Rates and energetics of intramolecular electron transfer processes in conjugated metallofullerenes

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In this paper, we report on the design, redox potentials, excited state energies and radical ion pair state energies in electron donor–acceptor conjugates comprising the electron-donating π-extended tetraithiafulvalene and several electron-accepting fullerenes. To this end, we contrast an empty fullerene, that is, C60, with two endohedral metallofullerenes, that is, open-shell La@C82 and closed-shell La2@C80, in terms of charge separation and charge recombination dynamics.

1. Introduction

In recent years, the great versatility and unique geometrical and electronic properties of empty fullerenes, namely C60 and C70, and to a considerably lesser extent higher fullerenes, as integrative building blocks
Figure 1. (a) C$_{60}$-exTTF, (b) La@C$_{82}$-exTTF and (c) La$_2$@C$_{80}$-exTTF electron donor–acceptor conjugates. (Online version in colour.)

in electron donor–acceptor conjugates and hybrids have been established. In particular, concepts have been developed to generate functional entities using the bottom-up approach, that is, to design, manipulate, characterize, examine and understand the potential of fullerenes as a platform for stable electron donor–acceptor conjugates and hybrids [1–19]. Reduced contact resistance, increased film conductivity and manipulation of interface molecular-level alignment, especially in the context of constructing more efficient optoelectronic devices, are recognized benefits of doping molecular materials [20–22].

Endohedral metallofullerenes bear, in contrast to empty fullerenes, additional atoms, ions or clusters within their inner spheres [23]. The latter possess impressive electronic structures that are governed by significant electron transfer between the encapsulated species and the fullerene cage. What renders endohedral metallofullerenes particularly appealing is that significant control over the chemical and physical properties has been realized by just changing the nature and composition of the encapsulated species [24–27]. However, it is only recently that endohedral metallofullerenes have begun to be used in electron donor–acceptor conjugates and hybrids [26, 28]. Many questions remain unanswered to date. For example, the influence of the incorporated metals and the number of incorporated metals on the overall excited state chemistry of the fullerene needs to be explored. Furthermore, the broad range of redox potentials found for the different endohedral metallofullerenes raises the question about their suitability as electron or energy acceptors as a function of the incorporated species. Important also are aspects that relate to the open-shell versus the closed-shell species in endohedral metallofullerenes. In this context, we compare the impact that different metallofullerenes, that is, La@C$_{82}$ and La$_2$@C$_{80}$, exert on the excited state energies, radical ion pair state energies, and, consequently, on the electron transfer dynamics relative to C$_{60}$.

