Evidence of Pronounced Electronic Coupling in a Directly Bonded Fullerene–Ferrocene Dyad


A new donor–acceptor dyad (7) involving a ferrocene moiety as donor and an azafullerene as acceptor has been synthesized by treating bisazafullerenyl (1) with ferrocenium hexafluorophosphate. This compound represents the first example of a fullerene-based dyad where two electroactive groups are connected by only a single σ-bond. The cyclic voltammetry of 7, in comparison to the corresponding reference systems, clearly reveals strong electronic coupling between the ferrocene and the azafullerene moiety in the ground state. For example, the Fc-based, reversible, one electron oxidation wave is significantly positively shifted by 183 mV with respect to that of the parent ferrocene. This indicates the existence of intramolecular charge transfer (ICT) from the donating Fc to the accepting azafullerenyl group. Photophysical studies on 7 were carried out by means of emission and transient absorption spectroscopy. An instantaneous deactivation of the fullerene singlet excited-state results in the formation of the charge-separated (C₅₉N⁺) – (Fc⁺⁺) radical pair. From the charge-transfer dynamics with a lower limit of ≥ 5 × 10¹⁰ s⁻¹, we infer strong electronic coupling (N) between the azafullerene and the ferrocene moiety of the order of 60 cm⁻¹ in benzonitrile.

KEYWORDS:
donor–acceptor systems • electron transfer • ferrocene • fullerene • photoinduced processes

Since fullerenes became accessible in bulk quantities,[1] chemists have been interested in the substitution of one or more cage carbon atoms by heteroatoms such as boron or nitrogen. Different electronic and chemical behavior induced by heteroatom substitution is expected to provide fine-tuning capabilities for materials derived from these fullerene systems. In 1995, Wudl et al. and our group succeeded in the isolation of the first nitrogen heterofullerene (C₅₉N)₂ (1), using two different synthetic strategies starting from C₆₀.[7, 8] Since then, this new class of compounds has been available in quantities large enough to investigate their chemical and physical properties.[8-6]

The substitution of one cage carbon atom by a nitrogen leads to an open-shell system. Consequently, the stable form of the simplest nitrogen heterofullerene is dimer 1. In this compound the two C₅₉N moieties are connected by a C–C bond between the two sp³ C atoms adjacent to the N atoms.[2] Various methods to substitute one C₅₉N moiety by other groups such as H atoms, alkyl chains, and aryl systems have been disclosed within the last few years.[6-10] Monomeric C₅₉N systems with suitable side chains exhibit several advantages over the parent system, such as a marked increase of the solubility, which is very important for further evolution of heterofullerene chemistry as well as the development of heterofullerene materials. In principle, two different pathways exist for the synthesis of C₅₉N derivatives starting from C₆₀ (Scheme 1).

The thermally or photochemically induced cleavage of the weak C₅₉N–C₅₉N bond leads to the formation of an azafullereny radical 2.[11, 12] This species can either dimerize back to 1 or it can be trapped by other radical-generating reagents, for example diphenylmethane, to form monomeric derivatives such as 3.[13] The reaction sequence to form the azafullerene derivatives that we developed is based on the oxidation of the azafullereny radical 2 to the azafullerium ion 4.[9] In this context, the oxidation is achieved by oxygen in the presence of an acid such as 4-methyl benzenesulfonic acid (p-TsOH). The resulting cationic intermediate 4 reacts subsequently with electron-rich...
aromatics or enolizable carbonyl compounds to form monomeric derivatives such as 5 and 6.\textsuperscript{10, 13} We have shown recently that other oxidizing reagents like chloroanil can also be employed for the generation of intermediate 4.\textsuperscript{10}

In the field of fullerene-based materials, the development of donor–acceptor (D–A) multicomponent molecular assemblies in which electron donors, such as porphyrins, are covalently linked to a C\textsubscript{60} cage has been demonstrated to lead to systems with unique electronic and photophysical properties. The challenge and long-range goal behind this concept is to promote efficient intramolecular energy or electron-transfer reactions and/or to generate long-lived charge-separated states.\textsuperscript{14–25} In all dyads reported so far the donor was, however, separated from the fullerene sphere by a minimum of at least two C\textsubscript{60}–bonds. Few of these therefore showed significant intramolecular electronic interactions in the neutral ground state due to the insulating effect of the C\textsubscript{60}–bonds.

