

Recent progress in the synthesis of regio-isomerically pure *bis*-adducts of empty and endohedral fullerenes[†]

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***Bis*-functionalized fullerenes have resulted in very effective acceptors in organic photovoltaic solar cells. Here we present a short overview of specific and recently reported pure *bis*-adduct regioisomers of C₆₀ using short tethers, a few recent examples of *bis*-adducts of C₇₀ and finally examples of *bis*-adducts of endohedral cluster fullerenes. We also discuss the unexpected reactivity differences of empty fullerenes (C₆₀ and C₇₀) compared with those of trimetallic nitride cluster endohedral fullerenes (M₃N@I_h-C₈₀, M = Sc, Lu) towards tethered-*bis*-addition reactions. Finally, we describe the remarkable endohedral-cluster regiochemical control of multiple additions. Copyright © 2016 John Wiley & Sons, Ltd.**

Keywords: empty fullerenes; endohedral fullerenes; *bis*-functionalization of fullerenes; tethered method

INTRODUCTION

Since the serendipitous discovery of the fullerenes in 1985,^[1] and the first detection of endohedral fullerenes almost immediately after,^[2] the first functionalization reactions were reported^[3–5] as soon as the fullerenes became available in macroscopic amounts in 1990.^[6] These derivatization reactions lead to products with substantially improved solubility and modified chemical and physical properties, increasing their potential applications in many different fields.^[7–10] Almost invariably, functionalization leads to the formation of multiple adducts, as it is very difficult, if not impossible, to control the conditions in order to limit the reactivity to a single addition. As will be discussed in the succeeding texts, both *mono*-functionalization and *bis*-functionalization can lead to compounds which act as excellent electron acceptors in organic photovoltaic (OPV) devices, yielding relatively high photoconversion efficiencies (PCEs). Given that multiple isomeric *bis*-adducts can be formed with C₆₀ and C₇₀, developing reagents and techniques to limit the accessible possibilities has led to a renaissance in this field, which was originally pioneered many years ago by Diederich *et al.*^[11,12] In this overview article we describe recent developments in the regiochemical control of *bis*-functionalizations of empty (C₆₀ and C₇₀) and of some endohedral cluster fullerenes.

We begin by briefly describing the number of statistically possible *bis*-adducts of C₆₀ and C₇₀ and describe a nomenclature that we recently introduced to systematically name the C₇₀ compounds.^[13–15]

Possible *bis*-adduct regioisomers

Empty fullerenes possess two different types of bonds, the [5,6]-bonds between a five-membered and a six-membered ring and [6,6]-bonds between two six-membered rings (Fig. 1a).^[11] The most reactive bonds on an empty fullerene are typically the [6,6]-junctions,^[16] thus multiple adducts of fullerenes normally involve [6,6]-bonds.^[11,15,17] If the two addends are identical and

the additions occur exclusively on [6,6]-bonds, the statistical number of possible regioisomers is 8 in the case of C₆₀ (refer to Fig. 1b for the nomenclature),^[15] and 64 in the case of C₇₀ (refer to Fig. 1c for the nomenclature).^[13]

Regioisomers observed

It has been shown that *bis*-adduct formation on C₆₀ is not statistical, and in most cases the *trans*-3 and *e*-isomers are the preferred products. If there is very low steric congestion between the addends, the *cis*-1 isomer is the preferred product. After the formation of the *mono*-adduct, no matter what the nature of the addend is, the *cis*-1 and *e*-bonds are the shortest; therefore, addition to these bonds is preferred. In addition, *bis*-adducts *cis*-1, *e* and *trans*-3 possess enhanced HOMO-LUMO coefficients, which explain the preferential formation of these specific regioisomers. For the case of C₇₀, the typically preferred isomers involve adducts on α -bonds on opposite poles of the D_{5h} symmetric compound because the α -bonds are the shortest and most strained. Thus, the 3 isomers that are normally obtained are the α -6- α' , the α -7- α' , and the α -9- α' following our recently introduced nomenclature (previously known as the 12-o'clock, 2-o'clock and 5-o'clock isomers, respectively).^[13,18] The

