

Account / Revue

# Tether-directed remote functionalization of fullerenes C<sub>60</sub> and C<sub>70</sub>

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Received 6 July 2005; accepted after revision 19 September 2005

Available online 19 January 2006

## Abstract

The article provides an overview of the work on regio- and, in the occurrence, stereoselective tether-directed remote functionalization of fullerenes in the Diederich group, from the initial stages in 1994 to the present. All bisaddition patterns of C<sub>60</sub>, except *cis*-1, have been realized with high selectivities, mainly by Bingel-type macrocyclizations. Particular emphasis is placed on the stereoselective generation of the inherently chiral *cis*-3, *trans*-3, and *trans*-2 addition patterns. Besides, one of the rare examples of direct threefold tether-directed cyclopropanation of C<sub>60</sub> is presented and the spacer-controlled derivatization of C<sub>70</sub> is reviewed. **To cite this article:** C. Thilgen, F. Diederich, *C. R. Chimie* 9 (2006).

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*Keywords:* Fullerenes; Multiple functionalization; Tether; Spacer; Template; Regioselectivity; Stereoselectivity

## 1. Introduction

The regio- and, if applicable, the stereoselective preparation of multiadducts of fullerenes is of prime importance for the preparation of functional fullerene derivatives and fullerene-based advanced materials [1]. This is related to the fact that the properties of the residual fullerene chromophore of derivatives critically depend on the functionalization pattern and that their geometry plays a crucial role in the relative arrangement of components, thereby determining the structure of such materials. Successive addition of independent reagent molecules to fullerenes generally leads to a mixture of regio- and/or stereoisomers, which are diffi-

cult to separate, and the desired compound may not even be formed at all [2,3]. In order to gain regio- and stereocontrol over bis- and multiadditions to fullerenes, Diederich and co-workers first applied the tether-directed remote functionalization [4] to the carbon spheroids in 1994 [5]. It consists in the attachment to the cage molecules of an anchor carrying a reactive group at the end of a tether (Fig. 1). Conformational preferences of the spacer and steric constraints ideally allow the reactive group to attack only a single, specific position within the molecular conjugate. In some cases, it has been possible to reduce the role of the tether to that of an auxiliary, which is removed after achievement of a selective bis- or multiaddition and is, therefore, termed a template [6]. The tether-directed remote functionalization has become the most generally applicable method for selective multiadditions to fullerenes [7,8]. The present account gives an overview of its de-

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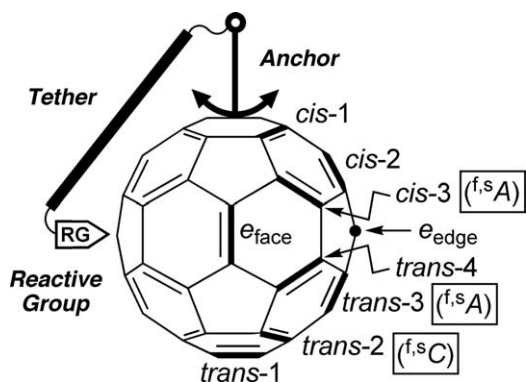


Fig. 1. Illustration of the concept of tether-directed remote functionalization of  $C_{60}$ , trivial nomenclature of possible bisadduct isomers [10], and stereodescriptors for the highlighted inherently chiral addition patterns [9,12].

velopment in the Diederich group over the past 11 years.

## 2. Isomerism of [60]fullerene bisadducts

Functionalization of one of the 30 identical 6–6 bonds (common edges of two six-member rings) of  $I_h$ - $C_{60}$  [2,3] by addition of a  $C_{2v}$ -symmetric addend (e.g. anchor in Fig. 1) lowers the symmetry of the derivatized carbon cage to  $C_{2v}$ , thereby eliminating the equivalence of the remaining 6–6 bonds. As a result, addition of a second, identical residue can, in principle, lead to eight different bisadduct regioisomers. They can be unambiguously named according to IUPAC (International Union of Pure and Applied Chemistry) nomenclature [9] or, in a more intuitive way, by indication of the relative arrangement of the addends as proposed by Hirsch et al. [10] (Fig. 1): the two addends can be located in the same hemisphere (*cis*) or in opposite hemispheres (*trans*) of the carbon cage and, in addition, there is a borderline case which is termed *equatorial* or *e*. There are three possible arrangements for two addends within a hemisphere (*cis*-1, *cis*-2, and *cis*-3) and four of them involving both hemispheres (*trans*-1, *trans*-2, *trans*-3, and *trans*-4). If two different,  $C_{2v}$ -symmetrical addends are considered, the structural degeneracy of *e* arrangements vanishes and the second addend can occupy two different *e* sites ( $e_{\text{face}}$  and  $e_{\text{edge}}$ , Fig. 1) in relation to the first. This leads to a total of nine possible constitutional bisadduct isomers.

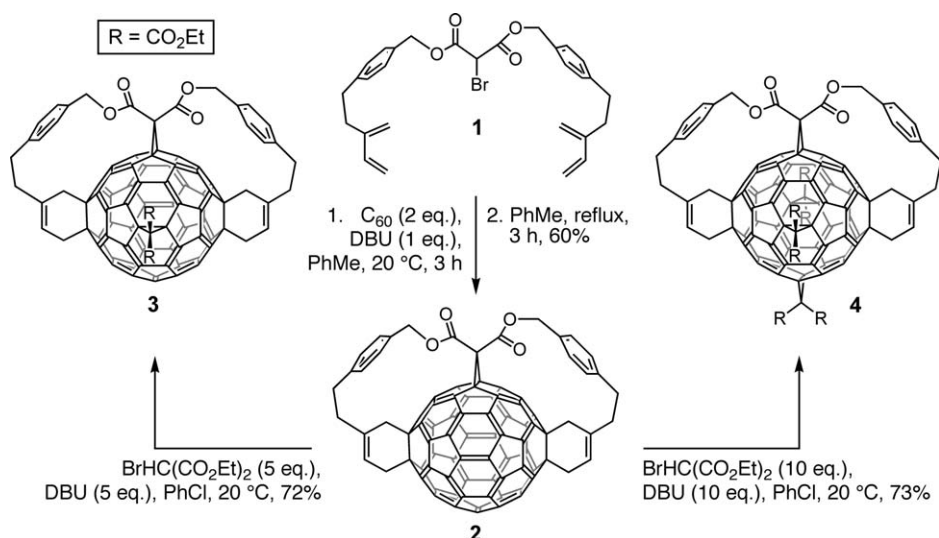
The number of bisadducts further increases if stereoisomers are included. In fact, the *cis*-3, *trans*-3, and *trans*-2 addition patterns are inherently chiral, that is, the corresponding functionalization with any two addends (identical or different, achiral or chiral) provides

a chiral molecule [11–13]. Other addition patterns (*cis*-1, *cis*-2, and *trans*-4) become chiral only with two different addends: they are termed noninherently chiral. As to the remaining functionalization patterns, *trans*-1 bisadducts are always achiral unless the addends include appropriate stereogenic units. In the case of *e* bisadducts with two identical,  $C_s$ -symmetrical methanotype addends, i.e., carrying two different substituents at the bridging C-atoms – the methano C-atom in  $e_{\text{face}}$  position is a stereogenic center but the addition pattern remains achiral [13]. In other cases of *e* bisadducts with identical,  $C_s$ -symmetrical addends, the addition pattern becomes noninherently chiral without new stereogenic centers appearing in the addends [13]. The situation in *e* bisadducts depends critically on structural details of the addends and shall not be discussed here exhaustively.

