The Addition Patterns of C_{60} Trisadducts Involving the Positional Relationships *e* and *trans-n* (n = 2–4): Isolation, Properties, and Determination of the Absolute Configuration of Tris(malonates) and Tris[bis(oxazolines)]

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A series of regioisomeric trisadducts of C_{60} (**5**–**11**, **14**–**18**) having the positional relationships *e* and *trans-n* (n = 2–4) resulting from successive additions of malonates or bis(oxazolines) to [6,6]-double bonds of the fullerene framework has been isolated and characterized. The new adducts **8**–**11** and **15**–**17** represent examples of unprecedented addition patterns. The addition patterns of the new trisadducts with C_2, C_s or C_1 symmetry have been assigned on the basis of the known positional relationships of the addends in their precursor bisadducts, and those of the C_2- or C_s-symmetric representatives have been verified by analysis of their NMR spectra. The absolute configurations of the adducts with inherently chiral addition patterns could be determined either by comparison of the calculated and experimental CD spectra of the bis(oxazoline) adducts or with knowledge of the absolute configurations of the chiral bisadduct precursors containing bis(oxazoline) addends. The CD spectra of the pairs of diastereomers with an enantiomeric addition pattern **^{f}*A*-15/^{f}*C*-15**, **^{f}*A*-16/^{f}*C*-16**, and **^{f}*A*-18/^{f}*C*-18** show mirror image behavior and pronounced Cotton effects.

Introduction

The synthesis and characterization of stereochemically defined oligoadducts of the polyfunctional molecule C_{60} is a fundamental aspect of fullerene chemistry.[1] In principle, the number of isomers that can be formed by multiple additions is huge. Even if one considers only subsequent 1,2-additions to [6,6]-double bonds, which is the predominant mode for cycloadditions or additions of sterically nondemanding addends, many different constitutional isomers are possible. For example, eight different positional relationships are available for bisadducts containing C_{2v}-symmetric addends of a single type, while nine are possible for a combination of two different C_{2v}-symmetric addends (Figure 1).

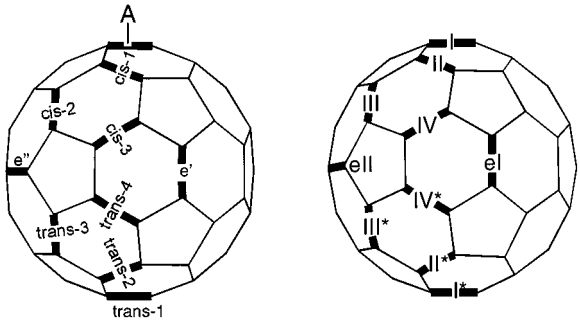

Figure 1. Relative positional relationships (left) and labelling (right) of [6,6]-bonds in C_{60} derivatives

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Examples of all such addition patterns have been reported and the regioselectivities associated with the formation of the corresponding bisadducts have been discussed.[1d–1k] Some of the addition patterns are inherently chiral;[1d,2] pure enantiomers of such dissymmetric structures have been isolated and their chiroptical properties have been investigated.[3–6] The synthesis of defined oligoadducts using tether-controlled techniques allows access to specific addition patterns in good yield.[1l,1m,3,7] A limited number of tris-, tetrakis-, pentakis- or hexakisadducts are also known.[1a,1e,1f,1h,1k–1s,6,7a,7b,7c,8] However, with just a few exceptions,[1e,1i,1q,6] only tris- to hexakisadducts with addends bound in octahedral positions (*e* and *trans*-1 relationships)[9] have been isolated and characterized. On the other hand, it is very desirable to take advantage of the multitude of possible addition patterns. This requires fundamental investigations of the regiochemistry, which may provide a basis for a systematic and at the same time flexible access to fullerene-based architectures with defined and tunable structures and functions. We report here on the isolation of all but one of the possible types of trisadducts having *trans-n*- (n = 2–4) and *e*-positional relationships.

Results and Discussion

Considering the case of threefold addition of C_{2v}-symmetric addends to [6,6]-double bonds of C_{60}, in principle 46 different regioisomers are possible. The number of regioisomers that can theoretically be formed starting from a given bisadduct depends on its existing addition pattern. For example, 14 different trisadducts can be produced from a precursor with the addends bound in *e* positions. However, our recent investigations into the regioselectivity of such additions[1d–1k] have shown that the number of preferably

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formed regioisomers is considerably smaller, since, for example, additions at *cis* positions, especially those of sterically demanding addends such as malonates, are very unfavorable. With the restriction that only *e* or *trans* additions to bisadducts having *e*- and *trans*-positional relationships are considered, the number of possible regioisomers is reduced to 10 (Table 1).

Table 1. Relative and absolute positional relationships, symmetry and number of possible formation pathways of trisadducts which can be formed out of *e* and *trans*-*n* ($n = 1-4$) bis[adducts] (first row) neglecting *cis* additions[a]

***trans*-1** I, I*	***trans*-2** I, II*	***trans*-3** I, III*	***trans*-4** I, IV*	***e*** I, eI
e, *e*, ***t*-1** (I) I, eI, I* C_s 2	*e*, *t*-4, ***t*-2** I, eI, IV* C_1 2	*e*, *t*-4, ***t*-3** I, eI, III* C_1 2	*e*, ***t*-4**, *t*-2 I, eI, IV* C_1 2	***e***, ***e***, ***e*** I, eI, eII C_3 2
e, *e*, ***t*-1** (II) I, eII, I* C_s 2	*e*, *t*-3, ***t*-2** I, eII, III* C_1 2	*e*, ***t*-3**, *t*-2 I, eII, III* C_1 2	*e*, ***t*-4**, *t*-3 I, eI, III* C_1 2	***e***, *t*-4, *t*-2 I, eI, IV* C_1 2
	t-4, *t*-4, ***t*-2** I, IV*[1], IV*[3] C_2 1	*t*-4, ***t*-3**, ***t*-3** I, IV*, III* C_s 1	***t*-4**, ***t*-4**, *t*-2 I, IV*[1], IV*[3] C_2 2	***e***, ***e***, *t*-1 (I) I, eI, I* C_s 1
		***t*-3**, ***t*-3**, ***t*-3** I, III*, III* D_3 1	***t*-4**, ***t*-4**, ***t*-4** I, IV*[1], IV*[4] C_{3v} 1	***e***, *t*-4, *t*-3 I, eI, III* C_1 2
			***t*-4**, *t*-3, *t*-3 I, IV*, III* C_s 1	***e***, *t*-3, *t*-2 I, eII, III* C_1 2
				e, ***e***, *t*-1 (II) I, eII, I* C_s 1

[a] *t* = *trans*.

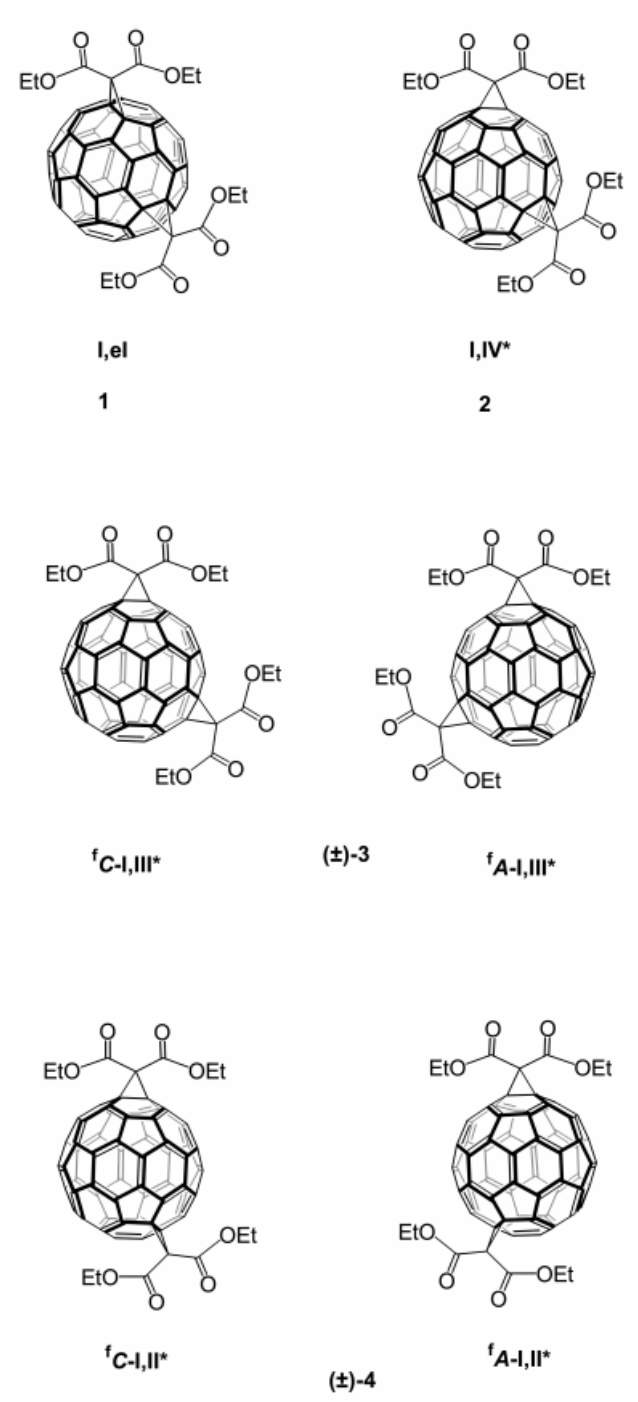
With regard to their symmetry and their possible formation pathways, three types of trisadducts can be distinguished (Table 1): (i) adducts with only one positional relationship, for example an *e,e,e* isomer [such highly symmetric adducts can only be formed from one regioisomeric bisadduct precursor]; (ii) adducts with two different positional relationships, for example a *trans*-4,*trans*-3,*trans*-3 isomer [an adduct of this type has two possible precursor bisadducts], and (iii) adducts with three different positional relationships, for example the *e,trans*-4,*trans*-3 isomer [such adducts may derive from three different precursor bisadducts]. All trisadducts] with one positional relationship exhibit threefold symmetry (D_3, C_3 or C_{3v}); those with two exhibit twofold symmetry (C_2 or C_s), while those with three are unsymmetrical (C_1). The relative positional relationship of addends within a bisadduct precursor must also be present in any trisadduct derived therefrom, provided that no rearrangements take place during the formation of the trisadduct. These stereochemical considerations not only provide a basis for an unambiguous structure assignment of trisadducts (Table 1), but also for higher adducts formed by subsequent additions to [6,6]-bonds.

