A Facile Way for Synthesis of High Performance Electron Receptor MCB: A Promising Replacer of PCBM

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Methyl 4-C₆₁-benzoate (MCB) series fullerene materials with low cost and high yield, including monoadduct (MCBM) and bisadduct (MCBB) compounds, were synthesized and their photophysical and electrochemical properties were investigated. Fabricated photovoltaic devices based on both two materials showed power conversion efficiency of 3.48% and 0.16%, respectively. The MCBM exhibited higher PCE relative to PCBM’s 3.40%. The LUMO energy level of MCBM was 0.03 eV lower than that of PCBM, and it was facile to be synthesized by two steps with high yield of 55% from low-cost industrial commercials, whose molecular weight was 868.0 g/mol. This work supplied new route to design fullerene materials as PCBM’s alternative.

Keywords Bulk heterojunction, fullerene, photovoltaic property, MCBM

 Fullerene derivatives are extensively used in the organic photovoltaics (OPVs) due to their high electron affinity and high mobility (1,2), in which [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) is the most widely employed material (3). Material scientists have done exhaustive research on improving the photovoltaic performance of fullerene materials in recent 10 years (2,4–19).

 Fullerene had a high conjugated 60 π electron structure, while addition onto the fullerene sphere would decrease the conjugated structure partly with the decrement of the π number of fullerene ball. In simplified mode, the V_OC is linear related to the bandgap between HOMO of donors (D) and LUMO of acceptors (A) (20). Many studies have shown that result in analogue materials (8-9,18). Herein, many works were reported to increase

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the LUMO energy level of A by reducing the \( \pi \) number of fullerene core (11,16,21–22). However, there were also enough cases indicating opposite or non-tight-related trend (2,15,16,22) because whether in nonsimplified theory or reality, \( V_{OC} \) depends on five main factors: energy gap between D and A, temperature, light intensity, work function of the electrode, and material microstructure. Wang et al. reviewed the related theoretical results and technology (23).

Higher LUMO energy levels may reduce the stability of the fullerene. The relation between the LUMO energy level of A and stability is a paradox situation (23,24). Is there certain fullerene material with the same or lower LUMO energy level than that of PCBM as well as competitive photovoltaic performance, that is, higher \( J_{SC} \) and \( FF \) to compensate the loss of \( V_{OC} \)? The answer may be yes. Previously (15), we developed t-BCB series of fullerene materials, which had a carbonyl (electron-withdrawing) group on the phenyl ring attached to the fullerene core bridged by a methano group. The best material of highest photovoltaic performance was the monoadduct compound, t-BCB-M, whose LUMO energy level was 0.03 eV lower than that of PCBM while it performed PCE of 2.43% compared with PCBM’s 3.8%. The materials with this backbone seemed promising and structure-tailored, albeit their solubility was relatively low and they did not display a high enough performance. Herein, we tried to obtain their analogue of high performance especially aimed at improving their solubility. When the tert-butyl group was substituted with the methyl group, namely, methyl 4-C\(_{61}\)-benzoate (MCB) series of fullerene materials, we found not only the solubility was much improved but also the photovoltaic performance of monoadduct compound (MCBM) was promoted comparable to that of PCBM. Here, we reported a facile strategy to synthesize a new series of fullerene derivatives as well as detailed photophysical, electrochemistry, and photovoltaic studies. Also, its synthesis was convenient and inexpensive (Figure 1).

The visible spectra of the MCB derivatives in c.a. \( 10^{-5} \) M toluene solution was calibrated to concentration to that of PCBM (Figure 2). Both fullerene derivatives having weak absorption in c.a. 700 nm were convinced that they were [6,6]methanofullerene conversed from [5,6] and [6,6] fullerene mixtures.(25) Because there were several isomers in multiadduct mixture of MCBB with varied electronic energy levels, no sharp peak but rather a broad band was observed in a visible region. The absorption of MCBM was weaker than that of PCBM; however, the band structure of PCBM and MCBM was similar. The absorption of MCBB was much stronger than that of MCBM and PCBM, indicating that the electron structures of C\(_{60}\) cage had been changed enormously by multiadducts with the relation of MCBB > PCBM > MCBM in respect of LUMO levels.

