Fullerenes

Chemical Reactions of Cationic Metallofullerenes: An Alternative Route for Exohedral Functionalization

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Abstract: The chemistry of cationic forms of clusterfullerenes remain less explored than that of the corresponding neutral or anionic species. In the present work, $M_3N@I_h$-C_{80} (M = Sc or Lu) cations were generated by both electrochemical and chemical oxidation methods. The as-obtained cations successfully underwent the typical Bingel–Hirsch reaction that fails with neutral $Sc_3N@I_h$-C_{80}. Two isomeric $Sc_3N@I_h$-C_{80} cation derivatives, [5,6]-open and [6,6]-open adducts, were synthesized, and the former has never been prepared by means of a Bingel–Hirsch reaction with neutral clusterfullerenes. In the case of the $Lu_3N@I_h$-C_{80} cation, however, only a [6,6]-open adduct was obtained. Density functional theory (DFT) calculations indicated that the oxidized $M_3N@I_h$-C_{80} was much more reactive than the neutral compound upon addition of the diethyl bromomalonate anion. The Bingel–Hirsch reaction of $M_3N@I_h$-C_{80} cations occurred by means of an unusual outer-sphere single-electron transfer (SET) process from the diethyl bromomalonate anion to the stable intermediate $[M_3N@C_{80}(C_2H_5COO)_2CBr]^•$. Remarkably, the diethyl bromomalonate anion was found to act as both a nucleophile and an electron donor.

The chemistry of fullerenes continues to attract the interest of synthetic and materials chemists due to their fascinating properties and promising applications in energy and materials science.[1] Thus, it is important to explore new strategies to synthesize fullerene derivatives that are difficult to prepare.

Compared to the neutral and anion chemistry of fullerenes, the chemistry of oxidized cationic forms remains rarely studied and far from well understood. Although C_{60}^+ was found to exist in interstellar space,[2] it is challenging to obtain stable fullerene cations compared to the generation of their reduced counterparts.[3] Electrochemically oxidizing C_{60} to its cations C_{60}^{n+} ($n = 1–3$) was observed in cyclic voltammetry (CV) under highly demanding conditions.[4] Fullerene carbocations, such as C_{76}^+, C_{60}^+ and HC_{60}^+ can be stabilized only in the presence of ultra-strong oxidants, under radiolytic oxidation or in superacids.[5] Thus, directly oxidizing C_{60} to C_{60}^{n+} is extremely difficult and challenging. Alternatively, the C_{60} radical cation and organo[60]fullerenyl cation can be generated chemically with the assistance of Lewis acids such as $FeCl_3$ or $AlCl_3$ on a laboratory scale by one- or multistep procedures.[6] Since the first organo[60]fullerenyl cation-mediated reaction was reported by Olah et al.,[7] versatile fullerene cation intermediates have afforded a variety of unique and unexpected fullerene derivatives.[6] Recently, Matsuo and co-workers reported the formation of ArC_{60}^+ by pyrolyzing the corresponding dimers in the presence of $CuBr_2$ or $CuCl_2$, and a series of 5- and 7-membered cyclo[60]fullerene derivatives mediated by ArC_{60}^+ were synthesized for applications in organic solar cells or perovskite solar cells.[8]

In contrast, endohedral metallofullerenes (EMFs) are relatively easy to oxidize, as measured by cyclic voltammetry under ambient conditions, suggesting the feasibility of studying cation reactivity. Akasaka et al. reported the stabilities and chemical reactivities of cationic $M@C_{82}$ (M = Y, La, or Ce) obtained by chemical oxidation or by controlled potential electrolysis (CPE). The reaction between $[M@C_{82}]^+SbCl_6$ and 1,1,2,2-tetrakis-(2,4,6-trimethylphenyl)-1,2-disilirane afforded the corresponding 1:1 adducts, which are not accessible from the neutral or the corresponding anionic forms.[9] Yang and co-workers studied the spectroelectrochemical properties of the $Sc_3N@C_{68}$ radical cation formed by CPE.[10] Nevertheless, additional information about cationic EMFs and their corresponding reactivities is very scarce.

