

Electron spin resonance spectroscopy of empty and endohedral fullerenes[†]

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Fullerene derivatives exhibit many interesting structural, electronic, and chemical properties, largely determined by the carbon cage's ability to accept electrons. Electron spin resonance spectroscopy is a very sensitive and important technique to detect open shell species and to determine HOMO and LUMO density distributions. Here we present a short overview of the most significant and informative reports of electron spin resonance studies of empty and endohedral fullerenes, classified on the basis of the entrapped moiety, cage size symmetry, and on the techniques used to generate the paramagnetic states. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: electron spin resonance spectroscopy; empty fullerenes; endohedral fullerenes

INTRODUCTION

Since the discovery of fullerenes in 1985^[1] by Kroto, Curl, and Smalley, an immediate question was posed: Is it possible to encapsulate atoms or molecules inside the hollow space of these carbon allotropes? It was quickly found that the answer was yes, and the same year, these authors reported the detection of La@C₈₂, where the symbol @ is used to denote the inclusion of La inside a C₈₂ cage.^[2] Since then, many examples of encapsulated moieties have been reported with many different fullerene cages containing a wide variety of atoms and clusters inside, and these compounds are collectively called endohedral fullerenes (EFs). The encapsulated species include non-metals; rare earth metals; metals of groups II, III, and IV; and also metallic clusters such as metallic carbides, nitrides, oxides, sulfides, cyanides, and even hydrocarbon have been reported.^[3]

Endohedral fullerenes exhibit many interesting structural, electronic, and chemical properties, largely determined by the EF carbon cage ability to accept electrons, generating stable systems with highly positive encapsulated species inside highly negative carbon cages with minimal reduction in symmetry.^[4] These compounds are typically studied by electrochemistry, a very useful tool for the characterization of their electronic properties. When electrochemistry is combined with electron spin resonance (ESR) detection of open shell species, a very sensitive tool results to probe the paramagnetic states and HOMO and LUMO density distributions. ESR spectroscopy is also an important technique to probe the structure of these interesting compounds. Herein, we have compiled the most significant and informative reports of ESR studies of empty and endohedral fullerenes, classified on the basis of the entrapped moiety, cage size symmetry, and on the techniques used to obtain the paramagnetic states. This is not an exhaustive review of the subject but rather an overview of some selected examples.

EMPTY FULLERENES

Although most fullerene derivatives are ESR-silent because they possess closed-shell electronic structures, there are several chemical and electrochemical techniques that can be used to

introduce unpaired spins *in situ* via electron reduction or oxidation. In 1991, the ESR study of the anion radical of C₆₀ generated by electrolysis was reported, which exhibited a g value of 1.9999. This spectrum exhibited two interesting features: (i) the g factor was significantly smaller than would be anticipated for a radical consisting of only carbon atoms; and (ii) there was a dramatic temperature effect on the line width.^[5] In addition, this spectrum (refer to Fig. 1) consisted of two types of signal, one very broad superimposed with a much sharper one, and the nature of the latter has been the subject of extensive controversy.^[6]

One of the most viable explanations for the presence of the sharp signal was presented by Reed *et al.* in 2000, who suggested that the existence of the sharp signal was caused by a C₁₂₀O impurity in solid C₆₀ samples that have been exposed to air and light (refer to structure in Fig. 1). This explanation was based on three main observations: (i) the ESR features of the anion radical of an authentic sample of C₁₂₀O perfectly matched those exhibited by the narrow line; (ii) the addition of C₁₂₀O to a solution of the anion radical of C₆₀ resulted in an increase of the relative intensity of this narrow signal only; and (iii) a sample of high purity (C₆₀)²⁻ showed a sharp line-free ESR spectrum at 100 K.

An alternative interpretation for the observation of the sharp ESR line was proposed by Dunsch *et al.* in 1998. Their interpretation was based on the idea that the anion radical of C₆₀ can undergo partial dimerization to produce the dimeric dianion (C₆₀)₂²⁻, which should be ESR silent but could be converted into the corresponding paramagnetic species (C₆₀)₂⁻ via disproportionation reactions (refer to structure in Fig. 1). In 2002, Dunsch and co-workers reported spectroelectrochemical studies of C₆₀

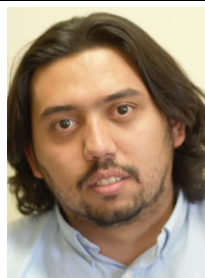
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Biography

Elkin L. Romero was born in Montería, Colombia, in 1988. He received his BSc and MSc in Chemistry from the Universidad del Valle in Cali, Colombia, in 2011 and 2014, under the supervision of Prof. Fabio Zuluaga and Prof. Manuel N. Chaur, respectively. In 2015, he joined the group of Prof. Luis Echegoyen at the University of Texas—El Paso. His current research involves the synthesis of new endohedral fullerenes and ESR studies of these fullerene derivatives.



Biography

Prof. Luis Echegoyen was born in La Habana, Cuba, in 1951. He obtained both his BSc and PhD from the University of Puerto Rico in Rio Piedras (1971 and 1974, respectively). After an industrial placement at Union Carbide and several professorships at the Universities of Puerto Rico, Maryland, and Miami, in 2002, he was appointed as Chair of the Department of Chemistry at Clemson University, in South Carolina. Later he served as Division Director for Chemistry at the National Science Foundation for 4 years (2006–2010) and more recently, he became the Robert A. Welch Professor of Chemistry at the University of Texas—El Paso in 2010. His research interests include fullerene chemistry, electrochemistry, and supramolecular chemistry, with special emphasis in photovoltaics and endohedral fullerenes.



with different electrolyte systems in order to determine the source of the ESR spike signal. The authors found that higher charged C_{60} anions are unstable and react easily with most organic solvents used in electrochemistry,^[7] which, of these interpretations for the nature of the species responsible for the sharp ESR signal, still remains unanswered.

Electron spin resonance spectroscopic studies for the anion radicals of higher empty fullerene are less abundant than for C_{60} . The ESR spectrum of the anion radical of C_{70} showed a g value of 2.005 with remarkable anisotropy as a result of the symmetry of the fullerene cage.^[8] In 2008, Dunsch and co-workers reported the ESR study of the anion radicals of two bis-adducts of C_{70} , $[C_{70}(CF_3)_2]^-$ and $[C_{70}(C_2F_5)_2]^-$, generated by electrolysis. The ESR spectrum spectra of the anion radicals showed a quartet with $hfcc$ of 0.324 G and an octet with $hfcc$ of 0.83 G for $C_{70}(CF_3)_2$ and $C_{70}(C_2F_5)_2$, respectively. These results suggested that the spin distribution is coupled to only one of the two CF_3 groups.^[9] The ESR spectrum of the anion radical of C_{76} exhibited a narrow signal with a g value of 2.002,^[10] which is close to the g value of 2.003 reported for

the cation radical of C_{76} by Reed in 1996,^[11] an expected result based on the lower symmetry of this fullerene cage. The ESR spectra of the anion radicals of two isomers of C_{78} showed notable differences, with g values of 2.002 and 2.004 for the C_{2v} and D_3 isomers, respectively.^[10] In 2008, Dunsch and co-workers reported the ESR studies of the mono, di, and trianion radicals of C_{82} isomer C_2 (3) generated via electrolysis, which showed a very sharp line with a g value of 2.0009 for $[C_{82}]^{3-}$; as expected, the di-anion was ESR-silent, and the tri-anion radical exhibited an ESR signal with a g value of 2.0020. Additionally, the cation radical of the C_2 (3) isomer of C_{82} exhibited a g value of 2.0029.^[12] Later, the same group reported ESR studies of the anion radicals of the C_s , C_2 , D_2 , and D_{2d} isomers of C_{84} .^[13] The ESR spectra of the C_s and C_2 isomers showed a sharp ESR line with g values of 2.0011 and 2.0004, respectively (refer to Fig. 2a and b). The anion radical of the D_2 isomer of C_{84} exhibited a sharp but not very intense line with a g value of 2.0008, as shown in the ESR spectrum of a mixture of C_2 and D_2 isomers (Fig. 2c). The D_{2d} isomer exhibited a broad signal with a g value of 2.0013, which also showed an impurity signal arising from the anion radical of the C_{82} – C_2 isomer. The authors concluded that the symmetry of the fullerene has a strong influence on the line width of the ESR signal of these anion radicals, as previously reported for fullerene dimers.

ENDOHEDEAL FULLERENES

Classical endohedral fullerenes

Unlike empty fullerenes, some endohedral fullerenes are intrinsically paramagnetic in their pristine form, so ESR studies have been important for their characterization. In 1992, La-EF extracts were characterized by ESR spectroscopy in solution and in the solid state, exhibiting octet signals as a result of coupling of the electron spin with a single $I = 7/2$ nucleus, with approximately equal intensities and a hyperfine coupling constant ($hfcc$) of 1.25 G and a g value of 2.0010. These studies revealed that the metal center has a formal charge of $3+$.^[14] Thus, the formal charge states for these endohedral compounds are best described by the formula $M^{3+}[C_{82}]^{3-}$. Similar results were reported by Weaver and co-workers for ESR measurements of Y-EF extracts, which exhibited two equal intensity lines as a result of electron spin coupling with the $I = 1/2$ metal nucleus with a small $hfcc$ (0.48 G) centered at a g value of 1.9999.^[15] In the same year, Shinohara *et al.* published the preparation of Sc-containing C_{82} species, and ESR spectroscopy helped to determine that it contained an encapsulated scandium trimer, $Sc_3@C_{82}$,^[16] which was later shown to correspond to $Sc_3C_2@C_{80}$. Both solution and solid-state ESR spectra of $Sc@C_{82}$ exhibited similar features to those reported by Weaver and Johnson, suggesting that Sc is present in a trivalent state,^[17] which was corroborated by DFT calculations.^[18] In 1995, Boonman and co-workers studied Er-EF extracts by high-frequency ESR spectroscopy.^[19] The ESR spectra showed two resonances; the first, at high magnetic fields, was assigned to a fullerene cage localized spin with a g value of 2.005, and the second, at lower magnetic fields, with an apparent g value of ~ 8.6 was assigned to transitions of the Er^{3+} ions in the fullerene system, which led to the conclusion that the electronic structure of these extracts was $[Er^{3+}][C_{82}^{3-}]$ even though there was no resolved hyperfine splitting.