Samples were kept at 100°C in vacuo for 24 hours before thermal analysis. TG/DTA were measured to understand the thermal stability of the fullerene derivatives as shown in Figure 3. The results indicated that the thermal decomposition temperature of all fullerene

![Figure 1. Structures of MCBM and MCBB fullerene derivatives.](image-url)
derivatives was higher than 350°C (onset temperature), which was 410°C and 380°C for MCBM and MCBB, respectively. High thermal decomposition temperature ensures that the thin film of OPV devices is safe during thermal annealing treatment. The analysis of DSC showed no crystallization ($T_c$) or glass transitions ($T_g$) between 20°C and 200°C, suggesting that the MCB series were amorphous materials (2).

The LUMO energy levels of the MCB derivatives were measured by cyclic voltammetry (CV) in $10^{-4}$ to $10^{-3}$ M α-DCB solution. $E_\text{red}^{\text{loneq}}$ was onset values in V vs. Fe/Fe$^+$ (internal standard); TBAPF$_6$ of 0.1 M was supporting electrolyte. Pt wire was counter electrode, Ag wire as reference electrode, glassy carbon as work electrode; scan rate was 50 mV·s$^{-1}$; room temperature was c.a. 25°C; and $\Delta$ was the difference between the LUMO energy level of materials and that of PCBM. All the reduction potentials of the two fullerene derivatives were measured as shown in Table 1 and Figure 4. The LUMO energy levels were estimated from onset value of their first reduction potential ($E_\text{red}^{\text{loneq}}$) according to equation (1).

$$\text{LUMO} = -e(E_{\text{red}}^{\text{loneq}} + 4.80)$$

The $E_{\text{red}}^{\text{loneq}}$ of MCB series decreased successively from MCBM to MCBB, and their LUMO energy levels increased successively. The LUMO energy level of MCBM was 0.03 eV lower than that of PCBM because of electron-withdrawing effects of the carbonyl group on the
Table 1
Electrochemistry properties of fullerene derivatives

| Fullerene | Reduction Potential (V) | LUMO (eV) | Δ (eV) |
|-----------|-------------------------|-----------|--------|
| C\(_{60}\) | −1.02                   | −3.78     | −0.07  |
| PCBM      | −1.09                   | −3.71     | 0.00   |
| MCBM      | −1.06                   | −3.74     | −0.03  |
| MCBB      | −1.15                   | −3.65     | 0.06   |

Δ was the difference between the LUMO energy level of materials and that of PCBM.

Figure 4. Cyclic voltammograms of MCBM and MCBB in o-DCB, calibrated to the Fe/Fe\(^+\).

phenyl ring. Both were electro-reversible testified by the symmetric peaks, equal \(i_{pa}\) and \(i_{pc}\), small Δ \(E_p\) of the red-ox couples.

The BHJ photovoltaic properties of MCB analogues as electron acceptors and P3HT as electron donors were measured. The performance was optimized in the contents of film thickness, thermal annealing time and temperature, weight ratio of donor versus acceptor, and organic addition; the optimized fabrication condition is shown in Table 2, performance indices in Table 3 and J-V curves in Figure 5, quantum efficiency in Figure S3. The performance of MCBB was much lower than that of MCBM with FF of 38%, which suggested that MCBB compound had non-ohmic contact with electrode, otherwise the hole mobility of P3HT and the electron mobility of MCBB were not match; and \(J_{SC}\) of 0.87 mA cm\(^{-2}\)

Table 2
Optimized fabrication technique of P3HT:MCB devices

| Fullerene | Coating | Con. Ratio | Rate | Coating Time | Thickness | Annealing Temp | Annealing Time | Addition |
|-----------|---------|------------|------|--------------|-----------|----------------|----------------|---------|
| MCBM      |         | 15 1:1     | 500  | 18           | 200       | 110            | 10             | none    |
| MCBB      |         | 15 1:1     | 500  | 45           | 200       | 110            | 10             | None    |
Facile Way for Synthesis of High Performance Electron Receptor MCB

Table 3
Photovoltaic performance indices of P3HT:MCB devices

| Fullerene | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | FF (%) | $R_S$ (Ω·cm$^2$) | $R_{SH}$ (Ω·cm$^2$) |
|-----------|---------|--------------|--------------------------|--------|------------------|---------------------|
| PCBM      | 3.40    | 0.63         | 8.57                     | 60     | 4.5              | 2566                |
| MCBM      | 3.48    | 0.60         | 8.43                     | 65     | 3.1              | 1754                |
| MCBB      | 0.16    | 0.50         | 0.87                     | 38     | 13.3             | 1149                |

$R_S$, series resistance; $R_{SH}$, Shunt resistance.

