Redox-active metal–metal bonds between lanthanides in dimetallofullerenes

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Abstract
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.

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•].

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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}\text{-}\text{i}_{h}(7) and C_{82}\text{-}\text{C}_{3v}(8) (fullerene isomers are designated by their point group symmetry and the number in accordance with Fowler–Manolopoulos spiral algorithm [13]). Characteristic feature of C_{80}\text{-}\text{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}\text{-}\text{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}\text{-}\text{i}_{h}(7) is thus an archetypical cage for EMFs with 6-fold electron transfer from endohedral species to the fullerene [3].

C_{82}\text{-}\text{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}\text{-}\text{C}_{3v}(8) (along with C_{82}\text{-}\text{C}_{6}(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^{2}(5d)\pi^{4} configuration) [16]. The energies of these MOs are considerably higher than the energy of the LUMO in C_{80}\text{-}\text{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^{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)$^2$(6p)$^2$(5d)$^2$[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)$^2$ 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$_{80}$h$_6$(7). As a result, the hypothetical Lu$_2$@C$_{80}$h$_6$(7) has an open-shell electronic structure with five electrons transferred from Lu$_2$ to the C$_{80}$h$_6$ cage [17•]. C$_{82}$−C$_{34}$(8) is a more suitable host for the Lu$_2$ dimer than C$_{80}$h$_6$(7). In Lu$_2$@C$_{82}$h$_6$C$_3$v(8), four electrons from the (6s)$^2$(5d)$^2$[17•] levels of Lu$_2$ are donated to the fullerene cage, whereas the (6s)$^2$ orbital of Lu$_2$ remains occupied. The formal charge distribution in the di-EMF is then (Lu$^{2+}$)$_2$@C$_{82}$$^{4-}$. The Lu–Lu bonding orbital resembling the (6s)$^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$_{80}$h$_6$(7) cage, several other fullerenes can act as acceptors of six electrons: La and/or Ce di-EMFs were reported for C$_{72}$h$_2$(10611) [18,19], C$_{76}$h$_6$(17490) [20], C$_{78}$h$_2$(5) [21,22], C$_{80}$h$_2$(6) [23], and C$_{100}$h$_4$(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).

Electrochemical studies of La$_2$@C$_{2n}$ (2$n$ = 72, 78, 80) showed that these di-EMFs exhibit 2–3 reversible single-electron reduction steps. The first reduction of La$_2$@C$_{80}$h$_6$ occurs at ≈−0.31 V (all redox potentials discussed hereafter are measured in o-dichlorobenzene and are referred to the Fe(Cp)$_2$+/0 redox couple) [25]. Likewise, the first reductions of La$_2$@C$_{72}$h$_2$ (−0.68 V) [26], La$_2$@C$_{78}$ (−0.40 V) [22], and La$_2$@C$_{80}$h$_2$(5) (−0.36 V) [23] are significantly more positive than for the EMFs with fullerene-based reductions (usually more negative than −1 V [1]). The first reduction potentials of analogous Ce di-EMFs are cathodically shifted by 0.04–0.13 V versus isostructural La di-EMFs (Table 1) [21,23,27,28].

Besides the value of the first reduction potential and its metal-dependence, another indication of the metal-based reduction in La and Ce di-EMFs is the difference between the first and second reduction potentials, which amounts to 1.23–1.44 V (Table 1). For a fullerene redox process based on the same MO, the difference between the first and second reduction steps is usually within 0.4–0.5 V. The metal-based redox process results in a much larger potential difference for the consequent redox steps, because these steps are either based on the M–M bonding MO (with a much higher on-site Coulomb interaction than in the fullerene) or affect different MOs (one metal-based, and one delocalized over the carbon cage). Thus, both the high potential of the first reduction step and the large gap between the first and the second reduction potentials point to the population of the M–M bonding MO and hence formation of the single-electron M–M bond at the first reduction step.

Formation of the single-occupied La–La bonding MO in the [La$_2$@C$_{80}$h$_6$]$^{−}$ anion radical is further confirmed by EPR spectroscopy [29]. The M–M bonding orbitals in di-EMFs have
hybrid spd character with large s-contribution, and population of such MOs by a single electron is expected to give paramagnetic species with large metal-based hyperfine constants [10••,11]. Indeed, huge isotropic $^{139}$La coupling constant of 364 G was reported in the radical anion $[La_2@C_{80}-I]_{-\bullet}$ [29,30].

