

Review

Capturing Unstable Metallofullerenes

Fupin Liu * and Alexey A. Popov *

Leibniz Institute for Solid State and Materials Research (IFW Dresden), 01069 Dresden, Germany

* Correspondence: liu_fupin@outlook.com (F.L.); a.popov@ifw-dresden.de (A.A.P.)

Abstract: Metallofullerenes are interesting molecules with unique structures and physicochemical properties. After they are formed in the arc-discharge process, they are first buried in the carbon soot, which requires solvent extraction to fish them out, normally followed by HPLC separation. In this minireview, we summarize the main procedures developed to obtain pure metallofullerenes, including well-established extraction with conventional fullerene solvents followed by HPLC (procedure **I**) as well as several methods developed for isolation and purification of unstable fullerenes insoluble in conventional fullerene solvents, including chemical modification followed by dissolution (**II.1**), chemical functionalization *during* extraction followed by HPLC (**II.2**), and chemical functionalization of ionic EMFs *after* redox-extraction followed by HPLC (procedure **II.3**). The main focus here is on procedure **II.3**, for which the current status and future perspective are discussed.

Keywords: endohedral metallofullerenes; extraction; open-shell electronic structure; electrophilic trifluoromethylation; benzylation

1. Introduction

Endohedral metallofullerenes (EMFs) are molecules with metal ions encapsulated in a fullerene cage, which are interesting because of their unique coordination between metal ions and the fullerene cage, resulting in fascinating physicochemical properties [1–52]. The pursuit of novel EMF structures has been a strong impetus in the field, not only for the discovery of a bizarre interplay between metal ions and fullerene cages, but also for their appealing application potentials endowed by this unique interaction. Metallofullerenes are usually prepared by direct current arc discharge of graphite rods embedded with a metal source. However, this process simultaneously produces EMFs, empty fullerenes, as well as other carbonaceous species, and the EMFs are then fished out of the carbon soot. The general procedure uses extraction with some organic solvents to dissolve metallofullerenes from the carbon soot, followed by separation procedures to obtain pure compounds (Procedure **I**, Figure 1). CS₂ is the most commonly used solvent during the extraction, although toluene, chlorobenzene and other aromatic solvents are also applied occasionally; we will refer to this group of solvents as **fullerene solvents** in the following discussion. Separation of the dissolved fullerenes is usually performed by high-performance liquid chromatography (HPLC), but may also include some non-HPLC steps.

Procedure **I** prevails in the EMF research because many fullerenes/metallofullerenes are well soluble in these solvents, and the extraction procedure is relatively straightforward. However, there is a certain fraction of fullerenes that show moderate to negligible solubility in fullerene solvents. These fullerenes therefore remain in the soot after extraction with fullerene solvents, but their formation in the arc-discharge synthesis could be demonstrated by extraction with other solvents or chemical functionalization, as will be discussed further in this review. In the following, we define **stable fullerenes** as those fullerenes that can be routinely obtained by Procedure **I**, while **unstable fullerenes** are those that cannot be obtained by this procedure due to poor solubility in fullerene solvents at the extraction and separation stages. The boundary between stable and unstable fullerenes is not clearly defined. Fullerenes are usually considered stable if their solution in



Citation: Liu, F.; Popov, A.A. Capturing Unstable Metallofullerenes. *Inorganics* **2024**, *12*, 48. <https://doi.org/10.3390/inorganics12020048>

Academic Editor: David Turner

Received: 18 January 2024

Revised: 27 January 2024

Accepted: 29 January 2024

Published: 31 January 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

fullerene solvents remains intact for months, i.e., long enough to complete the separation and characterization procedures.

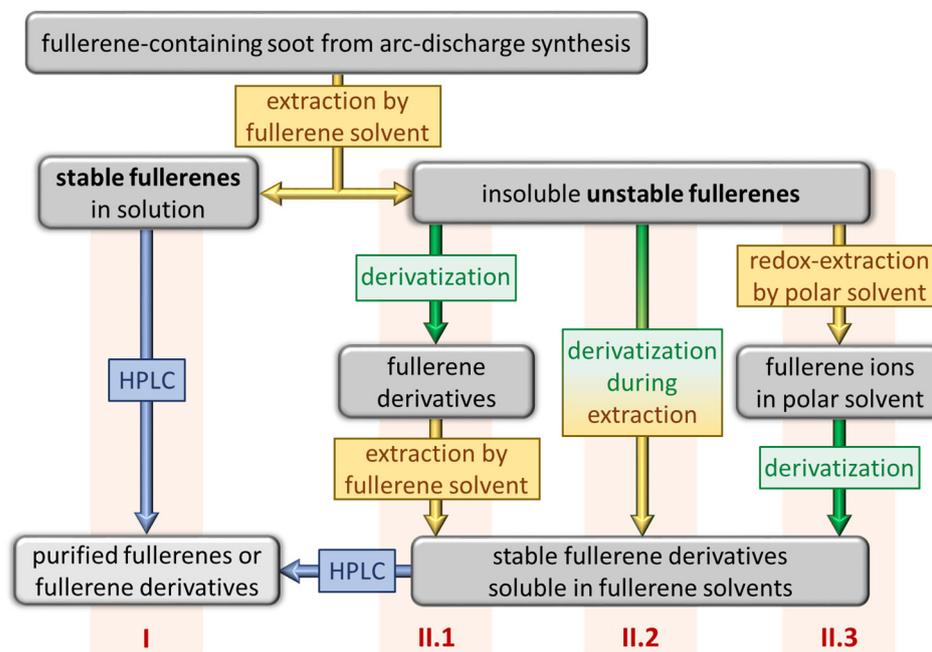


Figure 1. Schematic description of fullerene separation procedures discussed in this minireview.

2. Unstable Fullerenes

It should be emphasized that the stability discussed here is not stability in the thermodynamic sense. The **unstable fullerenes**, which are the focus of this review, are formed during synthesis, and if we assume that the yield of fullerenes in the arc-discharge process is controlled by thermodynamic factors, we should also assume **thermodynamic stability** of these unstable fullerenes. In other words, the relative energies of these structures with respect to different cage isomers should be low, and calculations of equilibrium concentration at the temperature of the synthesis will likely predict considerable concentration for these fullerenes. Therefore, it is their low **kinetic stability** or, equivalently, high reactivity, that poses the problem for their isolation and characterization. The high reactivity is usually related to the electronic structure and can be deduced from the analysis of the frontier orbital levels. Examples of frontier orbital situations in three types of fullerenes, which often have unstable structures among them, are shown in Figure 2:

- (1) Empty fullerenes. Soluble empty fullerenes have a large HOMO-LUMO gap and a closed-shell electronic structure with the singlet ground state. However, if the HOMO-LUMO gap is small, the triplet (biradical) state may be accessible or even become lower in energy than the singlet (Figure 2a). The molecule thus has an open-shell electronic structure, which is usually synonymous with enhanced reactivity. A typical example of an insoluble empty fullerene with a triplet ground state is $D_{3h}\text{-C}_{74}$ [53].
- (2) Monometallofullerenes with trivalent metals, $M^{\text{III}}@C_{2n}$ (Figure 2b). Since endohedral metal atoms transfer their electrons to the fullerene cage, the M^{III} state implies that the fullerene cage accepts three electrons and thus has a radical nature with one unpaired electron. Interestingly, some monometallofullerenes, such as $M^{\text{III}}@C_{2v}(9)\text{-C}_{82}$, behave as stable fullerenes and can be obtained in pure form by procedure I, while the others, such as $M^{\text{III}}@C_{60}$ or $M^{\text{III}}@C_{2v}(5)\text{-C}_{80}$, are insoluble in fullerene solvents and require special procedures for extraction and isolation. $M^{\text{III}}@C_s(6)\text{-C}_{82}$ is a good example of a dual behavior as it shows reasonable solubility and can be obtained by conventional procedure I, but tends to form dimers upon crystallization [54,55]. The boundary

- between the two types is blurred, indicating that the peculiarities of the π -system distribution for a given carbon cage also play an important role.
- (3) Dimetallofullerenes of trivalent metals (Figure 2c). Their situation in some way resembles that of empty fullerenes since the transfer of six electrons from the metal dimer to the host fullerene should result in a closed-shell electronic structure. Indeed, dimetallofullerenes of early lanthanides, such as $\text{La}_2@C_{2n}$ and $\text{Ce}_2@C_{2n}$, are soluble in fullerene solvents and can be purified using procedure I. The difference from empty fullerenes is that the LUMO of dimetallofullerenes is usually a metal–metal bonding orbital, and its energy depends on the metal. For heavier lanthanides, starting with Nd, the energy of the metal-based LUMO becomes so low that the triplet state, in which one unpaired electron occupies the metal-based MO and one occupies the fullerene MO, becomes more stable than the closed-shell singlet [56,57].
 - (4) Clusterfullerenes, i.e., metallofullerenes with endohedral clusters such as M_3N , M_2C_2 , M_2O , M_2S , etc., usually have a closed-shell electronic structure of the carbon cage, and the vast majority of them can be obtained from the soot and separated by procedure I. It is certainly possible that some of them are unstable due to the small HOMO–LUMO gap of the carbon cage, similarly to insoluble empty fullerenes, but we are not aware of any experimentally characterized examples of clusterfullerenes that are not soluble in fullerene solvents but could be extracted and separated by other approaches. Clusterfullerenes are therefore not discussed further in this review.