Figure 5. The $J$-$V$ curves of P3HT:MCB devices.

was attributed to low mobility because of rather many isomers, also inconsistent $V_{OC}$ with its LUMO energy level. Obviously, MCBM performed better than MCBB with PCE of 3.48%, slightly higher than PCBM’s 3.40%. $V_{OC}$ of MCBM was 0.03 V lower than that of PCBM, which was consistent with LUMO energy level relationship. Also, MCBM’s $J_{SC}$ was 8.43 mA·cm$^{-2}$ slightly lower than PCBM’s 8.57 mA·cm$^{-2}$, which was attributed to the lower absorption of MCBM compared with that of PCBM, as well as approaching high electron mobility of MCBM to that of PCBM. The $R_S$ of MCBM based device was 1.6 Ω·cm$^2$ lower than that of PCBM also much lower than that of MCBB, which was auxiliary evidence for the better performance of MCBM in semiconductor content while the $R_{SH}$ of MCBM-based device was not bigger than PCBM, which was another reason why the performance of MCBM was not much better than PCBM. The organic field effect transistor (OFET) based on MCBM was fabricated with electron mobility of 3×10$^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$ (Figure S4), 10 fold lower than PCBM’s 2×10$^{-3}$ cm$^2$·V$^{-1}$·s$^{-1}$. The FF value of MCBM based devices was 65% much higher than PCBM’s 60% leading to MCBM’s performance was slightly higher than PCBM’s. The QE spectra of MCBM based device showed that the photocurrent was mainly attributed to the absorption of polymers. We speculated that MCBM with smaller molecular volume than PCBM (molecular weight of MCBM was 868 g·mol$^{-1}$ smaller than PCBM’s 910 g·mol$^{-1}$) was a crucial factor. MCBM might tend to penetrate into interval among the alky chain of P3HT because of its smaller molecular volume compared with that of PCBM, then MCBM and P3HT had excellent miscibility and maybe a faster charge separation rate than that of recombination. To date, MCBM is the second-smallest fullerene derivatives whose PCE is higher than 3.4% (the smallest one...
is indene monoadduct fullerene compound (11)), while it is the smallest methanofullerene material with such high photovoltaic performance.

Optical microscope results clearly show that MCBM has a smooth surface (Figures 6a, b); however, a number of crystals precipitated on the surface of MCBB films (Figures 7a, b), which suggested that the miscibility between P3HT and MCBB was poorer than that of P3HT and MCBM. AFM showed that the scale of surface phase separation of MCBM-based devices was large and vague (Figures 6c, d), around 100∼200 nm, which were much bigger than PCBM’s 10∼30 nm. One possible explanation was that the vertical phase separation of MCBM-based devices was not homogeneous with higher content of polymer on the top of the active layer. It seemed that the rather big phase separation scale didn’t affect the performance of MCBM. Although the scale of phase separation of MCBB was smaller with 50∼100 nm (Figures 7a, b), but the miscibility problem led to low performance of MCBB as shown in OM pix. The device fabrication based on MCBM and other polymers was on the way.

Conclusions

We had successfully synthesized two novel fullerene derivatives; that is, monoadduct of MCBM and bisadduct of MCBB. MCBM was facile to synthesize by two steps with a high yield of 55% from low-cost industrial commercials. The monoadduct-based device exhibited a power conversion efficiency of 3.48%, which was slightly higher than PCBM’s
Facile Way for Synthesis of High Performance Electron Receptor MCB 295

Figure 7. Morphology images of MCBB based devices. OM pix: a, b, AFM pix: c, d, phase images, 500 nm × 500 nm (color figure available online).

3.40% in the same condition, though MCBM’s $V_{OC}$ was 0.03 V lower than that of PCBM. Possible favored explanation was its smaller molecular volume. Our results provided a new route to design fullerene material as PCBM’s alternative, according to the principle “the simpler, the better.”