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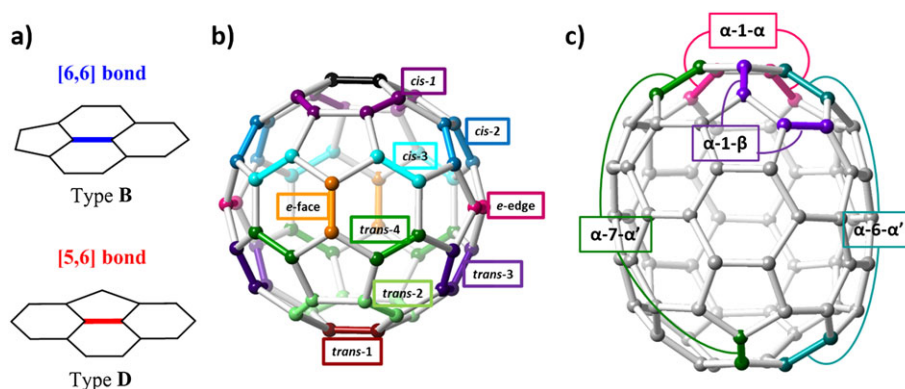


Figure 1. (a) Two different types of bonds on empty fullerenes. First addition site is designated with a black bond b) nomenclature for the eight possible regioisomers of C_{60} ; (c) some examples of *bis*-adduct regioisomers of C_{70} relevant to this work

nomenclature uses Greek letters to define the addition positions and a number that corresponds to the smallest number of bonds separating the additions sites. Same type bonds on opposite sides across the δ -bonds are differentiated using a prime designation.^[13]

Methods to control *bis*-adduct regioisomer formation

The challenge in the synthesis of *bis*-adducts is to obtain regioisomerically pure products that avoid complicated, costly, and inefficient purification methods such as HPLC.^[14,19–21] There are very few methods that provide control for the formation of specific *bis*-adduct regioisomers. The first to be reported and the one that continues to be the most general and effective was described by Diederich *et al.* in 1994, named tether-directed multifunctionalization.^[11] This method uses a variable length and rigidity tether that connects two or more reactive centers to direct the location of the additions on the fullerene surface, and it is still widely used and will be described in more detail later in this article, using new reagents.

The second method was reported by Kräutler *et al.* in 1996 and consists of a rather unique and very interesting topologically controlled reaction which lacks general applicability and has only been shown to work with C_{60} and more recently with C_{70} (Fig. 2).^[22,23] The method uses molten anthracene under vacuum at 240 °C in the presence of the corresponding fullerene and yields exclusively the *trans*-1 *bis*-Diels–Alder adduct in 48% yield with C_{60} (Fig. 2a) and exclusively the α -6- α' *bis*-adduct in 68% yield with C_{70} (Fig. 2b). This topologically controlled *bis*-addition reaction is completely specific, and no other isomers are obtained for either C_{60} or C_{70} and the products can be used to further

functionalize these fullerenes regioselectively, using what Prof. Kräutler has described as orthogonal transposition,^[24,25] where other groups are added to the *bis*-adducts, followed by thermal *retro* Diels–Alder of the anthracenes to afford compounds that are otherwise very difficult, if not impossible, to prepare in large quantities without observing multiple isomeric forms.^[26–31]

Why are fullerene *bis*-adducts important?

As briefly mentioned earlier, recently prepared *bis*-functionalized fullerenes have resulted in very effective acceptors in OPV solar cells.^[32–38] PCEs up to 10.6% have been achieved using isomeric mixtures of fullerene *bis*-adducts, such as indene- C_{61} -*bis*-adducts (IC₆₁BA) in a solution processed tandem solar cell.^[33] Although not all isomerically pure *bis*-regioisomers have been tested in solar cell devices, most of the reported cases have demonstrated that pure regioisomers many times perform better than the corresponding isomeric mixtures,^[39–43] although some exceptions have also been noted.^[21,41,44] These observations justify the necessity to synthesize pure *bis*-adducts, and this in turn has led to a renaissance of the methods and reagents available to decrease the number of fullerene multiadduct derivative isomers.

