Reduction of Regioisomers of Fullerene-Bisadducts by Tether-Directed Remote Functionalization: Investigation of Electronically and Sterically Isomeric Effects on Bulk-Heterojunction Solar Cells

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ABSTRACT: C_{60} bis-adduct containing a mixture of regioisomers with different LUMO energy levels and steric geometries could greatly affect the morphological and bulk properties. To investigate the regio-isomer effect on solar cell performance, we have successfully designed and synthesized a regio-selective 4-acetatephenyl-4'-methylphenylmethano C_{60} bis-adduct (S-APM-CBA) by “tether-directed remote functionalization” strategy and a random 4-acetatephenyl-4'-methylphenylmethano C_{60} bis-adduct denoted as R-APM-CBA by traditional cyclopropanation. The dramatic reduction in the number of regio-isomers in S-APM-CBA is confirmed by the ^1H NMR and HPLC measurements and theoretical calculations. Compared to the R-APM-CBA-based device with a J_{sc} of 6.63 mA/cm², an FF of 44.3% and a PCE of 2.46%, the device using S-APM-CBA yielded a much lower J_{sc} of 1.48 mA/cm², an FF of 32.2%, and a PCE of 0.38%. Consistently, the electron-only device using S-APM-CBA exhibited lower electron mobility than the R-APM-CBA-based device. These results imply that the electronic shallow-trap effect ascribed to the LUMO energy variations turned out to be insignificant in the AMP-CBA system. The lower efficiency and mobility of S-APM-CBA might due to the assumption that the most probable trans-4-III isomer in AMP-CBA prevents the intermolecular facial contact of fullerenes, thereby hindering the electron transporting. Furthermore, the nanomorphology of S-AMP-CBA and R-AMP-CBA active layers could be different because of their different three-dimensional structures. This research demonstrated that steric effect of regio-isomers in a given C_{60} bis-adduct is more crucial than electronic shallow-trap effect.

KEYWORDS: regioisomers, bis-adducts, tether, bulk-heterojunction, solar cells, shallow-trap effect

INTRODUCTION

Research on polymer solar cells (PSCs) has attracted tremendous scientific and industrial interest and attention in recent years. The power conversion efficiency (PCE) of a photovoltaic device is determined by open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF). Increasing V_{oc} is one of the approaches to improve PCEs. The magnitude of V_{oc} value is generally proportional to the energy difference between the highest occupied molecular orbital (HOMO) energy level of the donor and the lowest unoccupied molecular orbital (LUMO) level of the acceptor. Therefore, either raising the LUMO level of the fullerene material or lowering the HOMO level of the polymer can obtain higher V_{oc}. A straightforward strategy is to design new fullerene-based materials that possess intrinsically high-lying LUMO energy levels. Introduction of electron-donating groups on the addend of the fullerenes has been attempted to modulate the LUMO energy levels. However, the changes in LUMO energy level of fullerene derivatives are too small to affect V_{oc} because of the fact that the through-space interaction without direct π-conjugation is negligible. Development of bis-adduct C_{60} materials has become a more practical approach. The double functionalization on the C_{60} core structure to reduce the electron delocalization in the C_{60} makes bis-adduct C_{60} derivatives have larger electrochemical reduction potentials and thus higher-lying LUMO levels. For example, the bisPC_{61}BM with 56 π-electrons exhibits higher LUMO level by ca. 0.1 eV than the PC_{61}BM with 58 π-electrons. Consequently, the V_{oc} of the P3HT:bisPC_{61}BM-based device improves to 0.73 V compared to the P3HT:PC_{61}BM-based device with V_{oc} of 0.6 V. Based on the strategy, many fullerene bis-adduct derivatives, such as bisPC_{61}BM, IC_{61}BA, IC_{70}BA, and DMPBCBA, have been developed and applied in the PSCs.

