

Article

## Tethered Bis-Adducts of C60 and C70 with Addends on a Common Hexagonal Face and a 12-membered Hole in the Fullerene Cage

Maira R. Cerón, Marta Izquierdo, Amineh Aghabali, Juan A. Valdez, Kamran B. Ghiassi, Marilyn M. Olmstead, Alan L. Balch, Fred Wudl, and Luis Echegoyen

*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • DOI: 10.1021/jacs.5b03768 • Publication Date (Web): 18 May 2015

Downloaded from <http://pubs.acs.org> on May 28, 2015

### Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Publications  
High quality. High impact.

# Tethered *Bis*-Adducts of C<sub>60</sub> and C<sub>70</sub> with Addends on a Common Hexagonal Face and a 12-membered Hole in the Fullerene Cage

Maira R. Cerón,<sup>a‡</sup> Marta Izquierdo,<sup>a‡</sup> Amineh Aghabali,<sup>b</sup> Juan A. Valdez,<sup>a</sup> Kamran B. Ghiassi,<sup>b</sup> Marilyn M. Olmstead,<sup>\*b</sup> Alan L. Balch,<sup>\*b</sup> Fred Wudl,<sup>\*c</sup> Luis Echegoyen<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, University of Texas at El Paso, 500W University Ave, El Paso, TX 79968 (USA)

<sup>b</sup> Department of Chemistry, University of California at Davis, One Shields Ave, Davis, CA 95616 (USA)

<sup>c</sup> Department of Chemistry and Biochemistry & Center for Polymers and Organic Solids, University of California, Santa Barbara, CA 93106 (USA)

**ABSTRACT:** The regio-selective synthesis of easily isolable pure *bis*-methanoderivatives of C<sub>60</sub> and C<sub>70</sub> with high steric congestion is described using 1,3-dibenzoylpropane-*bis*-*p*-toluenesulfonyl hydrazone as the addend precursor. When the addition occurs at two [6,6] ring junctions within the same hexagon, *bis*-adducts with mirror symmetry are obtained for both C<sub>60</sub> and C<sub>70</sub>. When the addition occurs at two [5,6] ring junctions in C<sub>60</sub>, a symmetrical adduct is formed, which readily undergoes photooxidation and ring opening to yield a fullerene with a hole in the cage. In this work we also propose a simple and general system to name all of the possible [6,6] *bis*-adduct isomers on C<sub>70</sub>.

## 1. INTRODUCTION

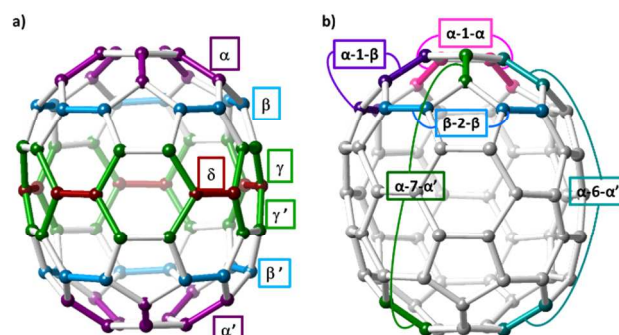
Since the discovery of fullerenes in 1985,<sup>1</sup> their functionalization has been extensively studied,<sup>1</sup> partly to increase their solubilities and to expand their applications in biomedicine, materials science and in organic photovoltaic (OPV) solar cells, among others.<sup>2</sup> The use of fullerene derivatives as electron acceptors is rapidly developing, mainly because of their low reduction potentials, their low recombination energies upon electron transfer and their high charge transport capabilities in three dimensions.<sup>2,3</sup>

Recently, *bis*-functionalization of fullerenes has resulted in compounds that are very effective in OPV solar cells.<sup>3-6</sup> Therefore, understanding and controlling the formation of specific regioisomers of *bis*- and multiple-adducts of fullerenes is crucial, because it has been shown that some regio-isomerically pure fullerene *bis*-adducts perform better in OPV solar cells than the corresponding isomeric mixtures.<sup>7</sup>

The synthesis of fullerene *bis*-adducts is challenging because of the many isomeric products that are typically obtained. If both addends are identical and symmetric, the number of possible isomers is 8 in the case of C<sub>60</sub><sup>8</sup> and 38 in the case of C<sub>70</sub> (Figure 1), provided that additions occur exclusively on [6,6]-bonds. To increase the yield of a specific *bis*-adduct regio-isomer and to avoid HPLC chromatographic separations, Diederich *et al.* introduced a very useful tool, the tether-directed remote multifunctionalization. This method involves the use of a variable length and rigidity tether that connects two or more reactive centers to direct the location of the multiple adducts on the fullerene surface.<sup>9</sup> The most abundant non-

tethered *bis*-addition products usually observed are the *trans*-3 and equatorial isomers for C<sub>60</sub> and the 12-, 2- or 5-o'clock for C<sub>70</sub>,<sup>10</sup> with very few examples of *cis*-1 or *cis*-2 on C<sub>60</sub> or  $\alpha$ -1- $\alpha$  and  $\alpha$ -2- $\alpha$  on C<sub>70</sub> because of the steric congestion see Figure 1 for the nomenclature used.<sup>11</sup> However, for *bis*-epoxides, C<sub>60</sub>O<sub>2</sub>, the isomer with both oxygen atoms bound to a single hexagonal surface is the most abundant isomer.<sup>12</sup>

Since no systematic way is currently available to define C<sub>70</sub> *bis*-adducts, we propose a simple and forward straight method to do so (Figure 1). The method uses Greek letters to define the addition positions and numbers corresponding to the smallest number of bonds separating the additions sites. This nomenclature applies for additions to [6,6]-bonds. Same type bonds on opposite sides across the  $\delta$ -bonds are differentiated using a prime designation. Using this system a 12-o'clock *bis*-adduct would be designated as  $\alpha$ -6- $\alpha'$ , a 2-o'clock would be  $\alpha$ -7- $\alpha'$  and a 5-o'clock would be  $\alpha$ -9- $\alpha'$ .<sup>13</sup>