Recent activity in this area has resulted in new and regioisomerically pure *bis*-adducts that have performed reasonably well in OPV devices.^[37,40,42] In some cases, even when using the tether-directed method, the number of isomers obtained is still rather large, for example, in the case of the synthesis of tethered *bis*-PC₆₁BM (phenyl butyric acid methyl ester- C_{61})^[45] and tethered *bis*-DPM- C_{60} (diphenyl methano)^[44] for which the number of isomers obtained was 7 and 12, respectively. The main reasons for these observations are the lack of symmetry of the addend, in which case diastereomers can also be observed and

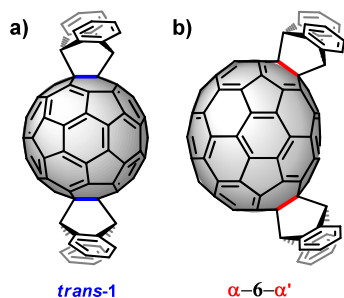


Figure 2. Topologically controlled *bis*-anthracene derivatives of (a) C_{60} (*trans*-1 isomer)^[22]; (b) C_{70} (12 o'clock or α -6- α' isomer)^[23]

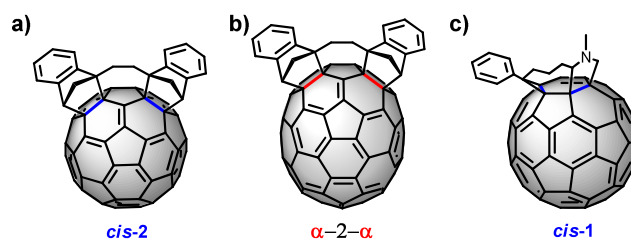


Figure 3. Pure *bis*-adducts synthesized using the tether-directed method (a) IC₆₁BA *cis*-2 isomer^[40]; (b) IC₆₁BA α -2- α isomer^[42]; (c) *N*-methyl-phenyl- C_{61} -propyl-2-fulleropyrrolidine *cis*-1a isomer^[37]

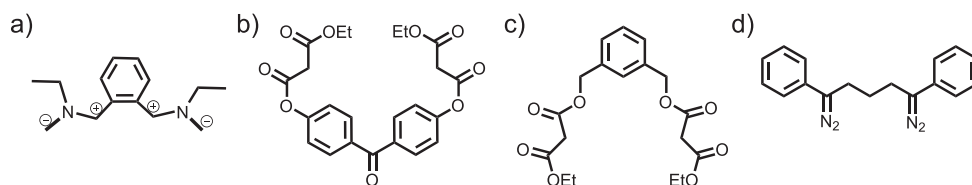


Figure 4. Reagents used to perform 1,3-dipolar, Bingel and diazo cycloadditions (a) tethered *bis*-ylide; (b) long tether *bis*-malonate; (c) short tether *bis*-malonate; (d) tethered *bis*-diazo

the extreme flexibility of the tether used.^[37] It is known that the use of shorter tethers and rigid addends decreases the number of observed isomers. To the best of our knowledge, the only pure *bis*-adducts synthesized using the tether-directed method and applied to OPV solar cells are the recently reported IC₆₁BA *cis*-2 isomer,^[40] IC₇₁BA α -2- α isomer,^[42] and the *N*-methyl-phenyl-C₆₁-propyl-2-fulleropyrrolidine *cis*-1a isomer^[37] with 1% and 2% higher PCEs than the corresponding isomeric mixtures using P3HT as the donor (refer to Fig. 3 for the structures).

Recent results

This article is not meant to be a comprehensive review of fullerene *bis*-adducts in general, but rather an account of specific and recently reported pure *bis*-adduct regioisomers of C₆₀ using short tethers, a few recent examples of *bis*-adducts of C₇₀ and finally examples of *bis*-adducts of endohedral cluster fullerenes. Part of the reason for introducing short tethers was to prepare more polar fullerene derivatives for enhanced solubility and ease of OPV device fabrication and also to explore C₇₀ derivatives where both addends are attached to one pole of the D_{5h} symmetric compound, because most *bis*-adducts reported for C₇₀ are located on opposite ends of the rugby-shaped molecule, on α - and α' -bonds.

The tether-directed method has been implemented using different types of reactions, such as addition-elimination (Bingel), 1,3-dipolar, Diels–Alder and diazo cycloadditions.^[46,47] Here we limit the examples for the most part to 1,3-dipolar and Bingel cycloadditions, with some exceptions, specifically employing the following reagents shown in Fig. 4.

