Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry C

Materials for optical and electronic devices
www.rsc.org/materialsC

ROYAL SOCIETY
OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/materialsC

Journal of Materials Chemistry C

RSCPublishing

Isobenzofulvene-Fullerene Mono-Adduct for Organic Photovoltaic Applications

Nai-Wen Tseng,[b] Yong Yu,[a] Yunke Li,[c] Jingbo Zhao,[c] Shu Kong So,[d] He Yan[c] and Ka Ming Ng[*a]

A family of three isobenzofulvene mono-adduct fullerene derivatives are synthesized and applied as the acceptor for organic photovoltaic (OPV) cells. PTB7-based OPV cells incorporating these new fullerene derivatives show increased V_{oc} compared to the corresponding $PC_{60}BM$-based cells. The best performing derivative in this fullerene family is $IC_{60}MA$-4C that contains the longest alkyl chain and that yields a power conversion efficiency of 6.5% when combined with PTB7.

The development of high performance organic photovoltaics (OPVs) has attracted tremendous amount of attention in recent years.[1-6] The most popular structure among OPVs is bulk-heterojunction (BHJ) cell, which comprises a bulk-heterojunction active layer constructed by a blend of polymer donor and organic acceptor.[7-10] In contrast to the large number of novel polymeric donor materials developed, only limited progress has been achieved in the development of new acceptors. Due to its high electron mobility, C_{60} was considered an excellent electron acceptor material for BHJ cell.[7] However, the poor processibility of C_{60} makes it very difficult to use the unsubstituted C_{60} during devices fabrication. To address such issue, C_{60} derivatives with improved processibility such as $PC_{60}BM$ has been developed and serving as electron acceptor for OPV devices.[11-13] With their outstanding solubility and electron mobility, $PC_{60}BM$ and $PC_{70}BM$ are still dominating acceptor materials for high performance OPV devices. With $PC_{70}BM$ as acceptor, over 9% PCE was achieved from a single junction solar cell and an over 10% PCE was achieved from tandem cells.[14,15] On the other side, in order to improve the V_{oc} of OPV devices, fullerene derivatives with high LUMO levels are highly desirable for quite a long time.

To up shift the LUMO level of fullerenes, a series of mono and multi substituted fullerene derivatives was developed. Cyclobutadienes were incorporated onto C_{60} and the resulting derivatives showed higher LUMO than C_{60}.[16] Silylmethyl[60]fullerene (SIMEF) was synthesized and OPV device based on SIMEF showed a 0.21V higher V_{oc} than $PC_{60}BM$ based device.[17] Bis-PCBM, Biindene-C_{60} adducts (BCMA, BCBA), di(4-methylphenyl)-methano-C_{60} bisadduct (DMPCBA), indene-C_{60} monoadduct (ICMA) and indene-C_{60} bisadduct (ICBA) have been developed with modified electrochemical and physical properties.[18] All of the derivatives exhibited good solubility with higher LUMO level than PCBM. In particular, much research progress has been done with ICBA on devices showing high open-circuit voltage (V_{oc}). Compared with the monoadduct, fullerene multiadduct ICBA has better solubility and higher LUMO but poorer electron mobility and thus J_{sc}. To balance solubility, LUMO level and electron mobility, fullerene monoadduct-ICBM was synthesized.[19] The ester group of ICBM enhanced its miscibility with donor materials and excellent performance was obtained for ICBM based OPV device. However, derivatives such as ICBA and ICBM both have isomeric structures. These isomers with different LUMO levels would increase the electron recombination and affect J_{sc} negatively as a result.

