

Fullerene Adducts

Tether-Directed Bisfunctionalization Reactions of C₆₀ and C₇₀Maira R. Cerón,^[a] Marta Izquierdo,^[a] Yunhong Pi,^[b] Sandra L. Atehortúa,^[a] and Luis Echegoyen^{*[a]}

Abstract: Four easily isolable regio- and stereoselective bis-adducts of C₆₀ and C₇₀, as well as a new C₇₀-dumbbell derivative, have been synthesized by using two different bismalonate tethered moieties. The derivatives that possess relative-

ly long-tethered moieties show highly symmetric addition patterns, as evidenced by spectroscopic measurements, whereas the derivatives possessing the shorter-tethered moiety exhibit interesting addition patterns on C₆₀ and C₇₀.

Introduction

Solar energy is a promising renewable resource alternative, and organic photovoltaic (OPV) solar cells are a promising technology for energy conversion since they can be prepared at relatively low cost.^[1] Bulk heterojunction (BHJ) solar cells are the most studied OPV devices exhibiting relatively high power conversion efficiencies (PCEs).^[2] The application of fullerene bis-adducts in BHJ solar cells is developing rapidly, mainly because of their higher LUMO levels compared with those of the mono-adducts; the cathodically shifted reduction potentials of the bis-adducts (LUMO level) increase the open-circuit voltage (V_{oc}) of the solar cells, thus leading to higher PCEs.^[3] Solar cells fabricated with isomeric mixtures of fullerene bis-adducts, such as indene-C₆₀ and indene-C₇₀ bis-adducts (IC₆₁BA and IC₇₁BA), show PCEs up to 10.6%.^[2a] Currently, not all isomerically pure bisindene derivatives have been tested in solar cells with different donors. The only few reported cases of regioisomerically pure bis-adducts clearly demonstrated that for both C₆₀ and C₇₀ bisindene isomers, some regioisomers perform better than the isomeric mixture (6.3% for the *trans*-3 IC₆₁BA and 5.9% for the 2 o'clock IC₇₁BA, compared with 5.3 and 4.7% for the respective isomeric mixtures).^[4] This justifies the need for pure fullerene bis-regioisomers.

Fullerene bis-functionalization typically leads to a large number of isomers. Bis-derivatization of C₆₀ can result in eight possible isomers and in the case of C₇₀, 38 is the number of possible isomers, with identical addends attached exclusively to [6,6] bonds.^[5] Diederich et al. reported tether-directed remote multifunctionalization as a method that restricts the lo-

cation of addition sites by selecting the length and rigidity of a tether moiety connecting the reacting centers, thus increasing the yield of a few bis-adduct isomers.^[6] There is a large number of examples of bis-derivatives of C₆₀ using either two independent additions or a bis-tether addend, and the most common bis-addition isomers for C₆₀ are the equatorial followed by the *trans*-3 isomer.^[5,7] In particular, the *trans*-3, *trans*-2, and *cis*-3 isomers are inherently chiral as a consequence of their C₂ symmetry.^[8,9] Of the three chiral bis-regioisomers of C₆₀ the most common one is the *cis*-3 regioisomer, and the *trans*-2 regioisomer is the least reported one. During the tether-directed preparation of the *trans*-2 isomer, the *trans*-1 and equatorial isomers are also formed.^[9,10]

The necessity to synthesize isomerically pure bis-adducts for potential applications in OPV solar cells has led to a renaissance of the tether-directed multifunctionalization method. In this work, we have focused on the development of a new tethered bis-Bingel reagent^[11] to synthesize three easily isolable regio- and stereoselective bis-adducts of C₆₀ and C₇₀ (1–3) and a new C₇₀-dumbbell derivative (5).^[12] Herein, we present the complete characterization of the derivatives by using spectroscopic and electrochemical measurements as well as computational studies.

