *J* = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 167.2, 142.9, 125.0, 70.1, 52.0, 45.5, 24.9, 23.4, 22.0.

S3t:[26] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.23 (s, 1H), 5.77 (s, 1H), 4.32 (q, *J* = 7.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.57 (d, *J* = 7.0 Hz, 1H), 1.66−1.74 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.7, 142.5, 124.9, 73.1, 60.9, 29.2, 14.2, 10.2.

S3u:[27] ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 6.13 (d, *J* = 1.2 Hz, 1H), 5.68 (t, *J* = 1.1 Hz, 1H), 4.26 (q, *J* = 6.3 Hz, 1H), 2.69 (d, *J* = 6.9 Hz, 1H), 1.65−1.70 (m, 2H), 1.50 (s, 9H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 166.1, 143.6, 124.3, 81.5, 73.5, 29.3, 28.2, 10.4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional text describing general procedures and meaterials; one figure showing UV−visible spectra; one table listing LUMO levels and comparison data in properties of OPVs; and ^{1}H and ^{13}C NMR spectra of **1a−1m**, **2a−2l**, and novel β-hydroxy esters (**S3g**, **S3i**, **S3j**, **S3k**, **S3l**, **S3s**, **S3v**, and **S3w**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The present work was supported by a Grant-in-Aid for Scientific Research of the GSC Center of Tottori University from the Ministry of Education, Culture, Sports, Science and Technology of Japan and was also supported by a fund for Environmental Research from Tottori Prefecture. We are grateful to Professor Hideyuki Murata and Ryo Itou of Japan Advanced Institute of Science and Technology for measurement of OPV properties of fullerene derivatives.

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