Neutral $Sc_3N@I_h$-C_{80}, which is the least reactive species of all endohedral fullerenes, does not undergo the typical Bingel–

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Hirsch reaction.[11] It only reacts in the presence of a strong base in more polar solvents and at elevated temperatures.[12] A [6,6]-open diethyl malonate derivative was the only product obtained. One of the steps of the Bingel–Hirsch reaction is the nucleophilic addition of the deprotonated bromomalonate anion to the fullerene cage.[13] Thus the introduction of a positive charge on $M_3N@I_h$-C_{80} (M = Sc or Lu) is expected to increase the reactivity of the cages, and the resulting cations should be more reactive toward nucleophiles than the neutral species. As a proof of concept, we conducted both the electrochemical and chemical oxidation of $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80} to generate $[Sc_3N@I_h$-$C_{80}]^+$ and $[Lu_3N@I_h$-$C_{80}]^+$ cations, respectively, and studied their reactivities under typical Bingel–Hirsch reaction conditions.[11]

$[M_3N@I_h$-$C_{80}]^+$ cations were obtained by controlled potential electrolysis of neutral $M_3N@I_h$-C_{80} at +1.0 V for M = Sc and +1.06 V for M = Lu versus a silver wire pseudoreference electrode in 15 mL o-dichlorobenzene (o-DCB) that contained 0.1 M tetrabutylammonium perchlorate (TBAP) under an argon atmosphere. The ultraviolet/visible/near-infrared (UV/Vis/NIR) spectra of the corresponding $[M_3N@I_h$-$C_{80}]^+$ ion generated by CPE are displayed in Figure S1 (Supporting Information). The as-formed $[M_3N@I_h$-$C_{80}]^+$ was then submitted to the typical Bingel–Hirsch reaction conditions[11] (Scheme 1, Route A, see the experimental details in the Supporting Information). Compounds **1** and **2** derived from $[Sc_3N@I_h$-$C_{80}]^+$ (Figure 1 a) and compound **3** from $[Lu_3N@I_h$-$C_{80}]^+$ (Figure S2, Supporting Information) were synthesized. Compounds $M_3N@I_h$-C_{80} (M = Sc or Lu) were also chemically oxidized to the corresponding cationic forms by treatment with a small excess tris(4-bromophenyl)aminium hexachloroantimonate ($(BrC_6H_4)_3NSbCl_6$, TPBAH), which has been used to oxidize $M@C_{82}$ (M = Y, La, or Ce) to the corresponding $[M@C_{82}]^+$ cations and to selectively separate I_h- and D_{5h}-$Sc_3N@C_{80}$ isomers by oxidation.[9,14] The as-obtained cationic $M_3N@I_h$-C_{80} compounds were then subjected to the typical Bingel–Hirsch reaction conditions (Scheme 1, Route B, see experimental details in the Supporting Information) and the same results were obtained as described in Route A. Two compounds (**1** and **2**) from $[Sc_3N@I_h$-$C_{80}]^+$ (Figure 1 a) and one (**3**) from $[Lu_3N@I_h$-$C_{80}]^+$ (Figure S2, Supporting Information) were isolated. These results clearly confirm the anticipated increased reactivity of cationic forms of $M_3N@I_h$-C_{80} toward the Bingel–Hirsch reaction.
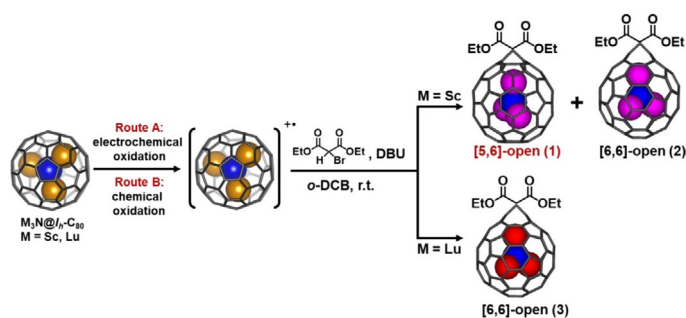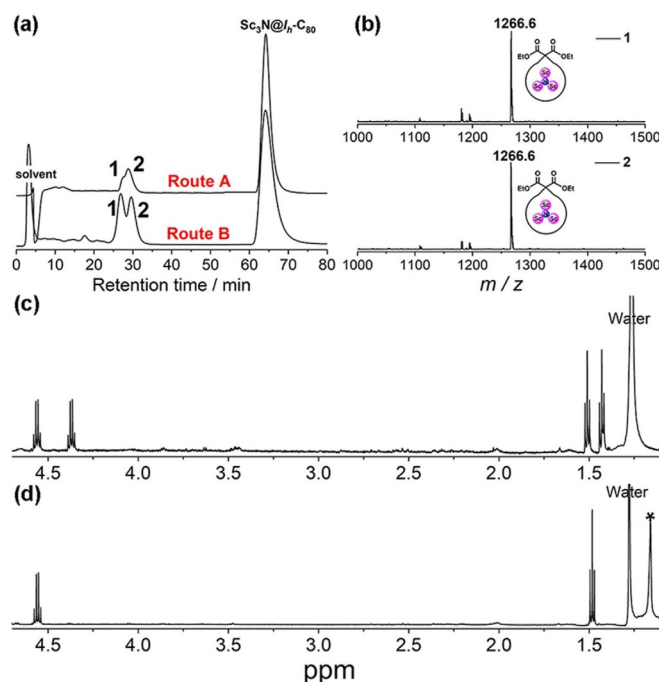