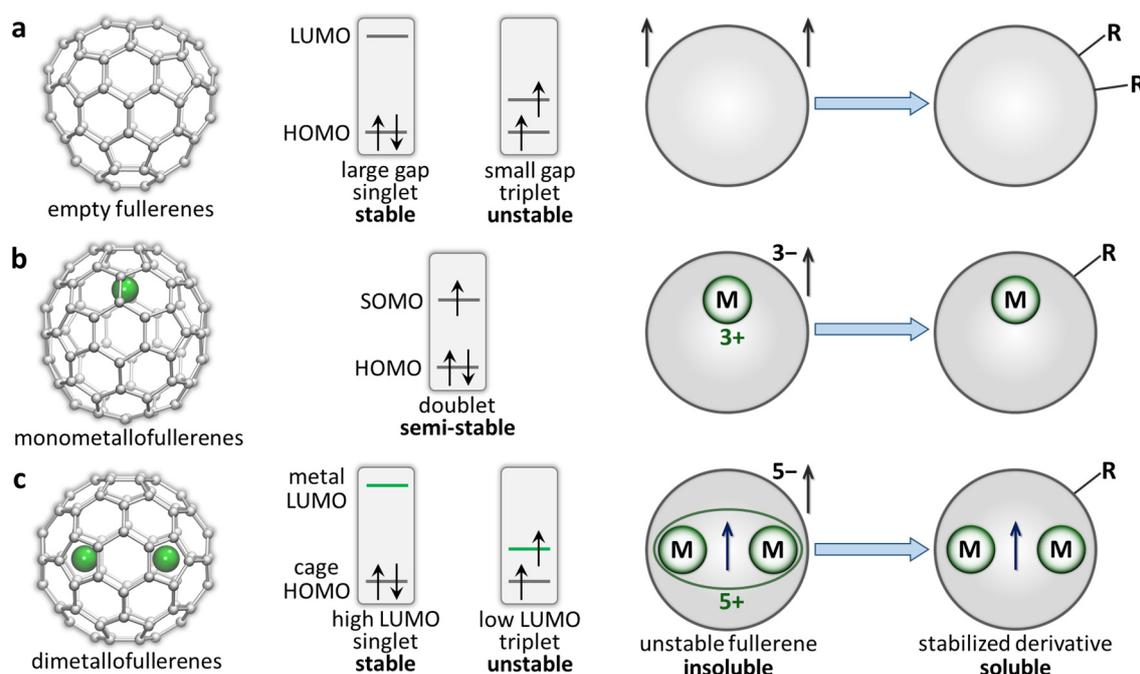


Figure 2. Major types of unstable fullerenes: (a) empty fullerenes, (b) monometallofullerenes with trivalent metals, (c) dimetallofullerenes with trivalent metals. For each type, the figure shows an example of a molecular structure (left), population of the frontier MOs (middle; fullerene MO levels are gray, metal-based MO levels are green), formal charge of the metal species and the cage (b,c) and stabilization of the open-shell electronic structure of the carbon cage by addition of radical groups (right). Vertical arrows denote unpaired electrons.

The low solubility of unstable fullerenes is likely caused by the tendency of fullerene cages to stabilize their open-shell structure by forming covalent bonds between fullerene molecules (dimerization/polymerization) or by forming bonds with other unidentified components of the soot. Either way, polymerization or binding to soot particles renders unstable fullerenes poorly soluble and causes them to remain in the soot during extraction with fullerene solvents. Importantly, it is the open-shell structure of the carbon cage

that is critical for kinetic stability and separation of EMFs. Endohedral species can also have an open-shell electronic structure, but it does not affect the kinetic stability if the fullerene cage has closed-shell electronic structure. For instance, dimetallo-azafullerenes $M_2@C_{79}N$ ($M = Y, Gd, Tb$) [58,59], trimetal-carbide clusterfullerenes $M_3C_2@C_{80}$ ($M = Sc, Dy, Er$) [60–62] or dimetallofullerenes derivatives $M_2@C_{80}(R)$ ($M = \text{rare earth elements}$) [63–67] have unpaired electrons localized on their endohedral species, but this does not hinder their solubility in fullerene solvents and their overall kinetic stability.

3. Redox Extraction

Extensive studies of metallofullerene synthesis in the late 1990s revealed that while the solubility of some metallofullerenes in fullerene solvents is low, it can be greatly enhanced if extraction is performed using polar nitrogen-containing solvents such as pyridine, *N,N*-dimethylformamide (DMF), or aniline [68–79]. Subsequent studies found that EMFs in these solvents adopt the negative charge state [80,81], suggesting that stabilization of insoluble EMFs, which allows their extraction, occurs via the electron transfer from the solvent. Indeed, since unstable metallofullerenes have an open-shell electronic structure in their pristine neutral form, the addition or removal of an electron can change the fullerene structure to the closed-shell, while endohedral metal species can still retain their spin structure. The process by which fullerenes are reduced or oxidized during extraction with a polar solvent is hereafter referred to as **redox extraction**. Redox extraction requires the presence of either reducing agents (amines [74–79], which can simultaneously be a solvent), or oxidizing agent (magic blue $(BrC_6H_4)_3NSbCl_6$, $AgSbF_6$) [82–85], or the use of electrolysis [70,86]. Ionic fullerenes are not soluble in most fullerene solvents and instead require the use of highly polar solvents, whereas uncharged fullerenes are conversely poorly soluble in many polar solvents. Therefore, redox extraction can be used not only for extraction of unstable fullerenes, but also for a partial separation of fullerenes based on their redox properties.

One of the most popular forms of redox extraction in EMF synthesis applies DMF [72,73,81,87–90], which undergoes partial thermal decomposition during extraction with the formation of amines. Hereby, amines act as mild reducing agents, facilitating the formation of EMF anions that are well soluble in DMF. Meanwhile, fullerenes with large HOMO-LUMO gap, including the majority of empty fullerenes, remain in the uncharged state. Since the solubility of neutral fullerenes in DMF is rather modest, extraction with hot DMF is quite efficient for dissolving of mono- and dimetallofullerenes and separating them from empty fullerenes [91,92].

Redox extraction helps to obtain unstable fullerenes from a soot as charged species, but their further separation is less straightforward. To date, $Li@C_{60}$ is the only unstable fullerene that has been isolated in a pure cationic form by redox methods [84,85]. HPLC procedures and column materials used for fullerene separation have been developed for uncharged fullerenes, and their efficiency for ionic species is not guaranteed. In addition, polar solvents normally used for unstable fullerenes, such as DMF or aniline, have high boiling points and are toxic, which adds obstacles for further separation by multi-step HPLC. Therefore, the separation of fullerenes extracted with DMF usually involves non-HPLC methods, such as electrochemical or chemical redox reactions, which change the charge state of the dissolved fullerenes and thus strongly affect their solubility [70,86,90,92,93]. The disadvantage of this strategy is that the redox reaction is not only controlled by the intrinsic redox potentials of the fullerenes, but also strongly affected by their concentrations. This means that very high purity separations can hardly be achieved by this method, and HPLC is still required in the final step. If dissolved anionic EMFs are also stable in the pristine form, they can be oxidized to the neutral form and then separated by HPLC [90]. However, if neutral EMFs are unstable, the oxidation of their anions will obviously produce open-shell species with ensuing low kinetic stability and solubility problems. For instance, attempts in our laboratory to obtain dimetallofullerenes of heavy lanthanides by oxidation

of their DMF-soluble anions immediately formed insoluble precipitates that could not be further processed.

4. Chemical Functionalization of Unstable Fullerenes

4.1. General Remarks

An alternative approach to stabilize fullerenes with open-shell electronic structure is their chemical derivatization by attachment of exohedral groups, which should quench unpaired electrons of the carbon cage. Obviously, each unpaired cage electron can be compensated by the addition of one radical group, and therefore, we will only consider derivatization with groups that form single bonds to the fullerene surface. Cycloaddition reactions, which usually introduce two bonds to a fullerene at once, are not suitable for stabilization of EMFs with the open-shell electronic structure of the fullerene cage. Figure 2 sketches the minimum number of groups that are required to stabilize different types of unstable fullerenes:

- (1) Empty fullerenes with triplet ground state require the addition of at least two radical groups to quench the cage biradical. However, it is not guaranteed that the bisadduct $C_{2n}(R)_2$ will have a large HOMO-LUMO gap. Depending on the MO structure of the molecule, the bisadduct may also have a small gap, thus requiring the addition of another pair of radical groups. However, regardless of how many pairs of radical groups are ultimately required to obtain a stable derivative, it is certain that the number of groups will be even.
- (2) Monometallofullerenes $M^{III}@C_{2n}$ have one unpaired electron, and therefore require the addition of at least one radical group. In general, the number of groups in the stable closed-shell $M^{III}@C_{2n}(R)_x$ derivative should be odd.
- (3) Open-shell dimetallofullerenes of trivalent metals are peculiar in that of the two unpaired valence electrons, one is localized on the fullerene cage and one on the metal dimer. The latter does not seem to be relevant for the kinetic stability, which means that only the unpaired electron of the cage should be quenched. Therefore, dimetallofullerenes require the addition of at least one and generally odd number of groups, similarly to monometallofullerenes.

Once unstable fullerenes are stabilized by derivatization, they can be processed akin to stable fullerenes, since derivatives are soluble in fullerene solvents and can be separated by conventional HPLC to achieve high-purity separation. This strategy will be referred to as Procedure II.

4.2. Derivatization Followed by Dissolution

Depending on the sequence of derivatization and extraction, three modifications of Procedure II can be distinguished, as shown in Figure 1. In method II.1, chemical derivatization is first applied to insoluble unstable fullerenes. A classic example is the thermal radical trifluoromethylation of a mixture of insoluble empty fullerenes (left after pre-extraction of stable fullerenes with *o*-dichlorobenzene) by CF_3I gas [94]. This procedure resulted in a series of $C_{2n}(CF_3)_{12}$ derivatives that exhibited high HOMO-LUMO gaps and good solubility in fullerene solvents. Separation of the mixture by HPLC and subsequent ^{19}F NMR and/or single-crystal X-ray diffraction studies of purified derivatives revealed the formation of some previously unreported empty fullerenes, such as $D_{3h}-C_{74}$, T_d-C_{76} , $D_{3h}(5)-C_{78}$, $C_{2v}(5)-C_{80}$, or $C_2(5)-C_{82}$ [94,95]. More recently, Shinohara et al. modified the method by adding polytetrafluoroethylene into the arc-discharge generator, thus performing the reaction in situ, before any extraction step [96]. Applying this procedure in the synthesis of Y, La, and Gd EMFs, they were able to isolate CF_3 derivatives of several elusive monometallofullerenes, including $M@C_{60}$, $M@C_{70}$, $M@C_{72}$, $M@C_{74}$, etc., and determine their molecular structures by single-crystal X-ray diffraction [96–99]. In situ chlorination [100–102] and hydrogenation [103–105] during fullerene formation, which allowed the capture of many unstable and nonclassical empty fullerenes in the form of chlorides and hydrides, can also be considered as a version of Procedure II.1, but its application to metallofullerenes has not

been very successful so far: halogenated EMF species have been detected in mass-spectra, but not yet isolated in bulk form [106].