As recommended by the IUPAC, the configuration of a fullerene derivative with a chiral functionalization pattern is specified by the stereodescriptors ( $^{f,s}C$ ) and ( $^{f,s}A$ ) ( $f$  = fullerene,  $s$  = systematic [numbering],  $C$  = clockwise,  $A$  = anticlockwise) [9,12].  $C$  and  $A$  correspond to the direction of an arc traced from C(1) via C(2) to C(3) in a fullerene derivative numbered according to IUPAC [9,14]. Observation of the rule of the lowest set of locants for the addends is of particular importance in the numbering procedure. Fig. 1 displays the stereodescriptors for the highlighted examples of inherently chiral *cis*-3, *trans*-3, and *trans*-2 addition patterns.

## 3. The tether-directed remote functionalization of $C_{60}$ : early developments

Although the various formal double bonds of a [60]fullerene monoadduct show somewhat different reactivities [3,15], selectivity in bisadduct formation is generally limited and regio- or stereoisomeric product mixtures result. These are often difficult to purify and, furthermore, the desired isomer may only be formed in minor amounts, if at all. Trying to remedy this unsatisfactory situation, the Diederich group tested the tether-directed remote functionalization [4] as a rational approach towards selectively multifunctionalized fullerenes that are difficult to obtain in thermodynamically or kinetically controlled successive additions of unconnected reagents [5,16]. The first step of this method consists in the attachment to the fullerene of an anchor carrying a reactive group at the end of a tether (Fig. 1). As a result of steric and conformational constraints imposed by anchor and tether, the reactive group should



Scheme 1. Regioselective formation of *e,e,trans*-1 trisadduct **2** by tether-directed remote functionalization and selective further transformation into tetrakisadduct **3** and hexakisadduct **4**.

ideally add to a single, precise position of the carbon spheroid.

Anchor–tether–reactive group conjugates such as **1** (Scheme 1) were designed by PM3 semiempirical calculations to afford the desired multiadduct with the lowest relative heat of formation [5,16]. Indeed, fixation of the anchor (malonate group of **1**) to the fullerene core by nucleophilic cyclopropanation in the presence of a non-nucleophilic base (Bingel reaction [17]) and subsequent addition of the reactive buta-1,3-diene groups by intramolecular Diels–Alder reactions under high dilution conditions afforded the predicted trisadduct **2** with complete regioselectivity [5,16]. Its *e,e,trans*-1 addition pattern is not attainable through successive additions of untethered reagents.

Bingel reaction of **2** with five and 10 equivalents of diethyl 2-bromomalonate and DBU (1,8-diazabicyclo [5.4.0]undec-7-ene) regioselectively afforded tetrakisadduct **3** and hexakisadduct **4**, respectively (Scheme 1) [5,16]. The latter displays a pseudo-octahedral addition pattern and its residual  $\pi$ -chromophore corresponds to a cubic cyclophane with eight benzenoid rings that are located at the corners of a cube and interconnected along its edges [5,16,18,19]. The generation of pentakisadducts by bromomalonate addition to tetrakisadduct **3** afforded unequal amounts of two regioisomers in which the fifth addend occupies either of the two remaining positions that become functionalized en route to hexakisadduct **4** [5,16,18–20]. In the more abundantly formed pentakisadduct, the bond functionalized last (*e* in relation to the original anchor) is positioned doubly

*e*<sub>face</sub> and singly *e*<sub>edge</sub> relative to the neighboring addends; reverse relationships are found for the minor pentakisadduct resulting from addition of the fifth group *trans*-1 to the anchor. It can be inferred that double bonds in *e*<sub>face</sub> position relative to an existing addend are more reactive than *e*<sub>edge</sub> bonds, a finding supported also computationally [21] and by other experimental work [22,23].

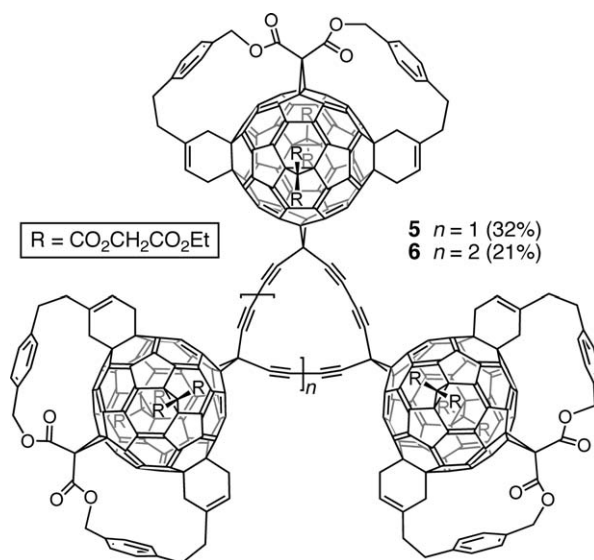
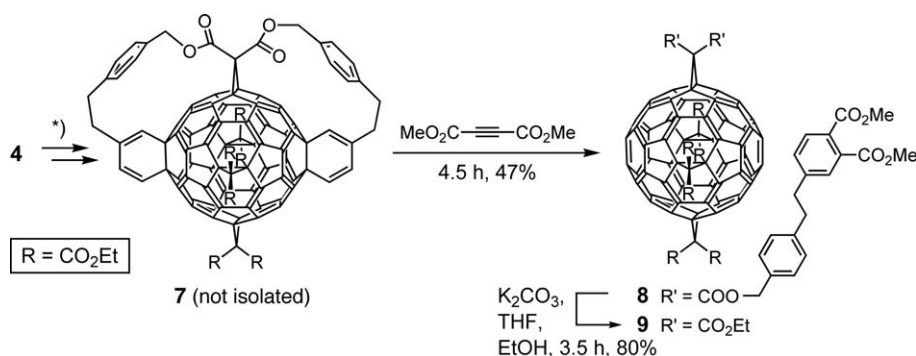


Fig. 2. Solubilized derivatives of fullerene-acetylene hybrid carbon allotropes C<sub>195</sub> and C<sub>260</sub>, obtained by Eglinton–Glaser coupling of the corresponding diethynylmethanofullerene precursors.