2. Results and discussion

(a) Synthesis

The target conjugates (exTTF = $\pi$-extended tetrathiafulvalene), C$_{60}$-exTTF, La@C$_{82}$-exTTF and La$_2$@C$_{80}$-exTTF (figure 1), were synthesized by 1,3-dipolar cycloaddition reactions of azomethine ylides generated \textit{in situ} from aminoacetic acids and 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF-CHO) [29] to C$_{60}$ [30], La@C$_{82}$ [31] and La$_2$@C$_{80}$ [29], respectively.
Table 1. Redox potentials of C_{60}-exTTF, La@C_{82}-exTTF and La_{2}@C_{80}-exTTF electron donor–acceptor conjugates.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>( E_{4}^{(1)} ) \textsuperscript{ox} (V)</th>
<th>( E_{3}^{(3)} ) \textsuperscript{ox} (V)</th>
<th>( E_{2}^{(2)} ) \textsuperscript{ox} (V)</th>
<th>( E_{1}^{(1)} ) \textsuperscript{ox} (V)</th>
<th>( E_{4}^{(1)} ) \textsuperscript{red} (V)</th>
<th>( E_{3}^{(3)} ) \textsuperscript{red} (V)</th>
<th>( E_{2}^{(2)} ) \textsuperscript{red} (V)</th>
<th>( E_{1}^{(1)} ) \textsuperscript{red} (V)</th>
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<tr>
<td>exTTF-CHO</td>
<td>+0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{60}</td>
<td></td>
<td>+1.21</td>
<td>−1.12</td>
<td>−1.50</td>
<td>−1.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La@C_{2}-C_{82}</td>
<td>+1.07</td>
<td>+0.07</td>
<td>−0.42</td>
<td>−1.37</td>
<td>−1.53</td>
<td>−2.62</td>
<td></td>
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</tr>
<tr>
<td>La@C_{80}</td>
<td>+0.95</td>
<td>+0.56</td>
<td>−0.31</td>
<td>−1.71</td>
<td>−2.13</td>
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<td></td>
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<tr>
<td>C_{60}-exTTF</td>
<td></td>
<td>+0.06</td>
<td>−1.06</td>
<td>−1.41</td>
<td>−2.07</td>
<td>−2.36</td>
<td></td>
<td></td>
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<tr>
<td>La@C_{82}-exTTF</td>
<td></td>
<td>−0.05</td>
<td>−0.04</td>
<td>−0.38</td>
<td>−1.32</td>
<td>−1.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La_{2}@C_{80}-exTTF</td>
<td>+0.95</td>
<td>+0.58</td>
<td>+0.19</td>
<td>+0</td>
<td>−0.45</td>
<td>−1.73</td>
<td>−2.23</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values are given in V relative to a Fc/Fc\textsuperscript{+} redox couple.

After a one-step high-performance liquid chromatography separation—using a recycling system and a Buckyprep column—single fractions of C_{60}-exTTF, La@C_{82}-exTTF and La_{2}@C_{80}-exTTF were obtained. In the case of La@C_{82}-exTTF only, the corresponding fraction contained two products. Owing to the asymmetric nature of azomethine ylides, cycloadditions at C21–C23 may generate diastereomers of four types. In fact, the results from the \( ^{1} \)H nuclear magnetic resonance (NMR) experiments indicated equivalent methylene protons and inequivalent methyne protons, strongly suggesting that both isomers feature methylene hydrogens linked to the carbon adjacent to either C21 or C23. The two most stable density functional theory-optimized structures possess methylene hydrogens linked to the carbon adjacent to C23.

Standard characterization methods, such as \( ^{1} \)H NMR, \( ^{13} \)C NMR, etc. provide unambiguous evidence for the \( [6,6]\)-closed character of C_{60}-exTTF, while La@C_{82}-exTTF and La_{2}@C_{80}-exTTF are of \( [5,6]\)-closed character [29–31].

(b) Electron spin resonance characterization

Importantly, electron spin resonance (ESR) measurements corroborate the open-shell nature of La@C_{82}-exTTF. In fact, the observed ESR spectrum reveals a broad asymmetric octet signal. The latter was, nevertheless, best fitted to two octet signals. In addition, the simulated spectrum points to the existence of two compounds in a 1:1 ratio.

