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Communication

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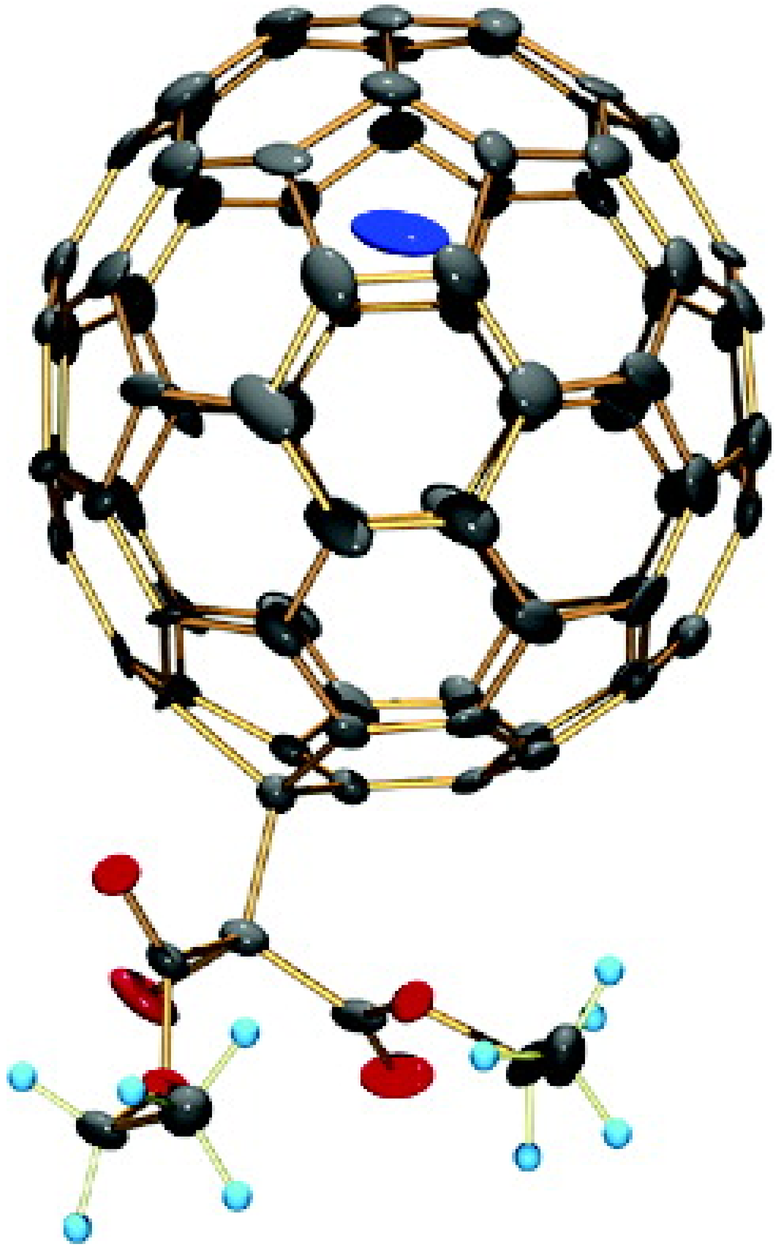

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A Singly Bonded Derivative of Endohedral Metallofullerene: $La@C_{82}CBr(COOC_2H_5)_2$

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Endohedral metallofullerenes (EMFs) are constructed by encapsulating metal atoms in the fullerene cages. Hybridization of the properties of fullerene and metal atoms makes EMFs very promising materials in the fields of chemistry, physics, bioscience, and nanoscience.[1,2] $M@C_{82}$ (M = La, Y, Ce, Pr, etc.) is one of most abundantly produced EMFs. Recently, the studies on their electronic structures and chemical functionalizations have attracted considerable interest to disclose how the endohedral metal atoms perturb the electron distribution of the fullerene cage and affect its reactivity.[1,2] It has been revealed that $M@C_{82}$ has an open-shell electronic structure as a result of electron transfer from M to C_{82}.[3] Meanwhile, several reactions of $M@C_{82}$ have been carried out to afford the cycloadducts, which retain the paramagnetic nature of the parent fullerene.[4] Recently, it has been reported that the fluoroalkylation reaction of $Y@C_{82}$ to afford $Y@C_{82}(CF_3)_5$ is very different from the cycloaddition reaction.[5] Three possible structures for the two diamagnetic isomers of $Y@C_{82}(CF_3)_5$ have been suggested by means of NMR spectroscopic analysis and theoretical calculation.[5] Herein, we present a novel singly bonded adduct of $La@C_{82}$, which was prepared from the Bingel−Hirsch reaction of $La@C_{82}$, and its unambiguous structural characterization.