In an attempt to enhance intramolecular electron (IET) or charge transfer (ICT), we report here the synthesis and properties of a novel D–A dyad 7 involving a directly bonded donor ferrocene connected to the electron-accepting azafullerene group.

Our approach is based on the following rationale: a) Azafullerene is a stronger acceptor than C\textsubscript{60}; b) ferrocene is a strong donor and the redox potential of its derivatives FeX–Fc denotes the ferrocenyl group [Fe(η\textsuperscript{5}–C\textsubscript{5}H\textsubscript{5})(η\textsuperscript{5}–C\textsubscript{5}H\textsubscript{4})]; c) ferrocenyl fulleropyrrolidine is known to exhibit small but evident ICT phenomena;\textsuperscript{26} and finally d) in contrast to homoatomic fullerenes the addition chemistry of 1 allows for the synthesis of closed-shell monoaducts involving one bond to one addend only. Hence the Fe group can be directly connected to the sphere through a single bond, which should, in principle, enhance the intramolecular D–A interactions relative to those found in ferrocenyl fulleropyrrolidines or other systems.\textsuperscript{25}

**Results and Discussion**

**Synthesis of Ferrocenyl Hydroazafullerene 7**

As pointed out above, the reaction of 1 with an electrophile in the presence of p-TsOH and an oxidizing reagent results in the synthesis of monozaheterofullerene derivatives.\textsuperscript{10, 13} Using ferrocenium hexafluorophosphate, both prerequisites for the formation of a monomeric C\textsubscript{59}N derivative are combined in one reagent. In particular, the ferrocenium moiety is a strong oxidizing reagent and the ferrocene generated in the redox process is available for the electrophilic attack on the cationic intermediate 4.

The reaction of 1 in 1,2-dichlorobenzene (ODCB) in the presence of a 25-fold excess of ferrocenium hexafluorophosphate at 150 °C in an argon atmosphere afforded the ferrocenyl hydroazafullerene dyad 7 in acceptable yields (Scheme 2).

The isolation of the product was achieved by flash chromatography on silica gel using toluene as the mobile phase. Ferrocenyl hydroazafullerene 7 elutes as the least polar olive-green colored fraction. This color is characteristic for all azafullerene derivatives bearing a carbon substituent.\textsuperscript{10} The solubility of the C\textsubscript{59}N–ferrocene dyad is high compared to that of 1.\textsuperscript{2} The separation from traces of ferrocene was carried out by preparative HPLC using a Cosmosil Buckyprep column. The
product was completely characterized by MS, UV, IR, and NMR spectroscopy.

The \( ^1H \) NMR spectrum of compound 7 shows one singlet for the five protons of the unsubstituted Cp ring at \( \delta = 4.55 \). The signal of the Cp ring attached to the C\(_{59}\)N moiety is shifted to lower field due to the influence of the electron-withdrawing fullerene moiety. The peak assignment is based on the expectation that the protons closer to the C\(_{59}\)N moiety are shifted more downfield than those that are more remote. The multiplet at \( \delta = 5.28 \) can therefore be assigned to the two ortho protons and the multiplet at \( \delta = 4.72 \) belongs to the two remaining protons of the substituted ring. The \( ^1H \) NMR spectrum shows a weak signal at \( \delta = 80 \), which is due to the sp\(^3\) carbon atom adjacent to the nitrogen. The remaining carbon atoms of the C\(_{59}\)N moiety resonate in the region of \( \delta = 123 - 155 \) (28 signals with double intensity, two signals with single intensity, \( C_s \) symmetry). The signal of the five carbon atoms of the unsubstituted Cp ring lies at \( \delta = 69.95 \). The ipso-C atom resonates at \( \delta = 92.07 \) and the two different groups of carbon atoms of the Cp ring that bears the C\(_{59}\)N moiety show signals at \( \delta = 69.88 \) and 67.26. Both NMR spectra clearly exhibit the \( C_s \) symmetry of the azafullerene–ferrocene dyad.