(c) Electrochemical characterization

In the oxidative range, C_{60}-exTTF shows only a quasi-reversible oxidation at +0.06 V (all values versus ferrocene Fc/Fc\textsuperscript{+}) involving a two-electron process to form the dication of exTTF [30], similar to that seen for the exTTF reference [32–35] (table 1). In the reductive range, the presence of four reductions resemble those seen for the C_{60} reference at −1.06, −1.41, −2.07 and −2.36 V [36–39]. In La@C_{82}-exTTF, the oxidative range is dominated by the oxidation of La@C_{82} at −0.04 V [40] and the two-electron oxidation of exTTF at +0.05 V. Theoretical calculations corroborate the fact that the singly occupied molecular orbital is localized on La@C_{82} rather than on exTTF. In the reductive range, the three La@C_{82} reductions evolve at −0.38, −1.32 and −1.66 V [40]. For La_{2}@C_{80}-exTTF, the first oxidation at +0.00 V is exTTF centred and again is a two-electron process. The following three oxidations at +0.19, +0.58 and +0.95 V involve La_{2}@C_{80}. In stark contrast, the reductive range only reveals La_{2}@C_{80} reductions at −0.45, −1.73 and −2.23 V [29]. The redox potentials, as found for C_{60}-exTTF, La@C_{82}-exTTF and La_{2}@C_{80}-exTTF, reveal, in agreement with the data stemming from the corresponding references, namely C_{60} [37], La@C_{82} [40], La_{2}@C_{80} [41] and exTTF [32–35], only weak electronic interactions between the electron donors and electron acceptors in their ground state.
Considering the exTTF centred oxidation and the lowest reduction of C\textsubscript{60}, La@C\textsubscript{82} and La\textsubscript{2}@C\textsubscript{80}, we derive radical ion pair state energies of 1.12 eV for C\textsubscript{60}-exTTF, 0.43 eV for La@C\textsubscript{82}-exTTF and 0.45 eV for La\textsubscript{2}@C\textsubscript{80}-exTTF (see below).

(d) Photophysical characterization of references

To evaluate the excited state interactions, we investigated C\textsubscript{60}-exTTF, La@C\textsubscript{82}-exTTF and La\textsubscript{2}@C\textsubscript{80}-exTTF, in relation to the C\textsubscript{60}, La@C\textsubscript{82}, La\textsubscript{2}@C\textsubscript{80} and exTTF references, by means of femtosecond pump–probe experiments following 387 nm excitation.

For example, 387 nm excitation of the exTTF reference (i.e. exTTF-CHO) generates a fairly short-lived exTTF centred excited state (2.7 eV). The spectral characteristics of the latter are transient maxima around 455, 615 and 915 nm, as well as transient bleaching at a wavelength below 450 nm. Owing to strong second-order spin couplings, exTTF centred excited states tend to decay fast, that is, within the time window of up to approximately 10 ps. From a mono-exponential fit of the decay at, for example, the 615 nm maximum, we derive a decay rate constant of \((1.2 \pm 0.2) \times 10^{12} \text{ s}^{-1}\) [31].

The singlet excited state (1.76 eV) of the C\textsubscript{60} reference lacking exTTF displays a distinct and characteristic singlet–singlet transition around 880 nm, which undergoes a quantitative intersystem crossing with a rate of \(5 \times 10^{8} \text{ s}^{-1}\). As a product, the long-lived triplet manifold, for which maxima are noted at 360 and 700 nm followed by a low-energy shoulder at 800 nm, evolves [42].

When turning to the La@C\textsubscript{82} reference, in which a phenyl group replaces exTTF, maxima at 455, 550, 695, 900 and 1140 nm and a minimum at 950 nm emerge as a consequence of forming the La@C\textsubscript{82} doublet excited state (0.88 eV). The latter maxima are subject to a mono-exponential decay in the form of a rapid intersystem crossing with rate \(5.0 \times 10^{10} \text{ s}^{-1}\) to yield the energetically lower-lying quartet excited state. The intersystem crossing is independent of the solvent polarity (i.e. toluene, tetrahydrofuran (THF) or benzonitrile). For the La@C\textsubscript{82} centred quartet excited state, we noted a several nanoseconds-lived transient spectrum with maxima at 450, 560, 705, 910 and 1140 nm [31].

For the La\textsubscript{2}@C\textsubscript{80} reference, where exTTF is replaced by a phenyl group, the following singlet excited features emerge: maxima 520, 580 and 1110 nm. This singlet excited state (1.4 eV) is, however, subject to a rapid intersystem crossing \((3 \times 10^{10} \text{ s}^{-1})\) to yield the energetically lower-lying triplet excited state. For the latter, we noted a several nanoseconds-lived transient maximum at 500 nm [29].

