Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in
Electrochemistry

Review Article

Redox-active metal–metal bonds between lanthanides in dimetallofullerenes

Alexey A. Popov*

The empty space inside a fullerene cage can be filled with a variety of species, including metal dimers. Encapsulation of Sc_2, Y_2, or lanthanide dimers leads to dimetallofullerenes featuring metal–metal bonding molecular orbital. Such an orbital can be either HOMO or LUMO of the dimetallofullerene molecule. In certain cases, single-occupied metal–metal bonding orbital can be also stabilized. This review is focused on redox processes involving variation of the electron population of metal–metal bonding orbitals in dimetallofullerenes.

Address
Leibniz Institute for Solid State and Materials Research,
Helmholtzstraße 20, 01069 Dresden, Germany

*Corresponding author: Popov, Alexey A. (a.popov@ifw-dresden.de)

Current Opinion in Electrochemistry 2017, **XX**:XX–XX

This review comes from a themed issue on **Organic and Molecular Electrochemistry**

Edited by **Flavio Maran**

For a complete overview see the Issue and the Editorial

Available online XX XXXX 2017

https://doi.org/10.1016/j.coelec.2017.12.003

Introduction

The encapsulation of metal atoms by carbon cages in endohedral metallofullerenes (EMFs) leads to a plethora of interesting chemical and physical phenomena [1–5]. High chemical and thermal stability of fullerene cage protects endohedral entities from the environment and can stabilize unusual species, which cannot exist otherwise. Metal atoms enclosed inside a fullerene transfer their valence electrons to the carbon cage, resulting in "salts" with cationic metals and anionic fullerene cages. Electrochemistry has been traditionally used as a relatively simple and yet very powerful technique to study electronic structures of EMFs [1,6•].

Empty fullerenes are good electron acceptors and undergo multiple single-electron redox steps in solutions [7]. Encapsulation of metal atoms and clusters results in more complex redox behavior of EMFs since both the carbon cage and the endohedral cluster can exhibit redox activity. Especially interesting are endohedral (*in cavea*) electron transfer processes, in which the endohedral cluster is redox-active, whereas the carbon cage acts as an inert container transparent to electrons [8,9•]. An obvious prerequisite for the endohedral redox activity in EMF molecules is a localization of frontier molecular orbitals (HOMO or LUMO) on endohedral species. Experimentally, the endohedral redox processes can be identified via unexpected redox behavior (e.g., shifted potential when compared to analogous molecules) or via spectroscopic characterization of the charged species. Electron paramagnetic resonance (EPR) spectroscopy is an especially powerful tool, since EMFs with endohedral redox activity often exhibit rich hyperfine structure with large coupling constants in their ion radicals [10•].

This review is focused on the electrochemistry of EMFs featuring redox-active metal–metal bonds, and in particular on dimetallofullerenes (di-EMFs hereafter). First, we describe the electronic structure of di-EMFs from the molecular orbital (MO) point of view. This description forms a basis for the understanding of the redox behavior of three types of di-EMF: di-EMFs without metal–metal bonds, but with metal-based LUMO; di-EMFs with two-electron metal–metal bonds; and di-EMF with single-electron metal–metal bonds. Discussion of electrochemical properties of di-EMF is accompanied by the results of EPR spectroscopic measurements of their radical species.

Metal–metal bonding in dimetallofullerenes: theoretical description

Computational studies of di-EMF with Sc, Y, or lanthanides (metal is designated as M hereafter) show that these molecules feature metal–metal bonding molecular orbital, whose energy is close to the energy of the frontier cage-based MOs [11,12]. Whether the M–M bonding MO in a given di-EMF is the HOMO or the LUMO depends on the energy match between the metal-based and fullerene-based orbitals.