Figure 1. a) HPLC profiles of the reaction mixtures of cationic $Sc_3N@I_h$-C_{80} obtained from electrochemical oxidation (Route A) and chemical oxidation (Route B) after reaction with diethyl malonate. Conditions: 5PBB column (ϕ 10×250 mm); eluent: toluene, 5 mL min^{-1}. b) Negative ionization mode APCI-MS of **1** and **2**. ^{1}H NMR spectra (magnified) of c) **1** and d) **2** in CS_2/$CDCl_3$ (v:v = 2:1). Peak marked with asterisk corresponds to an unknown impurity.

The atmospheric pressure chemical ionization mass spectrometry (APCI-MS) measurements of **1** and **2** obtained from electrochemical oxidation (m/z = 1266.6 for $Sc_3N@C_{80}C(CO_2C_2H_5)_2$, Figure 1 b) and MALDI-TOF MS of **1** (m/z = 1267.305) and **2** (m/z = 1267.404) generated from chemical oxidation (Figure S3) confirmed the presence of two mono-Bingel adducts of $Sc_3N@I_h$-C_{80}. There are four possible structures for the mono-Bingel adduct of $Sc_3N@I_h$-C_{80}, [5,6]-closed/open and [6,6]-closed/open (Scheme S1, Supporting Information). The addition of diethyl malonate to a [5,6] bond leads to different proton nuclear magnetic resonance (NMR) patterns of the two –$COOC_2H_5$ groups. The ^{1}H NMR signals for the ethyl group of **1** (Figure 1 c) display two quartets (δ = 4.57 and δ = 4.38 ppm) and two triplets (δ = 1.51 and δ = 1.43 ppm). The observation of two sets of signals indicates a [5,6]-addition for **1**, which has never been previously observed for a Bingel–Hirsch reaction of a neutral clusterfullerene. In contrast, **2** displays only one set of signals, a quartet (δ = 4.56 ppm) and a triplet (δ = 1.48 ppm) (Figure 1 d), in agreement with the previously reported symmetrical [6,6]-Bingel product of $Sc_3N@I_h$-C_{80}.[12] ^{13}C NMR spectra of **1** and **2** were not possible due to the low quantities of the samples obtained. The UV/Vis/NIR absorption spectra of **1** and **2** (Figure S5, Supporting Information) are almost identical to that of $Sc_3N@I_h$-C_{80}. The retained electronic structure of the C_{80} cage upon malonate addition implies an open-cage fulleroid structure.[12,15] Thus, **1** is assigned a [5,6]-open structure and **2** a [6,6]-open structure. This is the

Scheme 1. Bingel–Hirsch reaction of $M_3N@I_h$-C_{80} (M = Sc or Lu) radical monocation under conventional conditions.

first time that a [5,6]-open Bingel product was obtained from a clusterfullerene.