4.3. *In Situ Derivatization during Extraction*

One notable breakthrough in the stabilization and isolation of unstable metallofullerenes by their chemical derivatization was made by Akasaka and colleagues (Procedure II.2 in Figure 1). They found that halogenated benzenes, such as 1,2,4-trichlorobenzene [25] or iodobenzene [107], which act as good fullerene solvents for stable fullerenes, can also be a source of aryl radicals that functionalize unstable fullerenes and make them soluble in the form of aryl monoadducts. The solvent thus plays a dual role, as a reactant in the addition reaction of unstable fullerenes and simultaneously as a solvent for stable fullerenes and stable derivatives of unstable fullerenes. Conventional HPLC can then be used in further separation steps. This *in situ* chemical functionalization during the extraction was successful in fishing out a number of unstable metallofullerenes, such as La@C₇₂ [108] La@C₇₄ [109,110], La@C₈₀ [111], and minor isomers of La@C₈₂ [112]. Since these EMFs could not be isolated in their pristine form by Procedure I, they were dubbed as “missing fullerenes” by the authors. A detailed review of this strategy can be found in Ref. [25]. The success of procedure II.2 is limited by the reactivity of the applied solvent/reactant to the targeted metallofullerenes. It has not been possible to identify a universal solvent/reactant for all types of metallofullerenes, because the reactivity of metallofullerenes varies so much based on the topology of the π -electron distribution and the energetics of the frontier orbitals. For example, we have found that the derivatization and isolation of highly interesting dimetallofullerenes with a single-electron metal–metal bond is not feasible via the *in situ* chemical functionalization strategy.

4.4. *Redox-Extraction and Derivatization of Anions*

The stabilization/separation strategy that appeared to be successful for unstable dimetallofullerenes is denoted in Figure 1 as Procedure II.3. In the first step, EMFs are redox-extracted from the soot with hot DMF, resulting in a mixture of EMF anions. As discussed above, the separation of the EMF anions is not straightforward. Instead, EMF anions can be chemically functionalized to produce stable neutral derivatives. For instance, thermal trifluoroalkylation of a dried Y-EMF mixture extracted with DMF gave a mixture of EMF-CF₃ derivatives, from which pure Y@C₈₂(CF₃)₅ was isolated by HPLC and characterized by NMR [113].

Recently, we have developed two versions of Procedure II.3, which involved the functionalization of the metallofullerene anions with the formation of neutral compounds. Hereby, the insoluble metallofullerenes are converted into derivatives that are soluble in fullerene solvents and can be further separated by HPLC to obtain the derivatives of desired metallofullerenes in high purity. In the first method, we successfully applied benzyl bromide PhCH₂Br to react with the metallofullerene anions in DMF [66]. The reaction required mild heating and presumably proceeded as a nucleophilic substitution of bromide with metallofullerene anions, producing benzyl monoadducts of metallofullerenes (see Figure 3a for details). An alternative mechanism, proposed in Ref. [114], involves the electron transfer from the EMF anion to benzyl bromide in the first step, followed by the radical coupling reaction. The benzyl derivatives of metallofullerenes are well soluble in fullerene solvents, allowing their subsequent HPLC separation to yield the high-purity compounds. Using this strategy, we have synthesized and isolated a series of dimetallofullerene derivatives M₂@I_h-C₈₀(CH₂Ph) (M₂ = Sc₂, Y₂, Gd₂, Tb₂, TbY, TbGd, Dy₂, Ho₂, Er₂), among which Tb₂@C₈₀(CH₂Ph) and Dy₂@C₈₀(CH₂Ph) show particularly remarkable single-molecule magnetic properties [20,65–67].

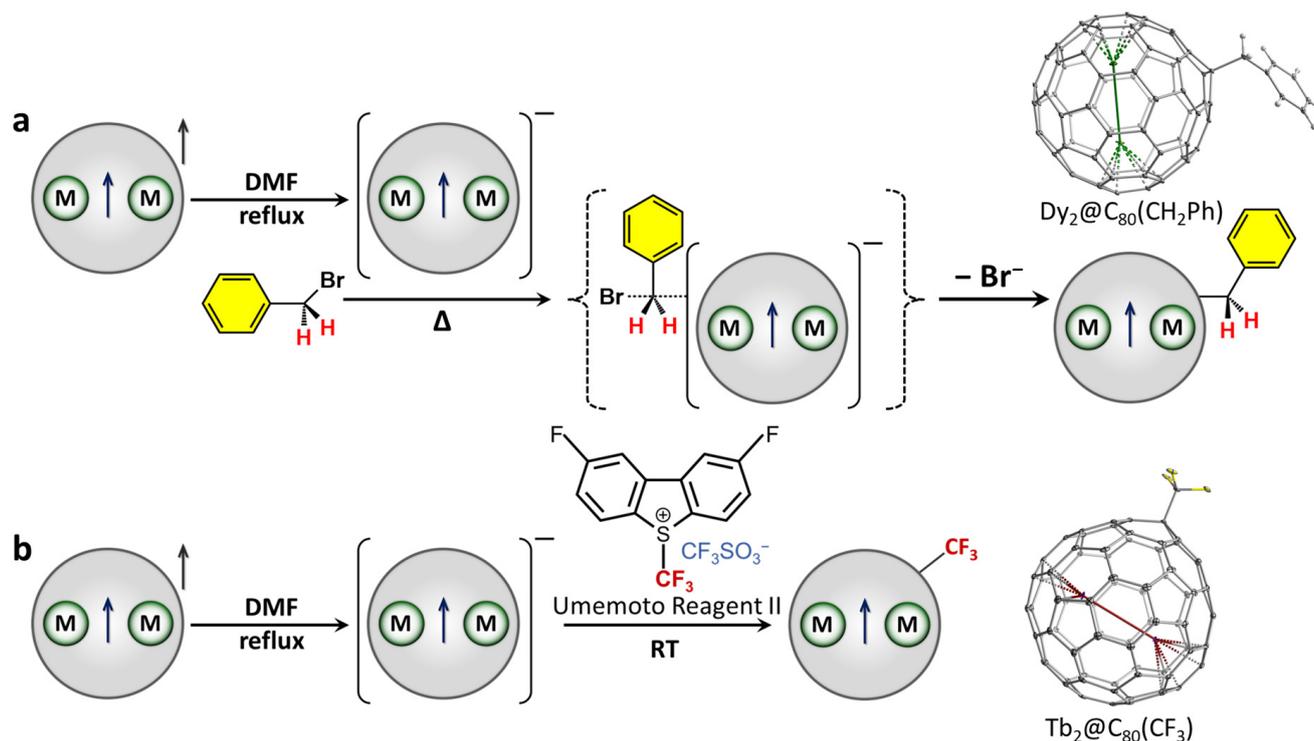


Figure 3. Two modifications of procedure II.3: (a) benzyl bromide route applied to stabilize $M_2@C_{80}$ in the form of $M_2@C_{80}(CH_2Ph)$; (b) CF_3 functionalization route leading to $M_2@C_{80}(CF_3)$. Also shown are molecular structures of $Dy_2@I_h-C_{80}(CH_2Ph)$ and $Tb_2@I_h-C_{80}(CF_3)$ determined by single-crystal X-ray diffraction in Refs. [66,115]. Vertical arrows denotes unpaired electron localized on the metal-metal bond.

The unusual magnetic properties are the reason why, until recently, the main focus in the exploitation of the anion functionalization strategy II.3 has been on the dimetallofullerenes $M_2@I_h-C_{80}$. However, $M_2@I_h-C_{80}$ with a single-electron metal–metal bond is not the only unstable EMF that can be solubilized in the anionic form during DMF extraction. In fact, the DMF extract contains anions of many monometallofullerenes, and, similarly to $M_2@C_{80}^-$, they also undergo mono-benylation in the reaction with benzyl bromide. This procedure can thus be used to fish out other unstable “missing” EMFs from the fullerene soot. Recently, Yang and colleagues used the benzyl bromide functionalization route to successfully isolate and structurally characterize $Dy@C_{80}(CH_2Ph)$ with the $C_{2v}(5)$ cage isomer [116]. Since $Dy@C_{2v}(5)-C_{80}$ is not soluble in fullerene solvents, it had never been properly characterized in the previous studies of Dy-EMFs. This example shows that the benzylation route can be very useful for the stabilization and structural elucidation of various unstable EMFs, and it is very likely that its exploration will help in the discovery of novel elusive fullerene structures.

The versatility of the thermal reaction with benzyl bromide in its application to EMF anions, while being very useful for exploratory studies, becomes a drawback when targeting a specific EMF derivative. The fact that the reaction works well with most of the known metallofullerene anions suggest that it has low selectivity to specific types of metallofullerenes. Furthermore, for EMFs with relatively low symmetry, benzylation does not show particularly high regioselectivity and can yield several isomers of adducts. Maeda et al. showed that the thermal reaction of $La@C_{2v}(9)-C_{82}$ anion with benzyl bromide produces two major and two minor isomers of $La@C_{82}(CH_2Ph)$ [114]. Thus, the benzylation of an anionic EMF extract that already contains many EMFs produces an even greater variety of benzyl adducts. The complexity of the product mixture then complicates the HPLC separation. Figure 4 illustrates that the isolation of $Tb_2@C_{80}(CH_2Ph)$ after benzylation

of the Tb-EMF anionic mixture is a rather tedious process, requiring three HPLC steps, including recycling HPLC [65].

