JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Enantioselective Synthesis of Endohedral Metallofullerenes

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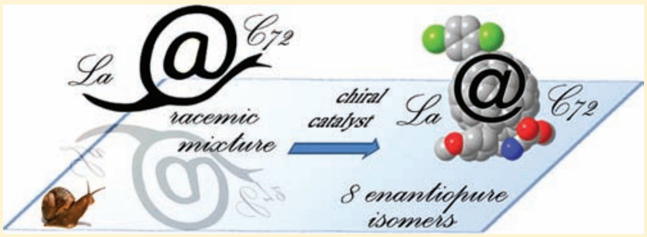
Supporting Information



ABSTRACT: Endohedral metallofullerenes are promising materials in biomedical and material sciences. In particular, they are of interest as agents for magnetic resonance imaging (MRI), photovoltaic devices, and semimetallic components. The synthesis of chiral endofullerenes represents one step further in the potential use of these carbon allotropes; however, this step has not been addressed so far. In this regard, enantiopure endofullerenes are expected to open new avenues in fields in which chirality is a key issue. Here, the synthesis and characterization of the first chiral endohedral metallofullerenes, namely, chiral bis-adducts of La@C_{72}, are reported. Eight optically active isomers were obtained by enantioselective 1,3-dipolar cycloaddition of a N-metalated azomethine ylide onto a non-isolated-pentagon rule metallofullerene derivative, La@C_{72}($C_6H_3Cl_2$), catalyzed by a copper chiral complex. The chiral bis-adducts of La@C_{72}, isolated by nonchiral HPLC, showed optical purities as high as 98% as revealed by the remarkable positive or negative Cotton effects observed in the circular dichroic spectra.

INTRODUCTION

The three-dimensional fullerene structure has inspired chemists to design and synthesize novel building blocks with unique chemical and physical properties.[1] Endohedral metallofullerenes, which encapsulate one or more metal atoms inside the fullerene cage, are promising molecules because they can radically enhance the molecular properties of fullerenes by changing the nature and composition of the encapsulated species.[2] In this regard, most of the knowledge on synthetic aspects and chemical reactivity of fullerenes has been focused on empty fullerenes, mostly C_{60}, whereas the chemistry of higher fullerenes is considerably less developed.[3] Endohedral fullerenes, on the other hand, exhibit a lower and more difficult to predict chemical reactivity, which is currently under study.[4] In fact, the limited availability and the reduced symmetry of endofullerenes make necessary the development of new and more efficient chemical strategies for the preparation of molecules with specific properties.

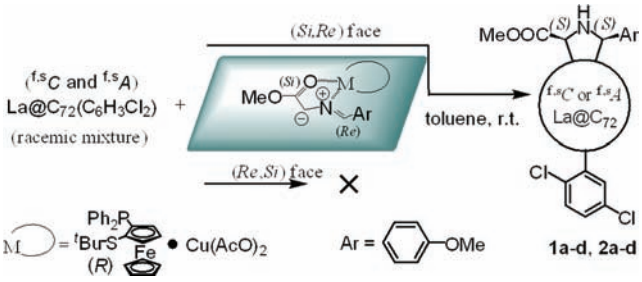
Several fullerene adducts have shown a broad range of promising biological activities. Remarkable examples are the use of C_{60} derivatives as inhibitors against HIV-protease[5] and chemically modified endohedral gadolinium metallofullerenes as efficient agents for enhancing magnetic resonance imaging (MRI).[6] Certain classes of fullerenes and their derivatives are chiral;[7] however, the lack of a general and selective method to induce chirality in the different carbon allotropes has hampered the preparation and use of chiral fullerenes for these purposes.[8]

To the best of our knowledge, only a few examples of enantiomerically pure fullerene derivatives have been investigated to date, namely, those used as helicity inducers in polymers[9] or in homochiral prolinofullerenes for peptide synthesis.[10] In these cases, chiral fullerenes were separated by expensive and time-consuming preparative HPLC on chiral stationary phases.

