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FEATURE ARTICLE

Chemistry of endohedral metallofullerenes: the role of metals

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Recent breakthroughs achieved in the chemical functionalization of endohedral metallofullerenes (EMFs), especially single crystallographic X-ray characterizations of their derivatives, have presented fundamentally new insights into the structures and properties of these metal–carbon hybrid molecules, and have also brought immense potential applications. In particular, the interplay between the encapsulated metallic species and the fullerene cage has been well investigated. On one hand, the position and motion of the encapsulated metals can be effectively controlled by exohedral modification. On the other hand, the cage structures, the chemical behaviours of cage carbons and thus the chemical reactivity of the whole molecule are also apparently influenced by the electronic configuration and geometrical conformation of the internal metals *via* strong metal–cage interactions. In this article, we contribute a systematic review of the important chemical transformations of EMFs reported to date, including disilylation, 1,3-dipolar cycloaddition with ylides, cyclopropanation with carbenes and carbanions, cycloaddition with dienes and benzyne, radical reactions, and other miscellaneous reactions, in addition to noncovalent interactions such as supramolecular complexation. The roles that internal metals play in controlling the reactivity of cage carbons are particularly emphasized. Finally, some applicable materials based on EMFs and their derivatives are summarized and practical perspectives are proposed.

1. Introduction

Fullerenes, emerged as the third but the only molecular form of the element carbon with marked differences from the well-known graphite and diamond, are a collection of spherical molecules comprising exactly 12 pentagonal carbon rings and a variable number of hexagonal rings.[1] The most prominent fullerene members are certainly C_{60} and C_{70} because of their high production yield, and to a certain degree, because of their high molecular symmetry as well.[2] The advent of fullerenes has not only presented a class of new all-carbon materials but also provided new insights into the knowledge of chemical transformation and the concept of molecule architecture. On one hand, the curved fullerene surfaces full

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of π-electrons are able to undergo a variety of chemical reactions, thereby creating a new sub-branch of organic chemistry termed as fullerene chemistry.[3] During the past two decades, numerous chemical reactions have been conducted on fullerenes and tremendous useful materials have been synthesized.[4] On the other hand, the internal vacancies of fullerene cages are capable of encapsulating a wide range of atoms, molecules and even otherwise unstable species, forming endofullerenes with more fascinating properties and intriguing functions than empty fullerenes.[5] In particular, when metal atoms or metallic clusters are encapsulated, a certain number of electrons transfer from the internal metal to the fullerene cage, hence resulting in unique structures, novel properties and vast potential applications in materials science, electronics, photovoltaics, catalysis, biomedicine and molecular devices.[6] This new family of metal–carbon hybrid materials is commonly called endohedral metallofullerenes (EMFs). During the past twenty years, EMFs have attracted great attention from chemists, physicists, materials scientists and even biologists.[5,6]

Recent ten years or so, thanks to the progress achieved in the synthesis and extraction/isolation of EMFs, chemical functionalization of EMFs has become a hot topic because (i) introducing different functional groups to EMFs will surely broaden their applications in various fields; (ii) chemical properties of EMFs are significantly different from those of empty fullerenes due to the presence of metallic species and the charge transfer; (iii) functionalized EMFs present the great opportunity to be characterized with X-ray crystallography, which is the ultimate solution for elucidating EMF structures with respect to the dynamic behaviors of internal metals. Indeed, many unexpected results that are characteristic of EMFs have been observed in recent studies and unambiguous X-ray results of EMF-adducts have provided valuable information of the function that the internal metals play in determining the cage structures and controlling the chemical reactivity of cage carbons. Several review articles on EMFs have been published recently, but none has specifically focused on the chemical properties of EMFs.[5–7] Herein, we present a

systematic review of the chemical reactions of EMFs, and the influences of internal metals on the chemical behaviors of cage carbons are particularly emphasized.

1.1 Classification, general structures and properties of EMFs

A detailed inspection of reported results engenders the conclusion that only metal elements of Groups 2, 3, and 4 can form EMFs in macroscopic amounts using the most effective arc discharge method.[8]

Regarding the composition of internal metallic species, one or two pure metal atoms and various metallic clusters have been identified for EMFs. Consequently, isolated EMFs are generally classified into three categories according to the type of encapsulated metallic species, and such a classification is helpful to understand their structures and inherent properties.

Mono-EMFs. As only one metal exists, mono-EMFs are viewed as the simplest prototype of EMFs and they are certainly ideal candidates for elucidating metal–cage interactions. When an alkali-earth metal or either of Sm, Eu, Tm, Yb is encapsulated, two electrons are transferred from the internal metal to the cage, and they are accordingly called divalent EMFs.[9] For these EMFs containing a rare earth metal other than the above, three electrons are donated; hence they are trivalent EMFs. These two groups differ significantly from each other in terms of structures and properties. For instance, divalent EMFs normally have a much lower production yield than trivalent ones, but they can form more isomers for a given cage, thereby providing more opportunities for disclosing metal–cage interactions and for applications.[9] For example, three isomers have been isolated for $Yb@C_{82}$ and four for $Yb@C_{84}$, but only two were found for $Sc@C_{82}$ and one for $Sc@C_{84}$.[10]

More interestingly, it was revealed that the single metal is not in the center of the cage, but it tends to coordinate strongly with the cage carbons. For example, the single metal in $M@C_{2v}(9)$-C_{82} (M = Sc, Y, La, Ce, Gd, *etc.*) prefers to stay off-center under a hexagonal ring along the C_2 axis, thus making the distribution of charge density and cage curvature highly anisotropic over the surface.[11] X-Ray results of $M@C_{3v}(134)$-C_{94} (M = Ca, Tm) also confirmed that the metal is localized near one end of the molecule.[12] Such off-center positions of the metal can be common in mono-EMFs.

Di-EMFs. Di-EMFs do not contain any non-metallic element but only two metal atoms. $M_2@C_{80}$ (M = La, Ce, *etc.*) is always the most accessible di-EMF; normally, two cage isomers (I_h and D_{5h}) are obtainable.[13]

In contrast to the nearly fixed localization of metal in mono-EMFs, the two metals in di-EMFs normally move rapidly. For example, NMR results of $La_2@I_h(7)$-C_{80} revealed that the two La atoms rotate freely inside the C_{80} cage;[14] single crystallographic X-ray results of $Er_2@C_s(6)$-C_{82} and $Er_2@C_{3v}(8)$-C_{82} revealed that the two Er atoms prefer to circulate along a cage ribbon consisting of purely hexagonal rings.[15] However, the rotation is more confined in relatively small cages such as $M_2@D_{3h}(5)$-C_{78} (M = La, Ce, *etc.*).[16]

Cluster EMFs. $Sc_2C_2@D_{2d}(23)$-C_{84} was the first identified carbide cluster EMF.[17] To date, carbide clusters with Sc, Y and Er have been frequently found in EMFs, presumably

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because of the small ionic radii of these metals.[18] Larger metals would prefer larger cages, for example $Gd_2C_2@D_3(85)$-C_{92}.[19] In addition, two C atoms are always necessary to stabilize the whole cluster whereas at least two metals are necessary to prevent the C_2 unit from interacting with the cage.

Metal nitride cluster (M_3N) EMFs are particularly intriguing because of the preferential formation of the highly symmetric $I_h(7)$-C_{80} cage.[20] Furthermore, the yield of $Sc_3N@C_{80}$ is astonishingly high, making it the third most abundant fullerene (after C_{60} and C_{70}), but the yield of other $M_3N@C_{2n}$ decreases dramatically with increasing metal size. In addition, bigger M_3N clusters prefer larger cages. For example, M_3N (M = Nd, Pr, and Ce) templates C_{88}, while the biggest La_3N prefers C_{96}.[21] X-Ray results revealed that the M_3N cluster prefers a planar conformation and it is generally rotating.[22] Recently, $Sc_3CN@C_{80}$ was reported as the first example of metal cyanide cluster EMF.[23]

Although early reports claimed that oxygen depresses the formation of fullerenes and EMFs, recent works showed that EMFs with metal oxide clusters could be macroscopically synthesized by doping metal oxide into the graphite rod or by introducing air into the discharge chamber. Reported examples include $Sc_4(\mu_3$-$O)_2@I_h$-C_{80}, $Sc_4(\mu_3$-$O)_3@I_h$-C_{80} and $Sc_2(\mu_2$-$O)@C_s(6)$-C_{82}, all of which have been characterized by X-ray crystallography.[24]

Similarly, EMFs containing a metal sulfide cluster (M_2S) were synthesized using sulfur-containing additives. It was proposed that the M_2S cluster tends to template the $C_s(6)$-C_{82} and $C_{3v}(8)$-C_{82} cages as a result of both electronic and geometrical effects.[25]

Encapsulation of three or more pure metals seems difficult. This can be presumably explained by the strong coulomb repulsions among three or more trications within the limited space of a normal cage (say C_{80}), so that nonmetallic elements are always necessary to partially neutralize the positive charge and to tighten the cluster. No example of $M_3@C_{2n}$ has been unambiguously characterized to date: the previously proposed $Sc_3@C_{82}$ was recently confirmed as $Sc_3C_2@C_{80}$,[18a] but a recent computational work indicated that $Y_3@C_{80}$ should be a real trimetallofullerene rather than a carbide EMF.[26]

