Organic Letters
Letter
pubs.acs.org/OrgLett

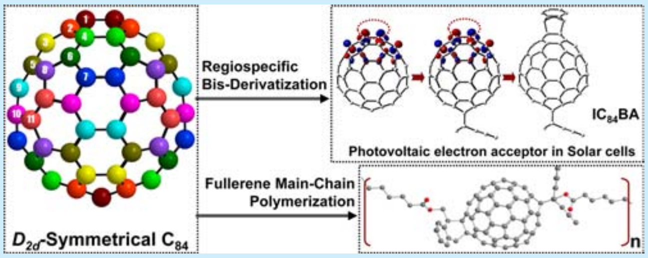
Regioselective Derivatization of C_{84} by Diels−Alder Reactions: Applications to Photovoltaic Solar Cells and Fullerene Polymerization

Jing-Shuang Dang,[†,‡] Wei-Wei Wang,[‡,†] Xiang Zhao,*[,†,‡] and Shigeru Nagase*[,‡]

[†]Institute for Chemical Physics & Department of Chemistry, Xi'an Jiaotong University, Xi'an 710049, China
[‡]Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

Ⓢ *Supporting Information*

ABSTRACT: Regioselective properties of a D_{2d}-C_{84} in multistep [4 + 2] cycloadditions and the applications of bis-functional C_{84} derivatives were investigated. Density functional calculations demonstrate that an indene−C_{84} bisadduct is a promising electron acceptor in organic solar cells and a C_{84}-bis-anthracene copolymer can be utilized as a charge-transfer material.



The Diels−Alder (DA) reaction has served as a powerful strategy for the derivatization of fullerenes to produce unprecedented properties.[1] However, the search for highly regioselective derivatizations remains an important objective because of the low regioselectivity of the C_{60} fullerene in multistep cycloadditions. Indene−C_{60} bisadducts ($IC_{60}BA$) have been reported as electron acceptors in solar cells because of their high photovoltaic performance.[2] However, the bisadducts have been produced as a mixture containing many monoadducts ($IC_{60}MA$) and trisadducts ($IC_{60}TA$).[2] Therefore, $IC_{60}BA$ must be separated from $IC_{60}MA$ and $IC_{60}TA$, for example, using column chromatography[2] to identify the structure and to use it as a pure sample for practical applications.[3] Another interest is fullerene polymerization. Various polymers have been synthesized with fullerenes attached on the main chain as pendants. However, polymers with fullerenes in the main chain remain unexplored.[4] For the polymerization of C_{60}, the products comprise undesirable oligomeric species and cross-linking structures with low molecular weights.[5] Therefore, finding fullerene derivatives that yield desirable polymers is important.

This study explored multistep derivatizations of D_{2d}−C_{84} (an abundantly produced isomer of C_{84}) by DA reactions using density functional theory (DFT) calculations. In contrast to C_{60} and C_{70}, D_{2d}−C_{84} exhibits a highly regioselective behavior in multiadditions. The bisadducts are useful for practical applications. Furthermore, the possible applications of C_{84}-based derivatives to photovoltaic solar cells and fullerene polymers are investigated.

The multistep additions of cyclopentadiene (Cp) to D_{2d}−C_{84} were first investigated to elucidate the regioselectivity: Cp was chosen because it acts as a nucleophile. Furthermore, its small size does not cause severe steric repulsions for multiadditions.[6] All symmetry-allowed addition sites with large LUMO coefficients on C_{84} were considered. These calculated results are presented in the Supporting Information. The activation barriers ($\Delta G^{\ddagger}$) and reaction free energies (ΔG) at room temperature were calculated using density functional theory at the M06-2X level (for details, see the Supporting Information).

The LUMOs of D_{2d}-C_{84} are degenerate with e symmetry.[7,8] A degenerate LUMO of D_{2d}-C_{84} is shown in Figure 1. The LUMO are mostly distributed at the upper part of D_{2d}-C_{84} (another LUMO is distributed similarly in the lower part). As might be apparent from frontier molecular orbital theory, it is expected that Cp adds to the carbons having large LUMO coefficients. In fact, the regioselective addition of Cp to the [6,6] bond with the largest LUMO coefficients at the top of D_{2d}-C_{84} was confirmed by performing calculations for several reaction sites (see Figure S1, Supporting Information). The activation barrier ($\Delta G^{\ddagger}$) calculated for the most favorable

