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Methanofullerenes, $C_{60}(CH_2)_n$ (n = 1, 2, 3), as Building Blocks for High-Performance Acceptors Used in Organic Solar Cells

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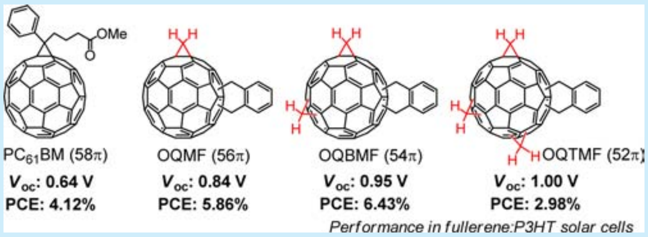
Ⓢ *Supporting Information*

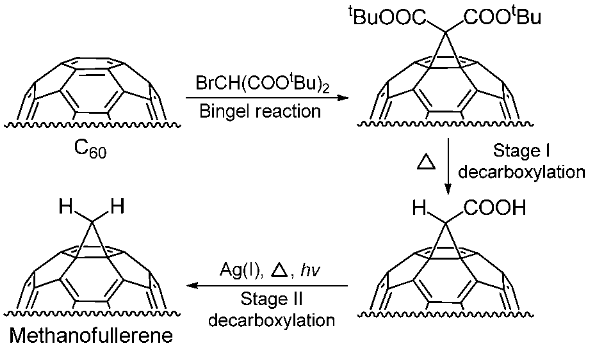
ABSTRACT: Selective preparation of $C_{60}(CH_2)_n$ (n = 1, 2, 3) was realized via a "Bingel-decarboxylation" route. A 54π-electron derivative of $C_{60}(CH_2)_2$, OQBMF, demonstrates an outstanding power conversion efficiency (PCE) of 6.43% (V_{oc} = 0.95 V, J_{sc} = 9.67 mA cm^{-2}, FF = 70%) in fullerene:P3HT solar cells since the small CH_2 addends lift up fullerene LUMO and increase V_{oc} significantly without decreasing mobility significantly.



Organic solar cells (OSCs) are promising devices for solar energy harvesting.[1] Recently, derivatives of 1,2-dihydromethano[60]fullerene ($C_{60}CH_2$) as acceptor materials in OSCs have attracted great interest. Unique properties for these molecules are as follows: (1) the CH_2 group effectively lifts up the fullerene LUMO level, leading to high open-circuit voltage (V_{oc}); (2) the sterically compact CH_2 addend does not affect fullerene packing in the solid state, guaranteeing good electron mobility and leading to high short-circuit current (J_{sc}) and fill factor (FF).[2] Two 56π-electron methanofullerene derivatives, $C_{60}(CH_2)$(indene) and *o*-quinodimethane-methano[60]fullerene (OQMF), performed well in fullerene:poly(3-hexylthiophene) (P3HT) solar cells, affording 5.9% and 5.74% PCE, respectively.[3] Using a small CH_2 addend can improve the performance of fullerene acceptors with high LUMO levels, such as 54π fullerenes. Replacing one bulky addend of a 54π C_{60} tris-adduct with a CH_2 addend led to a ~10 times increase in electron mobility and a ~4 times increase in PCE.[4] In this regard, methanofullerenes with more CH_2 addends (e.g., $C_{60}(CH_2)_2$ or $C_{60}(CH_2)_3$) might be better platforms than $C_{60}CH_2$ for developing efficient acceptors with high LUMO levels. However, pure $C_{60}(CH_2)_2$ or $C_{60}(CH_2)_3$ has not been obtained due to synthesis difficulty. In this work, we developed an innovative "Bingel-decarboxylation" approach to selectively prepare $C_{60}CH_2$, $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$. A 54π *o*-quinodimethane-bis-methano[60]fullerene (OQBMF) and a 52π *o*-quinodimethane-tris-methano[60]fullerene (OQTMF) were further synthesized by Diels−Alder derivatization of $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$, respectively. With a high LUMO level (−3.40 eV) and an electron mobility of 1.1×10^{-4} cm^2 V^{-1} s^{-1}, OQBMF exhibits an outstanding photovoltaic performance. The OQBMF:P3HT solar cells afforded a PCE of 6.43%, with good V_{oc} (0.95 V) and J_{sc} (9.67 mA cm^{-2}), and an impressive FF (70%).