With the development of better isolation and purification methods, it was later possible to study the paramagnetic properties of isomeric samples of EFs. Kikuchi *et al.* reported ESR studies of the major isomers of $M@C_{82}$, ($M = La, Y$),^[20]

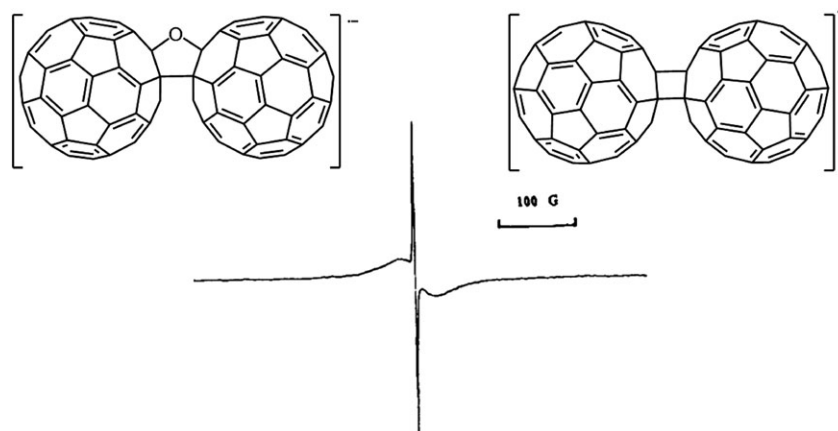


Figure 1. Representative Electron spin resonance (ESR) spectrum of the anion radical of C_{60} (major, broad signal) containing a minor, narrow signal. The two dimeric structures shown have been proposed to account for the sharp line. Reproduced with permission from ref 5. Copyright 1991 American Chemical Society

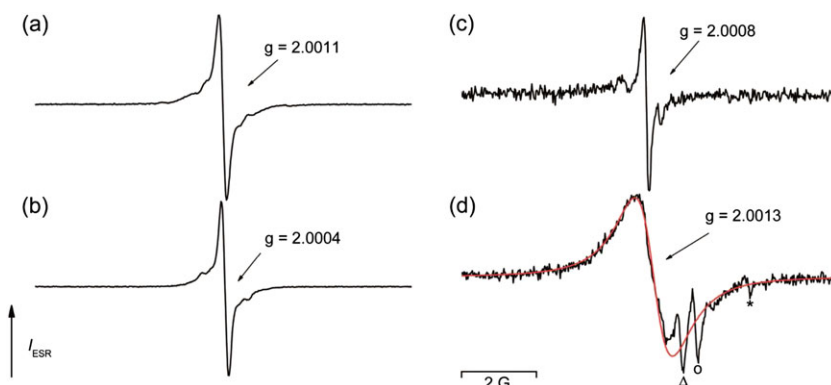


Figure 2. ESR spectra of the anion radicals of the (a) C_s (14), (b) C_2 (11), (c) D_2 (22), and (d) D_{2d} (23) isomers of C_{84} generated by electrolysis. Reproduced with permission from ref 13. Copyright 2009 American Chemical Society

which exhibited a hfcc of 1.159 G with eight symmetric lines and 0.48 G with two symmetric lines for La and Y, respectively. However, in agreement with previous measurements, the major C_{2v} isomer of La-EF extracts exhibited another octet signal with a smaller hfcc and at lower concentration. Akasaka and co-workers published the first isolation and characterization of this minor isomer of La@ C_{82} with a hfcc of 0.836 G, corresponding to C_s symmetry.^[21] Isomers of La@ C_{2n} ($2n = 76 - 90$) studied by ESR spectroscopy exhibited similar features to those reported previously, with small hfcc and g values centered around 2.003.^[22] ESR studies of pure samples of Sc@ C_{82} (C_{2v} , C_s) and Sc@ C_{84} were reported by Shinohara in 2000. The ESR spectra exhibited the typical octet as a result of the Sc nucleus hyperfine splitting ($I = 7/2$) and similar g values, but the corresponding hfccs were 3.82, 1.16, and 3.78 for Sc@ C_{82} (C_{2v}), Sc@ C_{82} (C_s), and Sc@ C_{84} , respectively. These values of hfcc suggested that the electron spin is localized mainly on the encapsulated Sc nucleus.^[23] Nevertheless, in 2005, a hyperfine structure study of Sc@ C_{82} was reported using electron density functional theory (DFT) calculations and ESR measurements and found that the electron density is distributed mainly around the carbon cage, with 5% of the spin eigenstate associated with the Sc d_{yz} orbital which leads to the anisotropy observed for the resultant g and hfcc values.^[24]

In 2003, Kato and co-workers examined the magnetic properties of Gd@ C_{82} by X- and W-band ESR spectroscopy in powder

form and in CS_2 and 1,2,4-tri-chlorobenzene solutions.^[25] The ESR spectrum of Gd@ C_{82} in tri-chlorobenzene solution exhibited the behavior of a monomer with $S = 3$, resulting from coupling between Gd^{3+} and the carbon cage. The intramolecular exchange coupling constant, $J = -1.8 \text{ cm}^{-1}$, was determined from the simulation. Multi-frequency ESR spectroscopy has been used to study a family of europium EFs, including Eu@ C_{74} and three isomers of Eu@ C_{82} .^[26] The spectra were fitted in order to obtain information about the zero-field splitting parameters up to fourth order with a g value of 1.995, 1.993, 1.9946; 1.9919, 1.9928, 1.9933; 1.9925, 1.9921, 1.9939; and 1.9938, 1.9891, 1.9883 for Eu@ C_{82} (C_s), Eu@ C_{82} (C_2), Eu@ C_{82} (C_{2v}), and Eu@ C_{74} (D_{3h}), respectively. ESR studies of Lu@ C_{82} were reported by two different groups in 1998 and 2000.^[27] Only a single broad peak was observed at room temperature and at liquid nitrogen temperature, which was attributed to fast nuclear spin relaxation. The spectra showed g values of 1.99705 and 2.0085 at room and liquid nitrogen temperatures, respectively. Moreover, the broad spectrum exhibited a characteristic Lorentzian line shape at room temperature, while the spectral shape was distorted with the low field part of the spectrum being more intense at 77 K.^[27]

Electron spin resonance spectroscopy has also helped to characterize classical endohedral fullerene derivatives, especially those of La@ C_{82} . Some of the studied derivatives

involve pyrrolidine addends, bis-silylated isomers, digermane compounds, and bis-adducts of La@C_{82} . These derivatives exhibited hfccs between 0.10–1.93 G and 0.52–3.81 G for C_{2v} (9) and C_s (6), respectively. M@C_{82} ($\text{M} = \text{Sc}$ and Y) derivatives studied by ESR spectroscopy exhibit hfccs close to the value for the pristine M@C_{82} , thus, chemical derivatization of M@C_{82} ($\text{M} = \text{La}$, Sc , and Y) does not result in significant electron spin redistributions.

Electron spin resonance studies of dimetallofullerenes have not been as fully explored because most of these EFs are diamagnetic. However, the chemical reduction of La_2C_{80} was reported by Kato in 2007,^[28] and the resulting ESR spectrum of the anion radical of La_2C_{80} was very complex, exhibiting very large hfcc for the La nuclei, clearly indicating high-spin localization on the metals. The ESR spectra of [5,6]- and [6,6]-pyrrolidine-derivatives of La_2C_{80} also exhibited complex spectra with high-spin localization on the $(\text{La}_2)^{5+}$ nuclei.^[29] Recently, Akasaka and co-workers published ESR studies of the derivatives of La_2C_{80} (I_h) and La_2C_{80} (D_{5h}), which showed very similar signal patterns as those of the two La_2C_{80} isomers in the pristine form.^[30] In 2013, Wang and co-workers reported the ESR study of the anion radical of Y_2C_{82} prepared by potassium reduction in tetrahydrofuran. The ESR spectrum showed three signals with a g value and a hfcc of 2.0025 and 34.3 G, respectively. These values suggested that the spin distribution is mainly localized on the Y nuclei.^[31]

Azafullerenes

When at least one fullerene cage carbon atom is replaced by a nitrogen atom, the ESR spectra exhibit similar features as those of simple radical centers on nitrogen. The ESR spectrum of $\text{Y}_2\text{C}_{79}\text{N}$ in toluene showed a 1:2:1 triplet with a g factor of 1.9740 and a large hfcc of 81.23 as a result of electron spin coupling with two equivalent Y nuclei (refer to Fig. 3).^[32] However, the ESR spectrum in the solid state showed a single broadened line as a result of Heisenberg exchange, which was confirmed by dilution of $\text{Y}_2\text{C}_{79}\text{N}$ with the empty fullerene C_{84} ,

which has a comparable size. Similar results were obtained by Dorn and co-workers for the ESR spectrum of $\text{Gd}_2\text{C}_{79}\text{N}$, which exhibited a g value of 1.978.^[33] In 2012, Wang *et al.* published the exohedral mono-derivatization and temperature dependence of the paramagnetic properties of $\text{Y}_2\text{C}_{79}\text{N}$. The ESR spectra at low temperature showed pronounced anisotropy, which suggests that the two Y nuclei exhibit restricted motion.^[34] While the ESR spectrum of a pyrrolidine derivative of $\text{Y}_2\text{C}_{79}\text{N}$ showed similar features to that of pristine $\text{Y}_2\text{C}_{79}\text{N}$, different hfcc values indicated that each Y nucleus is in a different electronic environment as a result of exohedral functionalization.