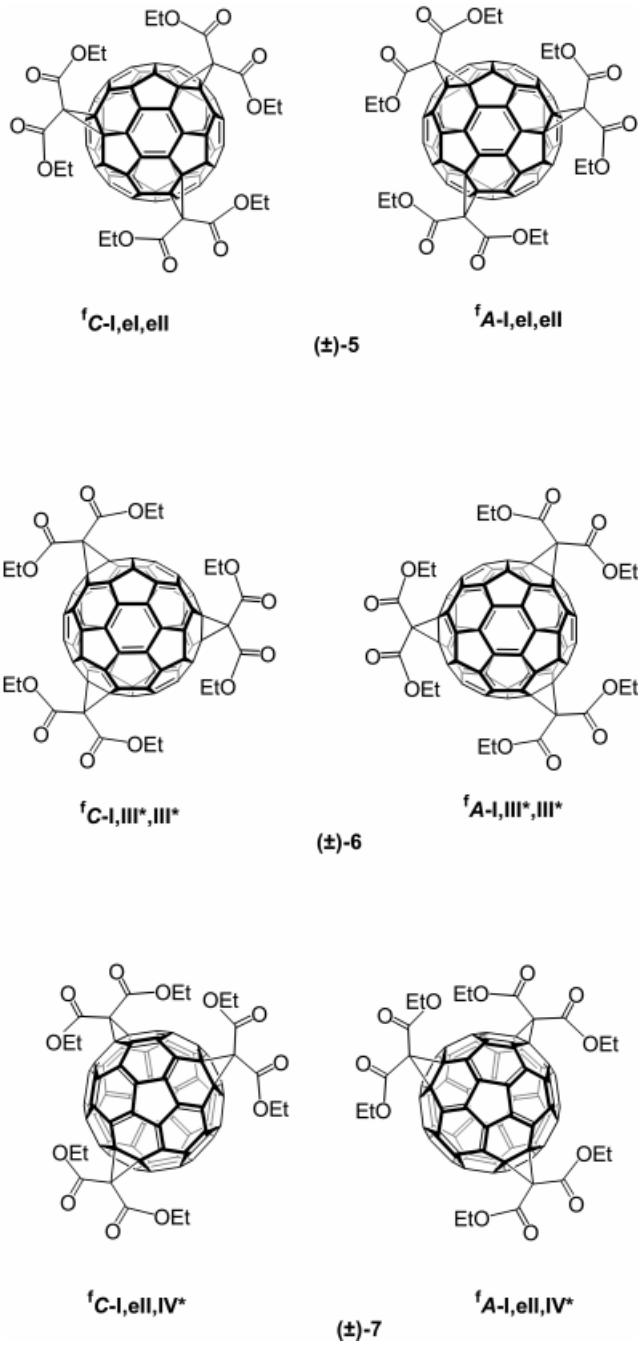
The absolute configuration of a trisadduct with an inherently chiral addition pattern is automatically determined by the absolute configuration of the precursor bisadduct. For example, the trisadduct formed from the *e*-, the *trans*-4-, and the *trans*-3-bisadduct must have the addition pattern *e*,*trans*-4,*trans*-3 and therefore its structure is predetermined. In this example, the addition pattern of the *trans*-3-bisadduct precursor is chiral (C_2 symmetry). By using an enantiomerically pure *trans*-3-bisadduct with known absolute configuration as the precursor, the C_1-symmetric *e*,*trans*-4,*trans*-3-trisadduct must be formed, since only an attack at one specific [6,6]-double bond leads to formation of this trisadduct. The only exceptions are the dissymmetric *e*,*e*,*e* isomers. Although their addition patterns can be unambiguously assigned on the basis of NMR data (only C_3-symmetric isomers are possible), their absolute configurations are not determined by the formation pathway because their *e*-bisadduct precursors are prochiral.[10]

Treatment of *e*-$C_{62}(COOEt)_4$ (**1**), *trans*-4-$C_{62}(COOEt)_4$ (**2**), *trans*-3-$C_{62}(COOEt)_4$ [(±)-**3**], and *trans*-*2*-$C_{62}(COOEt)_4$ [(±)-**4**] with a twofold excess of diethyl bromomalonate in the presence of NaH as base for 24 h in toluene at room temperature[11] leads to a mixture of regioisomeric trisadducts, namely *e*,*e*,*e*-$C_{63}(COOEt)_6$ [(±)-**5**], *trans*-3,*trans*-3,*trans*-3-$C_{63}(COOEt)_6$ [(±)-**6**], and *e*,*trans*-4,*trans*-3-$C_{63}(COOEt)_6$ [(±)-**7**], which we have isolated and characterized previously,[1d,1i] together with four new adducts **8**−**11** (Figures 2 and 3). All the trisadducts **5**−**11** were isolated by flash chromatography followed by HPLC on silica gel (toluene/ethyl acetate, 99.5:0.5). According to the topological considerations outlined above, the new isomers were assigned as *e*,*trans*-4,*trans*-2-$C_{63}(COOEt)_6$ [(±)-**8**], *e*,*trans*-3,*trans*-2-$C_{63}(COOEt)_6$ [(±)-**9**], *trans*-4,*trans*-4,*trans*-2-$C_{63}(COOEt)_6$ [(±)-**10**], and *trans*-4,*trans*-3,*trans*-3-$C_{63}(COOEt)_6$ (**11**) by (i) comparing the k' values of the product peaks in the elugrams (Figure 2) and (ii) isolating the products and comparing their spectroscopic properties.

As can be seen from Figures 2 and 3, the regioselectivity of the trisadduct formation depends strongly on the addition pattern of the bisadduct precursor. Cyclopropanation of the *trans*-3-adduct (±)-**3** shows almost no regioselectivity. The four possible trisadducts (±)-**6**, (±)-**7**, (±)-**9** and **11** are formed in similar yields (Figure 3c). Somewhat less unselective is the cyclopropanation of **2**. The four isomers (±)-**7**, (±)-**8**, (±)-**10** and **11** are isolated with (±)-**7** being the most abundant (Figure 3b).

The fifth possible isomer, with a C_{3v}-symmetric *trans*-4,*trans*-4,*trans*-4 addition pattern, is not found. Additions to **1** and (±)-**4** are much more regioselective. Only three of the six possible tris[adducts] are obtained upon cyclopropanation of **1** (Figure 3a). Although the relative yield of the *e*,*e*,*e*-adduct (±)-**5** only constitutes about 35% of the total amount of trisadducts formed and the yield of the *e*,*trans*-3,*trans*-2 isomer (±)-**9** is higher, the preferred mode of addition is *e* relative to the bound addends. Under the reaction conditions, substantial amounts of tetrakis-





and pentakisadducts with C_s or C_{2v} symmetry having exclusively the relative positional relationships *e* or *trans*-1 are formed. The overall yield of such adducts, formed by subsequent attack at the *e* positions of **1**, amounted to ca. 50%. Significantly, the cyclopropanation of (±)-**4** leads to only two trisadducts (±)-**8** and (±)-**9**. The formation of (±)-**9**, with an *e*,*trans*-3,*trans*-2 addition pattern, is clearly preferred (Figure 3d). Under the reaction conditions used in this study, no rearrangements of the addends on the C_{60} surface could be detected, since, for example, the *e*,*e*,*e*-trisadduct (±)-**5** was only found when the *e*-bisadduct **1** was used as the precursor, while the *trans*-3,*trans*-3,*trans*-3-adduct (±)-**6** was only formed with the *trans*-3-adduct (±)-**3** as starting material. Moreover, no *cis* additions were observed since no products other than the adducts **5**−**11** having only *e*- or *trans*-positional relationships were isolated.

The C_1 symmetry of compounds (±)-**8** and (±)-**9** is reflected in their NMR spectra. Thus, for example, six signals due to the sp^3-C atoms of the fullerene core and the carbonyl C atoms of addends are seen in the ranges δ = 70−73 and δ = 163−164, respectively, as well as three signals at δ = 47−51 for the methylene bridges. The C_2 symmetry of the *trans*-4,*trans*-4,*trans*-2 isomer (±)-**10** leads to 26 signals for the sp^2-C atoms of the fullerene core at δ = 135−138, three resolved signals for the sp^3-C atoms of the fullerene core at δ = 70−71, two signals at δ = 48−49 for the

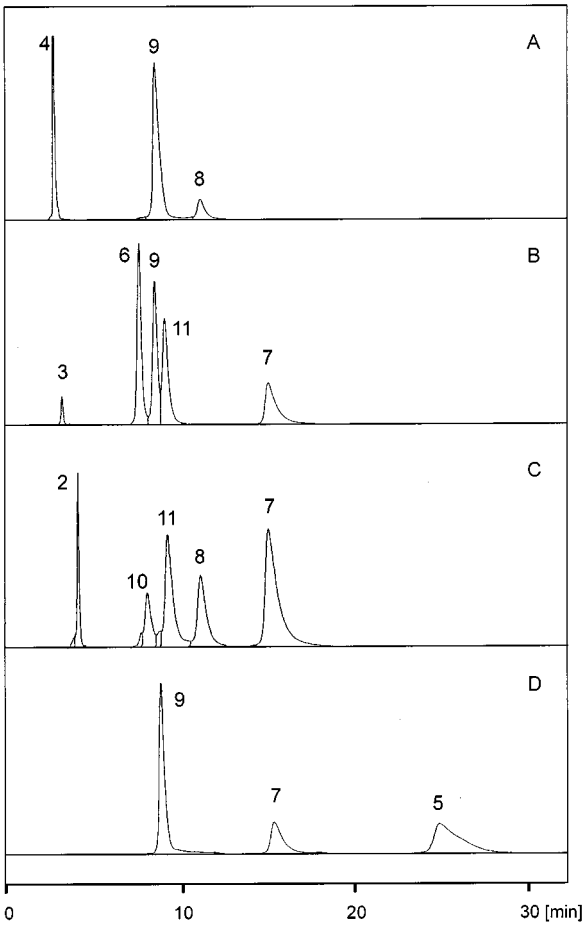
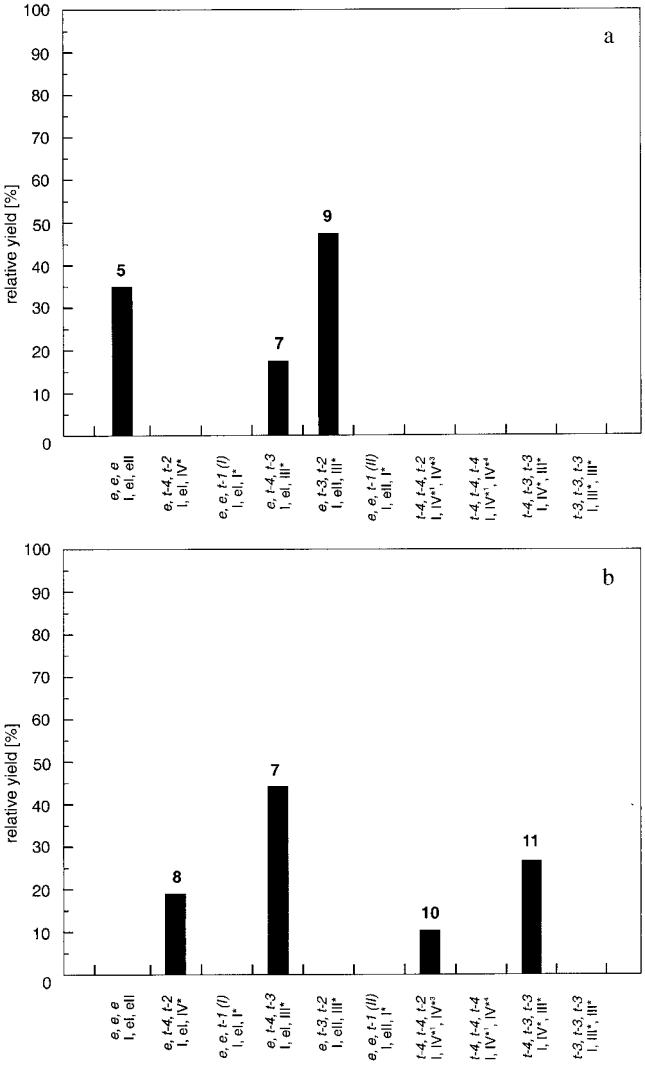


Figure 2. HPLC elugrams of the reaction mixtures obtained after cyclopropanation of **4** (A), **3** (B), **2** (C), and **1** (D)

methylene bridges, and three signals for the carbonyl C atoms at δ = 163−164. Similarly, the C_s symmetry of the *trans*-4,*trans*-3,*trans*-3 isomer **11** is unambiguously indicated by 25 resolved signals for the sp^2-C atoms of the fullerene core in the range δ = 137−149, two signals for the sp^3-C atoms of the fullerene core at δ = 70.95 (4 C) and 71.92 (2 C), two signals at δ = 49.87 (2 C) and 51.61 (1 C) for the methylene bridges, and two signals for the carbonyl C atoms at δ = 163.43 (2 C) and 163.59 (4 C). As we have demonstrated in previous investigations, the features of the fullerene absorption in the UV/Vis spectra of bis(malonates) and bis(aziridines) of C_{60} depend only on the addition pattern and not on the nature of the addend.[1j] As a consequence, the electronic absorption spectrum of a new adduct can be used as a "fingerprint" in order to assign its addition pattern. Similarly, the electronic absorption spectra of the trisadducts investigated in this study are determined by the addition pattern at the C_{60} chromophore (Figure 4).