**Dimetallofullerenes with metal-based HOMO**

Due to the lanthanide contraction, the metals close to the end of the lanthanide row exhibit more covalent character in their compounds. In di-EMFs, Er and Lu give away only two electrons to the fullerene cage (the formal charge of the fullerene cage is thus $-4$). The remaining metal-based valence electrons then form the M–M bond via the sigma-type spd-hybrid MO. The most abundantly produced di-EMFs with four-fold charged fullerene cages are the two isomers of C$_{82}$, C$_{5}\times(6)$ and $C_{3v}\times(8)$ [31–34]. Structural characterization was also reported for several other Lu di-EMFs, including Lu$_2@C_{76}$–$T_d(1)$ [35], Lu$_2@C_{84}$–$D_{2d}(23)$, and Lu$_2@C_{86}$–$C_{2v}(9)$ [31]. If the M–M bonding MO is the HOMO (as predicted by theory), these di-EMFs should feature a metal–metal bond already in the pristine non-charged state, and this bond should be electrochemically active in the oxidation processes.

The experimental confirmation of the metal–metal bonding in di-EMFs is not very straightforward. The formal charge of the fullerene cage in M$_2@C_{82}$ can be deduced from Vis-NIR spectroscopic measurements. UV-vis-NIR absorption spectra of the di-EMFs with the same fullerene cage and different metals are virtually identical. Presumably, the excitation originating from the metal-based HOMO have very low intensity and cannot be observed, resulting in the dominance of the $\pi \rightarrow \pi^*$ transitions in the fullerene cages. Similar spectra are also observed for sulfide clusterfullerenes M$_2S@C_{82}$ [32••,36] or carbide clusterfullerenes M$_2C_2@C_{82}$ [12,37]. In cluster-fullerenes, the non-metal endohedral entity bears a negative charge (C$_2^2-$, O$^{2-}$, or S$^{2-}$), the metal atoms are in their 3+ state, whereas the cage has the negative charge of $-4$. Such clusterfullerenes do not feature metal–metal bonds, and their frontier MOs are usually localized on the fullerene cage [6•]. The close resemblance of the absorption spectra of di-EMF and clusterfullerenes proves that the carbon cage in these EMFs has the same formal charge, $-4$. Thus, $+2$ oxidation state of metal atoms appears natural. However, the presence of the M–M bond does not automatically follow from the oxidation state. X-ray absorption spectra at the M$_{4,5}$ edge (3d→4f excitations commonly used in the studies of lanthanides) did not show substantial difference between Er$_2@C_{82}$ or Er$_2C_2@C_{82}$ [38]. However, both Er$^{2+}$ and Er$^{3+}$ states in EMFs feature the same 4f$^{12}$ occupation, and therefore absorption at the M$_{4,5}$ edge may be not sensitive enough to the difference in the valence orbital populations.

Electrochemistry provides more straightforward approach to the problem. If the M–M bonding MO is indeed the redox-active HOMO of di-EMFs, the first oxidation potential should exhibit pronounced metal-dependence in contrast to the first reduction potential, which corresponds to the cage-based LUMO and is not expected to vary much from metal to metal. Indeed, electrochemistry reveals pronounced differences in the electronic structure of Er$_3@C_{82}$ and Lu$_3@C_{82}$ [32••]. Their reduction potentials are rather similar (Figure 2a; note that C$_{82}$–$C_3$ isomer exhibits irreversible reduction steps, whereas reduction steps of C$_{82}$–$C_5$ isomers are fully reversible). Such a similarity of the potentials points to the fullerene-based
nature of the underlying redox steps, in agreement with DFT prediction. On the contrary, oxidation potentials of Er$_2$@C$_{82}$ and Lu$_2$@C$_{82}$ are strongly metal-dependent. Er$_2$@C$_{82}$ isomers have their first oxidation step at ca. 0.3–0.4 V lower potentials than Lu-counterparts (Table 1). The same trend was observed for M$_2$@C$_{82}$-C$_{3v}$ structures with other metals, including Sc$_2$@C$_{82}$ and mixed-metal ErSc@C$_{82}$ and YLu@C$_{82}$ di-EMFs [32••]. With almost identical reduction potential, they exhibit large variability of the first oxidation potentials (Figure 2b). Metal-dependence of the first oxidation potential in di-EMFs confirms the computationally predicted metal–metal bonding HOMO in these molecules (Figure 2c). Lu has the lowest energy of the M–M bonding HOMO, and hence Lu di-EMFs exhibit the highest oxidation potentials when compared to other metals. In fact, oxidation potentials of Lu-di-EMFs are close to the cage-based oxidation potentials of sulfide clusterfullerenes M$_2$S@C$_{82}$ (Table 1), and it is hard to distinguish if the first oxidation step of Lu$_2$@C$_{82}$ isomers is metal- or fullerene-based. Lower oxidation potentials of di-EMFs with other metals unequivocally point out the metal-based processes.