There are only a few methods developed for synthesizing methanofullerenes. Initially, C_{60} was treated with diazomethane to produce mono- and multiadducts of methanofullerene.[5] This reaction gave a mixture of products in low yield. The separation of pure multiadducts (e.g., $C_{60}(CH_2)_2$ or $C_{60}(CH_2)_3$) from the mixture was unsuccessful due to their similar polarity and low solubility.[5b] Other methods, such as the cyclopropanation of C_{60} by CH_2I_2/Zn[6] and the electrochemical synthesis,[7] met similar issues on yields and separation. Nakamura et al. developed an effective approach for selectively preparing $C_{60}CH_2$.[2a] The synthesis involves a monoaddition of a silylmethyl Grignard reagent to C_{60} and an oxidative cyclopropanation of the resulting silylmethylfullerene by using $CuCl_2$ in the presence of a base. However, this approach could not produce multiadducts of methanofullerene. Our "Bingel-decarboxylation" approach for preparing methanofullerenes includes three steps: (1) a Bingel reaction of C_{60} and di-*tert*-butyl 2-bromomalonate gives a cyclopropanation product in good yield;[8] (2) thermolysis of the Bingel product quantitatively removes the *tert*-butyl groups and cleaves one carboxylic acid group;[9] (3) a silver-mediated decarboxylation reaction cleaves the remaining carboxylic acid group and produces methanofullerene (Scheme 1). The advantage for this

Scheme 1. A "Bingel-Decarboxylation" Strategy for Synthesizing Methanofullerenes



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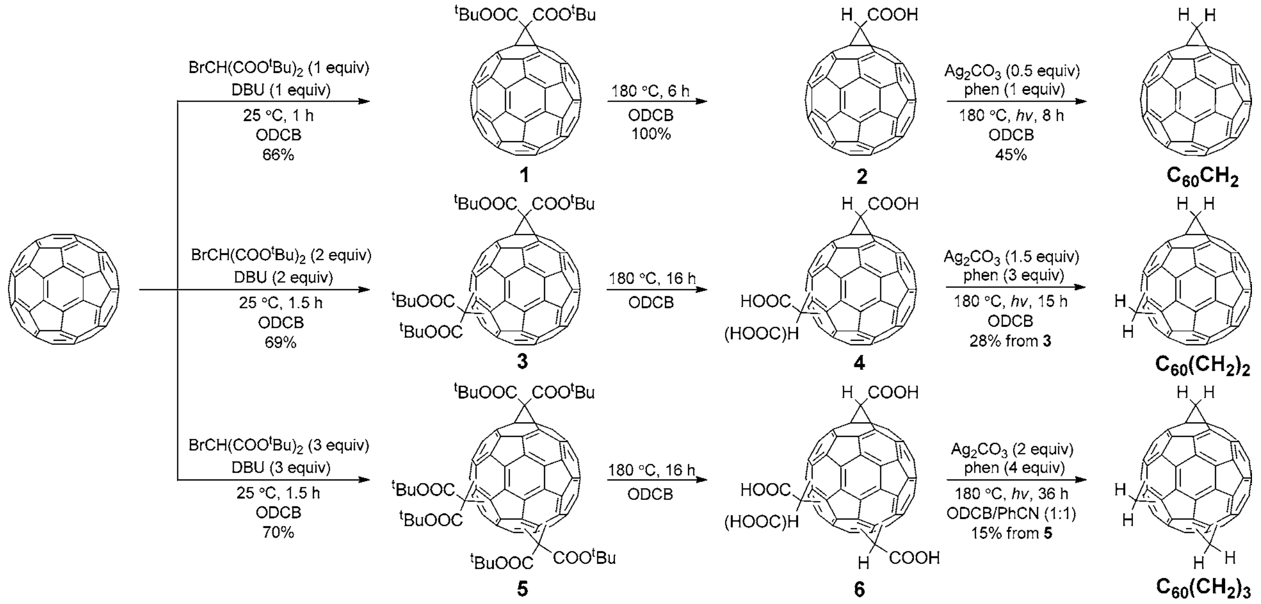
Scheme 2. Synthesis of $C_{60}CH_2$, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$[a]



[a] Compounds **3**–**6**, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$ contain regioisomers.

approach is that the mono-, bis-, and tris-adducts of the Bingel reaction can be selectively synthesized by controlling the equivalent of $BrCH(COO^tBu)_2$ from 1 to 2 to 3, and unlike methanofullerenes, these precursors can be easily purified through silica gel column chromatography due to their different polarity and good solubility. Consequently, it is easy to obtain pure $C_{60}CH_2$, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$, respectively.