The Bingel−Hirsch reaction was conducted with $La@C_{82}$ and diethyl bromomalonate in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in dry toluene over 2 h under Ar.[6] The crude reaction mixture was filtered to remove the small amount of precipitate of $[La@C_{82}]^-DBU^+$.[7] Then, by preparative HPLC, a mixture of monoadducts was separated from multiadducts and unreacted starting materials. Among them, one monoadduct (mono-A) was most abundantly produced and isolated in the yield of 40% based on the consumed $La@C_{82}$.

Although $La@C_{82}$ is ESR-active, mono-A affords no ESR signal. This diamagnetic property allows direct NMR characterization. In the ^{13}C NMR spectrum of mono-A, 81 signals are observed in the typical sp^2 carbon range of $[La@C_{82}]^-$ (160−130 ppm), suggesting the diversion of one sp^2 carbon and the reduced C_1 symmetry of the C_{82} cage after monoaddition. In another field, the spectrum exhibits two sets of signals for the ethoxycarbonyl groups (164.91, 164.71, 63.99, 63.71, 14.16, and 14.23 ppm) and another two signals (69.42 and 60.46 ppm) corresponding to the quaternary carbon for the C−C bond between the appended group and the C_{82} cage. In the ^1H NMR spectrum, two sets of signals for ethyl groups appear. All these NMR data suggest that a bromomalonate group is combined with the C_{82} cage by a single bond.

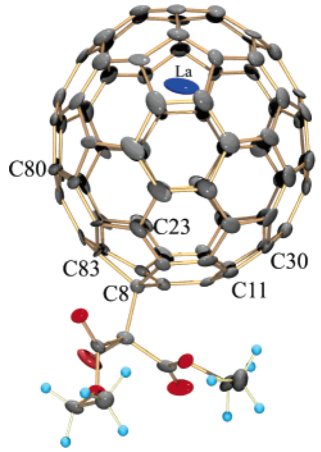

Figure 1. ORTEP drawing of mono-A (major enantiomer). The CS_2 molecules are omitted for clarity.

Finally, the structure of mono-A was unambiguously determined by the X-ray crystallographic analysis.[8] As clearly shown in Figure 1, a bromomalonate group is combined with the C_{82} cage by a single bond, as suggested by NMR analysis results. The addition takes place at the C8 position, the apex between two hexagons and one pentagon. Because of the formation of a single bond, the C_{82} cage undergoes deformation. In particular, the C8−C83 distance (1.592(10) Å) is significantly elongated, compared with the average C−C distance at the unaltered 6:5 ring junction (1.443(12) Å). Thus, C8 is observably pulled away from the C_{82} cage. Moreover, it is interesting that the La atom is located at a fixed position far from the bromomalonate group. The distance between the La atom and the nearest carbon atom (2.520 Å) agrees well with the calculation result (2.513 Å).[9]

The MALDI-TOF mass spectrum and the UV−visible−NIR absorption spectrum of mono-A are shown in Figure 2. The mass spectrum shows a distinct peak at m/z 1123 for $La@C_{82}$ from the single-bond cleavage and a weak peak at m/z 1281 due to the loss of the Br atom from mono-A. In the UV−visible−NIR spectrum, mono-A displays characteristic absorptions at 1416, 1198, 990, 820, and 509 nm, which are very different from those of the pristine $La@C_{82}$. The onset of mono-A shifts to a shorter wavelength, as compared with $La@C_{82}$. All these findings suggest that mono-A has a larger HOMO−LUMO gap than $La@C_{82}$. This result is in good agreement with the theoretical calculations shown in Figure 3.[9] Mono-A has a closed-shell electronic structure, unlike the

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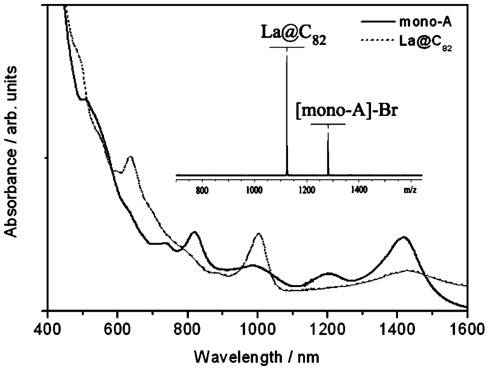

Figure 2. UV−vis−NIR spectra of La@C_{82} and mono-A. Inset: Negative mode MALDI-TOF mass spectrum of mono-A.

