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Regioselective Cycloaddition of $La_2@I_h$-C_{80} with Tetracyanoethylene Oxide: Formation of an Endohedral Dimetallofullerene Adduct Featuring Enhanced Electron-Accepting Character

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S *Supporting Information*

ABSTRACT: We describe the regioselective cycloaddition of $La_2@I_h$-C_{80} with tetracyanoethylene oxide (TCNEO), which enabled the formation of the corresponding adduct having a tetracyanotetrahydrofuran moiety. X-ray crystallographic analysis revealed that the cycloaddition took place as a [5,6] addition. Along with dynamic swing motion of the metal atoms, the results of this electrochemical study demonstrate that TCNEO addition enhanced the electron-accepting character of $La_2@I_h$-C_{80} and that the first reduction potential of the adduct reached −0.21 V versus the ferrocene/ferrocenium couple, which is the lowest value reported for endohedral metallofullerenes and their derivatives to date.

Fullerenes are currently of interest as excellent electron acceptors for organic electronics because of their high electron affinity and ability to transport carriers effectively.[1] In particular, the strong electron-accepting ability of C_{60} enables the preparation of superconducting alkali metal-intercalated complexes[2] and ferromagnetic charge-transfer salts.[3] Therefore, enhancement of the electron affinity of fullerenes by chemical functionalization remains a demanding goal in fullerene chemistry for applications in electroconducting materials. However, the electron affinity of fullerenes generally decreases upon functionalization.[4] To compensate for this loss and enhance the electron-accepting character, various chemical modifications of the fullerene surface have been explored to date. Wudl, Martin, and co-workers have taken the initiative in the design and synthesis of organofullerenes in this direction with the attachment of strongly electron-withdrawing groups,[5] the use of periconjugation mechanisms,[6] and heterofullerene synthesis.[7] Other strategies for improvement of the electron-accepting strength of fullerenes include polyfluorination,[8] trifluoromethylation,[9] and formation of fulleropyrrolidinium salts.[10] Higher fullerenes are also of interest as an alternative to C_{60} because they have a better electron-accepting character than C_{60} does.[11] However, the limitation is that higher fullerenes possess much lower symmetries than C_{60}, which causes difficulty in controlling the regioselectivity in functionalization.

A potent strategy for dramatic enhancement of the electron-accepting strength of fullerenes is endohedral metal-atom doping, which provides hybrid molecules of a new class, the so-called endohedral metallofullerenes (EMFs).[12] Among various EMFs, $La_2@I_h$-C_{80} is an amazing molecule. It is a promising candidate for future applications in the field of materials science because of its much stronger electron-accepting character in comparison with C_{60}. In fact, the first reduction potential of $La_2@I_h$-C_{80} is −0.31 V versus the ferrocene/ferrocenium couple (Fc/Fc^+), whereas that of C_{60} is −1.12 V vs Fc/Fc^+.[13] Furthermore, the high symmetry of the $La_2@I_h$-C_{80} cage (icosahedral) gives excellent chemical tunability. In this communication, we report the regioselective cycloaddition of $La_2@I_h$-C_{80} and tetracyanoethylene oxide (TCNEO), providing further enhancement of the electron-accepting character.

It is well-known that at temperatures greater than 100 °C, TCNEO generates a carbonyl ylide intermediate thermally via ring-opening. The intermediate reacts with alkenes, alkynes, and aromatic compounds to afford the corresponding cycloadducts bearing tetracyanotetrahydrofuran structures.[14] Because the reaction can introduce four cyano groups as a strong electron-withdrawing group all at once,[15] we applied the TCNEO addition to the dimetallofullerene $La_2@I_h$-C_{80} to improve the electron-accepting character. A toluene solution containing $La_2@I_h$-C_{80} and 7 equiv of TCNEO was heated under reflux for 1.5 h (Scheme 1). The mixture was analyzed using analytical high-performance liquid chromatography (HPLC), by which a single new peak was observed. Subsequently, matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) mass spectrometry revealed the product to be the $La_2@I_h$-C_{80}−TCNEO monoadduct (**1**). It is particularly interesting that the product was eluted after pristine $La_2@I_h$-C_{80} in an HPLC chromatogram using a Buckyprep-M column, suggesting that the product is a strongly polar molecule. This phenomenon also supports the introduction of cyano groups onto $La_2@I_h$-C_{80}. Preparative HPLC techniques allowed the isolation of **1**. It is noteworthy that the reaction proceeded in a regioselective manner. Two different types of C−C bond in $La_2@I_h$-C_{80} are available for reaction with 1,3-dipoles. One is a C−C bond that bisects pentagonal and hexagonal rings (a [5,6] junction), and