We started our work from $C_{60}CH_2$ synthesis (Scheme 2). The Bingel product **1** was prepared in 66% yield by treating C_{60} with 1 equiv of $BrCH(COO^tBu)_2$ and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU). Refluxing compound **1** in *o*-dichlorobenzene (ODCB) gave fullerene carboxylic acid **2** in 100% yield. Compound **2** was confirmed by NMR.[10] To obtain $C_{60}CH_2$ from **2**, we screened different reaction conditions (see Supporting Information). First, we found that decarboxylation only took place in the presence of Ag(I) and 1,10-phenanthroline (phen).[11] Other metal compounds (e.g., Cu, Pd) and ligands (or additives) did not help the reaction (Table S1, entries 1–17). Second, heating and light irradiation accelerate the reaction and improve the yield (Table S1, entries 18–25). Third, a catalytic version of this reaction failed (Table S1, entries 26–27). The best yield, 51%, was achieved with 0.5 equiv of Ag_2CO_3, 1 equiv of phen, and light irradiation at 180 °C. A 45% yield was achieved in a 500 mg-scale synthesis, suggesting that the decarboxylation reaction can be scaled up. Although the mechanism for the decarboxylation remains unclear at this stage, we speculate that $C_{60}CH_2$ was generated via a decomposition of silver carboxylate of compound **2**.[12] We applied this "Bingel-decarboxylation" approach for synthesizing $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$. Treating C_{60} with 2 or 3 equiv of $BrCH(COO^tBu)_2$ and DBU afforded bis-adduct **3** or tris-adduct **5** in 69% and 70% yields, respectively. Compounds **3** and **5** were further converted to fullerene carboxylic acids **4** and **6** via thermolysis. Although the heat-promoted decarboxylation in this step was incomplete (Figures S28 and S30), **4** and **6** were directly used as the starting materials for the next decarboxylation. Treating **4** with 1.5 equiv of Ag_2CO_3 and 3 equiv of phen, and **6** with 2 equiv of Ag_2CO_3 and 4 equiv of phen removed all –COOH groups on **4** and **6** and afforded $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ in 28% and 15% yields, respectively.

Methanofullerenes were characterized by spectroscopic methods. The C_{2v} symmetric $C_{60}CH_2$ shows one singlet peak at 3.92 ppm in the ^1H NMR spectrum and 17 peaks (15 in sp^2 region and 2 in sp^3 region) in the ^{13}C NMR spectrum.[5a] $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ consist of regioisomers as indicated by NMR spectra. $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ show peaks at 3–4 ppm for CH_2 protons, and without AB quartets at lower or higher field, indicating that there are no [5,6]-open fulleroid isomers existing in $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ products.[13] These results also indicate that no fullerene skeleton rearrangement took place during the decarboxylation processes. MALDI-TOF mass spectra gave molecular ion peaks (M^+) at 734, 748, and 762 (*m*/*z*), corresponding to $C_{60}CH_2$, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$, respectively (Figure 1a). The low-intensity peaks for $M^+ \pm 14$ suggested that some CH_2 addends were cleaved and re-added to methanofullerenes under MS conditions. HPLC profiles of C_{60}, $C_{60}CH_2$, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$ are shown in Figure 1b. The retention time decreases as CH_2 addends increase. Different from C_{60} and $C_{60}CH_2$, $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ show several chromatographic peaks due to the regioisomers. $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$ show low solubility in common organic solvents and cannot be directly used as acceptors in OSCs. They were further modified with *o*-quinodimethane diene through a Diels–Alder reaction (Figure 2b).[14] OQBMF and OQTMF were obtained in 40% and 46% yields, respectively. The integral ratios between aromatic protons (7–8 ppm) and aliphatic protons (2–5 ppm) on ^1H NMR are 1:2 and 1:2.5 for OQBMF and OQTMF, respectively, indicating that only 1 equiv of diene was added to fullerene. High resolution ESI mass spectra showed the expected molecular ion peaks ($M + H^+$), 853.0999 and 867.1152, for OQBMF and OQTMF, respectively (Figures S31–S32). Compared with $C_{60}(CH_2)_2$ and $C_{60}(CH_2)_3$, OQBMF and OQTMF show good solubility, 100 and 70 mg mL^{-1} in ODCB, respectively.