In 2014, Wang *et al.* reported a detailed ESR and DFT study of $\text{Y}_2\text{C}_{81}\text{N}$, which was detected by mass spectrometry, but it was difficult to separate from a mixture with Y_2C_{82} . The paramagnetic species $\text{Y}_2\text{C}_{81}\text{N}$ exhibited a g value of 1.97851 and two hfccs of 7.7 and 69.8 G for two inequivalent Y nuclei. This large hfcc value suggested that the unpaired spin is mainly localized in the encapsulated metal nuclei. The DFT calculations of three possible structures of $\text{Y}_2\text{C}_{81}\text{N}$ ($\text{Y}_2\text{CN@C}_{80}$, $\text{Y}_2\text{C}_2\text{C}_{79}\text{N}$, and $\text{Y}_2\text{C}_{81}\text{N}$) concluded that the only possible species where the unpaired spins are localized on the yttrium nuclei is $\text{Y}_2\text{C}_{81}\text{N}$.^[35]

Non-Metallic Endohedral Fullerenes

Endohedral fullerenes are usually prepared by adding the appropriate starting materials during the arcing process. However, Knapp and co-workers reported the serendipitous discovery of a new family of EFs by nitrogen implantation in C_{60} , which produces a paramagnetic species with similar hyperfine properties to those of atomic nitrogen, N@C_{60} , with the encapsulated nitrogen atom in its quartet state, with three unpaired electrons.^[36] Q-band ESR spectroscopy of N@C_{60} showed two different signals.^[37] A strong triplet signal with a g value of 2.0030 and a hardly detectable doublet corresponding to $^{14}\text{N@C}_{60}$ ($I = 1$) and $^{15}\text{N@C}_{60}$ ($I = 1/2$), respectively. The ESR signal from $^{15}\text{N@C}_{60}$ was clearly visible after enrichment with 99.9% ^{15}N (refer to Fig. 4a).^[37,38] The ESR spectrum of N@C_{70} exhibits the same g value with a smaller hfcc.^[39]

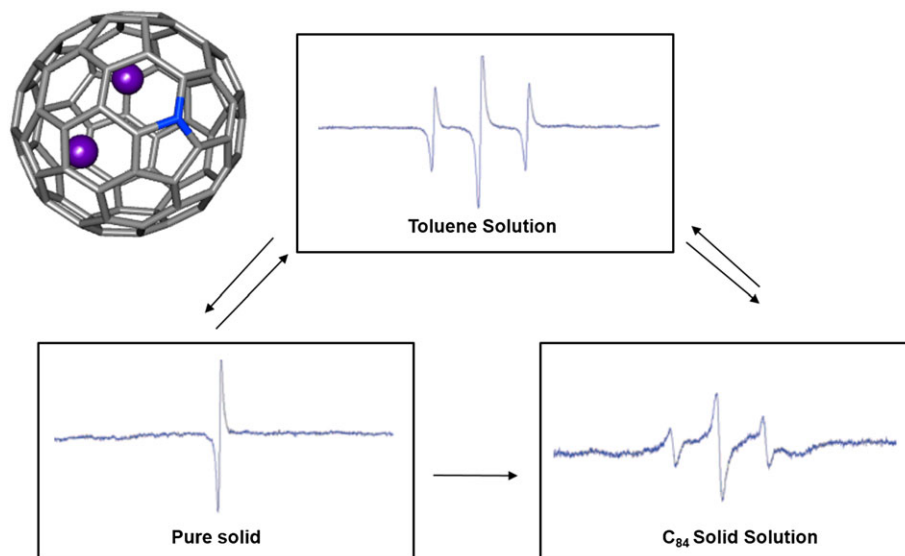


Figure 3. X-band ESR spectra of $\text{Y}_2\text{C}_{79}\text{N}$ samples in toluene solution, as a solid, and as a solid solution with C_{84} . Reproduced with permission from ref 32. Copyright 2008 American Chemical Society

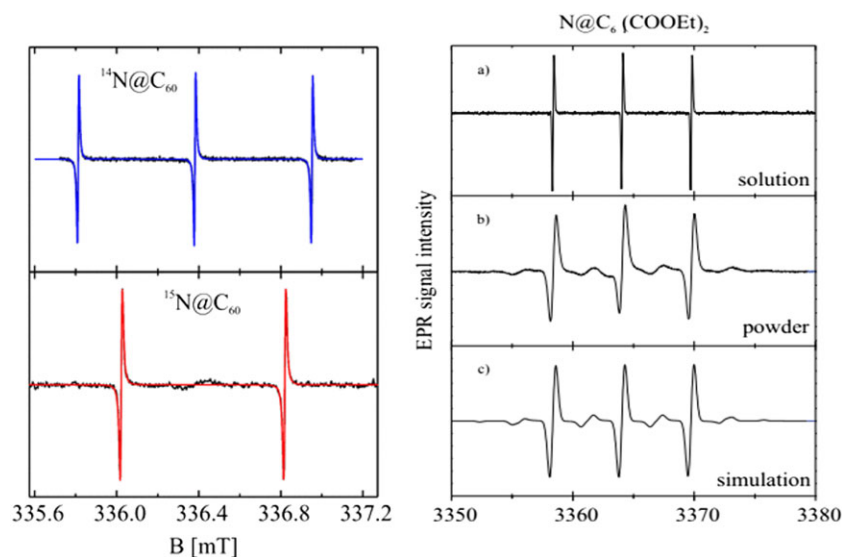


Figure 4. Left: X-band ESR spectra at 300 K of a C_{60} sample in CS_2 produced under a beam of $^{14}\text{N}_2$ (top) and $^{15}\text{N}_2$ (bottom). Right: X-band ESR spectra of $\text{N}@C_{61}(\text{COOEt})_2$ (a) in solution and (b) in the form of a powder at ambient temperature (c) simulation. Reproduced with permission from ref 38. Copyright 1998 Springer-Verlag

Functionalization of $\text{N}@C_{60}$ led to the observation of ESR spectra with interesting features: (i) smaller hfccs than that of pristine $\text{N}@C_{60}$; and (ii) broadened line widths and reduced relaxation times. In 1997, Weidinger and co-workers reported the ESR study of the first $\text{N}@C_{60}$ derivative, $\text{N}@C_{60}$ diethyl malonate monoadduct ($\text{N}@C_{61}(\text{COOEt})_2$).^[40] The ESR spectrum of $\text{N}@C_{61}(\text{COOEt})_2$ in solution showed similar features to that of pristine $\text{N}@C_{60}$; however, in the solid state, new lines were observed (refer to Fig. 4b) as a result of the distortion of the icosahedral cage symmetry by addition of the addend, resulting in the loss of the degeneracy of the nitrogen p-orbitals.

In 2006, Franco *et al.* reported the effect of the size and type of ring system fused to the fullerene cage on the ESR signals of $\text{N}@C_{60}$ derivatives.^[41] The ESR powder spectra of $\text{N}@C_{60}$ derivatives are similar but exhibiting significant differences in the line

widths (refer to Fig. 5), which was attributed to small dipolar interactions of the nitrogen unpaired electrons with the protons of the addends. The same year, Jones and co-workers reported the epoxidation of $\text{N}@C_{60}$, which resulted in a decay of the ESR signal intensity, likely as a result of a lower energy barrier for the loss of nitrogen.^[42] In 2011, Porfyraakis *et al.* studied the stability of two *N*-methyl-pyrrolidine- $\text{N}@C_{60}$ derivatives and found that both showed ESR signal losses when exposed to ambient temperature and light. ESR spectroscopy is the principal tool to study the stability of $\text{N}@C_{60}$ derivatives.^[43]

In 2012, Porfyraakis and co-workers reported the synthesis of a switch based on a covalently linked $\text{N}@C_{60}$ -porphyrin dyad (refer to structure 2N in Fig. 6). The $\text{N}@C_{60}$ ESR signals are modulated by demetalation of 2N with a decrease of the pH, resulting in the free-base porphyrin, which removes paramagnetic Cu and

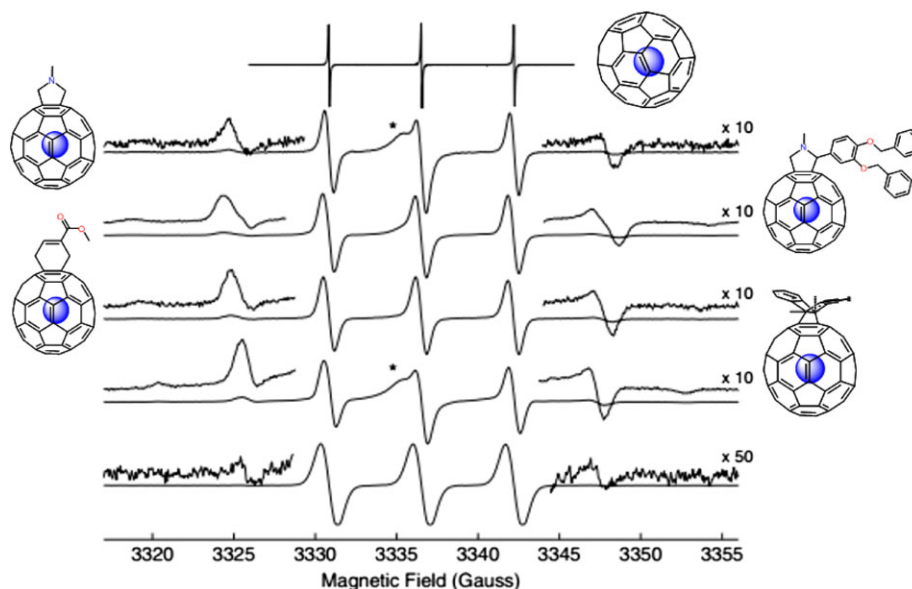


Figure 5. X-band ESR spectra at room temperature of different $\text{N}@C_{60}$ derivatives. Reproduced with permission from ref 41. Copyright 2006 Elsevier B. V