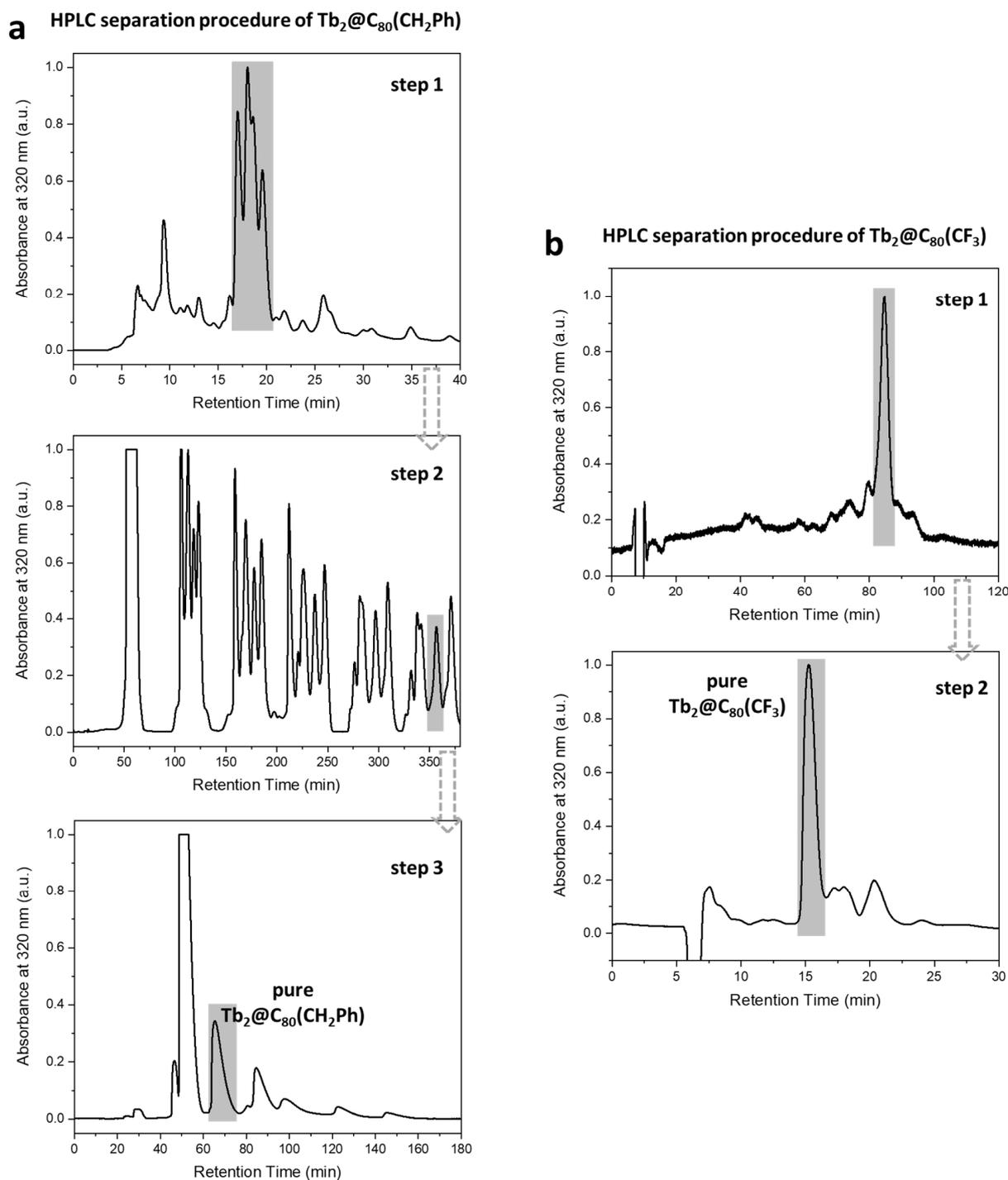


Figure 4. HPLC separation procedure of crude reaction products: (a) thermal benzylation of the Tb-EMF anionic extract in DMF, the target compound— $\text{Tb}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$ [65]; (b) electrophilic trifluoromethylation of Tb-EMF anions in DMF at room temperature, the target compound— $\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$ [115]. Shaded are the fractions containing the target compound and subjected to the next separation step. Note that $\text{Tb}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$ is only a small fraction of the crude product in (a), while $\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$ is the main component of the crude product in (b). Adapted with permission from Ref. [65]. Copyright 2019, Springer Nature. Adapted with permission from Ref. [115]. Copyright 2021 American Chemical Society.

Another possible source of complication in benzylation is that EMF monoanions do not react with benzyl bromide at room temperature, and the reaction requires heating to proceed. However, we have observed that even slight overheating changes the reaction mechanism from controllable monoaddition to uncontrolled polyaddition of benzyl groups. Presumably, heating facilitates homolytic cleavage of the C–Br bond and formation of benzyl radicals, which then react with fullerene anions by a radical addition mechanism. The latter appeared to be very unselective, and the resulting mixtures of benzyl multiadducts could not be separated into individual compounds. Lowering the reaction temperature requires an increase in the reactivity of EMF anions, which can be achieved by the reduction beyond the monoanionic state. Li et al. showed that benzyl bromide reacts with the $\text{Gd@C}_{2v}(9)\text{-C}_{82}^{3-}$ trianion already at room temperature to give several isomers of $\text{Gd@C}_{82}(\text{CH}_2\text{Ph})$ [117].

Seeking for a different functionalization reaction for EMF anions that would help to circumvent the drawbacks of the benzyl bromide route, we found that the electrophilic CF_3 addition can be particularly useful for the isolation of $\text{M}_2@I_h\text{-C}_{80}$ species [115]. Umemoto's Reagent II (Figure 3b), which can be formally described as a source of CF_3^+ , reacts with anionic EMF extract in DMF instantaneously and at room temperature. DMF is then removed under reduced pressure and the residue is extracted with toluene, in which neutral CF_3 derivatives are well soluble. The toluene solution can then be subjected to further analysis and HPLC separation. When the CF_3^+ reagent was taken in a large excess, the reaction gave CF_3 multiadducts. However, it showed remarkable selectivity toward $[\text{Tb}_2@I_h\text{-C}_{80}]^-$, and under an optimized reagent ratio, $\text{Tb}_2@I_h\text{-C}_{80}(\text{CF}_3)$ was obtained as the main toluene-soluble product. As a result, the time required to isolate the pure monoadduct was dramatically reduced compared to the isolation of $\text{Tb}_2@I_h\text{-C}_{80}(\text{CH}_2\text{Ph})$, since the HPLC isolation of $\text{Tb}_2@I_h\text{-C}_{80}(\text{CF}_3)$ required a much smaller number of injections and could be accomplished in two simple steps (see Figure 4, right panel for details). Electrophilic trifluoromethylation thus paves the way for further in-depth studies of the properties and applications of dimetallofullerenes $\text{M}_2@I_h\text{-C}_{80}$ with metal–metal bonds. The method is less efficient for EMFs with other carbon cages, as their trifluoromethylation is significantly less selective, and the yield of their monoadducts is considerably lower. Nonetheless, since CF_3 adducts crystallize easier than their benzyl analogs, the CF_3 route should be more efficient in the structural studies of unstable fullerenes.

In another recent work, we used electrophilic trifluoromethylation to elucidate the stability and molecular structures of Nd dimetallofullerenes [56]. A comparison of the extraction of arc-discharge soot containing Pr and Nd EMFs showed that while $\text{Pr}_2@C_{80}$ and other Pr dimetallofullerenes are soluble in CS_2 , Nd dimetallofullerenes could not be extracted by CS_2 , but were soluble in hot DMF. Thus, the boundary between stable and unstable lanthanide dimetallofullerenes was found to be between Pr and Nd. The anionic Nd-EMF extract in DMF was then reacted with Umemoto's Reagent II and showed similar selectivity toward $\text{Nd}_2@I_h\text{-C}_{80}$ as in the earlier study of Tb-EMFs. At the same time, analysis of minor HPLC fractions identified another isomer of $\text{Nd}_2@C_{80}(\text{CF}_3)$. Using single-crystal X-ray diffraction, the molecular structures of two isolated isomers were elucidated as $\text{Nd}_2@D_{5h}(6)\text{-C}_{80}(\text{CF}_3)$ and $\text{Nd}_2@I_h(7)\text{-C}_{80}(\text{CF}_3)$. Figure 5 illustrates the transition from unstable to stable forms of $\text{Nd}_2@C_{80}$ isomers by plotting the evolution of the spin density distribution from unstable $\text{Nd}_2@C_{80}$ to stable anion $[\text{Nd}_2@C_{80}]^-$ and stable neutral $\text{Nd}_2@C_{80}(\text{CF}_3)$. The presence of the single-electron Nd–Nd bond in all three forms is well evidenced by the spin density lobes localized between Nd atoms, while the spin density on the fullerene cage is present only in $\text{Nd}_2@C_{80}$, but is absent in the anion and CF_3 monoadduct.

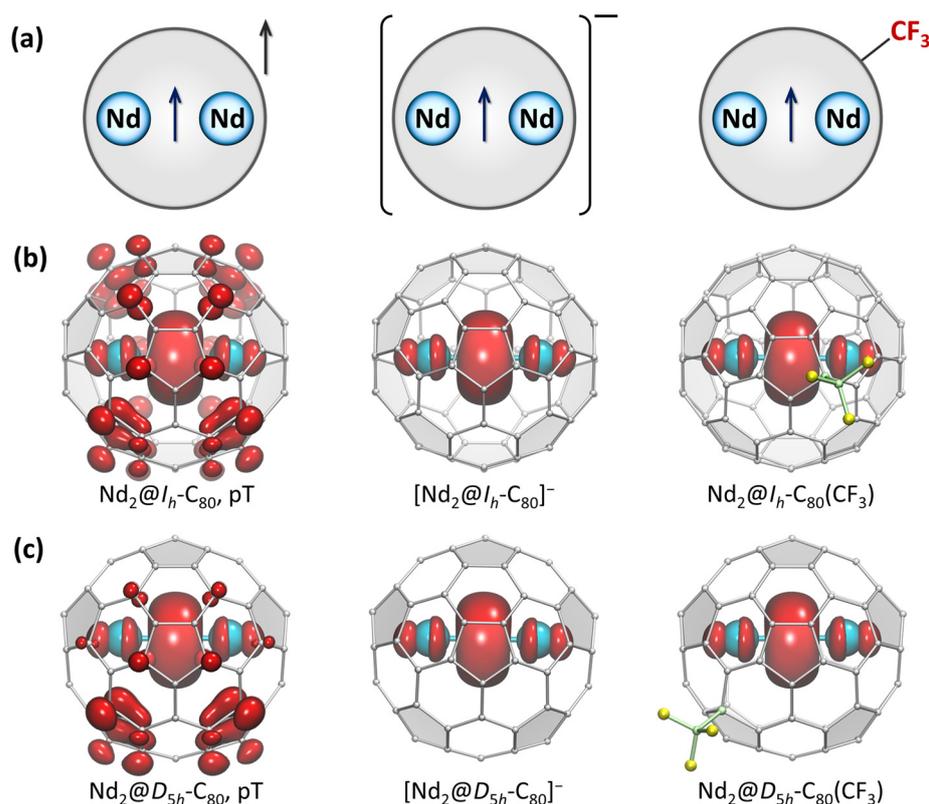


Figure 5. (a) Schematic description of neutral Nd₂@C₈₀ in pseudo-triplet (pT) state (two unpaired valence electrons), [Nd₂@C₈₀]⁻ anion with unpaired electron on the Nd–Nd bonding orbital, and Nd₂@C₈₀(CF₃) with unpaired electron on the Nd–Nd bonding orbital. (b) DFT-computed valence spin density distribution in Nd₂@C₈₀, [Nd₂@C₈₀]⁻ anion and Nd₂@C₈₀(CF₃) with I_h-C₈₀ cage. (c) DFT-computed valence spin density distribution in Nd₂@C₈₀, [Nd₂@C₈₀]⁻ anion and Nd₂@C₈₀(CF₃) with D_{5h}-C₈₀ cage. Adapted with permission from Ref. [56]. Copyright 2023 The Authors, published by Wiley-VCH GmbH.