2. The chemistry of EMFs

2.1 Structural considerations of two prototypical EMFs: $La@C_{2v}(9)$-C_{82} and $La_2@I_h(7)$-C_{80}

As can be inferred from above discussions, commonly available EMFs are generally larger than C_{60} and C_{70}. In particular, the $C_{2v}(9)$-C_{82} cage is always most abundantly produced for mono-EMFs forming $M@C_{2v}(9)$-C_{82}; and the $I_h(7)$-C_{80} cage is most suitable for trapping a nitride cluster or two metals forming $M_3N@I_h(7)$-C_{80} or $M_2@I_h(7)$-C_{80}. Accordingly, these EMFs have received more attention than others. In particular, almost all the reactions discussed in this context have been performed on these two cages with different metal contents. Therefore, we first furnish a brief description of their geometrical and electronic structures before reaching the chemical reactions; this is certainly helpful to elucidate their chemical behaviors.
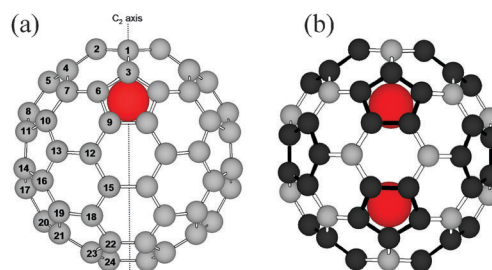

Fig. 1 Optimized structures of (a) $La@C_{2v}(9)$-C_{82} with the 24 types of nonequivalent carbons numerically labeled, and (b) $La_2@I_h(7)$-C_{80} with all PHHJ carbons and [5,6]-bonds marked in dark shade.

Fig. 1a portrays the optimized structure of $La@C_{2v}(9)$-C_{82} with numerical labels on each of the 24 types of nonequivalent carbons, which form 16 kinds of [5,6]-bonds and 19 kinds of nonequivalent [6,6]-bonds.[27] At first glance, this molecule is unsuitable for chemical functionalization because many regioisomers would be formed. However, because the La atom is localized off-center under a hexagonal ring along the C_2 axis, it influences the reactivity of the cage carbons effectively. As presented in Table 1, the p-orbital axis vector (POAV) values, an effective measure of the local strain of fullerene carbons, are obviously higher for carbons of type 1 and type 2, which form the hexagonal ring interacting strongly with the internal metal. These carbons are expected to be more reactive than others.[27b]

Furthermore, three electrons are transferred from La to C_{82} so that $La@C_{82}$ should be described as $[La]^{3+}@[C_{82}]^{3-}$. Calculated Mülliken charge density values (Table 1) showed that negative charges are mainly localized on the carbons close to the La^{3+} cation, while positive charges are also found, which belong to the carbons far from the metal, namely, C18, C21, and C23. Accordingly, electrophiles and

Table 1 POAV, Mülliken charge density, and SOMO spin density of the 24-nonequivalent carbons of $La@C_{2v}(9)$-C_{82} calculated at the B3LYP/6-31G(d)//B3LYP/3-21G level (all in arbitrary units)

Carbon number	POAV value	Charge density	Spin density
1	11.28	−0.170	0.016
2	11.20	−0.136	0.002
3	8.82	−0.099	0.021
4	9.62	−0.015	0.015
5	9.16	−0.045	0
6	10.49	−0.037	0.004
7	9.06	−0.092	0.001
8	8.89	−0.061	0
9	9.94	−0.022	0.026
10	10.66	−0.020	0.032
11	10.57	−0.021	0.009
12	7.66	−0.047	0.005
13	10.89	−0.006	0.003
14	11.00	0.000	0.023
15	7.36	−0.027	0.014
16	10.62	−0.012	0.013
17	8.24	−0.036	0.000
18	10.91	+0.004	0.030
19	11.01	−0.006	0.024
20	8.36	−0.026	0
21	10.50	+0.002	0
22	10.73	−0.006	0.001
23	8.31	+0.006	0.025
24	10.74	−0.025	0

nucleophiles would selectively attack the two different regions of La@C_{2v}(9)-C_{82}, respectively.[28]

In addition, one unpaired electron exists on the fullerene cage as a result of the three-electron transfer. Calculations show that the singly occupied molecule orbital (SOMO) spin density (Mülliken) is mainly localized on the equatorial region. In combination with POAV values, it can be concluded that C10 and C18 have the highest radical character and accordingly prefer radical reactions.[29]

The optimized structure of La$_2$@I_h(7)-C_{80} is shown in Fig. 1b. Since each La donates three electrons to the cage, its electronic structure is described as [La$_2$]$^{6+}$@[C_{80}]$^{6-}$. Because the two La atoms rotate freely inside the cage, they don't lower the high I_h-symmetry for the molecule.[14] This cage contains only two types of carbons: all the 20 triple-hexagon junctions (THJs) are mutually equivalent, so are the remaining 60 pentagon–pentagon–hexagon junctions (PPHJs). As a result, all the [5,6]- and [6,6]-bonds are, respectively, equal. Obviously, this cage is ideal for chemical modifications because it can form very few regioisomers of the monoadduct. The I_h-C_{80} cage is also suitable for M$_3$N@C_{80} (M = Sc, Y, Lu, etc.), and chemical reactions have been frequently reported for these species. Recent results revealed that the chemical reactivity of cage carbons is strongly dependent on the type and size of internal clusters, which will be addressed in greater detail later.
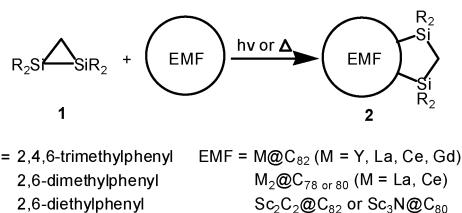
In addition, a minor isomer with the C_s(6)-C_{82} cage was also obtained for M@C_{82} (M = Y, La, Ce, Gd, etc.),[30] and the D_{5h}-C_{80} cage was found for Ce$_2$@C_{80} and M$_3$N@C_{80} (M = Sc, Y, Er, Lu, etc.).[31] However, because of their relatively low yield and low stability, few results relating to their chemical reactivity were reported. In the following text, M@C_{82} will only indicate the C_{2v}(9)-C_{82} cage, and La$_2$@C_{80} and M$_3$N@C_{80} will exclusively point to the I_h-C_{80} cage for clarity, unless otherwise noted.

2.2 Cycloaddition reactions of EMFs

Cycloaddition is the most effective way to generate covalent derivatives of fullerenes and EMFs, and accordingly it has been intensively investigated.

Disilylation. The first chemical reaction of EMFs was reported by Akasaka et al. in 1995, when they used 1,1,2,2-tetramesityl-1,2-disilirane (1) to functionalize La@C_{82}.[32] Formation of monoadducts was confirmed by mass spectrometry but ESR results disclosed the existence of several regioisomers. This methodology was soon extended to other EMFs with different metal contents and/or cage structures, such as M@C_{82} (M = Y, Ce, Pr, Gd), La$_2$@C_{80}, Sc$_2$C$_2$@C_{3v}(8)-C_{82} (which had been wrongly assigned as Sc$_2$@C_{84})[18b] and Sc$_3$N@C_{80}.[33] The results showed that mono- and di-EMFs react with 1 both photochemically and thermally, whereas cluster EMFs, resembling empty fullerenes (C_{60} and C_{70}), only undergo photochemical reactions (Scheme 1).

The high reactivity of mono- and di-EMFs results from their high electron affinities. From the redox potential values listed in Table 2, it is evident that the first reduction potentials of M@C_{82} (M = Y, La, Gd) and La$_2$@C_{80} are much more positive than those of empty fullerenes and cluster EMFs,

Scheme 1 Disilylation of EMFs with **1**.

R = 2,4,6-trimethylphenyl   EMF = M@C_{82} (M = Y, La, Ce, Gd)
2,6-dimethylphenyl   M$_2$@$C_{78 \text{ or } 80}$ (M = La, Ce)
2,6-diethylphenyl   Sc$_2$C$_2$@C_{82} or Sc$_3$N@C_{80}

Table 2 Redox potentials (V vs. Fc$^+$/Fc), and reactivity toward **1** of typical fullerenes and EMFs[33]

Compound	$^{Ox}E_1$	$^{Red}E_1$	Reactivity with **1**	
			Thermal	Photo
C_{60}	+1.21	−1.12	×	✔
C_{70}	+1.19	−1.09	×	✔
Y@C_{2v}(9)-C_{82}	+0.07	−0.42	✔	✔
La@C_{2v}(9)-C_{82}	+0.08	−0.41	✔	✔
Ce@C_{2v}(9)-C_{82}	+0.07	−0.39	✔	✔
Gd@C_{2v}(9)-C_{82}	+0.09	−0.39	✔	✔
La@C_s(6)-C_{82}	−0.07	−0.47	×	×
La$_2$@I_h(7)-C_{80}	+0.22	−0.36	×	✔
Sc$_3$N@I_h(7)-C_{80}	+0.62	−1.22	×	✔
Sc$_2$C$_2$@C_{3v}(7)-C_{80}	+0.16	−0.95	×	✔

corresponding to a high electron-accepting ability and accordingly high thermal reactivity toward **1**.