Herein, we report the new design of the fullerene derives, which combine the LUMO up-shifting property from ICBA with the improved processibility via incorporation of alkyl side chain with an ester group from PCBM. A series of fullerene derivatives ($IC_{60}MA$-2C, $IC_{60}MA$-3C and $IC_{60}MA$-4C) were synthesized and characterized. These $IC_{60}MA$ derivatives are attractive alternative electron acceptors to $PC_{60}BM$ with up-shifted LUMO level and decent material processibility for device fabrication. Photovoltaic devices were fabricated using PTB7 as donor materials, $PC_{60}BM$ and $IC_{60}MA$ derivatives as acceptor materials, respectively (structures shown in Scheme 1). Devices with $IC_{60}MA$-2C, $IC_{60}MA$-3C and $IC_{60}MA$-4C showed improved V_{oc} compared with the one using $PC_{60}BM$ acceptor. The highest V_{oc} of 0.79 V was achieved while $IC_{60}MA$-3C was employed as acceptor.
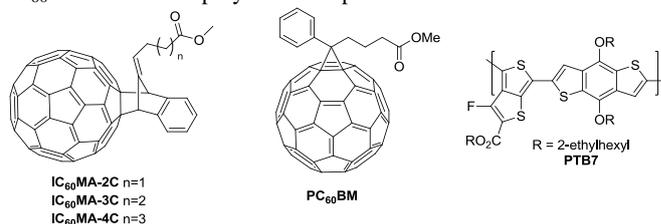
Scheme 1. Chemical structures of $IC_{60}MA$ derivatives $PC_{60}BM$ and PTB7.

The fullerene derivatives were synthesized via the Diels-Alder reaction between C_{60} and cyclic diene (Scheme 2). In contrast to the preparation of ICBA using large excess amount of the indene

reactant, this method only required up to ~2 equivalents of bicycle and tetrazine to generate the corresponding products in decent yield. The mild reaction condition (45 ^oC) is also considerably easy to handle compared with the temperature used for $IC_{60}BM$ preparation (~ 180 ^oC).
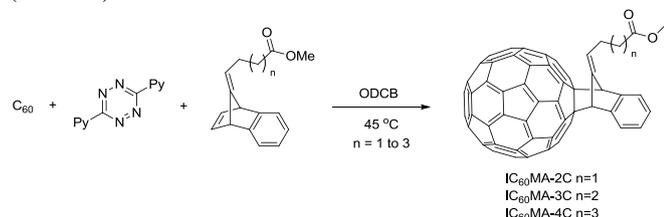
Scheme 2. Synthetic route of fullerene derivatives $IC_{60}MA$-2C, $IC_{60}MA$-3C and $IC_{60}MA$-4C.

The absorption spectra of active layers are shown in Fig. 1. The absorbance of all the acceptors is quite similar and slight differences came from wavelength before 500 nm.
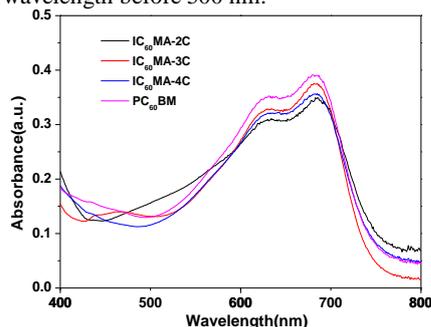
Fig 1. Absorption spectra of the active layer fabricated from blend of PTB7 and different acceptors

Cyclic voltammetry was employed to characterize the electrochemical properties of $IC_{60}MA$-2C, $IC_{60}MA$-3C and $IC_{60}MA$-4C. LUMO levels were then obtained from their onset reduction potentials indicated in the cyclic voltammograms (Fig 2).[20] Table 1 showed the half-wave potentials (defined as $E=0.5(E_{p,c}+E_{p,a})$, where $E_{p,c}$ is the cathodic peak potential and $E_{p,a}$ is the corresponding anodic peak potential) and the LUMO levels of the reduction processes of P $C_{60}BM$ and the three fullerene derivatives. 0.02 eV upshift LUMO levels were obtained for all the three new $IC_{60}MA$ derivatives compared with P $C_{60}BM$.
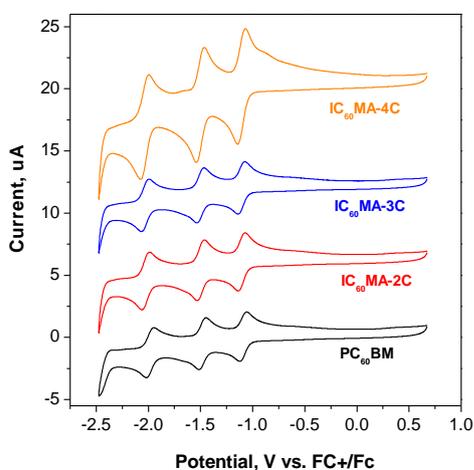
Fig 2. Cyclic voltammetry results of P $C_{60}BM$ and three $IC_{60}MA$ derivatives.

