Methane as a Selectivity Booster in the Arc-Discharge Synthesis of Endohedral Fullerenes: Selective Synthesis of the Single-Molecule Magnet Dy₂TiC@C₈₀ and Its Congener Dy₂TiC₂@Cₘₘ

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Abstract: The use of methane as a reactive gas dramatically increases the selectivity of the arc-discharge synthesis of M-Ti-carbide clusterfullerenes (M = Y, Nd, Gd, Dy, Er, Lu). Optimization of the process parameters allows the synthesis of Dy₂TiC@C₈₀-I and its facile isolation in a single chromatographic step. A new type of cluster with an endohedral acetylide unit, M₂TiC₆@C₈₀, is discovered along with the second isomer of M₂TiC₆@C₈₀ (II) and Dy₂TiC₆@C₈₀-I are shown to be single-molecule magnets (SMM), but the presence of the second carbon atom in the cluster Dy₂TiC₂@C₈₀ leads to substantially poorer SMM properties.

The field of endohedral metallofullerene (EMF) research was revolutionized in 1999, when it was discovered that the presence of small amounts of nitrogen gas in the arc-discharge generator afforded Sc₃N@C₈₀, a new type of EMF with a trimetalnitridide cluster inside the carbon cage.[1] The use of NH₃ as a reactive gas instead of molecular nitrogen resulted in much higher selectivity in the synthesis of nitride clusterfullerenes as the yield of empty fullerenes in such conditions decreased dramatically.[2] Discovery of nitride clusterfullerenes triggered exhaustive studies of other clusterfullerenes, resulting in a variety of EMFs with endohedral S,[3] O,[4] C₂,[5] CH,[6] CN,[7] and other nonmetal units.[8]

One of the advantages of the trimetallic cluster in nitride clusterfullerenes is the possibility of combining two or even three different metals within one EMF molecule. Mixed-metal nitride clusterfullerenes may exhibit new properties not present in homometallic nitride clusterfullerenes. Examples include unusual redox behavior,[9] stabilization of unconventional carbon cages,[10] and strong variation of chemical reactivity[11] and magnetization behavior[12] depending on the number of lanthanide ions in the cluster. However, a disadvantage of the mixed-metal EMFs is the increased complexity of their chromatographic separation.

Whereas nitride clusterfullerenes are usually formed with Group III metals, such as Sc, Y, and trivalent lanthanides,[13] Yang et al. demonstrated that a single Ti ion can be introduced into the mixed-metal nitride cluster together with Sc or Y.[14] Due to the trivalent Ti, M₂TiN@C₈₀ clusterfullerenes have unusual electronic and chemical properties.[15] Recently, in an attempt to obtain Ti-based nitride clusterfullerenes with Lu using NH₃ as a reactive gas or melamine as a solid organic nitrogen source, we have discovered a new type of clusterfullerene, Lu₂TiC@C₈₀, which has an endohedral µ₃-carbide ion and a Ti–C double bond.[16] The molecule is an isostructural analogue of Lu₂ScN@C₈₀ in which the Sc–N fragment is replaced by the isoelectronic Ti–C fragment. Unfortunately, in the Lu/Ti/NH₃ and Lu/Ti/melamine syntheses, Lu₂TiC@C₈₀ is only a minor by-product; the products are predominantly Lu₃N@C₈₀ nitride clusterfullerenes, which precludes further exploration of this new type of clusterfullerenes. Herein we demonstrate that 1) M₂TiC@C₈₀ clusterfullerenes can be synthesized with high selectivity for many lanthanides using methane as a reactive gas; 2) this synthetic route also affords appreciable amounts of another cage isomer of M₂TiC@C₈₀ as well as a new type of clusterfullerene, M₂TiC₂@Cₘₘ; 3) Dy₂TiC@C₈₀ exhibits single-molecule magnet (SMM) behavior, whereas the SMM properties of Dy₂TiC₂@Cₘₘ are less pronounced owing to the presence of the second carbon atom in the central unit.