5. Conclusions

In summary, we overviewed the general strategies to fish out metallofullerenes from the carbon soot, with the emphasis on the recently developed anion functionalization strategy (procedure II.3). The most appealing potential of this approach is that it specifically targets the novel structures missing in conventional separation routine (procedure I). This potential of the anion functionalization to stabilize and isolate “missing” metallofullerenes is not deeply exploited yet, and it is expected that many more novel metallofullerenes will be discovered with this strategy. The discovery of these novel structures will certainly renew our understandings to the coordination structures and physicochemical properties of metallofullerenes. It is worth noting that the chemical functionalization of metallofullerenes is a burgeoning field with a large variety of reactions already studied towards improved regioselectivity and physicochemical property modification [4,118–124]. In this regard, the PhCH₂ and CF₃ addition reactions merely exemplify a proof of concept, with the vast possibilities in this direction using the currently available versatile chemical functionalization methods yet to be explored.

Author Contributions: Writing, funding acquisition, F.L. and A.A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Deutsche Forschungsgemeinschaft (grants LI 3055/3-1, PO 1602/7-1, and PO 1602/11-1).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Popov, A.A.; Yang, S.; Dunsch, L. Endohedral Fullerenes. *Chem. Rev.* **2013**, *113*, 5989–6113. [[CrossRef](#)]
2. Lu, X.; Feng, L.; Akasaka, T.; Nagase, S. Current status and future developments of endohedral metallofullerenes. *Chem. Soc. Rev.* **2012**, *41*, 7723–7760. [[CrossRef](#)]
3. Yang, S.; Wei, T.; Jin, F. When metal clusters meet carbon cages: Endohedral clusterfullerenes. *Chem. Soc. Rev.* **2017**, *46*, 5005–5058. [[CrossRef](#)]
4. Wang, S.; Zhang, X.; Tan, X.; Li, H.; Dai, S.; Yao, B.; Liu, X.; He, Y.; Jin, F. Recent Progress on the Functionalization of Endohedral Metallofullerenes. *Inorganics* **2023**, *11*, 346. [[CrossRef](#)]
5. Li, Y.; Sun, Y.; Kopcha, W.P.; Zhang, J. Advances in Regioselective Functionalization of Endohedral Metallofullerenes. *Chin. J. Chem.* **2023**, *41*, 2025–2034. [[CrossRef](#)]
6. Kopcha, W.P.; Biswas, R.; Sun, Y.; Chueng, S.-T.D.; Dorn, H.C.; Zhang, J. Water-soluble endohedral metallofullerenes: New horizons for biomedical applications. *Chem. Commun.* **2023**, *59*, 13551–13561. [[CrossRef](#)] [[PubMed](#)]
7. Nie, H.; Zhao, C.; Shi, Z.; Jia, C.; Guo, X. Single-Molecule Fullerenes: Current Stage and Perspective. *ACS Mater. Lett.* **2022**, *11*, 1037–1052. [[CrossRef](#)]
8. Li, Y.; Kopcha, W.; Rodriguez-Fortea, A.; Zhang, J. Multicomponent Reactions Among Alkyl Isocyanides, sp reactants, and sp² Carbon Cages. *Synlett* **2022**, *33*, 907–912.
9. Li, W.; Wang, C.; Wang, T. Metallofullertube: From Tubular Endohedral Structures to Properties. *ChemPhysChem* **2022**, *23*, e202200507. [[CrossRef](#)]
10. Li, M.; Zhao, R.; Dang, J.; Zhao, X. Theoretical study on the stabilities, electronic structures, and reaction and formation mechanisms of fullerenes and endohedral metallofullerenes. *Coord. Chem. Rev.* **2022**, *471*, 214762. [[CrossRef](#)]
11. Shen, W.; Bao, L.; Lu, X. Endohedral Metallofullerenes: An Ideal Platform of Sub-Nano Chemistry. *Chin. J. Chem.* **2022**, *40*, 275–284. [[CrossRef](#)]
12. Li, W.; Wang, C.-R.; Wang, T. Molecular structures and magnetic properties of endohedral metallofullerenes. *Chem. Commun.* **2021**, *57*, 10317–10326. [[CrossRef](#)] [[PubMed](#)]
13. Akhanova, N.Y.; Shchur, D.V.; Pomytkin, A.P.; Zolotareno, A.D.; Zolotareno, A.D.; Gavrylyuk, N.A.; Ualkhanova, M.; Bo, W.; Ang, D. Methods for the Synthesis of Endohedral Fullerenes. *J. Nanosci. Nanotechnol.* **2021**, *21*, 2446–2459. [[CrossRef](#)] [[PubMed](#)]
14. Wang, S.; Chang, Q.; Zhang, G.; Li, F.; Wang, X.; Yang, S.; Troyanov, S.I. Structural Studies of Giant Empty and Endohedral Fullerenes. *Front. Chem.* **2020**, *8*, 607712. [[CrossRef](#)] [[PubMed](#)]
15. Shen, W.; Hu, S.; Lu, X. Endohedral Metallofullerenes: New Structures and Unseen Phenomena. *Chem. Eur. J.* **2020**, *26*, 5748–5757. [[CrossRef](#)] [[PubMed](#)]
16. Jalife, S.; Arcudia, J.; Pan, S.; Merino, G. Noble gas endohedral fullerenes. *Chem. Sci.* **2020**, *11*, 6642–6652. [[CrossRef](#)]
17. Guan, R.; Chen, M.; Jin, F.; Yang, S. Strain Release of Fused Pentagons on Fullerene Cage via Chemical Functionalization. *Angew. Chem. Int. Ed.* **2020**, *59*, 1048–1073. [[CrossRef](#)] [[PubMed](#)]
18. Wang, T.; Wang, C. Functional Metallofullerene Materials and Their Applications in Nanomedicine, Magnetics, and Electronics. *Small* **2019**, *15*, e1901522. [[CrossRef](#)]
19. Spree, L.; Popov, A.A. Recent advances in single molecule magnetism of dysprosium-metallofullerenes. *Dalton Trans.* **2019**, *48*, 2861–2871. [[CrossRef](#)]
20. Liu, F.; Spree, L.; Krylov, D.S.; Velkos, G.; Avdoshenko, S.M.; Popov, A.A. Single-Electron Lanthanide-Lanthanide Bonds Inside Fullerenes toward Robust Redox-Active Molecular Magnets. *Acc. Chem. Res.* **2019**, *52*, 2981–2993. [[CrossRef](#)]
21. Jin, P.; Li, Y.; Magagula, S.; Chen, Z. Exohedral functionalization of endohedral metallofullerenes: Interplay between inside and outside. *Coord. Chem. Rev.* **2019**, *388*, 406–439. [[CrossRef](#)]
22. Feng, L.; Hao, Y.; Liu, A.; Slanina, Z. Trapping Metallic Oxide Clusters inside Fullerene Cages. *Acc. Chem. Res.* **2019**, *52*, 1802–1811. [[CrossRef](#)] [[PubMed](#)]
23. Cai, W.; Chen, C.-H.; Chen, N.; Echegoyen, L. Fullerenes as Nanocontainers That Stabilize Unique Actinide Species Inside: Structures, Formation, and Reactivity. *Acc. Chem. Res.* **2019**, *52*, 1824–1833. [[CrossRef](#)] [[PubMed](#)]
24. Yang, W.; Li, X.; Chen, N. Recent Progress on Endohedral Metallic Fullerenes. *Gen. Chem.* **2018**, *4*, 180004.
25. Yamada, M.; Akasaka, T.; Nagase, S. Salvaging Reactive Fullerenes from Soot by Exohedral Derivatization. *Angew. Chem. Int. Ed.* **2018**, *57*, 13394–13405. [[CrossRef](#)]
26. Popov, A.A. Redox-active metal–metal bonds between lanthanides in dimetallofullerenes. *Curr. Opin. Electrochem.* **2018**, *8*, 73–80. [[CrossRef](#)] [[PubMed](#)]
27. Bao, L.; Peng, P.; Lu, X. Bonding inside and outside Fullerene Cages. *Acc. Chem. Res.* **2018**, *51*, 810–815. [[CrossRef](#)]
28. Li, T.; Dorn, H.C. Biomedical Applications of Metal-Encapsulated Fullerene Nanoparticles. *Small* **2017**, *13*, 1603152. [[CrossRef](#)] [[PubMed](#)]
29. Kako, M.; Nagase, S.; Akasaka, T. Functionalization of Endohedral Metallofullerenes with Reactive Silicon and Germanium Compounds. *Molecules* **2017**, *22*, 1179. [[CrossRef](#)]
30. Cerón, M.R.; Maffei, V.; Stevenson, S.; Echegoyen, L. Endohedral Fullerenes: Synthesis, Isolation, Mono and Bis-Functionalization. *Inorg. Chim. Acta* **2017**, *468*, 16–27. [[CrossRef](#)]