The formation of this dyad can be explained by the oxidation of the intermediate C\(_{59}\)N radical 2 by the ferrocenium ion, leading to ferrocene and to the azafullerionium ion 4 (Scheme 3). Subsequently, an electrophilic aromatic substitution of one proton of a Cp ring takes place. As described above, in this novel synthesis the ferrocenium ion acts as an oxidizing reagent and the resulting ferrocene serves as a nucleophile for the attack of the C\(_{59}\)N\(^+\) cation 4.

**Electrochemistry**

The solution phase electrochemical properties of the dyad 7 was investigated by cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV). The results were compared with those of the two related analogue compounds (diethyl-2-azafullerenyl malonate, 9, and \( p \)-(methoxy-ethoxy-ethoxy-ethoxy)-phenyl hydroazafullerene, 10) as well as with those of the parent ferrocene and two of its derivatives (ferrocenylcarboxaldehyde (Fc-CHO, 11) and ethyferrocene (Fc-Et, 12) as models Scheme 4). The synthesis of the two azafullerene derivatives 9 and 10 is described in ref. [11].

All the experiments were performed at room temperature in ODCB solutions containing tetra-n-butylammonium hexafluorophosphate (TBAPF\(_6\), 0.05 M) as the supporting electrolyte, with gold, platinum, or glassy carbon as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference. The cyclic voltammograms are presented in Figure 1 and the measured potentials are collected in Table 1.

![Scheme 3. Reaction mechanism leading to ferrocenyl hydroazafullerene 7](image)

![Scheme 4. Reference compounds used in this study.](image)

**Figure 1.** Oxidative and reductive CVs of a) 9, b) 10, c) 7, d) Fc-CHO, e) ferrocene, and f) Fc-Et in an ODCB-TBAPF\(_6\) (0.05 M) system at room temperature on a gold electrode.
As expected, ferrocene and its derivatives Fc-CHO and Fc-Et exhibit a single, chemically reversible (\( \eta_i/\eta_r = 1 \)) and electrochemically quasi-reversible (\( \Delta E_p = \eta_p - \eta_r = 75 \pm 1 \text{ mV} \)) one-electron redox wave at 543, 842, and 496 mV (\( E_{1/2} \) values), respectively. As shown in Figure 1 and Table 1, it is very clear that the redox potentials of the ferrocene derivatives, which contain a single ring substituent, are highly dependent on the nature of the substituent. If its ligating carbon atom is sp\(^3\) hybridized, with possible conjugation with the Cp ring, the redox potential is much more sensitive to the effect of the substituent than when the substituent is bonded to the Cp ring through a sp\(^3\) carbon.[26] For example, Fc-CHO has a much higher redox potential (\( \Delta E_{1/2} \) value of 299 mV), but Fc-Et has a slightly lower redox potential (47 mV) than the parent ferrocene due to the ability of the aldehydic CHO group to conjugate with the reaction center and act as an electron acceptor through a –I effect, rather than the +I effect for the ethyl group that cannot conjugate with the Cp ring.

The CVs of the dyad 7 and the other two azafullerene derivatives 9 and 10 show some common features with respect to those of ferrocene, Fc-CHO, Fc-Et, and C\(_{60}\) derivatives. All three azafullerene derivatives 7, 9, and 10 are electrochemically active in both anodic and cathodic sweeping directions between 1.62 and –2.05 V. In the anodic direction (between 0 and 1.62 V), 9 and 10 show one chemically irreversible (\( \eta_i = 50–600 \text{ mV s}^{-1} \)) oxidation peak at 1412 and 1347 mV (\( \eta_p \) values at 100 mV s\(^{-1} \)), respectively (Figure 1a,b). This oxidation is nitrogen based, judged from the value observed for the oxidation of the nitrogen atom in the pyrrolidine group attached to C\(_{60}\) in fulleropyrrolidine derivatives, which occurs at about 1460 mV at 100 mV s\(^{-1} \).