Despite that saturating fullerene is beneficial for obtaining high V_{oc}, double functionalization on the core of fullerene in a random fashion inevitably generates a mixture of regio-isomers...
that are difficult to isolate by typical chromatography. The synthesis of mixtures of fullerene bis-adduct suffers from batch-to-batch reproducibility, because the isomer ratio and distribution are highly dependent on synthetic conditions such as temperature, reaction time, and concentration of the reactants.

For two symmetrical A₂C-addends (two A substitutents on the carbon of cyclopropane shown in Figure 1a) functionalized on C₆₀ through cyclopropanation reaction, there are eight possible regio-isomers with different substituent locations. When the two A₂C-addends are located on the same hemisphere, there are three possible isomers defined as cis-1, cis-2, and cis-3. Similarly, if the two A₂C-addends are attached on opposite hemispheres, four possible isomers, denoted as trans-1, trans-2, trans-3, and trans-4, are generated. When one A₂C-addend is functionalized on the equator of the fullerene sphere, the only one possible isomer is defined as E. If addend is unsymmetrical (substituents are A and B), more possibilities are generated; for instance, 4 different stereoisomers are possible in the trans-4 configuration (trans-4-I, trans-4-II, trans-4-III, trans-4-IV in Figure 1b). Overall, there will be at most 27 probable regio-isomers and stereoisomers (see the Supporting Information for 27 detailed structures). Because the structures of C₆₀ bis-adduct are not well-defined, the structural change of isomers could lead to different steric and electronic properties, which in turn affects device performance.

First, the different isomeric structure of bis-adducts may alter the molecular packing and thereby the resultant morphology. Moreover, each regio-isomer is expected to possess different reduction potentials. The existence of variations in the LUMO energy levels of isomers may cause energetic traps (i.e., shallow traps) which are supposed to have negative impact on Jₚ and FF. Although the shallow-trap effect has been speculated to be detrimental, the in-depth and detailed studies are still limited. To investigate whether the shallow-trap effect, resulting from a bunch of regioisomers, is important in affecting

Figure 1. (a) Eight possible regio-isomers of a C₆₀ bis-adduct substituted with a symmetrical addend, (b) four possible stereoisomers of trans-4 bis-adduct functionalized with an unsymmetrical addend, (c) chemical structure of APM-CBA.
device performance or not, a straightforward method is to reduce the number of regioisomers of a given C₆₀-bis-adduct by chemical control. However, it is synthetically very challenging. To regulate specific regio-isomers within C₆₀ bis-adduct, Diederich et al. introduced a "tether-directed remote functionalization" (TDRF) based on the idea that two addend groups are covalently attached on a tether moiety.⁴⁰⁻⁴⁶ After the tether-induced regio-selective reaction with C₆₀, the tether group can be chemically removed to resume the specific fullerene bis-adduct. Herein, we attempt to investigate the effect of a new C₆₀ bis-adduct, APM-CBA, where two (4-acetatephenyl)-4-methylphenyl methano (APM) moieties are functionalized on a C₆₀ through cyclopropanation (Figure 1c). We deliberately synthesized APM-CBA by means of two independent approaches. Random APM-CBA (R-APM-CBA) was prepared by the standard cyclopropanation, whereas regio-selective APM-CBA (S-APM-CBA) was synthesized by the TDRF strategy. The difference in numbers of isomers between R-APM-CBA and S-APM-CBA provides a model to investigate the isomeric (i.e., shallow-trap and steric) effect in bulk heterojunction solar cells.

■ RESULTS AND DISCUSSION

The molecular design is shown in Figure 2. Two diphenylmethano-based anchoring groups are linked with a tether group. The tosylhydrazone functional groups are used to undergo cyclopropanation reaction with fullerene. The length and rigidity of a tether moiety play an important role in governing regio-selectivity of the two anchoring groups on C₆₀. By careful manipulation, the two anchoring groups can be located in the same hemisphere (cis form) or opposite hemisphere (trans form) of C₆₀. 1,6-Hexylene and 1,4-xylol moieties are selected as a soft tether and an rigid tether, respectively, to connect two 4-methylbenzophenone tosylhydrazone addends together (Scheme 1 and Figure 2) for preliminary study.