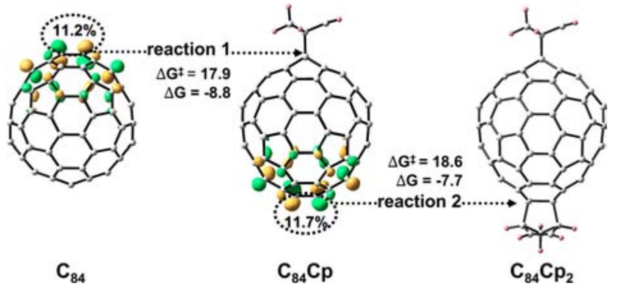


Figure 1. LUMO distribution of C_{84} and $C_{84}Cp$ and the $\Delta G^{\ddagger}$ and ΔG (in kcal mol^{-1}) values calculated for reactions 1 and 2.

Received: November 1, 2013
Published: December 9, 2013

addition (reaction 1 in Figure 1) is 17.9 kcal mol^{-1}. As shown in Figure 1, the LUMO of the C_{84}Cp monoadduct is distributed mostly at the opposite side of Cp. For this reason, Cp added to the carbons at the opposite side yield the $C_{84}Cp_2$ bisadduct. The activation barrier for the most favorable addition (denoted reaction 2 in Figure 1) is 18.6 kcal mol^{-1}. This barrier is much lower than those of 24−26 kcal mol^{-1} calculated for other possible reaction sites (see Figure S2, Supporting Information), which indicates that the addition of Cp to C_{84}Cp proceeds in a highly regioselective manner. In addition, the barrier for the addition of Cp to C_{84}Cp is only 0.7 kcal mol^{-1} larger than that of 17.9 kcal mol^{-1} for the addition of Cp to C_{84}. In other words, C_{84}Cp is as reactive toward Cp as C_{84}. Therefore, the addition of Cp to C_{84}Cp is followed without a break by the addition of Cp to C_{84}.

The LUMO of the $C_{84}Cp_2$ bisadduct is localized in the vicinity of the equator (see Figure S3, Supporting Information). Accordingly, Cp adds to the [6,6] bonds in the vicinity of the equator to yield the $C_{84}Cp_3$ trisadduct. The smallest barrier for the additions is 24.2 kcal mol^{-1} (see Figure S3, Supporting Information). Furthermore, as shown in Figures S4−S7 (Supporting Information), the smallest barrier for the addition of Cp to $C_{84}Cp_n$ is 24.5 ($n = 3$), 25.4 ($n = 4$), 25.2 ($n = 5$), 33.1 ($n = 6$) kcal mol^{-1}, respectively. All these barriers are larger than that for the addition of Cp to C_{84}Cp, suggesting that the $C_{84}Cp_2$ bisadduct is most abundantly produced. Therefore, similar bisadducts were examined for application to photovoltaic solar cells and fullerene polymers.

In the last two decades, derivatives of C_{60} such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and $IC_{60}BA$ shown in Figure 2[2,9] were widely used as electron acceptors for polymer solar cell (PSC) devices.[10] Recently, efforts have been undertaken to find the derivatives of other fullerenes. For example, a C_{84}-based derivative $PC_{85}BM$ (an analogue of $PC_{61}BM$) shown in Figure 2 was inferred as an alternative acceptor in PSC devices because of the strong and broad absorption in the visible region.[11] However, the lower LUMO energy level of $PC_{85}BM$ engenders poor power conversion efficiency (PCE) for the photovoltaic devices in practice.[11] Therefore, we tested the photovoltaic performance of an indene-C_{84} bisadduct ($IC_{84}BA$) obtainable by DA reactions, as shown in Figure 2. For comparison, the popular $PC_{61}BM$, $IC_{60}BA$, $IC_{60}MA$, and $PC_{85}BM$ shown in Figure 2 were also considered. $IC_{60}BA$ was obtained as a mixture because of its low regioselectivity.[3] Therefore, six isomers were considered for $IC_{60}BA$, which are denoted $IC_{60}BA$-x (x = a−f) in Figure S8 (Supporting Information). Energy differences among the isomers are only 0.5 kcal mol^{-1}. The barriers for the formation of the isomers are all of 10.8−11.2 kcal mol^{-1} (see Figure S8, Supporting Information).