Table 1. Electrochemical properties of PCBM, $IC_{60}MA$-2C, $IC_{60}MA$-3C and $IC_{60}MA$-4C.

Fullerenes	E_1 (V)	E_2 (V)	E_3 (V)	E_{LUMO} (eV)
P $C_{60}BM$	-1.09	-1.48	-1.98	-3.69
$IC_{60}MA$-2C	-1.10	-1.49	-2.02	-3.67
$IC_{60}MA$-3C	-1.10	-1.50	-2.03	-3.67
$IC_{60}MA$-4C	-1.10	-1.50	-2.03	-3.67

Photovoltaic devices were fabricated based on the $ITO/ZnO/PTB7$:acceptor/MoO_3/Al configuration. The morphology of donor/acceptor blend films were characterized by atomic force microscopy (AFM) and the height and phase images were shown in Fig. S1. All the surface topography of the BHJ films based on $IC_{60}MA$ derivatives was very similar to the one based on $PC_{60}BM$. The surface topography was quite smooth without any excessively large features that could be detrimental to the operation of a polymer solar cell device.

The current density–voltage (J–V) curves measured under AM1.5 G illumination were shown in Fig 3, and the performance of devices using different acceptors were summarized in Table 2. Device based on $PC_{60}BM$ still showed the best power conversion efficiency (PCE) of 6.8%, while two $IC_{60}MA$-based devices also had comparable performance (6.0% and 6.5%).
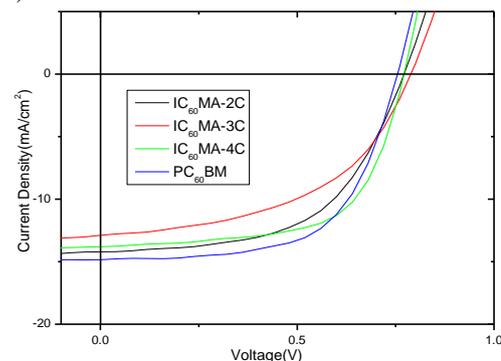
Fig 3. Current-Voltage curves of the photovoltaic devices based on PTB7 as donor, $IC_{60}MA$ derivatives and $PC_{60}BM$ as acceptors.

For the devices based on the $IC_{60}MA$ derivatives, the open circuit voltages (V_{oc}) are all higher than $PC_{60}BM$-based devices (Table 2). The results can be attributed to the difference in the LUMO levels of the acceptors (Table 1) and the increase in LUMO levels finally results in the higher V_{oc}. Moreover, devices based on $IC_{60}MA$-2C and $IC_{60}MA$-4C also obtained similar J_{sc} to PCBM based device.

Table 2. The open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) of photovoltaic devices based on different acceptors.

Active layer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	PCE [%]
PTB7/ $IC_{60}MA$-2C	0.77	14.2	0.55	6.0(±0.1)
PTB7/ $IC_{60}MA$-3C	0.79	12.9	0.50	5.1 (±0.1)
PTB7/ $IC_{60}MA$-4C	0.77	13.7	0.61	6.5 (±0.1)
PTB7/ $PC_{60}BM$	0.76	14.6	0.62	6.8(±0.1)

The external quantum efficiency (EQE) spectra of solar cell devices are shown in Fig 4. All the curves showed the highest peak at around 620 nm and then followed by a lower peak at around 690 nm. The EQEs matched quite well with the UV absorptions as well as the current densities for all devices. $IC_{60}MA$-2C and $IC_{60}MA$-4C based devices also showed comparable EQEs to $PC_{60}BM$ based device.
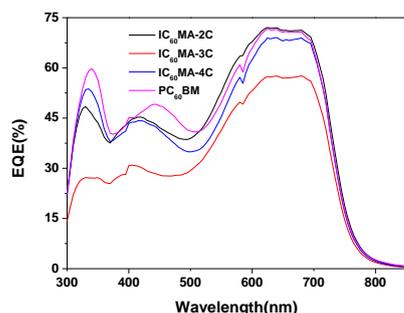
Fig 4. EQE curves of photovoltaic devices based on PTB7 as donor, three $IC_{60}MA$ derivatives and $PC_{60}BM$ as acceptor.