All trisadducts **5**−**10** with C_1, C_2, C_3 and D_3 symmetry have an inherently chiral addition pattern and were isolated as racemic mixtures. As we have shown recently,[6] enantiomerically pure bisadducts and trisadducts with a chiral addition pattern are readily accessible by addition of chiral bis(oxazolines) and subsequent chromatographic separation of the resulting diastereomers. In order to determine the absolute configurations of such chiral fullerene derivatives, we calculated the CD spectra[12] of the corresponding model systems containing the parent methylene addend and compared the results with the experimental CD spectra of the bisadducts ^{f}***C*-12**, ^{f}***A*-12**, ^{f}***C*-13** and ^{f}***A*-13** as well as of the trisadducts ^{f}***C*-14** and ^{f}***A*-14** (Figure 5).

For this purpose, high-level theoretical calculations of the first singlet excited states and rotatory strengths of the corresponding transitions from the ground state were required. Due to the importance of differential dynamic electron correlation effects in the case of aromatic chromophores,[13] standard ab initio techniques cannot be employed for systems as large as C_{60}. Recently, a new scheme for the theoretical description of excited states based on a combination of density functional theory (DFT) and the single excitation configuration interaction method (DFT/SCI) has been proposed by one of us.[14] The new method is clearly superior to the standard ab initio HF/SCI approach in that it implicitly takes into account dynamic electron correlation effects. Very good results have been obtained, especially for the prediction of CD spectra.[14−16] Calculations of the CD spectra were carried out for ^{f}*A-trans*-3-$C_{62}H_4$, ^{f}*C-trans*-2-



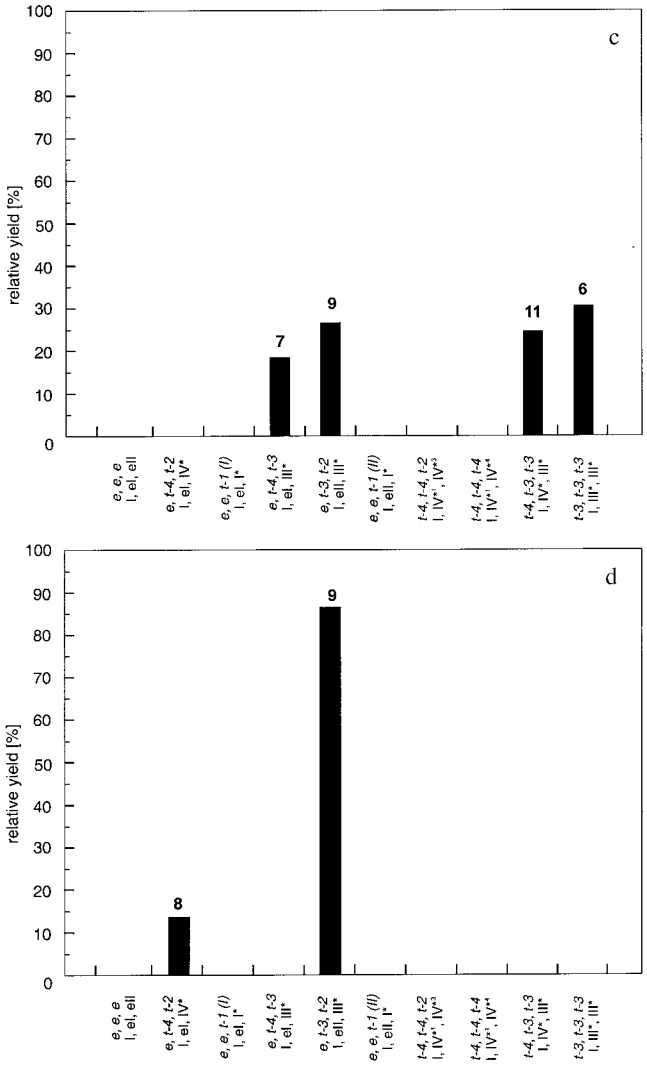
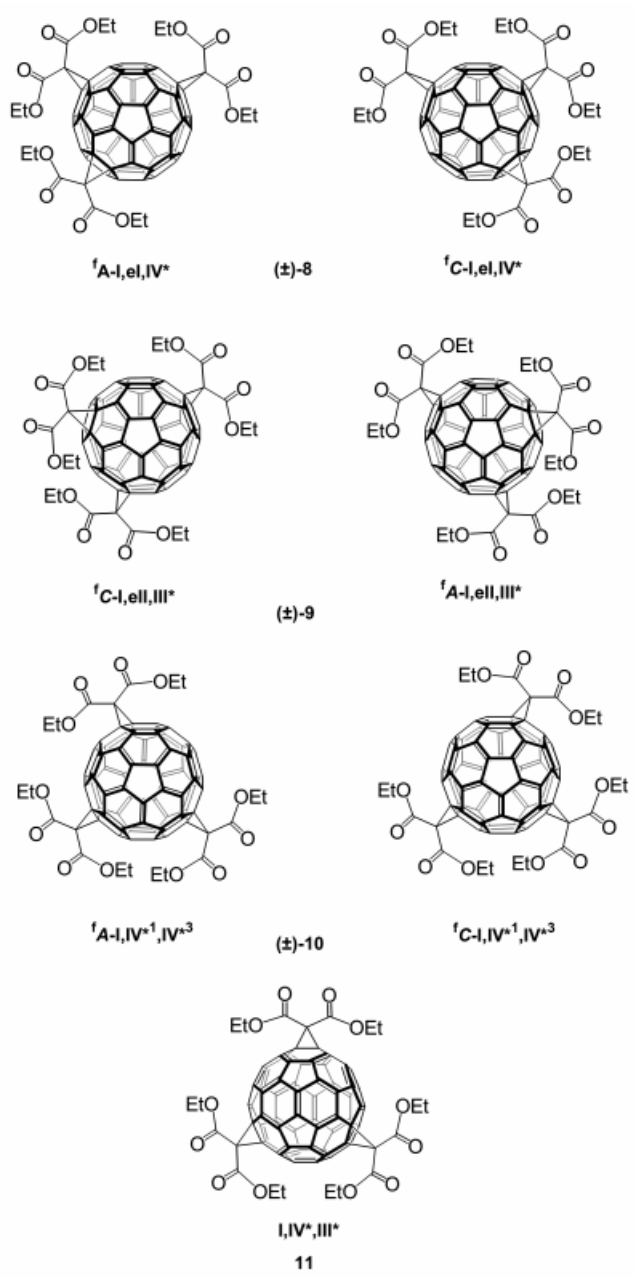


Figure 3. Relative yields of the trisadducts formed from **1** (a), **2** (b), **3** (c) and **4** (d), as determined by HPLC



$C_{62}H_4$, and ^{f}*A*-*e*,*e*,*e*-$C_{63}H_6$. For the bisadducts **12** and **13** with *trans*-3 and *trans*-2 addition patterns, the correlation between experimental and calculated CD spectra is excellent, since each of the mirror image CD spectra of the isolated diastereomers matches nicely with the theoretical curve (Figures 5a,b). In the case of the *e*,*e*,*e* addition pattern, the correlation between the spectrum and theory is still sufficiently good to allow an unambiguous assignment of the absolute configuration (Figure 5c). The lower accuracy of the simulation for the *e*,*e*,*e* isomer can be attributed to the inherently lower chirality of this compound compared to the corresponding *trans*-2- and *trans*-3-bisadducts, which is clearly visible from the spectrum showing CD intensities about 50% lower. With the assignment of the absolute configuration of one diastereomer of **12**−**14**, the stereochemistry of the other diastereomer having the addition pattern with opposite absolute configuration can be deduced.

As already pointed out, the absolute configuration of a trisadduct can be assigned when, besides its addition pattern, the absolute configuration of at least one of its chiral bisadduct precursors is known. For the determination of the absolute configurations of further enantiomerically pure trisadducts with inherently chiral addition patterns we therefore cyclopropanated the enantiomerically pure *trans*-3 and *trans*-2 precursors ^{f}***C*-12**, ^{f}***A*-12**, ^{f}***C*-13** and ^{f}***A*-13** with known absolute configurations and isolated and analyzed the corresponding trisadducts **15**−**18** (Schemes 1 and 2).

The addition patterns of the corresponding products were unambiguously assigned on the basis of the following facts: (a) All trisadducts **15**−**18** must contain at least one *trans*-3-positional relationship, since either ^{f}***C*-12** or ^{f}***A*-12**

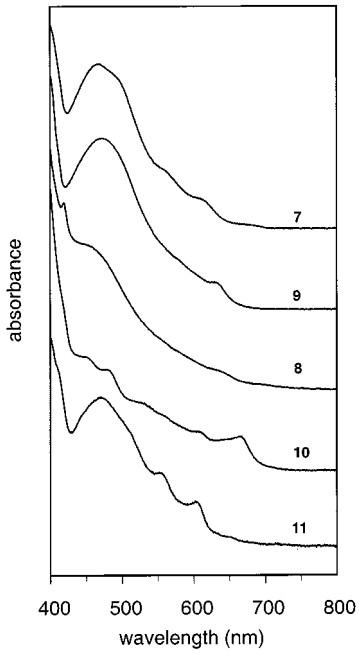
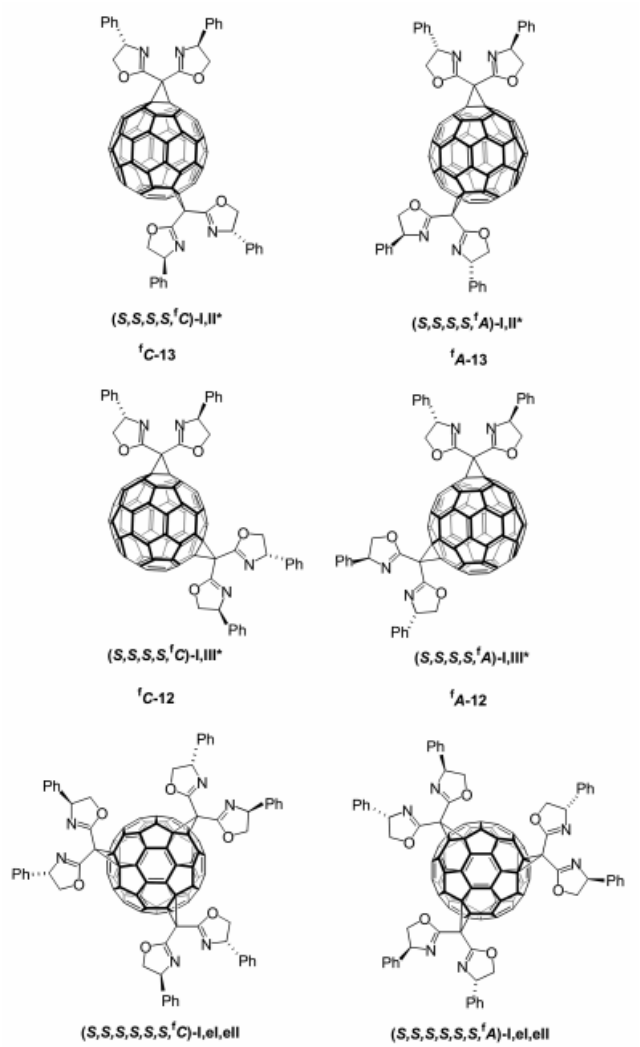