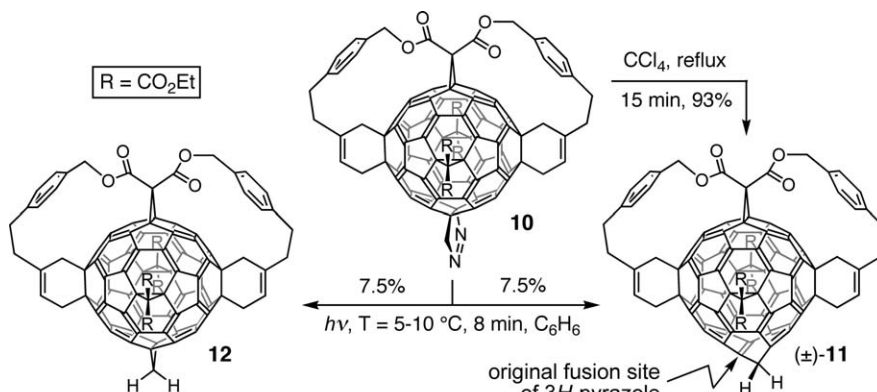
Scheme 2. Removal of the cyclohexene units and the tethers of hexakisadduct **4** (Scheme 1) under generation of tetrakisadduct **9** with all addends located on an equator of the carbon spheroid. \*) Synthetic details: see [25–27].

Introduction of a diethynylmethano residue *trans*-1 to the anchor of a slightly modified pentakisadduct and treatment of the resulting hexakisadduct under Eglinton–Glaser conditions afforded tri- and tetrameric macrocycles **5** and **6** (Fig. 2). They represent solubilized derivatives of fullerene-acetylene hybrid carbon allotropes with the general formula  $C_{65(n+2)}$  [16,18]. Their MALDI-TOF (matrix-assisted laser-desorption time-of-flight) mass spectra showed a sequential loss of fullerene units, leading to the ions of mono-fullerene adducts of cyclo[15]- and cyclo[20]carbon.

A truly templated method requires the final removal of directing auxiliaries employed in the course of a synthesis. To eliminate the tethers from **4** (Scheme 1), direct retro-Diels–Alder reaction was not feasible because of the high thermal stability of fullerene-fused cyclohexene rings [24]. However, following a multistep procedure by An et al. [25], transformation of the fullerene-fused cyclohexene to cyclohexadiene units (**7**, Scheme 2) and in situ treatment of the latter with dimethyl acetylenedicarboxylate, in a Diels–

Alder/retro-Diels–Alder sequence, tetrakisadduct **8** which was finally transesterified to octakis(ethyl ester) **9** [26,27]. As confirmed by X-ray crystallography [27], **9** includes two 6–6 bonds in all-*e* position relative to the addends in place which can be exploited for further molecular scaffolding [28,29]. Tetrakisadduct **9** was obtained independently by Kräutler and co-workers, as reported by Schwenninger et al. [22] and Kräutler et al. [30], through a completely different template-directed approach including, as a key step, a topochemically controlled, regioselective anthracene transfer in heated crystals of the monoadduct resulting from Diels–Alder addition of anthracene to  $C_{60}$  [22,30].

Derivatives with an added or inserted methylene group were obtained from pyrazolofullerene **10**, product of the [3 + 2] cycloaddition between the according pentakisadduct precursor and diazomethane [31]. Whereas thermal extrusion of dinitrogen afforded hexakisadduct ( $\pm$ )-**11**, photolysis of **10** led to a 1:1 mixture of homofullerene ( $\pm$ )-**11** and methanofullerene **12** (Scheme 3). On the basis of the analogy to the products



Scheme 3. Thermal and photochemical extrusion of dinitrogen from pyrazolofullerene **10**, affording homofullerene ( $\pm$ )-**11** and a mixture of the latter and methanofullerene **12**, respectively.



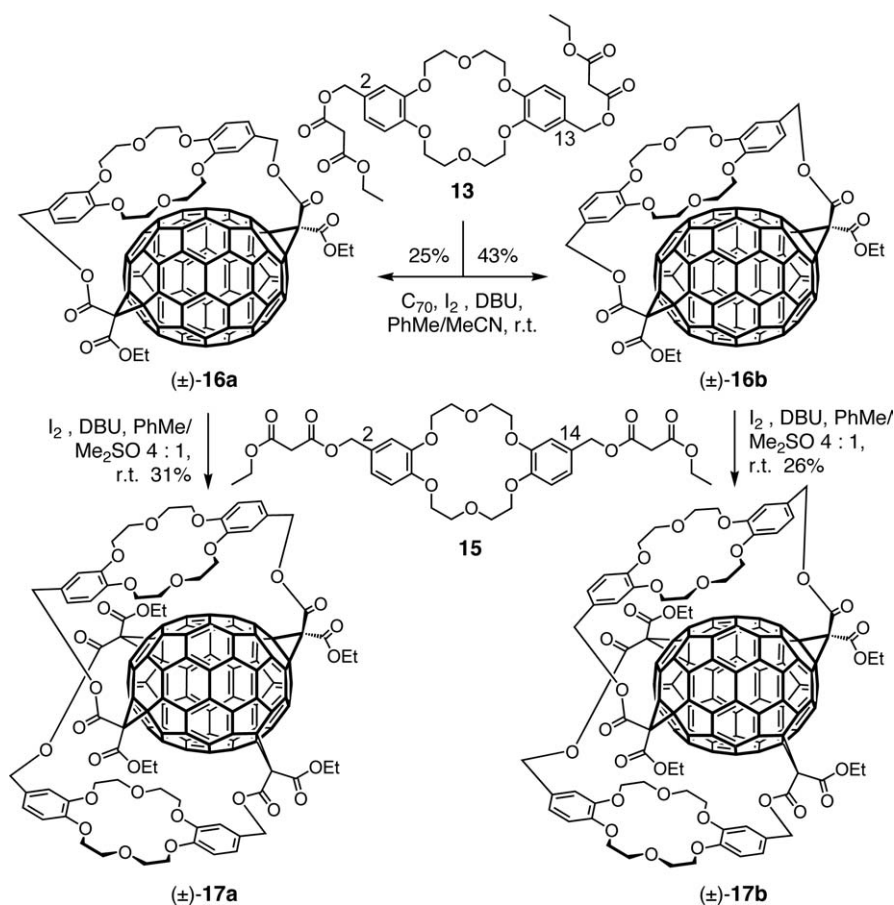
of  $N_2$ -elimination from diazoalkane–toluene adducts [32] as well as high-level calculations [33], thermolysis was proposed to pass through a Möbius aromatic transition state in an eight-electron orbital-symmetry-controlled  $[2\pi_s + 2\pi_s + 2\sigma_s + 2\sigma_a]$  process [31,33]. It leads to an intermediate norcaradiene substructure that cycloreverts to the cycloheptatriene unit of homofullerene derivative ( $\pm$ )-**11**. In contrast, photolysis of **10** presumably proceeds through a diradical mechanism, resulting in a 1:1 mixture of ( $\pm$ )-**11** and **12**. Further addition of diazomethane provided di- and trihomofullerene derivatives in which all inserted  $CH_2$  groups depart from the same central double bond. However, complete isolation of the latter from the residual fullerene chromophore by introduction of a fourth methylene group failed, presumably for steric reasons.