The reactions of the anions and cations of M@C_{82} (M = Y, La, Ce) with **1** were also investigated.[34a] The results showed that the cations react readily even at room temperature in the dark, but the anions do not react either thermally or photochemically, proving that the reactivity of EMFs is tunable upon oxidation and reduction. A recent work confirmed the above conclusion: electrochemically generated dianions of Lu$_3$N@C_{80} react readily with benzal bromide forming a [6,6]-open derivative while pristine Lu$_3$N@C_{80} does not react.[34b] However, the Sc$_3$N@C_{80} dianion generated under identical conditions shows no reactivity toward the electrophile, inferring a cluster-size dependent reactivity of nitride cluster EMFs.

It is noteworthy that the minor isomer of La@C_{82}, i.e. La@C_s(6)-C_{82}, does not react with **1**, or the reaction does not afford any detectable adducts. The low stability of La@C_s(6)-C_{82} is expected to be a main reason.

Although disilirane (**1**) is an effective probe for investigating the chemical reactivity of EMFs, it invariably generates many structural isomers when reacting with the low-symmetric M@C_{82}, which renders further isolation and structural elucidation of the adducts extremely difficult.[33b] Fortunately, the reaction of **1** with the highly symmetric Sc$_3$N@C_{80} and La$_2$@C_{80} gave rise to limited number of mono-adduct isomers: a 1,2-isomer and a 1,4-isomer are formed for Sc$_3$N@C_{80} and only a 1,4-isomer is formed for La$_2$@C_{80}. The 1,2-disilylated Sc$_3$N@C_{80} isomerizes to the 1,4-adduct under heating, proving that the latter is thermodynamically more stable.[33d] X-Ray structures of the corresponding 1,4-adducts, i.e. La$_2$@C_{80}CH$_2$(Dep$_2$Si)$_2$ and Sc$_3$N@C_{80}CH$_2$-(Mes$_2$Si)$_2$, present valuable information related to the motional control of the internal metals by the attachment of the disilirane moieties. As depicted in Fig. 2, the three-dimensional random motion of the two La
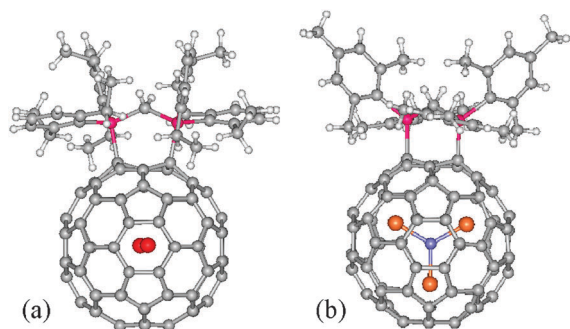
Fig. 2 X-Ray structures of (a) $La_2@C_{80}CH_2(Dep_2Si)_2$ and (b) $Sc_3N@C_{80}CH_2(Mes_2Si)_2$.

atoms in the parent $La_2@C_{80}$ is lowered down to a 2-D horizontal hopping, and the dynamic motion of Sc_3N in $Sc_3N@C_{80}$ is completely stopped in the adduct. Reaction of **1** with $M_2@D_{3h}(5)-C_{78}$ (M = La, Ce) showed unexpectedly high regioselectivity because only one mono-adduct is formed.[35] Its X-ray structure presents a 1,4-addition pattern with the two La atoms being fixed along the equator in the ellipsoidal cage.

Because silicon has a strong electron-donating ability, the redox potentials of the disilylated derivatives are generally more negative than the corresponding values of parent EMFs, rendering disilylation an efficient method for tuning the electrochemical properties of EMFs.[33b]

Diels–Alder reaction: cycloaddition of dienes to EMFs.
Cycloadditions between a conjugated diene and an alkene (termed as dienophile) to form a cyclohexene system are called Diels–Alder reactions. Fullerenes behave as conjugated poly-alkenes and are certainly reactive toward various dienophiles. Although [6,6]-bonds of empty fullerenes are generally more dienophilic, Diels–Alder reactions of EMFs exclusively take place on [5,6]-bonds.

Addition of an o-quinone reagent formed in situ by thermo-lysis of 6,7-dimethoxyisochroman-3-one to $Sc_3N@C_{80}$ represents the first Diels–Alder reaction of EMFs.[36a] Only one mono-adduct isomer was formed. NMR and X-ray results confirmed that the addition occurs at a [5,6]-bond and the Sc_3N cluster is nearly fixed inside the cage.[36b] The same reaction was also performed on $Gd_3N@C_{80}$ and a bis-adduct was isolated, but no detailed structural information was reported.[36c]

Addition of cyclopentadiene (Cp, **2**) to $La@C_{82}$ shows a surprisingly high selectivity: only one monoadduct isomer was formed (Scheme 2).[37] However, the adduct underwent a retro-reaction even at room temperature, thereby impeding its complete isolation and structural determination.

Fortunately, cycloaddition of pentamethylcyclopentadiene (C_5Me_5H, Cp*) to $La@C_{82}$ gave a stable monoadduct because of the substituent effect of the five methyl groups.[38] Its high
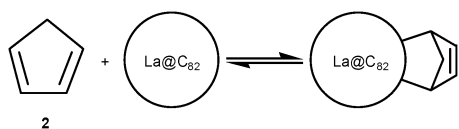
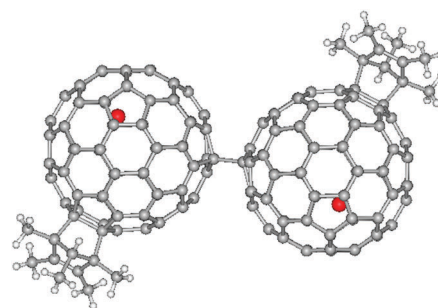**Scheme 2** Reaction of cyclopentadiene (**2**) with $La@C_{82}$.
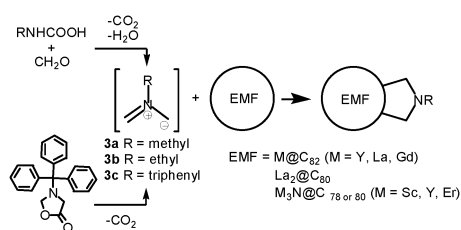

Fig. 3 X-Ray structure of $La@C_{82}Cp*$ dimer.

stability enabled further electrochemical and X-ray single crystallographic characterizations. The X-ray structure of $La@C_{82}Cp*$ is depicted in Fig. 3. The addition takes place on C21 and C23 (cf. Fig. 1a) which have both high POAV values and high positive charges. Though molecule orbital (MO) analysis found no large coefficients on C21 and C23, the positive charges act as the predominant driving force for the high selectivity because Cp* is an electron-rich diene which tends to attack the positively charged C21 and C23. Furthermore, DFT calculations confirmed that the C21–C23 adduct is at least 4.9 kcal mol^{-1} more stable than other possible isomers. More interestingly, $La@C_{82}Cp*$ tends to form a dimer in crystal state. The bond length between the two cages is 1.606 Å, a little longer than a typical C–C single bond in a fullerene cage. The dimerization results from the high POAV value (11.0) and high spin density (0.25) localized on the bonding carbons (C14).[38] Such a phenomenon might facilitate the use of these molecules as sensors and high-density memories.

A theoretical study of the addition of 1,3-butadiene to $Y_3N@D_{3h}(5)-C_{78}$ indicated that the addition should take place on a long [5,6]-bond with large pyramidalization angles (high POAV), confirming a strain-induced addition pattern.[39] Results also showed that the internal Y_3N cluster is so large that it distorts the cage, thereby influencing the addition pattern. Further examination of the more energetically favorable non-IPR $Y_3N@C_2(22010)-C_{78}$ (but not yet isolated) led to the conclusion that a [5,5]-adduct could be formed that is purely induced by bond strains.

Based on the fact that nitride cluster EMFs (especially $Sc_3N@C_{80}$) show lower kinetic reactivity with Cp than other fullerene species, a Cp-functionalized resin, and later a 9-methylanthracene or a cyclopentadienyl/amino-functionalized silica were adopted to isolate $M_3N@C_{80}$ from crude extract without HPLC separation.[40] These results are very useful for large-scale preparation of $M_3N@C_{80}$-type EMFs.

Prato reaction: 1,3-dipolar addition of azomethine ylides.
1,3-Dipolar cycloaddition of azomethine ylides with alkene is a very effective method for constructing pyrrolidine rings, which are important building blocks in pharmaceuticals and natural alkaloids. The most common way to get azomethine ylides (**3**) is the reaction of an immine with an aldehyde to form an iminium followed by the generation of a carbanion. Alternatively, thermal ring-opening of heterocyclic compounds, e.g. N-triphenylmethyl-5-oxazolidinone, can also give the corresponding 1,3-dipolar ylides, i.e., N-triphenylazomethine ylide (**3c**).

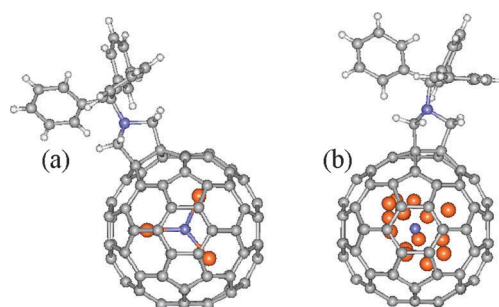**Scheme 3** Reaction of azomethine ylides **3** with different EMFs.