Figure 4. Electronic absorption spectra (CH_2Cl_2) of the trisadducts **7**–**11**



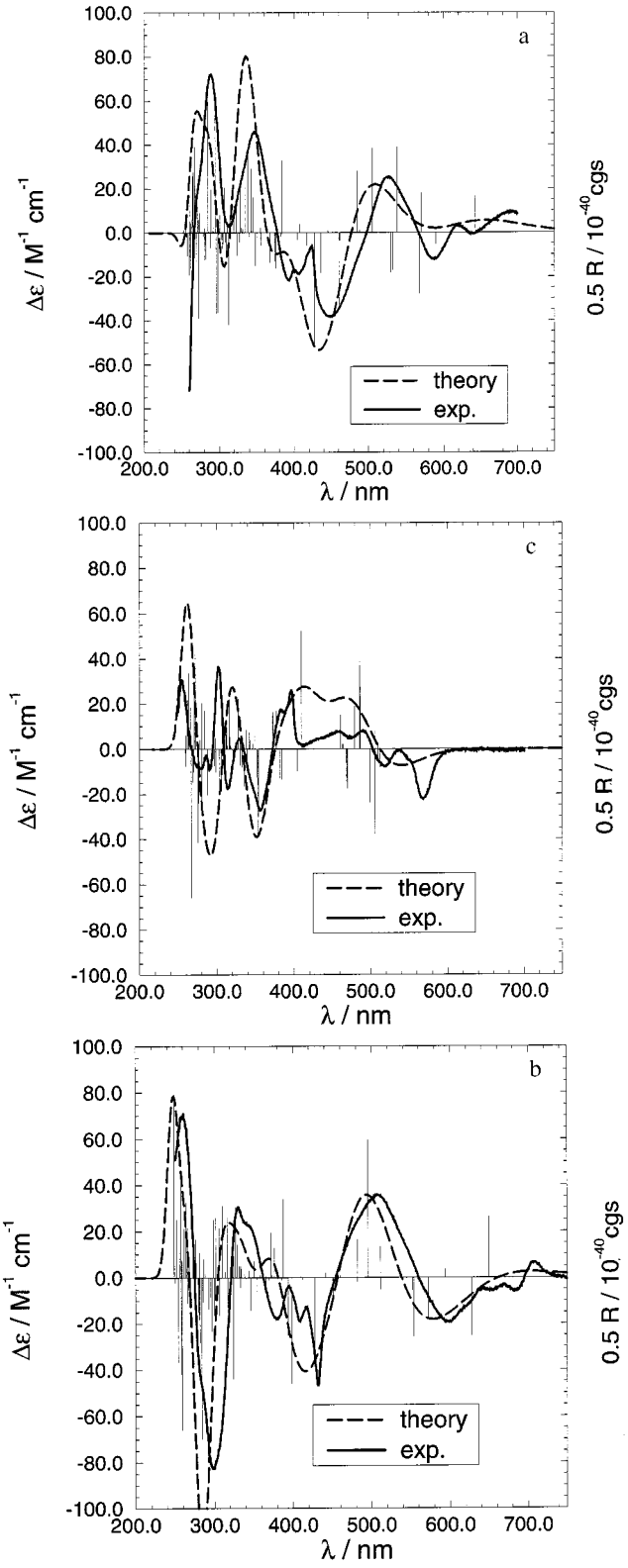
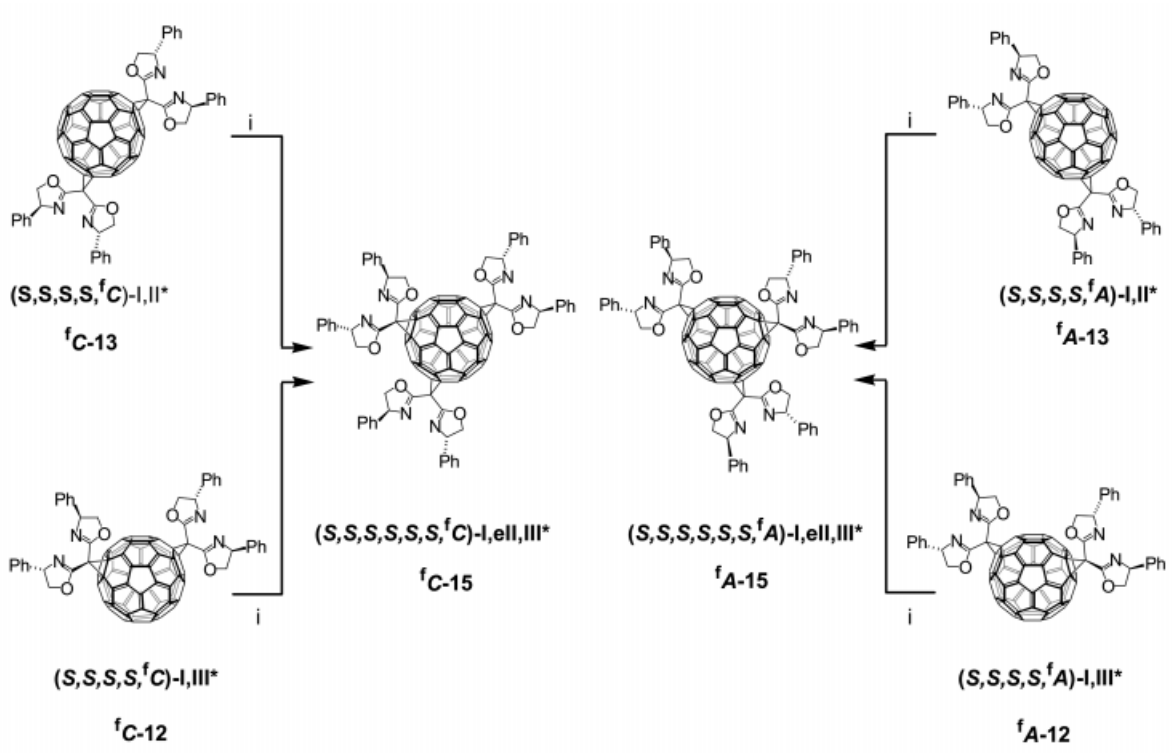


Figure 5. Calculated (dashed curve and solid sticks representing the position and intensities of the individual excited states) and experimental (solid curve) CD spectra of ^{f}***A*-12** (a), ^{f}***C*-13** (b), and ^{f}***A*-14** (c); for the calculations, the parent methanofullerenes $C_{63}H_6$ were used

was always used or identified as a potential precursor. (b) Four different addition patterns of trisadducts involving



Scheme 1. Synthesis of ^{f}***C*-15** from ^{f}***C*-12** and ^{f}***C*-13** and of ^{f}***A*-15** from ^{f}***A*-12** and ^{f}***A*-13**; conditions: (i) 4 equiv. DBU, 2 equiv. CBr_4, 2 equiv. bis(oxazoline), CH_2Cl_2/toluene, room temp.

Table 2. Symmetries and expected as well as experimentally (^{13}C-NMR) observed number of sp^2-C atoms, sp^3-C atoms and C=N groups of the adducts ^{f}***A*-15**, ^{f}***C*-15**, ^{f}***A*-16**, ^{f}***C*-16**, **17**, ^{f}***A*-18** and ^{f}***C*-18**

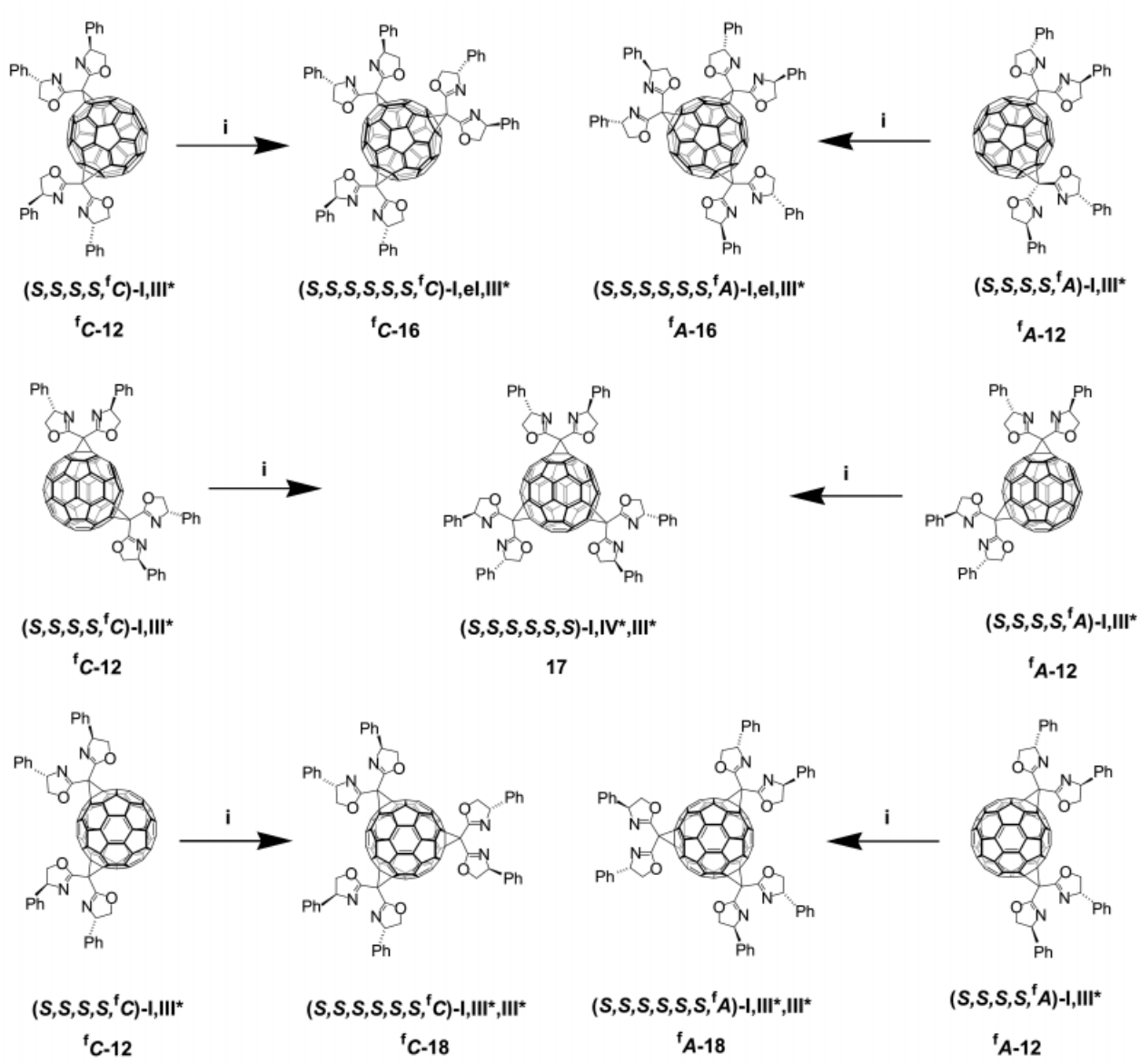
Adduct	Symmetry		sp^2-C atoms[a]		sp^3-C atoms[b]		C=N groups[c]	
	molecule	addition pattern	expected	observed	expected	observed	expected	observed
^{f}***A*-15**	C_1	C_1	54	44	6	6	6	6
^{f}***C*-15**	C_1	C_1	54	49	6	6	6	6
^{f}***A*-16**	C_1	C_1	54	38	6	3	6	5
^{f}***C*-16**	C_1	C_1	54	40	6	5	6	5
17	C_1	C_s	54	33	6	4	6	4
^{f}***A*-18**	D_3	D_3	9	9	1	1	1	1
^{f}***C*-18**	D_3	D_3	9	9	1	1	1	1

[a] Number of magnetically inequivalent sp^2-C atoms of the fullerene cage. – [b] Number of magnetically inequivalent sp^3-C atoms of the fullerene cage. – [c] Number of magnetically inequivalent C atoms within the C=N moieties of the addend.

trans-3 positions are possible and all four different diastereomeric products of each precursor ^{f}***C*-12** or ^{f}***A*-12** were found (Schemes 1 and 2). (c) The addition pattern of the two different diastereomers of **15** must be *e*,*trans*-3,*trans*-2, since this is the only addition pattern which has *trans*-3- and *trans*-2-positional relationships (Table 1). (d) Both ^{f}***C*-12** and ^{f}***A*-12** give rise to the same C_1-symmetric trisadduct **17**, as concluded from the identical chromatographic and spectroscopic behaviour (Table 2). This is only possible when the addition pattern of **17** is achiral; the only achiral addition pattern involving *trans*-3 positions is *trans*-4,*trans*-3,*trans*-3 (Table 1). (e) The addition pattern of the trisadducts **18** is *trans*-3,*trans*-3,*trans*-3 since they exhibit D_3 symmetry as evidenced by the small number of signals in the NMR spectra (Table 2). We have previously reported the isolation of one diastereomer of **18** without knowing its absolute configuration.[6] The assignments of the absolute configurations of both diastereomers of **18** will be explained below. (f) The remaining pair of diastereomers **16** must be *e*,*trans*-4,*trans*-3 since this is the only possibility left.