Results and Discussion

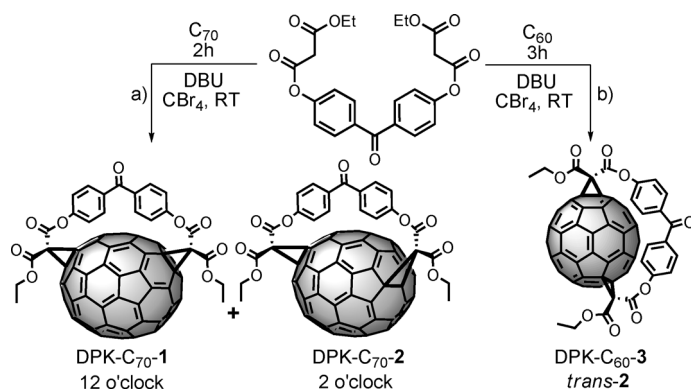
Bisfunctionalization of C₇₀ and C₆₀ with 4,4'-diethyl malonate-benzophenone

Bis-adducts 1 and 2 were synthesized by addition of a stable bis- α -halocarbanion resulting from an in situ base deprotonation of 4,4'-diethyl malonate-benzophenone (diphenyl ketone, DPK) in the presence of tetrabromomethane, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and C₇₀ (Scheme 1a and the Supporting Information). The crude mixture was purified by column chromatography on silica gel using carbon disulfide and chloroform to elute the unreacted pristine fullerene, followed by isomer 1 (DPK-C₇₀-1) in 42% yield, isomer 2 (DPK-C₇₀-2) in 29% yield, and finally a small fraction of mono-adduct.

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Scheme 1. One-step synthesis of a) bis-Bingel bis-adducts of [70]fullerene and b) bis-Bingel bis-adduct of [60]fullerene.

Compounds **1** and **2** were characterized by UV/Vis spectrophotometry, NMR spectroscopy, mass spectrometry, and cyclic voltammetry. Compounds **1** and **2** showed molecular peaks at 1278.0887 and 1278.0343 m/z , respectively, corresponding to bis-adduct regioisomers (Figures S1 and S2 in the Supporting Information), by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Because of the length of the DPK addend, after the first cycloaddition takes place the most accessible and reactive bonds for a second cycloaddition on C_{70} are on the opposite pole of the cage (α bonds); therefore, a total of three isomers are possible; the 12 o'clock, 2 o'clock, and 5 o'clock (Scheme 1).^[13]

The ^1H NMR spectrum of DPK- C_{70} -**1** showed half of the possible number of signals, with two doublets in the aromatic region evidencing the presence of a plane of symmetry (Figure 1a) and implying a 12 o'clock addition with C_s symmetry due to the rigidity of the addend. This constitutional isomer was confirmed by comparison with the UV/Vis absorption

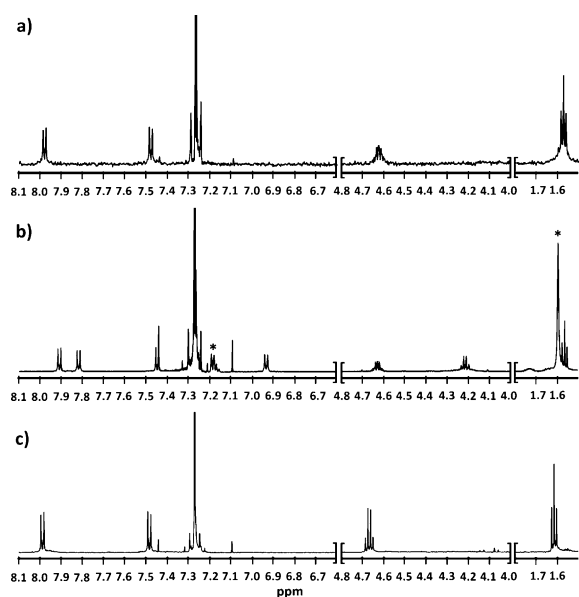


Figure 1. ^1H NMR spectra (600 MHz, CDCl_3 , 298 K) of a) DPK- C_{70} -**1**, b) DPK- C_{70} -**2** (* residual toluene and water), and c) DPK- C_{60} -**3**.