In addition to biomedical applications, endohedral metallofullerenes have exhibited their potential as materials for the preparation of artificial photosynthetic systems[11] as well as of photovoltaic devices surpassing the photocurrent efficiency (PCE) of C_{60}-based devices. In fact, organic solar cells from P3HT/Lu_3N@C_{80}-PCBH have achieved PCE values of 4.2% and an open circuit voltage value (V_{oc}) of 0.89 V under AM1.5G solar simulation conditions.[12] These values are higher than those reported for the well-known P3HT/C_{60}-PCBM reference devices under the same experimental conditions. Furthermore, among the reported organic conductors measured by flash-photolysis time-resolved microwave conductivity, the adamantylidene derivative of La@C_{82} in its single-crystal form exhibited the highest electron mobility ($\mu > 10\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$) reported to date.[13]

Received: July 6, 2011
Published: September 28, 2011

Scheme 1. Synthesis of Optically Pure Metallofullerenes (1a−d and 2a−d)



Recently, Martín and co-workers[14] have reported the first example of a catalytic enantioselective 1,3-dipolar cycloaddition affording chiral pyrrolidinofullerenes with controlled stereochemistry by using Cu(II)/Fesulphos and Ag(I)/BPE as chiral catalysts. This versatile methodology enables us to prepare fullerene derivatives in high enantiomeric excesses under very mild experimental conditions.

Establishing the methodology to synthesize enantiopure endohedral metallofullerene derivatives should add a new page in fullerene chemistry where chirality plays an important role in molecular design. This paper describes a highly enantioselective synthesis of chiral bis-adducts based on the non-isolated-pentagon rule (non-IPR) $La@C_{72}(C_6H_3Cl_2)$ (or La@[72]fullerene-($C_6H_3Cl_2$)).[15] To the best of our knowledge, this is the first example of enantioselective synthesis of endofullerenes reported so far.

In particular, we report the synthesis of optically active bis-adducts of the non-IPR metallofullerene $La@C_{72}$ by the highly enantioselective cycloaddition reaction of N-metalated azomethine ylides on a racemic mixture of $La@C_{72}(C_6H_3Cl_2)$. (Scheme 1). In such a reaction, the chiral catalyst formed by copper(II) acetate and Fesulphos chiral ligand directs the cycloaddition of both starting enantiomers, ($^{f,s}C$ and $^{f,s}A La@C_{72}$-($C_6H_3Cl_2$),[16] to the (*Si*,*Re*) face of the N-copper azomethine ylide. The high enantioface selectivity shown by this complex leads to eight optically active endofulleropyrrolidines **1a**−**d** and **2a**−**d** with a fixed (2*S*,5*S*) configuration of the pyrrolidine carbon atoms (Scheme 1).

Despite the presence of 71 free nonequivalent cage carbon atoms, 108 possible reaction sites, and no symmetric addend, only four isomers for each of the two enantiomeric starting compounds are formed. Circular dichroic measurements revealed the strong impact of chirality of the starting enantiomer on the observed values, which is in sharp contrast with that previously observed for the I_h-symmetrical C_{60}.

■ RESULTS AND DISCUSSION

Preliminary attempts to carry out the cycloaddition reaction of N-metalated azomethine ylide 1,3-dipoles on a series of pristine endofullerenes ($Sc_3N@C_{80}$, $La@C_{82}$, or $La_2@C_{80}$) were unsuccessful, probably due to the energy mismatch between the frontier orbitals of both reagents. Therefore, in order to modify the highest occupied and lowest unoccupied molecular orbital (HOMO−LUMO) energy levels, we used the endohedral $La@C_{72}$ endowed with a strong electron-withdrawing substituent such as dichlorophenyl radical. The non-IPR metallofullerene $La@C_{72}(C_6H_3Cl_2)$ endowed with a dichlorophenyl moiety was isolated after extraction of the soot containing lanthanum metallofullerene $La@C_{72}$ with 1,2,4-trichlorobezene, and it was formed by addition of a dichlorophenyl radical to the open-shell metallofullerene.[17] X-ray analysis revealed a racemic chiral structure of two enantiomers and the dichlorophenyl group attached to a carbon atom of one of the two fused pentagons (see Figure S1 in Supporting Information).[17] The nature of this endohedral fullerene and the electronic effect of this organic addend modifies significantly the LUMO level, thus increasing its further reactivity with N-metalated 1,3-dipoles.