Single-electron oxidation of di-EMF with M–M bonding HOMO produces a single-occupied metal-based orbital with unprecedented spin properties. Large contribution of metal s-atomic orbital to the M–M HOMO of M$_2$@C$_{82}$ yields a large isotropic hyperfine coupling constant for metals with non-zero nuclear spin in [M$_2$@C$_{82}$]$^{1+}$ cation radicals. A striking example is the cation radical of Sc$_2$@C$_{82}$, which at room temperature in o-dichlorobenzene solution exhibits well-resolved EPR spectrum with the hyperfine structure spanning 2800 G (Figure 2d). Instead of 15 lines expected for two equivalent Sc with nuclear spin of 7/2, experimental spectrum comprises 64 lines caused by additional splitting due to the large $^{45}$Sc hyperfine constant, $a(^{45}\text{Sc}) = 199.2$ G [32••]. Formation of the single-electron Er–Er bond in [Er$_2$@C$_{82}$-C$_{3v}$]$^{1+}$ was supported by SQUID magnetometry. The oxidation of Er$_2$@C$_{82}$ strongly modified the spin state of the endohedral Er$_2$ unit, presumably creating a three-center [Er$_{3+}$–e–Er$_{3+}$] system with stronger exchange interactions than in the pristine Er$_2$@C$_{82}$ [32••].

**Dimetallofullerenes with single-electron metal–metal bond**

Whereas early and late lanthanides tends to form di-EMFs with tri- and di-valent state of metals, respectively, yttrium and lanthanides in the middle part of the lanthanide row (Gd–Ho) give di-EMF with even more peculiar electronic structure. Computational studies of M$_2$@C$_{80}$-I$_6$ (M = Y, Lu) showed that the ground electronic state for these di-EMF is a triplet [17•]. The M–M bonding MO is occupied by a single electron, and another unpaired spin is delocalized over the fullerene cage. The formal charge distribution is then (M$_2$)$^{5+}$@C$_{80}$$^{5-}$. During the extraction of fullerenes from the arc-discharge soot by standard fullerene solvents (such as CS$_2$ or toluene) these molecules remain insoluble, presumably due to polymerization or aggregation with the soot particles.

Electronic structure of such M$_2$@C$_{80}$-I$_6$ di-EMFs can be stabilized by addition of an electron, which yields to closed-shell electronic structure of the fullerene cage, (M$_2$)$^{5+}$@C$_{80}$$^{6-}$ [39]. Indeed, the synthesis of M$_2$@C$_{80}$ derivatives was accomplished when EMFs were extracted from the soot with N,N-dimethylformamide, which is known to form fullerene anions during extraction (Figure 3a) [40,41]. Chemical derivatization with a single
radical group R (R = CF₃ or benzyl CH₂Ph) is another way to quench the cage-based radical in M₂@C₈₀-I₈ [17•,42••]. Finally, addition of an electron is equivalent to substitution of one carbon atom by nitrogen. C₇₉N⁵⁻ is isoelectronic to C₈₀⁶⁻, and stable M₂@C₇₉N compounds were obtained in Dorn’s group for M = Y, Gd, and Tb [43,44]. The common feature of M₂@C₈₀⁻, M₂@C₇₉N, or M₂@C₈₀(R) is the single-electron M–M bond stabilized inside the fullerene. For M = Y, localization of the spin density on the Y–Y bonding MO can be confirmed by EPR spectroscopy, which revealed similar spectra in all three types of EMFs with large isotropic ⁸⁹⁹Y hyperfine coupling constants near of 80 G (Figure 3b,c) [17•,42••,44]. Formation of the single-electron La–La bond in La₂@C₈₀(CH₂Ph) and similar radical monoadducts of La₂@C₈₀-I₈ was also confirmed by EPR spectroscopy and single-crystal X-ray diffraction [45••,46].