The assignments of the addition patterns of **15**–**18** are corroborated by their electronic absorption spectra, which are identical to those of $C_{63}(COOEt)_6$ and exhibit the same addition pattern (Figure 4). The absolute configurations of the different diastereomers **15**, **16** and **18** are depicted in Schemes 1 and 2. They were determined by the absolute configurations of the precursors **12** and **13**, since in each case only one possibility for an attack at a [6,6]-double bond leading to the corresponding trisadduct was available.

The enantiomeric relationships of the addition patterns of the pairs of diastereomers ^{f}***C*-15**/^{f}***A*-15**, ^{f}***C*-16**/^{f}***A*-16** and ^{f}***C*-18**/^{f}***A*-18** is clearly reflected by the mirror image behav-



Scheme 2. Synthesis of ^{f}*C*-**16**, **17** and ^{f}*C*-**18** from ^{f}*C*-**12** and of ^{f}*A*-**16**, **17** and ^{f}*A*-**18** from ^{f}*A*-**12**; conditions: (i) 4 equiv. DBU, 2 equiv. CBr_4, 2 equiv. bis(oxazoline), CH_2Cl_2/toluene, room temp.

iour of their circular dichroism (CD) spectra, which show strong Cotton effects (Figure 6). This shows that, as in the case of the bisadducts **12** and **13** and the corresponding C_3-symmetric *e*,*e*,*e*-trisadducts,[6] the chiral bis(oxazoline) addends do not make a significant contribution to the chiroptical properties, which are essentially due to the distorted π system of the C_{60} chromophore with a chiral addition pattern. The $[\alpha]_D$ values of compounds **15**, **16** and **18** lie in the range ±600 to ±2000. The magnitudes of the Cotton effects seen for **15**, **16** and **18** are comparable to those seen for the bisadducts **12** and **13** and are somewhat larger than those for the corresponding C_3-symmetric *e*,*e*,*e*-trisadducts.[6] Hence, as previously suggested,[6] a simple relationship between the magnitude of the Cotton effects, the number of π electrons, and the symmetry of the addition pattern cannot easily be deduced. Further systematic studies are required in order to clarify this matter. As expected, the Cotton effects in the CD spectrum of C_1-symmetric **17** are very weak and are almost negligible in the visible region. In this case, the fullerene chromophore is a priori achiral and the chirality of the whole molecule is provided only by the covalent binding of the C_2-symmetric bis(oxazoline) addends.

Summary and Conclusions

An almost complete series of regioisomeric trisadducts of C_{60} having the positional relationships *e* and *trans*-*n* (n = 2−4), formed by the successive addition of malonates to [6,6]-double bonds of the fullerene framework, has been isolated and characterized. The only remaining missing example is now an adduct with a *trans*-4,*trans*-4,*trans*-4 addition pattern. The addition patterns of such trisadducts with D_3, C_3, C_2, C_s or C_1 symmetry have been assigned on the basis of the known positional relationships of the ad-

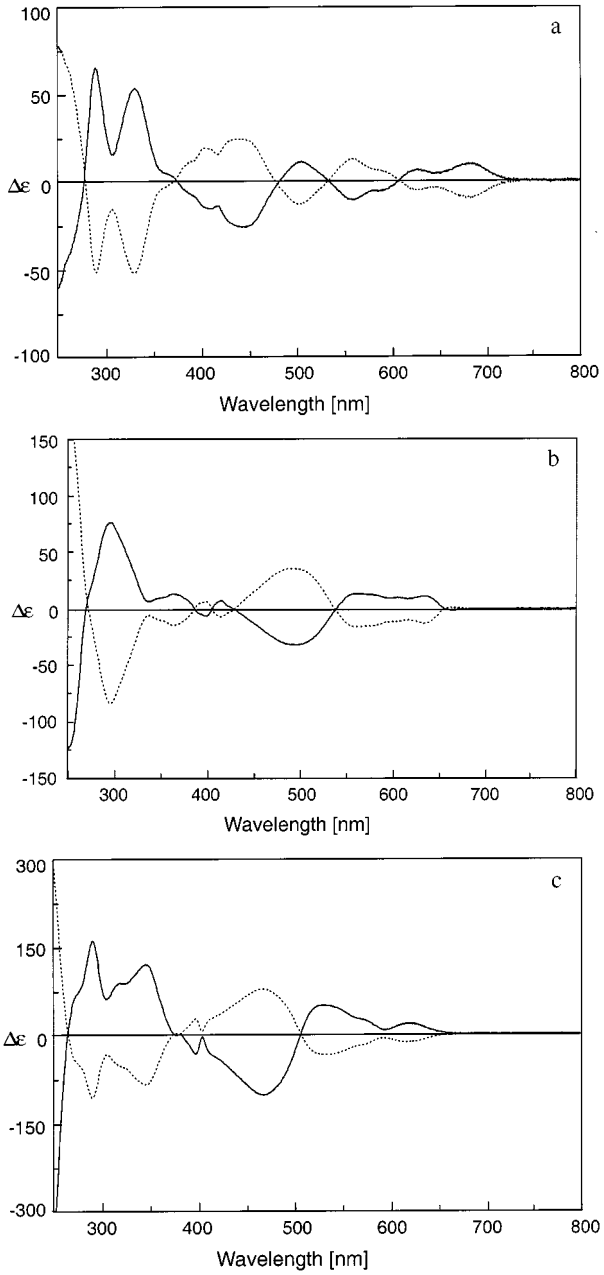


Figure 6. CD spectra (CH_2Cl_2) of the pairs of diastereomers of ^{f}***A*-16** (solid line) and ^{f}***C*-16** (dotted line) (a), ^{f}***A*-15** (solid line) and ^{f}***C*-15** (dotted line) (b), ^{f}***A*-18** (solid line) and ^{f}***C*-18** (dotted line) (c)

dends in their precursor bisadducts and, for the D_3-, C_3-, C_2- and C_s-symmetric representatives, have been corroborated by analysis of their NMR spectra. The determination of the absolute configuration of adducts with an inherently chiral addition pattern has proved possible either by comparison of calculated and experimental CD spectra of bis(oxazoline) adducts or with knowledge of the absolute configuration of the chiral bisadduct precursors containing bis(oxazoline) addends. Within these series of methanofullerenes, each addition pattern gives rise to its own "fingerprint" in the optical spectra. The collection of such characteristic UV/Vis and CD spectra of trisadducts should provide useful information for future structural assignments of new derivatives exhibiting the corresponding addition patterns. An investigation of the catalytic properties of such chiral bis(oxazoline) adducts in enantioselective reactions and the dependence of the selectivity on the addition pattern and the presence of additional addends such as dendrimers (dendrizymes) is currently in progress.

Experimental Section

General Remarks: ^{1}H- and ^{13}C-NMR: JEOL JNMEX 400 and JEOL JNMGX 400. − MS: Micromass Zabspec (FAB). − IR: Bruker Vektor 22. − UV/Vis: Shimadzu UV 3102 PC. − Preparative HPLC: Shimadzu SIL 10 A, SPD 10 A, CBM 10 A, LC 8 A, FRC 10 A (Grom-Sil 100 Si, NP1, 5 μm, 25 cm × 4.6 mm). − TLC (Riedel-de Haën silica gel F_{254} and Macherey−Nagel aluminum oxide N/UV_{254}). − CD: JASCO J-710. − Reagents were prepared according to standard procedures. Materials and solvents were obtained from commercial suppliers and were used without further purification. All reactions were carried out under nitrogen. Where possible, products were isolated by flash column chromatography (Merck silica gel 60, particle size 0.04−0.063 mm, or Aldrich STD grade Brockmann I neutral, activated aluminum oxide ca. 150 mesh, 58 Å). − $[\alpha]_D$ values were measured at 25°C.

Details of Calculations: All DFT calculations were performed with the TURBOMOLE suite of programs.[17][18] Valence double-ξ Gaussian AO basis sets ([3s2p]/[2s])[19] and Becke's hybrid exchange-correlation functional (B3LYP)[20][21] were used throughout. The geometries were taken from semiempirical PM3[22] optimizations of the ground states, for which the MOPAC 6.0 program[23] was used. To reduce the computational effort, the ethoxycarbonyl groups were replaced by hydrogen atoms. All DFT/SCI calculations were performed with an approximate resolution of the identity (RI) for the two-electron integrals.[24] The auxiliary basis sets used were the same as those used in ref.[24] According to previous experience, the errors introduced by the RI method amount to less than 0.01 eV in the excitation energies and the calculated properties are subject to correspondingly small uncertainties. All computed excitation energies correspond to vertical transitions, i.e. they are based solely on the optimized ground state geometries, and thus represent an approximation of the experimental transition energy at the band maximum. For the *trans*-2- and *trans*-3-adducts, all singly excited configurations (23820 in symmetries A and B) resulting from the distribution of all valence electrons in all virtual MOs were included. Due to technical reasons, in the calculations of the *e,e,e*-trisadduct with C_3 symmetry the 200 highest-lying virtual MOs were not considered, which left 21900 configurations for inclusion in the CI treatment. Standard diagonalization techniques were employed to extract the lowest 100 excited states [90 for the *e,e,e*-trisadduct] from the CI matrices. All transition moments were calculated in the mixed dipole lengths/dipole velocity form,[25] which is independent of the choice of the coordinate origin and is preferred to the pure dipole velocity form in the case of very approximate wavefunctions. Theoretical simulations of the CD spectra were obtained by summing Gaussian curves with constant half-widths of 0.45 eV for each electronic transition. Compared to the experimental data, the computed excitation energies were generally too high by approximately 0.8 eV. To allow a better comparison with the experimental data, the excitation energies were red-shifted

by this amount in the simulations of the CD spectra. Errors as large as 0.8 eV are quite unusual for the DFT/SCI method (rms errors in the vertical excitation energies of medium-sized aromatics are typically 0.2−0.3 eV),[14] but can tentatively be attributed to the use of a very small AO basis set, and to solvent effects (high polarizability of C_{60} derivatives) that are neglected in the theoretical treatment.