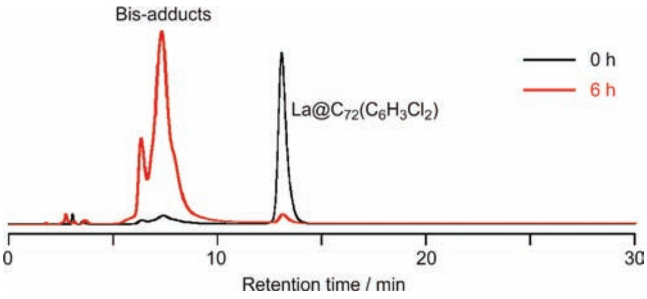


Figure 1. HPLC profiles of the crude reaction mixture of chiral bis-adducts of $La@C_{72}$. Conditions: Buckyprep column (ϕ 4.6 × 250 mm); eluent, toluene; flow rate, 1.0 mL/min; wavelength, 330 nm; temperature, 40 °C.

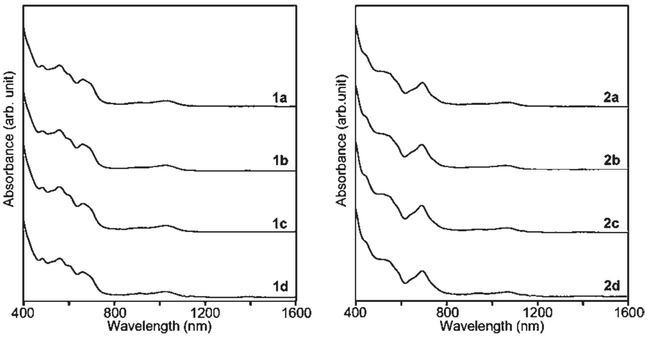


Figure 2. UV−Vis−NIR spectra of **1a**−**d** and **2a**−**d** in CS_2.

This reasoning was correct, and chiral bis-adducts of $La@C_{72}$ were synthesized by 1,3-dipolar cycloaddition of N-metalated azomethine ylides, catalyzed by a chiral copper complex, onto a racemic mixture of the non-IPR $La@C_{72}(C_6H_3Cl_2)$. The chiral bis-adducts (**1a**−**d** and **2a**−**d**) were formed under mild conditions at room temperature (Scheme 1). After the mixtures were stirred for 6 h, HPLC profiles of the resulting crude material showed new peaks, indicating formation of the target adducts (Figure 1). A multistep HPLC separation (Figure S2, Supporting Information) yielded eight bis-adducts (**1a**−**d** and **2a**−**d**). Compounds **1a**−**d** correspond to addition on C27−C28, and compounds **2a**−**d**, to addition on C13−C14 (see Figure S1 in Supporting Information). The product distribution was estimated to be approximately 10% for **1a**, 10% for **1b**, 7% for **1c**, 6% for **1d**, 24% for **2a**, 17% for **2b**, 13% for **2c**, and 13% for **2d** according to analyses of their HPLC profiles.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra confirmed formation of the target chiral bis-adducts of $La@C_{72}$. Thus, the peak at 1355 *m*/*z* was observed, together with fragmentation peaks at 1003 and 1148 *m*/*z*, corresponding to the loss of the organic addends (Figure S3, Supporting Information).

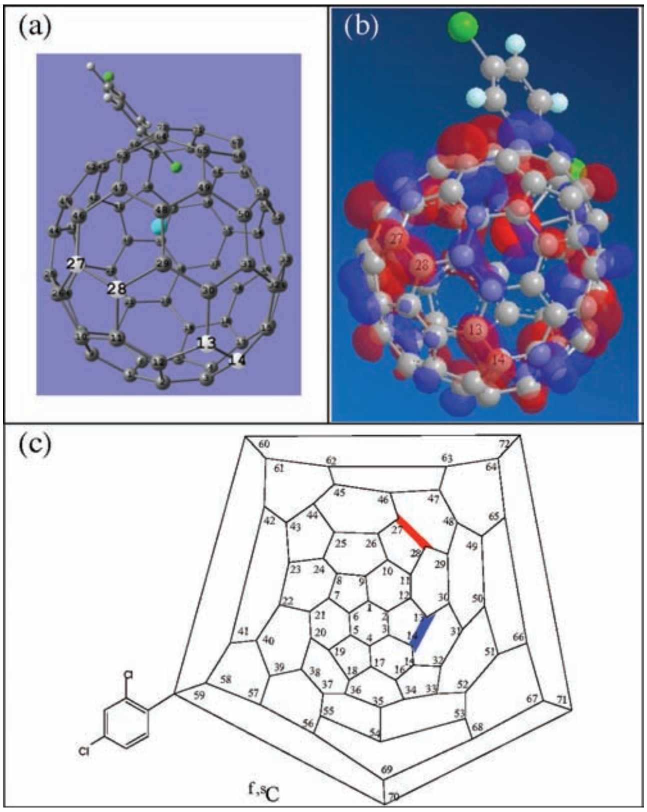


Figure 3. (a) Schematic drawings and systematic atom numbering of ^{f,s}C La@C_{72}($C_6H_3Cl_2$). (b) LUMO of La@C_{72}($C_6H_3Cl_2$). Geometries were optimized at the B3LYP/6-31G(d)∼hw level. (c) Schlegel diagram of ^{f,s}C La@C_{72}($C_6H_3Cl_2$): the two sites for 1,3 dipolar cycloadditions are marked in blue and red.