Dyad 7 shows two oxidation processes with a Fc-based, one-electron electrochemically reversible redox process (\( E_{1/2} = 726 \text{ and } \Delta \eta_p = 73 \text{ mV, Figure 1c dashed line} \) and a second N-based chemically irreversible oxidation peak (\( E_{1/2} = 1464 \text{ at 100 mV s}^{-1} \), Figure 1c solid line). In the cathodic direction between 0 and –2.05 V, all the compounds (9 shows some differences) show four successive and nearly equally spaced electrochemically reversible (the first three reductions, \( \Delta \eta_p < 80 \text{ mV} \)) or quasi-reversible (the fourth one, \( \Delta \eta_p = 100 \pm 10 \text{ mV} \)) redox waves, similar to the electrochemical behavior of C\(_{60}\)-based reductions. These reduction waves are thus based on the azafullerene moiety and can be easily assigned as four successive, one-electron reduction processes leading to the final formation of a tetraanion. It should be pointed out that the reduction potentials of these four azafullerene-based redox processes are generally more positive than those of the corresponding reduction processes of C\(_{60}\) derivatives, thereby indicating a better electron-accepting ability.

The main interest for the design of 7 and the electrochemical studies was the possible intramolecular electronic interactions between the Fc and azafullerene moieties in the ground state of 7. When comparing the electrochemical data of the dyad with those of 9, 10, and the parent ferrocene or its derivatives Fc-CHO and Fc-Et, although some common features exist as stated above, two points are clear: a) Both the oxidative and reductive CVs of 7 are not exactly the sum of those of the parent ferrocene or Fc-Et and that of the azafullerene derivatives 9 or 10; and b) the potentials measured are significantly different from those of the parent ferrocene or Fc-Et (oxidation) and 9 or 10 (oxidation and reduction). These two points are good indications that electronic interactions between the two moieties are present in 7.

The Fc-based, reversible, one-electron oxidation wave of 7 is significantly positively shifted by 183 mV with respect to that of the parent ferrocene (\( E_{1/2} \) values are 726 versus 543 mV). This indicates the existence of ICT from the donating Fc to the accepting azafullerenyl group in the neutral ground state due to the inductive electron-accepting effect (–I) of the C\(_{59}\)N moiety. However, this –I effect for the azafullerene group is smaller than that of the aldehyde group (\( E_{1/2}^{\text{7,Cho}} \) is larger by 116 mV with respect to that of the Fc-based oxidation for 7). In addition, the second chemically irreversible N-based oxidation of 7 is also positively shifted by 52 and 117 mV with respect to 9 and 10, respectively. However, the N-based oxidation for 7 should be negatively shifted with respect to 9, since diethyl malonate is a –I group, in contrast to Fc which is a +I group. This can be easily accounted for by the substantial –I effect of the positively charged Fc\(^+\) after the first Fc-based oxidation of 7. It is also evident that the –I effect of Fc\(^+\) is much bigger than that of the diethyl malonate group in 9, resulting in a 65 mV positive shift of the N-based oxidation for 9 with respect to 10, in which the p-(methoxy-ethoxy-ethoxy-ethoxy)phenyl moiety is a +I group.

Conversely, the azafullerene-based reduction potentials for 7 are negatively shifted with respect to those of 9 and 10 by about 50–57 and 36–51 mV, respectively, again showing significant intramolecular electronic interactions. The CVs or OSWVs for the

Table 1. Electrochemical data (\( E_{1/2}, \eta_p, \) and \( \Delta \eta_p \)) of the redox processes of compounds 1–3, ferrocene, Fc-CHO, and Fc-Et (about 1 mM) detected by CV in a ODCB-TBAPF\(_6\) system (0.05 \( \text{mM} \)) on a gold electrode at room temperature.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( E_{1/2}^{\text{ox}}/\Delta \eta_p^{\text{ox}} )</th>
<th>( E_{1/2}^{\text{red}}/\Delta \eta_p^{\text{red}} )</th>
<th>( E_{1/2}^{\text{ox}}/\Delta \eta_p^{\text{ox}} )</th>
<th>( E_{1/2}^{\text{red}}/\Delta \eta_p^{\text{red}} )</th>
<th>( E_{1/2}^{\text{ox}}/\Delta \eta_p^{\text{ox}} )</th>
<th>( E_{1/2}^{\text{red}}/\Delta \eta_p^{\text{red}} )</th>
<th>( E_{1/2}^{\text{ox}}/\Delta \eta_p^{\text{ox}} )</th>
<th>( E_{1/2}^{\text{red}}/\Delta \eta_p^{\text{red}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>583/68</td>
<td>953/69</td>
<td>1425/86</td>
<td>1884/120</td>
<td>1412</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>597/63</td>
<td>968/71</td>
<td>1439/74</td>
<td>1870/110</td>
<td>1347</td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>633/74</td>
<td>1004/76</td>
<td>1478/72</td>
<td>1921/110</td>
<td>1464</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc-CHO, 11</td>
<td>726/73</td>
<td>842/75</td>
<td>543/74</td>
<td>496/76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FcCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Fc-Et, 12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