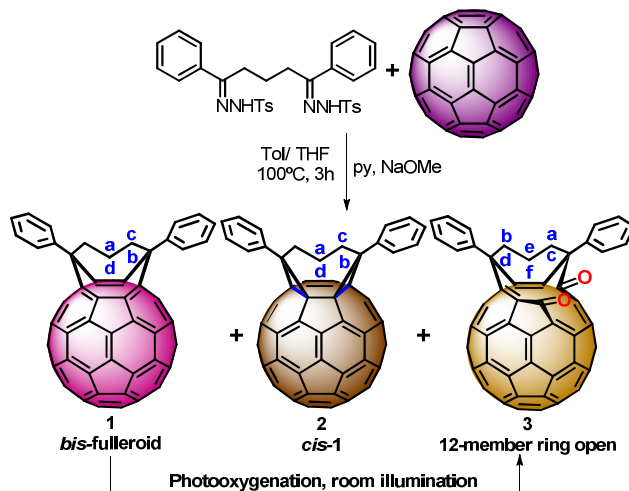
**Figure 1. a)** Types of double bonds on  $C_{70}$ . The equator contains the  $\delta$ -bonds, and in the north pole there are  $\alpha$ ,  $\beta$ , and  $\gamma$ -bonds and in the south pole  $\alpha'$ ,  $\beta'$ , and  $\gamma'$ -bonds. **b)** Some examples of possible *bis*-addition combinations relevant to this work.

Functionalization of fullerenes via diazo cycloaddition generates two types of derivatives: the fulleroids if the addition occurs on a [5,6]-bond or the methanofullerenes if the addition occurs on a [6,6]-bond.<sup>14</sup> Fulleroids are the kinetically controlled products, whereas the methanofullerenes are the thermodynamic products,<sup>15</sup> hence fulleroid derivatives are usually isomerized to the more stable methanofullerene derivatives via a  $\pi$ -methane transposition.<sup>16</sup> Both fulleroid and methanofullerene derivatives of  $C_{60}$  and  $C_{70}$  have been reported before, but there are only two examples of the synthesis of *bis*-methanofullerenes using a *bis*-diazo addend derived from a tether directed remote functionalization method, which yielded seven regio-isomers.<sup>17</sup> Here we designed a shorter, rigid and symmetric *bis*-diazo addend to limit the number of possible regio-isomers. To the best of our knowledge there are no reports of the synthesis of *bis*-fulleroids using *bis*-diazo cycloadditions.<sup>18</sup>

## 2. RESULTS AND DISCUSSION

**Synthesis of [60]Fullerene-Bis-Adducts 1, 2 and 3.** Pure *bis*-adducts **1** and **2** were synthesized from a *bis*-diazo precursor, resulting from the *in situ* base-induced decompositions of 1,3-dibenzoylpropane-*bis*-*p*-toluenesulfonyl hydrazone (DBP), in the presence of  $C_{60}$  as shown in Scheme 1.<sup>13</sup> To prevent the formation of *mono*-adducts, an excess of sodium methoxide (NaOMe) and pyridine (py) was added. Purification of the crude mixture using silica gel chromatography ( $CS_2$ :Hexanes 3:2) eluted unreacted pristine fullerene, followed by compounds **1** and **2** and finally by a mixture of multiadducts. The yield and ratio of compounds **1** and **2** were controlled by modifying the reaction conditions; under dilute conditions in toluene/THF the main product was compound **1** (19%) followed by compound **2** (3%); under more concentrated conditions in *o*-DCB the main product was compound **2** (13%) followed by compound **1** (4%). Characterization of compound **1** was difficult because of its unexpected high sensitivity to light; which quickly led to its conversion into a new compound **3** and a pronounced color change from pink to yellow, see details below.<sup>19</sup>

**Spectroscopic Characterization of [60]Fullerene-Bis-Adducts 1, 2 and 3.** Compounds **1**, **2** and **3** were characterized by UV-vis spectrophotometry, Nuclear Magnetic Resonance spectroscopy (NMR), Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry (MALDI-TOF MS), cyclic voltammetry and by X-ray single crystal diffraction, except where noted. Since the DBP group has a short alkane chain, after the first addition the most accessible bonds for a second addition on  $C_{60}$  are either one or two bonds away.



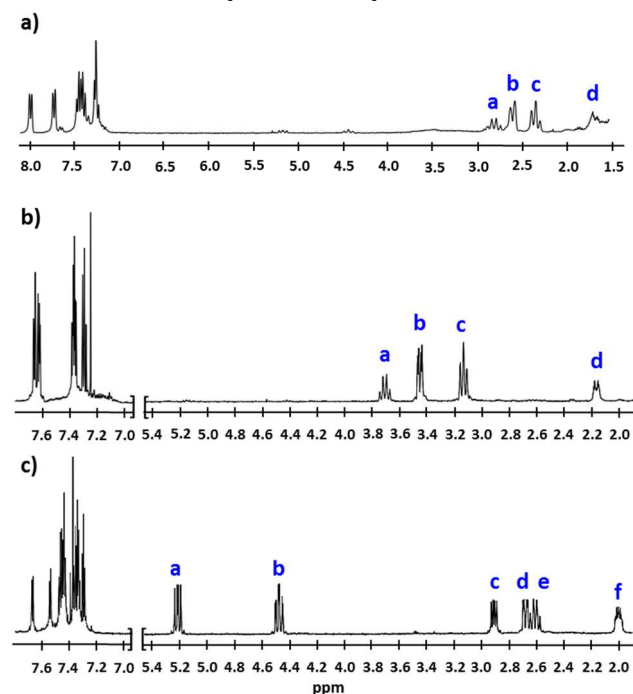
**Scheme 1.** One-step synthesis of *bis*-methanoderivatives [60]fullerene.

Compound **1** shows a molecular mass of 940.1364  $m/z$  by MALDI-MS. It has a UV-vis absorption spectrum that is essentially identical to that observed for pristine [60]fullerene, indicating that both additions on compound **1** have likely occurred on [5,6]-bonds. Thus, the assignment to a *bis*-fulleroid structure is based on the fact that the cages of *bis*-fulleroids and  $C_{60}$  are isoelectronic, since there is no loss of  $\pi$ -conjugation of the cage upon [5,6]-additions.<sup>13,20</sup> Surprisingly, the *bis*-fulleroid derivative compound **1** in the presence of air, quickly converted to a more stable derivative, compound **3**, with a molecular mass of 972.12572  $m/z$ , corresponding to an addition of two oxygen atoms to compound **1**.