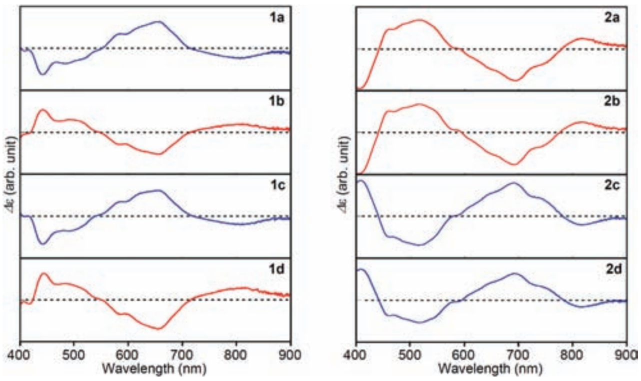


Figure 4. CD spectra of **1a**−**d** and **2a**−**d** in CS_2. The eight isomers display almost identical CD curves, where the differences stem from the different UV−vis spectra and therefore from the relative position of the addends (site isomers). The mirror-image shape of the CD spectra of **1b**, **1d**, **2a**, and **2b** (red curves) and of **1a**, **1c**, **2c**, and **2d** (blue curves) reveals the strong chiroptical contribution of the chiral core of the molecule.

UV−Vis−NIR absorption spectra of **1a**−**d** and **2a**−**d** can be classified into two groups (Figure 2). Compounds **1a**−**d** show more structured spectra with four characteristic absorption bands at around 480, 560, 660, and 1020 nm; compounds **2a**−**d** show three significant bands around 550, 690, and 1060 nm. These similarities strongly suggest that **1a**−**d** or **2a**−**d** have the same addition sites for the pyrrolidine ring. Otherwise, the electronic spectra of fullerene derivatives would have provided sufficiently distinctive fingerprints of the π-electron system topology. Therefore, despite the presence of 105 possible reaction sites in the starting La@C_{72}($C_6H_3Cl_2$), excluding three sites adjacent to the dichlorophenyl group, the metal-catalyzed cycloaddition of azomethine ylides to La@C_{72}($C_6H_3Cl_2$) occurs with remarkable site selectivity and *only two site isomers are formed*!

It is well-known that the driving force of chemical reactivity of fullerenes is attributed to the “strain-relief principle”, which consists of rehybridization from sp^2 to sp^3 occurring in the saturation of a double bond of the fullerene sphere.[18] Therefore, the site selectivity of the addition can be roughly estimated by considering the local spheroid curvature, which typically corresponds to the carbon atoms with a highest value of pyramidalization angle.[19] However, hybrid density functional theory (DFT) calculations provide a more accurate criterion to determine the two addition sites. The LUMO of La@C_{72}($C_6H_3Cl_2$) is regarded to play an important role in the addition of azomethine ylides. The optimized structure of La@C_{72}($C_6H_3Cl_2$), calculated at the B3LYP/6-31G(d)∼hw level, predicts that the LUMO is delocalized on the fullerene cage (Figure 3). More precisely, the LUMO is mainly localized on the carbon atoms showing higher POAV (π-orbital axis vector)[19] values and positive charge densities (C13−C14 and C27−C28; see Table S1 in Supporting Information). These positions are feasible targets for the attack by azomethine ylides to form the corresponding **1a**−**d** and **2a**−**d** bis-adducts (see Figure 3).

