Fullerenes

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# Bis-Carbene Adducts of Non-IPR $La_2@C_{72}$: Localization of High Reactivity around Fused Pentagons and Electrochemical Properties**

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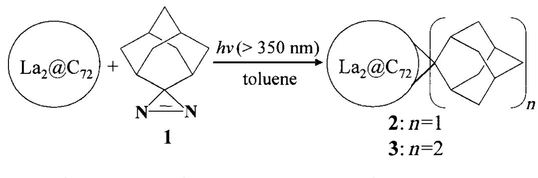
Endohedral metallofullerenes (EMFs) are generated by encapsulation of metal species in hollow fullerene cavities.[1] The strong interactions between the encaged metal species and the fullerene cage lead to novel structures and properties which are not found for empty fullerenes.[1]

An intriguing aspect of EMFs is their chemical properties, which clearly differ from those of empty fullerenes due to electron transfer from the encaged metal atoms to the fullerene cage. In addition, derivatives of EMFs are more useful than the parent EMFs in many fields,[2–9] and especially their adducts are generally more suitable for single-crystal X-ray diffraction (XRD) measurements, since pristine EMFs are orientationally disordered in the crystal phase due to their spherical shapes. Hence, chemical modification of EMFs has blossomed in recent years. Since the first exohedral adduct of $La@C_{82}$ was reported in 1995,[2] various derivatives have been synthesized by different reactions, and some of them have been isolated and structurally characterized.[3,5] Most reports focused on mono-adducts of EMFs, while only a few papers deal with bis-adducts. Stevenson and co-workers isolated a bis-adduct from a Diels–Alder reaction of $Gd_3N@C_{80}$, but no additional structural information was presented.[10] Feng et al.[11] reported regioselective synthesis of a bis-adduct of $La@C_{82}$ from the Bingel–Hirsch reaction. X-ray data showed that the bis-adduct tends to form a dimer in the single crystal. Cai et al. reported that Bingel–Hirsch reaction of $Sc_3N@C_{78}$ affords abundantly a bis-adduct, and an NMR study showed that the second reaction site is controlled by the internal metal cluster.[12] Investigations on bis-adducts provide deeper insight into the properties and chemical reactivities of EMFs.

Another fascinating aspect of EMFs is stabilization of carbon cages violating the isolated-pentagon rule (IPR) by the encaged metal species. These non-IPR EMFs are currently of considerable interest because the [5,5]-junction carbon atoms are expected to be very reactive due to the high surface curvature, so that they were previously thought to be unstable species.[13–18] In the last few years, some non-IPR fullerene derivatives and EMFs have been isolated and structurally characterized.[13–18] However, no investigations on the chemical behavior of non-IPR fullerenes and/or EMFs have been reported. Recently, we found that $La_2@C_{72}$, which has a $D_2$-symmetric non-IPR cage with two pairs of fused pentagons, reacts readily with 2-adamantane-2,3-[3*H*]-diazirine (**1**) to generate six isomers of mono-adduct $La_2@C_{72}Ad$ (**2**, Ad = adamantylidene).[19] Experimental and theoretical results suggested that the fused-pentagon regions are more reactive than other sites of the $C_{72}$ cage, and more interestingly it was found for the first time that the [5,5]-junction carbon atoms are less reactive than the adjacent ones, as they interact strongly with the encaged metal atoms and thus are stabilized.[19] Since two pairs of fused pentagons are available in $La_2@C_{72}$, it is natural to elucidate the reactivity of both. We now report the synthesis, isolation, and characterization of bis-carbene adduct $La_2@C_{72}Ad_2$ (**3**).

The reaction of $La_2@C_{72}$ with **1** was induced by a high-pressure mercury-arc lamp in anhydrous toluene (Scheme 1) and monitored by HPLC on a Buckyprep M column (Figure 1). Before irradiation, the retention times of **1** and $La_2@C_{72}$ were 3 and 15 min, respectively. After 5 min of



**Scheme 1.** Photoreaction between $La_2@C_{72}$ and **1**.

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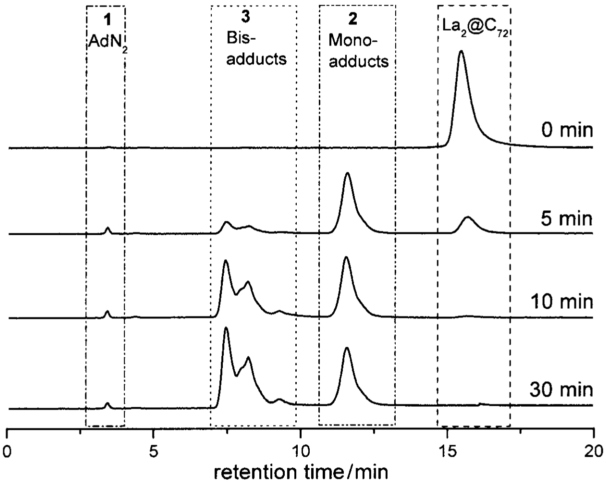