To achieve a high-performing bulk-heterojunction solar cell, good charge-carrier mobility and solubility is also required. The charge-carrier mobilities were calculated from the *J–V* characteristics using the space-charge-limited current (SCLC) method. Since PTB7 and $PC_{60}BM$ are commercialized molecules, we carried out experiment on the three $IC_{60}MA$ derivatives. The results of charge-carrier mobilities and solubility in chloroform are summarized in Table 3.

Table 3. The e-only mobility and solubility of three different $IC_{60}MA$ derivatives.

Fullerenes	E-only mobility/ $\times 10^{-4}$ cm^2 V^{-1} s^{-1}	Solubility in chloroform (mg/mL)
$IC_{60}MA$-2C	7.7	48
$IC_{60}MA$-3C	5.0	90
$IC_{60}MA$-4C	14.1	47.3

Three derivatives exhibit different e-only mobility. $IC_{60}MA$-4C has quite a high mobility of 1.41×10^{-3} cm^2 V^{-1} s^{-1} and thus a convincing fill factor (61%), while the other two derivatives have lower e-only mobilities and fill factors. In general, there is a negative correlation between solubility and electron mobility. Interestingly, $IC_{60}MA$-3C, which has the lowest electron mobility among the three derivatives, exhibits the highest solubility (Table 3). The relatively high solubility of $IC_{60}MA$-3C indicates that the intermolecular interaction is relatively weak for $IC_{60}MA$-3C molecules compared to other two derivatives, which then results in lower electron mobility for $IC_{60}MA$-3C.

Conclusions

In summary, three novel C_{60} derivatives without isomeric structures were designed and synthesized via the Diels-Alder reaction. They all show upshifted LUMO level compared with $PC_{60}BM$. All of the derivatives could be easily dissolved in common solvents and work well with PTB7 during photovoltaic device fabrications. $IC_{60}MA$-2C and $IC_{60}MA$-4C based device showed comparable EQEs, J_{sc}s and PCEs to $PC_{60}BM$ based device. Moreover, all devices base on $IC_{60}MA$ derivatives possessed higher V_{oc} than that base on $PC_{60}BM$. This new series of $IC_{60}MA$ derivatives will surely be a new choice in organic photovoltaic devices.

Notes and references

1. S. Guenes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324.
2. B. C. Thompson and J. M. J. Frechet, *Angew. Chem. Int. Ed.*, 2008, **47**, 58.
3. P. Peumans, A. Yakimov and S. R. Forrest, *J. Appl. Phys.*, 2003, **93**, 3693.
4. G. Li, R. Zhu and Y. Yang *Nat. Photon.*, 2012, **6**, 153.
5. L. M. Chen, Z. R. Hong, G. Li and Y. Yang, *Adv. Mater.*, 2009 **21**, 1434.
6. G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323.
7. G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.
8. (a) Z.He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, *Nat. Photon.*, 2012, **6**, 591. (b) J. Chen and Y. Cao, *Acc. Chem. Res.*, 2009, **42**, 1709.
9. (a) Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Comm.* 2014, **5**, 5293. (b) J. Zhao, Y. Li, H. Lin, Y. Liu, K. Jiang, C. Mu, T. Ma, J. Y. L. Lai and H. Yan, *Energy Environ. Sci.* 2014, DOI: 10.1039/C4EE02990A. (c) C. Mu, P. Liu, W. Ma, K. Jiang, J. Zhao, K. Zhang, Z. Chen, Z. Wei, Y. Yi, J. Wang, S. Yang, F. Huang, A. Facchetti, H. Ade and H. Yan, *Adv. Mater.*,2014, **26**, 7224.
10. Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*,2010, **22**, E135.
11. J.C. Hummelen, B. W. Knight, F. Lepeq, F. Wudl, J. Yao and C. L. Wilkins, *J Org. Chem.*, 1995, **60** 532.
12. M.M. Wienk, J. M. Kroon, W. J. H, Verhees, J. Knol, J.C. Hummelen , P. A. van Hal and R. A. J. Janssen, *Angew. Chem. Int. Ed.*, 2003, **42**, 3371.
13. P. A. Troshin, H. Hoppe, J. Renz, M. Egginger, J. Y. Mayorova, A. E. Goryachev, A. S. Peregudov, R. N. Lyubovskaya, G. Gobsch, N. S. Sariciftci and V. F. Razumov, *Adv. Funct. Mater.*, 2009, **19**, 779.
14. Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photon.*, 2012, **6**, 591.
15. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao, G. Li and Y. Yang, *Nat. Comm.*, 2013, **4**, 1446.
16. G. D. Han, W. R. Collins, T. L. Andrew, V. Bulović and T. M. Swager, *Adv. Funct. Mater.*, 2013, **23**, 3061
17. (a) Y. Matsuo, A. Iwashita, Y. Abe, C. Z. Li, K. Matsuo, M. Hashiguchi and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 15429; (b) Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka

and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 16048.

18. (a) M. Lenes, G. J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen and P. W. M. Blom, *Adv. Mater.* 2008, **20**, 2116; (b) Y. J. He, H. Y. Chen, G. J. Zhao, J. H. Hou and Y. F. Li, *Sol. Energy Mater. Sol. Cells.*, 2011, **95**, 899; (c) Y.J. Cheng, M.H. Liao , C.Y. Chang , W.S. Kao , C. E. Wu and C. S. Hsu, *Chem. Mater.*, 2011, **23**, 4056; (d) Y. J. He, H. Y. Chen, J. H. Hou and Y. F. Li, *J. Am. Chem. Soc.*, 2010, **132**,1377.

19. Y. J. He, M. Shao, K. Xiao, S. C. Smith and K. L.Hong, *Sol. Energy Mater. Sol. Cells.*, 2013, **118**, 171.

20. Y.F. Li, Y. Cao, J. Gao, D.L. Wang, G. Yu and A.J. Heeger, *Syn. Met.*, 1999, **99**, 243.

21. S. C. Chuang, M. Sander, T. Jarrosson, S. James, E. Rozumov, S. I. Khan and Y. Rubin, *J. Org. Chem.*, 2007, **72**, 2716.

[a] Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong (China). E-mail: kekmng@ust.hk

[b] Nano and Advanced Materials Institute Limited, The Hong Kong University of Science and Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong (China).

[c] Department of Chemistry, The Hong Kong University of Science and Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong (China).

[d] Department of Physics, Hong Kong Baptist University, Kowloon Tong, Hong Kong (China).
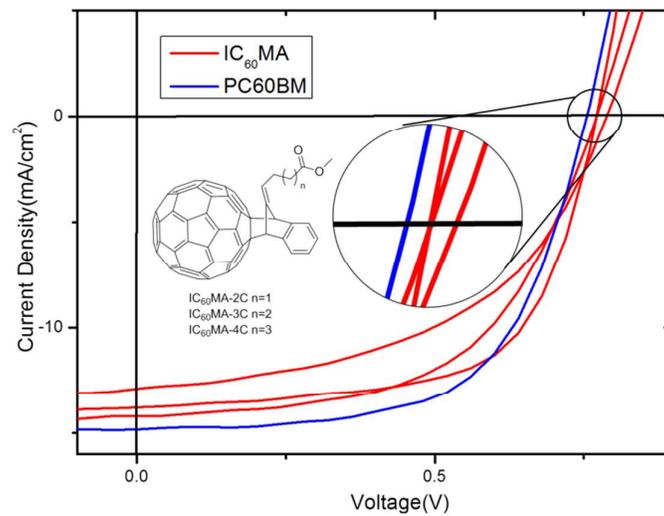
IC$_{60}$MA derivatives with up-shifted LUMO were synthesized and their OPV devices showed higher V_{oc} than the corresponding PC$_{60}$BM based device.