Fig. 4 X-Ray structures of (a) [5,6]-$Sc_3N@C_{80}(CH_2)_2NTrt$ with one set of Sc_3N (90% occupancy) and (b) [6,6]-$Sc_3N@C_{80}(CH_2)_2NTrt$ showing all possible Sc positions.

In 1993, Prato and coworkers reported the first reaction between **3a** and C_{60}.[41] This methodology is thus referred to as Prato reaction.

Since 2004, azomethine ylides (**3**) with different R groups have also been employed to functionalize EMFs (Scheme 3). Multiple adducts were always generated for $M@C_{82}$ (M = La, Y, Gd, *etc.*) but the maximum number of the pyrrolidine moieties was no more than eight, even under forced conditions.[42] Because many regioisomers were generated, no definitive structural characterization of the adducts has been reported yet.

Addition of **3c** to $La_2@C_{80}$ gave rise to both [5,6]- and [6,6]-adducts. Though exhaustive HPLC separations were invalid to separate them, the [5,6]-isomer was crystallized from the mixture and its structure was finally determined by the X-ray diffraction method. Moreover, it was revealed that the two La atoms are fixed at a slantwise position in the [6,6]-adduct while they still rotate in the [5,6]-adduct.[43]

Pronounced results were obtained from the reaction of **3** with $M_3N@C_{80}$: the size of the encapsulated clusters strongly affects the reactivity of the cage carbons and affects the stability of the resulting adducts as well. Addition of **3b** to $Y_3N@C_{80}$ afforded only a [6,6]-adduct, but it occurred regio-selectively on a [5,6]-bond of $Sc_3N@C_{80}$.[44] The unexpected reaction behavior of $Y_3N@C_{80}$ is attributed to the large cluster size, which distorts the cage and promotes the reactivity of [6,6]-bonds. Actually, the [6,6]-adduct of $Y_3N@C_{80}$ is merely a kinetically favored derivative which isomerizes into the thermodynamically more stable [5,6]-adduct under heating.[45] X-Ray structure of [5,6]-$Y_3N@C_{80}(CH_2)_2Net$ presents a slightly pyramidalized Y_3N cluster with the N atom extruding out of the Y_3-plane by 0.13 Å, presenting concrete support of the strong metal–cage interactions.[46]

Addition of **3c** to $Sc_3N@C_{80}$ also afforded two regio-isomers: the kinetic [6,6]-adduct isomerizes to the thermo-dynamic [5,6]-adduct under heating.[47] X-Ray structures of both isomers are shown in Fig. 4. It was found that the random motion of the Sc_3N unit in pristine $Sc_3N@C_{80}$ is more confined in the [5,6]-adduct, where the cluster orientates in such a fashion that two Sc atoms point to the *para* positions of each addition site, respectively, whereas the third Sc atom is rather dangling. However, the Sc_3N cluster is still rotating in the [6,6]-adduct.

Yet there is no definitive conclusion whether the orientation and motion of the internal cluster correlate with the stability of the adducts. Nevertheless, it was proved that the larger cluster size favors the formation of the [6,6]-pyrrolidino adducts for $M_3N@C_{80}$ (M = Sc, Y).[45b] A systematic study of the pyrrolidino reactions of $Sc_xGd_{3-x}N@C_{80}$ (x = 0–3) with **3** disclosed that the relative stability of the [6,6]-adduct *versus* the [5,6]-adduct increases concomitantly with increasing cluster size, and finally the [6,6]-adduct of $Gd_3N@C_{80}$ becomes more stable than the [5,6]-adduct.[48] These results are explainable by the coordination of bigger metals with THJ carbons so as to acquire a planar configuration of the cluster, which increases the reactivity of THJs and decreases that of PHHJs simultaneously.[49]

Reaction of **3c** with $Sc_3N@D_{3h}(5)$-C_{78} afforded only two [6,6]-adducts. Because the encaged cluster is more confined inside the small C_{78} cage, strong interactions between Sc and the adjacent cage carbons are responsible for such high selectivity, as supported by NMR results and DFT calculations.[50]

Addition of **3b** to $Sc_3C_2@C_{80}$ afforded only a [5,6]-adduct. More interestingly, the spin distribution on the Sc atoms was strongly changed upon exohedral modification.[51]

Additionally, treatment of $Dy@C_{82}$ with dimethyl acetylene-dicarboxylate (DMAD) and triphenylphosphine unexpectedly gave rise to only one monoadduct with a yield up to 90%. X-Ray structural analysis of the adduct confirmed an open-cage structure, and the addition sites are the same as those found for the major isomer of $M@C_{82}(Ad)$, *i.e.* C1 and C2 (see Fig. 1a).[52a] The carbene–ylide intermediate appears more reactive than the zwitterion toward the electron-rich region of the molecule.[52b]

Carbene addition. A Cu(I)-catalyzed carbene addition of aryldiazoacetates to $Tb@C_{82}$ afforded multiple methano-derivatives, mainly hexa-adducts.[53] Due to the complexity of the derivatives, no structural results were reported.

Photolysis/thermolysis of 2-adamantane-2,3-[3H]-diazirine (AdN_2) generates the corresponding carbene reagent (**4**, Ad), which shows both high reactivity and high selectivity toward EMFs, especially to $M@C_{82}$ (Scheme 4).[27,54]

As described above, disilylation and the Prato reaction of $M@C_{82}$ always generate many regioisomers, precluding their subsequent separation and structural characterization. In sharp contrast, addition of **4** to $La@C_{82}$ afforded only two
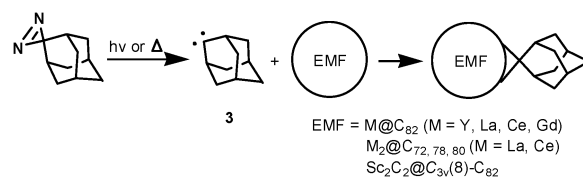
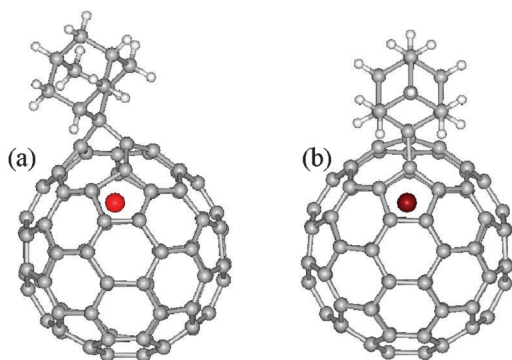**Scheme 4** Cycloaddition of carbene **4** to different EMFs.

Fig. 5 X-Ray structures of (a) La@C_{82}Ad-A and (b) Ce@C_{82}Ad-B.

mono-adduct isomers with an abundance ratio of 4 : 1. Single crystallographic X-ray results of the major isomer La@C_{82}Ad-A (Fig. 5a) disclosed that the Ad group is connected with the two carbons consisting of the hexagonal ring closest to the La atom (C1 and C2 in Fig. 1a), forming an open-cage structure.[27] NMR results of the minor isomer indicated C_s symmetry, suggesting that the addition takes place on C1 and C3. This was unambiguously confirmed by the X-ray results of Ce@C_{82}Ad-B (Fig. 5b).[54b] The high regioselectivity of this reaction can be rationally explained by the highest POAV value and charge density of C1 (Table 1), which engender it very reactive toward the electrophile **4**.

The reaction of **4** with M@C_{82} (M = Y, Ce, Gd) presented similar results: two isomers (abundance ratio = 4 : 1) were formed and their structures were fully characterized with NMR and single crystal X-ray crystallography.[54] These results confirm that the metal in M@C_{82} always tends to locate under the hexagonal ring along the C_2 axis. Such an off-center location plays a critical role in determining the chemical behaviors of the cage carbons.

Reaction of **4** with La@C_s(6)-C_{82} also showed high selectivity by forming only two mono-isomers. Experimental and theoretical characterizations revealed that the addition should have occurred at a place close to the La cation.[55]

Di-EMFs, M_2@C_{2n} (M = La, Ce; 2n = 72, 78 and 80), were also functionalized with **4** and high regioselectivity was observed in most cases. Although as many as six mono-adduct isomers were obtained for the non-IPR La$_2$@D_2(10611)-C_{72}Ad (IPR = isolated pentagon rule), X-ray analyses of the major isomers in combination with theoretical calculations revealed that **4** selectively attacks the carbons adjacent to the [5,5]-junctions, providing substantial evidence that the fused-pentagons are stabilized by the internal metals.[56] In addition, the X-ray structure of a bis-adduct La$_2$@D_2(10611)-C_{72}Ad$_2$ showed that the second Ad group tends to attack the unsubstituted fused-pentagon region, indicating the high reactivity induced by the high curvature.[57] Both photochemical and thermal reactions of **4** with La$_2$@D_{3h}(5)-C_{78} were investigated: the thermal reaction afforded more regioisomers than the photochemical reaction, indicating a more complicated thermal process. Four isomers were isolated from the photoirradiated mixture and one was firmly characterized with XRD.[58] Addition of **4** to La$_2$@C_{80} afforded both [5,6]- and [6,6]-adducts. The X-ray structure of the [6,6]-adduct showed that the random

motion of the La atoms is completely halted in the open-cage derivative such that the two La atoms are collinear with the spiro carbon of the Ad group.[59]

