Endofullerenes

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Radical Derivatives of Insoluble La@C_{74}: X-ray Structures, Metal Positions, and Isomerization**

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Fullerenes, the third allotrope of the element carbon, are spherical molecules comprising exactly 12 pentagonal carbon rings and a certain number of hexagons, which is dependent on fullerene size. The interior of fullerenes can host a variety of metal atoms or otherwise unstable metal clusters, forming endohedral metallofullerenes (EMFs), which show fantastic structures and properties with vast potential applications in biomedicine, photovoltaics, and electronics.[1]

Since the first solvent extraction of EMFs by Smalley and co-workers, reported in 1991,[2] investigations of fullerenes and EMFs have largely focused on soluble species, such as C_{60}, C_{70}, and La@C_{82}, although soot contains various fullerene species with cages ranging from C_{60} to larger than C_{400}.[3] In contrast, little is known about insoluble fullerenes, which are estimated to be more abundant than soluble species in soot.[3] Calculations revealed that insoluble fullerenes normally have small HOMO–LUMO bandgaps. Thus they are also termed "small-bandgap fullerenes" or "missing fullerenes".[4] An important example of insoluble fullerenes is C_{74}, which has a HOMO–LUMO bandgap of 0.05 eV, while the value of C_{60} is 1.72 eV.[5]

Considerable efforts have been devoted to accessing these insoluble fullerenes and EMFs during the past twenty years. Reduction or oxidation of soot sublimate proved effective to change the bandgaps of some insoluble compounds, and thereby make them soluble. In 1998, Diener and Alford obtained a soluble fraction dominated by C_{74} and Gd@C_{2n} ($2n = 60$, 74) using an electrochemical reduction method.[5] Later, a chemical oxidation method was proposed by Bolskar and Alford, which yielded distinct classes of both soluble and insoluble fullerenes and EMFs, including C_{74} and Gd@C_{74}.[6]

However, the redox methods only provide mixtures of insoluble fullerenes and EMFs, so that no definitive structural identification of any cage has been reported. Alternatively, exohedral derivatization was also found to be efficient in solubilizing some small-bandgap species. In 2004, Strauss, Boltalina, and co-workers reported the first synthesis, isolation, and characterization of a fluorinated derivative of insoluble C_{74}.[7] Soon afterwards, the same group reported trifluoromethylated C_{74} derivatives and detailed structural characterization by NMR, DFT, and single-crystal XRD.[8] The reports concluded that empty C_{74} adopts the only IPR (IPR = isolated pentagon rule) isomer with D_{3h} symmetry.[9]

For the derivatization of C_{74}-based EMFs, only one example has been reported. In 2005, we accidentally found that during the 1,2,4-trichlorobenzene (TCB) extraction process, dichlorophenyl radicals generated by refluxing TCB react readily with some insoluble EMFs. Consequently, several missing-cage species, namely, La@C_{2n} ($2n = 72$, 74, 80, 82), are solubilized and isolated as dichlorophenyl derivatives.[10–13] Herein we report our recent findings that addition of dichlorophenyl radical to La@C_{74} actually generates two series of regioisomers of La@C_{74}($C_6H_3Cl_2$), each of which has been identified by X-ray crystallography. Our results show that two neighboring cage carbon atoms, both of which are very close to the internal metal atom, are highly reactive toward radicals as a result of strong metal–cage interactions. Furthermore, isomerization between the two series of isomers was observed.

La@C_{74} also adopts the D_{3h}-symmetric IPR cage, but its overall symmetry is reduced to C_{2v} because the La atom resides closely under a [6,6] bond at one pole of the molecule (Figure 1).[11] The La^{3+} cation has an important influence on the chemical properties of the cage carbon atoms. The p-orbital axis vector (POAV) value,[14] an effective index of the bond strain of fullerenes, is particularly prominent for these carbon atoms closest to La, including Carbon I and Carbon II. In addition, SOMO spin density, an indicator of the radical character of cage carbon atoms of paramagnetic EMFs, is also prominent for Carbon I and Carbon II. Consequently, both Carbon I and Carbon II are highly reactive toward radicals.