The crystallographic determination of **2** provided solid evidence of the structure assigned based on the MS, NMR and UV/Vis/NIR measurements (Figure 2a). The C1—C2 bond of **2** at a [6,6] ring junction is broken and elongated to 2.159(15) Å,
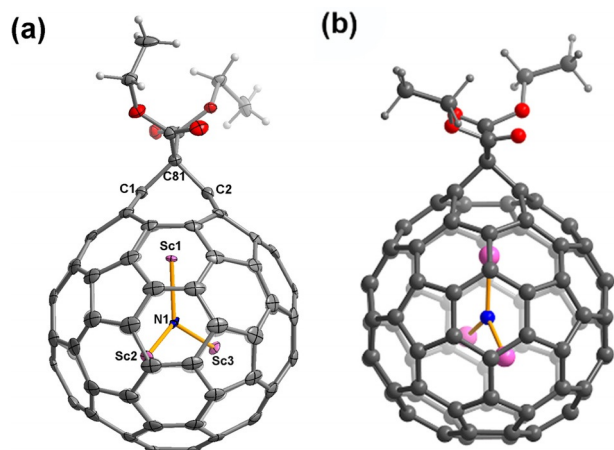

Figure 2. a) Crystal structure of **2** with 20% thermal contours for those atoms refined anisotropically. Only the predominant orientation of the Sc$_3$N group is shown. b) DFT optimized structure of **1**.

which is much longer than the average [6,6] C—C bond length in parent Sc$_3$N@I_h-C$_{80}$ (1.421 Å).[16] The inner Sc$_3$N cluster shows four disordered orientations, and only the major orientation with an occupancy of 0.4 is shown (see Figure S6 and detailed descriptions of the cluster in Supporting Information). The Sc$_3$N cluster is nearly planar with the sum of the three Sc-N-Sc angles being 358.8°. Notably, the Sc1 atom is adjacent to the broken bond, suggesting that this is the lowest energy orientation, which is in good agreement with the computed results.[13a] Although attempts to crystallize the [5,6]-adduct were not successful, the calculations showed that the [5,6]-open Bingel adduct was much more stable than the corresponding [5,6]-closed one.[13b] The density functional theory (DFT) optimized structure of the [5,6]-open adduct **1** is displayed in Figure 2b. The C—C bond at the open [5,6] ring junction is calculated to be 2.147 Å, which is very similar to the crystallographically determined bond length of **2** at the open [6,6] ring junction. Interestingly, the DFT optimized structure of **1** implies a reaction symmetry at addition site. Namely, no matter the addition site is at [5,6] bond or [6,6] bond, there is always a Sc atom that is oriented toward the open site. Similarly, the inner Sc$_3$N cluster is calculated to be a planar structure, of which the sum of three Sc-N-Sc angles is 360.0°.

The electrochemical properties of the [5,6]-open adduct (**1**) were studied by CV (Figure S7a, Supporting Information). Compound **1** displays electrochemically irreversible cathodic behavior resembling that of the [6,6]-isomer (Figure S7b and Table S1, Supporting Information), which is dramatically different from the reversible cathodic behavior of the [5,6]-pyrrolidino and [5,6]-benzyne monoadducts of Sc$_3$N@I_h-C$_{80}$.[11b,17] The

first and second reduction peak potentials are cathodically shifted by 50 and 140 mV, respectively, and the third is anodically shifted by 390 mV, relative to those of the parent Sc$_3$N@I_h-C$_{80}$. In 2013, Echegoyen et al. reported the first [5,6]-open methanofullerene derivative of Sc$_3$N@I_h-C$_{80}$,[15e] in which no oxidation processes were observed in the CV. However, the [5,6]-open Bingel adduct (**1**) exhibited quasi-reversible anodic electrochemical behavior with E_{pa} values of +0.53 and +1.01 V versus Fc/Fc$^+$ (Figure S7a and Table S1, Supporting Information).

All of the Bingel products of neutral M$_3$N@C$_{80}$ (M=Y,[11a,18] Er,[11b] Lu or Sc)[12] obtained under traditional or modified reaction conditions were [6,6]-adducts, and the [5,6]-isomer was never detected before. This indicates that either the [5,6]-adduct was not formed or it was converted to the corresponding [6,6]-adduct during thermal processing. Surprisingly, when the [Sc$_3$N@I_h-C$_{80}$]$^+$ cation is subjected to the Bingel–Hirsch reaction, the [5,6]-isomer is obtained, and it is thermally stable. After heating the [5,6]-adduct at 120°C for 3 h, neither conversion to the [6,6]-isomer nor decomposition of the product was observed (see Figure S8, Supporting Information).