31. Abella, L.; Wang, Y.; Rodríguez-Forteza, A.; Chen, N.; Poblet, J.M. Current status of oxide clusterfullerenes. *Inorg. Chim. Acta* **2017**, *468*, 91–104. [[CrossRef](#)]
32. Shinohara, H. Another big discovery—Metallofullerenes. *Philos. Trans. R. Soc. Lond. A Math. Phys. Eng. Sci.* **2016**, *374*, 20150325. [[CrossRef](#)]
33. Romero, E.L.; Echegoyen, L. Electron spin resonance spectroscopy of empty and endohedral fullerenes. *J. Phys. Org. Chem.* **2016**, *29*, 781–792. [[CrossRef](#)]
34. Zhang, Y.; Popov, A.A. Transition-Metal and Rare-Earth-Metal Redox Couples inside Carbon Cages: Fullerenes Acting as Innocent Ligands. *Organometallics* **2014**, *33*, 4537–4549. [[CrossRef](#)]
35. Zhang, J.; Dorn, H.C. NMR Studies of the Dynamic Motion of Encapsulated Ions and Clusters in Fullerene Cages: A Wheel Within a Wheel. *Fuller. Nanotub. Carbon Nanostruct.* **2014**, *22*, 35–46. [[CrossRef](#)]
36. Wang, T.; Wang, C. Endohedral Metallofullerenes Based on Spherical I_h -C₈₀ Cage: Molecular Structures and Paramagnetic Properties. *Acc. Chem. Res.* **2014**, *47*, 450–458. [[CrossRef](#)] [[PubMed](#)]
37. Lu, X.; Bao, L.; Akasaka, T.; Nagase, S. Recent progress in the chemistry of endohedral metallofullerenes. *Chem. Commun.* **2014**, *50*, 14701–14715. [[CrossRef](#)] [[PubMed](#)]
38. Jin, P.; Tang, C.; Chen, Z. Carbon Atoms Trapped in Cages: Metal Carbide Clusterfullerenes. *Coord. Chem. Rev.* **2014**, *270–271*, 89–111. [[CrossRef](#)]
39. Ghiassi, K.B.; Olmstead, M.M.; Balch, A.L. Gadolinium-containing endohedral fullerenes: Structures and function as magnetic resonance imaging (MRI) agents. *Dalton Trans.* **2014**, *43*, 7346–7358. [[CrossRef](#)] [[PubMed](#)]
40. Garcia-Borras, M.; Osuna, S.; Luis, J.M.; Swart, M.; Sola, M. The role of aromaticity in determining the molecular structure and reactivity of (endohedral metallo)fullerenes. *Chem. Soc. Rev.* **2014**, *43*, 5089–5105. [[CrossRef](#)]
41. Cerón, M.R.; Li, F.-F.; Echegoyen, L.A. Endohedral fullerenes: The importance of electronic, size and shape complementarity between the carbon cages and the corresponding encapsulated clusters. *J. Phys. Org. Chem.* **2014**, *27*, 258–264. [[CrossRef](#)]
42. Zhang, J.; Stevenson, S.; Dorn, H.C. Trimetallic Nitride Template Endohedral Metallofullerenes: Discovery, Structural Characterization, Reactivity, and Applications. *Acc. Chem. Res.* **2013**, *46*, 1548–1557. [[CrossRef](#)] [[PubMed](#)]
43. Xie, Y.-P.; Lu, X.; Akasaka, T.; Nagase, S. New features in coordination chemistry: Valuable hints from X-ray analyses of endohedral metallofullerenes. *Polyhedron* **2013**, *52*, 3–9. [[CrossRef](#)]
44. Lu, X.; Akasaka, T.; Nagase, S. Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin. *Acc. Chem. Res.* **2013**, *46*, 1627–1635. [[CrossRef](#)] [[PubMed](#)]
45. Cong, H.; Yu, B.; Akasaka, T.; Lu, X. Endohedral metallofullerenes: An unconventional core–shell coordination union. *Coord. Chem. Rev.* **2013**, *257*, 2880–2898. [[CrossRef](#)]
46. Yang, S. Synthesis, Separation, and Molecular Structures of Endohedral Fullerenes. *Curr. Org. Chem.* **2012**, *16*, 1079–1094. [[CrossRef](#)]
47. Popov, A.A.; Avdoshenko, S.M.; Pendas, A.M.; Dunsch, L. Bonding between strongly repulsive metal atoms: An oxymoron made real in a confined space of endohedral metallofullerenes. *Chem. Commun.* **2012**, *48*, 8031–8050. [[CrossRef](#)]
48. Akasaka, T.; Lu, X. Structural and electronic properties of endohedral metallofullerenes. *Chem. Rec.* **2012**, *12*, 256–269. [[CrossRef](#)]
49. Yang, S.; Liu, F.; Chen, C.; Jiao, M.; Wei, T. Fullerenes encaging metal clusters-clusterfullerenes. *Chem. Commun.* **2011**, *47*, 11822–11839. [[CrossRef](#)]
50. Rodríguez-Forteza, A.; Balch, A.L.; Poblet, J.M. Endohedral metallofullerenes: A unique host-guest association. *Chem. Soc. Rev.* **2011**, *40*, 3551–3563. [[CrossRef](#)]
51. Popov, A.A.; Dunsch, L. Electrochemistry In Cavea: Endohedral Redox Reactions of Encaged Species in Fullerenes. *J. Phys. Chem. Lett.* **2011**, *2*, 786–794. [[CrossRef](#)]
52. Liu, G.; Wu, Y.; Porfyrakis, K. Synthesis and Chemistry of Endohedral Fullerenes. *Curr. Org. Chem.* **2011**, *15*, 1197–1207. [[CrossRef](#)]
53. Kovalenko, V.I.; Khamatgalimov, A.R. Open-shell fullerene C₇₄: Phenalenyl-radical substructures. *Chem. Phys. Lett.* **2003**, *377*, 263–268. [[CrossRef](#)]
54. Hu, S.; Liu, T.; Shen, W.; Slanina, Z.; Akasaka, T.; Xie, Y.; Uhlik, F.; Huang, W.; Lu, X. Isolation and Structural Characterization of Er@C_{2v}(9)-C₈₂ and Er@C_s(6)-C₈₂: Regioselective Dimerization of a Pristine Endohedral Metallofullerene Induced by Cage Symmetry. *Inorg. Chem.* **2019**, *58*, 2177–2182. [[CrossRef](#)]
55. Bao, L.; Pan, C.; Slanina, Z.; Uhlik, F.; Akasaka, T.; Lu, X. Isolation and Crystallographic Characterization of the Labile Isomer of Y@C₈₂ Cocrystallized with Ni(OEP): Unprecedented Dimerization of Pristine Metallofullerenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 9234–9238. [[CrossRef](#)]
56. Yang, W.; Velkos, G.; Rosenkranz, M.; Schiemenz, S.; Liu, F.; Popov, A.A. Nd-Nd Bond in I_h and D_{5h} Cage Isomers of Nd₂@C₈₀ Stabilized by Electrophilic CF₃ Addition. *Adv. Sci.* **2024**, *11*, 2305190. [[CrossRef](#)]
57. Wang, Z.; Kitaura, R.; Shinohara, H. Metal-Dependent Stability of Pristine and Functionalized Unconventional Dimetallofullerene M₂@I_h-C₈₀. *J. Phys. Chem. C* **2014**, *118*, 13953–13958. [[CrossRef](#)]
58. Fu, W.; Zhang, J.; Fuhrer, T.; Champion, H.; Furukawa, K.; Kato, T.; Mahaney, J.E.; Burke, B.G.; Williams, K.A.; Walker, K.; et al. Gd₂@C₇₉N: Isolation, Characterization, and Monoadduct Formation of a Very Stable Heterofullerene with a Magnetic Spin State of S = 15/2. *J. Am. Chem. Soc.* **2011**, *133*, 9741–9750. [[CrossRef](#)]