EMFs were obtained by arc-discharge synthesis under He atmosphere with a small amount of CH₄ gas using graphite rods packed with a mixture of Ti, lanthanide (Y, Ce, Nd, Gd, Dy, Er, or Lu), and a graphite powder. The role of CH₄ in this type of synthesis is similar to that of NH₃[17] in the synthesis of nitride clusterfullerenes: the reactive gas increases selectivity of the process by suppressing the formation of empty fullerenes and making the EMFs with desired central atom(s) the main products. Figure 1 shows that under optimized conditions, carbide clusterfullerenes are
the most abundant EMF products for Lu, Dy, Er, Y, and Gd. M\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (Roman number denotes the isomer) is the major or the sole component of the fraction eluting at 36 min. Thus, pure M\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (Lu, Dy, Gd) was obtained from the EMF extract in a single HPLC separation step. For other metals, the main fraction also included a small amount of M\textsubscript{2}C\textsubscript{60}, which could be then easily removed at the second HPLC step (see the Supporting Information (SI), Figures S2 and S4).

The ionic radius of the lanthanide ion (R\textsuperscript{3+}) plays a crucial role in the absolute yield of EMFs. Lu (R\textsuperscript{3+} = 0.86 Å), Er (0.90 Å), and Dy (0.91 Å) afford similar amounts of M\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} per synthesis, the yields of Gd\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (0.94 Å) and Nd\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (0.98 Å) are roughly 6 and 20 times lower than that of Dy\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I}, respectively, whereas Ce\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (1.01 Å) is not produced at all. Yttrium (R\textsuperscript{3+} = 0.90 Å) stands apart as the yield of Y\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} is about 4 times lower than that of Dy\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I}, despite the similar ionic radii of Dy\textsuperscript{3+} and Y\textsuperscript{3+}.

Significant amounts of M\textsubscript{2}C\textsubscript{60} and M\textsubscript{2}C\textsubscript{94} (presumably dimetallofullerenes M\textsubscript{2}C\textsubscript{60} and carbides M\textsubscript{2}C\textsubscript{94}) are formed for Lu and Er. Besides, the presence of traces of nitrogen in the generator leads to the formation of nitride clusterfullerenes M\textsubscript{2}N@C\textsubscript{60}. However, the yield of these EMFs decreases with the ionic radius faster than the yield of M\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I}, and Dy\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} can be produced with a high degree of selectivity and relatively high absolute yield. Equally high selectivity is also achieved for Y and Gd (Figure 1), but their overall yield is lower.

The molecular structure of Lu\textsubscript{2}TiC@C\textsubscript{80} determined by single-crystal X-ray diffraction and \textsuperscript{13}C NMR spectroscopy was reported earlier.\textsuperscript{[19]} The Lu\textsubscript{2}TiC cluster rotates inside the C\textsubscript{80}\textsuperscript{-I} fullerene resulting in a simple two-line \textsuperscript{13}C NMR spectrum of the cage carbons. The use of \textsuperscript{13}C powder for the synthesis of Lu\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} in this work allowed detection of the \textsuperscript{13}C resonance of the central carbon atom at 340.98 ppm (Figure 2). This value is much more positive than the chemical shift of endohedral carbon atoms reported before: 220–260 ppm in M\textsubscript{2}C\textsubscript{60} clusterfullerenes,\textsuperscript{[8a]} 292.4 ppm in YCN@C\textsubscript{60},\textsuperscript{[17]} and 328.3 ppm in the Sc\textsubscript{2}C\textsubscript{60}@C\textsubscript{60} anion.\textsuperscript{[18]} Note that large downfield shifts for metal-bonded carbon atoms are not unusual in Ti alkylidynes with a Ti=C bond.\textsuperscript{[19]} Particularly large shifts in the range of 400–600 ppm are reported for α-C atoms in μ-bridging alkylidynes of titanium in titanocubane frameworks.\textsuperscript{[20]}