In most subsequent applications of the tether-directed remote functionalization of fullerenes, the formal distinction between anchor and reactive group did no longer make sense. In fact, a practical simplification

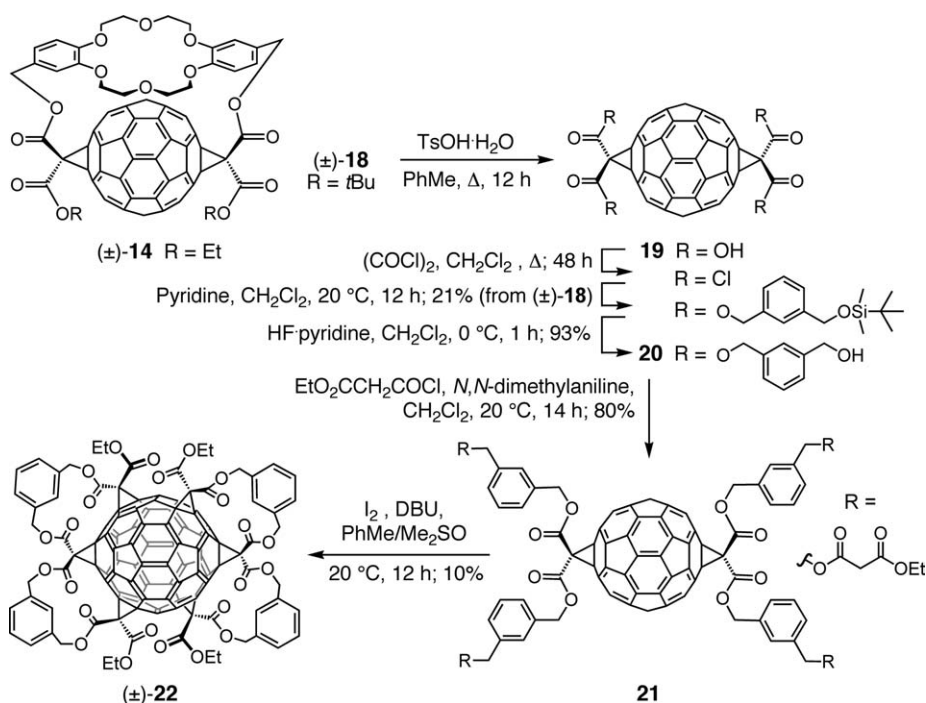
of the method consists in treating the carbon cage with a reagent in which two or several identical functional groups are interconnected by a tether; in such one-pot multi-stage additions, each addend already attached to the fullerene acts as an anchor for the remaining reactive groups.

#### 4. Crown ether tethers

Among the isomers obtained by addition of monofunctional, independent reagents, *trans*-1 bisadducts of  $C_{60}$  (Fig. 1) are generally the least abundant for both kinetic and statistical reasons [10,21]. Also, the design of a tether sufficiently large to span the distance between two poles of the carbon sphere and conformationally homogeneous enough to provide good regioselectivity posed a considerable challenge. The dibenzo[18]crown-6 macrocycle which can act simultaneously as a spacer and an ionophore was found to present an elegant solution to this problem.



Scheme 4. Single and double addition of dibenzo [18]crown-6-derived bismalonates to  $C_{70}$ .



Scheme 5. Multistep transformation of *trans*-1 bis-adduct ( $\pm$ )-**18** into hexakisadduct ( $\pm$ )-**22** with a double-helical, inherently chiral addition pattern.

Addition of a bismalonate derived from *anti*-disubstituted dibenzo [18]crown-6 (**13**, Scheme 4) to  $\text{C}_{60}$  afforded *trans*-1 bismethanofullerene derivative ( $\pm$ )-**14** (Scheme 5) in 30% yield together with 3% of the corresponding *trans*-2 isomer [34]. Addition of  $\text{KPF}_6$  to the reaction mixture led to an enhanced yield (50%) and regioselectivity (only *trans*-1) through an additional template effect originating from the complexation of  $\text{K}^+$  ions by the ionophore which reduces its conformational flexibility [35]. The complex between ( $\pm$ )-**14** and  $\text{KPF}_6$  was characterized by X-ray crystal-structure analysis which confirmed the close tangential orientation of the ionophore atop the carbon cage. Reaction of  $\text{C}_{60}$  with a constitutionally isomeric tether derived from *syn*-disubstituted dibenzo [18]crown-6 (**15**, Scheme 4) regioselectively afforded a *trans*-3 bisadduct.

Although the *trans*-1 addition pattern is  $D_{2h}$ -symmetric and bismalonate **13** is achiral, the product of the double Bingel addition of **13** to  $\text{C}_{60}$  is a racemate (( $\pm$ )-**14**, Scheme 5). The chirality of the  $C_2$ -symmetric bisadduct results from the restricted conformational mobility of the crown ether fixed in close proximity of the fullerene sphere to which it can expose only a single face and, in conjunction with the substitution pattern of the dibenzo-fused heterocycle, constitutes an element of planar chirality. The racemic nature of ( $\pm$ )-**14** was demonstrated in  $^1\text{H-NMR}$ -based complexa-

tion studies with enantiomerically pure potassium (*S*)-1,1'-binaphthalene-2,2'-diyl phosphate and potassium (1*S*)-camphorsulfonate [35].

Dibenzo [18]crown-6-derived bismalonates were also successfully used in the first tether-directed remote functionalization of  $\text{C}_{70}$  [36–38]. Macrocyclization of this fullerene with bismalonate **13** afforded four stereoisomers, namely racemates ( $\pm$ )-**16a** and ( $\pm$ )-**16b**, with complete regioselectivity (Scheme 4) [36,38]. The chirality of the [70]fullerene–crown ether conjugates is associated with an inherently chiral fullerene addition pattern in combination with the planar chiral unit of the *anti*-disubstituted crown ether. Interestingly, the addition pattern of ( $\pm$ )-**16a** and ( $\pm$ )-**16b** differs from that of the major product of two independent additions of untethered diethyl malonate units to  $\text{C}_{70}$  [39]. A sizeable template effect was noted when the synthesis of ( $\pm$ )-**16a** and ( $\pm$ )-**16b** was carried out in the presence of  $\text{KPF}_6$ : whereas the regioselectivity remained unaffected, the diastereoselectivity increased and the total yield went up from 41% to 68%.

When bisadducts ( $\pm$ )-**16a** and ( $\pm$ )-**16b** were allowed to separately react with *syn*-disubstituted dibenzo[18]crown-6 derivative **15**, tetrakisadducts ( $\pm$ )-**17a** and ( $\pm$ )-**17b**, respectively, with  $\text{C}_{70}$  sandwiched between two crown ethers, were obtained regio- and stereoselectively [37,38]. It should be pointed out that the *syn* substitu-

tion pattern of **15** avoids introduction of another planar chiral unit.