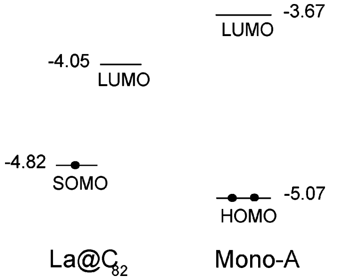

Figure 3. The orbital levels of La@C_{82} and mono-A in eV.

Table 1. Redox Potentials (*V*)^a of La@C_{82} and Mono-A

compound	$_{ox}E_2$	$_{ox}E_1$	$_{red}E_1$	$_{red}E_2$	$_{red}E_3$
La@C_{82}	1.07	0.07	−0.42	−1.37	−1.53
mono-A	0.85	0.38	−0.66	−1.31	−1.47

^{a} Versus Fc/Fc$^+$. In *o*-dichlorobenzene with 0.1 M (*n*-Bu)$_4$NPF$_6$ at a Pt working electrode. DPV: pulse amplitude, 50 mV; scan rate, 20 mV s^{-1}.

pristine La@C_{82}. The higher LUMO and lower HOMO levels of mono-A suggest that mono-A is less easily reduced or oxidized than La@C_{82}.

Table 1 shows redox potentials of mono-A obtained by differential pulse voltammetry (DPV). The salient feature is the wider gap between its first redox potentials. As compared with those of pristine La@C_{82}, the first reduction and oxidation potentials of mono-A shift negatively by 240 mV and positively by 310 mV, respectively. The cyclic voltammetry (CV) study shows that the first reduction is irreversible, though the first oxidation is reversible. This suggests that the anion of mono-A is unstable.

Theoretical calculations of the Mulliken charge densities of La@C_{82} show that the C8 atom is most positively charged.[9] The π-orbital axis vector (POAV) analysis[10] shows that the local strain is the second largest at the C8 atom, as compared with other positively charged carbon atoms. These make the C8 atom most reactive toward the nucleophilic attack. Therefore, it is reasonable to assume that a nucleophilic reaction takes place at the first step, followed by the oxidation of an intermediate [La@C_{82}Br($COOC_2H_5)_2]^-$ with oxidants (La@C_{82} or trace oxygen in solvent) to afford the final adduct, mono-A.

In conclusion, a novel singly bonded adduct of La@C_{82} (mono-A) has been synthesized by the reaction with diethyl bromomalonate in the presence of DBU. Its structure has been fully determined by NMR spectroscopic and X-ray crystallographic analyses. Since mono-A is very different from the conventional Bingel adduct of empty fullerenes, this study may suggest a new aspect in the chemistry of endohedral metallofullerenes.

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Supporting Information Available: The complete list of authors for ref 4d. HPLC profile, ^{1}H NMR and ^{13}C NMR spectral data, CV and DPV spectrum of mono-A. Selected X-ray crystallographic data of mono-A in CIF format at 93 K. Calculation data of La@C_{82} and mono-A at the B3LYP level. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) La@C_{82} was found to be reduced by DBU to form [La@$C_{82}]^-$DBU$^+$. [La@$C_{82}]^-$DBU$^+$ is insoluble in toluene but soluble in the mixture of acetone and CS_2 (1:1). Its feature absorptions in the UV−vis−NIR region are very similar to those of [La@$C_{82}]^-$TBA$^+$.

(8) Crystal data of a black block of mono-A·2.5(CS_2): FW = 1552.12, 0.40 mm × 0.33 mm × 0.32 mm, monoclinic, $P2_1/c$ (No. 14), a = 11.4183(8) Å, b = 20.7335(15) Å, c = 21.8982(16) Å, β = 95.8990(10)°, V = 5156.8(6) Å^3, Z = 4, D_{calcd} = 1.999 g cm^{-3}, μ (Mo Kα) = 1.407 mm^{-1}, Bruker SMART, θ = 1.36−28.43°, T = 93 K, No. observations (all reflections): 11 872. No. variables: 1185, reflection/parameter ratio: 12.47, $R1$ (8466 $F_o > 4\sigma(F_o)$) 0.0784, R (for all 11 872 data) 0.1109, $wR2$ (all reflections) 0.2087. Goodness of fit indicator 1.076, restrained goodness of fit indicator 1.086 for all data. The full list of coordinates of the other atomic sites and the X-ray data at 93 K are available in the Supporting Information.

(9) Geometries were optimized with hybrid density functional theory at the B3LYP level using the Gaussian 03 program. The effective core potential (ECP) and LANL2DZ basis set were used for La and Br. The split-valence d-polarized 6-31G(d) basis set was used for C, O, and H. For B3LYP, see: (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. For ECP and LANL2DZ, see: (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310. For 6-31G-(d), see: (e) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654−3665.

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