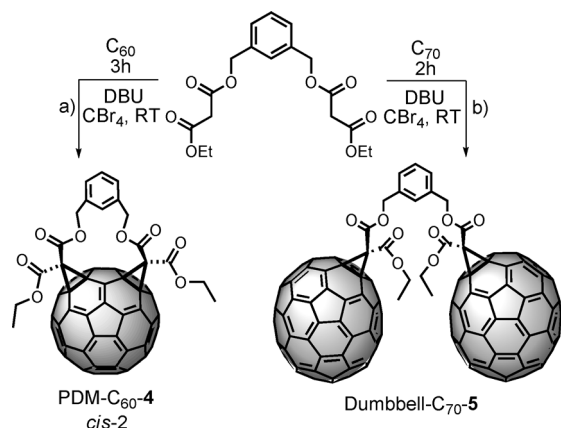
spectra of previously reported 12 o'clock bis-adducts (Figure S4 in the Supporting Information).^[13] Different diastereoisomers can also be obtained (in-in, in-out, and out-out).^[14] Diastereoisomers in-in or out-out for DPK- C_{70} -**1** would explain the observed C_s symmetry in the ^1H NMR spectrum, whereas the in-out configuration would introduce C_1 symmetry. DFT calculations showed that the out-out configuration has a lower energy than the in-in configuration (Figure S24 in the Supporting Information). We thus assign DPK- C_{70} -**1** to a 12 o'clock regioisomer with the EtO_2C groups in an out-out orientation. The ^{13}C NMR spectrum of DPK- C_{70} -**1** showed 33 signals for the sp^2 carbon atoms and the bridgehead and bridge carbon atoms appeared at $\delta = 62.93$ and 62.98 ppm, corresponding to typical Bingel adducts (Figure S6 in the Supporting Information),^[9] in agreement with the C_s symmetry observed by ^1H NMR spectroscopy.

In contrast, the ^1H NMR spectrum of DPK- C_{70} -**2** exhibits no symmetry (Figure 1 b), thus indicating one of two possible isomeric structures, the 2 o'clock or the 5 o'clock. The ^{13}C NMR spectrum showed a total of 60 signals, which account for the 66 sp^2 carbon atoms of the cage (three double-intensity signals correspond to six carbon atoms with accidental overlap). The remaining four carbon atoms of the C_{70} cage, bridgehead, and bridge carbon atoms resonated between $\delta = 75$ and 64 ppm (Figure S9 in the Supporting Information). Unfortunately, all attempts to grow single crystals for structural assignment of DPK- C_{70} -**2** were unsuccessful, but the UV/Vis absorption spectrum of DPK- C_{70} -**2** was very similar to that of 2 o'clock bis-adducts reported in the literature.^[13] In this case, all diastereoisomers would exhibit C_1 symmetry; therefore, DFT calculations^[15] using the B3LYP functional and the 3-21G basis set^[16] were used to assign the addition pattern of DPK- C_{70} -**2** as the 2 o'clock regioisomer with the EtO_2C groups in an out-out orientation (Figures S23 and S25 in the Supporting Information). These theoretical studies were in agreement with the relative yield of the symmetric and unsymmetric isomers.

When the bis-addition reaction was performed using C_{60} instead of C_{70} , only one isomer was obtained (Scheme 1 b and the Supporting Information). Compound **3** (DPK- C_{60} -**3**) with a molecular mass of 1158.0723 m/z (Figure S3 in the Supporting Information) has an essentially identical UV/Vis absorption spectrum to that reported for a *trans*-2 bis-regioisomer (Figures S4 and S27 in the Supporting Information). Thus, the assignment to a *trans*-2 addition pattern was based on the unique UV/Vis absorption patterns of each C_{60} bis-adduct.^[17] The ^1H NMR spectrum of DPK- C_{60} -**3** showed a similar number and displacement of the signals to those observed for DPK- C_{70} -**1** (Figure 1 c). In this case the number of signals observed results from the C_2 symmetry of the *trans*-2 isomer with the ethoxycarbonyl groups in an out-out orientation (Figures S26 and S27 in the Supporting Information), which renders the protons of the *para*-substituted aromatic systems equivalent.^[18] Of the few reported examples of a *trans*-2 addition pattern on C_{60} ,^[9] this is the only example for which a *trans*-2 regioisomer was the only product obtained.

Bisfunctionalization of C₇₀ and C₆₀ with 1,3-phenylenedi-methyl-diethyl malonate (PDM)

Bis-adduct **4** (PDM-C₆₀-**4**) was synthesized and purified in 34% yield, by following the same procedure as that described by Nierengarten et al. (Scheme 2).^[6e,14a] The purity of PDM-C₆₀-**4**



Scheme 2. One-step synthesis of a) bis-Bingel bis-adduct [60]fullerene and b) bis-Bingel dumbbell [70]fullerene.

was checked by UV/Vis spectrophotometry, ¹H NMR spectroscopy, and mass spectrometry (Figures S15, S17, and S18 in the Supporting Information).