[a] \( \Delta \eta_p = (\eta_p + \eta_r)/2 \). \( \eta_p \) and \( \eta_r \): cathodic and anodic peak potential. \( \eta_p = \eta_p - \eta_r \). All data in mV versus Ag/AgCl. Errors are estimated at about ±5 mV.
[b] Potential data on platinum or glassy carbon electrodes are the same as on gold electrode. [c] \( E_{1/2} \) values. [d] Fc-based redox potential. [e] Nitrogen-based oxidation peak potential of the hydroazafullerenyl group. [f] The ratio \( \eta_p/\eta_r > 1 \) (\( \eta_p \) and \( \eta_r \) are cathodic and anodic peak currents).
mixtures of ferrocene and 9, 10, or 7 with different molar ratios (2:1, 1:1, or 1:2) are simply the sum of the constituents and no potential shifts (oxidations or reductions) were observed under the CV conditions and timescale. Thus no intermolecular electronic interactions are observed between ferrocene and the C59N moieties in 9, 10, or 7. In addition, comparison of the reduction potentials ($E_{1/2}$) between 9 and 10 shows a small but evident trend, that is, the $E_{1/2}$ values of 9 are generally more positive than those of 10 by about 15 mV (Table 1). This is due to the $-I$ effect of the diethyl malonate group in 9 and the $+I$ effect of the $p$-(methoxy-ethoxy-ethoxy-ethoxy)phenyl group in 10.

Absorption Spectra

The absorption spectrum of dyad 7 in toluene, for example, reveals significant deviations from a simple superposition of the component chromophores comprising this donor–acceptor pair, namely C59N and ferrocene. As a representative example, the 500–850 nm region of dyad 7 is shown in Figure 2, together with those of reference compounds 10 and 12. This supports the notion that indeed electronic perturbation exists within the dyad structure. The latter may stem from the short linkage between the redox- and photoactive blocks, leading to an electronic coupling even in their ground state configuration (see below).

**Photophysical Studies**

By means of emission and transient absorption spectroscopy, a variety of excited-state measurements were conducted in an effort to characterize azafullerene derivatives 9, 10, and ferrocene–azafullerene dyad 7. Special attention was directed to the potential interaction between the photoexcited electron acceptor, namely the C59N core, and the covalently linked ferrocene donor. This was carried out to complement the electrochemical studies (see above), which revealed a significant electronic interaction in a fullerene-based donor–acceptor dyad in the ground state for the first time.

**Fullerene References—Emission Studies**

The substantial red shift to about 800 nm displayed by the long-wavelength absorption of the C59N core in 9 (800 nm), 10 (810 nm), and 7 (810 nm) compared to that of pristine C60 and various monofunctionalized fullerene derivatives (around 700 nm) results in notable effects on the emission properties. For instance, in parallel with the absorption shift observed, the room-temperature emission of azafullerene derivatives 9 and 10 were found in the long-wavelength region, namely, at 815 and 825 nm (see Table 2).

The emission also clearly mirrors the singlet ground-state absorption and is insignificantly impacted by molecular oxygen. The above experiments, considered together, indicate that the origin of this emission is the radiative depopulation of the fullerene singlet excited state, namely, fluorescence. It is also worthwhile to point out that the 0-0 transitions (0*0 absorption and *0-0 emission) of the investigated diethyl malonate analog 9 reveal slightly higher energies than those of 10, corroborating a trend seen earlier in comparing a methanofullerene with a 4-hydroxycyclohexano adduct of C60. The shift in 0-0 energy gap is also in reasonable accord with the $-I$ versus $+I$ effects, which change the HOMO–LUMO gaps of 9 and 10, respectively.