Sc$_2$C$_2$@C_{3v}(8)-C_{82} has been wrongly assigned as Sc$_2$@D_{2d}(23)-C_{84} but a recent NMR study disclosed its true carbide nature.[18b] To obtain concrete structural information, Sc$_2$C$_2$@C_{3v}(8)-C_{82} was first functionalized with **4** so that the random rotation of the spherical molecules in the crystal lattice could be effectively restrained by the covalent attachment of the rigid addend. X-Ray results of a mono-adduct disclosed a symmetric [5,6]-open structure. Several Sc positions were identified, but none was close to the broken bond, indicating a rotating Sc$_2$C$_2$ cluster inside.[60a] Similarly, Sc$_3$C$_2$@C_{80}, which has been wrongly assigned as Sc$_3$@C_{82}, was also functionalized with **4** under photoirradiation. X-Ray results revealed a [6,6]-open addition pattern. More interestingly, the five atoms of the internal Sc$_3$C$_2$ cluster are coplanar with one Sc atom being trapped inside the broken bond and collinear with the C_2 unit and the spiro carbon of Ad.[18a] Very recently, we reported the carbene derivatives of Sc$_2$C$_2$@C_{2v}(5)-C_{80} and found that the motional behavior of the internal Sc$_2$C$_2$ cluster inside the cage is highly temperature-sensitive, thus this molecule can be used as a molecule thermometer.[60b]

Electrochemical results revealed that the Ad group grafted to EMFs has a mild reduction effect, thereby providing an efficient method for designed control of the molecular levels of EMFs.[54–60] These are expected to be useful in future works dealing with the generation of EMF-based materials such as photovoltaics and electronics. In addition, because of the high stability of the adducts and the high symmetry of the rigid Ad group, the resulting derivatives are very suitable for single-crystal growth and X-ray analysis.

Bingel–Hirsch reaction: cyclopropanation of carbanion. Dehydrogenation of bromodiethylmalonate with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) generates the corresponding carbanion (**5a**), which adds to fullerenes forming cyclopropanated adducts with close-cage structures. However, addition of **5a** to La@C_{82} unexpectedly afforded four singly bonded adducts, but only one cycloadduct.[28a] As depicted in Fig. 6a, the X-ray structure of a singly bonded adduct revealed that the addend is linked to a carbon with the highest positive charge (C23 in Fig. 1a), which is certainly very reactive toward the carbanion **5a**. Because the singly-bonded adducts have a close-shell electronic structure, they are too stable to undergo further cycloaddition. These results indicate that paramagnetic EMFs such as La@C_{82} tend
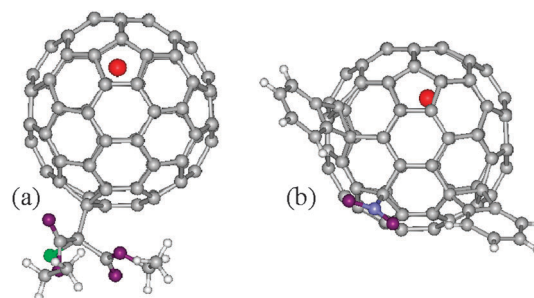

Fig. 6 X-Ray structures of (a) La@C_{82}CBr(COOC$_2$H$_5$)$_2$ and (b) La@C_{82}NO$_2$(C$_6$H$_4$)$_2$.

to pursue a close-shell configuration whenever possible, which is also supported by the larger electrochemical bandgap of the close-shell adduct (1.04 V) than that of La@C$_{82}$ (0.49 V).[28b]

Because of the lower acidity of the methylene proton in malonate, its reaction with DBU was conducted under elevated temperatures. Addition of the corresponding carbanion **5b** to La@C$_{82}$ also generated four singly bonded adducts and one cycloadduct. Unexpectedly, a dominant bis-adduct was also formed in high yield and high selectivity.[28c] Its X-ray structure showed that the two malonate groups are bonded to two adjacent carbons (C23 and C21 in Fig. 1a) far from the internal La^{3+} cation, each having high positive charges and high POAV values. The fact that no bis-adduct was formed in the reaction of **5a** with La@C$_{82}$ is explainable by the steric hindrance of the Br atom to the second addend. Furthermore, results showed that the bis-adduct tends to form a dimer in solid state, a case very similar to La@C$_{82}$Cp* (see Fig. 3). The dimerization also occurs on C14.

Reaction of **5** with diamagnetic EMFs, *e.g.* cluster EMFs, afforded only cycloadducts (Scheme 5). The size effect of M$_3$N cluster on the reactivity of cage carbons was observed again. For instance, cycloaddition of **5a** to Sc$_3$N@C$_{80}$ failed to give any identifiable adduct, but to Y$_3$N@C$_{80}$ gave rise to an unexpected [6,6]-open adduct.[44c,61] X-Ray data of Y$_3$N@C$_{80}$C(COOCH$_2$Ph)$_2$ unveiled that the Y$_3$N cluster is planar with one Y atom positioning inside the open cavity of the broken bond but the rest two Y atoms still move. This cluster orientation is obviously different from that of the Prato-adduct, [5,6]-Y$_3$N@C$_{80}$(CH$_2$)$_2$Net, indicating that the exohedral addition pattern is effective to control the motion and position of the internal metals.

Bingel–Hirsch reaction is a versatile and effective strategy to synthesize cyclopropanated derivatives of EMFs. Reactions of a wide range of bromo-substituted reagents in the presence of DBU (or NaH) with M$_3$N@C$_{80}$ (M = Sc, Lu) have been investigated, and stable [6,6]-adducts were obtained and characterized with NMR or CV techniques.[62]

Addition of **5a** to Sc$_3$N@D_{3h}(5)-C$_{78}$ showed high selectivity: only one mono-adduct and a dominant bis-adduct were obtained. Theoretical calculations and NMR results confirmed that the addition site of the malonate group(s) is controlled by the encaged Sc$_3$N cluster by distorting some regions of the C$_{78}$ cage.[63] Furthermore, closed propane rings between the addend and the fullerene cage are formed, while cyclopropanation of other EMFs always produces open-cage structures.

The non-IPR Sc$_3$N@D_3(6140)-C$_{68}$ was also functionalized with **5a**, and up to penta-adducts were generated. Experimental and theoretical results of an isolated mono-adduct indicated that the addition should occur at the [6,6]-junction next to the fused-pentagon junction, presenting evidence for the stabilization of [5,5]-bonds by the internal metals.[64]
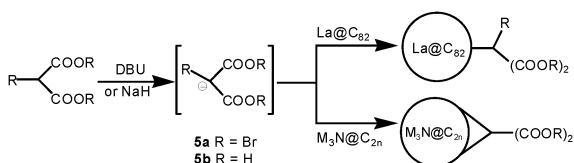
[2 + 2] cycloaddition of benzyne. Addition of benzyne to C$_{60}$ formed exclusively a [6,6]-adduct, but to C$_{70}$ afforded four different isomers with the 1,2-[6,6]-adduct being the major one.[65] Bis- and multi-adducts of C$_{60}$ and C$_{70}$ were also readily obtained, making benzyne an ideal reagent for the cyclobutanation of fullerenes.[66]

Diazotization of anthranilic acid with isoamyl nitrite is a convenient method to generate benzyne *in situ,* which added to Gd@C$_{82}$ forming not only mono-adducts but unavoidably multiple adducts. Two mono-adduct isomers were isolated and characterized with electrochemical methods, which showed that the electronic structure of pristine Gd@C$_{82}$ has been altered dramatically upon benzyne addition. Unfortunately, no distinct structural information of the adducts was available.[67]

Recently, addition of benzyne to La@C$_{82}$ was also investigated. Unexpectedly, aside from the addition of 1–10 benzene rings, a NO$_2$ group was also singly bonded onto the cage, thus quenching the magnetic property of La@C$_{82}$. A pure isomer containing one NO$_2$ group and two benzene rings was isolated and characterized using various methods. Its structure was firmly established using single crystal X-ray crystallography, as depicted in Fig. 6b. The nitro group is added to C18 (*cf.* Fig. 1a) which has a high spin density and a high POAV value, while the two benzynes are cycloadded, respectively, to two [5,6]-junctions involving the *para*-carbons of C18. These confirm that the NO$_2$ group has a positional directing effect on the subsequent addition of the two benzynes. Origin of the NO$_2$ group was from the trace NO/NO$_2$ radicals in isoamyl nitrite as confirmed through several control experiments.[68]

The same methodology was also adopted to modify Sc$_3$N@C$_{80}$ but no nitrated derivatives were formed. Both [5,6]- and [6,6]-adducts were obtained and characterized using many techniques including single crystal X-ray crystallography. Moreover, the high stability of the benzyne derivatives of Sc$_3$N@C$_{80}$ ensures their future applications as photovoltaics and molecule devices.[69]

2.3 Radical addition of EMFs

Radical reactions of EMFs normally generate singly bonded adducts. Moreover, paramagnetic EMFs tend to form a closed-shell configuration so that an odd number of singly bonded addends are always attached, whereas an even number of new bonds are formed for diamagnetic EMFs.