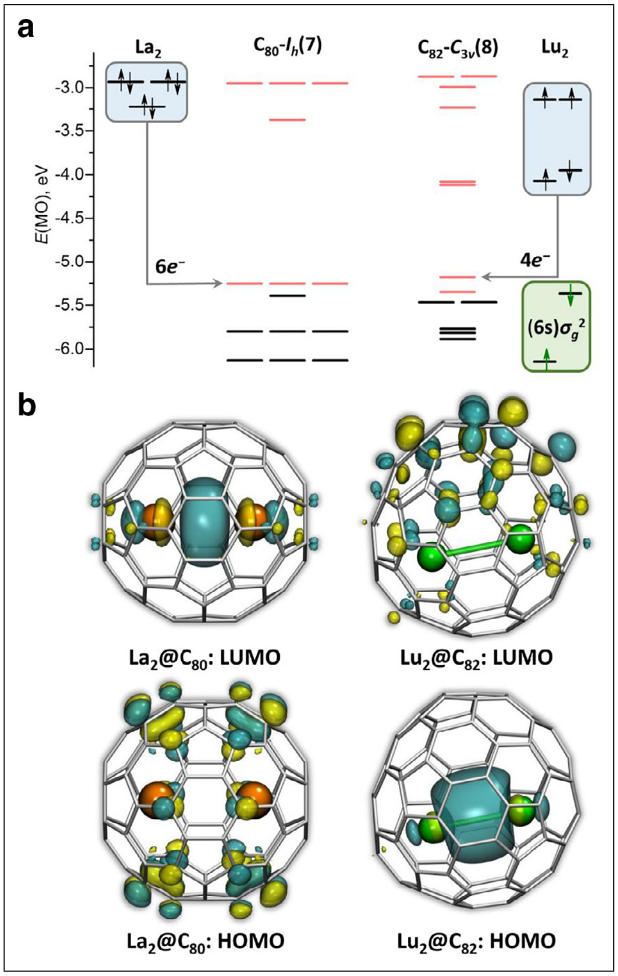
Figure 1a shows MO energy levels of two fullerene cages typical for di-EMFs, C_{80}-I_h(7) and C_{82}-C_{3v}(8) (fullerene isomers are designated by their point group symmetry and the number in accordance with Fowler–Manolopoulos

---

Abbreviations: EMF, endohedral metallofullerene; di-EMF, dimetallofullerene; MO, molecular orbital; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; EPR, electron paramagnetic resonance; M–M bond, metal–metal bond; Vis-NIR, visible and near-infrared; DFT, density functional theory.

Please cite this article as: Popov, Redox-active metal–metal bonds between lanthanides in dimetallofullerenes, Current Opinion in Electrochemistry (2018), https://doi.org/10.1016/j.coelec.2017.12.003

Figure 1



(a) Molecular orbital energy level of empty fullerene C$_{80}$-I_h(7) and C$_{82}$-C_{3v}(8) compared to those of the metal dimers La$_2$ and Lu$_2$ (DFT calculations at the PBE/TZ2P level). Occupied MO levels of fullerenes are shown as black lines, unoccupied levels–as pink lines. Gray arrows indicate donation of six or four electrons from metal dimer to fullerene in corresponding dimetallofullerenes. (b) Frontier molecular orbitals (HOMO and LUMO) of La$_2$@C$_{80}$-I_h(7) and Lu$_2$@C$_{82}$-C_{3v}(8).

spiral algorithm [13]). Characteristic feature of C$_{80}$-I_h(7) is the 4-fold degenerate orbital occupied by only two electrons. Jahn–Teller distortion reduces the symmetry and introduces a small gap between the HOMO and the 3-fold degenerate LUMO. The electronic structure of the molecule is very unstable, and C$_{80}$-I_h(7) has never been obtained as an empty fullerene. However, if the LUMO is filled with six electrons, a stable structure with large band gap is obtained [14]. C$_{80}$-I_h(7) is thus an archetypical cage for EMFs with 6-fold electron transfer from endohedral species to the fullerene [3].