Trisadducts (±)-8 and (±)-9: To a solution of 80 mg (77 μmol) of bis(adduct) **4** in 40 mL of toluene, 19 mg (770 μmol, 10 equiv.) of sodium hydride and 27 μL (155 μmol, 2 equiv.) of diethyl bromomalonate were added under a protective gas. The mixture was stirred for 24 h at room temperature and then quenched with 2 N sulfuric acid. The products were separated by means of preparative HPLC (Grom-Sil 100 Si, NP1, toluene/ethyl acetate, 99.5:0.5). The relative yields (HPLC) of the trisadducts were: (±)-**8** (13.5%) and (±)-**9** (86.5%); isolated yields: (±)-**8** (5 mg), (±)-**9** (23 mg).

Trisadduct (±)-8: k' (HPLC, SiO_2, toluene/ethyl acetate, 99.5:0.5) = 10.84. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.44 (m, 18 H, CH_3), 4.43 (m, 12 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 14.08 (2 C, CH_3), 14.18 (2 C, CH_3), 14.25 (2 C, CH_3), 47.56 (1 C, methylene-C), 49.13 (1 C, methylene-C), 51.03 (1 C, methylene-C), 63.07 (1 C, CH_2), 63.13 (1 C, CH_2), 63.16 (1 C, CH_2), 63.22 (1 C, CH_2), 63.31 (2 C, CH_2), 70.22 (1 C), 70.22 (1 C), 70.44 (1 C), 71.07 (1 C), 71.86 (1 C), 72.03 (1 C), 135.36, 137.17, 137.62, 138.35, 139.32, 139.71, 140.20, 140.51, 141.00, 141.08 (2 C), 141.31, 141.37, 141.77, 141.97, 142.10 (2 C), 142.21, 142.37, 142.59, 142.72, 142.76, 142.79, 143.18, 143.25, 143.45, 143.54, 143.65, 143.74, 143.82 (2 C), 144.04, 144.11, 144.29, 144.71, 144.78 (2 C), 145.01 (2 C), 145.28 (2 C), 145.73, 145.79 (2 C), 145.95, 146.08, 146.47, 146.90, 147.11, 147.31 (2 C), 147.67 (2 C), 149.28, 163.51 (1 C, CO), 163.64 (1 C, CO), 163.71 (1 C, CO), 163.77 (1 C, CO), 163.99 (2 C, CO). − IR (KBr): $\tilde{\nu}$ = 2978, 2932, 1745 (CO), 1638, 1463, 1443, 1367, 1296, 1236, 1099, 1063, 1020, 858, 706, 546, 527 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 236 (89000), 265 (sh, 70000), 298 (sh, 44000), 395 (sh, 5700), 418 (4800), 463 (sh, 3000), 646 nm (300). − MS (FAB/3-NBA): *m/z* (%) = 1194 [M^+] (40), 720 [C_{60}] (100); calcd. for $^{12}C_{81}H_{30}O_{12}$ 1194.

Trisadduct (±)-9: k' (HPLC, SiO_2, toluene/ethyl acetate, 99.5:0.5) = 8.27. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.42 (m, 18 H, CH_3), 4.50 (m, 12 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 14.14 (1 C, CH_3), 14.18 (3 C, CH_3), 14.21 (1 C, CH_3), 14.27 (1 C, CH_3), 49.33 (1 C, methylene-C), 51.03 (1 C, methylene-C), 51.23 (1 C, methylene-C), 63.13 (2 C, CH_2), 63.16 (1 C, CH_2), 63.29 (2 C, CH_2), 63.38 (1 C, CH_2), 70.16 (1 C), 70.98 (2 C), 71.33 (1 C), 71.88 (1 C), 71.92 (1 C), 137.11, 137.20, 140.09, 140.14, 141.15, 141.22, 141.35, 141.57 (2 C), 141.62, 141.77, 141.88, 141.92, 142.17, 142.23, 142.52 (2 C), 143.01, 143.10, 143.30, 143.65, 143.78, 143.91, 144.02 (2 C), 144.27, 144.35, 144.49, 144.58 (3 C), 144.69, 144.95, 145.33, 145.50, 145.73 (2 C), 145.94 (2 C), 146.17, 146.50, 146.67, 146.74 (2 C), 146.79 (2 C), 146.92, 147.09, 147.16, 147.65, 148.29, 148.71 (2 C), 149.19, 163.31 (1 C, CO), 163.42 (1 C, CO), 163.51 (1 C, CO), 163.55 (1 C, CO), 163.90 (1 C, CO), 163.93 (1 C, CO). − IR (KBr): $\tilde{\nu}$ = 2976, 2925, 1744 (CO), 1444, 1442, 1366, 1233, 1102, 1061, 1020, 858, 805, 735, 708, 526 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (102000), 292 (sh, 54000), 402 (4600), 472 (3400), 635 nm (500). − MS (FAB/3-NBA): *m/z* (%) = 1194 [M^+] (42); calcd. for $^{12}C_{81}H_{30}O_{12}$ 1194.

Trisadducts (±)-6, (±)-7, (±)-9 and 11: To a solution of 125 mg (120 μmol) of bis(adduct) **3** in 63 mL of toluene, 29 mg (1.2 mmol, 10 equiv.) of sodium hydride and 52 μL (241 μmol, 2 equiv.) of diethyl bromomalonate were added under a protective gas. The mixture was stirred for 24 h at room temperature and then quenched with 2 N sulfuric acid. The products were separated by means of preparative HPLC (Grom-Sil 100 Si, NP1, toluene/ethyl acetate, 99.5:0.5). The relative yields (HPLC) of the trisadducts were: (±)-**6** (28.5%), (±)-**7** (19.7%), (±)-**9** (27.5%) and **11** (24.3%); isolated yields: (±)-**6** (22 mg), (±)-**7** (12 mg), (±)-**9** (19 mg), **11** (15 mg).

Trisadduct (±)-7: k' (HPLC, SiO_2, toluene/ethyl acetate, 99.5:0.5) = 13.97. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.42 (m, 18 H, CH_3), 4.50 (m, 12 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 14.07 (2 C, CH_3), 14.10 (2 C, CH_3), 14.14 (1 C, CH_3), 14.21 (1 C, CH_3), 49.04 (1 C, methylene-C), 49.40 (1 C, methylene-C), 53.26 (1 C, methylene-C), 63.04 (1 C, CH_2), 63.09 (3 C, CH_2), 63.18 (1 C, CH_2), 63.24 (1 C, CH_2), 69.63 (1 C), 70.82 (2 C), 70.98 (1 C), 71.55 (1 C), 72.10 (1 C), 135.72, 138.35, 138.43, 138.81, 139.03, 139.61, 140.16, 140.58, 141.08, 141.29, 141.66, 141.93, 142.15, 142.19, 142.34, 142.41, 142.63, 142.79, 143.30, 143.76 (2 C), 143.91, 144.04, 144.09 (2 C), 144.22, 144.33, 144.40, 144.64, 144.93 (2 C), 145.02 (2 C), 145.19, 145.24, 145.68 (2 C), 145.72 (2 C), 146.08, 146.26, 146.45 (2 C), 146.52, 146.65, 146.72, 147.03 (2 C), 147.07, 147.11, 147.45, 147.60, 147.95, 148.79, 163.46 (1 C, CO), 163.50 (2 C, CO), 163.59 (3 C, CO). − IR (KBr): $\tilde{\nu}$ = 2978, 2927, 2360, 1745 (CO), 1443, 1637, 1244, 1106, 1066, 1022, 860, 708, 520 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (107000), 294 (53000), 403 (sh, 4000), 466 (3300), 494 (sh, 3500), 558 (sh, 1100), 611 nm (500). − MS (FAB/3-NBA): *m/z* (%) = 1194 [M^+] (68), 720 [C_{60}] (100); calcd. for $^{12}C_{81}H_{30}O_{12}$ 1194.

Trisadduct 11: k' (HPLC, SiO_2, toluene/ethyl acetate, 99.5:0.5) = 9.49. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.42 (m, 18 H, CH_3), 4.50 (m, 12 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 14.12 (2 C, CH_3), 14.16 (3 C, CH_3), 14.25 (1 C, CH_3), 49.87 (2 C, methylene-C), 51.61 (1 C, methylene-C), 63.15 (2 C, CH_2), 63.20 (3 C, CH_2), 63.32 (1 C, CH_2), 70.95 (4 C), 71.92 (2 C), 137.88 (2 C), 138.96 (4 C), 139.17 (2 C), 140.92 (1 C), 141.21 (2 C), 141.80 (2 C), 142.21 (2 C), 142.67 (2 C), 142.82 (2 C), 143.23 (2 C), 143.62 (2 C), 144.08 (4 C), 144.44 (2 C), 145.51 (4 C), 145.73 (2 C), 145.95 (1 C), 146.08 (2 C), 146.64 (4 C), 146.69 (2 C), 146.96 (2 C), 146.99 (2 C), 147.51 (2 C), 148.51 (1 C), 148.92 (2 C), 148.98 (1 C), 163.43 (2 C, CO), 163.59 (4 C, CO). − IR (KBr): $\tilde{\nu}$ = 2978, 1745 (CO), 1443, 1442, 1366, 1296, 1238, 1109, 1061, 1020, 860, 735, 706, 529 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (130000), 300 (53000), 398 (sh, 5500), 414 (sh, 4200), 471 (11200), 553 (2000), 607 nm (1200). − MS (FAB/3-NBA): *m/z* = 1194 [M^+] (24), 720 [C_{60}] (100); calcd. for $^{12}C_{81}H_{30}O_{12}$ 1194.

Trisadducts (±)-7, (±)-8, (±)-10 and 11: To a solution of 250 mg (0.24 mmol) of bis(adduct) **2** in 125 mL toluene, 58 mg (2.4 mmol, 10 equiv.) of sodium hydride and 104 μL (482 μmol, 2 equiv.) of diethyl bromomalonate were added under a protective gas. The mixture was stirred for 24 h at room temperature and then quenched with 2 N sulfuric acid. The products were separated by means of preparative HPLC (Grom-Sil 100 Si, NP1, toluene/ethyl acetate, 99.5:0.5). The relative yields (HPLC) of the trisadducts were: (±)-**7** (44.15%), (±)-**8** (18.93%), (±)-**10** (10.31%) and **11** (26.61%); isolated yields: (±)-**7** (22 mg), (±)-**8** (12 mg), (±)-**10** (12 mg), **11** (18 mg).

Trisadduct (±)-10: k' (HPLC, SiO_2, toluene/ethyl acetate, 99.5:0.5) = 8.27. − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.38 (t, 6 H, J = 7.33 Hz, CH_3), 1.43 (t, 6 H, J = 6.83 Hz, CH_3), 1.49 (t, 6 H, J = 6.83 Hz, CH_3), 4.43 (q, 4 H, J = 6.84 Hz, CH_2), 4.48 (q, 4 H, J = 7.33 Hz, CH_2), 4.57 (q, 4 H, J = 6.84 Hz, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 14.13 (2 C, CH_3), 14.18 (2 C, CH_3), 14.25 (2 C, CH_3), 48.53 (1 C, methylene-C), 48.59 (2 C, methylene-C), 63.15 (2 C, CH_2), 63.23 (2 C, CH_2), 63.33 (2 C, CH_2), 70.38 (2 C), 70.48 (2 C), 71.08 (2 C), 135.59 (2 C), 137.09 (2

C), 137.16 (2 C), 137.75 (2 C), 140.15 (4 C), 140.63 (2 C), 140.98 (2 C), 141.30 (2 C), 141.98 (2 C), 142.18 (2 C), 142.56 (2 C), 143.26 (2 C), 143.73 (2 C), 143.90 (2 C), 144.03 (2 C), 144.26 (2 C), 145.11 (2 C), 145.17 (2 C), 145.95 (2 C), 146.04 (2 C), 146.17 (2 C), 146.42 (2 C), 146.54 (2 C), 147.01 (2 C), 147.37 (2 C), 147.48 (2 C), 163.63 (2 C, CO), 163.69 (2 C, 2 CO), 163.98 (2 C, 2 CO). − IR (KBr): $\tilde{\nu}$ = 2977, 2928, 1745 (CO), 1462, 1443, 1368, 1366, 1297, 1236, 1184, 1108, 1058, 1023, 858, 806, 763, 737, 520 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (108000), 309 (sh, 45000), 343 (sh, 18000), 376 (sh, 10000), 395 (sh, 6500), 451 (2100), 479 (1800), 529 (sh, 1200), 610 (700), 667 nm (600). − MS (FAB/3-NBA): *m*/*z* = 1194 [M^+] (96), 720 [C_{60}] (100); calcd. for $^{12}C_{81}H_{30}O_{12}$ 1194.