59. Zuo, T.; Xu, L.; Beavers, C.M.; Olmstead, M.M.; Fu, W.; Crawford, T.D.; Balch, A.L.; Dorn, H.C. $M_2@C_{79}N$ ($M = Y, Tb$): Isolation and Characterization of Stable Endohedral Metallofullerenes Exhibiting M...M Bonding Interactions inside Aza[80]fullerene Cages. *J. Am. Chem. Soc.* **2008**, *130*, 12992–12997. [[CrossRef](#)]
60. Jin, F.; Xin, J.; Guan, R.; Xie, X.-M.; Chen, M.; Zhang, Q.; Popov, A.A.; Xie, S.-Y.; Yang, S. Stabilizing Three-Center Single-Electron Metal-Metal Bond in a Fullerene Cage. *Chem. Sci.* **2021**, *12*, 6890–6895. [[CrossRef](#)]
61. Hu, S.; Zhao, P.; Li, B.; Yu, P.; Yang, L.; Ehara, M.; Jin, P.; Akasaka, T.; Lu, X. Cluster-Geometry-Associated Metal–Metal Bonding in Trimetallic Carbide Clusterfullerenes. *Inorg. Chem.* **2022**, *61*, 11277–11283. [[CrossRef](#)]
62. Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; et al. Structural determination of metallofullerene Sc_3C_{82} revisited: A surprising finding. *J. Am. Chem. Soc.* **2005**, *127*, 12500–12501. [[CrossRef](#)] [[PubMed](#)]
63. Yamada, M.; Kurihara, H.; Suzuki, M.; Saito, M.; Slanina, Z.; Uhlik, F.; Aizawa, T.; Kato, T.; Olmstead, M.M.; Balch, A.L.; et al. Hiding and Recovering Electrons in a Dimetallic Endohedral Fullerene: Air-Stable Products from Radical Additions. *J. Am. Chem. Soc.* **2015**, *137*, 232–238. [[CrossRef](#)] [[PubMed](#)]
64. Bao, L.; Chen, M.; Pan, C.; Yamaguchi, T.; Kato, T.; Olmstead, M.M.; Balch, A.L.; Akasaka, T.; Lu, X. Crystallographic Evidence for Direct Metal–Metal Bonding in a Stable Open-Shell $La_2@I_h-C_{80}$ Derivative. *Angew. Chem. Int. Ed.* **2016**, *55*, 4242–4246. [[CrossRef](#)]
65. Liu, F.; Velkos, G.; Krylov, D.S.; Spree, L.; Zalibera, M.; Ray, R.; Samoylova, N.A.; Chen, C.-H.; Rosenkranz, M.; Schiemenz, S.; et al. Air-stable redox-active nanomagnets with lanthanide spins radical-bridged by a metal–metal bond. *Nat. Commun.* **2019**, *10*, 571. [[CrossRef](#)]
66. Liu, F.; Krylov, D.S.; Spree, L.; Avdoshenko, S.M.; Samoylova, N.A.; Rosenkranz, M.; Kostanyan, A.; Greber, T.; Wolter, A.U.B.; Büchner, B.; et al. Single molecule magnet with an unpaired electron trapped between two lanthanide ions inside a fullerene. *Nat. Commun.* **2017**, *8*, 16098. [[CrossRef](#)]
67. Zaripov, R.B.; Kandrashkin, Y.E.; Salikhov, K.M.; Büchner, B.; Liu, F.; Rosenkranz, M.; Popov, A.A.; Kataev, V. Unusually large hyperfine structure of the electron spin levels in an endohedral dimetallofullerene and its spin coherent properties. *Nanoscale* **2020**, *12*, 20513–20521. [[CrossRef](#)]
68. Bubnov, V.P.; Laukhina, E.E.; Kareev, I.E.; Koltover, V.K.; Prokhorova, T.G.; Yagubskii, E.B.; Kozmin, Y.P. Endohedral Metallofullerenes: A Convenient Gram-Scale Preparation. *Chem. Mater.* **2002**, *14*, 1004–1008. [[CrossRef](#)]
69. Huang, H.; Yang, S. Toward Efficient Synthesis of Endohedral Metallofullerenes by Arc Discharge of Carbon Rods Containing Encapsulated Rare Earth Carbides and Ultrasonic Soxhlet Extraction. *Chem. Mater.* **2000**, *12*, 2715–2720. [[CrossRef](#)]
70. Diener, M.D.; Alford, J.M. Isolation and properties of small-bandgap fullerenes. *Nature* **1998**, *393*, 668–671. [[CrossRef](#)]
71. Kubozono, Y.; Noto, T.; Ohta, T.; Maeda, H.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. Extractions of $Ca@C_{60}$ and $Sr@C_{60}$ with Aniline. *Chem. Lett.* **1996**, *25*, 453–454. [[CrossRef](#)]
72. Fuchs, D.; Rietschel, H.; Michel, R.H.; Fischer, A.; Weis, P.; Kappes, M.M. Extraction and Chromatographic Elution Behavior of Endohedral Metallofullerenes: Inferences Regarding Effective Dipole Moments. *J. Phys. Chem.* **1996**, *100*, 725–729. [[CrossRef](#)]
73. Ding, J.; Yang, S. Efficient N,N-Dimethylformamide Extraction of Endohedral Metallofullerenes for HPLC Purification. *Chem. Mater.* **1996**, *8*, 2824–2827. [[CrossRef](#)]
74. Kubozono, Y.; Ohta, T.; Hayashibara, T.; Maeda, H.; Ishida, H.; Kashino, S.; Oshima, K.; Yamazaki, H.; Ukita, S.; Sogabe, T. Preparation and Extraction of $Ca@C_{60}$. *Chem. Lett.* **1995**, *24*, 457–458. [[CrossRef](#)]
75. Xiao, J.; Savina, M.R.; Martin, G.B.; Francis, A.H.; Meyerhoff, M.E. Efficient HPLC Purification of Endohedral Metallofullerenes on a Porphyrin-Silica Stationary Phase. *J. Am. Chem. Soc.* **1994**, *116*, 9341–9342. [[CrossRef](#)]
76. Anderson, M.R.; Dorn, H.C.; Stevenson, S.A. Making connections between metallofullerenes and fullerenes: Electrochemical investigations. *Carbon* **2000**, *38*, 1663–1670. [[CrossRef](#)]
77. Liu, B.B.; Zou, G.T.; Yang, H.B.; Yu, S.; Lu, J.S.; Liu, Z.Y.; Liu, S.Y.; Xu, W.G. Synthesis, extraction and electronic structure of $Ce@C_{2n}$. *J. Phys. Chem. Solids* **1997**, *58*, 1873–1876. [[CrossRef](#)]
78. Sun, D.Y.; Liu, Z.Y.; Guo, X.H.; Xu, W.G.; Liu, S.Y. High-yield extraction of endohedral rare-earth fullerenes. *J. Phys. Chem. B* **1997**, *101*, 3927–3930. [[CrossRef](#)]
79. Kubozono, Y.; Maeda, H.; Takabayashi, Y.; Hiraoka, K.; Nakai, T.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. Extractions of $Y@C_{60}$, $Ba@C_{60}$, $La@C_{60}$, $Ce@C_{60}$, $Pr@C_{60}$, $Nd@C_{60}$ and $Gd@C_{60}$ with aniline. *J. Am. Chem. Soc.* **1996**, *118*, 6998–6999. [[CrossRef](#)]
80. Kareev, I.E.; Shulga, Y.M.; Bubnov, V.P.; Kozlovski, V.I.; Dodonov, A.F.; Martynenko, M.V.; Yagubskii, E.B. Investigation of composition of endometallofullerene extracts. *Fuller. Nanotub. Carbon Nanostruct.* **2004**, *12*, 59–63. [[CrossRef](#)]
81. Kareev, I.E.; Bubnov, V.P.; Laukhina, E.E.; Dodonov, A.F.; Kozovski, V.I.; Yagubskii, E.B. Experimental evidence in support of the formation of anionic endohedral metallofullerenes during their extraction with N,N-dimethylformamide. *Fuller. Nanotub. Carbon Nanostruct.* **2004**, *12*, 65–69. [[CrossRef](#)]
82. Raebiger, J.W.; Bolskar, R.D. Improved Production and Separation Processes for Gadolinium Metallofullerenes. *J. Phys. Chem. C* **2008**, *112*, 6605–6612. [[CrossRef](#)]
83. Bolskar, R.D.; Alford, J.M. Chemical oxidation of endohedral metallofullerenes: Identification and separation of distinct classes. *Chem. Commun.* **2003**, *11*, 1292–1293. [[CrossRef](#)] [[PubMed](#)]
84. Aoyagi, S.; Nishibori, E.; Sawa, H.; Sugimoto, K.; Takata, M.; Miyata, Y.; Kitaura, R.; Shinohara, H.; Okada, H.; Sakai, T.; et al. A layered ionic crystal of polar $Li@C_{60}$ superatoms. *Nat. Chem.* **2010**, *2*, 678–683. [[CrossRef](#)] [[PubMed](#)]