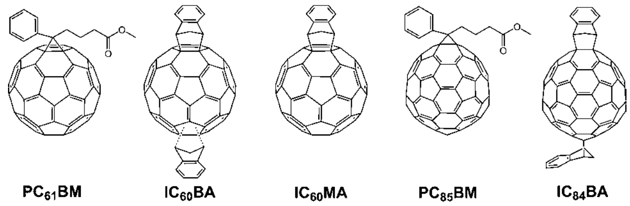


Figure 2. Fullerene derivatives.

The PCE of PSC devices is proportional to the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), and fill factor (FF) of the device.[12] For the PSC device with P3HT[13] as a representative polymer donor, the high LUMO level, broad visible-NIR absorption, and high charge carrier mobility of the acceptor are essential to achieve a high photovoltaic efficacy.[14] The calculated LUMO energy levels are presented in Table 1.

Table 1. LUMO Energy Levels (in eV) and Reorganization Energies (λ, in eV) of Fullerene Derivatives

	$PC_{61}BM$	$IC_{60}MA$	$IC_{60}BA$-x[a]	$PC_{85}BM$	$IC_{84}BA$
LUMO	−2.57	−2.54	−2.28 to −2.29	−3.02	−2.61
λ_e	0.184	0.173	0.191 to 0.193	0.247	0.146
λ_h	0.220	0.219	0.208 to 0.244	0.226	0.217
λ_{sum}	0.404	0.392	0.399 to 0.417	0.473	0.353

[a] Each value of $IC_{60}BA$-x (x = a−f) is listed in Table S1 (Supporting Information).

Apparently, $IC_{60}BA$ has the highest LUMO level (ca. −2.28 eV), irrespective of the kind of isomer (Table S1, Supporting Information). In contrast, $PC_{85}BM$ has the lowest LUMO level (−3.02 eV). Additionally, the LUMO level (−2.61 eV) of $IC_{84}BA$ is lower than that of $IC_{60}BA$ but differs little from that (−2.57 eV) of $PC_{61}BM$. For the two derivatives with the similar property of LUMO level, the density of states (DOS) were calculated and we found that $IC_{84}BA$ possesses a slightly higher Fermi level than that of $PC_{61}BM$ (see Figure S9, Supporting Information).[15] These results suggest that $IC_{84}BA$ and $PC_{61}BM$ may exhibit very similar V_{oc}'s in PSCs.

For solar cells, the charge mobility is as important as the open circuit voltage. The experimental value of J_{sc} is correlated with the reorganization energy (λ), which is defined as a sum of electron and hole components: $\lambda_{sum} = \lambda_e + \lambda_h$.[16,17] Small λ values correspond to large J_{sc} values for devices.[17] The calculated λ values are presented in Table 1. It is noteworthy that $IC_{84}BA$ shows the smallest λ_e and λ_{sum} values. In contrast, $PC_{85}BM$ exhibits the largest λ_e and λ_{sum}: the λ_e is even larger than the λ_h, which suggests that $PC_{85}BM$ is unsuitable as an electron carrier in solar cells.

Absorption spectra of the fullerene derivatives shown in Figure 3, as calculated using the time-dependent (TD) M06-2X method, are shown in Figure 3. Figure S10 (Supporting Information) shows that the absorption spectra of $IC_{60}BA$-x (x = a−f) are very similar. Therefore, the absorption spectrum calculated for ICBA-a is shown in Figure 3 as a representative example. Figure 3 shows that $PC_{61}BM$, $IC_{60}MA$, and $IC_{60}BA$ show the absorption bands in the UV region and only $IC_{60}BA$ shows weak absorptions in the visible region at 400−800 nm.

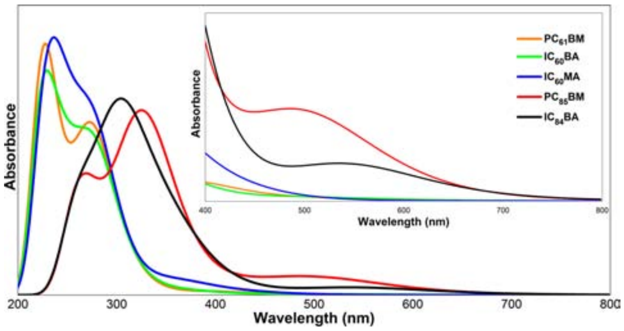
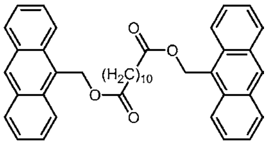


Figure 3. Calculated absorption spectra of fullerene derivatives. Inset: Enlarged absorption spectra in the visible region at 400−800 nm.