***Figure 1.*** HPLC profiles of the reaction mixture of $La_2@C_{72}$ and **1**. Conditions: Buckyprep M column, 1.0 mL min⁻¹, 330 nm detection, 25 °C.

irradiation, two new peaks appeared at retention times of 7 and 11 min, which are ascribed to bis-adduct **3** and mono-adduct **2**, respectively.[19] After irradiation for 10 min, disappearance of the peak at 15 min indicated that all of the starting $La_2@C_{72}$ was consumed. Then the mixture was further irradiated for 20 min. Surprisingly, no new peaks arising from multiple adducts were observed by HPLC, and only bis- and mono-adducts were detected by mass spectrometry. For bis-adduct **3**, more than fifteen isomers were distinguishable, but only seven were isolated by recycling preparative HPLC and characterized (see the Supporting Information for details). The structure of the most abundant isomer **3a** was determined by single-crystal XRD analysis.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of the seven isolated bis-adduct isomers display only one molecular ion peak at $m/z$ 1410, ascribed to the 1:2 adduct. Figure 2a shows the mass spectrum of **3a** as a representative. The absence of the peaks of $La_2@C_{72}$ and the mono-adduct indicates that the two Ad groups in the bis-adduct isomers are both tightly attached to the $C_{72}$ cage and can not be peeled off even by laser irradiation, as in the case of mono-adducts **2**.[19]

The Vis/NIR spectra of the bis-adduct isomers are similar to each other, so only that of **3a** is shown in Figure 2b together with those of $La_2@C_{72}$ and **2c** (which is the most abundant mono-adduct isomer and has a similar addition pattern to **3a**) for comparison, and others can be found in the Supporting Information. All of them show prominent absorbance bands at 510, 590, and 720 nm. These similar spectra indicate that the electronic structure of $La_2@C_{72}$ is not significantly changed even after covalent attachment of two Ad groups, and hence the bis-adducts should also have open-cage structures.[19] Interestingly, electrochemical data show that the Ad group has a mild reductive effect on $La_2@C_{72}$. As summarized in Table 1, the redox potentials of **3a** are about 0.2 and 0.1 V more negative than those of $La_2@C_{72}$ and **2c**,[19] respectively, that is, the electrochemical properties of $La_2@C_{72}$ can be tuned by stepwise addition of Ad groups. Accordingly, this Ad cycloaddition method is expected to be very useful, since it meets the requirements for changing the electrochemical properties by chemical modification while retaining the essential electronic structures of the pristine metallofullerene. These Ad derivatives will surely find fundamental applications in many fields, especially in photovoltaics and donor–acceptor systems.