Compound **3** showed a similar UV-vis absorption spectrum to that reported for a photooxidized open cage fullerene.<sup>21</sup> Thus photooxygenation of compound **1** is favored over isomerization to a *bis*-methanofullerene (Scheme 2).<sup>14</sup> Compound **2**, with a molecular ion peak at 940.12571  $m/z$ , showed a similar absorption spectrum as that reported for a *cis*-1 *bis*-isomer.<sup>22</sup> Thus initial structural assignments for these compounds were made solely based on the unique UV-vis absorption patterns exhibited by each  $C_{60}$  *bis*-adduct in the 300 to 700 nm region.

The  $^1H$ -NMR spectrum of compound **1** showed 4 sets of signals with integrals of 1:2:2:1 (Figure 2), which could correspond to the presence of two protons with different chemical environments attached to the same carbon (protons **a** and **d**). Due to the proximity of the two additions, the alkane chain is not free to rotate and this restriction generates different environments for the protons, with proton **d** probably closer to the cage, which shifts its signal to a higher field.<sup>23</sup> For compound **1** it was not possible to obtain a reasonable  $^{13}C$ -NMR spectrum due to the fast photooxygenation of the compound. DFT calculations using the B3LYP functional and the 6-311G\* basis set,<sup>24</sup> suggested that the isomer with the lowest energy of the *bis*-fulleroid has the addition pattern shown in Scheme 1, with the phenyl rings in a symmetric configuration.<sup>25</sup> Although a *bis*-fulleroid structure with a similar addition pattern has been reported,<sup>17</sup> to the best of our knowledge

there is no precedent for a tether-directed *bis*-functionalization that gives rise directly to a sterically congested *bis*-fulleroid. *Bis*-fulleroids are typically obtained from cyclohexadiene-fused derivatives upon irradiation; after the [4+4] intramolecular photocycloadditions these are followed by [2 + 2 + 2] cycloreversions.<sup>17</sup>



**Figure 2.** <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> (1/1), 298 K) of **a**) Compound **1** **b**) Compound **2** and **c**) Compound **3**.

Although compound **2** contains a plane of symmetry (Scheme 1), the <sup>1</sup>H-NMR spectrum showed 4 sets of signals with integrals of 1:2:2:1 (Figure 2). Analogously to compound **1**, the COSY-NMR and the HMQC-NMR spectra of compound **2** showed that proton **d** is likely closer to the cage than **a**, which results in an upfield shift. The <sup>13</sup>C-NMR spectrum clearly established the existence of a plane of symmetry, with 28 signals observed for sp<sup>2</sup> carbons. The bridgehead and bridge carbons were observed at 55.86, 65.38 and 70.69 ppm, corresponding to a typical methanofullerene structure.<sup>19</sup>

The FT-IR spectrum of compound **3** showed two carbonyl absorptions at 1738 cm<sup>-1</sup> and 1689 cm<sup>-1</sup>, in agreement with the observation of two extra oxygen atoms in the LD FT-ICR spectrum of compound **3**, resulting from the photooxygenation of compound **1**. The <sup>1</sup>H-NMR spectrum of compound **3** showed 6 sets of signals in the aliphatic region and an integral value of 10 in the aromatic region (Figure 2), consistent with an oxygen addition to an unsymmetric bond close to one of the [5,6]-additions. The COSY-NMR and the HMQC-NMR of compound **3** support the assignment of the signals, as well as the observation of an upfield shift for proton **f**. The <sup>13</sup>C-NMR spectrum exhibited no plane of symmetry with 54 signals for sp<sup>2</sup> carbons (four double intensity signals corresponding to carbons with accidental overlap), and the bridgehead carbons at 60.14 and 64.07 ppm, corresponding to a *bis*-

fulleroid structure and the carbonyl at 162.20 and 157.52 ppm.<sup>19</sup>

Calculations were performed to determine the structure of compound **3**. Analysis of the experimental data and DFT calculations suggested that the addition of one oxygen molecule to compound **1** occurred at one of the two bonds next to the fulleroid addition, in agreement with the loss of symmetry of compound **1**. Fullerenes are known to self-sensitize their photooxygenation.<sup>26</sup> Such a photooxygenation of an azafulleroid was used to create the first example of a fullerene containing a hole in the cage.<sup>20</sup> Here we report the one step photooxygenation of a *bis*-fulleroid to obtain a 12-membered opened *bis*-fulleroid (Scheme 1).

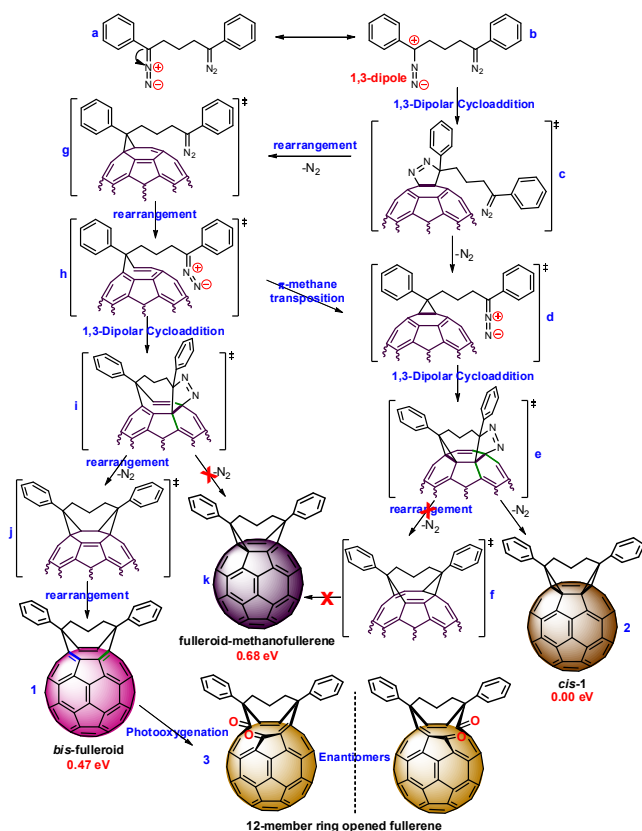
Bis-diazo compound (**a**) is stabilized by the formation of a 1,3-dipole (**b**) see Scheme 2. 1,3-dipolar cycloaddition of **b** to a [6,6]-bond of the fullerene leads to the formation of a pyrazoline intermediate (**c**), which can rearrange to **h** or undergo nitrogen elimination to yield **d**, see Scheme 2. Depending on which step predominates will determine the type of addition that occurs on the fullerene; either a *bis*-fulleroid (rearrangement) or a *bis*-methanofullerene derivative (after nitrogen elimination).