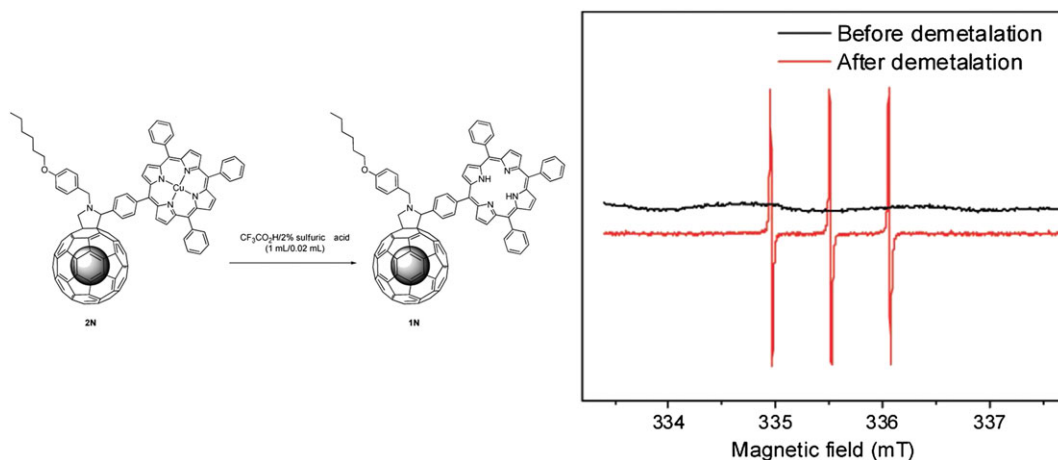


Figure 6. Molecular switch based on a covalently linked N@C₆₀-porphyrin dyad controlled by metalation/demetalation. Reproduced with permission from ref 44. Copyright 2012 American Chemical Society

the associated enhanced relaxation of the unpaired spin.^[44] The authors also studied the concentration dependence of these signals and found that Cu[TPP] shows a remarkable effect in the sample at high concentrations; thereby, they concluded that the intramolecular dipolar coupling plays an important role in the relaxation properties of this endohedral fullerene dyad. Recently, Porfyakis and co-workers reported a spin dipolar coupling study between N@C₆₀ and Cu spins for different N@C₆₀-phthalocyanine dyads. The authors established that the chemical modification and length of the spacer can change the magnitude of the dipolar coupling. These systems also showed concentration dependence as previously reported.^[45]

Electron spin resonance studies of C₆₀ dimers with a nitrogen atom included in one of the C₆₀ cages were reported in 2001 by Dinse *et al.*^[46] They showed that the dimers are ESR-active and exhibited similar features to those of N@C₆₀; however, the intensity of the observed signals is lower than that for a mixture of N@C₆₀/C₆₀. Retention of spin activity of N@C₆₀ derivatives has proven to be a serious challenge. Recently, Porfyakis and co-workers reported modified Bingel reaction conditions that led to retain 94% of the retention of spin activity of N@C₆₀,^[47] much better than those previously reported for 1,3-dipolar cycloadditions (73–79%). In 2011, Porfyakis *et al.* also found that there is no change in the hfcc and g value for a nitrogen-containing fullerene dimer, which suggests that the nitrogen atom is still in the center of the cage, confirming the previous report by Dinse.^[48] Two years later, the same group reported the synthesis of two dimers ¹⁴N@C₆₀-C₆₀ and ¹⁵N@C₆₀-C₆₀.^[49] According to the ESR studies, these dimers are more stable in solution than other N@C₆₀ derivatives previously reported. In addition, ESR studies of dimers with a nitrogen atom in both fullerene cages suggested that there is no effect on the stability of the endohedral nitrogen species by the proximity the two N@C₆₀ units.^[50]

In 2013, Akasaka and co-workers reported the preparation of HeN@C_{2n} (*n* = 30, 35) by nitrogen insertion in He@C_{2n} (*n* = 30, 35). The ESR spectra showed overlapped ESR signals for both fullerene cages (refer to Fig. 7), which corroborated the generation of HeN@C_{2n} (*n* = 30, 35) with a hfcc of 5.99 G for HeN@C₆₀, a little larger than that of N@C₆₀ (5.67 G). In the case of HeN@C₇₀, the hfcc measured was 5.59 G compared with 5.38 G for N@C₇₀. These results revealed that the encapsulated helium atom influences

the paramagnetic properties of the nitrogen atom coexisting inside of the fullerene cages.^[51]

NON-CLASSICAL ENDOHEDRAL FULLERENES

Metallic nitride EFs

The first report of an ESR spectrum for a member of this family of EFs was published in 2001 by Dinse *et al.*, who prepared the corresponding anion radical of Sc₃N@C₈₀ by reduction with potassium metal. The ESR spectrum (refer to Fig. 8) exhibited 22 lines as a result of hyperfine coupling with three equivalent scandium nuclei with a large hfcc of 55.6 G and a g value of 1.9984. The spectrum suggested that the spin distribution is mainly localized on the Sc₃N moiety.^[52] Later, Echegoyen *et al.* were able to generate this anion radical by electrolysis and obtained similar results.^[53] In 2006, Dunsch *et al.* reported the first study of the stable paramagnetic cation of a non-IPR EF, Sc₃N@C₆₈. These species were electrochemically generated *in situ*, and the ESR spectrum showed 22 lines from three equivalent Sc nuclei. In contrast to the previous results for [Sc₃N@C₈₀]⁻, [Sc₃N@C₆₈]⁺ exhibited a very small Sc hfcc of 1.289 G, indicating that the spin distribution is largely localized on the fullerene cage.^[54] Similar results were obtained for the corresponding anion radical [Sc₃N@C₆₈]⁻, which had a hfcc of 1.75 G.

Sc₃N@C₈₀ derivatives show more complex ESR spectra as a result of the correspondingly lower symmetries. Dunsch and co-workers reported ESR spectroscopic studies for the anions of Sc₃N@C₈₀-(CF₃)_{2n} derivatives (*n* = 2, 10, 12).^[55] They showed that chemical functionalization with two CF₃ groups led to a g value of 1.9958 and a hfcc of 9.3 G for two equivalent Sc nuclei and 10.7 G for another Sc nucleus for the anion radical of Sc₃N@C₈₀-(CF₃)₂. The trion radical of Sc₃N@C₈₀-(CF₃)₂ showed the most complex spectrum within this family of trifluoromethyl derivatives (refer to Fig. 9), exhibiting a g value of 2.0006 and hfcc of 49.2 G for one of the Sc nuclei and 10.8 G for two equivalent Sc nuclei, indicating that the spin distribution is preferentially localized on one of the Sc nuclei. Additionally, the addition of more CF₃ groups caused a change of the spin distribution evidenced by the low values of the ESR parameters for three different Sc nuclei in all studied derivatives, for example, 0.6, 11.1, and 21.5 G for Sc₃N@C₈₀-(CF₃)₁₀ with g values of 2.0009 and 0.6, 7.4 and 8.1 G for Sc₃N@C₈₀-(CF₃)₁₂ with a g value of 2.0012.

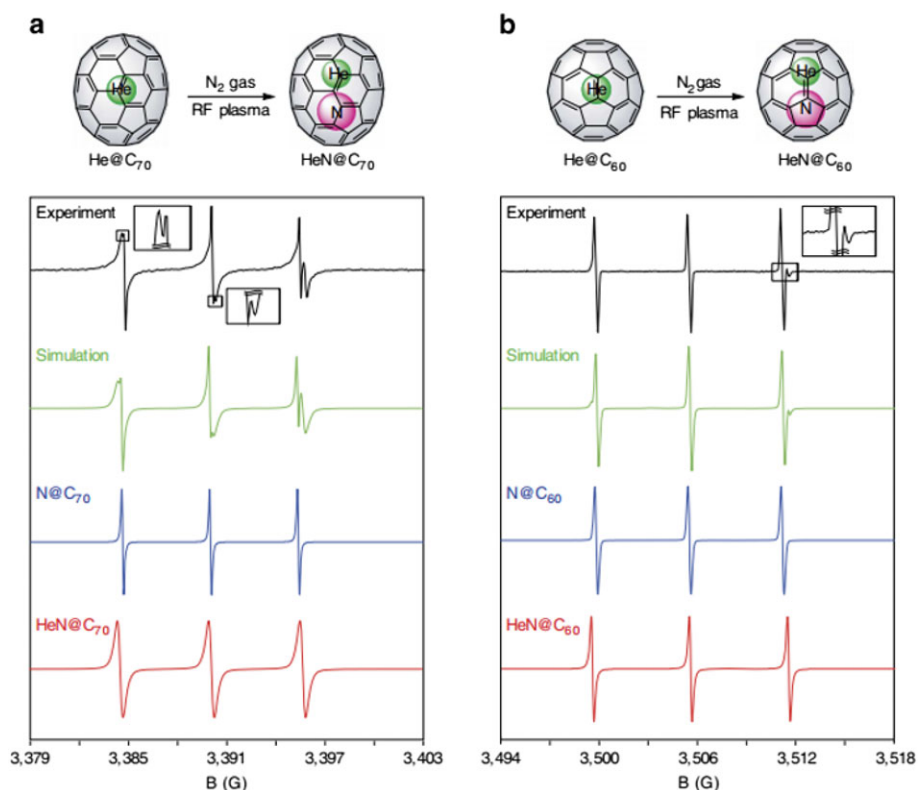


Figure 7. X-band ESR spectra of HeN@C_{2n} ($n = 30, 35$) and N@C_{2n} ($n = 30, 35$). Reproduced with permission from ref 51. Copyright 2013 Nature