Potentially, the half-occupied M–M bonding orbital can be redox active both in reduction and oxidation processes. However, DFT calculations predict large energy difference between occupied and unoccupied counterparts of the MO [42••]. As a result, the occupied component of the M–M bonding MO in La₂@C₈₀(CH₂Ph) is predicted to be the HOMO, whereas the LUMO is localized on the fullerene cage. In Y₂@C₈₀(CH₂Ph), analogous calculations showed metal-based LUMO and fullerene-based HOMO.

Y and Gd–Ho M₂@C₈₀(CH₂Ph) derivatives exhibit virtually identical oxidation potential at +0.51–0.52 V (Table 1, Figure 3d) [32••,47]. The lack of the metal dependence is an indication of the fullerene-based oxidation in these di-EMFs, in agreement with DFT prediction for Y₂@C₈₀(CH₂Ph). With the first oxidation potential at +0.15 V [45••], La₂@C₈₀(CH₂Ph) is an obvious outlier exhibiting the metal-based oxidation. Thus, the metal–metal bonding MO of La₂@C₈₀(CH₂Ph) is depopulated in the oxidation process, whereas for other metals the single-electron M–M bond is not affected.

The first reduction potentials of M₂@C₈₀(CH₂Ph) derivatives are different and span the range from −0.52 V in Y₂@C₈₀(CH₂Ph) to −0.92 V in La₂@C₈₀(CH₂Ph). In the Gd–Ho row, the potential is changing gradually with the size of the lanthanide, more negative values corresponding to larger ionic radii. This behavior is consistent with the metal-based reduction for Y and medium-size lanthanides. Hence, the single-electron M–M bond turns to a two-electron bond in their monoanions. In La₂@C₈₀(CH₂Ph), the process switches to the fullerene-based reduction.

Electrochemical studies of other di-EMFs with single-electron M–M bond were reported so far only for Gd₂@C₇₉N [43]. Its first oxidation potential at +0.51 V is very close to that of M₂@C₈₀(CH₂Ph) derivatives with fullerene-based oxidation (Table 1). The first reduction at −0.96 V is more negative than in any M₂@C₈₀(CH₂Ph), including La₂@C₈₀(CH₂Ph). Computational studies showed that Gd₂@C₇₉N has two low-energy unoccupied MOs, one Gd-based and one delocalized over the fullerene, thus making it hard to distinguish between the fullerene- and metal-based reductions. However, the large difference between the first and the second reduction potentials of almost 1 V (Table 1) indicates that the first reduction of Gd₂@C₇₉N may indeed involve the Gd–Gd bonding MO.
Outlook

The unique environment of endohedral fullerene provides a possibility to stabilize exotic species with unconventional bonding situation, such as lanthanide dimers with metal–metal bonds. Whereas many lanthanide complexes with low oxidation states have been synthesized [48••], no other molecular compounds with lanthanide–lanthanide bonds have been reported so far [49••]. Furthermore, the M–M bonding MOs in dimetallofullerenes are redox active and undergo single-electron reduction or oxidation, which leads to radical species with single-electron M–M bonding MOs. Electrochemistry is thus found to be a convenient technique to study metal–metal bonds in fullerenes. Redox variability of the population of the lanthanide–lanthanide bonding MOs in di-EMFs is very useful for tuning their magnetic properties. The presence of the unpaired valence electron in lanthanide-based di-EMFs results in giant exchange interactions and coupling of local 4f-derived spins and unpaired spin in the M–M bonding MO into a larger “superspin”. If lanthanides with large magnetic anisotropy (such as Dy or Tb) are coupled this way, single molecule magnets with high blocking temperature of magnetization can be obtained [42••]. Semi-occupied M–M bonding MO is also essential for the spin-polarized electronic transport through single fullerene molecules, which can lead to single-molecule electronic and spintronic devices.

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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.