After formation of the first pyrazoline and nitrogen elimination, the methanofullerene monoadduct (**d**) can undergo a second 1,3-dipolar cycloaddition to a [6,6]-bond in the same six membered ring to yield **e**, see supporting information. A second nitrogen elimination would then yield compound **2**, *bis*-methanofullerene *cis*-1, see Scheme 2. Rearrangement of the second pyrazoline could result in the formation of a fulleroid-methanofullerene *bis*-adduct (**k**). Rearrangement to either of the two possible [5,6]-bonds (green bonds in **e**) would result in the formation of an energetically less stable fulleroid-methanofullerene *bis*-adduct, which does not form, see supporting information.

On the other hand, rearrangement of pyrazoline (**c**) yields fulleroid monoadduct (**h**), which can undergo a  $\pi$ -methane transposition to yield monoadduct (**d**), or a second 1,3-dipolar cycloaddition to a [6,6]-bond in the same six membered ring (**i**). Rearrangement of the second pyrazoline (**i**) would yield compound **1**, the *bis*-fulleroid, see Scheme 2. Nitrogen elimination could give rise to the fulleroid-methanofullerene *bis*-adduct (**k**), which is not observed. Photooxygenation of compound **1** at the green or blue bonds (Scheme 2, compound **1**) gives rise to compound **3** as a pair of enantiomers.

**Electrochemical Characterization of [60]Fullerene Compounds **2** and **3**.** The redox potentials of *bis*-derivatives of C<sub>60</sub> (compounds **2** and **3**) were measured by cyclic voltammetry (CV) and square wave voltammetry (SWV) in *o*-DCB solutions using 0.05M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. The SWV results are summarized in Table 1.





**Scheme 2.** Suggested Mechanism for the synthesis of *bis*-derivatives [60]fullerene.

Previous studies showed that  $C_{60}$  methanofullerenes typically exhibit reversible cathodic electrochemical behavior,<sup>27</sup> analogous to those observed for  $C_{60}$ .<sup>28</sup> The CV of compound **2** showed three reduction waves with electrochemically reversible behavior, and compound **3** showed five reversible reduction waves. The reduction potentials of all *bis*-fullerene derivatives were shifted cathodically compared to the values for  $C_{60}$ . It is well known that the additions to double bonds on  $C_{60}$  cathodically shift the reduction potentials by approximately 100–150 mV.<sup>29</sup> Since compound **2** is a *bis*-adduct, cathodic shifts around 200–250 mV were anticipated. Compound **2** exhibits a shift of 210 mV. For the case of compound **3**, the cathodic shift is less evident with very similar redox properties compared to those of  $C_{60}$ .

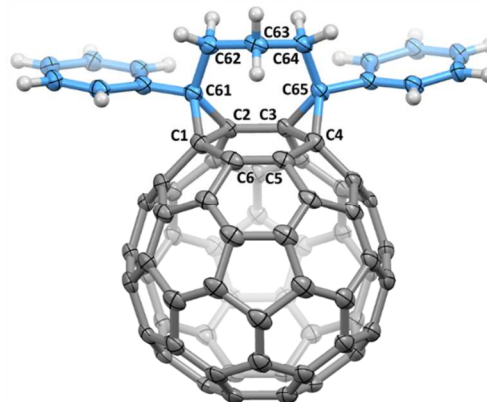
**Table 1.** Redox potential<sup>[a]</sup> of  $C_{60}$  *bis*-derivatives **2** and **3**.

Compound	$C_{60}$	Compound <b>2</b>	Compound <b>3</b>
$E^{0/-}$	-1.12	-1.33	-0.96
$E^{-1/-2}$	-1.49	-1.73	-1.37
$E^{-2/-3}$	-1.93	-2.22	-1.72
$E^{-4/-5}$	-2.40	-	-1.96
$E_{\text{onset, red}}$	-1.02	-1.19	-0.88

LUMO <sup>[b]</sup>	-4.08	-3.91	-4.22
[a] Values obtained by square wave and cyclic voltammetry in volts vs Fc/Fc <sup>+</sup> couple. [b] Values obtained using the following formula $E_{\text{LUMO}} = (E_{\text{onset, red vs Fc}^+/\text{Fc}} + 5.1) \text{ eV}$ . <sup>30</sup>			

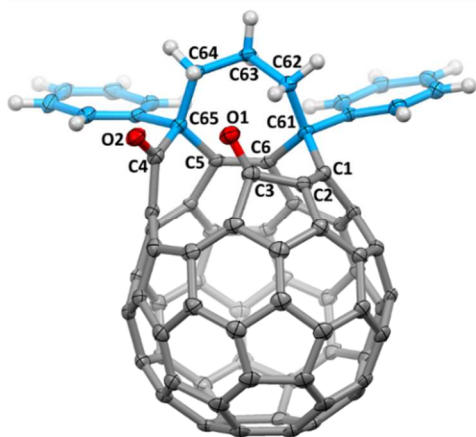
### Crystallographic Analysis of Compounds **2** and **3**.

Single crystals of compound **2**•toluene were grown by slow evaporation of a toluene solution of the compound. The results of the X-ray structure determination are shown in Figure 3. In this drawing the carbon atoms of the addend are colored blue. This molecule has no crystallographic symmetry, but a virtual mirror plane bisects the C2–C3 and C6–C5 bonds. The bond distances for the fullerene cage fall within normal ranges. However, at the point of addition across the two 6:6 double bond, significant bond lengthening has occurred, yielding distances over 1.6 Å for the C1–C2 and C3–C4 bonds (see Figure 3).



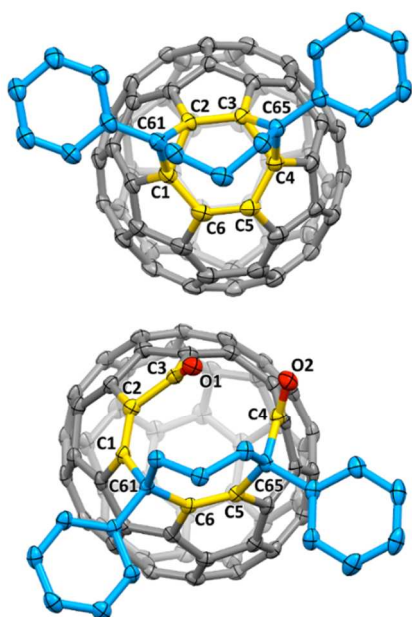
**Figure 3.** The molecular structure of the *bis*-methanofullerene derivative of  $C_{60}$ , compound **2**•toluene. Thermal contours are drawn at the 50% probability level. A molecule of toluene is omitted for clarity. Selected distances (Å): C1–C2, 1.620(3) Å; C3–C4, 1.616(4) Å; C2–C3, 1.535(3) Å; C5–C6, 1.380(4) Å.