Tethered *bis*-1,3-dipolar cycloadditions to C₆₀ and C₇₀

We recently reported the regioselective tethered *bis*-1,3-dipolar cycloaddition of a *bis*-ylide reagent to C₆₀ (Fig. 4a), by using a short and rigid *bis*-aldehyde (*o*-phthalaldehyde). This decreased

the number of possible regioisomers from 8 to 2, but because of the presence of two chiral centers on the *bis*-ylide the statistical number of possible diastereomers is 6 (Fig. 5). Interestingly, we only observed the formation of three regioisomeric *bis*-adducts out of the six possible isomers. The structures of the products were unambiguously assigned by X-ray crystallography and by spectroscopic techniques as two *meso* forms of the *cis*-2 isomer (compounds **1** and **2** in Fig. 6) and the racemic mixture (*RR* and *SS*) of the *cis*-1 isomer (compound **3** in Fig. 6).^[48]

We also reported the unexpected isomerism of the two *meso*-forms upon thermal treatment of compound **1** at 180 °C in *o*-dichlorobenzene solutions and the resulting quantitative conversion to compound **2**. We proposed a retro-1,3-dipolar cycloaddition reaction mechanism to account for the interconversion process, followed by migration of the corresponding ylide to a different *cis*-2 bond, which yields compound **2** exclusively with an inverted stereochemistry (Fig. 6).^[48]

The redox properties of compounds **1**, **2**, and **3** were previously reported but not discussed.^[48] Cyclic voltammetry

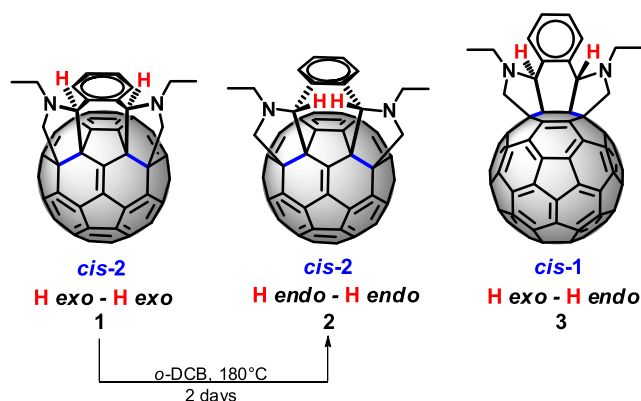


Figure 6. Reported *bis*-C₆₀-pyrrolidine regioisomers^[48]

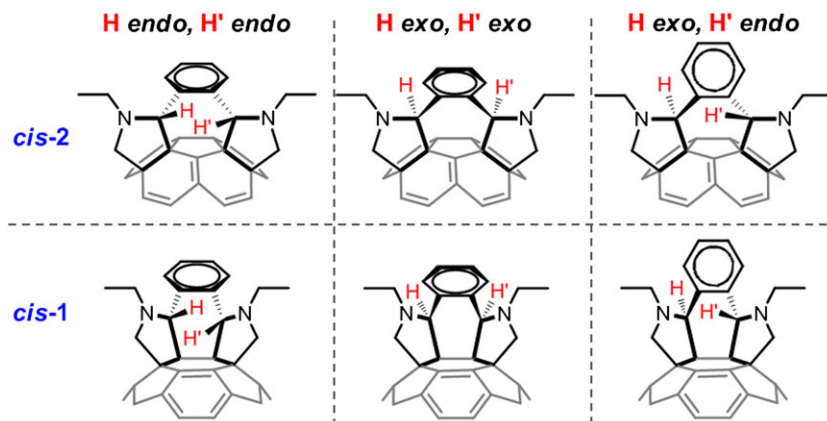


Figure 5. Structure of the six possible diastereomers that can be obtained from the 1,3-dipolar cycloaddition of a *bis*-ylide (Fig. 4a) to C₆₀

Table 1. Redox potentials (V)^a of **1**, **2**, **3** and C₆₀

Compound	C ₆₀	Isomer 1	Isomer 2	Isomer 3
$E^{0/-}$	-0.977	-1.218	-1.282	-1.224
$E^{-1/-2}$	-1.369	-1.574	-1.658	-1.608
$E^{-2/-3}$	-1.817	-2.158	-2.197	-2.222
$E^{-3/-4}$	-2.253	—	—	—

^aValues obtained by square wave voltammetry in V versus Fc/Fc⁺.

and square wave voltammetry were measured in dichloromethane solutions using 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte. The cyclic voltammetry of compounds **1**, **2**, and **3** showed three reduction waves with electrochemically reversible behavior. The first, second, and third reduction potentials of derivatives **1**, **2**, and **3** were cathodically shifted compared with the values for C₆₀ (Table 1).^[48] It is well known that addition to a double bond on C₆₀ cathodically shifts the reduction by approximately 100 mV.^[49] Because **1**, **2**, and **3** are *bis*-adducts, cathodic shifts around 200 mV were anticipated and compounds **1** and **3** exhibit shifts of 240 and 247 mV, respectively. Compound **2** exhibited a shift of 305 mV (Table 1).^[48] Thus, higher open circuit voltages (V_{oc}) could be expected for these compounds in OPV solar cells.