Radical reactions of paramagnetic M@C$_{82}$. Reactions of CF$_3$ radicals (**6**), generated by the thermolysis of CF$_3$I or Ag(CF$_3$CO$_2$), with empty fullerenes have been intensively investigated. More meaningfully, some new higher fullerene isomers, such as C_2(61)-C$_{94}$ and C_1(145)-C$_{96}$, have been accessed using these reactions.[70]

Trifluoromethylation of EMFs was first achieved on a Y@C$_{82}$-enriched sample (Scheme 6).[71] An odd number of CF$_3$ groups—up to five—were attached, as identified by mass spectroscopy, indicating that the paramagnetic Y@C$_{82}$ tends to form a closed-shell electronic structure upon radical addition. Two Y@C$_{82}$(CF$_3$)$_5$ isomers were isolated and characterized with ^{19}F NMR. Calculations proposed a 1,4-chain addition

Scheme 5 Reaction of carbanion **5** with different EMFs.
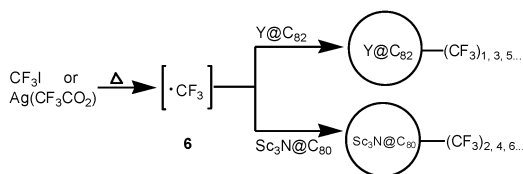
Scheme 6 Trifluoromethylation of different EMFs.

pattern of the five CF_3 groups, as frequently found for empty fullerenes.

Surprisingly, it was found that paramagnetic EMFs are able to undergo radical coupling reactions in toluene or 1,2-dichlorobenzene under photoirradiation. The attempt to synthesize pyrrolidino adducts of La@C_{82} using **3c** unexpectedly resulted in the singly bonded benzyl adducts La@$C_{82}(CH_2C_6H_5)$. Similar phenomena were also observed for the paramagnetic La@C_s(6)-C_{82} and Ce@C_{82}, but only pyrrolidino derivatives were found for the diamagnetic La$_2$@C_{80} and Sc$_3$N@C_{80}.[43,47] Formation of the benzyl adducts results from the addition of benzyl radicals generated under irradiation of toluene. These results confirmed that paramagnetic M@C_{82} prefers radical coupling reactions to 1,3-dipolar reactions because they tend to form closed-shell electronic configurations whenever possible. X-Ray structure of La@$C_{82}(CHClC_6H_3Cl_2)$ synthesized by irradiation of La@C_{82} in 1,2-dichlorobenzene showed that the addend is singly bonded to a cage carbon with a high spin density and a high POAV value (C10 in Fig. 1a). However, benzene is not suitable for such radical reactions because no radicals could be generated under photoirradiation. The radical adducts of La@C_{82} underwent retro-reactions under heating with the presence of a radical trapping reagent, affording the pristine La@C_{82} in high yields (up to 96%). Therefore, such radical reactions are useful for selective isolation of paramagnetic EMFs.[29]

Multiple addition of phosphoryl radicals or phenyl radicals to La@C_{82} and perfluoroalkylation of La@C_s(6)-C_{82} were reported earlier, but no clear structural information was presented in these reports.[72]

Radical reactions of diamagnetic EMFs. No radical reactions of divalent mono-EMFs or di-EMFs have been reported to date, but several examples of the radical derivatives of cluster EMFs are available.

Although Sc$_3$N@D_{5h}(6)-C_{80} is always more reactive than the I_h(7)-isomer, both showed essentially the same reaction rate toward CF_3 radicals at 520 °C (Scheme 6).[73] All the trifluoromethylated adducts contain an even number of CF_3 groups (from 2 to 12). A bis-adduct was isolated and NMR results indicated a 1,4-addition pattern. Calculations showed that the Sc$_3$N cluster is nearly fixed in the derivative with two Sc atoms coordinating with the *para* carbons of the addition sites. Moreover, it was disclosed that the two CF_3 groups have dramatically changed the molecule orbital levels of Sc$_3$N@C_{80}. With an obvious decrease of HOMO/LUMO bandgap, several new redox processes were observed in Sc$_3$N@$C_{80}(CF_3)_2$. Thus, trifluoromethylation is an effective method for tuning the electronic structures of EMFs.[74]

Recently, Sc$_3$N@$C_{80}(CF_3)_x$ (x = 14, 16) were synthesized by heating the EMF with Ag(CF_3CO_2) and their molecule
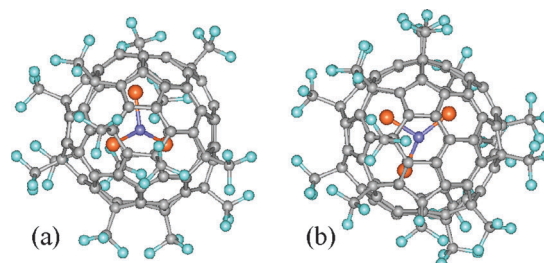
Fig. 7 X-Ray structures of (a) Sc$_3$N@$C_{80}(CF_3)_{14}$ and (b) Sc$_3$N@$C_{80}(CF_3)_{16}$.

structures were firmly determined by single crystal X-ray crystallography (Fig. 7), which provided valuable information about the mutual influence between the internal cluster and the exohedral substituents.[75a] It has been commonly accepted that THJs are always less reactive than fullerene carbons of other types (*e.g.* PHHJs or PPHJs) because of their low degree of pyramidalization. However, four and eight THJs are substituted for x = 14 and x = 16, respectively. Detailed structural analyses coupled with theoretical calculations disclosed that formation of isolated aromaticity and their coordination with the internal metals are the main reasons for such addition patterns. Similar results were also obtained by other researchers later.[75b] These results are informative for designated multiple additions to EMFs in future. A recent study of a series of Sc$_3$N@$C_{80}(CF_3)_n$ (n = 2–16) isomers, both experimentally and computationally, further confirms the mutual influence between the internal cluster's orientation and the multiple addition sites.[75c]

Heating diethyl malonate in the presence of manganese(III) acetate generates the corresponding carbon radicals which added to M$_3$N@C_{80} (M = Sc, Lu) forming cyclopropanated adducts. NMR results of an isolated mono-adduct proposed a [6,6]-open structure, similar to the corresponding Bingel–Hirsch adduct.[76] It would be interesting to perform the reaction on paramagnetic EMFs and singly bonded adducts could be expected.

Benzyl radicals generated by photoirradiation of benzyl bromide added to M$_3$N@C_{80} (M = Sc, Lu) producing only one dibenzyl adduct in high yield. NMR and X-ray results confirmed a 1,4-addition pattern. The planar Sc$_3$N cluster is nearly fixed inside the cage with two Sc atoms closest to the *para* carbons of addition, respectively, similar to that proposed for Sc$_3$N@$C_{80}(CF_3)_2$.[77]

Dichlorophenyl derivatives of insoluble EMFs. During past years, great efforts have been devoted to achieve insoluble EMFs, but successful results reporting explicit molecule structures were only available for La@C_{2n} ($2n$ = 72, 74, 80, 82).[78] These insoluble EMFs were obtained in forms of their dichlorophenyl derivatives during the 1,2,4-trichlorobenzene extraction process.

X-Ray structures of La@$C_{2n}(C_6H_3Cl_2)$ ($2n$ = 72, 74, 80, 82) are presented in Fig. 8. All have cage structures different from corresponding empty fullerenes and di- or cluster EMFs, indicating that the formation of fullerene cages is dictated by the internal metals. La@C_2(10612)-C_{72} has a non-IPR cage with one pair of fused-pentagons. The La atom is localized

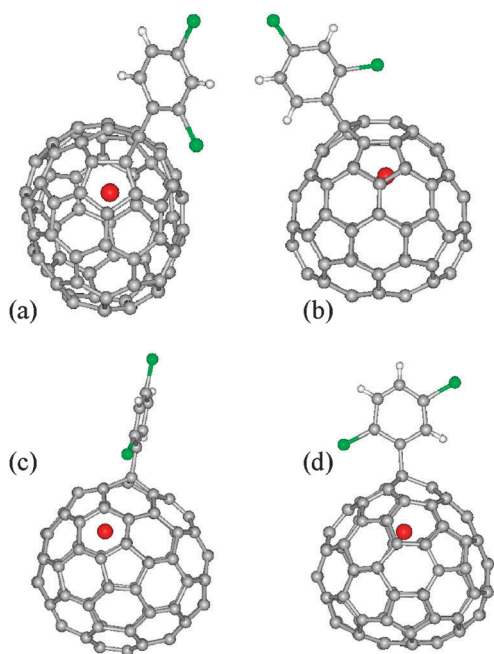**Fig. 8** X-Ray structures of (a) La@C_2(10612)-$C_{72}C_6H_3Cl_2$, (b) La@D_{3h}-$C_{74}C_6H_3Cl_2$, (c) La@C_{2v}(3)-$C_{80}C_6H_3Cl_2$, (d) La@C_{3v}(7)-$C_{82}C_6H_3Cl_2$.

close to the fused-pentagon junction. The dichlorophenyl group is not added to either of the [5,5]-carbons, but singly bonded to an adjacent one, confirming that the fused-pentagon has been stabilized by the internal metal.[78a] La@C_{74} has the only D_{3h} IPR cage. The addend is bonded to a PHHJ carbon close to the metal.[78b] La@C_{80} takes the C_{2v}(3) cage which has never been found or even predicted because earlier theoretical calculations proposed that the D_{5h}(6), I_h(7), and C_{2v}(5) cages are more stable for C_{80}^{3-}.[78c] La@C_{3v}(7)-C_{82} is also unexpected because it is theoretically less stable than La@C_{3v}(8)-C_{82}, but dichlorophenyl substitution changes the stability order. Remarkably, the dichlorophenyl group is singly bonded to a THJ carbon, which has the highest radical character because of strong metal–cage interactions.[78d] In contrast, THJ carbons of other fullerene and EMFs are always less reactive than carbons of other types.