In accordance with the above prediction, two series of dichlorophenyl derivatives of La@C_{74}($C_6H_3Cl_2$) were isolated by three-step HPLC separation (Figure S1, Supporting Information). Each category contains three distinct isomers with different substitution patterns of the dichlorophenyl group. According to the ^{1}H NMR data (Figure S4, Supporting

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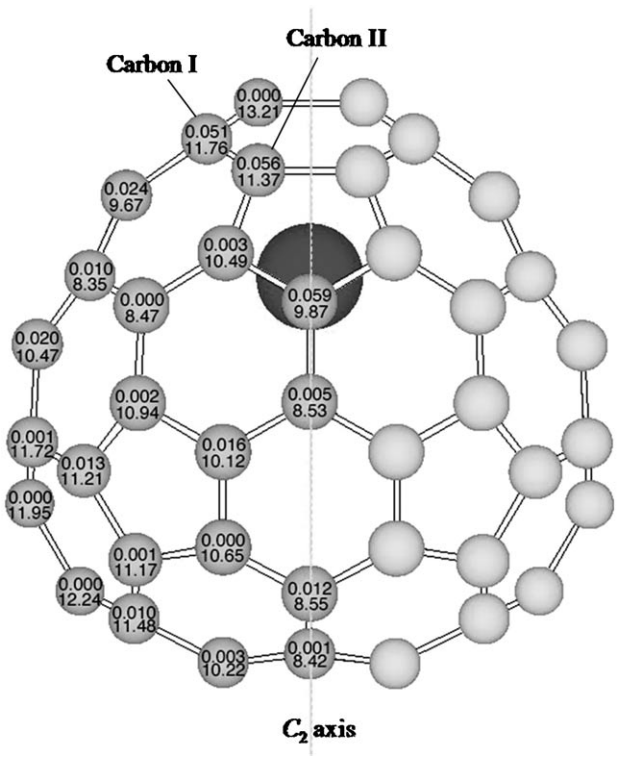

Figure 1. Optimized structure of La@D_{3h}-C_{74} with spin densities (top) and POAV values (bottom) labeled on nonequivalent carbon atoms. The overall symmetry is C_{2v} because of the off-center location of La.

Information), isomers **A**, **B**, and **C** have 2,4-, 2,5-, and 3,4-dichlorophenyl groups, respectively.

However, ^{13}C NMR data (Figures S5–S7, Supporting Information) indicate that these isomers have C_1 symmetry, so that only single-crystal XRD can give definite structural information. We obtained single crystals suitable for X-ray analysis of both La@C_{74}($C_6H_3Cl_2$)-**IA** and La@C_{74}($C_6H_3Cl_2$)-**IIB**. Their molecular structures are depicted in Figure 2.[11,15] La@C_{74}($C_6H_3Cl_2$)-**IA** has a 2,4-dichlorophenyl moiety singly bonded to Carbon I, as already reported, while in La@C_{74}($C_6H_3Cl_2$)-**IIB**, a 2,5-dichlorophenyl group is linked to Carbon II. More interestingly, although only one metal position is observed in La@C_{74}($C_6H_3Cl_2$)-**IA**, up to seven positions of La, with occupancies of 0.52, 0.18, 0.10, 0.07, 0.06, 0.04, and 0.03, are distinguished in La@C_{74}($C_6H_3Cl_2$)-**IIB**. Detailed analyses reveal that the seven La positions are nearly coplanar within a plane that is perpendicular to the single bond between the cage and the addend (Figure S8, Supporting Information). Thus, not only the internal metal atom can dictate the addition patterns, but the addends and the addition sites can also have a marked influence on the location and motion of the internal metal atom.[1]