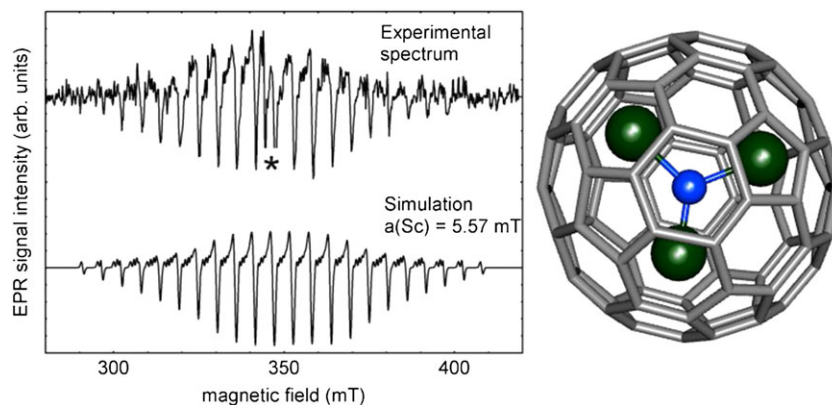


Figure 8. X-band ESR spectrum of the anion radical Sc₃N@C₈₀ obtained by potassium reduction, reported by Dinse and co-workers. Reproduced with permission from ref 52. Copyright 2001 American Chemical Society

Electron spin resonance measurements for the radical anion of *N*-ethyl-[5,6]-pyrrolidine derivative of Sc₃N@C₈₀—generated both via chemical and electrochemical methods showed non-equivalent Sc nuclei with one hfcc for a single scandium nucleus of 9.6 G and for two equivalent Sc nuclei of 33.4 G, respectively (refer to Fig. 10c).^[56] Echegoyen and co-workers studied two isomeric benzoadducts of Sc₃N@C₈₀ with [5,6] and [6,6] addition patterns, the only difference being the addition site on the C₈₀ cage (refer to Fig. 10a and b). The ESR spectra of the anion radicals obtained by reaction of these isomers with cobaltocene showed a hfcc of 9.1 for one Sc nucleus and 33.3 G for two equivalent Sc nuclei for the [5,6] adduct and 0.6 for one Sc nucleus and 47.9 G for two equivalent Sc nuclei for the [6,6] adduct. Interestingly, the ESR data indicated that the

position of the exohedral derivatization resulted in drastic changes of the spin density distributions.^[57]

Mixed metal nitride fullerenes have also been studied by ESR spectroscopy. Dunsch and co-workers reported ESR measurements of TiSc₂@C₈₀, which is a neutral radical, and shows a broad ESR line at room temperature in toluene solution, but cooling results in a well-defined signal with a *g* value of 1.9454.^[58] Two years later, the same group reported an ESR study at different temperatures for TiY₂N@C₈₀ in toluene solution, which has an electronic structure represented by [TiY₂N]⁶⁺[C₈₀]⁶⁻ and showed a spectrum with *g* factor of 1.9579 and significant anisotropy. They also compared the results with those previously reported for TiSc₂N@C₈₀^{58a} and found that the line width of the ESR lines of TiSc₂N@C₈₀ was much larger than

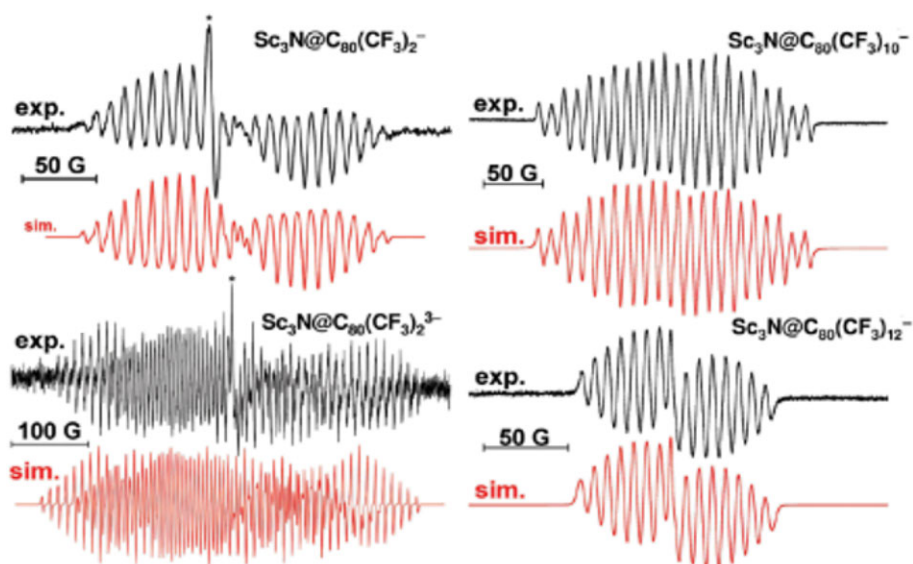


Figure 9. ESR spectra of anion radical of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_{2n}$ derivatives ($2n = 2, 10, 12$). Reproduced with permission from ref 55. Copyright 2011 American Chemical Society

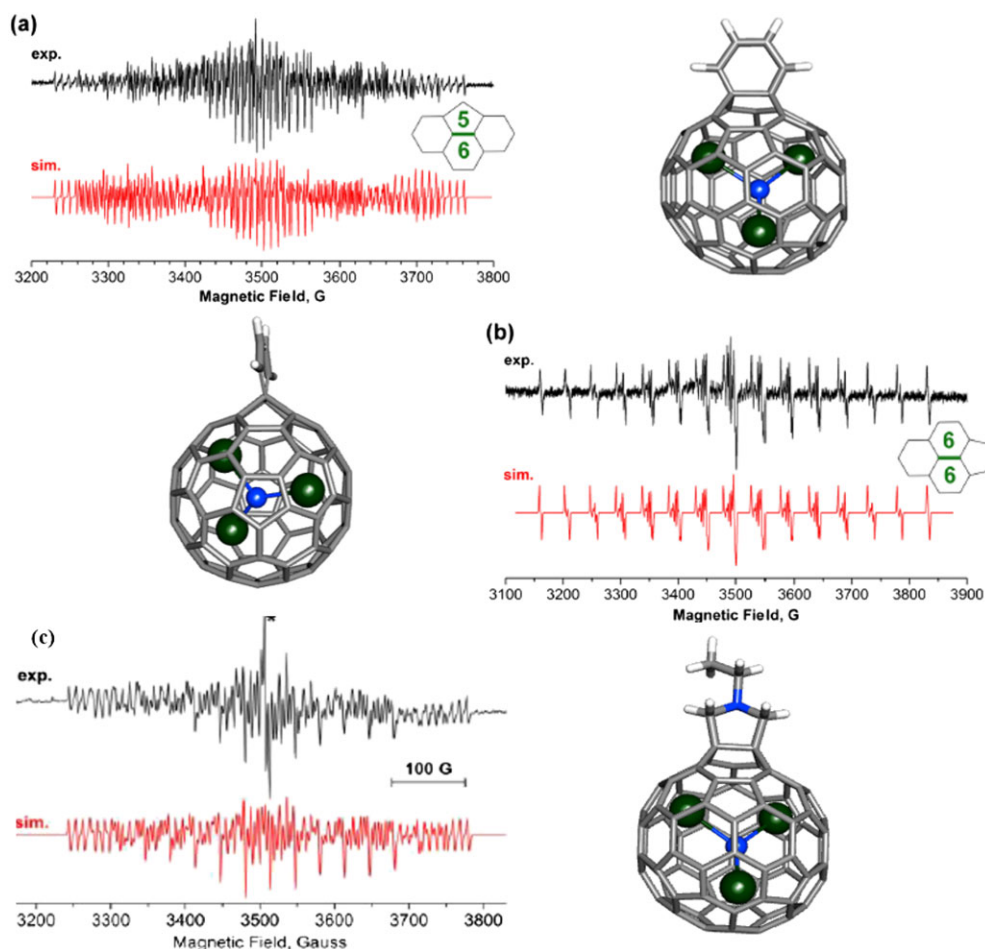


Figure 10. ESR spectra of the anion radicals of (a) [5,6]-benzoadduct, (b) [6,6]-benzoadduct, and (c) *N*-ethylpyrrolidine of $\text{Sc}_3\text{N}@C_{80}$. Reproduced with permission from ref 56. Copyright 2001 American Chemical Society. Reproduced with permission from ref 57. Copyright 2014 American Chemical Society

that of $\text{Ti}_2\text{N}@C_{80}$, showing that these Ti-based mixed metal nitride fullerenes have different electronic structures attributed to the difference of the spin distribution of these species resulting from the different electronic configurations of Y^{3+} and Sc^{3+} and the consequent geometric structures of the cluster encapsulated. Recently, Yang and co-workers reported the synthesis of two paramagnetic species, $\text{V}_x\text{Sc}_{3-x}\text{N}@C_{80}$ ($x=1,2$).^[59] The ESR spectra show broad signals at 130 K with g factors of 2.1998 and 1.9998 for $\text{V}_2\text{ScN}@C_{80}$ and $\text{VSc}_2\text{N}@C_{80}$, respectively. They suggested that the smaller g factor and line width of the ESR signal of $\text{VSc}_2\text{N}@C_{80}$ compared with that of $\text{V}_2\text{ScN}@C_{80}$ may be a result of the entrapment of the additional paramagnetic V^{3+} ion.