We have applied the same tethered *bis*-1,3-dipolar cycloaddition reaction on C₇₀ and obtained four regioisomeric *bis*-adducts, which are currently being purified and characterized. It is clear from the results observed with C₆₀ and C₇₀ that the 1,3-dipolar cycloaddition reaction is not particularly regioselective because it leads to the formation of three regioisomers in the case of C₆₀ and four in the case of C₇₀, an observation that has been previously noted.^[8,50–52]

Tethered *bis*-Bingel cycloadditions to C₆₀ and C₇₀

Because the short-tethered 1,3-dipolar *bis*-cycloadditions were not particularly regioselective, we also explored reactions involving different *bis*-malonate tethered addends (Fig. 4b and c) with C₆₀ and C₇₀, in which case not only regioisomers but diastereomers can be observed, depending on the orientation of the ethoxycarbonyl groups (in-in, in-out, and out-out).^[53,54]

Using a long and rigid tethered moiety with C₆₀ we observed only one product out of the 24 possible isomers that was assigned by spectroscopic techniques, symmetry considerations and DFT calculations as the *trans*-2 regioisomer with the ethoxycarbonyl groups (EtO₂C-) in an out-out orientation (compound **4**; Fig. 7).^[55] For the case of the less symmetric *D*_{5h}-C₇₀ we obtained two products, a C_s-symmetric *bis*-adduct assigned as the α -6- α' regioisomer and a C₁-symmetric *bis*-adduct assigned as the α -7- α' regioisomer based on spectroscopic data and DFT calculations, both with the EtO₂C- groups in an out-out orientation (compounds **5** and **6**; Fig. 7, respectively).^[55]

Interestingly, when we used a previously reported short tether moiety to perform a *bis*-Bingel cycloaddition on C₆₀ and C₇₀ (Fig. 4c), we observed a pronounced difference in the reactivity exhibited by the fullerenes.^[12,53,55] For C₆₀ the *cis*-2 isomer was the only one observed (compound **7**; Fig. 7),^[12,53] but using C₇₀ instead of C₆₀ did not lead to the formation of *bis*-adducts but to a dumbbell compound as the major product in 54% yield (compound **8**; Fig. 7).^[55] All attempts to obtain C₇₀ *bis*-adducts with this reagent were unsuccessful. These results indicate that after the first addition to a C₇₀ molecule, which preferentially occurs at an α -bond, the length and rigidity of the tether would direct a second addition at a γ -bond, but these bonds are highly unreactive. Therefore, the α *mono*-adduct reacts preferentially with another α -bond on a different C₇₀ molecule, leading predominantly to the dimeric dumbbell compound.^[55]

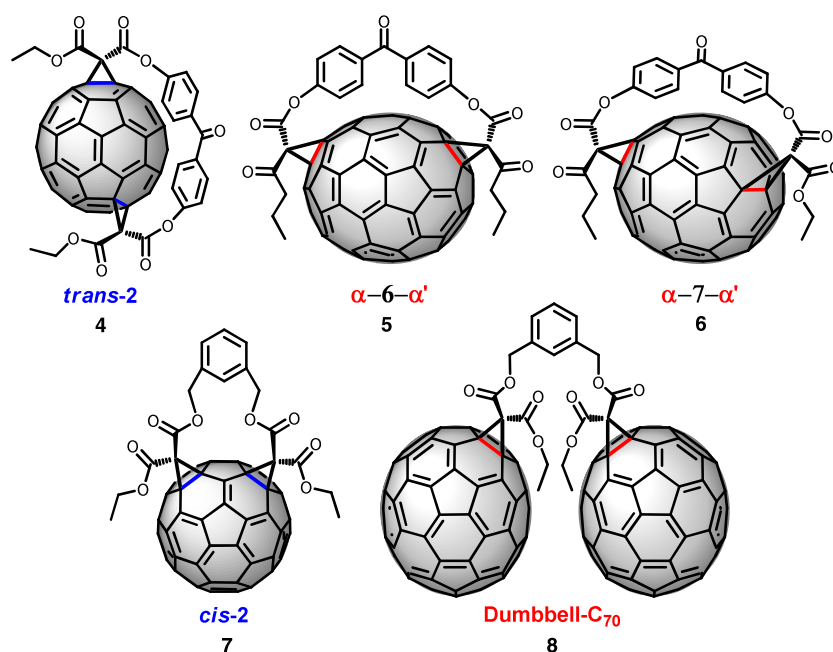


Figure 7. *Bis*-Bingel regioisomers of C₆₀ and C₇₀.^[55]