Single crystals of compound **3**•2.5CS<sub>2</sub> were grown by slow diffusion of ethanol into a carbon disulfide solution of the compound. The structure, which is shown in Figure 4, reveals the 12-member ring opened cage structure of compound with the addition of two oxygen atoms. Three of the C–C bonds (C4–C5, C4–C3, and C1–C6) in the original fullerene have been broken. Thus, these non-bonded separation are: C4–C5, 2.470(5) Å; C4–C3, 3.138(5) Å; and C1–C6, 2.345(5) Å, and the non-bonded O1–O2 distance is 2.705(4) Å.



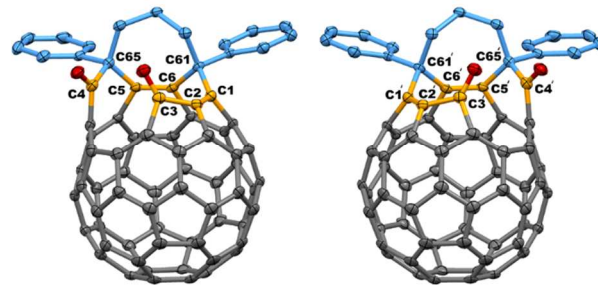
**Figure 4.** The molecular structure of one enantiomer of the ring-opened adduct, compound **3**, with the carbon atoms of the addend colored blue. Thermal contours are drawn at the 50% probability level. Solvate carbon disulfide molecules are omitted for clarity. Selected atom distances (Å): C1-C2, 1.384(5); C5-C6, 1.368(5); C3-O1, 1.199(4); C4-O2, 1.218(4).

Figure 5 compares the sites of adduct formation of the *bis*-adduct compound **2** and the ring opened adduct compound **3**. In this figure, the yellow carbon atoms belonged to the original hexagonal face of the C<sub>60</sub> molecule that underwent addition.



**Figure 5.** A comparison of compounds compound **2** (top) and compound **3** (bottom) as viewed from the perspective of oxygen addition. Thermal contours are drawn at the 50% probability level.

Compound **3** is a chiral molecule. The two enantiomers that are present in the centrosymmetric space group *Pi* are depicted in Figure 5.<sup>31</sup>



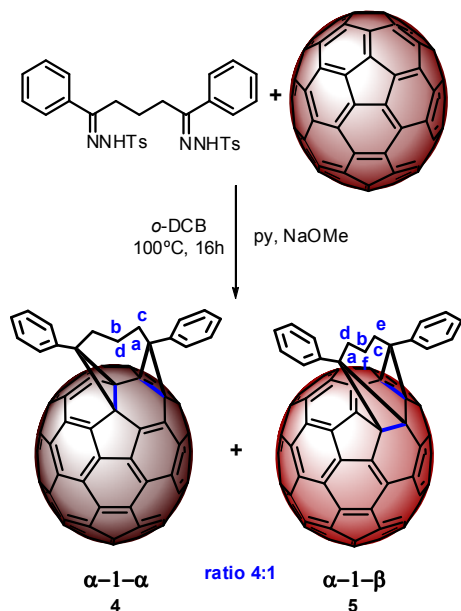
**Figure 6.** Enantiomers of the 12-member ring opened cage in compound **3**. Thermal contours are drawn at the 50% probability level. Both enantiomers occur in the crystal structure due to the instance of a centrosymmetric space group.

Based on the X-ray data, spectroscopic analysis and DFT calculations, it was possible to assign the addition pattern (summarized in Scheme 1) for the pure *bis*-fulleroid **1**, *bis*-methanofullerene **2** (*cis*-1) and the 12-membered opened *bis*-fulleroid **3**.

**Synthesis of [70]Fullerene-Bis-Adducts 4 and 5.** Pure *bis*-adducts **4** and **5** were synthesized using the same method described above but using C<sub>70</sub> instead of C<sub>60</sub> (Scheme 3). Purification of the crude mixture using silica gel chromatography (CS<sub>2</sub>:Hexanes 3:2) eluted the unreacted pristine fullerene, followed by a mixture of compounds **4** and **5** and finally by a fraction of multiadducts. Compounds **4** and **5** were further purified by preparative TLC (CS<sub>2</sub>:Hexanes 1:1). The major product of the reaction was *bis*-adduct compound **4**, which was isolated in 22% yield, followed by compound **5** in 6% yield. In contrast to the results observed with C<sub>60</sub>, varying the reaction conditions did not significantly affect the yield or ratio of the final products.

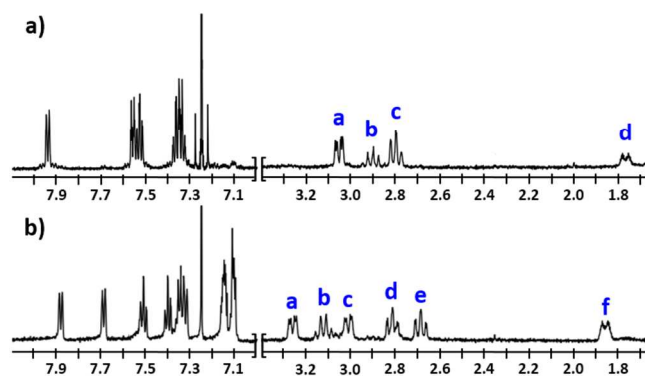
**Characterization of [70]Fullerene-Bis-Adducts 4 and 5.** Compounds **4** and **5** were characterized by UV-vis spectrophotometry, NMR spectroscopy, MALDI-TOF mass spectrometry and cyclic voltammetry. To estimate the number of possible isomers in this reaction, we assume that the first addition occurs at an  $\alpha$ -bonds, since it exhibits the highest reactivity compared to the  $\beta$ ,  $\gamma$  and  $\delta$  bonds on C<sub>70</sub>.<sup>32</sup> Due to the short alkane chain of the DBP group, after the first addition takes place, the most likely *bis*-adducts are:  $\alpha$ -1- $\alpha$ ;  $\alpha$ -2- $\alpha$ ;  $\alpha$ -1- $\beta$  and  $\alpha$ -3- $\beta$  (Figure 1).