Structural characterizations of **3** by MS, NMR and UV/Vis/NIR (Figure S9, Supporting Information) confirmed that **3** is a pure product. The APCI-MS of **3** (m/z = 1656.843 from Route A) and MALDI-TOF MS of **3** (m/z = 1657.731 from Route B) (Figure S9a) and a single set of ^{1}H NMR signals for **3** (Figure S9b) suggested a [6,6]-mono-Bingel product of Lu$_3$N@I_h-C$_{80}$.[12] The very similar absorption spectrum of **3** when compared to that of the pristine Lu$_3$N@I_h-C$_{80}$ confirmed that **3** is a [6,6]-open mono-Bingel adduct.[15a,c,19] Interestingly, the cationic form of Lu$_3$N@I_h-C$_{80}$ exhibited a different regioselectivity to that of the cationic Sc$_3$N@I_h-C$_{80}$.

The Bingel–Hirsch reactions of cationic forms of M$_3$N@C$_{80}$ (M=Sc or Lu) provide an alternative synthetic pathway to new derivatives through oxidation. A previous study of the Bingel–Hirsch reaction of clusterfullerenes revealed a gradual decrease in reactivity when the fullerene cage increased in size.[20] For example, Gd$_3$N@C$_{88}$, unlike Gd$_3$N@C$_{80}$ and Gd$_3$N@C$_{84}$, was completely unreactive under Bingel–Hirsch reaction conditions.[20] The findings presented here of oxidizing fullerene cages may be a viable way to increase the reactivity of larger-cage clusterfullerenes.

The mechanism of the Bingel–Hirsch reaction of neutral clusterfullerenes is well established.[13] Here, we propose an unusual but plausible mechanism for the Bingel–Hirsch reaction of the cationic clusterfullerenes. The proposal is based on a comparison between the reaction energy profiles for the addition of a diethyl bromomalonate anion to the [6,6] bond of neutral and cationic Sc$_3$N@I_h-C$_{80}$ (Figure 3). Initially, a proton is abstracted from diethyl bromomalonate (**I**) by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The deprotonated diethyl bromomalonate anion (**II$^-$**) can then attack a 666 carbon at a triplehexagon junction of the positively charged Sc$_3$N@I_h-C$_{80}$ (**4$^{+•}$**) to form the neutral intermediate [Sc$_3$N@I_h-C$_{80}$(C$_2$H$_5$COO)$_2$CBr]$^•$ (**5$^•$**), in which **II$^-$** is singly bonded to the cage. This process is strongly stabilized by approximately 40 kcal mol^{-1} (Figure 3 bottom); therefore, it is not expected to be reversible. Notably,
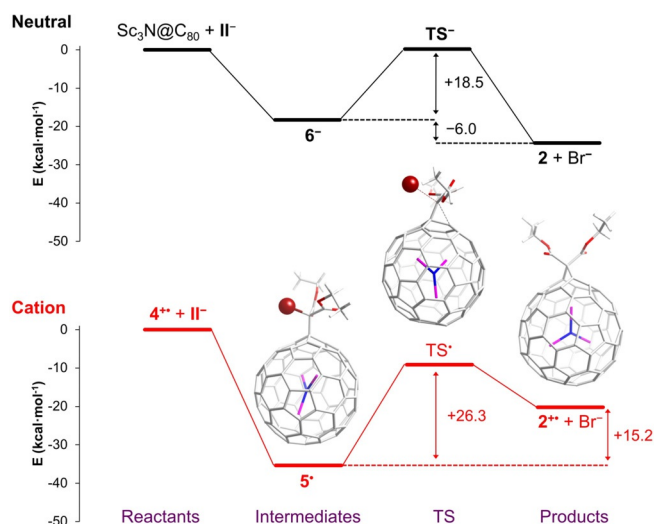
Figure 3. Top: Energy profile for a classical Bingel–Hirsch addition of bromomalonate to a [6,6] bond of neutral $Sc_3N@C_{80}$. Bottom: hypothetical equivalent reaction mechanism for $[Sc_3N@C_{80}]^+$.