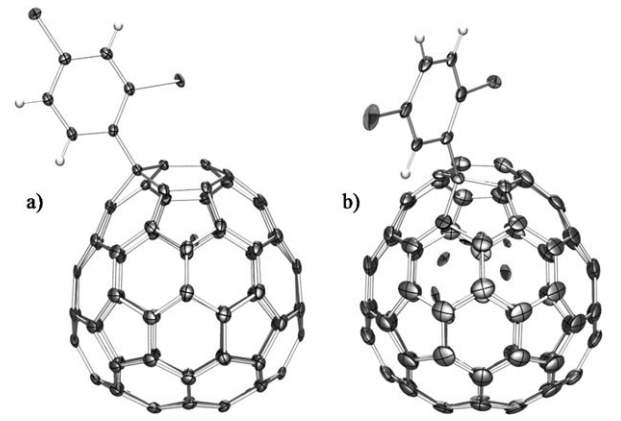

Figure 2. ORTEPs of a) La@C_{74}($C_6H_3Cl_2$)-**IA** and b) La@C_{74}($C_6H_3Cl_2$)-**IIB** with thermal ellipsoids at 50% probability. All La positions are shown.

Electronic properties differ between the two series of La@C_{74}($C_6H_3Cl_2$) isomers. The Vis/NIR spectra in Figure 3

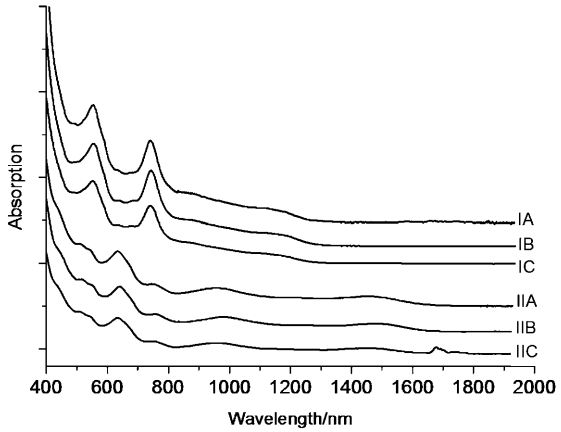

Figure 3. Vis/NIR spectra of La@C_{74}($C_6H_3Cl_2$)-**IA–C** and -**IIA–C** isomers.

show that the isomers with a dichlorophenyl group attached on the same site of the cage are fundamentally identical. This is consistent with our previous conclusions that the substitution pattern of the dichlorophenyl group has a negligible effect on the electronic structures of the adducts.[13] In detail, the **A**, **B**, and **C** isomers of La@C_{74}($C_6H_3Cl_2$)-**I** feature distinct absorption bands at 555, 740, and 1135 nm with an onset at 1350 nm, corresponding to a medium optical bandgap (0.92 eV). In contrast, the isomers with a substituent attached on Carbon II show absorption peaks at 630, 750, 960, and 1475 nm; the onset at 1690 nm indicates a relatively small bandgap (0.73 eV).

Electrochemical properties of La@C_{74}($C_6H_3Cl_2$)-**IA–C** and La@C_{74}($C_6H_3Cl_2$)-**IIA–C** show less difference. Both series exhibit two or three reversible reduction processes and one less reversible oxidation process (Figure S9, Supporting Information), again confirming that EMF anions are generally more stable than the cations.[5,8] The redox potentials are listed in Table 1. No marked differences exist between the two categories in view of both reduction and oxidation potentials, which implies that the mixture of these isomers can be directly employed for constructing donor–acceptor systems useful as photovoltaics.

We also investigated the thermal stability of these isomers and observed isomerization from La@C_{74}($C_6H_3Cl_2$)-**IA** to

Table 1: Redox potentials (V vs. Fc/Fc^+) of La@$C_{74}(C_6H_3Cl_2)$-**IA**–**C** and -**IIA**–**C** isomers.[a]