Experimental

Materials and Methods

All solvents were purified and freshly distilled prior to use according to literature procedures and purification handbook. Commercially available materials were used as received. Synthesis, experimental and characterization conditions, and detailed data were showed in the supporting information. C$_{60}$, 99.9% purity, was provided by Henan Yongxin Company (China); ferrocene (A.R.) was bought from China National Medicines Corporation Ltd. and then extracted by hexane; $o$-DCB for synthesis and CV was HPLC grade supplied by Ouhe Chemicals Corp. (Beijing, China), and for device fabrication supplied by Aldrich with 98+% purity of Extra Dry and acroseal; poly (3-hexylthiophene-2,5-diyl) (P3HT) was bought from Aldrich. Poly (ethylene dioxythiophene):polystyrenesulfonic acid (PEDOT:PSS) was CLEVIOS A1 4083; TBAPF$_6$ (A.R.) was bought from Alfa and then recrystallized in EtOH for two times and dried in vacuo at 80°C. $^1$H NMR and $^{13}$C NMR
spectra were measured on Bruker Avance 400 and 600 spectrometers, calibrated using signals from trimethylsilane (TMS) and reported downfield from TMS. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured on Bruker Biflex III MOLDI-TOF spectrometer which gave the M⁻, consistent with the calculated mass of all synthesized C₆₀ derivatives. The Fourier transform infrared (FT-IR) spectra were measured on Bruker Tensor-27 and showed absorption features at 526 cm⁻¹ c.a. indicative the [60]fullerene core. Thermo Gravimetric/Differential Thermal Analysis (TG/DTA) was measured on Shimadzu DTG-60 and Differential Scanning Calorimetry (DSC) on PerkinElmer Diamond DSC (N536-0022) F.T. Thickness of film was tested by profilometer on Tencor ALFA-Step 500 or Ambios Technology XP-2. AFM was measured on SEIKO SPA400, tapping mode (DFM). HPLC was tested on JAI LC-9104, Cosmoil Buckyprep 20 mm (ID) × 250 mm for preparation and Waters 660, Cosmoil Buckyprep Waters 4.6 mm (ID) × 250 mm for analysis. Cyclic Voltammetry (CV) was measured on Chi660d. Optical Microscope (OM) was measured on Olympus BX51. UV-Vis spectra were tested on JASCO V-570.

The device structure used in this study was a classic sandwich structure Glass/ITO/PEDOT:PSS/P3HT:Fullerens/Ca/Al (Figure S2). Indium/tin oxide (ITO, 150 nm thick) glasses were cleaned by supersonic treatment in deionized water, acetone, and i-propanol for at least 10 minutes, respectively, and then by O₂ plasma treatment for 6 minutes at 300 W, which was used as the anode and a thin layer of PEDOT:PSS was incorporated between the ITO and the active layer to reduce device leakage, which was around 35 nm thick spin-coated at 3000 rpm for 60 s, baked at 140°C and then 10 minutes to dry. Methanofullerenes and P3HT in different weight ratio were mixed and then dissolved in o-DCB solution around 17 mg·mL⁻¹, respectively. The solution was filtered by 0.25 μm filter or not to optimize morphology, and then spin-coated onto PEDOT:PSS at different rates for varied time to optimize device performance. In the structure of the devices, the active layer had a thickness of around 90~200 nm. Time for solvent annealing (SA) was around 30 minutes, then prethermal annealed (PTA) at 110°C for 30 minutes or 150°C for 10 minutes in a glove box and then cooled in air in a glove box. At last, Ca layer of 25 nm and Al layer of 80 nm as an electron-collecting electrode were thermally deposited on the active layer respectively in vacuo. The deposition rates, usually 0.05~0.10 nm·s⁻¹, and the thickness of the evaporation layers was monitored by a thickness/rate meter (FTM-V). The crossing area between the cathode and the anode defined the sensing area. Device area was around 0.044 cm² or 0.168 cm² calibrated by OM. All the fabrication steps were carried out in a nitrogen glove box with H₂O < 0.1 ppm and O₂ < 0.1 ppm. The J–V measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in a glove box under simulated AM 1.5G irradiation (100 mW·cm⁻²) using a Newport xenon lamp-based solar simulator. The QE measurements of the OPVs were performed using a Newport QE System. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. We tried diverse weight ratio of polymer versus fullerene, film thickness, additive (1-bromothiophene or 1,12-diiodooctane), temperature and time of thermal annealing to optimize the devices to best performance.

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Supplemental Material
Supplemental data for this article can be accessed on the publisher’s website.