**Synthesis.** The synthesis of S-APM-CBA is shown in Scheme 1. Friedel–Craft acylation of 4-methoxy benzoyl chloride with toluene afforded 4-methoxy-4′-methylbenzophenone (1).⁴⁷ Demethylation of compound 1 by boron tribromide led to 4-hydroxy-4′-methylbenzophenone (2). Under basic conditions, compound 2 was reacted with a tether molecule, 1,4-bis(bromomethyl) benzene or 1,6-dibromohexane, to give 3a or 3b, respectively. Condensation of compound 3a and 3b with p-toluenesulfonhydrazide furnished bis-tosylhydrazone 4a and 4b in good yield, respectively. In the presence of sodium hydride at 130 °C, cyclopropanation of tosylhydrazone groups in compound 4a and 4b with C₆₀ led to the formation of tether-directed C₆₀ bis-adduct intermediate 5. Dealkylation of compound 5a by BBr₃ successfully yielded compound 6 with two hydroxy groups that were allowed to react with acetyl chloride to yield the desired S-APM-CBA.

On the other hand, the synthesis of R-APM-CBA is shown in Scheme 2. Compound 7 reacted with C₆₀ to yield C₆₀ bis-adduct 8. In a similar manner, demethylation of compound 8 followed by acylation generated the final R-APM-CBA.

**Proton NMR and HPLC Measurements.** We first studied the effect of the different tether linkers on the regio-selectivity by measuring NMR spectra of compound 5a and 5b shown in a and b in Figure S1 in the Supporting Information, respectively. Compared to 5b, 5a with p-xylene as the tether exhibited less complicated peaks in the NMR spectrum, implying that the rigid 1,4-xylyl tether results in less regio-isomers than the soft n-hexyl tether. As a result of the better regio-selectivity, we selected only compound 5a for the following synthetic steps to make the final S-APM-CBA. The NMR spectra of S-APM-CBA and R-APM-CBA were measured to evaluate the effectiveness of tether-directed approach, as shown in panels a and b in Figure 3, respectively. Again, R-APM-CBA showed very complicated peaks from 2.0 to 2.6 ppm, which ascribed to the methyl groups of toluene as well as the methyl groups of ester. In contrast, S-APM-CBA showed much simpler and clearer peaks. Similar phenomena were observed in the aromatic region from 7 to 8.5 ppm, indicating that S-APM-CBA synthesized by the TDRF approach indeed contains many fewer regio-isomers than R-APM-CBA made by the typical method.

The stereochemistry of two 4-acetatephenyl-4′-methylphenylmethano groups in S-APM-CBA is determined by its precursor 5a. S-APM-CBA should inherit the stereochemistry of 5a and the number of stereoisomers should be identical for S-APM-CBA and 5a. 5a was then used to estimate the possible isomers of S-APM-CBA. With the help of a molecular-structure visualization program-GaussView 5.0, we found that 5a has at most 7 stereoisomers on account of the fact that the presence of the 1,4-xylyl tether forbids sterically the formation of the other isomers. The optimized structures of the 7 isomers are depicted in Figure 4, which includes cis-2-I, cis-2-III, cis-3-I, cis-3-II, E-II, E-III, and trans-III. Roman numerals are used to symbolize the stereoisomers resulting from the same class of regio-isomer illustrated in Figure 1 (also see the Supporting Information, Figure S1, for nomenclature). Since the interconversion between these isomers is nearly impossible, the distribution of isomers for 5a should be govern primarily by the activation barrier for the reaction from 4a to 5a among isomers. For this reaction, we reason that 4a would first react with C₆₀ to form a monoadduct with exclusive stereochemistry. Subsequently, the monoadduct would undergo another cycloaddition to give 5a. The second cycloaddition is expected to be the rate-determining step for this reaction and therefore the energy difference in the transition state for the second cycloaddition among the isomers would determine the relative product distribution. Furthermore, it can be envisaged that the energy difference between either the transition states or the resultant isomers would highly correlate with the strain resulting from the cyclic tether-addend. In light of this assumption, the energy difference between the isomers could