In addition to the noted red shift, the fluorescence quantum yields ($\Phi$ approximately $1.6 \times 10^{-4}$) are decreased relative to those of a pristine C60 sample ($\Phi = 2.0 \times 10^{-4}$) and, for example, of a methanofullerene ($\Phi = 6.0 \times 10^{-4}$) in nonpolar toluene ($\epsilon = 2.48$). In benzonitrile (bzc; $\epsilon = 24.8$), a nucleophilic solvent, the fluorescence quantum yield exhibits a further

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**Table 2. Photophysical properties of hydroazafullerenes 9, 10, and 7 in various solvents at room temperature.**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>solvent</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\Phi$/fluorescence</th>
<th>$\tau$/fluorescence [ns]</th>
<th>$\tau$/singlet [ns]</th>
<th>$\tau$/triplet [ns]</th>
<th>$\lambda_{\text{max}}$/CT [nm]</th>
<th>$\tau$/CT [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>toluene</td>
<td>813</td>
<td>1.6</td>
<td>1.01</td>
<td>0.97</td>
<td>16.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ODCB</td>
<td>817</td>
<td>1.6</td>
<td>1.10</td>
<td>[a]</td>
<td>[a]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bzc$^{[c]}$</td>
<td>823</td>
<td>1.2</td>
<td>0.91</td>
<td>0.9</td>
<td>19.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>toluene</td>
<td>825</td>
<td>1.35</td>
<td>0.93</td>
<td>0.9</td>
<td>13.1</td>
<td></td>
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<tr>
<td></td>
<td>ODCB</td>
<td>827</td>
<td>1.35</td>
<td>0.93</td>
<td>[a]</td>
<td>[a]</td>
<td></td>
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<tr>
<td></td>
<td>bzc$^{[c]}$</td>
<td>831</td>
<td>1.0</td>
<td>0.88</td>
<td>0.85</td>
<td>15.1</td>
<td></td>
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</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>818</td>
<td>0.05</td>
<td>[b]</td>
<td>[b]</td>
<td>575</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ODCB</td>
<td>820</td>
<td>0.04</td>
<td>[b]</td>
<td>[b]</td>
<td>647</td>
<td>0.34</td>
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</tr>
<tr>
<td></td>
<td>bzc$^{[c]}$</td>
<td>821</td>
<td>0.03</td>
<td>[b]</td>
<td>[b]</td>
<td>600</td>
<td>0.40</td>
<td></td>
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</tbody>
</table>


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**Figure 2. Absorption spectra of 7, 10, and 12.**
reduction by approximately 10% (Figure 3), although the pattern of the photoexcited C$_5$N moiety (specifically *0-0 emission around 820 nm) is still preserved.

To observe possible evidence for a polarity-dependent quenching of the emission, we examined extra sets of fluorescence experiments in THF ($\varepsilon$ = 9.93)–not listed—and ODCB ($\varepsilon$ = 7.6). While the latter set revealed virtually the same emission quantum yields as derived from the corresponding toluene solutions, the former were identical to the benzonitrile case. Based on the current results a simple polarity dependence can be ruled out, which leaves, in turn, a scenario that implies possible, but weak, interactions between the nucleophilic solvents (THF and benzonitrile) and the fullerene core.

As can be seen from a closer inspection of Table 2 and Figure 3, a red shift of the *0-0 transition in polar solvents (ODCB, benzonitrile) versus nonpolar solvents (toluene) occurs. This is, however, in accordance with the nature of the singlet excited-state emission, namely, a $\pi-\pi^*$ transition. As stated above, the fluorescence quantum yields of 9 and 10, especially in THF and benzonitrile, follows a surprising trend. To the extent that this characterization is accurate, the fluorescence lifetimes are expected to exhibit different decay dynamics. Interestingly, relating the lifetimes (typically of the order of 1 ns, see Table 2) in benzonitrile with those, for example, in toluene or ODCB led to values that are about 10% smaller. This is again in good agreement with the above-described steady-state emission studies.

Fullerene References—Transient Absorption Studies

Another important spectroscopic technique to characterize dynamic processes that are associated with the generation and fate of photoexcited states in closed-shell molecules, such as azafullerene derivatives 9, 10, and 7, is transient absorption changes following short laser pulses. Consequently, to probe the singlet and triplet excited-state properties of 9, 10, and 7, time-resolved differential absorption spectra were recorded following picosecond (18 ps) and nanosecond (8 ns) excitation.