Trisadduct ^{f}*C*-15: To 50 mg (38 μmol) of ^{f}***C*-13** in 100 mL of dry toluene, 23 mg (2 equiv.) of 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] in 25 mL of dry dichloromethane was added by means of a dropping funnel. Then, a solution of 25 mg (2 equiv.) of CBr_4 in 10 mL of dry dichloromethane and 17 μL (4 equiv.) of DBU were added under vigorous stirring. After 24 h at room temperature, the solution was concentrated and separated by column chromatography (SiO_2, toluene/ethyl acetate, 9:1), furnishing pure **^{f}*C*-15**. The relative yield (HPLC) of the trisadduct ^{f}***C*-15** was 80.2%; isolated yield 21 mg.

Trisadduct ^{f}*C*-15: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.3−4.6 (m, 6 H, CH_2), 4.8−5.1 (m, 6 H, CH_2), 5.4−5.7 (m, 6 H, CH), 7.2−7.6 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 38.45 (1 C, methylene-C), 40.02 (1 C, methylene-C), 40.62 (1 C, methylene-C), 70.42 (2 C, oxaz-CH), 70.56 (2 C, oxaz-CH), 70.63 (2 C, oxaz-CH), 71.04 (1 C), 71.64 (1 C), 71.67 (1 C), 71.94 (1 C), 72.61 (1 C), 72.68 (1 C), 75.67 (1 C, oxaz-CH2), 75.80 (2 C, oxaz-CH2), 75.89 (1 C, oxaz-CH2), 75.99 (1 C, oxaz-CH2), 76.18 (1 C, oxaz-CH2), 126.89 (2 C, Ph-C), 126.97 (2 C, Ph-C), 127.06 (6 C, Ph-C), 127.12 (2 C, Ph-C), 127.85 (3 C, Ph-C), 127.90 (3 C, Ph-C), 128.72 (2 C, Ph-C), 128.75 (6 C, Ph-C), 128.82 (2 C, Ph-C), 128.93 (2 C, Ph-C), 136.99 (3 C, Ph-C), 137.19 (3 C, Ph-C), 140.19, 140.27, 141.06, 141.18, 141.21, 141.27, 141.30 (3 C), 141.36, 141.44, 141.51, 141.65, 141.91, 142.03, 142.09 (2 C), 142.45, 142.95, 143.12, 143.53, 143.91 (2 C), 144.29, 144.35, 144.43, 144.46, 144.52, 144.65, 144.69, 144.76, 144.82, 145.13, 145.79, 145.87, 146.02 (2 C), 146.14, 146.17, 146.25, 146.51, 146.67, 146.73, 146.77, 146.89, 147.11, 147.34, 147.43, 147.80, 148.12, 148.47, 149.73, 149.86, 150.01, 160.37 (1 C, C=N), 160.61 (1 C, C=N), 160.75 (1 C, C=N), 160.87 (1 C, C=N), 160.91 (1 C, C=N), 161.07 (1 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2958, 2923, 2898, 1662 (C=N), 1493, 1471, 1453, 1353, 1267, 1191, 1104, 1081, 1029, 985, 965, 930, 755, 739, 698, 527 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (116000), 292 (64000), 404 (sh, 6100), 470 (4400), 636 nm (sh, 500). − CD ($CHCl_3$): λ (Δε) = 250 (163), 295 (−84), 345 (sh, −9), 363 (−15), 397 (7), 415 (−7), 490 (35), 557 (−15), 605 (sh, −11), 637 (−12) nm. − $[\alpha]_D$ = +640 (*c* = 1 mg/10 mL, $CHCl_3$). − MS (FAB/3-NBA): *m*/*z* (%) = 1632 [M^+] (5), 720 [C_{60}] (100); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadduct ^{f}*A*-15: To 55 mg (42 μmol) of ^{f}***A*-13** in 100 mL of dry toluene, 25 mg (2 equiv.) of 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] in 25 mL of dry dichloromethane was added by means of a dropping funnel. Then, a solution of 28 mg (2 equiv.) of CBr_4 in 10 mL of dry dichloromethane and 25 μL (4 equiv.) of DBU were added under vigorous stirring. After 24 h at room temperature, the solution was concentrated and separated by column chromatography (SiO_2, toluene/ethyl acetate, 9:1), furnishing pure **^{f}*A*-15**. The relative yield (HPLC) of the trisadduct ^{f}***A*-15** was 78.9%; isolated yield 24 mg.

Trisadduct ^{f}*A*-15: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.3−4.6 (m, 6 H, CH_2), 4.8−5.1 (m, 6 H, CH_2), 5.4−5.7 (m, 6 H, CH), 7.2−7.6 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 38.51 (1 C, methylene-C), 40.07 (1 C, methylene-C), 40.65 (1 C, methylene-C), 70.42 (2 C, oxaz-CH), 70.45 (2 C, oxaz-CH), 70.58 (1 C, oxaz-CH), 70.62 (1 C, oxaz-CH), 71.06 (1 C), 71.66 (1 C), 71.73 (1 C), 71.97 (1 C), 72.57 (1 C), 72.63 (1 C), 75.75 (3 C, oxaz-CH2), 75.90 (1 C, oxaz-CH2), 75.99 (1 C, oxaz-CH2), 76.17 (1 C, oxaz-CH2), 126.95 (6 C, Ph-C), 127.04 (2 C, Ph-C), 127.10 (2 C, Ph-C), 127.13 (2 C, Ph-C), 127.83 (4 C, Ph-C), 127.88 (2 C, Ph-C), 128.69 (2 C, Ph-C), 128.78 (6 C, Ph-C), 128.81 (2 C, Ph-C), 128.92 (2 C, Ph-C), 137.11 (6 C, Ph C), 140.27 (2 C), 141.08, 141.17, 141.24 (3 C), 141.33 (3 C), 141.39 (2 C), 141.46, 141.51 (2 C), 141.61, 141.72, 141.86, 142.01, 142.08, 142.21, 142.43, 143.07, 143.16, 143.56, 143.80, 143.91, 144.31, 144.35, 144.44, 144.51, 144.57, 144.71 (2 C), 144.80 (2 C), 145.17, 145.79, 145.97, 146.03, 146.08, 146.16 (2 C), 146.76, 146.85, 146.94, 147.09, 147.32, 147.84, 148.11, 148.57, 149.75 (2 C), 150.14, 160.46 (1 C, CN), 160.50 (1 C, C=N), 160.74 (1 C, C=N), 160.86 (1 C, C=N), 160.90 (1 C, C=N), 161.07 (1 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3060, 3028, 2960, 2898, 1662, 1493, 1471, 1453, 1353, 1267, 1191, 1030, 985, 964, 929, 755, 740, 698, 594, 527 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (113000), 290 (63000), 403 (sh, 6100), 471 (4000), 636 nm (450). − CD ($CHCl_3$): λ (Δε) = 250 (−122), 295 (77), 345 (sh, 9), 390 (sh, −3), 398 (−6), 415 (7), 494 (−32), 558 (13), 608 (sh, 10), 635 nm (11). − $[\alpha]_D$ = −680 (*c* = 1 mg/10 mL, $CHCl_3$). − MS (FAB/3-NBA): *m*/*z* = 1632 [M^+] (5), 720 [C_{60}] (100); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadducts ^{f}*A*-15, ^{f}*A*-16, 17, ^{f}*A*-18: To 175 mg (132 μmol) of ^{f}***A*-12** in 200 mL of dry toluene, 80 mg (2 equiv.) of 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] in 50 mL of dry dichloromethane was added by means of a dropping funnel. Then, a solution of 88 mg (2 equiv.) of CBr_4 in 10 mL of dry dichloromethane and 80 μL (4 equiv.) of DBU were added under vigorous stirring. After 24 h at room temperature, the solution was concentrated. The tris[-adducts] were first roughly separated by HPLC (Grom-Sil 100 Si, NP1, toluene/ethyl acetate, 85:15). The first-eluted, least-polar compound could be obtained essentially pure. The other three adducts had to be further separated by HPLC on a Buckyclutcher phase (eluent: toluene/ethyl acetate, 9:1). It should be noted that the fourth-eluted compound from the silica phase was eluted first from the Buckyclutcher phase. The two other adducts could be isolated in pure form by HPLC on an Al_2O_3 phase (eluent: toluene/ethyl acetate, 85:15). The relative yields (HPLC) of the trisadducts were: ^{f}***A*-15** (29.38%), ^{f}***A*-16** (22.54%), **17** (24.88%) and ^{f}***A*-18** (23.20%); isolated yields: ^{f}***A*-15** (26 mg), ^{f}***A*-16** (11 mg), **17** (14 mg), ^{f}***A*-18** (12 mg).

Trisadduct ^{f}*A*-16: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.2−4.6 (m, 6 H, oxaz-CH_2), 4.8−5.1 (m, 6 H, oxaz-CH_2), 5.4−5.7 (m, 6 H, oxaz-CH), 7.1−7.6 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 38.24 (2 C, methylene-C), 42.68 (1 C, methylene-C), 70.27 (2 C, oxaz-CH), 70.36 (2 C, oxaz-CH), 70.42 (4 C, oxaz-CH), 70.51 (2 C, oxaz-CH), 70.60 (2 C, oxaz-CH), 71.57 (2 C), 71.66 (2 C), 72.54 (2 C), 75.70 (3 C, oxaz-CH_2), 75.77 (3 C, oxaz-CH_2), 75.95 (3 C, oxaz-CH_2), 76.08 (3 C, CH_2), 126.80 (2 C, Ph-C), 126.93 (4 C, Ph-C), 126.99 (2 C, Ph-C), 127.06 (2 C, Ph-C), 127.12 (2 C, Ph-C), 127.70 (2 C, Ph-C), 127.81 (2 C, Ph-C), 127.90 (2 C, Ph-C), 128.63 (2 C, Ph-C), 128.69 (2 C, Ph-C), 128.74 (2 C, Ph-C), 128.80 (2 C, Ph-C), 128.85 (2 C, Ph-C), 128.89 (2 C, Ph-C), 135.63 (1 C, Ph-C), 138.50 (2 C, Ph-C), 138.99 (1 C, Ph-C), 139.08 (1 C, Ph-C), 139.32 (1 C, Ph-C), 140.25, 141.02, 141.35 (4 C), 141.50 (3 C), 141.59 (2 C), 142.12 (2 C), 142.24, 142.63, 142.92, 143.29, 143.67, 143.85, 144.02, 144.11 (2 C), 144.27, 144.35, 144.51 (2 C), 144.60 (2 C), 144.71, 144.97, 145.08, 145.33, 145.53, 145.66 (2 C), 145.92,