(e) Photophysical characterization of electron donor–acceptor conjugates

Following excitation of C\textsubscript{60}-exTTF with 387 nm, the instantaneous formation of both singlet excited states, that is, C\textsubscript{60} with its 880 nm maximum and exTTF with its maximum at 600 nm, is seen to evolve. In contrast to what is seen for the references, the singlet excited state decays in C\textsubscript{60}-exTTF rather quickly, that is, within 10 ps. A likely mechanism for the deactivation is an intramolecular electron transfer from the C\textsubscript{60} singlet excited state. On the one hand, it is noteworthy to mention the newly formed maximum at 660 nm and the ground state bleaching around 430 nm. We ascribe these changes in oscillator strength to the oxidation of exTTF, since both features are characteristic markers seen upon pulse radiolytical one-electron oxidation of exTTF [43]. On the other hand, the 1005 nm maximum relates to the one-electron reduced form of C\textsubscript{60} [42]. In conclusion, the C\textsubscript{60}\textsuperscript{−}–exTTF\textsuperscript{+} radical ion pair state (1.12 eV) is formed intramolecularly as a consequence of photexciting C\textsubscript{60}-exTTF before reinstating the singlet ground state.

Considering the absorption features of both constituents at the 387 nm excitation wavelength in La@C\textsubscript{82}-exTTF, we must also assume the excitation of the La@C\textsubscript{82} and the exTTF constituents. Indeed, when turning to transient absorption measurements with La@C\textsubscript{82}-exTTF and 387 nm
excitation (figure 2), we note the instantaneous formation of exTTF and La@C\textsubscript{82} centred excited states all throughout the visible and the near-infrared regions, respectively. Most notable in the visible region are the maxima at 465 and 645 nm, which attests the successful exTTF excitation. In fact, the latter bears great resemblance with the 455 and 615 nm maxima seen in experiments with exTTF-CHO that lacks La@C\textsubscript{82}. Within less than 10 ps, the exTTF excited state transforms into the one-electron oxidized exTTF. Evidence for the oxidative electron transfer comes from the 670 nm maximum and the ground state bleaching around 430 nm. The additional feature at 460 nm relates to the one-electron reduced form of La@C\textsubscript{82}. In terms of the La@C\textsubscript{82} centred doublet excited state, maxima at 455, 550, 895 and 1160 nm as well as a minimum at 950 nm are in perfect agreement with the transient features seen for the La@C\textsubscript{82} reference that lacks exTTF and, thus, corroborate the successful La@C\textsubscript{82} excitation. Within approximately a time frame of 10 ps, the La@C\textsubscript{82} doublet excited state characteristics decay. A closer look at the absorption characteristics sheds light onto the nature of the photoproduct that evolves as a consequence of the fast La@C\textsubscript{82} excited state decay (figure 2). Of particular importance is that the spectroscopic pattern with maxima at 860 and 1220 nm as well as a minimum at 945 nm are a good match to that developing during the electrochemical one-electron reduction of La@C\textsubscript{82}. Taking all of the aforementioned into account, we reach the important conclusion that the exTTF and La@C\textsubscript{82} excited states power an intramolecular electron transfer to yield an energetically low-lying La@C\textsubscript{82}−-exTTF\textsuperscript{+} radical ion pair state (0.43 eV). The latter is semistable and decays to the doublet ground state [31].
Likewise in La$_2@C_{80}$-exTTF, we must assume that 387 nm photoexcites both La$_2@C_{80}$ and exTTF. Evidence for this assumption was borrowed from the transient absorption spectra (figure 3) as they develop, for example, in THF at time delays close to the initial excitation, namely up to 5 ps. In the visible region, we noted short-lived features around 530 nm that are associated with the excited state features of exTTF. When turning to the near-infrared region, a broad transient is detected that bears great resemblance with that seen for La$_2@C_{80}$. Common to the visible and near-infrared characteristics in La$_2@C_{80}$-exTTF, namely the maxima at 530 and 1300 nm, is a mono-exponential decay. Here, a global analysis leads to a rate constant of $6.0 \times 10^{10} \text{s}^{-1}$. A closer look at the absorption characteristics sheds light on the nature of the photoproduct that evolves as a consequence of the fast excited state decay (figure 3). Again, in the visible range, we note an absorption that corresponds unambiguously to the marker of the one-electron oxidized exTTF. The radical cation absorption maximizes in the current case at 610 nm. The reduction of fullerenes is typically associated with characteristic changes in the near-infrared region—1200 nm. Implicit are the absorption pattern of the one-electron reduced form that depends on the nature of the fullerene and the specific addition pattern of the fullerene derivatives. Notable is that the ground state absorption of La$_2@C_{80}$ lacks what has been seen, for example, for C$_{60}$, C$_{70}$, etc. transitions in the near-infrared region. In fact, at times that relate to the formation of the radical cation of exTTF in the visible range, we see a transient maximum in the near-infrared window. The maximum is centred around 1200 nm, which is ascribed to the reduction of La$_2@C_{80}$. Of particular importance is the close resemblance of the near-infrared part with the radiolytically and spectroelectrochemically generated spectrum of the one-electron reduced form of La$_2@C_{80}$. In other words, upon photoexciting La$_2@C_{80}$-exTTF in THF, a rapid intramolecular electron transfer leads to the formation of a radical ion pair state, namely La$_2@C_{80}^-\text{exTTF}^+\text{+}$ (0.45 eV). A quantitatively similar picture evolves in the less polar toluene with kinetics that are virtually superimposable onto those in THF. The decay of the La$_2@C_{80}^-\text{exTTF}^+\text{+}$ radical ion pair state is associated with the re-formation of the singlet ground state [29].