C$_{82}$-C_{3v}(8) has small HOMO–LUMO gap, two low-lying unoccupied MOs, and a significant gap between the LUMO+1 and LUMO+2. The electronic structure of this fullerene is stabilized by addition of four electrons [15]. C$_{82}$-C_{3v}(8) (along with C$_{82}$-C_s(6), which has similar electronic structure) is therefore the most abundant fullerene cage for EMFs with 4-fold electron transfer.

Also shown in Figure 1 are the energy levels of the occupied valence MOs in the two lanthanide dimers, La$_2$ and Lu$_2$. La$_2$ has closed-shell electronic structure with six electrons occupying three MOs (hence (6s)$\sigma_g{}^2$(5d)$\pi_u{}^4$ configuration) [16]. The energies of these MOs are considerably higher than the energy of the LUMO in C$_{80}$-I_h(7), so when the La$_2$ dimer is encapsulated inside this cage, a complete transfer of all six valence electrons to the fullerene occurs. The formal charge distribution in the resulting di-EMF molecule is then (La^{3+})$_2$@C$_{80}{}^{6-}$, the HOMO is localized on the fullerene, whereas the LUMO resembles the (6s)$\sigma_g{}^2$ orbital of the pristine La$_2$ dimer (Figure 1b). Thus, there is no La–La bonding in the non-charged La$_2$@C$_{80}$, but the LUMO of the molecule has the La–La bonding character, and the bond between metal atoms can be formed if the LUMO is populated by a surplus electron.

The lanthanide contraction results in a substantially different electronic structure of Lu$_2$ when compared to that of La$_2$. The ground state of Lu$_2$ is a triplet, (6s)$\sigma_g{}^2$(6s)$\sigma_u{}^2$(5d)$\pi_u{}^2$ [16], with a significant splitting of the spin-up and spin-down orbitals (Figure 1a). These orbitals span a broader energy range than in La$_2$. In particular, the (6s)$\sigma_g{}^2$ level in Lu$_2$ is ca. 2 eV lower in energy than in La$_2$ and, even more importantly, it has lower energy than the LUMO of C$_{80}$-I_h(7). As a result, the hypothetical Lu$_2$@C$_{80}$-I_h(7) has an open-shell electronic structure with five electrons transferred from Lu$_2$ to the C$_{80}$-I_h cage [17•]. C$_{82}$-C_{3v}(8) is a more suitable host for the Lu$_2$ dimer than C$_{80}$-I_h(7). In Lu$_2$@C$_{82}$-C_{3v}(8), four electrons from the (6s)$\sigma_u{}^2$(5d)$\pi_u{}^2$ levels of Lu$_2$ are donated to the fullerene cage, whereas the (6s)$\sigma_g{}^2$ orbital of Lu$_2$ remains occupied. The formal charge distribution in the di-EMF is then (Lu^{2+})$_2$@C$_{82}{}^{4-}$. The Lu–Lu bonding orbital resembling the (6s)$\sigma_g{}^2$ MO of Lu$_2$ is the HOMO of Lu$_2$@C$_{82}$, whereas the LUMO is localized on the fullerene cage (Figure 1b).

Redox-active metal–metal bonds in dimetallofullerenes

Dimetallofullerenes with the metal-based LUMO

Early lanthanides, such as La, Ce, and less studied Pr and Nd, form di-EMFs with the transfer of all six valence electrons to the carbon cage. In addition to the C$_{80}$-I_h(7) cage, several other fullerenes can act as acceptors of six electrons: La and/or Ce di-EMFs were reported for C$_{72}$-D_2(10611) [18,19], C$_{76}$-C_s(17490) [20], C$_{78}$-D_{3h}(5) [21,22], C$_{80}$-D_{5h}(6) [23], and C$_{100}$-D_5(450) [24]. In all these di-EMFs, the M–M bonding MO is the LUMO, and hence metal–metal bonds are expected to be formed in the anionic state(s).

Please cite this article as: Popov, Redox-active metal–metal bonds between lanthanides in dimetallofullerenes, Current Opinion in Electrochemistry (2018), https://doi.org/10.1016/j.coelec.2017.12.003