The results presented above indicate that only paramagnetic mono-EMFs are obtainable using this method because localized high spin and pyramidalization on some special carbons are necessary to ensure the dichlorophenyl addition. Furthermore, considering the fact that no dichlorophenyl derivatives of the more abundant La@C_{82} are isolated, the derivatization process may involve a heterogeneous catalytic process: La@C_{82} is highly soluble in TCB and is exempted from dichlorophenyl addition.[78]

2.4 Noncovalent functionalization of EMFs

Inclusion of the spherical fullerenes inside the cavity of bowl-shaped hosts, such as calixarenes, has opened a new way for creating supramolecular complexes with novel functionalities.[79] The host–guest complex of Dy@C_{82} with *p-tert*-butylcalix[8]arene (C8A, **7e**) was prepared in solution by Yang *et al*. in 2002. It was confirmed that it is more difficult for

Dy@C_{82} to form a supramolecular complex than C_{60}, probably due to its larger size. However, once formed, Dy@C_{82}-C8A is more stable than C_{60}-C8A.[80]

Azacrown ethers were found to be more effective for constructing supramolecular systems with EMFs. A series of macrocyclic compounds including calix[*n*]arenes (*n* = 4–8, **7**), hexaazacyclooctadecane with or without N-substituted methyls (**8**), mono-aza-18-crown-6 ether (**9**), and 18-crown-6 ether (**10**) were investigated. The results showed that only these N-substituted compounds can form stable 1 : 1 host–guest complexes with La@C_{82} accompanying with one electron-transfer to the EMF, but empty fullerenes do not form stable complexes with any of these compounds. Consequently, some of the cyclic compounds were used to isolate EMFs from the extract selectively, and successful results were obtained (Fig. 9).[81]

Similarly, unsaturated thiacrown ethers (**11**) are also good host molecules for EMFs such as La@C_{82} but the saturated one (**12**) shows no affinity. The inclusion behaviors of 15-, 18, 21-, and 24-membered unsaturated thiacrown ethers with La@C_{82} and the ring-size effect were investigated thoroughly. All showed high affinity to La@C_{82} and the electron transfer from these ether molecules to the EMF was confirmed by absorption spectroscopy. Size matching was found to be critical to the stability of the resulting complexes. The most suitable one is **11c** with a ring size of 8.9 Å, which best fits La@C_{82} (8.6 Å).[82]

More pronouncedly, N-substituted *p*-phenylenediamine (**13**) can form stable radical ion pairs with La@C_{82} and La$_2$@C_{80}, respectively. Such spin-site exchange processes are reversible in solution, which provides useful concepts for developing promising materials for optical and magnetic applications.[83]

Recently, a porphyrin dimer was adopted to recognize La@C_{82}, and formation of 1 : 1 adduct was evidenced by means of electronic and electrochemical techniques.[84]

2.5 Encapsulation of EMFs inside carbon nanotubes (CNTs)

Fullerenes and EMFs are ideal guest molecules to be inserted inside carbon nanotubes (CNTs), forming the so-called nano 'peapods'.[85] Strong interactions between the inserted fullerene or EMF molecules and the CNT inner wall were evidenced from many experimental results. In addition, with the
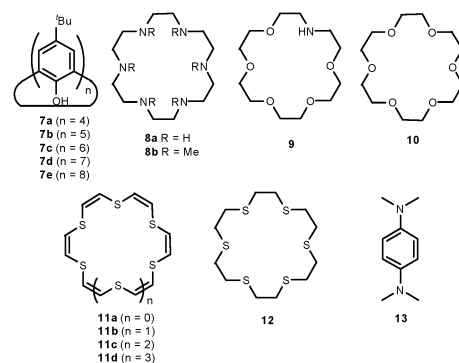

Fig. 9 Organic molecules used to construct supramolecular complexes with EMFs.

confinement of CNTs, the EMFs are uniformly arranged inside, which enables direct observation of the movements of metals and/or the cages and promises several novel applications such as quantum computing units, high-density memories, drug carriers and nano reactors.[86]

However, the insertion of EMF-derivatives inside CNTs is rarely reported.[86e] Since exohedral modification is very effective to alter the conformation and motion of the internal metals, such hybrid materials of CNTs filled with well-defined EMF-derivatives would be very fantastic and useful in many fields.

Polyhydroxylation and others. EMFs are only soluble in organic solvents so that several methods were developed to synthesize water-soluble derivatives by attaching a great number of hydrophilic groups such as hydroxyl and amino acid. Treatment of EMFs with either a reductant such as potassium or sodium or an oxidant such as nitric acid or peroxide followed by hydrolysis proved effective toward poly-hydroxylated EMFs.[87] Alternatively, the 'tetrabutylammonium hydroxide (TBAH) phase-transfer method' is more common for laboratory synthesis of water-soluble EMF derivatives because it requires milder conditions and shows higher efficiency.[88]

Furthermore, additions of glycine esters or amino acids to EMFs were also reported.[89] The resulting water-soluble derivatives have shown promising applications in clinical diagnostic/therapeutic purposes, as discussed below.

3. Potential applications of EMFs and their derivatives

The metal–carbon hybrid character of EMFs makes them more attractive and more useful than empty fullerenes. Preliminary results have presented many promising applications of EMFs in fields such as biomedicine, photovoltaics and materials science.

3.1 Water-soluble derivatives of EMFs: useful materials in biomedicine

MRI contrast reagent. Water-soluble derivatives of gadolinium-EMFs are promising magnetic resonance imaging (MRI) contrast reagents with high relaxivity and low toxicity. Numerous successful results have been reported.[89–95]

Table 3 summarizes the longitudinal proton relaxivity (r_1) of some typical MRI contrast reagents. The clinically used Gd–DTPA (DTPA = diethylenetriaminepentaacetic acid) reagent (Magnevist®) has an r_1 value of 3.9 mM^{-1} s^{-1}.[90] In contrast, the polyhydroxylated Gd-EMFs show much higher r_1 values, generally 10–50 times higher than that of Gd–DTPA.[89–93] Apparently, more OH groups on the fullerene cage correspond to higher r_1 values because highly hydroxylated EMF–(OH)$_n$ molecules aggregate into large particles in solution. However, large particles may cause relevant diseases such as thrombosis in living bodies so that several studies on their aggregation behaviors were conducted.[91,96] Results showed that the aggregation is largely dependent on the environment, particularly the pH value and the salt concentration. Thus, varying pH values and adding salts are effective solutions to destroy the aggregations.

Table 3 Longitudinal proton relaxivity (r_1/mM^{-1} s^{-1}) and hydro-dynamic radius (R_{hyd}/nm) of some Gd-containing MRI contrast reagents

Compound	r_1	R_{hyd}	Ref.
Gd–DTPA	3.9	92.8	90
Gd@C$_{60}$[C(CO$_2$H)$_2$]$_{10}$	6.8–24.0	30–700	91
Gd@C$_{60}$(OH)$_{27}$	14.1–83.2	50–1200	91
Gd@C$_{82}$(OH)$_{40}$	81	—	92
Gd@C$_{82}$(OH)$_{22}$	37.7–61	65–95	89b,93
Gd@C$_{82}$(OH)$_6$(NHC$_2$H$_4$SO$_3$H)$_8$	4.5	—	89b
Gd@C$_{82}$O$_6$(OH)$_{16}$(NHC$_2$H$_4$CO$_2$H)$_8$	9.1	30	89c
Gd$_3$N@C$_{80}$-Hydrochalarone	205	10–15	94a
Gd$_3$N@C$_{80}$[DiPEG(OH)$_x$]	232–460	37–96	95

Although the amino acid derivatives of Gd-EMFs show no markedly higher relaxation ability than Gd–DTPA, their *in vivo* metabolizing behaviors differ from those of Gd–DTPA and the polyhydroxylated Gd-EMFs.[91] Accordingly, they can be used as alternatives to the commercial Gd–DTPA with decreased uptake by the reticuloendothelial system (RES) and facile excretion *via* the urinary tract.

Remarkably, Gd$_3$N@C$_{80}$-derivatives show the highest relaxivities among these reagents, and accordingly they are very promising in future applications. It was proposed that the high relaxivity of Gd$_3$N@C$_{80}$-Hydrochalarone is not only due to the greater number of Gd^{3+} cations, but also because of its different relaxation mechanism from that of the Gd@C$_{2n}$-derivatives.[95] Utilizing the high contrasting ability of Gd$_x$Sc$_{3-x}$N@C$_{80}$-BioShuttle, single cell detection becomes possible.[94b]

In summary, Gd-EMFs appear to be the next-generation high-efficiency MRI contrast reagents because of advantages such as: (i) high stability and low toxicity. The toxic metal ions are protected by the fullerene cages and the whole molecule shows no obvious toxicity to living bodies. (ii) High relaxivity. Water soluble Gd-EMFs provide the same contrast at a lower dosage and in a shorter exposure time, reducing the exposure risk but giving highly efficient therapy. (iii) Multifunctionality. The surface of Gd-EMFs can carry various biomolecules (*e.g.* tumor antibodies) along with the hydrophilic groups, allowing target-directing diagnosis; while the internal can host different metals with multiple functions.