(f) Energetics

As scheme 1 and table 2 reflect, we have derived, for C$_{60}$-exTTF, from multi-wavelength analyses of the C$_{60}^-\text{exTTF}^+$ radical ion pair state (1.12 eV), the charge separation and charge recombination dynamics in dichloromethane, by following the maxima in the visible and the near-infrared regions, as $2.1 \times 10^{10} \text{s}^{-1}$ and as $1.4 \times 10^7 \text{s}^{-1}$, respectively (table 2). In this context, the C$_{60}$ singlet excited state (1.76 eV) triggers the intramolecular electron transfer. Notably, the singlet ground state emerges as the product of charge recombination with a thermodynamic driving force of 1.12 eV. Interestingly, in the more polar benzonitrile, the charge recombination is significantly slowed down with $4.9 \times 10^6 \text{s}^{-1}$ despite a reduced thermodynamic driving force.

We take this finding as support for the hypothesis that charge recombination dynamics in C$_{60}$-exTTF are located in the normal range of the Marcus parabola. Here, the reorganization energy exceeds the thermodynamic driving force. It is likely that the large structural changes associated with the oxidation of exTTF are responsible for a reorganization energy of greater than 1.1 eV.

Please note that this trend has been established in a large number of electron donor–acceptor conjugates featuring a C$_{60}$ electron acceptor and an exTTF electron donor.

Both excited states—exTTF (2.7 eV) and La@C$_{82}$ (0.88 eV)—power in La@C$_{82}$-exTTF an intramolecular electron transfer to yield an energetically low-lying La@C$_{82}^-\text{exTTF}^+$ ion and radical ion pair state (0.43 eV). In line with the different excited state energies, the La@C$_{82}^-\text{exTTF}^+$ ion and radical ion pair state evolve from the exTTF centred and the La@C$_{82}$ centred excited states with $2.3 \times 10^{11} \text{s}^{-1}$ and $1.5 \times 10^{11} \text{s}^{-1}$, respectively (table 2). Interesting is the fact that the charge recombination, which reinstates the doublet ground state, is $9.1 \times 10^8 \text{s}^{-1}$ in cyclohexylisonitrile and $4.1 \times 10^8 \text{s}^{-1}$ in THF. Considering the small thermodynamic driving force of 0.43 eV, the charge recombination dynamics follow the aforementioned trend, that is, being placed in the normal region of the Marcus parabola.
Figure 3. (a) Differential absorption spectrum (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of La$_2$@C$_{80}$ ($10^{-5}$ M) in argon-saturated THF with a time delay of 10 ps at room temperature. (b) Time–absorption profile of the spectrum shown above at 520 nm monitoring the charge separation.