The high selectivity makes Dy\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} a suitable synthetic target for further studies of its properties. Comparison of the Vis/NIR and IR absorption spectra prove that the Dy and Lu compounds are isostructural (Figure 2). Both have very similar Vis/NIR spectra with the lowest energy band at 910 nm (Figure 2b) and almost identical vibrational pattern of the fullerene cage (Figure 2c). However, the larger ionic radius of Dy\textsuperscript{3+} pushes the central carbon atom closer to Ti, which results in a higher Ti=C stretching frequency in Dy\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} (834 cm\textsuperscript{-1} versus 821 cm\textsuperscript{-1} in Lu\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I}). Analogous variations of the vibrational frequency with an increase of the lanthanide ionic radius was observed for the Sc–N stretching mode in M\textsubscript{2}ScN@C\textsubscript{60}.\textsuperscript{[21]} In a similar fashion, isostructurality of other M\textsubscript{2}TiC@C\textsubscript{80}\textsuperscript{-I} EMFs can be established via their absorption spectra (Figure S7). Besides, all compounds show similar redox behavior with the reversible Ti-based reduction near −1.0 V (vs. Fe(Cp)\textsubscript{2} as the couple) and cage-based oxidation at +0.6 V (Figure 3, Figure S8, and Table 1). Note that reduction potential depends on the size of the lanthanide, whereas the oxidation process is metal-independent.
Owing to the higher selectivity in the synthesis with CH₄ as the reactive gas, other Ln–Ti carbide clusterfullerenes could be detected; this was not possible in the first report on Lu₂TiC@C₈₀-I.⁴² Mass spectrometry studies proved the formation of M₂TiC@C₈₀ with larger cages (C₁₀₂, C₁₄₈), albeit in rather small amounts making their isolation impractical at this moment (see SI). More importantly, we identified the second isomer of M₂TiC@C₈₀ and a new type of M-Ti-carbide cluster with one more carbon atom in the structure, M₃TiC@C₈₀ (the new clusterfullerene also has two isomers, see Figures S1b and S2a). M₂TiC@C₈₀-II and M₃TiC@C₈₀-I have very similar retention times and elute in one fraction (Figures 1 and 4). Dy and Lu EMFs were separated by recycling HPLC as shown in Figures S1 and S3. Figure 4 compares HPLC traces and mass spectra of isolated Dy₂TiC@C₈₀-II and Dy₂TiC@C₈₀-I (each sample still contains a few percent of the other compound). Absorption spectra of M₂TiC@C₈₀-II and M₃TiC@C₈₀-I (M = Dy, Lu) shown in Figure 4b,c lack well-defined features and extend to ca. 1000 nm for the former and ca. 1100 for the latter. The close similarity of the M₂TiC and M₃ScN clusters suggest that M₃TiC@C₈₀-II is likely to have a D₃d(6) cage. The ¹³C NMR spectrum of Lu₂TiC@C₈₀-I (Figure 4c inset) has two ¹³C signals at 143.20 and 136.05 ppm (versus 143.46 and 136.60 ppm in Lu₂TiC@C₈₀-I). Thus, the cage symmetry of M₃TiC@C₈₀-I can be assigned as I₃d(7).

DFT calculations show that the M₂TiC₂ cluster has two conformations with similar energies. In the most stable one, the C₃ unit is perpendicular to the M₂Ti plane and has μ₃-coordination with all metal atoms (Figure 3). In the second one (9 kJ mol⁻¹ higher in energy), the C₃ fragment is tilted out of the M₂Ti plane, has μ₃-coordination with Ti and one lanthanide, and μ₁-coordination with another lanthanide. C₃ is likely to exhibit fluxional motion at room temperature. The structure and dynamics of the M₂TiC₂ cluster are similar to those of M₂C₂ clusters in Sc₂C@C₇₀ and Lu₂C₂@C₇₀.

M₂TiC@C₈₀-I has a cluster-localized LUMO with large contribution of Ti and a fullerene-based HOMO,⁴¹ and similar spatial distribution of the frontier MOs is predicted for M₃TiC@C₈₀-II. In Lu₂TiC@C₈₀-I, both HOMO and LUMO are predominantly localized on the endohedral cluster and have a large contribution of the acetylide fragment. The LUMO of Lu₂TiC@C₈₀-I is to a large extent localized on Ti, whereas in the HOMO both Lu and Ti have comparable contributions (Figure 3). Thus, both reduction and oxidation of M₂TiC@C₈₀-I are cluster-based processes. Dy₂TiC@C₈₀-I exhibits two reversible reductions and one oxidation; in

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**Table 1:** Redox potentials (V) of M₂TiC@C₈₀-I, Dy₂TiC@C₈₀-II, and Dy₂TiC@C₈₀-I.⁴¹

| EMF       | Ox-I | Ox-II | Red-I | Red-II | Red-III | Red-IV |
|-----------|------|-------|-------|--------|---------|--------|
| Lu₂TiC@C₈₀-I | 1.07 | 0.62  | 0.60  | 0.60   | 0.61    | 0.47   |
| Dy₂TiC@C₈₀-I | 1.07 | 0.60  | 0.60  | 0.60   | 0.61    | 0.47   |
| Gd₂TiC@C₈₀-I | 1.07 | 0.60  | 0.60  | 0.60   | 0.61    | 0.47   |

[a] All potentials are determined by square-wave voltammetry and are reference to the Fe(Cp)₂⁺/⁻ redox couple; the values for Lu₂TiC@C₈₀-I are from Ref. [16].