Metallic Carbide EFs

Electron spin resonance studies of metallic carbide endohedral fullerenes have mainly focused on compounds with three metals in the endohedral cluster, such as $\text{Sc}_3\text{C}_2@C_{80}$ and its derivatives, which are paramagnetic in their pristine form. The ESR spectrum of $\text{Sc}_3\text{C}_2@C_{80}$ showed a well-resolved hfcc of 6.22 G and a g value of 1.9985, resulting in 22 lines from three equivalent Sc nuclei.^[60] In 2007, Kato and co-workers reported ESR measurements of two isomers of the adamantylidene derivatives of $\text{Sc}_3\text{C}_2@C_{80}$. ESR measurements of the [5,6] and [6,6]-adducts showed dramatically different spectra from that of the pristine metallic carbide, with a pattern of 15 lines with similar hfcc for two non-equivalent Sc nuclei of 7.33 and 1.96 G for the [6,6]-adduct and 7.90 and 1.70 G for the [5,6]-adduct.^[61] Exohedral functionalization of $\text{Sc}_3\text{C}_2@C_{80}$ via a 1,3-dipolar cycloaddition reaction to yield a fulleropyrrolidine derivative led to a higher spin density on a unique Sc nucleus and a lower spin density on the other two Sc nuclei.^[62] The ESR spectrum showed a g value of 2.0007 and a hfcc of 8.6 G corresponding to one Sc nucleus and 4.82 G for the two equivalent Sc nuclei. Upon a second addition to $\text{Sc}_3\text{C}_2@C_{80}$, six isomers exhibited very complex ESR spectra in comparison

with the pristine $\text{Sc}_3\text{C}_2@C_{80}$ and its mono-adduct (refer to Fig. 11). Nevertheless, one of the bis-adducts exhibited three different hfccs for the Sc atoms with values of 8.207, 4.822, and 4.734 G and a g value of 2.0006, which clearly showed that the spin distribution is unequally localized on the encapsulated cluster.^[63] The ESR detection of non-equivalent Sc nuclei has also been reported by Kato *et al.* in 1994.^[64] The ESR spectrum from a fraction of Sc-EF extract showed a g value of 2.005 and hfccs of 3.19, 5.73 G, and 5.75 G for the Sc nuclei.

Wang *et al.* recently reported the design of a molecular magnetic switch based on a derivative of $\text{Sc}_3\text{C}_2@C_{80}$ (refer to structure in Fig. 12). The compound contains two spin centers, one localized on an exohedral nitroxide radical adduct and the other on the $\text{Sc}_3\text{C}_2@C_{80}$ unit, which exhibit strong coupling. The ESR signals of the two radical centers were broadened, and only three resonant lines from the nitroxide radical were observed with a g value of 2.0026 and hfcc of 15.5 G. The spin-spin interaction between the endohedral fullerene and the nitroxide radical can be reversibly modulated by reduction reactions of the nitroxide group that result in the observation of the signals for $\text{Sc}_3\text{C}_2@C_{80}$ (refer to Fig. 12), with a g value of 1.9948 and hfcc of 8.5 G. They also showed that the ESR signals of $\text{Sc}_3\text{C}_2@C_{80}$ are modulated by varying the distance between these spin centers or by changing the temperature of system.^[65]

The generation of paramagnetic species by chemical methods allowed the characterization of two different metallic carbide EFs, $\text{M}_2\text{C}_2@C_{82}$ ($\text{M}=\text{Y}, \text{Sc}$). The ESR spectra of both $[\text{Y}_2\text{C}_2@C_{82}]^-$ and $[\text{Sc}_2\text{C}_2@C_{82}]^-$ showed unsymmetrical features with hfcc and g values of 0.45 and 0.40 G and 2.00383 for Yttrium and 0.48 and 0.97 G and 2.00261 for scandium. The small hfcc values (<1 G) suggested that the spin distribution is largely localized on the carbon cages.^[31] Similar results were reported for the anion radical of non-IPR metallic carbide $\text{Sc}_2\text{C}_2@C_{72}$.^[66] The ESR spectrum showed 15 symmetrical lines with a g value of 2.0050 and

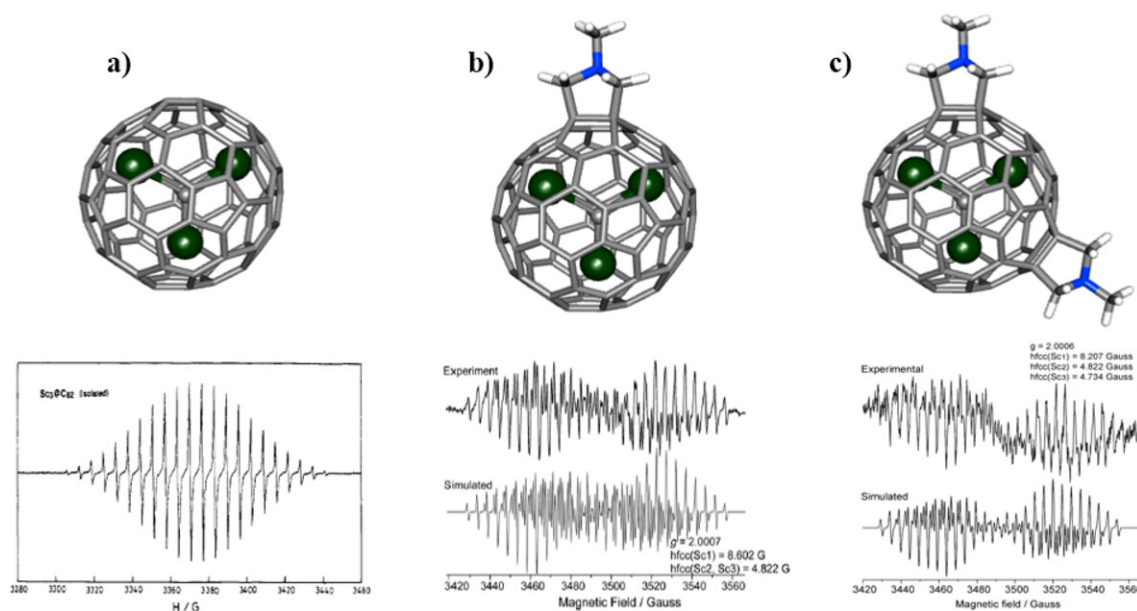


Figure 11. ESR Spectra of (a) pristine, (b) [5,6]-pyrrolidine, and (c) [5,6],[5,6]-bis-pyrrolidine of $\text{Sc}_3\text{C}_2@C_{80}$. Reproduced with permission from ref 60. Copyright 1994 American Chemical Society. Reproduced with permission from ref 62. Copyright 2010 The Royal Society of Chemistry. Reproduced with permission from ref 63. Copyright 2012 The Royal Society of Chemistry

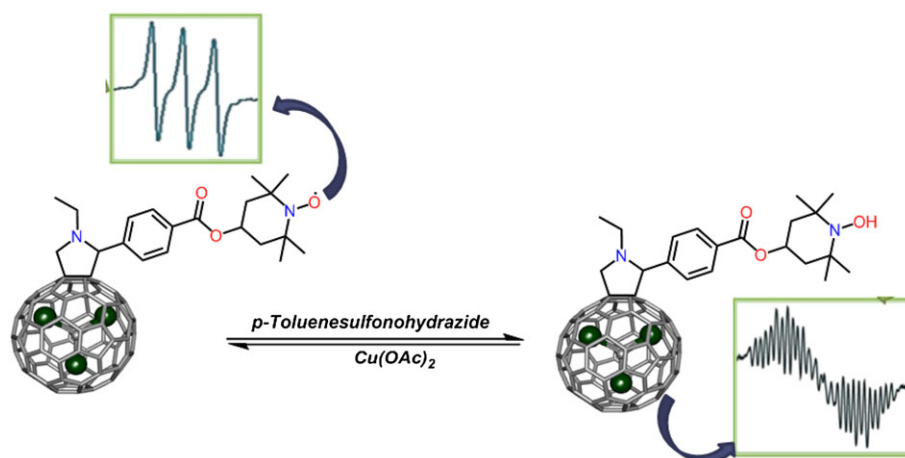


Figure 12. Molecular switch of paramagnetic properties of $\text{Sc}_3\text{C}_2@\text{C}_{80}$. Reproduced with permission from ref 65. Copyright 2015 Nature

a hfcc of 0.77 G for two equivalent Sc nuclei, which reflects the higher molecular symmetry compared with that of $\text{Sc}_2\text{C}_2@\text{C}_{82}$.