the stabilizing character of this process in the neutral form of $Sc_3N@C_{80}$ is relatively low (18.5 kcal mol^{-1}) (Figure 3 top). These results indicate that the attack of II^- on the oxidized fullerene is highly favored, which accounts for the enhanced reactivity of cationic clusterfullerenes toward the Bingel–Hirsch reaction. In addition, the association of the anionic malonate fragment with a positively charged fullerene should be more favored than the fragment with a neutral cage due to the pairwise electrostatic attraction between both fragments. Previous DFT studies identified this step as a barrierless process.[13] To complete the reaction, a neighboring carbon atom of the fullerene must perform a nucleophilic attack on the malonate carbon atom to eliminate the Br^- anion through a classical S_N2 substitution mechanism.[13a] Attaining this process from the neutral intermediate $5^•$ in the cation profile requires overcoming a significantly high energy barrier of 26.3 kcal mol^{-1} (from $5^•$ to $TS^•$) compared to that of 18.5 kcal mol^{-1} (from 6^- to TS^-) in the neutral profile. This fact was ascribed to the higher nucleophilic character of the fullerene cage in 6^- than that of the electron-deficient $5^•$ species. In addition, we found that the given products in the cation profile, $2^{+•}$ and Br^-, were higher in energy than intermediate $5^•$ (15.2 kcal mol^{-1}), in contrast to what was observed for the Bingel–Hirsch reaction of neutral $Sc_3N@I_h$-C_{80} (products 2 and Br^-, are 6 kcal mol^{-1} below intermediate 6^-). Therefore, intermediate $5^•$ was very stable with respect to reactants and products, implying that the mechanism displayed for the cation profile was not possible for the $[Sc_3N@I_h$-$C_{80}]^+$ cation reaction. Thus, as an alternative, we propose a key step for this cation reaction: the use of DBU or diethyl bromomalonate anion (II^-) as an organic electron donor that transfers one electron to the cage of $5^•$, that is, an outer-sphere single-electron transfer (SET) process. Once the intermediate $5^•$ is reduced to 6^-, the reaction proceeds as a conventional Bingel–Hirsch reaction.

Both DBU and diethyl bromomalonate anion are potential electron donors. However, the reaction energy for DBU trans-

ferring one electron to $5^•$ is much higher than that with the diethyl bromomalonate anion (II^-) ($\Delta E = +32.3$ vs. $+0.9$ kcal mol^{-1}, respectively). Thus, II^- is more likely the electron donor in the proposed mechanism. To evaluate its ability to reduce the fullerene radical, the free energy barrier associated with SET from II^- to the 666 intermediate $5^•$ to obtain 6^- was estimated by the Marcus theory.[21] This theory has been successfully employed to study SET processes between endohedral metallofullerenes[22] and between a wide variety of complexes by means of DFT.[23] It relates the free energy barrier of an electron transfer process to the reaction free energy and to the reorganization energy (more detailed description of the Marcus theory and the computational strategy used here can be found in the Supporting Information). The reaction free energy from $5^•$ to 6^- at the M06 level is 0.5 kcal mol^{-1}, and the free energy barrier predicted by Marcus theory is rather small (2.7 kcal mol^{-1}, Table S2, Supporting Information), which suggests that the SET step is fast and thus is not a rate-determining process. In general, SET processes involving fullerenes are fast due to the small reorganization energies, which is the consequence of the delocalization of the extra electron over the cage that manifests in small geometrical changes in the structure and the solvent distribution upon reduction. Table S2 shows the reorganization energies obtained for $5^•$ and II^- that are within the range of values reported in the literature.[22, 24] Other hybrid functionals (B3LYP, Table S2) confirm these conclusions. When M = Lu, the reaction became endergonic ($\Delta G_r =$ 2.3 kcal mol^{-1}), and the free energy barrier was slightly higher (5.4 kcal mol^{-1}) than that with M = Sc as a consequence of an elevated reorganization energy of the fullerene (Table S2). Therefore, the SET process was slightly slower than that for M = Sc. The SET from II^- to $5^•$ generates a diethyl bromomalonate radical ($III^•$), which can then convert to a malonate dimer (IV) via a radical coupling reaction. As expected, the formation of IV was highly exothermic (reaction energy of -40.7 kcal mol^{-1}), which represents the driving force for the electron transfer and made the process irreversible. The formation of dimeric IV was confirmed by a high-resolution liquid chromatography coupled to mass spectrometry (LC-MS) measurement of the mixture of the Bingel–Hirsch reaction of $[Sc_3N@I_h$-$C_{80}]^+$. The LC signal of the diethyl bromomalonate dimer and its mass spectrum were observed (Figure S11, Supporting Information). A diethyl bromomalonate anion was found, for the first time, to act as a nucleophile and also as an electron donor during the Bingel–Hirsch reaction of the cationic $M_3N@I_h$-C_{80} (M = Sc or Lu).