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**Figure 2.** Rigid and soft tether moieties in this research for tether-directed remote functionalization.
be used to roughly approximate the energy difference between the transition states and thus the distribution of isomers. Theoretical calculations on the PM3 level of theory were employed to calculate the electronic energy and Gibbs free energy (25 °C in kcal mol⁻¹) for the 7 isomers. Trans-4-III has the lowest energy which is set as zero for calibration. The electronic energy and Gibbs free energy relative to trans-4-III for the rest of 5a isomers (i.e., ΔE and ΔG) are shown in Table 1. It was found that there is no significant difference between the electronic energy and Gibbs free energy. We therefore
choose the electronic energy for the following discussion. Comparison of the optimized geometries with the corresponding electronic energies revealed that an isomer with highly strained conformation also possesses high energy. The energy of an isomer appears to be determined by the strain of the cyclic addend. The electronic energy of the isomers follows the order: trans-4-III < cis-2-I < cis-2-III < cis-3-II < E-III < E-II < cis-3-I. On the basis of the calculated energies, trans-4-III, cis-2-
Table 1. Electronic Energy Difference (ΔE) and Gibbs Free Energy Difference (25 °C) (ΔG) in kcal mol⁻¹ Relative to trans-4-III for the 5a Isomers

<table>
<thead>
<tr>
<th></th>
<th>trans-4-III</th>
<th>cis-2-I</th>
<th>cis-2-III</th>
<th>cis-3-I</th>
<th>cis-3-II</th>
<th>E-II</th>
<th>E-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE</td>
<td>0</td>
<td>1.85</td>
<td>4.02</td>
<td>16.09</td>
<td>7.29</td>
<td>12.74</td>
<td>9.33</td>
</tr>
<tr>
<td>ΔG</td>
<td>0</td>
<td>1.30</td>
<td>4.50</td>
<td>17.90</td>
<td>7.40</td>
<td>12.50</td>
<td>11.40</td>
</tr>
</tbody>
</table>

I, and cis-2-III are the more likely isomers for 5a. The computational results support that the tether-directed remote functionalization can significantly reduce the number of regio-isomers.

High-performance liquid chromatography (HPLC) was also employed to estimate the regio-isomers of bis-adduct C₆₀. The HPLC chromatogram of R-APM-CBA showed very broad distribution containing at least 12 distinct peaks ranging from 20 to 60 min retention time (Figure 5). To roughly identify the composition of the isomers in the normal phase of the HPLC, it is expected that the short-time signals belong to the trans-based isomers with lower polarity, whereas the long-time signals are assigned to the cis-based isomers with higher polarity. In contrast, the S-APM-CBA chromatogram showed only two major signals peaked at 38 and 47 min without observation of signals around shorter time (22–33 min) and longer time (50–60 min). These results are fairly consistent with the theoretical calculations suggesting that trans-4-III, cis-2-III, cis-3-I, and cis-3-II are the most probable isomers whose polarities are relatively moderate among the full isomers. HPLC data again indicated that a bis-adduct C₆₀ with significantly reduced regio-isomers can be achieved by applying the tether-directed approach.

Optical Properties. The optical absorption of R-APM-CBA, S-APM-CBA, and PC₆₁BM was characterized in THF with a concentration of 1 × 10⁻⁵ M (Figure 6). The absorption profiles of R-APM-CBA and S-APM-CBA without shoulders around 260 and 330 nm are dissimilar to that of PC₆₁BM. Interestingly, the absorption intensity of R-APM-CBA is much higher than that of S-APM-CBA under the same concentration, indicating that different regio-isomers can possess very distinct absorption coefficients.