Other families of EFs

Electron spin resonance studies of metallic oxide clusters have been reported only for the anion and cation radicals of $\text{Sc}_2\text{O}_4@\text{C}_{80}$, and the values of the hfcc are the highest reported for a metallic cluster encapsulated in a fullerene cage to date.^[67] In 2012, Dunsch and co-workers generated the anion and cation radicals of $\text{Sc}_2\text{O}_4@\text{C}_{80}$ by electrolysis. Fifteen lines were observed in the ESR spectrum of $[\text{Sc}_2\text{O}_4@\text{C}_{80}]^+$ (refer to Fig. 13), indicating the presence of two pairs of equivalent Sc nuclei with a hfcc of 18 and 150.4 G, with a g value of 1.9960, and the spin mainly localized on the metallic cluster. The anion radical exhibited also a complex pattern with a g value of 1.9956 and a hfcc of 2.6 and 27.4 G. The anion radical of the first metallic cyanide endohedral fullerene $\text{Sc}_3\text{NC}@\text{C}_{80}$ was also

characterized by ESR spectroscopy. Wang *et al.* reported the generation of the anion radical by reduction with potassium metal. The ESR spectrum exhibited a small hfcc of 3.89 G for two equivalent Sc nuclei and 1.95 G for the third Sc nucleus, suggesting that the spin distribution is mainly localized on the cyanide moiety.^[68] In 2014, Wang and co-workers reported the ESR study of $\text{Sc}_4\text{C}_2\text{H}@\text{C}_{80}$.^[69] The ESR signal was not detected in CS_2 solution at room temperature, but when the temperature was decreased, a distinguishable ESR line was observed with a line width of about 500 G; unfortunately, it was not possible to measure any hfcc; however, the large peak width suggested a strong spin-metal coupling for the Sc(3d)-based unpaired spin distributions.

OUTLOOK

Empty and endohedral fullerene research has been very active in the last couple of decades, and this trend will likely continue, as reflected by the increasing number of publications in this field.

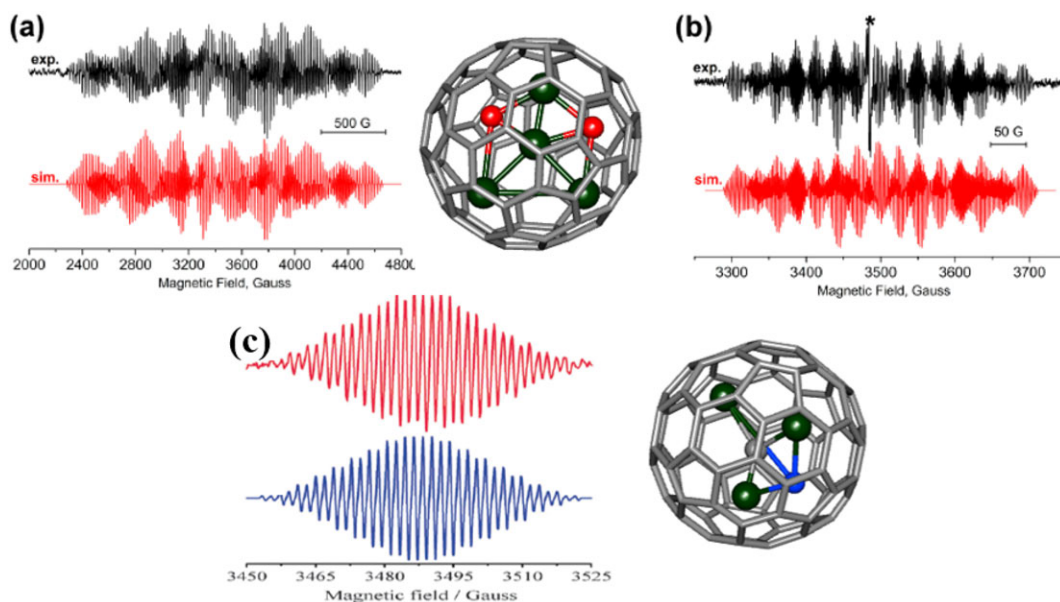


Figure 13. ESR Spectra of (a) anion, (b) cation radical of $\text{Sc}_2\text{O}_2@\text{C}_{80}$, and (c) anion radical of $\text{Sc}_3\text{NC}@\text{C}_{80}$. Reproduced with permission from ref 67. Copyright 2012 American Chemical Society. Reproduced with permission from ref 68. Copyright 2013 The Royal Society of Chemistry

These materials exhibit interesting properties based both on the fullerene cages and on the encapsulated moieties or functionalized addends. Undoubtedly, ESR spectroscopy has become on one of the most important tools to identify, characterize, and study the paramagnetic properties of fullerene compounds. ESR spectroscopy is the only technique capable of providing detailed electron spin densities for open shell fullerene systems, thus allowing detailed descriptions of their HOMO and LUMO levels, which are important to assess the potential photovoltaic properties of these compounds.