85. Okada, H.; Komuro, T.; Sakai, T.; Matsuo, Y.; Ono, Y.; Omote, K.; Yokoo, K.; Kawachi, K.; Kasama, Y.; Ono, S.; et al. Preparation of endohedral fullerene containing lithium (Li@C_{60}) and isolation as pure hexafluorophosphate salt ($[\text{Li}^+\text{@C}_{60}][\text{PF}_6^-]$). *RSC Adv.* **2012**, *2*, 10624–10631. [[CrossRef](#)]
86. Tsuchiya, T.; Wakahara, T.; Shirakura, S.; Maeda, Y.; Akasaka, T.; Kobayashi, K.; Nagase, S.; Kato, T.; Kadish, K.M. Reduction of endohedral metallofullerenes: A convenient method for isolation. *Chem. Mat.* **2004**, *16*, 4343–4346. [[CrossRef](#)]
87. Laukhina, E.E.; Bubnov, V.P.; Estrin, Y.I.; Golod, Y.A.; Khodorkovskii, M.A.; Koltover, V.K.; Yagubskii, E.B. Novel proficient method for isolation of endometallofullerenes from fullerene-containing soots by two-step o-xylene-N,N-dimethylformamide extraction. *J. Mater. Chem.* **1998**, *8*, 893–895. [[CrossRef](#)]
88. Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. Isolation of an ESR-Active Metallofullerene of La@C_{82} . *J. Phys. Chem.* **1994**, *98*, 2008–2011. [[CrossRef](#)]
89. Solodovnikov, S.P.; Tumanskii, B.L.; Bashilov, V.V.; Lebedkin, S.F.; Sokolov, V.I. Spectral study of reactions of La@C_{82} and Y@C_{82} with amino-containing solvents. *Russ. Chem. Bull.* **2001**, *50*, 2242–2244. [[CrossRef](#)]
90. Tsuchiya, T.; Wakahara, T.; Lian, Y.F.; Maeda, Y.; Akasaka, T.; Kato, T.; Mizorogi, N.; Nagase, S. Selective extraction and purification of endohedral metallofullerene from carbon soot. *J. Phys. Chem. B* **2006**, *110*, 22517–22520. [[CrossRef](#)]
91. Tagmatarchis, N.; Shinohara, H. Production, Separation, Isolation, and Spectroscopic Study of Dysprosium Endohedral Metallofullerenes. *Chem. Mater.* **2000**, *12*, 3222–3226. [[CrossRef](#)]
92. Sun, B.; Gu, Z. Solvent-dependent Anion Studies on Enrichment of Metallofullerene. *Chem. Lett.* **2002**, *31*, 1164–1165. [[CrossRef](#)]
93. Lu, X.; Li, H.; Sun, B.; Shi, Z.; Gu, Z. Selective reduction and extraction of Gd@C_{82} and $\text{Gd}_2\text{@C}_{80}$ from soot and the chemical reaction of their anions. *Carbon* **2005**, *43*, 1546–1549. [[CrossRef](#)]
94. Shustova, N.B.; Kuvychko, I.V.; Bolskar, R.D.; Seppelt, K.; Strauss, S.H.; Popov, A.A.; Boltalina, O.V. Trifluoromethyl derivatives of insoluble small-HOMO-LUMO-gap hollow higher fullerenes. NMR and DFT structure elucidation of $\text{C}_2\text{-(C}_{74}\text{-D}_{3h})(\text{CF}_3)_{12}$, $\text{C}_s\text{-(C}_{76}\text{-T}_d(2))(\text{CF}_3)_{12}$, $\text{C}_2\text{-(C}_{78}\text{-D}_{3h}(5))(\text{CF}_3)_{12}$, $\text{C}_s\text{-(C}_{80}\text{-C}_{2v}(5))(\text{CF}_3)_{12}$, and $\text{C}_2\text{-(C}_{82}\text{-C}_2(5))(\text{CF}_3)_{12}$. *J. Am. Chem. Soc.* **2006**, *128*, 15793–15798. [[CrossRef](#)]
95. Shustova, N.B.; Newell, B.S.; Miller, S.M.; Anderson, O.P.; Bolskar, R.D.; Seppelt, K.; Popov, A.A.; Boltalina, O.V.; Strauss, S.H. Discovering and verifying elusive fullerene cage isomers: Structures of $\text{C}_2\text{-}p^{11}\text{-(C}_{74}\text{-D}_{3h})(\text{CF}_3)_{12}$ and $\text{C}_2\text{-}p^{11}\text{-(C}_{78}\text{-D}_{3h}(5))(\text{CF}_3)_{12}$. *Angew. Chem. Int. Ed.* **2007**, *46*, 4111–4114. [[CrossRef](#)]
96. Wang, Z.; Nakanishi, Y.; Noda, S.; Niwa, H.; Zhang, J.; Kitaura, R.; Shinohara, H. Missing Small-Bandgap Metallofullerenes: Their Isolation and Electronic Properties. *Angew. Chem. Int. Ed.* **2013**, *52*, 11770–11774. [[CrossRef](#)] [[PubMed](#)]
97. Nakagawa, A.; Nishino, M.; Niwa, H.; Ishino, K.; Wang, Z.; Omachi, H.; Furukawa, K.; Yamaguchi, T.; Kato, T.; Bandow, S.; et al. Crystalline functionalized endohedral C_{60} metallofullerides. *Nat. Commun.* **2018**, *9*, 3073. [[CrossRef](#)]
98. Nakagawa, A.; Aoyagi, S.; Omachi, H.; Ishino, K.; Nishino, M.; Rio, J.; Ewels, C.; Shinohara, H. Isolation and structure determination of missing fullerenes $\text{Gd@C}_{74}(\text{CF}_3)_n$ through in situ trifluoromethylation. *R. Soc. Open Sci.* **2018**, *5*, 181015. [[CrossRef](#)] [[PubMed](#)]
99. Wang, Z.; Aoyagi, S.; Omachi, H.; Kitaura, R.; Shinohara, H. Isolation and Structure Determination of a Missing Endohedral Fullerene La@C_{70} through In Situ Trifluoromethylation. *Angew. Chem. Int. Ed.* **2016**, *55*, 199–202. [[CrossRef](#)] [[PubMed](#)]
100. Xie, S.-Y.; Gao, F.; Lu, X.; Huang, R.B.; Wang, C.R.; Zhang, X.; Liu, M.L.; Deng, S.L.; Zheng, L.S. Capturing the labile fullerene[50] as $\text{C}_{50}\text{Cl}_{10}$. *Science* **2004**, *304*, 699. [[CrossRef](#)] [[PubMed](#)]
101. Tan, Y.-Z.; Chen, R.-T.; Liao, Z.-J.; Li, J.; Zhu, F.; Lu, X.; Xie, S.-Y.; Li, J.; Huang, R.-B.; Zheng, L.-S. Carbon arc production of heptagon-containing fullerene[68]. *Nat. Commun.* **2011**, *2*, 420. [[CrossRef](#)]
102. Zhong, Y.-Y.; Chen, Z.-C.; Du, P.; Cui, C.-H.; Tian, H.-R.; Shi, X.-M.; Deng, S.-L.; Gao, F.; Zhang, Q.; Gao, C.-L.; et al. Double Negatively Curved C_{70} Growth through a Heptagon-Involving Pathway. *Angew. Chem. Int. Ed.* **2019**, *58*, 14095–14099. [[CrossRef](#)] [[PubMed](#)]
103. Wang, C.R.; Shi, Z.Q.; Wan, L.J.; Lu, X.; Dunsch, L.; Shu, C.Y.; Tang, Y.L.; Shinohara, H. C_{64}H_4 : Production, isolation, and structural characterizations of a stable unconventional fulleride. *J. Am. Chem. Soc.* **2006**, *128*, 6605–6610. [[CrossRef](#)]
104. Tian, H.-R.; Chen, M.-M.; Wang, K.; Chen, Z.-C.; Fu, C.-Y.; Zhang, Q.; Li, S.-H.; Deng, S.-L.; Yao, Y.-R.; Xie, S.-Y.; et al. An Unconventional Hydrofullerene C_{66}H_4 with Symmetric Heptagons Retrieved in Low-Pressure Combustion. *J. Am. Chem. Soc.* **2019**, *141*, 6651–6657. [[CrossRef](#)]
105. Xie, F.-F.; Chen, Z.-C.; Zhang, M.; Xie, X.-M.; Chen, L.-F.; Tian, H.-R.; Deng, S.-L.; Xie, S.-Y.; Zheng, L.-S. Capturing nonclassical C_{70} with double heptagons in low-pressure combustion. *Chem. Commun.* **2022**, *58*, 9814–9817. [[CrossRef](#)] [[PubMed](#)]
106. Moreno-Vicente, A.; Mulet-Gas, M.; Dunk, P.W.; Poblet, J.M.; Rodríguez-Fortea, A. Probing the formation of halogenated endohedral metallofullerenes: Predictions confirmed by experiments. *Carbon* **2018**, *129*, 750–757. [[CrossRef](#)]
107. Maeda, Y.; Tsuchiya, T.; Kikuchi, T.; Nikawa, H.; Yang, T.; Zhao, X.; Slanina, Z.; Suzuki, M.; Yamada, M.; Lian, Y.; et al. Effective Derivatization and Extraction of Insoluble Missing Lanthanum Metallofullerenes La@C_{2n} ($n=36\text{--}38$) with Iodobenzene. *Carbon* **2016**, *98*, 67–73. [[CrossRef](#)]
108. Wakahara, T.; Nikawa, H.; Kikuchi, T.; Nakahodo, T.; Rahman, G.M.A.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; et al. La@C_{72} having a non-IPR carbon cage. *J. Am. Chem. Soc.* **2006**, *128*, 14228–14229. [[CrossRef](#)]
109. Nikawa, H.; Kikuchi, T.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Rahman, G.M.A.; Akasaka, T.; Maeda, Y.; Yoza, K.; Horn, E.; et al. Missing metallofullerene La@C_{74} . *J. Am. Chem. Soc.* **2005**, *127*, 9684–9685. [[CrossRef](#)]

110. Lu, X.; Nikawa, H.; Kikuchi, T.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. Radical Derivatives of Insoluble La@C₇₄: X-ray Structures, Metal Positions, and Isomerization. *Angew. Chem. Int. Ed.* **2011**, *50*, 6356–6359. [[CrossRef](#)]
111. Nikawa, H.; Yamada, T.; Cao, B.P.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Akasaka, T.; Yoza, K.; Nagase, S. Missing Metallofullerene with C₈₀ Cage. *J. Am. Chem. Soc.* **2009**, *131*, 10950–10954. [[CrossRef](#)]
112. Akasaka, T.; Lu, X.; Kuga, H.; Nikawa, H.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Yoza, K.; Nagase, S. Dichlorophenyl Derivatives of La@C_{3v}(7)-C₈₂: Endohedral Metal Induced Localization of Pyramidalization and Spin on a Triple-Hexagon Junction. *Angew. Chem. Int. Ed.* **2010**, *49*, 9715–9719. [[CrossRef](#)]
113. Kareev, I.E.; Lebedkin, S.F.; Bubnov, V.P.; Yagubskii, E.B.; Ioffe, I.N.; Khavrel, P.A.; Kuvychko, I.V.; Strauss, S.H.; Boltalina, O.V. Trifluoromethylated endohedral metallofullerenes: Synthesis and characterization of Y@C₈₂(CF₃)₅. *Angew. Chem. Int. Ed.* **2005**, *44*, 1846–1849. [[CrossRef](#)]
114. Maeda, Y.; Akita, S.; Suzuki, M.; Yamada, M.; Akasaka, T.; Kobayashi, K.; Nagase, S. Controlling the reactivity of La@C₈₂ by reduction: Reaction of the La@C₈₂ anion with alkyl halide with high regioselectivity. *Beilstein J. Org. Chem.* **2023**, *19*, 1858–1866. [[CrossRef](#)]
115. Wang, Y.; Velkos, G.; Israel, N.J.; Rosenkranz, M.; Büchner, B.; Liu, F.; Popov, A.A. Electrophilic Trifluoromethylation of Dimetallofullerene Anions en Route to Air-Stable Single-Molecule Magnets with High Blocking Temperature of Magnetization. *J. Am. Chem. Soc.* **2021**, *143*, 18139–18149. [[CrossRef](#)] [[PubMed](#)]
116. Han, X.; Xin, J.; Yao, Y.; Liang, Z.; Qiu, Y.; Chen, M.; Yang, S. Capturing the Long-Sought Dy@C_{2v}(5)-C₈₀ via Benzyl Radical Stabilization. *Nanomaterials* **2022**, *12*, 3291. [[CrossRef](#)] [[PubMed](#)]
117. Zhou, X.; Yao, Y.-R.; Hu, Y.; Yang, L.; Yang, S.; Zhang, Y.; Zhang, Q.; Peng, P.; Jin, P.; Li, F.-F. Reactivity of Open-Shell Metallofullerene Anions: Synthesis, Crystal Structures, and Electrochemical Properties of Benzylated Gd@C_{2v}-C₈₂. *Inorganics* **2023**, *11*, 349. [[CrossRef](#)]
118. Yang, S.; Ioffe, I.N.; Troyanov, S.I. Chlorination-Promoted Skeletal Transformations of Fullerenes. *Acc. Chem. Res.* **2019**, *52*, 1783–1792. [[CrossRef](#)] [[PubMed](#)]
119. Lebedeva, M.A.; Chamberlain, T.W.; Khlobystov, A.N. Harnessing the Synergistic and Complementary Properties of Fullerene and Transition-Metal Compounds for Nanomaterial Applications. *Chem. Rev.* **2015**, *115*, 11301–11351. [[CrossRef](#)]
120. Boltalina, O.V.; Popov, A.A.; Kuvychko, I.V.; Shustova, N.B.; Strauss, S.H. Perfluoroalkylfullerenes. *Chem. Rev.* **2015**, *115*, 1051–1105. [[CrossRef](#)] [[PubMed](#)]
121. Yamada, M.; Akasaka, T.; Nagase, S. Carbene Additions to Fullerenes. *Chem. Rev.* **2013**, *113*, 7209–7264. [[CrossRef](#)] [[PubMed](#)]
122. Tzirakis, M.D.; Orfanopoulos, M. Radical Reactions of Fullerenes: From Synthetic Organic Chemistry to Materials Science and Biology. *Chem. Rev.* **2013**, *113*, 5262–5321. [[CrossRef](#)]
123. Lu, X.; Akasaka, T.; Nagase, S. Chemistry of endohedral metallofullerenes: The role of metals. *Chem. Commun.* **2011**, *47*, 5942–5957. [[CrossRef](#)] [[PubMed](#)]
124. Yamada, M.; Akasaka, T.; Nagase, S. Endohedral Metal Atoms in Pristine and Functionalized Fullerene Cages. *Acc. Chem. Res.* **2010**, *43*, 92–102. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.