Electrochemical Properties. The electrochemical properties of the R-APM-CBA and S-APM-CBA were investigated by cyclic voltammetry (CV) in Figure 7. The cyclic voltammetry showed three well-defined and reversible redox waves in the potential ranging from 0 to −2.5 V. In the negative potential region, R-APM-CBA and S-APM-CBA showed similar reduction potentials which shift more negatively by 0.15 eV compared to PC₆₁BM. The LUMO energy levels of S-APM-CBA, R-APM-CBA, and PC₆₁BM are estimated to be −3.77, −3.76, and −3.91 eV, respectively. The higher LUMO energy level of the bis-adducts would be advantageous for improving Voc. Notably, the energetic difference of 0.01 eV between S-APM-CBA and R-APM-CBA might cause the shallow-trap effect. Besides, we found that the CV profile of R-APM-CBA is slightly broader than that of S-APM-CBA, which is consistent with the fact that R-APM-CBA contains more regio-isomers with small variations of energetic energy levels.

![Figure 5. High-performance liquid chromatography (HPLC) chromatogram of R-APM-CBA and S-APM-CBA using toluene and ethyl acetate (4:1, v/v) as eluents at a flow rate of 1 mL/s.](image)

![Figure 6. Absorption spectra of S-APM-CBA, R-APM-CBA and PC61BM in THF solution under the concentration of 1 × 10⁻⁵ M. Inset: Enlarged absorption spectra from 400 to 800 nm.](image)

![Figure 7. Cyclic voltammetry of R-APM-CBA, S-APM-CBA, and PC61BM at a scan rate of 100 mV/S.](image)

### Table 2. Onset Reduction Potentials and LUMO Energy Levels of Fullerene Derivatives

<table>
<thead>
<tr>
<th>fullerene derivatives</th>
<th>E₁ (V)</th>
<th>E₂ (V)</th>
<th>E₃ (V)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-APM-CBA</td>
<td>−0.92</td>
<td>−1.33</td>
<td>−1.83</td>
<td>−3.77</td>
</tr>
<tr>
<td>R-APM-CBA</td>
<td>−0.94</td>
<td>−1.33</td>
<td>−1.85</td>
<td>−3.76</td>
</tr>
<tr>
<td>PC₆₁BM</td>
<td>−0.81</td>
<td>−1.22</td>
<td>−1.73</td>
<td>−3.91</td>
</tr>
</tbody>
</table>

*Potential values in this table are versus Ag/Ag⁺ reference electrode.

Photovoltaic Characteristics. Bulk heterojunction solar cells with configuration (ITO/PEDOT:PSS/P3HT:fullerene derivatives/Ca/Al) were fabricated and characterized under simulated 100 mW cm⁻² AM 1.5 G illumination (Figure 8). The device characteristics with the optimal blending ratio are shown in Table 3. The device using P3HT-R-APM-CBA blend (1:1 in wt %) showed a Voc of 0.84 V, FF of 44.3%, and Jsc of...
respectively. The di
P3HT:S-APM-CBA thin
Figure 10. The surface roughness of P3HT:R-APM-CBA and
studied by atomic force microscope (AFM) and showed in the
APM-CBA and P3HT:S-APM-CBA (1:1 in wt%) blends are
BHJ solar cells in comparison of the steric e
folds (1.8
higher than the corresponding S-APM-CBA-based device by 4-
sterically suppress the facial contact between the fullerene
isomers. The di
shallow-trap e
performance of S-APM-CBA implies that the electronic
S-APM-CBA is the number of isomers, the inferior device
Considering that the only di
CBA. As a result, the shallow-trap e
fect is insigni
fi
order molecular and morpho-
logic properties in PSCs. To investigate the isomer effect of a
C60 bisadduct, random (4-acetatephenyl)-4-methylphenyl
methano C60 bis-adduct (R-APM-CBA) was synthesized by
the traditional reaction, whereas regio-selective S-APM-CBA
was achieved by a “tether-directed remote functionalization
strategy. The significant reduction in the number of
regioisomers in S-APM-CBA is manifested by the 1H NMR,
HPLC measurements and theoretical calculation. Surprisingly,
the PSC using S-APM-CBA turned out to yield much lower
Jsc of 1.48 mA/cm² and FF of 32.16% compared to the R-APM-
CBA-based device with Jsc of 6.63 mA/cm² and FF of 44.3%.
Consistently, the electron-only device of S-AMP-CBA showed
much lower electron mobility than that of R-AMP-CBA by 4-
folds. These results imply that the electronic shallow traps as a
result of the LUMO energy variations are insignificant in the
AMP-CBA system. The structural geometry of trans-4-III, the
most probable isomer in S-AMP-CBA, might prevent the
most probable isomer in S-AMP-CBA, might prevent the
fullerene materials, which plays a key role in making
breakthrough of organic solar cells.