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comparison to Dy$_2$TiC@C$_{80}$-I, the redox potentials are shifted cathodically by ca. 0.15 V (Figure 3, Table 1).

Recently we have discovered that mixed-metal nitride clusterfullerenes Dy$_2$Sc$_x$N@C$_{80}$ (x = 1–3) exhibit slow relaxation of the magnetization with a temperature-dependent decay rate, that is, they behave as single-molecule magnets (SMMs).\(^{12,24}\) Of the three nitride clusterfullerenes, Dy$_2$ScN@C$_{80}$ is the strongest SMM due to the ferromagnetic exchange and dipolar interaction of the two Dy$^{3+}$ ions. Unfortunately, selective synthesis of mixed-metal nitride clusterfullerenes is not possible. The arc-discharge synthesis in the Dy–Sc system always produces a mixture of Dy$_2$Sc$_x$N@C$_{80}$ (x = 0–3) compounds with different isomeric structures as well as other cage sizes\(^{25}\) and isolation of Dy$_2$ScN@C$_{80}$ is quite a tedious process. Therefore, the selective synthesis of Dy$_2$TiC@C$_{80}$-I, which is isostructural to Dy$_2$ScN@C$_{80}$-I, opens a more convenient route to EMF-based Dy-SMMs as along as the magnetic properties of the two EMFs are similar.

Figure 5 displays the magnetization curve of Dy$_2$TiC@C$_{80}$-I recorded for different temperatures at a field sweep rate of 5 mT s$^{-1}$. The system shows magnetic hysteresis with a temperature-dependent opening. The observation indicates that the system exhibits a slow relaxation of the magnetization with a decay rate that depends on the temperature. At a constant temperature, the opening is also determined by the field sweep rate as demonstrated in Figure S9. Similar behavior was observed for Dy$_2$ScN@C$_{80}$ and is characteristic for SMMs. The stability of the remnant magnetization can be quantified by determining the temperature at which the zero-field magnetization relaxation time is 100 s, the so-called 100 s blocking temperature ($T_{B(100)}$).\(^{26}\) In the present case, we obtain $T_{B(100)}$ = 1.7 K for Dy$_2$TiC@C$_{80}$ as compared to $T_{B(100)}$ = 3.6 K for Dy$_2$ScN@C$_{80}$.\(^{12,24}\) The higher $T_{B(100)}$ value for the nitride clusterfullerene indicates that the nitride ion in the endohedral cluster is advantageous for stronger SMMs.

Isolation of Dy$_2$TiC@C$_{80}$-II and Dy$_2$TiC@C$_{80}$-I allows us to study how the cage isomerism and the carbide cluster composition affect magnetic properties. Corresponding magnetization curves measured at 1.8 K are shown in Figure 5. The two isomers of Dy$_2$TiC@C$_{80}$ have a similar field dependence and the same $T_{B(100)}$ value to within 0.1 K. In contrast, Dy$_2$TiC@C$_{80}$-I exhibits a narrower hysteresis than the Dy$_2$TiC@C$_{80}$-II isomers. The $T_{B(100)}$ value of Dy$_2$TiC@C$_{80}$-I is below 1.5 K demonstrating that it is the softest magnet in the series. Thus, substitution of a single carbide ion by an acetylide unit in the endohedral cluster has an obvious deleterious effect on the SMM properties.

This work shows that lanthanide–Ti carbide clusterfullerenes can be synthesized with high selectivity using methane as a reactive gas. In particular, Dy$_2$TiC@C$_{80}$-I is the first mixed-metal EMF obtained as a main fullerene product and separated without elaborate chromatographic procedures. Similar to its Dy$_2$ScN@C$_{80}$ analogue, Dy$_2$TiC@C$_{80}$-I is a single-molecule magnet. Thus, the class of EMF-SMMs is expanded to carbide clusterfullerenes. The study of the second isomer of Dy$_2$TiC@C$_{80}$ showed that the carbon cage isomerism has little effect on the magnetic behavior as the two isomers behave similarly. At the same time, we found a strong dependence of SMM properties on the central nonmetal unit: the strength of Dy$_2$-SMMs is decreases in the series Dy$_2$Sc > Dy$_2$Ti > Dy$_2$C.

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