To determine the molecular structures of **1a**−**d** and **2a**−**d**, ^{1}H and ^{13}C NMR spectroscopic measurements were performed. The ^{1}H NMR spectra of **1a**−**d** and **2a**−**d** exhibit resonances corresponding to the 2,5-dichlorophenyl group and the pyrrolidine ring (Figures S4−S11, Supporting Information). The ^{13}C NMR spectrum of **2b** shows a total of 89 signals (72 signals for the C_{72} cage, 6 signals for the dichlorophenyl group, and 11 signals for the pyrrolidine ring), in agreement with the C_1 symmetry of **2b** (Figure S12, Supporting Information). The signals at 58.75, 73.04, and 77.13 ppm are attributed to the sp^3 carbon atoms of the C_{72} cage connected to the two addends. These assignments were confirmed by distortionless enhancement of polarization transfer (DEPT) 135 and 2D NMR heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple-bond correlation (HMBC) spectroscopic measurements (Figures S13−S15, Supporting Information).

The cis stereochemistry of the methine hydrogens of pyrrolidine ring was partially determined from rotating-frame Overhauser enhancement spectroscopy (ROESY) measurements for **2a**, **2c**, and **2d** (Figures S16−S18, Supporting Information). In the ^{1}H NMR spectra of **1a**−**d** and **2a**−**d**, the methine proton signals of the pyrrolidine ring appeared at around 4.5 ppm. The ROESY measurements of **2a**, **2c**, and **2d** show ROE correlations between these two methine protons , thus indicating that they are all cis adducts. These results are in good agreement with the previously reported 1,3-dipolar cycloaddition reaction of N-metalated azomethine ylides to C_{60} and C_{70}.[3,14] Although ROESY measurements have not been performed for the remaining isomers (**1a**−**d** and **2b**), cis stereochemistry is assigned by analogy with **2a**, **2c**, and **2d**. Moreover, a cis configuration is formed by the same addition mechanism of the azomethine ylides on different dipolarophiles.[20] Furthermore, copper−Fesulphos directs the cycloaddition toward 2,5-*cis*-pyrrolidine independently of the dipolarophile used (see also below).[3,14,20] This is in good

Table 1. **Yields and Enantiomeric Ratios of Compounds 1a−d and 2a−d**

compd	yield,[a] %	CD sign (660−690 nm)	enantiomeric ratio
1a	10	(+)	97:3
1b	10	(−)	94:6
1c	7	(+)	96:4
1d	6	(−)	92:8[b]
2a	24	(−)	99:1
2b	17	(−)	97:3
2c	13	(+)	95:5
2d	13	(+)	99:1

[a] Product distribution based on the recovered starting material. [b] The lower ratio is due to the presence of traces of **1c** in the sample.

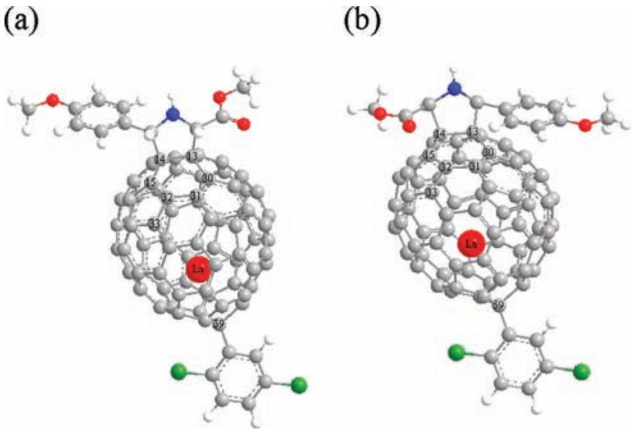


Figure 5. Optimized structure [M06-2X/6-31G(d)~hw level] of two of the feasible structures for chiral bis-adducts of La@C_{72}, formed as a result of addition to the C13−C14 double bond of $^{f,s}C$ La@C_{72}-($C_6H_3Cl_2$). (a) 2*S*-Methoxycarbonyl-5*S*-(*p*-methoxyphenyl)pyrrolidino-[3,4:13′,14′] $^{f,s}C$ La@[72]fullerene and (b) 2*S*-methoxycarbonyl-5*S*--(*p*-methoxyphenyl)pyrrolidino[3,4:14′,13′] $^{f,s}C$ La@[72]fullerene) feature the same UV and CD spectra since both stem from addition to the same double bond of the same optical antipode core. The newly generated asymmetric carbon atoms (2 and 5) of the pyrrolidine ring have the same configuration (*S*,*S*) in both regioisomers.

agreement with the ^{1}H NMR data for products **1a**−**1d** and **2b**, for which H2 and H5 protons of the pyrrolidine ring appear as doublets, in sharp contrast with that reported for the corresponding methine protons of the trans isomers that appear as singlets and always exhibit larger differences in chemical shifts (typically Δcis ≈ 0.4 ppm and Δtrans ≈ 0.8 ppm).[21] Therefore, **1a**−**d** and **2b** can reasonably be inferred to have a cis structure.