Addition of  $\text{KPF}_6$  to solutions of fullerene-crown ether conjugates ( $\pm$ )-**14** (Scheme 5), ( $\pm$ )-**16a**, ( $\pm$ )-**16b**, ( $\pm$ )-**17a**, or ( $\pm$ )-**17b** (Scheme 4) led to an anodic shift of the first reduction potential of the fullerene moiety, as shown by CV (cyclic voltammetry). These first-observed cases of cation-complexation-induced alterations of the redox potentials of fullerene derivatives are due to an electrostatic effect of the  $\text{K}^+$  ion fixed in close proximity of the carbon spheroid. The measured shift is particularly large for ( $\pm$ )-**17a** and ( $\pm$ )-**17b** (+170 mV, 0/–1 redox couple) in which cases the fullerene is sandwiched between two cations [37,38]. Incorporation of  $\text{C}_{60}$  derivative ( $\pm$ )-**14** in the membrane of an ion-selective electrode showed that  $\text{K}^+$  forms the strongest complex among the alkali metal ions [34,35].

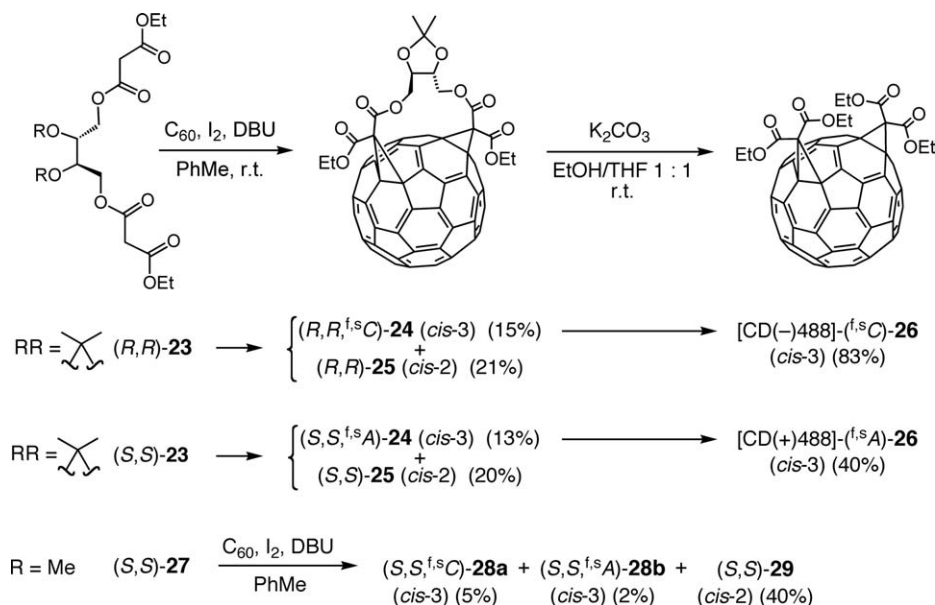
Conjugate ( $\pm$ )-**18**, a di-*tert*-butyl ester analog of ( $\pm$ )-**14** (Scheme 5), was prepared as a key intermediate en route to a hexakisadduct of  $\text{C}_{60}$  with an inherently chiral addition pattern. Acid-catalyzed cleavage of the *tert*-butyl ester groups and the crown ether template afforded the corresponding tetracarboxylic acid **19** which was transformed over several steps into tetrol **20** and further into tetrakisalonate **21**. The final step of the sequence, affording  $D_2$ -symmetric hexakisadduct ( $\pm$ )-**22** as sole product [29,40], consisted of two double tether-directed remote Bingel additions, multiple macrocyclizations which had previously been described

as ‘clipping reactions’ and given access to tris- and tetrakisadducts of  $\text{C}_{60}$  [41]. X-ray crystallography of ( $\pm$ )-**22** confirmed all six cyclopropane rings to be arranged in a double-helical fashion with the corresponding axis passing through the unfunctionalized poles of the carbon sphere.  $\pi$ -Electron conjugation is maintained between the two hemispheres of shiny red ( $\pm$ )-**22** via two (*E*)-stilbene-like bridges. This constitution leads to rather different chemical reactivity and physical properties in comparison to the pale yellow hexakisadducts with a pseudo-octahedral addition pattern (e.g., **4**, Scheme 1). Hexacyclopropafullerene ( $\pm$ )-**22** readily undergoes further Bingel additions at the two sterically most accessible polar 6–6 bonds under formation of orange-yellow heptakis- and octakisadducts [29,40].

## 5. Stereoselective synthesis of multiadducts of $\text{C}_{60}$

### 5.1. Stereoselective targeting of *cis* addition patterns

The  $C_2$ -symmetric addition patterns *cis*-2, *trans*-2, and *trans*-3 (Fig. 1) are distinguished by their inherent chirality [11–13], and their stereoselective generation by use of chiral, enantiopure tethers is of high interest. Our first attempts towards this goal were based on spacers derived from easily available enantiopure threitol, which, in the meantime, has proven to be a versatile



Scheme 6. Regio- and diastereoselective addition to  $\text{C}_{60}$  of bismalonates derived from enantiopure threitol and cleavage of the tether auxiliary from the *cis*-3 bisadducts (*R,R,f,s*C)-**24** and (*S,S,f,s*A)-**24**, affording (*f,s*C)-**26** and (*f,s*A)-**26**, respectively, as pure enantiomers with an inherently chiral addition pattern.

chiral auxiliary for the stereoselective multifunctionalization of fullerenes [8,13].

Bingel reaction between  $C_{60}$  and either (*R,R*)-**23** or (*S,S*)-**23** afforded the enantiomeric *cis*-3 bisadducts (*R,R*,<sup>*f,s*</sup>*C*)-**24** and (*S,S*,<sup>*f,s*</sup>*A*)-**24** (Scheme 6), respectively, as minor products besides the corresponding *cis*-2 (Fig. 1) bisadducts (*R,R*)-**25** and (*S,S*)-**25**, the addition pattern of which is achiral [41,42]. Removal of the chiral tethers from (*R,R*,<sup>*f,s*</sup>*C*)-**24** and (*S,S*,<sup>*f,s*</sup>*A*)-**24** by transesterification with ethanol yielded tetraethyl esters (<sup>*f,s*</sup>*C*)-**26** and (<sup>*f,s*</sup>*A*)-**26**, respectively, as pure enantiomers exhibiting strong CD (circular dichroism) bands between 250 and 750 nm with  $\Delta\epsilon$  values approaching  $150\text{ M}^{-1}\text{ cm}^{-1}$ . Such strong Cotton effects are typical for chiral  $\pi$ -chromophores of fullerene derivatives with an inherently chiral addition pattern [11–13]. Absolute configurations could be assigned as [CD(–)488]-(<sup>*f,s*</sup>*C*)-**26** and [CD(+488)]-(<sup>*f,s*</sup>*A*)-**26** by a comparison between experimental and calculated CD spectra [43].

On the other hand, the open-chain L-threitol-derived tether of bis-malonate (*S,S*)-**27** afforded the diastereoisomeric *cis*-3 bisadducts (*S,S*,<sup>*f,s*</sup>*A*)-**28a** and (*S,S*,<sup>*f,s*</sup>*C*)-**28b** (Scheme 6) as minor products, next to *cis*-2 bisadduct (*S,S*)-**29**, in a 5:2 ratio which reflects a rather poor diastereoselectivity [44]. It can be concluded that the reduced conformational flexibility of tethers (*R,R*)-**23** and (*S,S*)-**23**, associated with their cyclic acetal function, is essential for the quasi-complete diastereoselectivity observed in the formation of (*R,R*,<sup>*f,s*</sup>*C*)-**24** and (*S,S*,<sup>*f,s*</sup>*A*)-**24**.