Assignments of the addition pattern of *bis*-adducts on C<sub>70</sub> were not based on the corresponding UV-vis absorption spectra because there are very few examples of [70]fullerene-*bis*-adducts reported in the literature.<sup>11</sup> Here we report the characterization of two new *bis*-adducts of C<sub>70</sub> for which both additions occur on the same pole of C<sub>70</sub>, unlike most [70]-fullerene-*bis*-adducts reported, where the additions occur on opposite poles of the molecule.



**Scheme 3.** One-step synthesis of *bis*-methanoderivates of [70]fullerene.

The MALDI-MS of compound **4** showed the parent molecular peak at 1060.1322  $m/z$ , corresponding to a *bis*-adduct. The  $^1\text{H}$ -NMR spectrum of compound **4** was very similar to that for compound **2**; 4 sets of signals with integrals of 2:1:2:1 were observed (Figure 7). This result, along with the UV-vis absorption spectrum suggests an  $\alpha$ -1- $\alpha$  addition pattern. The COSY-NMR and the HMQC-NMR spectra of compound **4** showed that protons **b** and **d** are bonded to the same carbon, with an upfield shift for proton **d**. The  $^{13}\text{C}$ -NMR spectrum showed the presence of a plane of symmetry with 32 signals corresponding to  $\text{sp}^2$  carbons (one with double intensity at 147.94 ppm due to accidental overlap), and the bridgehead and bridge carbons at 41.53, 64.14 and 57.46 ppm, which correspond to a typical methanofullerene structure.<sup>19</sup>



**Figure 7.**  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3/\text{CS}_2$  (1/1), 298 K) of **a)** Compound **4** and **b)** Compound **5**.

The MALDI-MS spectrum of compound **5** showed the parent molecular peak at 1060.1383  $m/z$ , corresponding to a *bis*-adduct. The  $^1\text{H}$ -NMR spectrum of compound **5** exhibited diastereotopic behavior with 6 sets of signals in the aliphatic region (Figure 7). COSY-NMR and HMQC-NMR

spectra of compound **5** supported the assignment of the signals, with the observation of upfield shifts for proton **f**. The  $^{13}\text{C}$ -NMR spectrum exhibited no plane of symmetry with 63 signals for the  $\text{sp}^2$  carbons (three double intensity signals corresponding to carbons with accidental overlap). The bridgehead and bridge carbons at 42.38, 43.84, 54.52 and 62.39 ppm, correspond to methanofullerene structures.<sup>19</sup> Calculations were performed to determine the structures of compound **5**. Analysis of the experimental data and DFT calculations suggest that the addition on compound **5** is  $\alpha$ -1- $\beta$  (Scheme 3).

**Electrochemical Characterization of [70]Fullerene-Bis-Adducts 4 and 5.** The redox potentials of *bis*-methanofullerene **4** and **5** were also measured by CV and SWV using the same conditions for the  $\text{C}_{60}$  derivatives. The SWV results are summarized in Table 2.

Previous studies showed that  $\text{C}_{70}$  methanofullerene typically exhibit reversible cathodic electrochemical behavior,<sup>33</sup> analogous to those observed for  $\text{C}_{60}$  and  $\text{C}_{70}$ .<sup>25</sup> The CV of compounds **4** and **5** showed three reduction waves with electrochemically reversible behavior. The reduction potentials of all *bis*-methanofullerene derivatives were shifted cathodically around 300 mV compared to the corresponding values for  $\text{C}_{70}$ .<sup>34</sup>

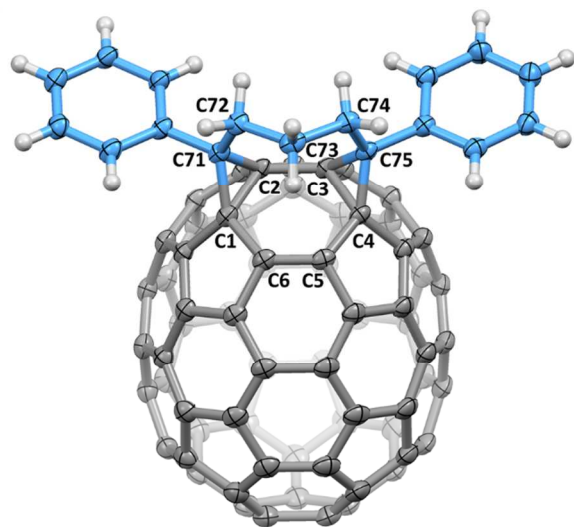
**Table 2.** Redox Potentials (V)<sup>[a]</sup> of  $\text{C}_{70}$  *bis*-derivatives **4** and **5**.

Compound	$\text{C}_{70}$	Compound <b>4</b>	Compound <b>5</b>
$E^{0/-}$	-0.98	-1.31	-1.27
$E^{-1/-2}$	-1.34	-1.47	-1.64
$E^{-2/-3}$	-1.75	-1.99	-1.99
$E_{\text{onset, red}}$	-0.88	-1.22	-1.14
LUMO (eV)	-4.22	-3.88	-3.96

[a] Values obtained by square wave voltammetry in volts vs Fc/Fc<sup>+</sup> couple. [b] Values obtained using the following formula  $E_{\text{LUMO}} = (E_{(\text{onset, red vs Fc}^+/\text{Fc})} + 5.1) \text{ eV}$ .<sup>30</sup>

**Crystallographic Analysis of Compound 4.** Single crystals of compound **4**•toluene were grown by slow evaporation of a toluene solution of the compound. As shown in Figure 8, the adduct with the carbon atoms colored blue occupies a symmetrical position near the cap of the  $D_{5h}$ - $\text{C}_{70}$  fullerene. As was the case for the  $\text{C}_{60}$ , addition across the double bonds of the fullerene has caused bond lengthening but not bond-breaking. The other fullerene C-C bonds were not greatly affected by adduct formation. Although the molecule has no crystallographically imposed symmetry, it does have effective mirror symmetry with the virtual mirror plane perpendicular to the plane of Figure 8, passing through C73 and bisecting the C2-C3 and C6-C5 bonds.