Analysis of the eight isomers by circular dichroism (CD) spectroscopy confirms that these adducts are all chiral (Figure 4). The spectra of **1a**−**d** and **2a**−**d** display strong Cotton effects at around 440, 660, and 810 nm and around 520, 690, and 815 nm, respectively. The spectra for **1a** and **1c** (or **2a** and **2b**), are similar in shape but opposite in sign to those of **1b** and **1d** (or **2c** and **2d**). This cannot represent an enantiomeric relationship, as all eight isomers were separated on achiral columns. It is likely that the CD spectra are dominated by the chiral endohedral fullerene core,[22] and thus, isomers (**1a**, **1c**, **2c**, and **2d**) that yield CD spectra with similar sign derive from fullerenes having the same configuration ($^{f,s}C$ or $^{f,s}A$), regardless of the type of site isomer or regioisomer considered. Isomers that yield CD spectra of similar shape (**1a**−**d** and **2a**−**d**) are assigned to adducts derived from the two different site isomers (C13−C14 or C27−C28, Figure 3), as implied by the UV spectra.

The optical purity of the eight isomers was analyzed by HPLC on a chiral column (REGIS Whelk 02) and all of them are formed in high enantiomeric excess (90−98%; see Table 1 and Supporting Information). The copper−Fesulphos complex directs cycloaddition of the carbon cage toward the (*Si*, *Re*) face of the N-metalated azomethine ylide, giving rise to 2*S*,5*S*-pyrrolidinofullerenes, regardless of the type of dipole used.[4,14,20] It is also worth noting that, due to the larger size of the cage, La@C_{72}-($C_6H_3Cl_2$) presents better facial discrimination and, therefore, higher enantioselectivity compared to that observed with [70]- and [60]fullerenes.[3,14] Despite the fact that the reaction has been carried out at room temperature, the copper−Fesulphos complex leads to the formation of chiral endohedral derivatives with high optical purity, up to 98%, as in the case of **2a** and **2d**.

Therefore, due to the fixed configuration (2*S*,5*S*) of the new generated stereocenters in the pyrrolidine ring, cycloaddition on the racemic starting material produces four pairs of diastereomers: the four isomers formed from the optical antipode $^{f,s}C$ will have a configuration (2*S*,5*S*, $^{f,s}C$) and all of them feature a Cotton effect of the same sign and opposite to the four isomers formed from the opposite optical antipode $^{f,s}A$ with configuration (2*S*,5*S*, $^{f,s}A$). Figure 5 displays the chemical structures of two of the four isomers stemming from ($^{f,s}C$) La@C_{72}($C_6H_3Cl_2$), showing the relative position between the organic addends and the La metal. Figure 6 shows the Schlegel diagram for these four isomers. The four $^{f,s}C$ isomers are constituted by two site isomers featuring the same UV−vis spectrum. The major site isomer (C13−C14) is constituted by two regioisomers, 2*S*-methoxycarbonyl-5*S*-(*p*-methoxyphenyl)pyrrolidino[3,4:13′,14′] $^{f,s}C$ La@[72]fullerene and 2*S*-methoxycarbonyl-5*S*-(*p*-methoxyphenyl)pyrrolidino-[3,4:14′,13′] $^{f,s}C$ La@[72]fullerene. Similarly, the minor site isomer (C27−C28) is formed by the regioisomers 2*S*-methoxycarbonyl-5*S*-(*p*-methoxyphenyl)pyrrolidino[3,4:28′,27′] $^{f,s}C$ La@[72]fullerene and 2*S*-methoxycarbonyl-5*S*-(*p*-methoxyphenyl)pyrrolidino[3,4:27′,28′]$^{f,s}C$ La@[72]fullerene (see also the other members of the diastereomeric pairs in Supporting Information).