References
1. Yu, G., Gao, J., Hummelen, J. C., Wudl, F., and Heeger, A. J. (1995) Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science*, 270(5243): 1789–1791.
2. Liu, C., Xiao, S., Shu, X., Li, Y., Xu, L., Liu, T., Yu, Y., Zhang, L., Liu, H., and Li, Y. (2012) Synthesis and photovoltaic properties of novel monoadducts and bisadducts based on amide methanofullerene. *ACS Appl. Mater. Interfaces*, 4(2): 1065–1071.
3. Hummelen, J. C., Knight, B. W., Lepeq, F., Wudl, F., Yao, J., and Wilkins, C. L. (1995) Preparation and characterization of fulleroid and methanofullerene derivatives. *J. Org. Chem.*, 60(3): 532–538.
4. Matsuo, Y., Sato, Y., Niinomi, T., Soga, I., Tanaka, H., and Nakamura, E. (2009) Columnar structure in bulk heterojunction in solution-processable three-layered p-i-n organic photovoltaic devices using tetrabenzo[60]porphyrin precursor and silylmethyl[60]fullerene. *J. Am. Chem. Soc.*, 131(44): 16048–16050.
5. Li, C.-Z., Matsuo, Y., Niinomi, T., Sato, Y., and Nakamura, E. (2010) Face-to-face C6F5[π][60]fullerene interaction for ordering fullerene molecules and application to thin-film organic photovoltaics. *Chem. Commun.*, 46(45): 8582–8584.
6. Cheng, Y.-J., Liao, M.-H., Chang, C.-Y., Kao, W.-S., Wu, C.-E., and Hsu, C.-S. (2011) Di(4-methylphenyl)methano-C60 bis-adduct for efficient and stable organic photovoltaics with enhanced open-circuit voltage. *Chem. Mater.*, 23(17): 4056–4062.
7. Zhang, C., Chen, S., Xiao, Z., Zu, Q., and Ding, L. (2012) Synthesis of mono- and bisadducts of thieno-o-quinodimethane with C60 for efficient polymer solar cells. *Org. Lett.*, 14(5): 1508–1511.
8. Meng, X., Zhang, W., Tan, Z. a., Li, Y., Ma, Y., Wang, T., Jiang, L., Shu, C., and Wang, C. (2012) Highly efficient and thermally stable polymer solar cells with dihydronaphthyl-based [70]fullerene bisadduct derivative as the acceptor. *Adv. Funct. Mater.*, 22(10): 2187–2193.
9. Meng, X., Zhang, W., Tan, Z. a., Du, C., Li, C., Bo, Z., Li, Y., et al. (2012) Dihydronaphthyl-based [60]fullerene bisadducts for efficient and stable polymer solar cells. *Chem. Commun.*, 48(3): 425–427.
10. Mikroyannidis, J. A., Tsagkournos, D. V., Sharma, S. S., and Sharma, G. D. (2011) Synthesis of a broadly absorbing modified PCBM and application as electron acceptor with poly(3-hexylthiophene) as electron donor in efficient bulk heterojunction solar cells. *J. Phys. Chem. C*, 115(15): 7806–7816.
11. Laird, D. W., Richter, H., Vejins, V., Scott, L. T., Lada, T. A. (2009) Organic photovoltaic devices comprising fullerene and derivatives thereof and improved methods of making fullerene derivatives. World Intellectual Property Organization WO 2009/086210.
12. Lenes, M., Shelton, S. W., Sieval, A. B., Kronholm, D. F., Hummelen, J. C., and Blom, P. W. M. (2009) Electron trapping in higher adduct fullerene-based solar cells. *Adv. Funct. Mater.*, 19(18): 3002–3007.
13. Ross, R. B., Cardona, C. M., Guldi, D. M., Sankaranarayanan, S. G., Reese, M. O., Kopidakis, N., Peet, J., et al. (2009) Endohedral fullerenes for organic photovoltaic devices. *Nat Mater.*, 8(3): 208–212.
14. Lenes, M., Wetzel, G. J. A. H., Kooistra, F. B., Veenstra, S. C., Hummelen, J. C., and Blom, P. W. M. (2008) Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells. *Adv. Mater.*, 20(11): 2116–2119.
15. Liu, C., Xu, L., Chi, D., Li, Y., Liu, H., and Wang, J. (2013) Synthesis of novel accepotor molecules of mono- and multiadduct fullerene derivatives for improving photovoltaic performance. *ACS Appl. Mater. Interfaces*, 5(3): 1061–1069.
The table of contents

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