**Figure 8.** Molecular structure of first highly steric congested *bis*-methanofullerene derivative of  $C_{70}$ , compound **4** showing thermal displacement parameters at the 50% probability level and selected atom numbers. The molecule of toluene is omitted for clarity. Selected distances (Å): C1-C2, 1.633(3); C3-C4, 1.626(3); C2-C3, 1.524(3); C5-C6, 1.374(3).

## CONCLUSION

New double addition products of both  $C_{60}$  and  $C_{70}$  have been prepared with both additions occurring within one six-membered ring of the fullerene through the use of 1,3-dibenzoylpropane-*bis*-*p*-toluenesulfonyl hydrazone as the addend precursor. When the addition occurs at two [6,6] ring junctions within a hexagon, the *bis*-adducts **2** and **4** with mirror symmetry have been obtained for both  $C_{60}$  and  $C_{70}$ .

When the addition occurs at two [5,6] ring junctions of  $C_{60}$ , symmetrical *bis*-fulleroid is formed. This adduct readily undergoes photooxidation and ring opening to yield a fullerene with a 12-membered hole in the cage.

Electrochemical measurements showed that the reduction potentials of all synthesized *bis*-adducts were shifted cathodically between 200–300 mV compared to the corresponding values for the pristine fullerenes.

## ASSOCIATED CONTENT

**Supporting Information.** Detailed synthesis and characterization of compounds **1** to **5** are presented in the supporting information including X-ray .cif files and DFT calculations results, this material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\* Department of Chemistry, University of Texas at El Paso  
500W University Ave, El Paso, TX, 79968 (USA)

E-mail: [echegoyen@utep.edu](mailto:echegoyen@utep.edu)

\* Department of Chemistry, University of California, Davis,  
CA 95616 (USA)

E-mail: [albalch@ucdavis.edu](mailto:albalch@ucdavis.edu), [mmolmstead@ucdavis.edu](mailto:mmolmstead@ucdavis.edu)

\* Department of Chemistry and Biochemistry & Center for  
Polymers and Organic Solids, University of California, Santa  
Barbara, CA 93106 (USA)

E-mail: [wudl@chem.ucsb.edu](mailto:wudl@chem.ucsb.edu)

## Author Contributions

‡These authors contributed equally.

## Funding Sources

PREM Program DMR-1205302. The Robert A. Welch Foundation grant AH-0033. NSF grant CHE-1011760. US Department of Energy DE-AC02-05CH11231.

## ACKNOWLEDGMENT

We thank the NSF for generous support of this work under the PREM Program (DMR-1205302) and for grant CHE-1408865. The Robert A. Welch Foundation is also gratefully acknowledged for an endowed chair to L.E. (grant AH-0033). A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by the NSF Agreement No. DMR-1157490 and the State of Florida. A.L.B. and M.M.O. acknowledge the NSF for grant CHE-1011760, the Advanced Light Source, supported by the Director, Office of Science, Office of Basic Energy Sciences of the US Department of Energy under contract no. DE-AC02-05CH11231, for beam time, and Dr. Simon J. Teat and Dr. Christine M. Beavers for their assistance and fellowship to KBG.

## ABBREVIATIONS

LUMO, low unoccupied molecular orbital; HPLC, high performance liquid chromatography; *o*-DCB, *ortho*-dichlorobenzene; TLC, thin layer chromatography; NMR, nuclear magnetic resonance; COSY, correlation spectroscopy; HMQC, Heteronuclear multiple-quantum correlation spectroscopy.

## REFERENCES

- (1) a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. b) Kraetschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. c) Hirsch, A. In *The Chemistry of the Fullerenes*; Hirsch A., Ed.; Thieme, Stuttgart: 2002; p 79.
- (2) a) Chen, N.; Ortiz, A. L.; Echegoyen, L. In *Fullerenes: Principles and Applications (2)*; The Royal Society of Chemistry: 2012, p 12. b) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2008**, *47* (1), 58-77.
- (3) Mishra, A.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2012**, *51*, 2020-2067.
- (4) Sun, Y.; Cui, C.; Wang, H.; Li, Y. *Adv. Energy Mater.* **2012**, *2*, 966-969.
- (5) Lenes, M.; Wetzelaer, G.-J. A. H.; Kooistra, F. B.; Veenstra, S. C.; Hummelen, J. C.; Blom, P. W. M. *Adv.Mater.* **2008**, *20*, 2116.
- (6) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct.Mater.* **2001**, *11*, 374.
- (7) a) Meng, X.; Zhao, G.; Xu, Q.; Tan, Z. a.; Zhang, Z.; Jiang, L.; Shu, C.; Wang, C.; Li, Y. *Adv. Funct. Ma-*