X-Ray imaging contrast reagent. Lu$_3$N@C$_{80}$ demonstrates sharp X-ray contrast under irradiation, but C$_{60}$ does not, confirming that the contrast is originated from the internal cluster instead of the carbon cage. Consequently, it is expected that such EMFs encapsulating mixed-metal clusters (*e.g.* Gd and Lu) will be multimodality contrast agents suitable for both MRI and X-ray diagnoses.[97]

Radiopharmaceuticals for biolabeling/biotracing. Bio-distribution of EMFs was investigated using ^{166}Ho$_x$@C$_{82}$(OH)$_{16}$ as a radiotracer. *In vivo* studies revealed that this material was presented to all the organs of BALB/c mice 1 h after injection, except to tissues with limited blood flow such as brain and fat, indicating a blood-delivery character. However, it was difficult to completely metabolize Ho$_x$@C$_{82}$(OH)$_{16}$ within 48 h from liver, bone, kidney and spleen, but slow and steady clearance

over 5 days was observed in Fischer rats, implying low toxicity in living bodies.[88b,c]

Using a modified Krätschmer–Huffman apparatus, $^{177}Lu_xLu_{3-x}N@C_{80}$ (x = 1–3) was synthesized and then conjugated with an interleukin-13 peptide. The results showed that the cage is sufficiently stable to survive the β-decay process and therefore such materials are very promising as radiotherapeutic/radiodiagnostic reagents.[98]

Chemotherapeutic pharmaceuticals. Several reports about the therapeutic use of $Gd@C_{82}(OH)_{22}$ nanoparticles are exciting.[99] For example, these nanoparticles were found to be good antioxidants and free radical scavengers superior to the C_{60} analogues intercepting all the major physiologically relevant reactive oxygen species (ROS).[99a] Furthermore, they can reverse tumor resistance to the clinically used chemotherapeutic cisplatin by reactivating the impaired endocytosis of cisplatin-resistant human prostate cancer cells by restoring defective endocytosis.[99b] In addition, $Gd@C_{82}(OH)_{22}$ nanoparticles are also antineoplastic pharmaceuticals with high efficiency and low toxicity.[99c]

3.2 Donor–acceptor conjugates for photovoltaics

Donor–acceptor systems based on empty fullerenes have been widely investigated; some useful materials have been synthesized.[3,4] Because the abundant electronic features of EMFs resulted from the charge transfer, they are expected to be more useful than empty fullerenes.[5]

In 2008, the first donor–acceptor dyad of EMFs was generated using the Prato reaction of $Sc_3N@C_{80}$ with sarcosine and ferrocene carboxaldehyde.[100] Subsequent NMR and electrochemical measurements indicated a [5,6]-adduct. Time-resolved transient absorption spectroscopy confirmed the successful formation of a radical ion pair state. Other $Sc_3N@C_{80}$-based donor–acceptor conjugates with a triphenylamine group linking to different sites of the pyrrolidine ring were also synthesized using the Prato reaction.[101] It was found that the N-substituted dyad is more stable than the 2-substituted one. More importantly, the former produces a significantly longer lived radical pair than the latter. These $Sc_3N@C_{80}$-based dyads have considerably longer lived charge separated states than the corresponding C_{60} analogues, proving the superiority of $Sc_3N@C_{80}$ to C_{60} in the application of organic solar cells.

In addition, dyads of $M_3N@C_{80}$ (M = Sc, Y) bearing different donors such as tetrathiafulvalene, phthalocyanine, and ferrocene were obtained using 1,3-dipolar or Bingel–Hirsch reactions. Photophysical investigations of some compounds confirmed the existence of photoinduced electron-transfer processes with obviously longer life times than the C_{60} analogues, but most of them show low stability compared to the corresponding C_{60} analogues.[102]

Reaction of $La_2@C_{80}$ with azomethine ylides containing a π-extended tetrathiafulvalene (exTTF) moiety, a widely used electron donor in fullerene-based dyads, afforded a [5,6]-adduct exclusively. Though very weak interactions between exTTF and $La_2@C_{80}$ exist at ground state, fast formation of a radical ion-pair state was observed at excited state by means of transient absorption spectroscopy.[103]

Diazoalkane additions of benzoylbutyrate p-tosylhydrozones to $Lu_3N@C_{80}$ afforded a series of $Lu_3N@C_{80}$-PCBX (X = M: methyl, B: butyl, H: hexyl, O: octyl) compounds with cyclopropanated open structures. They were adopted to construct high-performance organic photovoltaic devices. Very exciting results were obtained for the $P3HT/Lu_3N@C_{80}$-PCBH system, which shows a high open circuit voltage of 890 mV and a power conversion efficiency (PCE) value >4%. It is expected that using other low-bandgap polymers as donors, PCE greater than 10% will be achieved in the near future.[104] Similar compounds were also obtained for $M_3N@C_{80}$ (M = Sc, Lu), and [6,6]-open structures were unambiguously confirmed by NMR and X-ray data, but no photophysical experiments were conducted.[105]

A novel electron donor–acceptor conjugate, $Ce_2@I_h-C_{80}$-ZnP, was synthesized using a diazo precursor. Interestingly, photochemical studies disclosed unprecedented charge transfer pathways in this compound. In non-polar solvents, a reductive charge transfer takes place, forming $(Ce_2@I_h-C_{80})^{\bullet-}–(ZnP)^{\bullet+}$; while in polar solvents, the process is oxidative, generating $(Ce_2@I_h-C_{80})^{\bullet+}–(ZnP)^{\bullet-}$.[106]

3.3 Nanomaterials

EMFs can form nanoclusters in the mixture involving a good solvent (e.g. CS_2) and a poor solvent (e.g. acetonitrile). Nanoclusters of $Sc@C_{82}$ (15–35 nm) formed in toluene/acetonitrile were used to synthesize corresponding 1-D and 2-D nanostructures in AAO template with an electrochemical method. By adjusting the deposition time, nanotubes and nanowires were obtained respectively. HRTEM and XRD results confirmed a non-crystalline form in both nanostructures.[107]

The carbene derivative of $La@C_{82}$ forms crystalline nanorods during the process of single-crystal growth, which shows an unusual p-type FET property in contrast to the well-known n-type semiconductive thin films or whiskers of empty fullerenes. Results further showed that these nanorods made of paramagnetic $La@C_{82}Ad$ orient with their axis perpendicular to the magnetic field, indicating that the nanorods have a negative magnetic anisotropy. Such materials are expected to be useful as nanoelectronics and for magnetic purposes.[108]

Nanostructures of pristine $Sc_3N@C_{80}$ were recently prepared using a liquid–liquid interfacial precipitation method. By changing the good solvent from toluene to CS_2, the morphology was tailored from nanowhiskers to nanosheets. In both structures, crystalline form was confirmed.[109]

3.4 Others

Because high-yield EMFs generally contain rare earth ions which are the mainstay of many optoelectronic applications, investigations of the optical properties of EMFs have been of considerable interest.

Large third-order nonlinear optical responses were found for $Dy@C_{82}$ and $Gd_2@C_{80}$ either in solution or as solid thin films attributable to metal–cage charge transfer.[110] Photoluminescence corresponding to the f–f transition of Er^{3+} is frequently reported for Er-containing EMFs.[111] A recent study revealed that the photoluminescence from a single $Y_3N@C_{80}$ molecule could be enhanced by 100 times when

associated with a gold nanoparticle, thus engendering such molecules practically useful as solar-cell materials and organic light emitting devices.[112]

Magnetic properties of EMFs are also intriguing but there is lack of investigation except for Gd-EMFs as MRI contrast reagents.

4. Conclusions and perspectives

We have drawn a systematic sketch of the chemical transformations and possible applications of the distinctive EMFs. Although considerably less studied than empty fullerenes, EMFs have exhibited numerous novel properties, interesting phenomena/function and huge potential applications, most of which are associated with the internal metals and their influences on the whole molecules.

Frankly speaking, the chemistry of EMFs has mainly resembled the better-established fullerene chemistry. However, only a small percentage of reactions reported for empty fullerenes has been successfully copied to EMFs, and many details remain unexplored. The low selectivity of some low-symmetric EMFs could be sufficiently improved by choosing suitable reagents and utilizing the role that internal metals play in differentiating the reactivity of cage carbons. This strategy will be continuously useful in future works.

Multiple addition, multi-step reactions, and catalytic reactions of EMFs are of high importance but represent great challenges. Complexes of EMFs with transition metals are intriguing for the dual effects of the inner and outer metals, which may provide unexpected properties. Preparations of thin films, self-assembled monolayers, and well-defined nanostructures of EMFs are also interesting because these are technical groundwork for construction of organic nanodevices. Consequently, supramolecular chemistry of EMFs will receive continuous attention.

More challenging and more important is the work to promote the availability of EMFs. To light up the future of EMFs, concrete efforts must be devoted to increasing the production yield by, for example, searching for more efficient catalysts or inventing new synthetic methods. Furthermore, more powerful extraction methods and more convenient separation processes are necessary for industrial production of EMFs in future.

Through multidisciplinary endeavors, fruitful results and more and more applicable materials based on EMFs will appear soon.

Acknowledgements

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