■ EXPERIMENTAL SECTION
Synthesis of Compound 1. A solution of aluminum chloride (2 g,
15 mmol) in dry toluene was added slowly p-methoxybenzoyl chloride
(2 g, 10 mmol) at 0 °C. The mixture was stirred at room temperature
for 10 h. The reaction was quenched by pouring the mixture into ice/
water and then extracted with ethyl acetate/H2O. The crude product
was purified by silica column to give the product (hexane:ethyl acetate
= 5:1, v/v, 4.2 g, 93%). 1H NMR (300 MHz, CDCl3) δ = 2.44 (s, 3H),
3.89 (s, 3H), 6.96 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.68
(d, J = 7.8 Hz, 2H), 7.81 (d, J = 9.0 Hz, 2H).

Table 3. Device Characteristics of (ITO/PEDOT:PSS/
P3HT:S-APM-CBA or P3HT:R-APM-CBA (1:1 wt%)/Ca/
Al)

<table>
<thead>
<tr>
<th>acceptor</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-APM-CBA</td>
<td>0.80</td>
<td>1.48</td>
<td>32.16%</td>
<td>0.38</td>
</tr>
<tr>
<td>R-APM-CBA</td>
<td>0.84</td>
<td>6.63</td>
<td>44.30%</td>
<td>2.46</td>
</tr>
</tbody>
</table>

6.63 mA/cm², resulting in a PCE of 2.46%. Surprisingly, under
similar conditions, the device with S-APM-CBA containing less
regioisomers turned out to exhibit a much lower PCE of 0.38%
with a Voc of 0.80 V, an FF of 32.16%, and a Jsc of 1.48 mA/cm².
Considering that the only difference between R-APM-CBA and
S-APM-CBA is the number of isomers, the inferior device
performance of S-APM-CBA implies that the electronic
shallow-trap effect in R-APM-CBA is not pronounced. The
discrepancy is thus ascribed to the steric effect of the regio-
isomers. The different structural geometry of the regio-isomers
causes different intermolecular interaction and morphology of
the composite. We speculated that the trans-4-III isomer where
the two addends locate on different hemispheres of C60 might
sterically suppress the facial contact between the fullerene
cages. Therefore, the electron transportation in R-APM-CBA
might be significantly hindered within the fullerene phase. On
the basis of the speculation, the electron-only devices (ITO/
ZnO/P3HT:bisadducts (1:1 in wt%)/Al) were fabricated to
study the charge transporting capability of S-APM-CBA and
R-APM-CBA-based blends (Figure 9). The R-APM-CBA-based
device yielded a mobility of 8.01 × 10⁻⁶ cm² V⁻¹ s⁻¹, which is
higher than the corresponding S-APM-CBA-based device by 4-
folds (1.8 × 10⁻⁶ cm² V⁻¹ s⁻¹). The smaller electron mobility is
responsible for the inferior solar cell performance of S-APM-
CBA. As a result, the shallow-trap effect is insignificant in the
BHJ solar cells in comparison of the steric effect.

Morphological Study. The morphology of the P3HT:R-
APM-CBA and P3HT:S-APM-CBA (1:1 in wt%) blends are
studied by atomic force microscopy (AFM) and showed in the
Figure 10. The surface roughness of P3HT:R-APM-CBA and
P3HT:S-APM-CBA thin films are 14.7 and 12.6 nm,
respectively. The difference in roughness is probably due to the
different composition of the regioisomers of APM-CBA.