CONCLUSIONS

In summary, we have carried out the first asymmetric synthesis of the functionalized endohedral fullerene derivative La@C_{72}-($C_6H_3Cl_2$) by 1,3-cycloaddition reaction of an N-metalated azomethine ylide under very mild experimental conditions. Eight different compounds, **1a**−**d** and **2a**−**d**, have been obtained and characterized by spectroscopic techniques and circular dichroic measurements. Selective cycloaddition at C13−C14 and C27−C28 double bonds of La@C_{72}($C_6H_3Cl_2$) is supported by spectroscopic studies and theoretical calculations (B3LYP and M06-2X functionals). The four pairs of diastereomers feature a Cotton effect that is dominated by the inherent chirality of the carbon core. The four isomers formed from the $^{f,s}C$ (2*S*,5*S*, $^{f,s}C$) fullerene adduct exhibit CD spectra that are opposite in sign to those derived from the $^{f,s}A$ (2*S*,5*S*, $^{f,s}A$) fullerene adduct.

Work is currently in progress to obtain suitable monocrystals in order to determine the absolute configuration and, therefore, the unambiguous structural assignment of the enantiomerically pure endofullerenes formed.

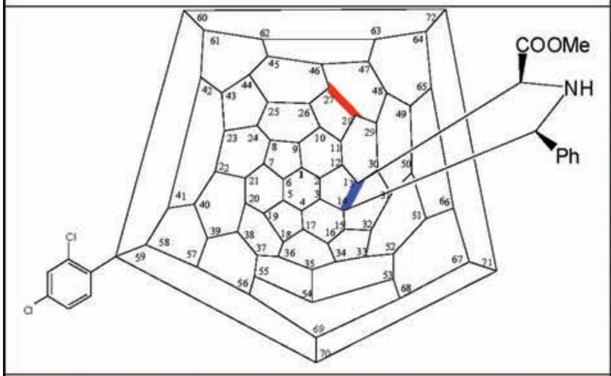
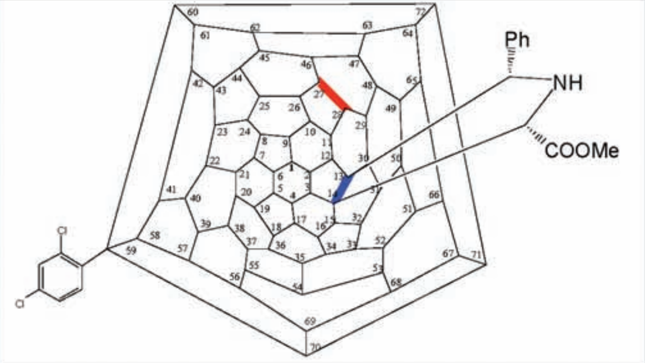
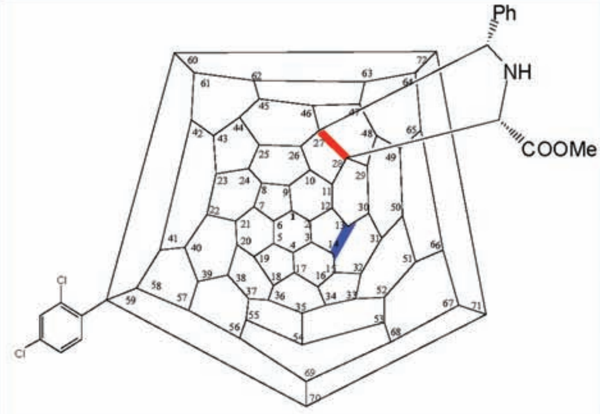
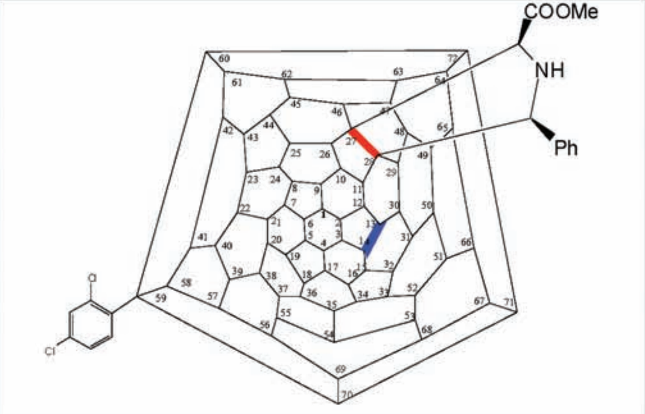
Major regioisomer	Minor regioisomer	
		Major siteisomer
2S-methoxycarbonyl-5S-(p-methoxyphenyl) pyrrolidino[3,4:13',14'] ^{f,s}C La@[72]fullerene	2S-methoxycarbonyl-5S-(p-methoxyphenyl) pyrrolidino[3,4:14',13'] ^{f,s}C La@[72]fullerene	name
		Minor siteisomer
2S-methoxycarbonyl-5S-(p-methoxyphenyl) pyrrolidino[3,4:28',27'] ^{f,s}C La@[72]fullerene	2S-methoxycarbonyl-5S-(p-methoxyphenyl) pyrrolidino[3,4:27',28'] ^{f,s}C La@[72]fullerene	name

Figure 6. Structures of the four isomers formed from the clockwise ^{f,s}C La@[72]fullerene($C_6H_3Cl_2$) by using Schlegel diagrams. Observe that all isomers have similar CD spectra. However, an unambiguous assignment between the CD spectrum (Figure 4) and chemical structure (this figure) cannot be carried out so far.