Compound	$^{ox}E_1$	$^{red}E_1$	$^{red}E_2$	$^{red}E_3$
La@$C_{74}(C_6H_3Cl_2)$-**IA**	0.30	−1.05	−1.36	−1.92
La@$C_{74}(C_6H_3Cl_2)$-**IB**	0.24	−1.08	−1.38	−2.32
La@$C_{74}(C_6H_3Cl_2)$-**IC**	0.30	−1.06	−1.40	
La@$C_{74}(C_6H_3Cl_2)$-**IIA**	0.23	−0.95	−1.34	−2.00
La@$C_{74}(C_6H_3Cl_2)$-**IIB**	0.24	−0.90	−1.39	
La@$C_{74}(C_6H_3Cl_2)$-**IIC**	0.23	−1.05	−1.48	

[a] Determined by differential pulse voltammetry in 1,2-dichlorobenzene with 0.1 M $(n\text{Bu})_4NPF_6$ at a Pt working electrode.

La@$C_{74}(C_6H_3Cl_2)$-**IIA** on heating. A degassed solution of pure La@$C_{74}(C_6H_3Cl_2)$-**IA** in *o*-dichlorobenzene (ODCB) sealed in a glass tube was heated at 100 °C for 10 h, and the resulting solution was characterized by HPLC (Figure 4). The

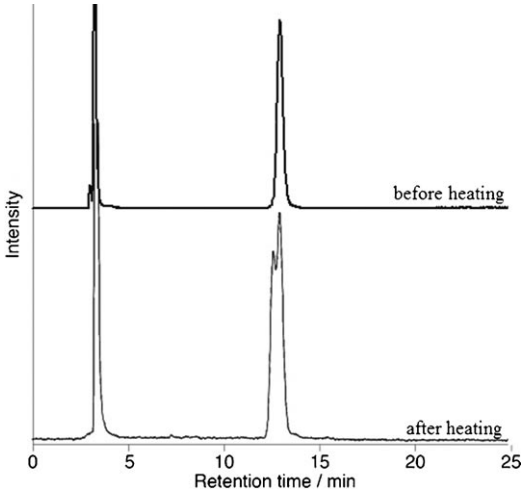

Figure 4. HPLC profiles showing the isomerization from La@C_{74}-$(C_6H_3Cl_2)$-**IA** to La@$C_{74}(C_6H_3Cl_2)$-**IIA**.

two peaks exhibited by the heated solution correspond to La@$C_{74}(C_6H_3Cl_2)$-**IA** and -**IIA**, respectively, as confirmed by means of Vis/NIR and ^1H NMR spectrometry. The isomerization process should be similar to the retro-radical reaction of singly bonded La@C_{82} derivatives in which the bond between the addend and the fullerene cage is broken.[16] This conclusion is further confirmed by calculations showing that La@$C_{74}(C_6H_3Cl_2)$-**IIA** is 2.50 kcal mol^{-1} less stable than La@$C_{74}(C_6H_3Cl_2)$-**IA**.

In summary, we have examined the reaction of dichlorophenyl radicals with insoluble La@C_{74} systematically. Six isomers were isolated, which can be assigned as regioisomers in which dichlorophenyl groups with different substitution patterns are singly bonded to one of two adjacent cage carbon atoms. The addition pattern is markedly dictated by the internal metal atom and, in turn, additions to different sites of the cage change the motional behavior of the internal metal atom effectively, as well as the electronic structures of the resulting adducts. Our results provide new insights into the chemistry of insoluble fullerenes and will evoke greater interest in investigations of these small-bandgap fullerenes and their applications as solar-cell materials and quantum computing units.

Experimental Section

Experimental details and HPLC separation charts are presented in the Supporting Information.

Black single crystals were obtained by layering a saturated CS_2 solution of La@$C_{74}(C_6H_3Cl_2)$-**IIB** beneath hexane in a glass tube (∅ 7.0 mm). X-ray data were collected at 100 K with an AXS SMART APEX machine (Bruker Analytik, Germany). CCDC 808585 (La@$C_{74}(C_6H_3Cl_2)$-**IIB**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical calculations were conducted with the Gaussian 03 program package.[17] The molecular structures were optimized at the B3LYP level[18] with the relativistic effective core potential (ECP)[19] and the LANL2DZ basis set for La and 6-31G(d) basis set[20] for C, H, and Cl.

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