Scheme 1. Energy diagrams for photoexcitation, charge separation and charge recombination in (a) C$_{60}$-exTTF, (b) La@C$_{82}$-exTTF and (c) La$_2$@C$_{80}$-exTTF. (Online version in colour.)
Table 2. Charge separation and charge recombination dynamics in C_{60}-exTTF, La@C_{82}-exTTF and La_{2}@C_{80}-exTTF electron donor–acceptor conjugates.

<table>
<thead>
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<th>solvent</th>
<th>charge separation (s^{-1})</th>
<th>charge recombination (s^{-1})</th>
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<tr>
<td>C_{60}-exTTF</td>
<td>2.1 \times 10^{10}</td>
<td>1.4 \times 10^{7}</td>
</tr>
<tr>
<td></td>
<td>dichloromethane</td>
<td></td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>4.9 \times 10^{6}</td>
</tr>
<tr>
<td>La@C_{82}-exTTF</td>
<td>2.3 \times 10^{11}</td>
<td>4.1 \times 10^{8}</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>1.5 \times 10^{11}</td>
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<tr>
<td></td>
<td>cyclohexylisonitrile</td>
<td>9.1 \times 10^{8}</td>
</tr>
<tr>
<td>La_{2}@C_{80}-exTTF</td>
<td>5.0 \times 10^{10}</td>
<td>3.0 \times 10^{8}</td>
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<tr>
<td></td>
<td>toluene</td>
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</tr>
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</table>

Photoexcitation of La_{2}@C_{80}-exTTF in toluene and THF is the starting point for a rapid intramolecular electron transfer yielding the La_{2}@C_{80}^{--}exTTF^{++} radical ion pair state (0.45 eV). It is mainly the La_{2}@C_{80} singlet excited state (1.4 eV), from which the La_{2}@C_{80}^{--}exTTF^{++} radical ion pair state evolves with 5.0 \times 10^{10} s^{-1} (table 2). From the corresponding time–absorption profile, kinetics of 3.0 \times 10^{8} s^{-1} were derived for the charge recombination process, during which the latter re-forms the singlet ground state. Relative to La@C_{82}^{--}exTTF^{++}, this constitutes a significant stabilization at approximately the same thermodynamic driving force.

3. Conclusions

We have shown via a fully fledged photophysical investigation focusing on three different electron donor–acceptor conjugates, namely C_{60}-exTTF, La@C_{82}-exTTF and La_{2}@C_{80}-exTTF, that C_{60}, La@C_{82} and La_{2}@C_{80} are all versatile electron acceptors. It is, however, the electron-donating exTTF that imposes rather large reorganization energies of at least 1.1 eV, and that, in turn, forces the charge recombination dynamics into the normal region of the Marcus parabola. In other words, more polar solvents are desirable to stabilize the radical ion pair states. The limited solubility and stability of La@C_{82}-exTTF and La_{2}@C_{80}-exTTF in common organic solvents hampers, however, a more thorough analysis. Thus, with the data in hand, we summarize as follows. On the one hand, the low reduction potentials of La@C_{82} and La_{2}@C_{80} are clear assets in terms of stabilizing ion and radical ion pair states. On the other hand, the electronic structures of La@C_{82} and La_{2}@C_{80} seem to contradict the aforementioned and, as such, hinder a significant stabilization.

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