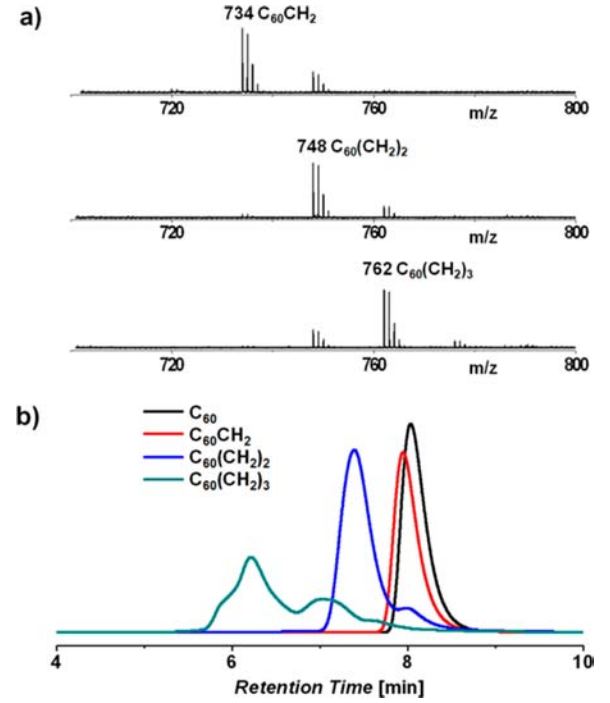


Figure 1. (a) MALDI-TOF mass spectra for $C_{60}CH_2$, $C_{60}(CH_2)_2$, and $C_{60}(CH_2)_3$; (b) HPLC analysis. Retention time: C_{60} 8.03 min; $C_{60}CH_2$ 7.95 min; $C_{60}(CH_2)_2$ (major peak) 7.39 min; $C_{60}(CH_2)_3$ (major peak) 6.21 min.

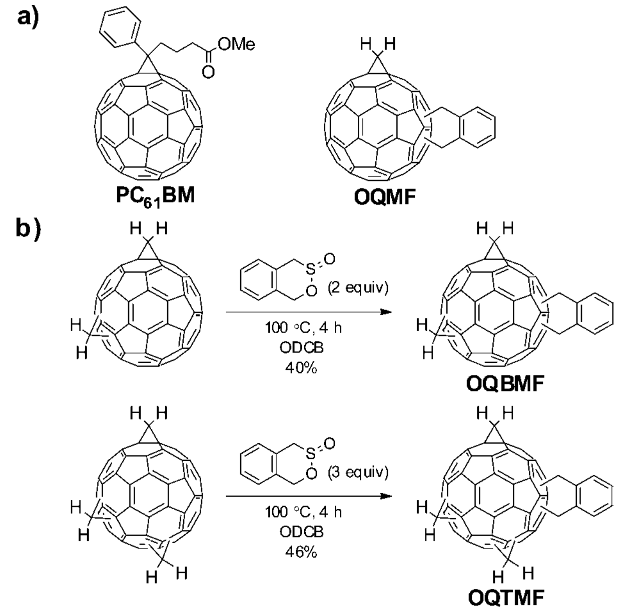


Figure 2. (a) Structures of $PC_{61}BM$ and OQMF; (b) synthesis of OQBMF and OQTMF.

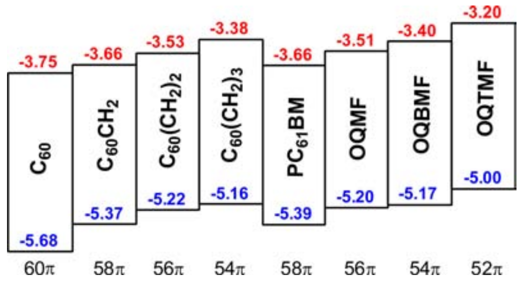


Figure 3. LUMO (red) and HOMO (blue) energy levels of fullerenes (eV).

We studied the energy levels of the new fullerenes, $C_{60}(CH_2)_2$, $C_{60}(CH_2)_3$, OQBMF, and OQTMF, as well as the references, C_{60}, $C_{60}CH_2$, $PC_{61}BM$, and OQMF, by cyclic voltammetry (CV) and UV−vis absorption (Figures S33−S36, Table S2).[15,16] All the LUMO and HOMO levels of the fullerenes are compared in Figure 3. The LUMO level is lifted up as the fullerene π-system shrinks.[2,4] From 60π C_{60} to 52π OQTMF, reducing two π-electrons on fullerene lifts the LUMO level up for 0.1−0.2 eV. It is very interesting to note that the optical band gap (E_g^{opt}) increases as the π-system shrinks from 56π OQMF to 52π OQTMF, while it decreases as the π-system shrinks from 60π C_{60} to 56π $C_{60}(CH_2)_2$. 56π $C_{60}(CH_2)_2$ and OQMF possess the smallest band gaps (1.69 eV). Fullerenes with the same number of π-electrons, such as $C_{60}CH_2$ and $PC_{61}BM$ (58π), $C_{60}(CH_2)_2$ and OQMF (56π), and $C_{60}(CH_2)_3$ and OQBMF (54π), show similar LUMO and HOMO levels. 54π OQBMF and 52π OQTMF with a higher LUMO level are expected to provide higher V_{oc} for solar cells compared with 58π $PC_{61}BM$ and 56π OQMF.