For 9 and 10 (2.0 $\times$ 10$^{-5}$ M in deoxygenated toluene), concomitant with the completion of the picosecond laser pulse, formation of a broadly absorbing transient was registered. A set of distinct maxima at 511, 745, and 940 nm, as displayed in Figure 4a, characterizes the spectrum of the new species.

The long-wavelength maximum around 940 nm reveals a close spectral resemblance to those of various C$_{60}$ derivatives. Implicit in this picture is the assumption that the new transient corresponds to the fullerene singlet–singlet absorption, evolving from the instantaneous conversion of the singlet ground state to the singlet excited state. In the 940 nm range, the singlet–singlet absorption decays monoeXponentially with rate constants of 1.03 $\times$ 10$^9$ s$^{-1}$ (9; Figure 4b) and 1.1 $\times$ 10$^9$ s$^{-1}$ (10). In contrast, around 860 nm (similar to Figure 5), a region where the singlet–singlet absorption minimizes, a synchronous development of a new transient dominates the absorption changes.

The following time constants were derived from the kinetic development profiles in toluene: 0.95 $\times$ 10$^9$ s$^{-1}$ 9 and 1.2 $\times$ 10$^9$ s$^{-1}$ 10. The good similarity between decay and development kinetics suggests that an ISC from the singlet excited state to the triplet excited state takes place. Additional proof for this hypothesis stems from the nearly identical fluorescence lifetimes...
(see above) as the second major deactivation pathway for the singlet excited state. Interestingly, control experiments with 9 and 10 (2.0 × 10⁻³ M) in deoxygenated benzonitrile yielded the same acceleration (about 10%) of the ISC dynamics as seen in the emission studies (see Table 2).

To confirm the triplet–triplet absorption and to explore their inherent decay dynamics, we examined the excited states of 9 and 10 with an 8 ns laser pulse under similar conditions to those employed in the picosecond experiments. In general, the nanosecond and picosecond results are in excellent agreement with each other, disclosing the strongest triplet–triplet absorption at 860 nm (Figure 5) accompanied by a much weaker shoulder at 1040 nm. A clean monoeponential recovery of the singlet ground state follows at low substrate concentration and low laser power, affording a triplet lifetime of nearly 20 ms. Employing higher concentrations of 9 and 10 and/or higher laser power, the kinetics became more complicated: efficient triplet–triplet and also triplet ground state annihilation processes became important. The triplet quantum yields were determined to be around 30%.

The long-lived nature and the low-lying energies of the fullerene triplet excited states encouraged us to probe its reactivity with molecular oxygen by monitoring the fate of the singlet–triplet absorption upon adding variable concentrations of oxygen to toluene solutions of 9 and 10 (1.0 × 10⁻³ M). The decay in question was, in fact, found to involve a pseudo first-order process. The determination of the rate constant for the intermolecular energy transfer reaction was possible by following the accelerated decay of the triplet–triplet absorption. The observed rates (kₜₙₒ = ln2/τ₁₀₀) were all linearly dependent on the oxygen concentration. From this, we propose that under the experimental conditions probed a nearly diffusion-controlled reaction (k ≈ 10⁴ m⁻¹ s⁻¹) of the fullerene triplet state occurs with molecular oxygen, generating singlet oxygen (¹O₂). The latter was confirmed by its characteristic ¹Δₒ O₂ phosphorescence at 1270 nm.

With regard to the possible electron transfer evolving in dyad 7 from the electron donor (ferrocene) to the fullerene singlet excited state (see below), models 9 and 10 were reduced in a set of complementary radiolytic experiments. This was deemed necessary to simulate the spectral characteristics of the one-electron reduced azafulerene moiety and to compare them to those noted following the excitation of dyad 7. The π-radical anion exhibits fingerprint absorption at 1010 nm (not shown), bathochromically shifted to that of the π-radical anion spectrum of pristine C₆₀.