146.17 (2 C), 146.30 (2 C), 146.45 (2 C), 146.69, 146.79 (2 C), 147.00, 147.38, 147.43, 147.49, 147.62, 147.73, 148.09 (2 C), 148.91, 160.61 (1 C, C=N), 160.72 (1 C, C=N), 160.81 (2 C, C=N), 160.88 (1 C, C=N), 161.14 (1 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3060, 3028, 2923, 2851, 1666 (C=N), 1533, 1493, 1471, 1452, 1343, 1267, 1219, 1190, 1029, 987, 965, 930, 756, 698, 548, 524 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (10000), 297 (55000), 404 (sh, 7000), 485 (6000), 571 nm (sh, 3000). − CD ($CHCl_3$): λ (Δε) = 252 (−58), 263 (sh, −38), 288 (64), 329 (52), 367 (sh, 3), 384 (sh, −6), 403 (−15), 439 (−26), 504 (11), 558 (−11), 593 (sh, −5), 624 (6), 681 nm (9). − $[\alpha]_D$ = −2000 (*c* = 1 mg/25 mL, $CHCl_3$). − MS (FAB/3-NBA): *m/z* (%) = 1632 [M^+] (5), 720 [C_{60}] (55); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadduct 17: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.40 (m, 4 H, oxaz-CH_2), 4.55 (dd, 2 H, *J* = 8.79 Hz, oxaz-CH_2), 4.90 (m, 4 H, oxaz-CH_2), 5.06 (dd, 2 H, *J* = 10.26 Hz, oxaz-CH_2), 5.50 (m, 4 H, oxaz-CH), 5.66 (dd, *J* = 10.26 Hz, 2 H, oxaz-CH), 7.2−7.6 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 39.04 (1 C, methylene-C), 39.10 (1 C, methylene-C), 40.72 (1 C, methylene-C), 70.38 (3 C, oxaz-CH), 70.45 (2 C, oxaz-CH), 70.65 (1 C, oxaz-CH), 71.59 (1 C), 71.66 (1 C), 71.75 (1 C), 72.72 (3 C), 75.79 (2 C, oxaz-CH_2), 75.86 (2 C, oxaz-CH_2), 75.99 (2 C, oxaz-CH_2), 126.90 (3 C, Ph-C), 126.97 (6 C, Ph-C), 127.13 (2 C, Ph-C), 127.81 (4 C, Ph-C), 127.92 (2 C, Ph-C), 128.67 (3 C, Ph-C), 128.74 (6 C, Ph-C), 128.83 (3 C, Ph-C), 137.64 (1 C, Ph-C), 137.68 (1 C, Ph-C), 138.81 (2 C, Ph-C), 139.12 (1 C, Ph-C), 141.15, 141.19 (2 C), 141.29 (3 C), 141.33 (2 C), 141.42 (4 C), 141.93 (2 C), 142.67 (2 C), 142.99 (2 C), 143.16 (2 C), 143.32, 143.62 (2 C), 144.18, 144.24, 144.64, 144.71 (2 C), 144.88, 144.99 (2 C), 145.81, 145.90, 146.05, 146.41 (2 C), 146.48 (2 C), 146.81 (2 C), 146.85, 146.98 (2 C), 147.34 (2 C), 147.71, 147.82 (2 C), 147.89, 148.09, 148.17, 148.68, 149.13 (2 C), 160.66 (1 C, C=N), 160.83 (3 C, C=N), 160.97 (1 C, C=N), 161.08 (1 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2958, 2896, 1666 (C=N), 1493, 1471, 1452, 1353, 1266, 1220, 1196, 1104, 984, 954, 929, 756, 698, 530 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (140000), 300 (60000), 382 (sh, 9500), 403 (sh, 6500), 475 (4500), 557 (2200), 607 nm (1300). − MS (FAB/3-NBA): *m/z* (%) = 1632 [M^+] (5), 720 [C_{60}] (43); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadduct ^{f}*A*-18: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.62 (dd, *J* = 8.33 Hz, 6 H, oxaz-CH_2), 4.82 (dd, *J* = 9.76 Hz, 6 H, oxaz-CH_2), 5.39 (dd, *J* = 9.77 Hz, 6 H, CH), 7.1−7.3 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 43.28 (3 C, methylene-C), 73.43 (6 C, oxaz-CH), 75.42 (6 C, oxaz-CH_2), 79.01 (6 C), 130.11 (12 C, Ph-C), 131.10 (6 C, Ph-C), 131.98 (12 C, Ph-C), 144.36 (6 C, Ph-C), 144.69 (6 C), 145.41 (6 C), 145.52 (6 C), 146.37 (6 C), 148.77 (6 C), 150.45 (6 C), 150.85 (6 C), 151.09 (6 C), 151.66 (6 C), 163.66 (6 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3060, 3027, 2958, 2923, 2898, 1662 (C=N), 1534, 1493, 1471, 1453, 1348, 1267, 1216, 1193, 1178, 1104, 1029, 985, 957, 928, 757, 698, 530 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (120000), 299 (52000), 374 (sh, 8700), 405 (sh, 5100), 478 (4500), 572 nm (1900). − CD (CH_3Cl): λ (Δε) = 250 (−377), 274 (sh, 67), 291 (160), 318 (sh, 85), 346 (118), 398 (−35), 413 (sh, −34), 469 (−104), 526 (48), 575 (sh, 23), 621 nm (17). − $[\alpha]_D$ = +477 (*c* = 1 mg/10 mL, $CHCl_3$). − MS (FAB/3-NBA): *m/z* (%) = 1632 [M^+] (5), 720 [C_{60}] (100); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadducts ^{f}*C*-15, ^{f}*C*-16, 17, ^{f}*C*-18: To 190 mg (132 μmol) of ^{f}***C*-12** in 200 mL of dry toluene, 88 mg (2 equiv.) 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] in 50 mL dry dichloromethane was added by means of a dropping funnel. Then, a solution of 95 mg (2 equiv.) of CBr_4 in 10 mL of dry dichloromethane and 86 μL (4 equiv.) DBU were added under vigorous stirring. After 24 h at room temperature, the solution was concentrated. The tris[adducts] were first roughly separated by HPLC (Grom-Sil 100 Si, NP1, toluene/ethyl acetate, 85:15). The first-eluted, least-polar compound could be obtained essentially pure. The other three adducts had to be further separated by HPLC on a Buckyclutcher phase (eluent: toluene/ethyl acetate, 9:1). It should be noted that the fourth-eluted compound from the silica phase was eluted first from the Buckyclutcher phase. The two other adducts could be isolated in pure form by HPLC on an Al_2O_3 phase (toluene/ethyl acetate, 85:15). The relative yields (HPLC) of the trisadducts were: ^{f}***C*-15** (30.11%), ^{f}***C*-16** (18.23%), **17** (27.49%) and ^{f}***C*-18** (24.17%); isolated yields: ^{f}***C*-15** (13 mg), ^{f}***C*-16** (24 mg), **17** (13 mg), ^{f}***C*-18** (15 mg).

Trisadduct ^{f}*C*-16: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.2−4.6 (m, 6 H, oxaz-CH_2), 4.8−5.0 (m, 6 H, oxaz-CH_2), 5.4−5.7 (m, 6 H, oxaz-CH), 7.1−7.6 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 38.26 (1 C, methylene-C), 38.53 (1 C, methylene-C), 40.61 (1 C, methylene-C), 70.29 (2 C, oxaz-CH), 70.36 (1 C, oxaz-CH), 70.42 (1 C, oxaz-CH), 70.47 (1 C, oxaz-CH), 70.60 (1 C, oxaz-CH), 71.51 (1 C), 71.59 (2 C), 71.62 (1 C), 72.37 (1 C), 73.01 (1 C), 75.62 (1 C, oxaz-CH_2), 75.73 (1 C, oxaz-CH_2), 75.77 (2 C, CH_2), 75.90 (1 C, oxaz-CH_2), 76.08 (1 C, oxaz-CH_2), 126.79 (2 C, Ph-C), 126.88 (2 C, Ph-C), 126.95 (2 C, Ph-C), 127.02 (2 C, Ph-C), 127.08 (2 C, Ph-C), 127.13 (2 C, Ph-C), 127.68 (1 C, Ph-C), 127.74 (1 C, Ph-C), 127.81 (2 C, Ph-C), 127.85 (1 C, Ph-C), 127.90 (1 C, Ph-C), 128.61 (2 C, Ph-C), 128.72 (4 C, Ph-C), 128.76 (2 C, Ph-C), 128.85 (2 C, Ph-C), 128.89 (2 C, Ph-C), 135.78 (1 C, Ph-C), 138.35 (2 C, Ph-C), 139.01 (2 C, Ph-C), 139.49 (1 C, Ph-C), 140.34, 140.95, 141.29 (2 C), 141.33 (3 C), 141.37 (2 C), 141.40 (3 C), 141.57 (2 C), 142.06 (2 C), 142.10, 142.28, 142.68, 142.81, 143.47, 143.87, 144.09 (3 C), 144.38, 144.51 (2 C), 144.57, 144.91, 145.04, 145.31, 145.46, 145.63, 145.73, 145.90, 146.14, 146.25 (2 C), 146.32, 146.43, 146.47, 146.70, 146.78 (2 C), 146.92, 147.31, 147.43 (2 C), 147.56, 147.71, 148.06, 148.09, 148.88, 160.61 (1 C, C=N), 160.83 (1 C, C=N), 160.86 (2 C, C=N), 160.94 (1 C, C=N), 161.03 (1 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2959, 2897, 1666 (C=N), 1493, 1471, 1452, 1353, 1267, 1191, 1102, 1048, 986, 965, 930, 756, 698, 595, 547, 522 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 241 (141000), 296 (63000), 402 (5900), 480 (5200), 570 nm (sh, 2500). − CD ($CHCl_3$): λ (Δε) = 252 (76), 288 (−52), 329 (−53), 364 (sh, −3), 384 (sh, 10), 403 (19), 438 (24), 501 (−13), 559 (12), 588 (sh, 6), 622 (−5), 681 (−10). − $[\alpha]_D$ = 1825 (*c* = 1 mg/25 mL, $CHCl_3$). − MS (FAB/3-NBA): *m/z* (%) = 1632 [M^+] (3), 720 [C_{60}] (25); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

Trisadduct ^{f}*C*-18: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.29 (dd, *J* = 8.33 Hz, 6 H, oxaz-CH_2), 4.81 (dd, *J* = 9.76 Hz, 6 H, oxaz-CH_2), 5.40 (dd, *J* = 9.77 Hz, 6 H, CH), 7.1−7.3 (m, 30 H, Ph). − ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 43.19 (3 C, methylene-C), 73.52 (6 C, oxaz-CH), 75.40 (6 C, oxaz-CH_2), 78.95 (6 C), 130.20 (12 C, Ph-C), 131.42 (6 C, Ph-C), 131.96 (12 C, Ph-C), 144.28 (6 C, Ph-C), 144.81 (6 C), 145.34 (6 C), 145.51 (6 C), 146.33 (6 C), 148.83 (6 C), 150.30 (6 C), 150.86 (6 C), 151.17 (6 C), 151.62 (6 C), 163.69 (6 C, C=N). − IR (KBr): $\tilde{\nu}$ = 3061, 3028, 2923, 1662 (C=N), 1493, 1471, 1453, 1352, 1266, 1216, 1178, 1103, 1080, 1029, 928, 757, 698, 530, 516 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (128000), 297 (59000), 321 (sh, 40000), 375 (sh, 10000), 401 (sh, 5600), 483 (4700), 575 nm (2200). − CD ($CHCl_3$): λ (Δε) = 250 (290), 271 (sh, −40), 290 (−107), 318 (sh, −54), 345 (−86), 398 (24), 411 (24), 467 (76), 530 (−36), 573 (sh, −20), 621 nm (−15). − $[\alpha]_D$ = −750 (*c* = 1 mg/10 mL, $CHCl_3$) . − MS (FAB/3-NBA): *m/z* = 1632 [M^+] (5), 720 [C_{60}] (43); calcd. for $^{12}C_{117}H_{48}N_6O_6$ 1632.

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