The importance of the conformational homogeneity of the tethers used in multifunctionalizations of fullerenes is also nicely illustrated by the following example: Macrocyclization between enantiopure (*R,R*)-butane-2,3-diyl [45] bismalonate and  $C_{60}$  afforded *cis*-3 bisadduct (*R,R*,<sup>*f,s*</sup>*A*)-**30** (Fig. 3) as sole regioisomer in 24% yield and with > 97% de (=  $100 \times (([R,R,\sup{f,s}A]-30] - [(R,$

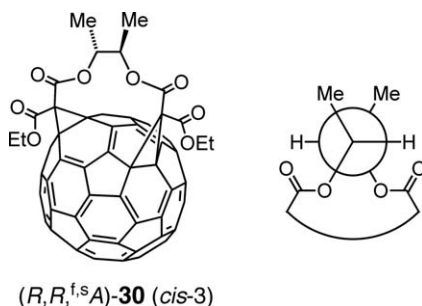


Fig. 3. Bisadduct (*R,R*,<sup>*f,s*</sup>*A*)-**30**, obtained by diastereoselective addition of (*R,R*)-butane-2,3-diyl bismalonate to  $C_{60}$  (left) and Newman projection of the preferred conformation of the tether fragment (right).

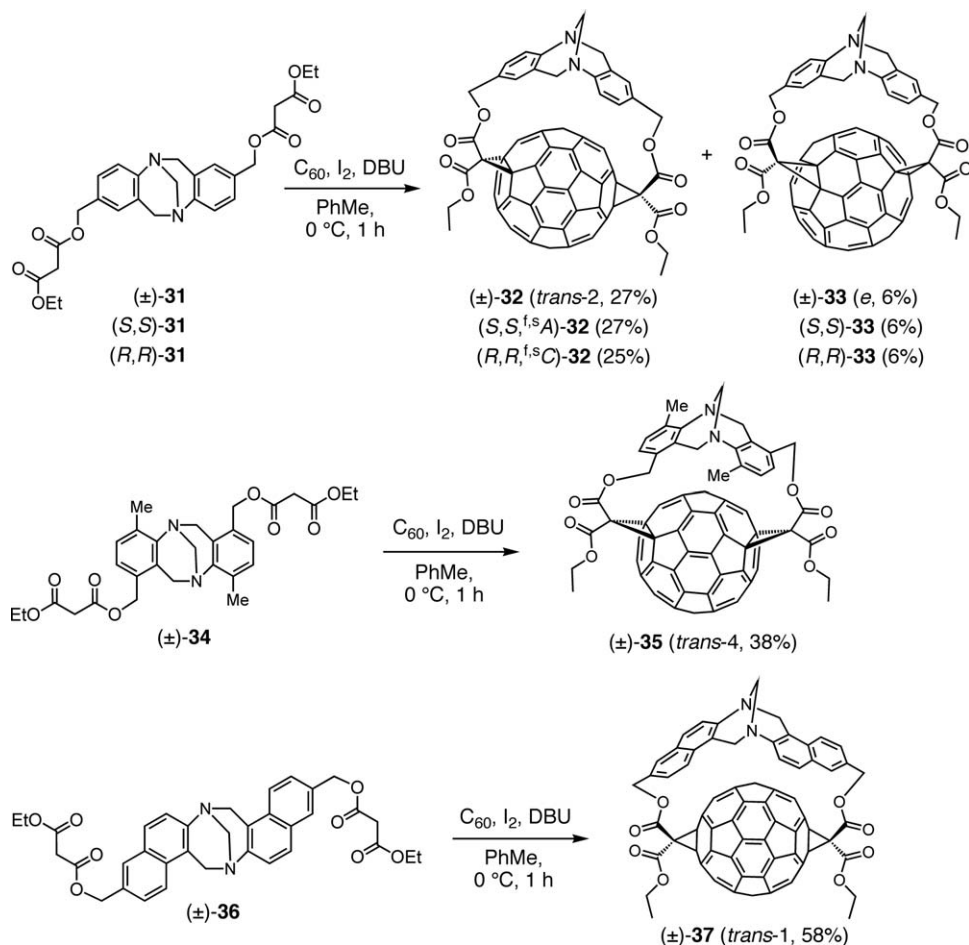
*R*,<sup>*f,s*</sup>*C*)-**30**]/([(*R,R*,<sup>*f,s*</sup>*A*)-**30**] + [(*R,R*,<sup>*f,s*</sup>*C*)-**30**])) [46]. According to semiempirical calculations, the substituents of the ethylene tether fragment of (*R,R*,<sup>*f,s*</sup>*A*)-**30** adopt a staggered conformation with *gauche* relationships between the two methyl as well as between the two ester groups and an antiperiplanar (*ap*) arrangement of the H-atoms (Newman projection of Fig. 3). Fixation of the ethylene unit of the tether in this conformation by incorporation in a bismalonate derived from *trans*-cyclohexane-1,2-diol even led to an increased yield (32%) of exclusively and diastereoselectively formed *cis*-3 regioisomer upon reaction with  $C_{60}$ . Conversely, when the glycolic fragment is locked in an unproductive conformation, for example in *trans*-cyclopentane-1,2-diyl or *exo,cis*- and *exo,trans*-norbornane-2,3-diyl bismalonates, Bingel macrocyclization with  $C_{60}$  failed almost completely. The absolute configuration of (*R,R*,<sup>*f,s*</sup>*A*)-**30** was determined by comparing the results of an NMR-spectroscopic and a computational conformational analysis of the tether fragment [46]. The result is in accord with the near-identity of the CD spectra of (*R,R*,<sup>*f,s*</sup>*A*)-**30** and (<sup>*f,s*</sup>*A*)-**26** (Scheme 6) which reflects their matching chiral  $\pi$ -chromophores.

## 5.2. Stereoselective targeting of *trans* addition patterns: tethers derived from various Tröger-type bases

The difficulty of finding tethers spanning the two hemispheres of  $C_{60}$  and simultaneously inducing a high regioselectivity was mentioned above. Regio- and stereoselective targeting of the inherently chiral *trans*-2 and *trans*-3 addition patterns seemed all the more challenging since it requires large and conformationally constrained chiral tethers. Derivatives of the  $C_2$ -symmetric Tröger base were envisaged as suitable for this purpose: they are characterized by rigidity and a folded geometry with nearly orthogonal aromatic rings as distinctive structural features. In addition to the attainment of the inherently chiral *trans*-2 and *trans*-3 functionalization patterns, such tethers allowed the high-yielding regioselective preparation of *trans*-1 and *trans*-4 bisadducts of  $C_{60}$  [47].