Based on the results presented above, we propose the following mechanism for the formation of the [6,6]-open fulleroid 2 by the $[Sc_3N@I_h$-$C_{80}]^+$ cation reaction. As shown in Scheme 2, the neutral $Sc_3N@I_h$-C_{80} is oxidized to the radical monocation $4^{+•}$, which can be attacked by a diethyl bromomalonate anion (II^-) to form intermediate $5^•$. An additional diethyl bromomalonate anion (II^-) then acts as an organic electron donor to cage of $5^•$, that is, a SET process. Once the intermediate $5^•$ is reduced to 6^- by electron transfer, the reaction proceeds as a conventional Bingel–Hirsch reaction. The anion in 6^- attacks the bromomalonate carbon to substitute for Br^-.
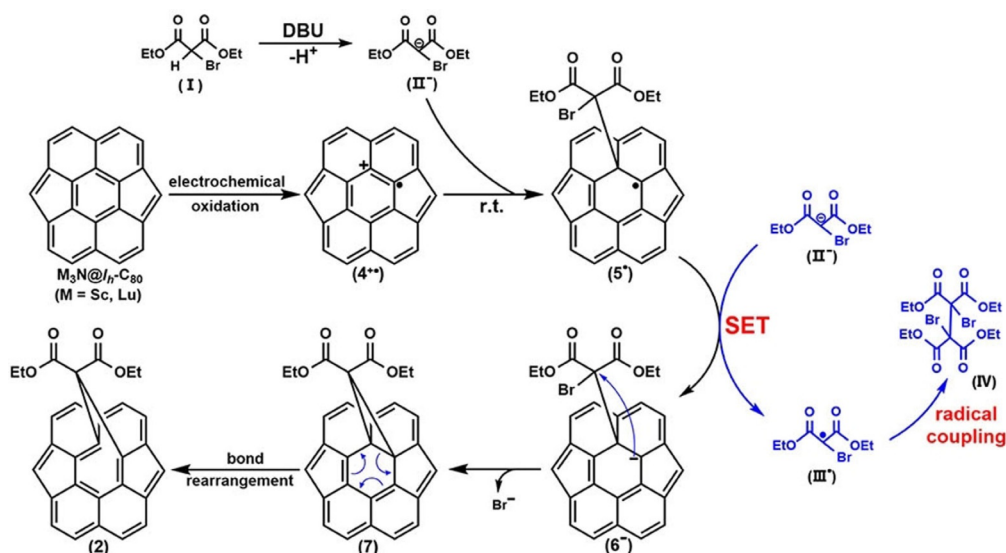
Scheme 2. Proposed reaction mechanism of Bingel–Hirsch reaction of $M_3N@I_h$-C_{80} (M = Sc, Lu) monocations.

The methano-adduct **7** then converts to the open-cage fulleroid **2** through a bond rearrangement process involving the cleavage of the cyclopropane ring. The proposed mechanism for the formation of the [5,6]-open fulleroid **1** is completely analogous.