The photovoltaic performance of OQBMF and OQTMF and the references, $PC_{61}BM$ and OQMF, in solar cells with a structure of ITO/PEDOT:PSS/fullerene:P3HT/Ca/Al were investigated. V_{oc}, J_{sc}, FF, and PCE data are listed in Table 1. J–V curves and EQE spectra are shown in Figure S37. 54π OQBMF solar cells gave the best performance. OQBMF cells afforded not only a high V_{oc} of 0.95 V, which is 0.11 V higher than that of OQMF cells and 0.31 V higher than that of $PC_{61}BM$ cells, but also a good J_{sc} of 9.67 mA cm^{-2} and a high FF of 70%, which are comparable to those of OQMF cells (J_{sc} = 9.96 mA cm^{-2}, FF = 70%) and $PC_{61}BM$ cells (J_{sc} = 9.47 mA cm^{-2}, FF = 68%). The 6.43% PCE of OQBMF cells is among the highest PCEs reported for fullerene:P3HT solar cells.[3,17] Compared with the indene C_{60} bis-adduct ($IC_{60}BA$) developed by Li et al., the OQBMF acceptor shows great potential in enhancing the V_{oc} of OSCs due to its high LUMO level.[18] A high V_{oc} of 1.00 V was obtained for 52π OQTMF cells, with a J_{sc} of 5.52 mA cm^{-2} and an FF of 54%, leading to a PCE of 2.98%.

Table 1. Performance of the Solar Cells Based on P3HT and Different Fullerene Acceptors under AM 1.5G Illumination (100 mW cm^{-2})[a]

fullerene	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	mobility (cm^2 V^{-1} s^{-1})
$PC_{61}BM$	0.64	9.47	68	4.12	1.6×10^{-4}
OQMF	0.84	9.96	70	5.86	1.5×10^{-4}
OQBMF	0.95	9.67	70	6.43	1.1×10^{-4}
OQTMF[b]	1.00	5.52	54	2.98	2.2×10^{-5}

[a] Blend concentration: 24 mg/mL in ODCB; donor/acceptor ratio (w/w): 1:0.6; annealed at 150 °C. [b] Annealed at 90 °C.

The J_{sc} and FF for OQBMF solar cells are the best results for 54π-fullerene-based devices, suggesting OQBMF's decent electron mobility.[4] The electron mobilities for $PC_{61}BM$, OQMF, OQBMF, and OQTMF were measured by the space charge limited current (SCLC) method (Figure S38, Table 1). As expected, OQBMF possesses a good electron mobility of 1.1 × 10^{-4} cm^2 V^{-1} s^{-1}, which is slightly lower than that of OQMF

(1.5×10^{-4} cm^2 V^{-1} s^{-1}) and PC$_{61}$BM (1.6×10^{-4} cm^2 V^{-1} s^{-1}). This result indicates that a fullerene derivative with two CH$_2$ addends can still maintain high electron mobility. The low electron mobility of OQTMF (2.2×10^{-5} cm^2 V^{-1} s^{-1}) accounts for the low J_{sc} and FF of OQTMF devices.

In summary, we have developed an innovative "Bingel-decarboxylation" approach for preparing methanofullerenes. This method employs no explosive or air- and moisture-sensitive reagents and selectively synthesizes C$_{60}$(CH$_2$)$_2$ and C$_{60}$(CH$_2$)$_3$. C$_{60}$(CH$_2$)$_2$ is a promising building block for developing efficient fullerene acceptors. A Diels–Alder derivative of C$_{60}$(CH$_2$)$_2$, OQBMF, demonstrates a 6.43% PCE in fullerene:P3HT solar cells. Compared with 58π and 56π fullerene acceptors, 54π OQBMF shows a great advantage in enhancing V_{oc} due to its high LUMO level. The two sterically compact CH$_2$ addends on OQBMF are the key to realizing high performance since they can significantly increase the fullerene LUMO level while maintaining decent electron mobility, while suppressing V_{oc}–J_{sc} and V_{oc}–FF trade-offs which always accompany solar cells based on high-LUMO-level fullerenes. Future work will focus on using methanofullerenes as building blocks to develop outstanding fullerene acceptors for highly efficient OSCs.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details including synthesis, measurements, and instruments. 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.

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