EXPERIMENTAL SECTION

General. All solvents were dried according to standard procedures. Reagents were used as purchased unless otherwise specified. High-performance liquid chromatography (HPLC) was performed on a LC-9204 apparatus (Japan Analytical Industry Co. Ltd.). HPLC-grade solvents were used as the eluents. Injection volumes of samples were 20 μL for analysis and 10 mL for separation. The ^{1}H and ^{13}C NMR measurements were conducted on a spectrometer (Avance 300 or Avance 500 with a Cryo-Probe system; Bruker) in carbon disulfide with a capillary tube of acetone-d_6 as an external lock. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) experiments were recorded (Biflex III; Bruker) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. Absorption spectra were recorded on a UV spectrophotometer (UV-3150; Shimadzu Corp.). Circular dichroic spectra were recorded on a spectrophotometer (J-820; Jasco Corp.). Methyl (*E*)-*N*-[(*p*-methoxyphenyl)methylene]glycinate[14] and La@C_{72}($C_6H_3Cl_2$)[17] were synthesized according to procedures reported in the literature.

Synthesis of Chiral Bis-adducts of La@C_{72} (1a−d and 2a−d). (*R*)-2-(*tert*-butylthio)-1-(diphenylphosphino)ferrocene (18.3 mg, 20.0 μmol) and Cu(AcO)$_2$ (3.6 mg, 20.0 μmol) were dissolved in toluene (40 mL), and the solution was stirred at room temperature for 1 h under argon atmosphere. A solution of methyl (*E*)-*N*-[(*p*-methoxyphenyl)methylene]glycinate (4.1 mg, 20.0 μmol) in toluene (20 mL) was added and the solution was stirred for 1 h at room temperature. Finally, a solution of a racemic mixture of endohedral metallofullerenes, La@C_{72}($C_6H_3Cl_2$) (11.5 mg, 10.0 μmol) in toluene (115 mL) was added and stirred for 6 h at room temperature. The eight chiral bis-adducts of La@C_{72} (**1a**−**d** and **2a**−**d**) were isolated from the unreacted starting materials by multistep HPLC, as shown in Figure S2 (Supporting Information). (For spectral data of **1a**−**d** and **2a**−**d**, see Supporting Information.)

Theoretical Calculations. Geometries were optimized by use of the Gaussian 09 program[23] with the B3LYP[24] and M06-2X[25] functionals. The basis set with relativistic effective core potential suggested by Hay and Wadt[26] was used for La atom. The split valence 3-21G(d)[27] or 6-31G(d)[28] basis sets were used for C, H, O, N, and Cl (for short, e.g., B3LYP/6-31G(d)∼hw).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional text, 21 figures, and one table showing spectral data of **1a**−**d** and **2a**−**d**; Schlegel diagrams, schematic drawings, and atom numbering of La@C_{72}($C_6H_3Cl_2$); charge densities and POAV angles in La@C_{72}($C_6H_3Cl_2$); and the complete list of authors for ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research on Innovation Areas (20108001, 'pi-Space'), a Grant-in-Aid for Scientific Research (A) (20245006), The Next Generation Super Computing Project (Nanoscience Project), Nanotechnology Support Project, Grants-in-Aid for Scientific Research on Priority Area (20036008 and 20038007), Specially Promoted Research (No. 22000009) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and The Strategic Japanese−Spanish Cooperative Program funded by JST and MICINN (fullsol@r PLE2009-0039; Endosol@r PIB2010JP00196). The Ministerio de Ciencia e Innovación (MICINN) of Spain (Project CTQ2008-00795/BQU; Consolider-Ingenio CSD2007-00010; Ramón y Cajal grant to S.F.), and the CAM (MADRISOLAR-2 Project S2009/PPQ-1533) are also acknowledged.

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