These are consistent with experimental observations.[2] The C_{84} derivatives, $PC_{85}BM$ and $IC_{84}BA$, show red-shifted absorptions of 300−400 nm and strong absorptions in the visible region. As the inset of Figure 3 shows, $PC_{85}BM$ and $IC_{84}BA$, respectively, exhibit strong absorption peaks near 550 and 500 nm. These results suggest that $PC_{85}BM$ and $IC_{84}BA$ provide better sunlight absorption and higher current output for devices than $PC_{61}BM$, $IC_{60}MA$, or $IC_{60}BA$.

In fact, the proposed $IC_{84}BA$ exhibits much higher charge mobility and stronger absorptions in the visible region than the widely used $PC_{61}BM$ and $IC_{60}BA$. Therefore, $IC_{84}BA$ is expected to act as a much better electron acceptor in solar cells. In addition, it is noteworthy that $IC_{84}BA$ is obtainable in a highly regioselective manner (see Figure S11, Supporting Information), as in the $C_{84}Cp_2$ case: the purification is easy for practical use, which contrasts against the fact that six isomers are produced in the same yield for the widely used $IC_{60}BA$.[3]



1

Figure 4. Bis-anthracene derivative, labeled as **1**.

In addition to the promising photovoltaic performance, we investigated the application of C_{84} to fullerene polymerization. Because of the regioselective bisaddition property, C_{84} can react with bis-diene molecules that contain two diene units in each monomer to generate the linear copolymers.[18] Here the bis-anthracene derivative **1** shown in Figure 4 was chosen as a bis-diene monomer because it does not cause the undesirable diene−diene homocoupling reactions and because it has been proved to react readily with C_{60} to afford the fullerene-bis-diene alternating copolymers.[18]

The copolymerization processes are depicted in Figure 5, together with the HOMO and LUMO of each reactant. As emphasized already, C_{84} has highly localized LUMOs. As Figure 5a shows, the HOMO of **1** is localized on one of two anthracene units. Because of the HOMO−LUMO interaction, the cycloaddition of **1** to C_{84} proceeds in a highly stereoselective way to yield the cycloadduct **2** shown in Figure 5b, with a low activation barrier of $\Delta G^{\ddagger} = 18.1$ kcal mol^{-1}. The HOMO and LUMO of **2** are localized, respectively, on the anthracene and C_{84} moieties. Therefore, dimerization of **2** by the DA reaction takes place in a stereoselective manner to yield adduct **3** shown in Figure 5c. The barrier of 20.2 kcal mol^{-1} for the dimerization is only 2.1 kcal mol^{-1} higher that for the addition of **1** to C_{84}. It is noteworthy that the HOMO and LUMO of **3** are again localized, respectively, on the anthracene and C_{84} moieties. In addition, the HOMO and LUMO levels of **3** differ little from those of **2**. Therefore, **3** can also dimerize in a stereoselective way with a low barrier, as does **2**. Apparently, repetition of such dimerization engenders a polymer with C_{84} in the main chain, as shown in Figure 5d.

The HOMO and LUMO of the polymer are expected to be spatially separated, as is apparent from those of **2** and **3**. Therefore, the polymer simultaneously possesses hole-transporting and electron-transporting properties.[19] Integrating different types of charge-transporting groups into a single molecular material can enhance the charge transfer performance because of the balanced transports of both carriers. It is therefore inferred that the designed C_{84} main-chain polymers might be useful as charge transfer bipolar materials in field effect transistors (FETs) and polymer memory devices.[20,21]

In summary, the regioselective derivatization of C_{84} and applications of the bisadducts were investigated. A newly designed $IC_{84}BA$ was demonstrated as a promising electron-accepting component in high-performance solar cells. Moreover, a C_{84}-bis-anthracene Diels−Alder copolymerization strategy was elucidated theoretically, thereby providing new insights into the synthesis of functionalized fullerene main-chain polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculation methods, LUMO energy levels and reorganization energies of $IC_{60}BA$-x (x = a−f), detailed calculation results of C_{84} + Cp, C_{60} + indene, and C_{84} + indene, DOS of $IC_{84}BA$ and $PC_{61}BM$, and calculated absorption spectra of fullerene derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: xzhao@mail.xjtu.edu.cn.
*E-mail: nagase@fukui.kyoto-u.ac.jp.