Thus, double Bingel cyclopropanation of  $C_{60}$  with bismalonate ( $\pm$ )-**31** including a Tröger base assembled from a *para*-substituted aniline, afforded *trans*-2 bisadduct ( $\pm$ )-**32** as major regioisomer next to a minor amount of *e* isomer ( $\pm$ )-**33** (Scheme 7) [47]. The addition patterns of these regioisomers as well as those of the compounds described below were unequivocally established by UV/Vis and NMR spectroscopies. The absorption spectra of malonate bisadducts of  $C_{60}$  in the





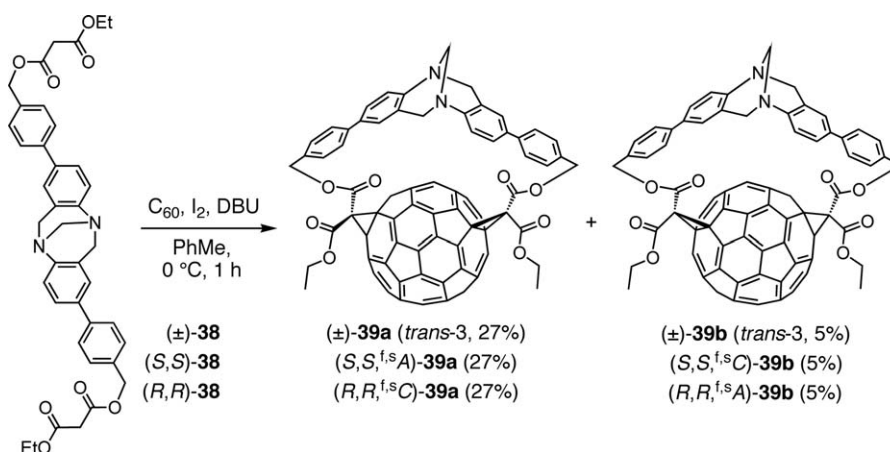
Scheme 7. Regio- and stereoselective Bingel macrocyclizations between  $C_{60}$  and racemic or enantiopure bismalonates derived from various Tröger-type bases.

region between 400 and 800 nm are mainly determined by the structure of the fullerene chromophore and can, therefore, be used as fingerprints for the corresponding addition patterns [48]. When the above Bingel addition was carried out with enantiomerically pure malonates (*S,S*)-**31** and (*R,R*)-**31**, obtained from the racemate by HPLC (high performance liquid chromatography) on a chiral stationary phase, bisadducts (*S,S,f,sA*)-**32** and (*R,R,f,sC*)-**32**, respectively, were obtained with complete diastereoselectivity. The absolute configurations of the enantiomers were determined by comparison of their CD spectra with those of previously reported enantiomerically pure derivatives of  $C_{60}$  with the same functionalization pattern [48,49]. Under the assumption that the thermodynamic stability of such bisadducts is reflected in the transition state of the second cyclopropanation, the relative heats of formation of (*S,S,f,sA*)-**32** and its hypothetical diastereoisomer (*S,S,f,sC*)-**32'** were calculated using the semiempirical PM3 method. The

computed difference  $\Delta\Delta H = 29.4 \text{ kcal mol}^{-1}$  in favor of the actually formed (*S,S,f,sA*)-**32** rationalizes the experimental observation very well.

Variation of the geometry of the tether by attachment of the malonate residues to the *meta* position of the aniline subunits of the Tröger base ((±)-**34**) afforded exclusively *trans*-4 regioisomer (±)-**35** upon reaction with  $C_{60}$  (Scheme 7) [47].

Alteration of the core of the Tröger base, on the other hand, by switching from an aniline derivative as precursor to a naphthyl-2-amine substituted at C(6) (bismalonate (±)-**36**) led to completely regioselective and high-yielding formation of *trans*-1 bisadduct (±)-**37** (Scheme 7) [47]. Although crystallization of this compound is tricky, a single crystal suitable for X-ray analysis could be isolated from a solution of (±)-**37**. Remarkably, it contained only the (*R,R*)-configured enantiomer and this seems to be the first case of spontaneous resolution of a racemic fullerene derivative.



Scheme 8. Regio- and stereoselective synthesis of *in,out trans*-3 bisadducts of  $C_{60}$  using enantiopure or racemic extended Tröger bases including biphenyl units.

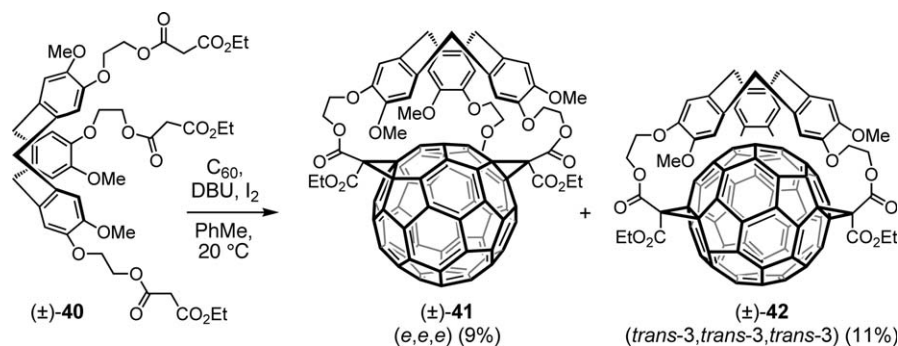
In an attempt to achieve also the inherently chiral *trans*-3 functionalization pattern, bismalonate  $(\pm)$ -**38**, including two 4'-substituted 4-aminobiphenyl units in the Tröger base core, was added to  $C_{60}$ . The reaction was completely regioselective, affording only the targeted *trans*-3 addition pattern, but in the form of four stereoisomers consisting of two pairs of enantiomers, namely  $(\pm)$ -**39a** and  $(\pm)$ -**39b** (Scheme 8) [47]. Whereas all the above Tröger base-fullerene conjugates are *out, out* isomers (*out* refers to the orientation of the ethoxycarbonyl substituents of the cyclopropane rings), the  $C_1$  symmetry of  $(\pm)$ -**39a** and  $(\pm)$ -**39b** points at *in,out* isomers. Separate syntheses with enantiomerically pure starting materials,  $(S,S)$ -**38** and  $(R,R)$ -**38**, allowed the isolation of all four stereoisomers, i.e.  $(S,S,^{f,s}A)$ -**39a** and  $(S,S,^{f,s}C)$ -**39b**, as well as  $(R,R,^{f,s}C)$ -**39a** and  $(R,R,^{f,s}A)$ -**39b**, respectively. Absolute configurations were assigned by comparison of the CD spectra with the published data of enantiomerically pure  $C_{60}$  derivatives with the same addition pattern [48,49]. Whereas the CD spectra of enantiomers are exact mirror images,

those of diastereoisomers show some deviation from this relationship due to the superposition of the Cotton effects originating from the fullerene and the Tröger base chromophores.

These asymmetric syntheses using the structural motif of the Tröger base as a 'chiral auxiliary' allowed the first stereoselective targeting of the inherently chiral *trans*-2 and *trans*-3 addition patterns of buckminsterfullerene. Tröger-type bases with different angles between the planes of the arene rings as well as representatives derived from thiophene and benzothiophene were successfully used by Ishida et al. [50] in a different study on the regio- and stereocontrolled addition of accordingly tethered bismalonates to  $C_{60}$ .