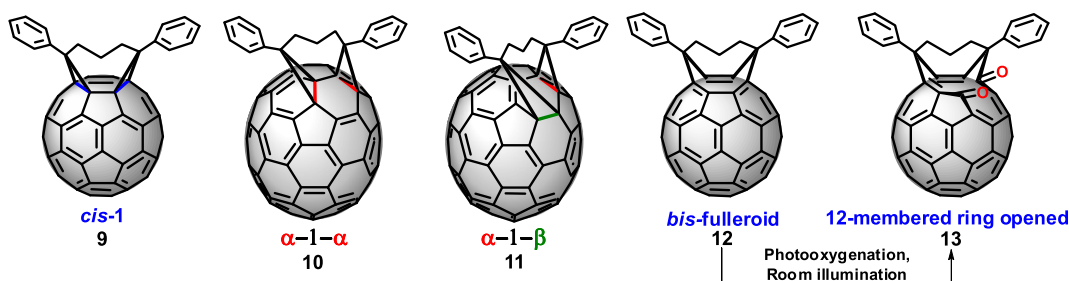


Figure 8. Previously reported *bis*-methano derivatives and *bis*-fulleroids of C_{60} and C_{70} ^[13]

Tethered *bis*-diazo cycloadditions to C_{60} and C_{70}

Because of the higher thermal stability and redox reversibility of methanofullerenes compared with those of the pyrrolidine or Bingel derivatives, we explored the functionalization of C_{60} and C_{70} using a *bis*-diazo reagent. Diazo cycloaddition reactions can generate two types of derivatives: the kinetically controlled product defined as a fulleroid, which involves addition at a [5,6]-bond, and the thermodynamic product defined as a methanofullerene, which results from addition at a [6,6]-bond.^[56–58] Fulleroid derivatives usually isomerize quickly to the more stable methanofullerene derivatives via a π -methane transposition.^[59,60] We recently designed a short, rigid, and symmetric *bis*-diazo addend and reported the regio-selective synthesis of easily isolable and highly sterically congested *bis*-derivatives of C_{60} and C_{70} with both additions on a common hexagonal face.^[13]

We observed that when the addition occurred at two [6,6]-bonds, a C_s -symmetric *bis*-adduct was obtained for C_{60}

(compound **9**, *cis*-1 isomer; Fig. 8) and C_s - and C_1 -symmetric *bis*-adducts for C_{70} (compounds **10** and **11**, α -1- α and α -1- β isomers, respectively; Fig. 8). Somewhat unexpectedly, when the addition occurred at two [5,6]-bonds on one hexagon ring on C_{60} , forming a *bis*-fulleroid, we observed that the C_s -symmetric derivative underwent fast photooxygenation in air, to yield a 12-membered ring opened *bis*-fulleroid (compounds **12** and **13**, respectively; Fig. 8).^[13]

Endohedral cluster fullerene *bis*-adducts

Given that there is only one example of an OPV solar cell based on an endohedral fullerene *mono*-adduct acceptor (PCBH-Lu₃N@I_h-C₈₀) and that reasonable efficiencies were obtained,^[61] there seem to be many possibilities for many rooms in the exploration of new endohedral fullerene derivatives as potential acceptors in solar cells. Thus, we were interested in exploring the