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REFERENCES

- H. W. Kroto, J. R. Heath, C. O. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163.
- J. R. Heath, C. O. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, F. K. Tittle, R. E. Smalley, *J. Am. Chem. Soc.* **1985**, *107*, 7779–7780.
- a) M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen, *Angew. Chem. Int. Ed.* **2009**, *48*, 7514–7538; b) X. Lu, L. Feng, T. Akasaka, S. Nagase, *Chem. Soc. Rev.* **2012**, *41*, 7723; c) A. A. Popov, S. Yang, L. Dunsch, *Chem. Rev.* **2013**, *113*, 5989–6113.
- a) Q. Xie, E. Perez-Cordero, L. Echegoyen, *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980; b) P. Paul, Z. Xie, R. Bau, P. D. W. Boyd, C. A. Reed, *J. Am. Chem. Soc.* **1994**, *116*, 4145–4146; c) W. C. Wan, X. Liu, G. M. Sweeney, W. E. Broderick, *J. Am. Chem. Soc.* **1995**, *117*, 9580–9581.
- a) P. M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc.* **1991**, *113*, 2780–2781; b) M. A. Greaney, S. M. Gorun, *J. Phys. Chem.* **1991**, *95*, 7142–7144; c) T. Kato, T. Kodama, M. Oyama, S. Okazaki, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, Y. Achiba, *Chem. Phys. Lett.* **1991**, *186*, 35–39.
- C. A. Reed, R. D. Bolskar, *Chem. Rev.* **2000**, *100*, 1075–1120.
- P. Rapta, A. Bartl, A. Gromov, A. Staško, L. Dunsch, *Chem. Phys. Chem.* **2002**, *3*, 351–356.
- D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufler, L. P. F. Chibante, L. J. Wilson, *J. Am. Chem. Soc.* **1991**, *113*, 4364–4366.
- A. A. Popov, N. B. Shustova, O. V. Boltalina, S. H. Strauss, L. Dunsch, *Chem. Phys. Chem.* **2008**, *9*, 431–438.
- J. A. Azamar-Barrios, E. Munoz, P. A. Penicaud, *J. Chem. Soc. Faraday T.* **1997**, *93*, 3119–3123.
- R. D. Bolskar, R. S. Mathur, C. A. Reed, *J. Am. Chem. Soc.* **1996**, *118*, 13093–13094.
- M. Zalibera, A. A. Popov, M. Kalbac, P. Rapta, L. Dunsch, *Chem. Eur. J.* **2008**, *14*, 9960–9967.
- M. Zalibera, P. Rapta, A. A. Popov, L. Dunsch, *J. Phys. Chem. C.* **2009**, *113*, 5141–5149.
- R. D. Jhonson, M. De Vries, J. Salem, D. Bethune, C. Yannoni, *Nature* **1992**, *355*, 239–240.
- J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, R. E. Smalley, *Chem. Phys. Lett.* **1992**, *190*, 460–464.
- H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, *Nature* **1992**, *357*, 52–54.
- C. S. Yannoni, M. Hoiniki, M. S. de Vries, D. S. Bethune, J. R. Salem, M. S. Crowder, R. D. Johnson, *Science* **1992**, *256*, 1191–1192.
- a) G. W. Morley, B. J. Herbert, S. M. Lee, K. Porfyrakis, T. J. S. Dennis, D. Ngu yen-Manh, R. Scipioni, J. van Tol, A. P. Horsfield, A. Ardavan, D. G. Pettifor, J. C. Green, G. A. D. Briggs, *Nanotechnology* **2005**, *16*, 2469–2472; b) J. Lu, X. Zhang, X. Zhao, S. Nagase, K. Kobayashi, *Chem. Phys. Lett.* **2000**, *332*, 219–224.
- M. E. J. Boonman, P. H. M. van Loosdrecht, D. S. Bethune, I. Holleman, G. J. M. Meijer, P. J. M. van Bentum, *Physica B. Condensed Matter* **1995**, *211*, 323–326.
- a) K. Kikuchi, Y. Nakao, S. Suzuki, Y. Achiba, T. Suzuki, Y. Maruyama, *J. Am. Chem. Soc.* **1994**, *116*, 9367–9368; b) K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, Y. Achiba, *Chem. Phys. Lett.* **1993**, *216*, 67–71.
- K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, T. Suzuki, Y. Masuyama, *J. Phys. Chem.* **1994**, *98*, 12831–12833.
- S. Okubo, T. Kato, *Appl. Magn. Reson.* **2003**, *23*, 481–493.
- M. Inakuma, H. Shinohara, *J. Phys. Chem. B.* **2000**, *104*, 7595–7599.
- G. W. Morley, B. J. Herbert, S. M. Lee, K. Porfyrakis, T. J. S. Dennis, D. Nguyen-Manh, R. Scipioni, J. van Tol, A. P. Horsfield, A. Ardavan, D. G. Pettifor, J. C. Green, G. A. D. Briggs, *Nanotechnology* **2005**, *16*, 2469–2473.
- K. Furukawa, S. Okubo, H. Kato, H. Shinohara, T. Kato, *J. Phys. Chem. A.* **2003**, *107*, 10933–10937.
- H. Matsuoka, N. Ozawa, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kikuchi, K. Furukawa, K. Sato, D. Shiomi, T. Takui, T. Kato, *J. Phys. Chem. B.* **2004**, *108*, 13972–13976.
- a) H. Huang, S. Yang, *J. Phys. Chem. Solids* **2000**, *61*, 1105–1110; b) C. Knapp, N. Weiden, K. P. Dinse, *Appl Phys A.* **1998**, *66*, 249–255.
- T. Kato, *J. Mol. Struct.* **2007**, *838*, 84–88.
- M. Yamada, M. Okamura, S. Sato, C. I. Someya, N. Mizorogi, T. Tsuchiya, T. Akasaka, T. Kato, S. Nagase, *Chem. Eur. J.* **2009**, *15*, 10533–10542.
- M. Yamada, H. Kurihara, M. Suzuki, M. Saito, Z. Slanina, F. Uhlik, T. Aizawa, T. Kato, M. M. Olmstead, A. L. Balch, Y. Maeda, S. Nagase, X. Lu, T. Akasaka, *J. Am. Chem. Soc.* **2015**, *137*, 232–238.
- Y. Ma, T. Wang, J. Wu, Y. Feng, H. Li, L. Jiang, C. Shu, C. Wang, *J. Phys. Chem. Lett.* **2013**, *4*, 464–467.
- T. Zuo, L. Xu, C. M. Beavers, M. M. Olmstead, W. Fu, D. Crawford, A. L. Balch, H. C. Dorn, *J. Am. Chem. Soc.* **2008**, *130*, 12992–12997.
- W. Fu, J. Zhang, T. Fuhrer, H. Champion, K. Furukawa, T. Kato, J. E. Mahaney, B. G. Burke, K. A. Williams, K. Walker, C. Dixon, J. Ge, C. Shu, K. Harich, H. C. Dorn, *J. Am. Chem. Soc.* **2011**, *133*, 9741–9750.
- Y. Ma, T. Wang, J. Wu, Y. Feng, L. Jiang, C. Shu, C. Wang, *Chem. Commun.* **2012**, *48*, 11570.
- Z. Zhang, T. Wang, B. Xu, C. Wang, *Dalton Trans.* **2014**, *43*, 12871.
- C. Knapp, K. P. Dinse, B. Pietzak, M. Waiblinger, A. Weidinger, *Chem. Phys. Lett.* **1997**, *272*, 433–437.
- T. Almeida Murphy, T. Pawlik, A. Weidinger, M. Höhne, R. Alcalá, J. M. Spaeth, *Phys. Rev. Lett.* **1996**, *77*, 1075–1078.
- A. Weidinger, M. Waiblinger, B. Pietzak, T. Almeida Murphy, *Appl. Phys. A.* **1998**, *66*, 287–292.
- a) M. Waiblinger, K. Lips, W. Harneit, A. Weidinger, E. Dietel, A. Hirsch, *Phys. Rev. B.* **2001**, *63*, 045421-1–045421-1; b) E. Dietel, A. Hirsch, B. Pietzak, M. Waiblinger, K. Lips, A. Weidinger, A. Gruss, K.-P. Dinse, *J. Am. Chem. Soc.* **1999**, *121*, 2432–2437.
- B. Pietzak, M. Waiblinger, T. A. Murphy, A. Weidinger, M. Höhne, E. Dietel, A. Hirsch, *Chem. Phys. Lett.* **1997**, *279*, 259–263.
- L. Franco, S. Ceola, C. Corvaja, S. Bolzonella, W. Harneit, M. Maggini, *Chem. Phys. Lett.* **2006**, *422*, 100–105.
- M. A. G. Jones, D. A. Britz, J. J. L. Morton, A. N. Khlobystov, K. Porfyrakis, A. Ardavan, G. A. D. Briggs, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2083.
- G. Liu, A. N. Khlobystov, A. Ardavan, G. A. D. Briggs, K. Porfyrakis, *Chem. Phys. Lett.* **2011**, *508*, 187–190.
- G. Liu, A. N. Khlobystov, G. Charalambidis, A. G. Coutsolelos, G. A. D. Briggs, K. Porfyrakis, *J. Am. Chem. Soc.* **2012**, *134*, 1938–1941.
- S. Zhou, M. Yamamoto, G. A. D. Briggs, H. Imahori, K. Porfyrakis, *J. Am. Chem. Soc.* **2016**, *138*, 1313–1319.
- B. Goedde, M. Waiblinger, P. Jakes, N. Weiden, K. P. Dinse, A. Weidinger, *Chem. Phys. Lett.* **2001**, *334*, 12–17.
- S. Zhou, I. Rasovic, G. A. D. Briggs, K. Porfyrakis, *Chem. Commun.* **2015**, *51*, 7096–7099.
- F. Hörmann, A. Hirsch, K. Porfyrakis, G. A. D. Briggs, *Eur. J. Org. Chem.* **2011**, *2011*, 117–121.
- S. R. Plant, M. Jevric, J. J. L. Morton, A. Ardavan, A. N. Khlobystov, G. A. D. Briggs, K. Porfyrakis, *Chem. Sci.* **2013**, *4*, 2971.
- B. J. Farrington, M. Jevric, G. A. Rance, A. Ardavan, A. N. Khlobystov, G. A. D. Briggs, K. Porfyrakis, *Angew. Chem. Int. Ed.* **2012**, *51*, 3587–3590.
- Y. Morinaka, S. Sato, A. Wakamiya, H. Nikawa, N. Mizorogi, F. Tanabe, M. Murata, K. Komatsu, K. Furukawa, T. Kato, S. Nagase, T. Akasaka, Y. Murata, *Nat. Commun.* **2013**, *4*, 1554.
- P. Jakes, K.-P. Dinse, *J. Am. Chem. Soc.* **2001**, *123*, 8854–8855.

- [53] B. Elliott, L. Yu, L. Echegoyen, *J. Am. Chem. Soc.* **2005**, *127*, 10885–10888.
- [54] P. Rapta, A. A. Popov, S. Yang, L. Dunsch, *J. Phys. Chem. A* **2008**, *112*, 5858–5865.
- [55] a) A. A. Popov, N. B. Shustova, A. L. Svitova, M. A. Makey, C. E. Coumbe, J. P. Phillips, S. Stevenson, S. H. Strauss, O. V. Boltalina, L. Dunsch, *Chem. Eur. J.* **2010**, *16*, 4721–4724; b) N. B. Shustova, D. V. Peryshkov, I. V. Kuvychko, Y.-S. Chen, M. A. Mackey, C. E. Coumbe, D. T. Heaps, B. S. Confait, T. Heine, J. P. Phillips, S. Stevenson, L. Dunsch, A. A. Popov, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc.* **2011**, *133*, 2672–2690; c) A. A. Popov, L. Dunsch, *J. Phys. Chem. Lett.* **2011**, *2*, 786–794.
- [56] B. Elliott, A. D. Pykhova, J. Rivera, C. M. Cardona, L. Dunsch, A. A. Popov, L. Echegoyen, *J. Phys. Chem. C* **2013**, *117*, 2344–2348.
- [57] A. A. Popov, A. D. Pykhova, I. N. Ioffe, F.-F. Li, L. Echegoyen, *J. Am. Chem. Soc.* **2014**, *136*, 13436–13441.
- [58] a) A. A. Popov, C. Chen, S. Yang, F. Lipps, L. Dunsch, *ACS Nano* **2010**, *4*, 4857–4871; b) S. Yang, C. Chen, A. A. Popov, W. Zhang, F. Liu, L. Dunsch, *Chem. Commun.* **2009**, *42*, 6391–6393.
- [59] T. Wei, S. Wang, X. Lu, Y. Tan, J. Huang, F. Liu, Q. Li, S. Xie, S. Yang, *J. Am. Chem. Soc.* **2016**, *138*, 207–214.
- [60] H. Shinohara, M. Inakuma, N. Hayashi, H. Sato, Y. Saito, T. Kato, S. Bandow, *J. Phys. Chem.* **1994**, *98*, 8597–8599.
- [61] Y. Iiduka, T. Wakahara, T. Nakahodo, T. Tsuchiya, A. Sakuraba, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, T. Kato, M. T. H. Liu, N. Mizorogi, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 12500–12501.
- [62] T. Wang, J. Wu, W. Xu, J. Xiang, X. Lu, B. Li, L. Jiang, C. Shu, C. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 1786–1789.
- [63] T. Wang, J. Wu, Y. Feng, Y. Ma, L. Jiang, C. Shu, C. Wang, *Dalton Trans.* **2012**, *41*, 2567–2570.
- [64] S. Suzuki, Y. Kojima, Y. Nakao, T. Wakabayashi, S. Kawata, K. Kikuchi, Y. Achiba, T. Kato, *Chem. Phys. Lett.* **1994**, *229*, 512–516.
- [65] B. Wu, T. Wang, Y. Feng, Z. Zhang, L. Jiang, C. Wang, *Nat. Commun.* **2015**, *6*, 6468.
- [66] Y. Feng, T. Wang, J. Wu, L. Feng, J. Xiang, Y. Ma, Z. Zhang, L. Jiang, C. Shu, C. Wang, *Nanoscale* **2013**, *5*, 6704.
- [67] A. A. Popov, N. Chen, J. R. Pinzón, S. Stevenson, L. A. Echegoyen, L. Dunsch, *J. Am. Chem. Soc.* **2012**, *134*, 19607–19618.
- [68] Y. Feng, T. Wang, J. Wu, Y. Ma, Z. Zhang, L. Jiang, C. Ge, C. Shu, C. Wang, *Chem. Commun.* **2013**, *49*, 2148–2150.
- [69] Y. Feng, T. Wang, J. Wu, Z. Zhang, L. Jiang, H. Han, C. Wang, *Chem. Commun.* **2014**, *50*, 12166–12168.