## 6. Addition of tethered tris- and tetrakis-malonates to $C_{60}$

The first direct threefold Bingel macrocyclization consisted in the addition to  $C_{60}$  of tripodal trismalonate  $(\pm)$ -**40** in which three propanedioate moieties are at-



Scheme 9. Products of the first one-pot direct addition of a trismalonate to  $C_{60}$ .

tached to a chiral CTV (cyclotrimeratriylene) core (Scheme 9) [51]. The two racemic trisadducts isolated from this reaction were assigned as *e,e,e* and *trans-3,trans-3,trans-3* regioisomers ( $\pm$ -**41** and ( $\pm$ -**42**). Both structures present an interesting superposition of an inherently chiral fullerene addition pattern (possible configurations ( $^{f,s}C$ ) and ( $^{f,s}A$ )) and a conformationally chiral CTV unit (possible configurations (*P*) and (*M*)) which can lead to a total of four stereoisomers (two pairs of enantiomers) for each regioisomer. Intriguingly, a detailed mathematical analysis revealed that the corresponding topological stereoisomers, besides being topologically chiral, amount to four in the case of the *e,e,e* adduct but only to two in that of the *trans-3,trans-3,trans-3* isomer [52]. This is a consequence of the fact that the median plane including the addends cuts the carbon sphere into unequal fractions in the former (( $\pm$ -**41**), but into equal halves in the latter (( $\pm$ -**42**) structure.

Another interesting approach towards regioselective bis-, tris-, and tetrakis-functionalization of  $C_{60}$  is based on the Bingel reaction with flexible cyclooligomalonates and was developed by Reuther et al. [53]. Whereas fullerene adducts resulting from addition of oligomalonate macrocycles with identical oligomethylene chains between the carboxy groups are generally characterized by rotational symmetry, those produced from cyclooligomalonates with unequal oligomethylene chains lead to other addition patterns.

## 7. Further tethers

Due to their easy availability, xylylene tethers have been applied to a large variety of tether-directed multiple functionalizations of  $C_{60}$  by the Diederich group [41,54] and by others [8]. They show different regioselectivities depending mainly on the substitution pattern of the core benzene ring but also on other factors such as the specific functional groups involved. A particularly elaborate example is catenane ( $\pm$ -**43**) (Fig. 4), the *p*-xylylene tether of which induces a *trans-4* pattern of biscyclopropanation, thereby becoming an element of planar chirality due to its restricted conformational mobility in combination with its particular substitution pattern [55]. Tethers derived from *m*-xylylene have been extensively used over the past years for the synthesis of a large structural variety of fullerene-derived dendrimers; these appear to be very promising tectons with regard to supramolecular chemistry and materials science applications [56].

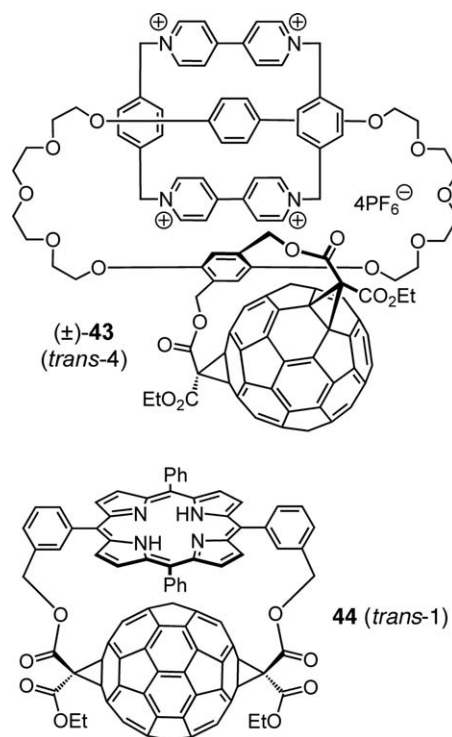


Fig. 4. Planar-chiral fullerene-derived catenane ( $\pm$ -**43**) and fullerene–porphyrin conjugate ( $\pm$ -**44**) — examples of [60]fullerene bisadducts with interesting structure and function, obtained regioselectively by tether-directed remote functionalization.

Fullerene–porphyrin conjugates continue to be one of the hottest research topics in fullerene chemistry due to their potential as model systems mimicking natural photosynthetic reaction centers by converting photonic excitation energy to chemical potential in the form of long-lived charge-separated states [57]. The use of porphyrins as tethers in the synthesis of such dyads, e.g. ( $\pm$ -**44**) (Fig. 4), allows not only for regioselective addition to the fullerene but also for precise control of the geometric parameters which have a crucial influence on the photophysical and electron-transfer properties [58]. Interestingly, extension of the chains linking the porphyrin to the malonates by one C-atom on each side leads to exclusive formation of the corresponding *trans-2* bisadduct [59].

Further bismalonates used by the Diederich group in Bingel macrocyclizations include tether residues such as *trans*-but-2-ene-1,4-diyl [42,60], 1,10-phenanthroline-2,9-dimethylene, 1,10-phenanthroline-2,9-bis(1,4-phenylene), and 9,9'-spirobifluorene-2,2'-dimethylene [41]. They afforded fullerene adducts showing interesting structural features with varying regio- and, in the occurrence, stereoselectivities.

## 8. Conclusion

Roughly a decade after the introduction of the tether-directed remote functionalization into fullerene chemistry [5], this method has made all addition patterns of C<sub>60</sub> available with fair to high regioselectivity [7,8]. Among them, the *cis*-1 pattern is limited to particular cases most of which can be considered as multiple anellations of the fullerene [8]. The reason for this limitation is the steric hindrance between most addends in such an arrangement, which precludes, for example, the formation of Bingel-type *cis*-1 bisadducts. As to the inherently chiral *cis*-3, *trans*-3, and *trans*-2 functionalization patterns, they are now available not only regio- but also diastereoselectively when enantiopure tethers are used in the macrocyclizations. Broader avenues to regio- and/or stereoselectively formed *trans* bisadducts have opened up only recently through the introduction of a variety of tethers derived from the Tröger base [47]. If one makes abstraction of the inaccessible *cis*-1 bisadducts, Bingel-type chemistry has proven to be particularly versatile and adaptable to the various functionalization patterns. As to *e* bisadducts, tether-directed bicyclopropanation usually generates a new stereogenic center [13], the stereocontrol of which has to be further investigated. Also, the stereoselective generation of non-inherently chiral functionalization patterns calls for more profound exploration. The same accounts for the selective generation of higher adducts of C<sub>60</sub> by tether-directed remote functionalization although some important progress in this area has been made during the past few years [51–53].

In the chemistry of C<sub>70</sub>, the tether-based methodology has provided access to only a few functionalization patterns, albeit with good regio- and stereoselectivities [36–38]. As to the spacer-controlled multifunctionalization of other higher fullerenes, it remains a terra incognita.

## Acknowledgements

The authors thank the co-workers whose names appear in the references for their valuable contributions. Continuing support of fullerene research by the Swiss National Science Foundation is gratefully acknowledged.

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