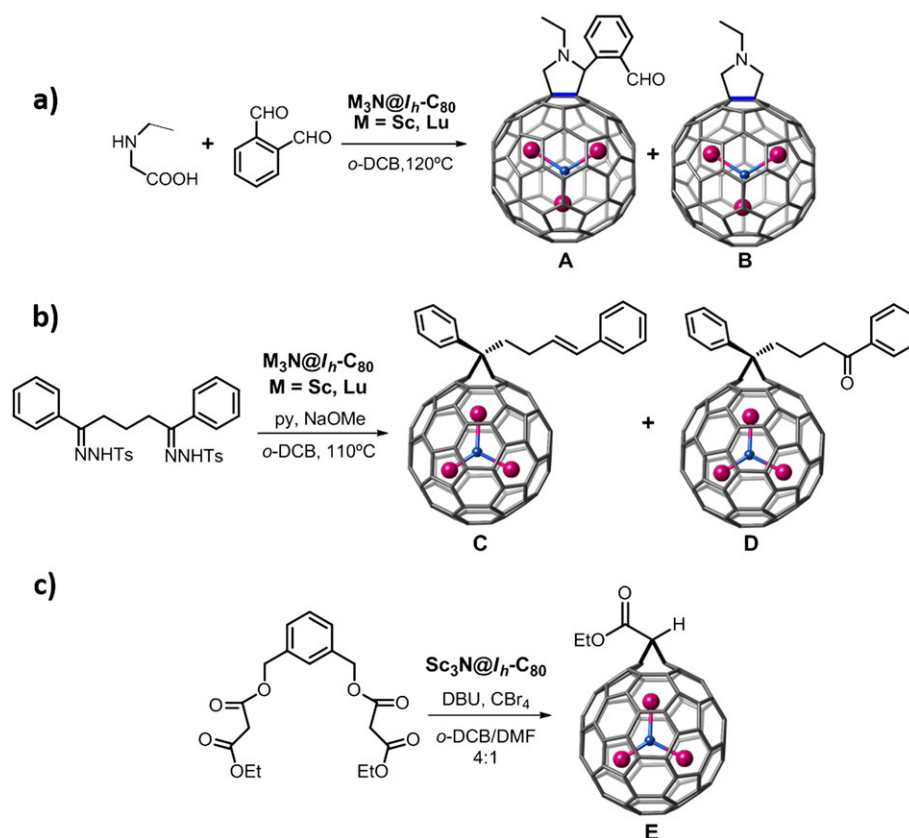


Figure 9. Attempts to use tether-controlled *bis*-addition reactions with endohedral cluster fullerenes $M_3N@I_h-C_{80}$ ($M = Sc$ and Lu)^[62]

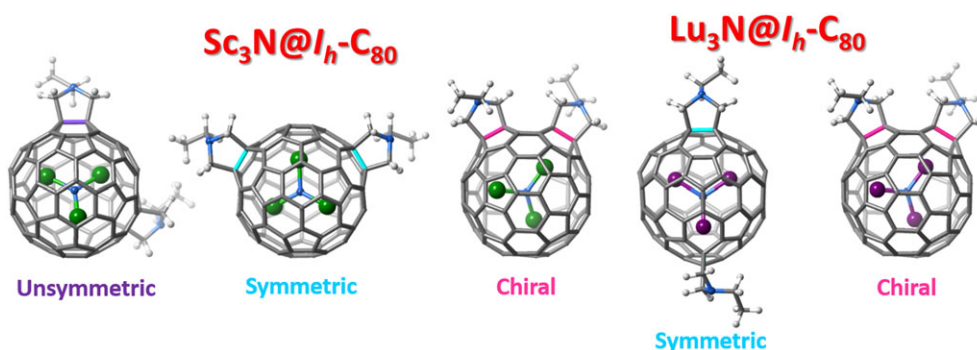


Figure 10. Addition patterns of the *bis*-adducts obtained for $M_3N@I_h-C_{80}$ ($M = Sc$ and Lu)^[62]

synthesis and regiochemistry of *bis*-additions to endohedral fullerenes.

Because the tethered *bis*-1,3-dipolar, *bis*-Bingel, and *bis*-diazo cycloadditions exhibited reasonable degrees of regioselectivity and gave rise to easily isolable *bis*-adducts of [60]- and [70]-fullerenes,^[3,13,48,55] we decided to use the same reactions to prepare *bis*-adducts of $Sc_3N@I_h-C_{80}$ and $Lu_3N@I_h-C_{80}$. Interestingly and totally unexpectedly, we discovered that the reactions that worked so well with C_{60} and C_{70} did not proceed at all with the trimetallic nitride endohedral fullerenes; we were only able to observe the formation of *mono*-adducts in all cases (Fig. 9). The obvious explanation for these observations is that the encapsulated cluster must exert a very strong directing effect, totally preventing the addition of the second tethered group. This apparent directing control coming from the cluster inside led us to consider independent (non-tethered) *bis*-additions, an experiment that should have naturally preceded the tethered one.^[62]