■ CONCLUSIONS
Fullerene bis-adducts with intrinsically high-lying LUMO
energy levels are superior N-type materials for PSCs to

![Figure 8. J–V curves of the PSCs based on (ITO/PEDOT:PSS/
P3HT:S-APM-CBA or R-APM-CBA (1: 1 wt %)/Ca/Al) under illumination of AM 1.5G (100 mW/cm²).](image1)

![Figure 9. J–V curves of the electron-only devices based on the ITO/
ZnO/P3HT:S-APM-CBA or P3HT:R-APM-CBA (1: 1 wt %)/Al configuration.](image2)
A solution of compound 1 (10 g, 44 mmol) in dry dichloromethane was slowly added boron tribromide (1 M, 44 mL, 44 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h. The resulting solution was poured into ice/water and then extracted with CH2Cl2/NaOH. The organic phase was dried by anhydrous MgSO4 and then concentrated in vacuo. The crude product was purified by silica column to give the product (hexane:ethyl acetate = 1: 1, v/v, 8.4 g, 90%).1H NMR (300 MHz, CDCl3) δ = 2.44 (s, 6H), 5.17 (s, 4H), 7.03 (d, δ = 7.8 Hz, 4H), 7.28 (d, δ = 7.8 Hz, 4H), 7.49 (s, 4H), 7.68 (d, δ = 8.1 Hz, 4H), 7.81 (d, δ = 9 Hz, 4H), 8.10 (d, δ = 9 Hz, 4H), 8.20 (m, δ = 8.2 Hz, 2H), 8.31 (m, δ = 8.3 Hz, 16H).13C NMR (100 MHz, CDCl3) δ = 127.7, 128.1, 129.5, 129.9, 130.2, 130.7, 131.0, 131.3, 131.8, 134.1, 134.2, 134.7, 144.6, 144.7, 144.9, 145.1, 145.3, 145.4, 145.6, 145.7, 146.2, 146.6, 146.9, 147.8, 147.9, 150.0, 150.1, 169.1, 169.2. FAB-MS (m/z): 1113.

Synthesis of Compound 8. In a similar manner for compound 5a, compound 8 was obtained in a yield of 58%.1H NMR (300 MHz, CDCl3) δ = 2.17–2.46 (m, 6H), 3.68–3.90 (m, 6H), 6.61–7.32 (m, 10H), 7.37–8.14 (m, 6H). FAB-MS (m/z): 1140.

Synthesis of Compound 9. In a similar manner for compound 6, compound 9 was obtained in a yield of 93%.1H NMR (300 MHz, CDCl3) δ = 2.04–2.46 (m, 6H), 3.75–5.08 (m, 2H), 6.76–8.20 (m, 16H). FAB-MS (m/z): 1113.

Synthesis of R-APM-CBA. In a similar manner for S-APM-CBA, R-APM-CBA was obtained in a yield of 87%.1H NMR (400 MHz, CDCl3) δ = 2.08–2.47 (m, 12H), 7.10–8.31 (m, 16H).13C NMR (100 MHz, CDCl3) δ = 21.3, 27.6, 30.0, 51.7, 54.5, 54.8, 56.3, 121.7, 126.0, 127.7, 128.1, 129.5, 129.9, 130.2, 130.7, 131.0, 131.1, 131.8, 132.1, 134.1, 135.0, 135.6, 136.2, 136.5, 137.1, 137.8, 138.7, 139.7, 140.0, 140.6, 140.9, 141.5, 141.8, 142.2, 142.5, 143.0, 143.3, 144.3, 145.3, 145.8, 146.2, 146.5, 147.1, 147.9, 148.8, 149.4, 150.0, 151.0, 169.1. FAB-MS (m/z): 1197.

ASSOCIATED CONTENT

Supporting Information

Device fabrication and characterization, NMR spectra, all the possible structures of stereoisomers for a C60 bis-adduct, theoretical calculations, hole-only devices, and open circuit light intensity measurement. This material is available free of charge via the Internet at http://pubs.acs.org.
REFERENCES