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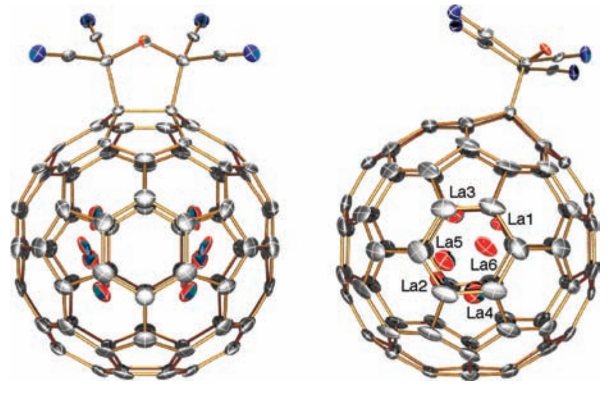
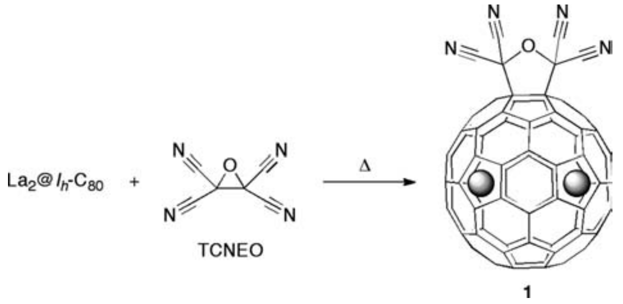


Figure 1. Two orthogonal views of the ORTEP plot of **1** at 90 K with thermal ellipsoids shown at the 50% probability level. Solvate molecules have been omitted for clarity.

Scheme 1



the other bisects two hexagonal rings (a [6,6] junction). We recently examined the reactivity of $La_2@I_h$-C_{80} with *N*-triphenylmethyl azomethine ylide and subsequently obtained both [6,6] and [5,6] adducts in a ratio of ~4:1.[16] In contrast, the presented TCNEO addition took place only at the [5,6] junction, showing that the carbonyl ylide and the azomethine ylide possess different reactivities toward $La_2@I_h$-C_{80}. Although the ^{13}C NMR spectrum provided no meaningful information related to the molecular structure because of the low solubility, the similarity in the absorption spectra of **1** and the [5,6]-pyrrolidino derivative gave positive evidence of possession of the [5,6] addition pattern (see Figures S2 and S4 in the Supporting Information). Finally, the molecular structure of **1** was observed unambiguously using single-crystal X-ray structure analysis. The crystal structure was solved with a space group of *Pnma*, in which the molecular structure of **1** has mirror-plane symmetry. The crystal structure shown in Figure 1 confirms that the addition took place at the [5,6] junction.

The obtained tetracyanotetrahydrofuran structure has an envelope conformation in which the oxygen atom is above the pentagon ring. Disorder involving the La atom locations is apparent in the cage interior, as found in the X-ray structure of a carbosilylated derivative.[17] As shown in Table 1, 12 La atoms have site occupation factors (SOFs) of 0.046−0.378 at 90 K. Because of the mirror plane symmetry, the 12 La sites come from six original locations, labeled as La1−La6. The symmetric expansion generates the other six sites, labeled as La1*−La6*, at the corresponding mirror positions. The La−La distances, in the range 3.811−3.816 Å, resemble those of the reported $La_2@I_h$-C_{80} derivatives.[16−18] The observation of the disordered La sites suggests that the La atoms have a large-amplitude motion inside the fullerene cage. The ^{139}La NMR spectrum of **1** exhibited a single signal, indicating that the two La atoms are magnetically equivalent. In addition, signal broadening with increasing temperature was observed, indicating that the La atoms have dynamic motion, as found in pristine $La_2@I_h$-C_{80} (see Figure S3).[19] The crysZtal packing shows an interesting short intermolecular contact. The CN groups of one molecule interact with the C−C bond of the cage of its neighbor with a shortest interatomic distance of 3.23 Å [CN···C(cage)] (see Figure S6). The intermolecular cyano−fullerene interaction is expected to be valuable for construction of a supramolecular network.

Table 1. Site Occupancy Factors (SOFs)^a and La−La Distances Determined Using Single-Crystal X-ray Crystallographic Analysis

La site	SOF	La pair	La−La distance (Å)
La1	0.378	La2*	3.816
La2	0.360	La1*	3.816
La3	0.076	La4*	3.816
La4	0.083	La3*	3.816
La5	0.057	La6*	3.811
La6	0.046	La5*	3.811

[a] SOFs were obtained independently for La1−La6.

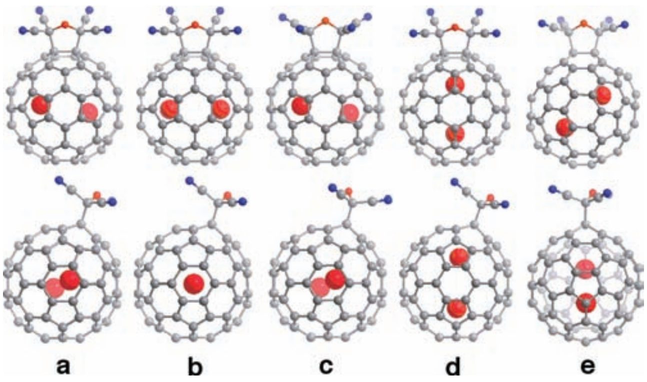


Figure 2. Optimized structures of $La_2@I_h$-C80−TCNEO adducts at the B3LYP/6-31G*~dz level (the LANL2DZ basis set was used for La; for further computational details, see the Supporting Information). Structures **a**−**d** correspond to [5,6] adducts, and structure **e** is a [6,6] adduct.