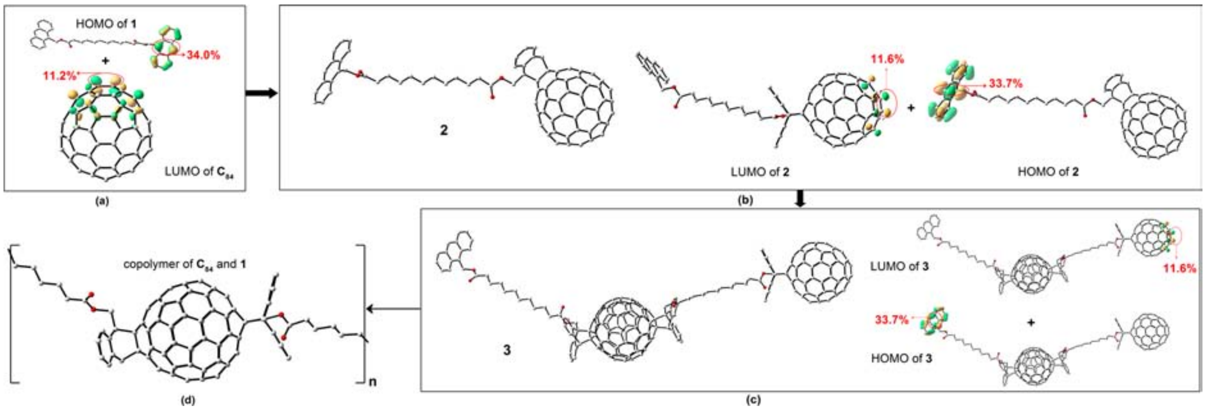


Figure 5. Copolymerization processes between C_{84} and bis-anthracene **1**. Hydrogens are omitted for clarity.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21171138), the National Key Basic Research Program of China (2011CB209404, 2012CB720904), and a Grant-in-Aid for Specially Promoted Research (No. 22000009) from MEXT of Japan.

■ REFERENCES

(1) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.

(2) He, Y.; Chen, H.-Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1377.

(3) He, Y.; Chen, H.-Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 5532.

(4) Giacalone, F.; Martín, N. *Chem. Rev.* **2006**, *106*, 5136.

(5) Gügel, A.; Belik, P.; Walter, M.; Kraus, A.; Harth, E.; Wagner, M.; Spickermann, J.; Müllen, K. *Tetrahedron* **1996**, *52*, 5007.

(6) Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561.

(7) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *231*, 319.

(8) (a) Boulas, P.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1994**, *116*, 9393. (b) Crassous, J.; Rivera, J.; Fender, N. S.; Shu, L.; Echegoyen, L.; Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1613.

(9) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(10) (a) Wong, W.-Y.; Ho, C.-L. *Acc. Chem. Res.* **2010**, *43*, 1246. (b) Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723.

(11) Kooistra, F. B.; Mihailetchi, V. D.; Popescu, L. M.; Kronholm, D.; Blom, P. W. M.; Hummelen, J. C. *Chem. Mater.* **2006**, *18*, 3068.

(12) Hermans, P.; Cheyns, D.; Rand, B. P. *Acc. Chem. Res.* **2009**, *42*, 1740.

(13) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85.

(14) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.

(15) Garcia-Belmonte, G.; Boix, P. P.; Bisquert, J.; Lenes, M.; Bolink, H. J.; La Rosa, A.; Filippone, S.; Martín, N. *J. Phys. Chem. Lett.* **2010**, *1*, 2566.

(16) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339.

(17) Köse, M. E.; Mitchell, W. J.; Kopidakis, N.; Chang, C. H.; Shaheen, S. E.; Kim, K.; Rumbles, G. *J. Am. Chem. Soc.* **2007**, *129*, 14257.

(18) Ilhan, F.; Rotello, V. M. *J. Org. Chem.* **1999**, *64*, 1455.

(19) Ge, Z.; Hayakawa, T.; Ando, S.; Ueda, M.; Akiike, T.; Miyamoto, H.; Kajita, T.; Kakimoto, M. *Org. Lett.* **2008**, *10*, 421.

(20) Yu, H.; Cho, H.-H.; Cho, C.-H.; Kim, K.-H.; Kim, D. Y.; Kim, B. J.; Oh, J. H. *ACS Appl. Mater. Inter.* **2013**, *5*, 4865.

(21) Ouyang. *J. Org. Electron.* **2013**, *14*, 665.