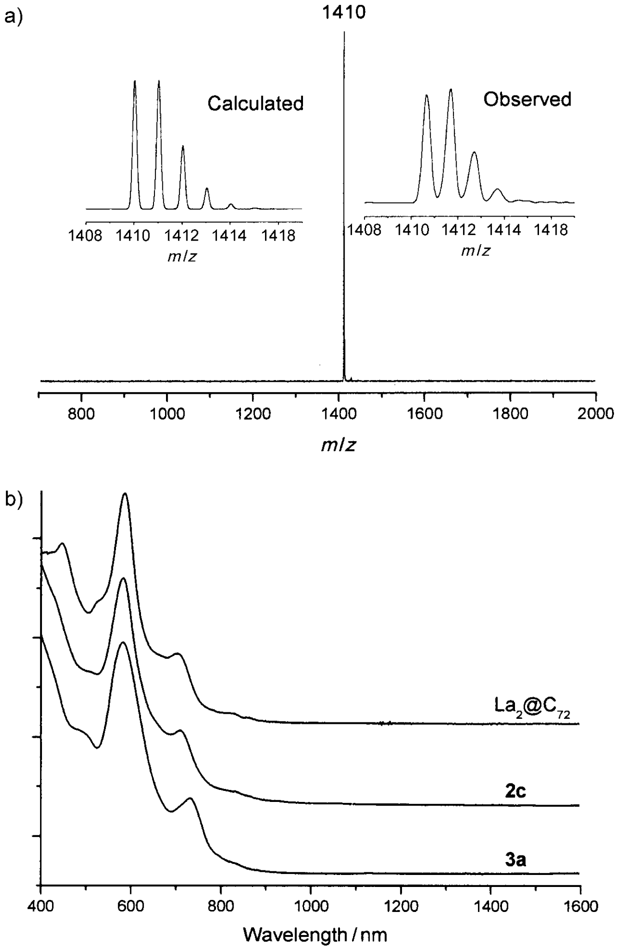

***Figure 2.*** a) Mass spectrum of **3a** in negative-reflection mode. Insets show the calculated and observed isotopic distributions. b) Vis/NIR spectra of $La_2@C_{72}$, **2c**, and **3a**.

***Table 1:*** Redox potentials of $La_2@C_{72}$, **2c**, and **3a**.[a]

| Compound | ${}^{ox}E_2$ | ${}^{ox}E_1$ | ${}^{red}E_1$ | ${}^{red}E_2$ |
|---|---|---|---|---|
| $La_2@C_{72}$ | +0.75[b] | +0.24 | −0.68 | −1.92 |
| **2c**[19] | +0.67 | +0.15 | −0.76 | −2.00[b] |
| **3a** | +0.57 | +0.02 | −0.86 | −2.08 |

[a] Half-cell potentials unless otherwise noted. Values are relative to ferrocene/ferrocenium couple. In 1,2-dichlorobenzene with 0.1 M $n\mathrm{Bu_4NPF_6}$ at a Pt working electrode. [b] Irreversible. Values obtained by DPV.

Figure 3a shows the molecular structure of **3a**, determined by single-crystal XRD,[20] while Figure 3b shows that of pristine $La_2@C_{72}$ for comparison. The two Ad groups are attached to the fused-pentagon regions on each side of the $C_{72}$ cage. The addition sites correspond to that previously found

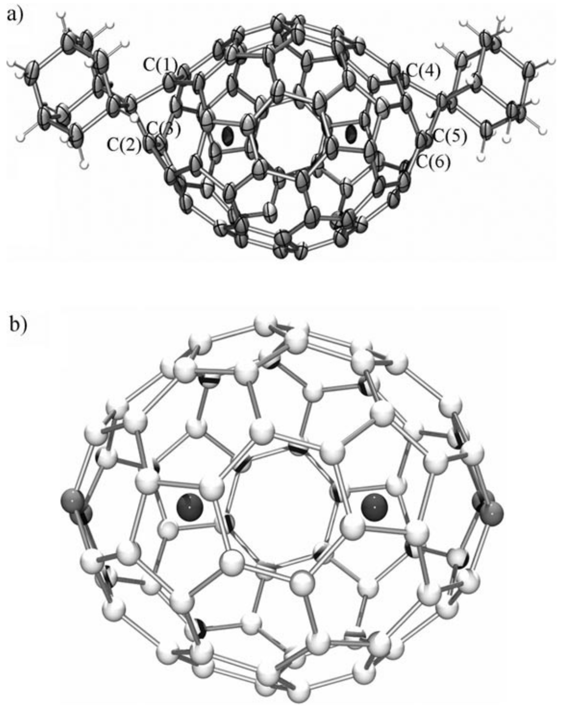

*Figure 3.* a) ORTEP drawing of one enantiomer of **3a** showing thermal ellipsoids at the 50% probability level. The $CS_2$ molecules are omitted for clarity. b) Molecular structure of $La_2@C_{72}$ (#10611) with the four [5,5]-junction carbon atoms highlighted as darker spheres.

for **2c**, that is, the [5,6]-bond junctions next to the [5,5]-bonds,[19] so that **3a** has a structure with $C_2$ symmetry. As indicated by the C(1)–C(2) and C(4)–C(5) separations of 2.138 and 2.120 Å, respectively, **3a** has an open-cage structure. The two La cations reside close to the two fused-pentagon pairs of $La_2@C_{72}$ at the poles of the $C_{72}$ cage. The La–La distance of 4.300 Å is longer than those for **2b–d** (4.171–4.178 Å);[19] this indicates that the two open parts in **3a** help to relieve the strong repulsion between the two La cations. The two [5,5]-bonds (which in fact are [5,6]-bonds because of ring opening) in **3a** are similar in length (C(2)–C(3) 1.429, C(5)-C(6) 1.458 Å). These values are close to that of **2b** (1.453 Å), but slightly shorter than those of **2c** (1.465 Å) and **2d** (1.535 Å).[19]