The experimental results are well-supported by density functional theory (DFT) calculations. Figure 2 depicts the fully optimized structures of the [5,6] adducts (**a**−**d**) together with that of the [6,6] adduct (**e**). Structures **a**, **c**, and **e** are local energy minima, while **b** and **d** represent activated complexes. Their relative potential energies are presented in Table 2. As the X-ray analysis shows, the [5,6] adduct having the oxygen atom above the pentagon ring of the carbon cage (structure **a**) is most stable. Structure **e** is 3.06 kcal mol^{-1} higher in energy than **a**, indicating that the [5,6] adduct is the thermodynamically stable product. Flipping of the envelope conformation of the tetracyanotetrahydrofuran ring changes the thermodynamic stability by just 1.89 kcal mol^{-1}. It is particularly interesting that the two La atoms in **a** are not equivalent and that the locations deviate from the horizontal plane. The [5,6] adduct with the equivalent La−La

Table 2. Ground-State Relative Energies Computed at the B3LYP/6-31G*∼dz Level[a] for Structures a−e

structure	La−La distance (Å)	relative energy (kcal mol^{-1})
a	3.720	0.00
b	3.746	4.44
c	3.721	1.89
d	3.715	17.18
e	3.718	3.06

[a] Values were obtained using the LANL2DZ basis set for La. For further computational details, see the Supporting Information.

Table 3. Redox Potentials[a] of $La_2@I_h$-C_{80} and Its Derivatives

compound	$^1E_{ox}$	$^1E_{red}$
1	+0.64[b]	−0.21
2a[c]	+0.11[b]	−0.50
2b[c]	+0.13[b]	−0.53
3[d]	−0.04[b]	−0.70
$La_2@I_h$-C_{80}[e]	+0.56	−0.31

[a] Values are given in V vs Fc/Fc^+ and were obtained using differential pulse voltammetry. [b] Irreversible. [c] Data from ref 17. [d] Data from ref 18b. [e] Data from ref 13.

orientation (structure **b**) is 4.44 kcal mol^{-1} higher in energy than **a**. However, the [5,6] adduct with the "vertical" La−La orientation (structure **d**) is 17.18 kcal mol^{-1} higher in energy than **a**. Therefore, it is reasonable to infer that the La atoms swing inside the cage because of this large energy difference in La−La orientation.

The remaining question was whether the electron-accepting character would be improved by the "indirect" introduction of the cyano groups. Our recent investigation into the electrochemistry of functionalized EMFs revealed that electron affinity of EMFs decreases upon functionalization, as found for empty fullerenes such as C_{60}.[12,20] In particular, the results showed that incorporation of a silyl substituent strongly affected the electronic properties of $La_2@I_h$-C_{80}: the reduction potentials of $La_2@I_h$-C_{80} were shifted cathodically to a great degree by silylation.[17,18b] In addition, the electronic modulation took place step-by-step according to the number of silicon atoms introduced on the cage. In fact, the first reduction potentials of the carbosilylated derivatives $La_2@I_h$-C_{80}($Dep_2Si(CH_2)CHtBp$) (two diastereomers **2a** and **2b**; Dep = 2,6-diethylphenyl, tBp = 4-*tert*-butylphenyl) were shifted cathodically to 190−220 mV, whereas that of the bis-silylated derivative $La_2@I_h$-C_{80}($Dep_2Si(CH_2)SiDep_2$) (**3**) was shifted cathodically by 390 mV relative to the reduction potential of pristine $La_2@I_h$-C_{80}.

In contrast to silylation, we found that addition of TCNEO strongly enhances the electron-accepting character. One irreversible oxidation and one reversible reduction processes were observed in the cyclic voltammograms of **1** (see Figure S5). As shown in Table 3, the results demonstrated that the first reduction potential of **1** was shifted anodically by 100 mV, reaching −0.21 V vs Fc/Fc^+. This finding underscores the fact that the electron-accepting character of EMFs, which are much stronger electron acceptors than C_{60}, can be improved further by TCNEO addition. It is noteworthy that this reported reduction potential is the lowest value reported to date for EMFs and their derivatives. The DFT calculations showed that the Mulliken charge of the addendum is −0.114, whereas those of the cage skeleton and two La atoms are −5.274 and +5.388, respectively. The results prove that the tetracyanotetrahydrofuran moiety withdraws charge density from $La_2@I_h$-C_{80} effectively. It is particularly interesting that the calculations showed the LUMO to be localized mainly on the two La cations (see Figure S8). Therefore, the results suggest that the addendum attached to the outer surface can affect the energy level of the LUMO. Further research based on this strategy will specifically examine the preparation of conducting organic salts containing derivatized EMFs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, spectroscopic data, crystallographic data (CIF), and theoretical results for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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