Surprisingly, the use of C₇₀ instead of C₆₀ with this reagent did not lead to bis-adducts but to dumbbell-C₇₀-**5** as the major product (Scheme 2) in 54% yield and a small fraction of some bis-adducts (2% yield) and a mono-adduct (9% yield). All attempts to obtain bis-adducts as major products with C₇₀ were unsuccessful. Dumbbell-C₇₀-**5** was characterized by UV/Vis spectrophotometry, NMR spectroscopy, mass spectrometry, and cyclic voltammetry.

Based on the observed exclusive formation of the *cis-2* regioisomer on C₆₀ and assuming that the first addition of PDM on C₇₀ occurs on an α bond, the length and rigidity of the bis-tether linker would be expected to direct the second addition to a γ bond on C₇₀. However, due to the lower reactivity of the γ bond on the flatter equatorial region, before reacting at that position it prefers to react with the α bond of another C₇₀ molecule.^[8] The ¹H NMR spectrum of dumbbell-C₇₀-**5** showed the presence of a plane of symmetry with half of the possible number of signals (Figure 2b). MALDI-TOF MS and ¹³C NMR spectroscopy confirmed the dumbbell structural assignment, with a molecular mass of 2042.1226 *m/z* (Figure S16 in the Supporting Information) and 63 signals for the sp² carbon atoms of the cage (five double-intensity peaks correspond to ten carbon atoms exhibiting coincidental overlap). The bridgehead and bridge carbon atoms

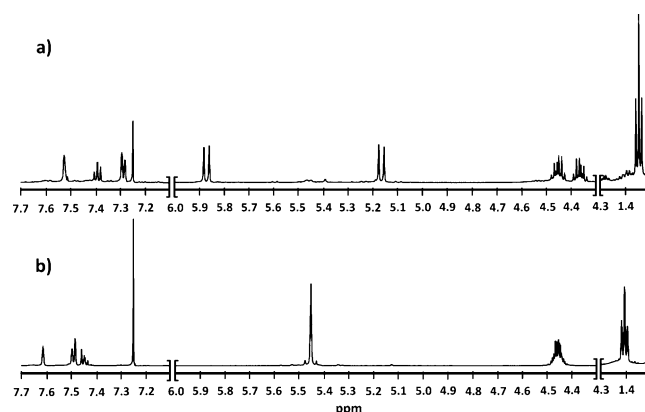


Figure 2. ¹H NMR spectra (600 MHz, CDCl₃, 298 K) of a) PDM-C₆₀-**4** and b) dumbbell-C₇₀-**5**.

appeared at $\delta = 66.09$ and 65.41 ppm, respectively, corresponding to a typical Bingel addition on C₇₀ (Figure S20 in the Supporting Information).

The redox potentials of the bis-Bingel derivatives of C₇₀ and C₆₀, as well of the dumbbell compound, were measured using cyclic voltammetry on a glassy carbon minielectrode in *o*-dichlorobenzene (*o*-DCB) solutions with 0.05 M *n*Bu₄NPF₆ as supporting electrolyte. The cyclic voltammetry results are summarized in Table 1.

Previous studies showed that Bingel derivatives of C₇₀ exhibit reversible cathodic electrochemical behavior between -1.0 and -1.2 V, whereas more negative potentials lead to irreversible retro-cycloadditions.^[19] Compounds DPK-C₇₀-**1** and DPK-C₇₀-

Table 1. Redox potentials^[a] of C₆₀ and C₇₀ bis derivatives.

DPK-C ₇₀ - 1		DPK-C ₇₀ - 2		DPK-C ₆₀ - 3		Dumbbell-C ₇₀ - 5	
<i>E</i> _p ^{red}	<i>E</i> _p ^{ox}	<i>E</i> _p ^{red}	<i>E</i> _p ^{ox}	<i>E</i> _p ^{red}	<i>E</i> _p ^{ox}	<i>E</i> _p ^{red}	<i>E</i> _p ^{ox}
-1.15	-1.06	-1.11	-1.05	-1.03	-0.95	–	-0.62
-1.52	-1.39	-1.52	-1.39	-1.43	-1.31	-1.23	-1.10
-1.89	-1.80	-1.88	-1.76	-1.74	-1.83	-1.57	-1.45
-2.10	-1.95	-2.04	-1.96	–	–	-1.95	-1.63

[a] Values obtained by cyclic voltammetry in volts versus the ferrocene/ferrocenium (Fc/Fc⁺) couple.