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Figure 1.
(a) Molecular orbital energy level of empty fullerene $C_{80}^-$-$I_6(7)$ 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 $La_2@C_{80}$: LUMO and $Lu_2@C_{82}$: LUMO, $La_2@C_{80}$: HOMO and $Lu_2@C_{82}$: HOMO.
Figure 2.
(a) Cyclic voltammetry of Er$_2$@C$_{82}$ and Lu$_2$@C$_{82}$ dimetallofullerenes with $C_{3v}$ (8) and $C_6$ cage isomers in o-dichlorobenzene/TBAPF$_6$ solution at 100 mV s$^{-1}$; whereas the first reduction potentials of Lu$_2$@C$_{82}$ and Er$_2$@C$_{82}$ with the same fullerene cage are virtually identical (denoted by blue dashed line), the first oxidation potentials are different by more than 0.3 V (red lines); (b) square wave voltammetry of several M$_2$@C$_{82}$ - C$_{3v}$ (8) at the first oxidation step (M$_2$ = Lu$_2$, YLu, Er$_2$, ErSc, Sc$_2$); (c) HOMO orbitals for Lu$_2$@C$_{82}$, Y$_2$@C$_{82}$, and YLu@C$_{82}$; (d) EPR spectrum of Sc$_2$@C$_{82}^+$ cation in o-dichlorobenzene at room
temperature, $a^{15}\text{Sc} = 199.2\text{ G}$, $g = 1.994$; the lines show assignment of the peaks in terms of $|I, m_I$ nuclear spin quantum numbers of the Sc$_2$ dimer. Reproduced with permission from the Ref. [32••].
Figure 3.
(a) Schematic description of the electron distribution between M–M bonding MO and fullerene cage in dimetallofullerenes $M_2@C_{80}^-$ (M = Y, Tb, Dy, etc.) and a chemical route to stabilize these structures via reduction and subsequent nucleophilic substitution yielding air-stable $M_2@C_{80}(CH_2Ph)$ monoadduct. (b) EPR spectra of the toluene solution of $Y_2@C_{80}(CH_2Ph)$ at room temperature and at 150 K (below the freezing point of the solvent); the isotropic RT spectrum has g-factor of 1.9733 and the $g_{iso}^{(89Y)}$ value of 223.8 MHz; the axial spectral pattern in frozen solution is reproduced by $g_\perp = 1.9620$, $g_\parallel = 1.9982$. 

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$\alpha_{\perp}^{(89)Y} = 208.0 \text{ MHz}, \quad \alpha_{\parallel}^{(89)Y} = 245.9 \text{ MHz};$ (c) spin density distribution in $Y_2@C_{80}(\text{CH}_2\text{Ph})$ computed at the PBE0/TZVP level; (d) square wave voltammetry of $M_2@C_{80}(\text{CH}_2\text{Ph})$ ($M = Y, \text{Dy, and Tb}$), black vertical bars denote redox potentials of $\text{La}_2@C_{80}(\text{CH}_2\text{Ph})$ from Ref. [45••], dotted lines denote the first oxidation (cyan) and the first reduction (red) potentials. Based on the data from Ref. [42••].
Table 1
Redox potentials of di-EMFs featuring the M–M bonding HOMO or LUMO in comparison to selected clusterfullerenes<sup>a</sup>