Independent (non-tethered) *bis*-additions to endohedral fullerenes have been reported before but very few details about their regiochemistry have been discussed.^[63–68] We recently described the statistically possible number of *bis*-adduct isomers that could in principle be formed on an I_h-C_{80} cage, assuming that the two addends are identical and that both [5,6] and [6,6] additions can occur. This analysis predicts that the total number of possible isomers is 91, of which 63 are C_1 -symmetric, 18 are C_5 -symmetric and 10 are C_2 -symmetric.^[62]

Yamakoshi *et al.* recently reported regioselective *bis*-1,3-dipolar cycloaddition reactions using $M_3N@I_h-C_{80}$ ($M = Y$ and Gd) and described one predominant and unsymmetrical *bis*-pyrrolidine isomer, which corresponds to one of the 63 possible C_1 -symmetric *bis*-adducts.^[69] The particular structure that was proposed was based on computational studies, but given that there are 63 possible isomeric forms, the specific definitive assignment is somewhat tentative, because the calculated energy differences are very small between different isomers. This group also reported that using $M_3N@I_h-C_{80}$ ($M = Sc$ and Lu) did not result in the formation of substantial amounts of *bis*-adducts to be isolated and characterized.^[69]

Fortunately, using the same *bis*-1,3-dipolar cycloaddition reaction with $M_3N@I_h-C_{80}$ ($M = Sc$ and Lu) in our hands resulted in the formation and successful isolation of five new *bis*-adducts, three for $Sc_3N@C_{80}$ and two for $Lu_3N@C_{80}$ (Fig. 10).^[62] We were very lucky to observe that out of these five *bis*-adduct isomers, four had either C_5 or C_2 symmetry, thus lowering the number of possible structures and providing a more definitive computationally-aided assignment of the specific structures, mainly based on 1H -NMR spectroscopy. For $Sc_3N@C_{80}$ we

obtained one C_1 -symmetric, one C_5 -symmetric, and one C_2 -symmetric *bis*-adduct. For $Lu_3N@C_{80}$ we obtained one C_5 -symmetric and one C_2 -symmetric *bis*-adduct (Fig. 10). Remarkably, for both Sc and Lu endohedral fullerenes, we observed the same C_2 -symmetric *bis*-adduct and these are the first examples of intrinsically chiral endohedral compounds, because of the resulting symmetry based solely on the addition pattern, not on the presence of chiral centers on the addends.^[62]

Based exclusively on the NMR observations, we assigned the structure of the C_5 -symmetric isomer for $Lu_3N@C_{80}$ to one of only four possible [5,6]-[6,6] *bis*-adducts, with mutually perpendicular pyrrolidines. To the best of our knowledge this is the first mixed (hybrid) *bis*-addition compound ever observed for an endohedral system, a rather unanticipated and very interesting result.^[62]

CONCLUSIONS

We described several reagents that were recently reported which were designed for regioselective tethered *bis*-additions to C_{60} and C_{70} . These are part of a renaissance of the use of the tethered-controlled method to decrease the number of *bis*-adduct isomers obtained for potential applications in OPV solar cells. Different types of reactions, such as tethered *bis*-Bingel, *bis*-1,3-dipolar, and *bis*-diazo cycloadditions, were described, which lead to unique and highly sterically congested *bis*-adducts of C_{60} and C_{70} . The shorter tethers were designed to result in more polar fullerene *bis*-adducts for enhanced solubility and processability in the construction of OPV devices.

We also described the interesting observation that the same tethered-*bis*-addition reactions that work well with C_{60} and C_{70} do not work at all with trimetallic nitride cluster fullerenes, indicative of very strong directing and controlling effects by the encapsulated clusters on the sites of exohedral additions. Four of the five isolated and characterized *bis*-adducts of $Sc_3N@I_h-C_{80}$ and $Lu_3N@I_h-C_{80}$ using non-tethered *bis*-1,3-dipolar cycloaddition reactions unexpectedly and remarkably exhibited relatively high symmetry, two exhibiting an intrinsically chiral addition pattern, and one exhibiting the first hybrid [5,6]-[6,6] *bis*-addition on a cluster fullerene. These results clearly show that the regiochemistry of multiple additions to endohedral fullerenes is strongly determined/controlled by the encapsulated cluster and not by exohedral tethered multi additions.

Given that the encapsulated clusters inside endohedral fullerenes control the regiochemistry of the exohedral functionalizations, the next step in the field of

bis-functionalization of endohedral fullerenes will involve the design of mixed metallic clusters to synthesize well-defined bis-adduct regioisomers.

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