2 (Figure S10 in the Supporting Information) showed chemical reversibility for the first reduction step at a scan rate of 100 mV s⁻¹, followed by three chemically and electrochemically irreversible waves. To effect retro-cycloaddition, DPK-C₆₀-**3** requires more negative potentials, close to -1.6 V. The reduction potentials of all bismethanofullerene derivatives were cathodically shifted relative to the values for their corresponding pristine fullerene.^[20]

Conclusion

We have reported the synthesis of a new long-tethered bis-Bingel reagent to synthesize three easily isolable regio- and stereoselective bis-adducts of C₆₀ and C₇₀ (**1–3**) as well the use of a reported short-tethered bis-Bingel reagent to synthesize

a new C₇₀-dumbbell derivative (5). We have also reported the first example of a regioselective *trans*-2 isomer as the only product obtained on C₆₀. In addition, we have presented the complete characterization of the derivatives by using spectroscopic and electrochemical measurements, as well as computational studies.

Experimental Section

Synthesis of DPK-C₇₀-1 and DPK-C₇₀-2

DBU (2 drops, 11.56 mg, 0.076 mmol) was added to a solution of C₇₀ (50 mg, 0.059 mmol, 1 equiv), 4,4'-diethyl malonate-benzophenone (39.5 mg, 0.089 mmol, 1.5 equiv), and tetrabromomethane (59.2 mg, 0.178 mmol, 3 equiv) in *o*-DCB (8 mL) under a N₂ atmosphere and the mixture was stirred at room temperature for 2 h. The reaction was stopped by using two drops of acetic acid, followed by extraction with a saturated sodium bicarbonate solution and sodium chloride solution. The solvent from the reaction mixture was removed under vacuum and the crude product was purified by column chromatography on silica gel, initially using CS₂ to collect the unreacted fullerene, followed by CS₂/CHCl₃ (7:3) to collect DPK-C₇₀-1 and DPK-C₇₀-2 (29 and 45 %, respectively), and finally CHCl₃/ethyl acetate (7:3) to collect a small fraction of mono-adduct.

Synthesis of DPK-C₆₀-3

DBU (2 drops, 11.56 mg, 0.076 mmol) was added to a solution of C₆₀ (50 mg, 0.069 mmol, 1 equiv), 4,4'-diethyl malonate-benzophenone (46.0 mg, 0.104 mmol, 1.5 equiv), and tetrabromomethane (69.1 mg, 0.208 mmol, 3 equiv) in *o*-DCB (12 mL) under a N₂ atmosphere and the mixture was stirred at room temperature for 2 h. The reaction was stopped by using two drops of acetic acid, followed by extraction with a saturated sodium bicarbonate solution and sodium chloride solution. The solvent from the reaction mixture was removed under vacuum and the crude product was purified by column chromatography on silica gel, initially using CS₂ to collect the unreacted fullerene, followed by CS₂/CHCl₃ (1:1) to collect DPK-C₆₀-3 (39%), and finally CHCl₃/ethyl acetate (7:3) to collect a small fraction of mono-adduct.

Synthesis of dumbbell-C₇₀-5

DBU (2 drops, 11.56 mg, 0.076 mmol) was added to a solution of C₇₀ (50 mg, 0.059 mmol, 1 equiv), 1,3-phenylenedimethyl-diethyl malonate (8.7 mg, 0.024 mmol, 1 equiv), and tetrabromomethane (23.7 mg, 0.071 mmol, 3 equiv) in *o*-DCB (7 mL) under a N₂ atmosphere and the mixture was stirred at room temperature for 1 h. The reaction was stopped by using two drops of acetic acid, followed by extraction with a saturated sodium bicarbonate solution and sodium chloride solution. The solvent from the reaction mixture was removed under vacuum and the crude product was purified by column chromatography on silica gel, initially using CS₂ to collect the unreacted fullerene, followed by CS₂/CHCl₃ (7:3) to collect dumbbell-C₇₀-5 (54%), and finally CHCl₃/ethyl acetate (9:1) to collect a small fraction of mono-adduct.

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Keywords: bis-adducts • cycloaddition • fullerenes • regioselectivity • stereoselectivity

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