| EMF                        | $E^{2+/1}$ | $E^{1+/0}$ | $E^{0/-1}$ | $E^{-1/-2}$ | $E^{-2/-3}$ | $\text{gap}_{cc}$<sup>b</sup> | Ref. |
|----------------------------|------------|------------|------------|------------|------------|----------------------|------|
| **Metal-based LUMO**       |            |            |            |            |            |                      |      |
| La<sub>2</sub>@C<sub>72</sub>-D<sub>2</sub>(10611) | 0.75       | 0.24       | $-0.68$    | $-1.92$    | 0.92       | [26]                 |      |
| Ce<sub>2</sub>@C<sub>72</sub>-D<sub>2</sub>(10611) | 0.82       | 0.18       | $-0.81$    | $-1.86$    | 0.99       | [27]                 |      |
| La<sub>2</sub>@C<sub>50</sub>-C<sub>7</sub>(17490) | 0.65       | 0.21       | $-0.63$    | $-1.83$    | 0.84       | [20]                 |      |
| La<sub>2</sub>@C<sub>50</sub>-D<sub>4d</sub>(5) | 0.62       | 0.26       | $-0.40$    | $-1.84$    | 0.66       | [22]                 |      |
| Ce<sub>2</sub>@C<sub>50</sub>-D<sub>4d</sub>(5) | 0.79       | 0.25       | $-0.52$    | $-1.86$    | 0.77       | [21]                 |      |
| La<sub>2</sub>@C<sub>50</sub>-D<sub>4d</sub>(6) | 0.78       | 0.22       | $-0.36$    | $-1.72$    | 0.58       | [23]                 |      |
| Ce<sub>2</sub>@C<sub>50</sub>-D<sub>4d</sub>(6) | 0.66       | 0.20       | $-0.40$    | $-1.76$    | 0.60       | [23]                 |      |
| La<sub>2</sub>@C<sub>50</sub>-I<sub>g</sub>(7) | 0.95       | 0.56       | $-0.31$    | $-1.72$    | 0.87       | [25]                 |      |
| Ce<sub>2</sub>@C<sub>50</sub>-I<sub>g</sub>(7) | 0.95       | 0.57       | $-0.39$    | $-1.71$    | 0.96       | [28]                 |      |
| **Metal-based HOMO**       |            |            |            |            |            |                      |      |
| Er<sub>2</sub>@C<sub>52</sub>-C<sub>7</sub>(6) | 0.65       | 0.02       | $-1.01$    | $-1.31$    | 1.03       | [32••]               |      |
| Lu<sub>2</sub>@C<sub>52</sub>-C<sub>7</sub>(6) | 0.74       | 0.34       | $-1.00$    | $-1.32$    | 1.34       | [32••]               |      |
| Er<sub>2</sub>S@C<sub>52</sub>-C<sub>7</sub>(6)<sup>c</sup> |            | 0.39       | $-1.16$    | $-1.49$    | 1.19       | [32••]               |      |
| Sc<sub>2</sub>S@C<sub>52</sub>-C<sub>7</sub>(6)<sup>c</sup> | 0.65       | 0.39       | $-0.98$    | $-1.12$    | 1.37       | [50]                 |      |
| Sc<sub>2</sub>@C<sub>52</sub>-C<sub>7</sub>(8) |            | 0.02       | $-1.16$    | $-1.53$    | 1.18       | [32••]               |      |
| ErSc@C<sub>52</sub>-C<sub>7</sub>(8) |            | 0.08       | $-1.11$    | $-1.49$    | 1.19       | [32••]               |      |
| Er<sub>2</sub>@C<sub>52</sub>-C<sub>7</sub>(8) |            | 0.13       | $-1.14$    | $-1.41$    | 1.27       | [32••]               |      |
| YLu@C<sub>52</sub>-C<sub>7</sub>(8) |            | 0.23       | $-1.13$    | 1.36       |            | [32••]               |      |
| La<sub>2</sub>@C<sub>52</sub>-C<sub>7</sub>(8) | 0.95       | 0.50       | $-1.16$    | $-1.46$    | 1.66       | [32••]               |      |
| ErSc@C<sub>52</sub>-C<sub>7</sub>(8)<sup>c</sup> | 0.88       | 0.51       | $-0.98$    | $-1.21$    | 1.49       | [32••]               |      |
| Sc<sub>2</sub>S@C<sub>52</sub>-C<sub>7</sub>(8)<sup>c</sup> | 0.96       | 0.52       | $-1.04$    | $-1.19$    | 1.56       | [50]                 |      |
| Lu@C<sub>52</sub>-C<sub>7</sub>(9) |            | 0.31       | $-1.01$    | $-1.34$    | 1.35       | [31]                 |      |
| Sc<sub>2</sub>C<sub>52</sub>-C<sub>7</sub>(9)<sup>c</sup> |            | 0.47       | $-0.84$    | $-1.11$    | 1.31       | [51]                 |      |
| **Single-electron M–M bonding MO** |           |            |            |            |            |                      |      |
| Gd<sub>2</sub>@C<sub>900</sub>-I<sub>g</sub>(7) |            | 0.51       | $-0.96$    | $-1.98$    | 1.45       | [43]                 |      |
| La<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> |            | 0.15       | $-0.92$    | $-1.34$    | 0.97       | [45••]               |      |
| Y<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> | 0.98       | 0.52       | $-0.52$    | $-1.29$    | 1.04       | [42••]               |      |
| Gd<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> |            | 0.52       | $-0.86$    | $-1.35$    | 1.38       | [47]                 |      |
| Tb<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> |            | 0.51       | $-0.79$    | $-1.36$    | 1.71       | [47]                 |      |
| Dy<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> | 0.98       | 0.52       | $-0.60$    | $-1.28$    | 1.12       | [42••]               |      |
| Ho<sub>2</sub>@C<sub>900</sub>-CH<sub>Ph</sub> |            | 0.51       | $-0.54$    | $-1.33$    | 1.05       | [47]                 |      |

<sup>a</sup>All potentials are measured in o-dichlorobenzene solution and referenced versus Fe(Cp)<sub>2</sub><sup>4+/0</sup> redox pair; redox processes involving M–M bonding orbitals are highlighted in bold.

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\[ \text{gap}^{EC} \text{ is defined as } E^{+1/0} - E^{0/-1}. \]

Clusterfullerenes with cage-based first oxidation steps, listed here for comparison to di-EMFs with the same fullerene cages.