The tendency of the two Ad groups to add to the two fused-pentagon regions of $La_2@C_{72}$ confirms that they are more reactive than other parts of the molecule. Moreover, we found that no multi-adducts $La_2@C_{72}(Ad)_n$ ($n \geq 3$) are formed even if the reaction mixture is further irradiated for 20 min after all the $La_2@C_{72}$ starting material has been consumed. This indicates that only the two fused-pentagon sites are reactive toward **1**, and no further reaction of $La_2@C_{72}Ad_2$ with **1** occurs after the two active sites are occupied. In other words, the high reactivity of $La_2@C_{72}$ toward **1** is localized in the two fused-pentagon regions. Accordingly, it is reasonable to speculate that in all of the bis-adduct isomers, the two Ad groups should be located in the two fused-pentagon regions of each pole of $La_2@C_{72}$.

In conclusion, bis-carbene adducts of $La_2@C_{72}$ were synthesized, isolated, and characterized as the first examples of non-IPR EMFs. Electrochemical results revealed that the Ad groups have an electron-donating nature with respect to $La_2@C_{72}$. Thus, we expect that a series of useful materials based on fullerenes and EMFs which retain the essential electronic structures of the pristine EMF but have different redox potentials can be generated by using this synthetic strategy and could find more applications than the precursors.[19] Furthermore, structural characterization of the most abundant isomer **3a** showed that the two Ad groups are covalently bonded to the [5,6]-junctions adjacent to the two fused-pentagon bonds in a symmetric open-cage structure. The fused-pentagon sites in $La_2@C_{72}$ are clearly more reactive than other sites, as only mono- and bis-adducts were formed. A variety of bis-adducts of non-IPR metallofullerenes will not only provide new understanding of the chemical properties of EMFs, but also will enrich the chemistry of fullerenes and supply more applicable materials.

## Experimental Section

A toluene solution (12 mL) containing both $La_2@C_{72}$ ($M = 1142$, 1.0 mg, $7.30\times10^{-5}$ M) and **1** ($C_{10}H_{14}N_2$, $M = 162$, 2.8 mg, $1.44\times10^{-3}$ M) in a degassed sealed tube was irradiated with an ultrahigh-pressure mercury-arc lamp (cutoff < 350 nm) at room temperature. Isomers of bis- and mono-adducts were isolated by multistage recycling HPLC. Detailed HPLC separation profiles can be found in the Supporting Information and reference [19].

Preparative HPLC was conducted on a LC-908 instrument (Japan Analytical Industry Co., Ltd) with toluene as mobile phase. MALDI-TOF MS was performed on a BIFLEX III (Bruker, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) as matrix. UV/Vis/NIR spectra were measured on a UV 3150 (Shimadzu, Japan) in $CS_2$. $^1$H NMR spectra were determined with Bruker AVANCE-300 in [$D_4$]-1,2-dichlorobenzene, and chemical shifts were calibrated according to the solvent. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were obtained in 1,2-dichlorobenzene with 0.1 M $(n\mathrm{Bu})_4NPF_6$ at Pt working electrode on a potentiostat/galvanostat (BAS CW-50). The scan rate for CV was 20 mV s$^{-1}$. Conditions for DPV: pulse amplitude, 50 mV; scan rate, 20 mV s$^{-1}$.

A black single crystal of **3a** was obtained by layering a solution of **3a** in $CS_2$ with hexane. CCDC 694662 (**3a**) 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

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[20] Crystal data for $La_2@C_{72}(Ad)_2 \cdot 2\,CS_2$: $M_r = 1563.22$, black plate, $0.13 \times 0.10 \times 0.04$ mm$^3$, triclinic, $P\bar{1}$ (no. 2), $a = 10.8457(8)$, $b = 14.6076(11)$, $c = 17.9994(17)$ Å, $\alpha = 103.786(5)$, $\beta = 96.811(5)$, $\gamma = 103.265(4)°$, $V = 2649.9(4)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.959$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 1.813$ mm$^{-1}$, $\theta = 5.51$–$140.73°$, $T = 100$ K; 28415 reflections collected, 13335 of which were unique ($R_{int} = 0.0248$) and included in the refinement; full-matrix least-squares calculation based on $F$ gave final $R = 0.2084$, $R1 = 0.0704$ for 9110 reflections ($I > 2.0\sigma(I)$) with 911 variable parameters. For the structural analysis, X-ray intensity data were collected on a Rigaku DSC imaging plate system by using Si-monochromated synchrotron radiation ($\lambda = 0.99830$ Å) at beam line BL-1A of Photon Factory (PF), High-Energy Accelerator Research Organization (KEK).