- ter. **2014**, *24*, 158-163. b) Wong, W. W. H.; Subbiah, J.; White, J. M.; Seyler, H.; Zhang, B.; Jones, D. J.; Holmes, A. B. *Chem. Mater.* **2014**, *26*, 1686. c) Tao, R.; Umeyama, T.; Kurotobi, K.; Imahori, H. *ACS Appl. Mater. Interfaces* **2014**, *6*, 17313.
- (8) a) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem. Int. Ed.* **1994**, *33*, 437. b) Diederich, F.; Kessinger, R. *Acc. Chem. Res.* **1999**, *32*, 537. c) Hirsch, A. *Chem. Rec.* **2005**, *5*, 196. d) Kessinger, R.; Thilgen, C.; Mordasini T.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 3069.
- (9) Hirsch, A.; Brettreich, M. In *Fullerenes*, Wiley-VCH, Weinheim, 2005; Chapter 10, p 289.
- (10) a) Sander, M.; Jarrosson, T.; Chuang, S.-C.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **2007**, *72*, 2724. b) Tzirakis, M. D.; Alberti, M. N.; Orfanopoulos, M. *Org. Lett.* **2011**, *13*, 3364. c) van Eis, M. J.; Seiler, P.; Muslinkina, L. A.; Badertscher, M.; Pretsch, E.; Diederich, F.; Alvarado, R. J.; Echegoyen, L.; Pérez Núñez, I. *Helv. Chim. Acta* **2002**, *85*, 2009. d) Neti, V. S. P. K.; Cerón, M. R.; Duarte-Ruiz, A.; Olmstead, M. M.; Balch, A. L.; Echegoyen, L. *Chem. Commun.* **2014**, *50*, 10584. e) Cerón, M. R.; Izquierdo, M.; Pi, Y.; Atehortúa, S. L.; Echegoyen, L. *Chem. Eur. J.* **2015**, *21*, 7881. f) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049.
- (11) a) Izquierdo, M.; Cerón, M. R.; Alegret, N.; Metta-Magaña, A. J.; Rodríguez-Forteza, A.; Poblet, J. M.; Echegoyen, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 12928. b) Ni, L.; Yang, W.-W.; Li, Z.-J.; Wu, D.; Gao, X. *J. Org. Chem.* **2012**, *77*, 7299. c) Martin, N.; Altable, M.; Filippone, S.; Martin-Domenech, A. *Chem. Commun.* **2004**, *0*, 1338. d) Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Poater, A.; Solà, M. *Chem. Eur. J.* **2005**, *11*, 2716. e) Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 1439. f) Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M.; Martín, N. *Org. Lett.* **2006**, *8*, 5959. g) Izquierdo, M.; Osuna, S.; Filippone, S.; Martín-Domenech, A.; Sola, M.; Martin, N. *J. Org. Chem.* **2009**, *74*, 6253.
- (12) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 8926.
- (13) van Eis, M. J.; Alvarado, R. J.; Echegoyen, L.; Seiler, P.; Diederich, F. *Chem. Comm.* **2000**, 1859.
- (14) a) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479. b) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532.
- (15) Hall, M. H.; Shevlin, P.; Lu, H.; Gichuhi, A.; Shannon, C. *J. Org. Chem.* **2006**, *71*, 3357.
- (16) a) Gonzalez, R.; Hummelen, J. C.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 2618. b) Matsuo, Y.; Okada, H.; Maruyama, M.; Sato, H.; Tobita, H.; Ono, Y.; Omote, K.; Kawachi, K.; Kasama, Y. *Org. Lett.* **2012**, *14*, 3784.
- (17) a) Liao, M.-H.; Lai, Y.-Y.; Lai, Y.-Y.; Chen, Y.-T.; Tsai, C.-E.; Liang, W.-W.; Cheng, Y.-J. *ACS Appl. Mater. & Interfaces* **2013**, *6*, 996. b) Bouwer, R. K. M.; Hummelen, J. C. *Chem. Eur. J.* **2010**, *16*, 11250.
- (18) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817.
- (19) Inoue, H.; Yamaguchi, H.; Iwamatsu, S.-i.; Uozaki, T.; Suzuki, T.; Akasaka, T.; Nagase, S.; Murata, S. *Tetrahedron Lett.* **2001**, *42*, 895.
- (20) Hirsch, A. In *The Chemistry of the Fullerenes*; Hirsch A., Ed.; Thieme, Stuttgart: 1994; p 203.
- (21) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003.
- (22) a) Djojo, F.; Herzog, A.; Lamparth, I.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1996**, *2*, 1537. b) Kordatos, K.; Bosi, S.; Da Ros, T.; Zambon, A.; Lucchini, V.; Prato, M. *J. Org. Chem.* **2001**, *66*, 2802.
- (23) Murata, M.; Ochi, Y.; Tanabe, F.; Komatsu, K.; Murata, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 2039.
- (24) a) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, and M. S. Gordon, *J. Chem. Phys.* 1982, *77*, 3654-3665. b) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* 1972, *56*, 2257.
- (25) Xiao, Y.; Zhu, S.-E.; Liu, D.-J.; Suzuki, M.; Lu, X.; Wang, G.-W. *Angew. Chem. Int. Ed.* **2014**, *53*, 3006.
- (26) Zhang, X.; Romero, A.; Christopher S. Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024.
- (27) a) Samoylova, N. A.; Belov, N. M.; Brotsman, V. A.; Ioffe, I. N.; Lukonina, N. S.; Markov, V. Y.; Ruff, A.; Rybalchenko, A. V.; Schuler, P.; Semivrazhskaya, O. O.; Speiser, B.; Troyanov, S. I.; Magdesieva, T. V.; Goryunkov, A. A. *Chem. - Eur. J.* **2013**, *19*, 17969. b) Carano, M.; Marcaccio, M.; Paolucci, F. *RSC Nanosci. Nanotechnol.* **2012**, *20*, 237. c) Kessinger, R.; Fender, N. S.; Echegoyen, L. E.; Thilgen, C.; Echegoyen, L.; Diederich, F. *Chem. - Eur. J.* **2000**, *6*, 2184. d) Deng, F.; Wang, G.-W.; Zhang, T.-H.; Jiao, L.-J.; Chen, S. *Chem. Comm.* **2004**, 1118.
- (28) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593.
- (29) Lenes, M.; Wetzelaer, G.-J. A. H.; Kooistra, F. B.; Veenstra, S. C.; Hummelen, J. C.; Blom, P. W. M. *Adv. Mater.* **2008**, *20*, 2116.
- (30) C. Hummelen, J.; Keshavarz-K, M.; L. J. van Dongen, J.; A. J. Janssen, R.; W. Meijer, E.; Wudl, F. *Chem. Comm.* **1998**, 281.
- (31) Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem. Int. Ed.* **1997**, *36*, 2268.
- (32) a) Samoylova, N. A.; Belov, N. M.; Brotsman, V. A.; Ioffe, I. N.; Lukonina, N. S.; Markov, V. Y.; Ruff, A.; Rybalchenko, A. V.; Schuler, P.; Semivrazhskaya, O. O.; Speiser, B.; Troyanov, S. I.; Magdesieva, T. V.; Goryunkov, A. A. *Chem. - Eur. J.* **2013**, *19*, 17969. b) Carano, M.; Marcaccio, M.; Paolucci, F. *RSC Nanosci. Nanotechnol.* **2012**, *20*, 237. c) Kessinger, R.; Fender, N. S.; Echegoyen, L. E.; Thilgen, C.; Echegoyen, L.; Diederich, F. *Chem. - Eur. J.* **2000**, *6*, 2184.
- (33) Lenes, M.; Wetzelaer, G.-J. A. H.; Kooistra, F. B.; Veenstra, S. C.; Hummelen, J. C.; Blom, P. W. M. *Adv. Mater.* **2008**, *20*, 2116.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

(34) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367.

Insert Table of Contents artwork here