The cationic forms of $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80} were found to display different regioselectivity, which has never been observed for the corresponding neutral forms. In order to gain additional understanding of this observation, the reaction energy profiles for both M = Sc and Lu and for both the formation of the [6,6]-adduct and the [5,6]-adduct were calculated (Figure 4). The addition of **II⁻** to the cationic fullerene was strongly exothermic in all cases; thus, it was reasonable to presume an equal distribution among 566 and 666 addition sites for intermediate **5·** (see structures in Scheme S2, Supporting Information). As the reduction does not involve bond breaking or formation within the fullerene structure, this site distribution should be maintained for **6⁻**. The energy barrier to form the [6,6]-open fulleroid product was 18.5 kcal mol⁻¹ when M = Sc (Figure 4), while the formation of the analogous [5,6]-product needs to overcome a slightly elevated energy barrier (by 3.8 kcal mol⁻¹), although it was still moderate. When M = Lu, the energy barrier for the formation of the [6,6]-adduct (20.5 kcal mol⁻¹) was very similar to that of M = Sc (18.5 kcal mol⁻¹). Nevertheless, the difference between the energy barriers to yield the [6,6] and the [5,6] product was significantly higher for M = Lu (8.3 kcal mol⁻¹) than for M = Sc (3.8 kcal mol⁻¹), which can explain the different regioselectivity of $[Sc_3N@I_h$-$C_{80}]^+$ and $[Lu_3N@I_h$-$C_{80}]^+$ for the Bingel–Hirsch reaction.

In summary, the chemistry of cationic forms of clusterfullerenes was explored in terms of formation, reactivity and regioselectivity. The positive charge on the cage of $M_3N@I_h$-C_{80} (M = Sc or Lu) enhanced their reactivity toward the classical Bingel–Hirsch reaction, and the reaction proceeded after an outersphere SET process occurred. The diethyl bromomalonate
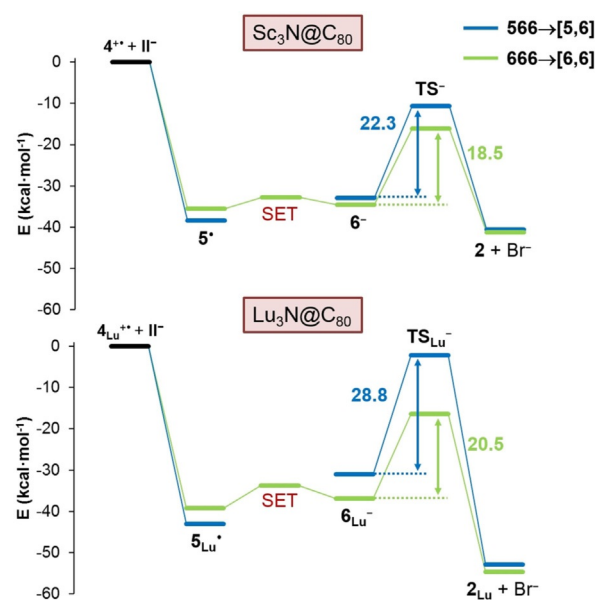

Figure 4. Comparison of the energy profiles for the Bingel–Hirsch additions on $M_3N@C_{80}^+$ cations for M = Sc (top) and Lu (bottom). Blue and green lines represent the energy profiles for Bingel–Hirsch additions to 566 and 666 C atoms of the fullerene, respectively. The free energy barrier for the SET process from **5·** to **6⁻** was estimated by means of the Marcus theory (see Computational details section). As the SET process is not expected to be rate-limiting in any case, it was only computed for isomer 666 (green line).

anion was found to play a dual role as both a nucleophile and as a reducing agent. For the first time, the missing [5,6]-open Bingel adduct of $Sc_3N@I_h$-C_{80} was synthesized and was shown to be stable. Furthermore, the different regioselectivity of $[M_3N@I_h$-$C_{80}]^+$, in which M = Sc (with the [6,6] and [5,6] products) and M = Lu (with only the [6,6] product), was explained on the basis of their reaction energy profiles. Cationic forms of clusterfullerenes exhibited chemical properties that are different from those of the corresponding neutral and anionic

forms. These findings promote a better understanding of EMFs cations and offer a complementary strategy to activate and functionalize EMFs.

Experimental Section

Material and methods, the experimental details, the computational details and the characterizations of products **1**, **2** and **3** were in the Supporting Information.

Conflict of interest

The authors declare no conflict of interest.

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