### Ferrocene Reference

Probing a toluene solution of 11 or 12 under similar conditions (that is, following a 18 ps laser pulse) led to very weak absorption changes in, for example, the 500–760 nm range (see Figure 6 and compare the intensity to that in Figure 4a). In fact, previously an extinction coefficient ε of less than 500 M⁻¹ cm⁻¹ was estimated, using laser flash photolysis, for the triplet–triplet absorption in the visible region.¹⁰ The broad and featureless transitions serve as an important reference point, due to the possible energy-transfer process within photoexcited donor–acceptor dyad 7. In agreement with the rapid triplet–ground state deactivation (triplet lifetimes of 0.6 ns²⁰), we could not detect any appreciable triplet features at time delays exceeding 2 ns.

### Donor–Acceptor Dyad 7

The singlet excited-state properties of fullerene derivatives (fluorescence and singlet–singlet absorption) are sensitive measures for intramolecular transfer dynamics in the present donor–acceptor system. As reported above, azafulerene derivatives 9 and 10 give rise to singlet excited-state emissions near 820 nm, which fit a singlet excited-state energy of around 1.50 eV. In addition, the close spatial separation between the C₅₉N core and the electron donor (ferrocene) is expected to lead to an efficient deactivation of the fullerene singlet excited state. We decided to investigate 7 first in a solvent of low polarity, namely toluene, and then complement these data with experiments in moderately polar ODCB and strongly polar benzonitrile.

In case of an intramolecular electron transfer, using this
progression helps to vary the free energy change associated with the electron transfer event and, in turn, to modulate the underlying dynamics. On the contrary, an energy transfer event should be only marginally, if at all, affected by solvent polarity, since the excited-state energies remain nearly constant in the solvents studied (see above).

Emission yields of dyad 7 in various aerated solvents were compared to those of the model compounds 9 and 10. Interestingly, dyad 7 reveals a nearly quantitative quenching of the fullerene fluorescence in nonpolar toluene (see Figure 7 and Table 2) relative to the reference model compounds employed. In this context it is important to note that, despite the weak fluorescence, the emission patterns of the azafullerene remain unchanged and are not noticeably affected by the presence of the attached ferrocene. This serves as crucial testimony for the unequivocal excitation of the azafullerene.

Figure 7. Emission spectra of dyad 7 in toluene.

An estimate for the rate constants $k$ of the intramolecular deactivation in dyad 7 was obtained by correlating the fluorescence quantum yields ($\Phi = 1.6 \times 10^{-3}$) and the lifetime ($\tau = 1.01$ ns) of photoexcited 9 with that of 7 ($\Phi \approx 0.05 \times 10^{-4}$), Equation (1). For toluene we calculate a rate constant of $k_{\text{toluene}} \approx 3.1 \times 10^{9}$ s$^{-1}$, which corresponds to a lifetime of approximately 32 ps.

$$k = \frac{\Phi(9) - \Phi(7)}{\tau(9)\Phi(7)}$$

Not surprisingly, complementary measurements in ODCB and benzonitrile led to the same quantitative emission quenching (see Table 2). A complete cancellation of the fullerene emission implies an extremely rapid intramolecular deactivation of the underlying singlet excited state. Corresponding to this hypothesis is the fact that several attempts to measure the fluorescence lifetimes of dyad 7 proved unsuccessful within our 100 ps resolution, due to the lack of any detectable emission.

At first glance the quenching is not surprising, in view of the short donor–acceptor separation (center-to-center separation 6.406 Å) and the favorable free energy changes ($-\Delta G_{C_{60}}$ values are 0.41 in ODCB and 0.49 eV in benzonitrile) for an electron transfer to occur. A possible energy transfer to the ferrocene singlet (about 2.46 eV)$^{39}$ is, due to the low-lying nature of the fullerene excited states at energies of approximately 1.5 (singlet) and <1.35 eV (triplet), endothermic and, therefore, unlikely to proceed. By contrast, a singlet–triplet excited state transfer (ferrocene triplet excited-state energies as low as 1.12 eV have been reported)$^{29, 31}$ cannot be ruled out with a simple thermodynamic argument (see below). However, it should be emphasized that the energy gap for this energy transfer is, at least in ODCB and benzonitrile, markedly smaller than that of an intramolecular electron transfer.$^{32}$

In summary, the fluorescence experiments indicate that the instantaneous deactivation of the fullerene singlet excited state in dyad 7 appears to result from an electron transfer mechanism yielding the charge-separated (C$_{60}$N$^-$)–(Fc$^+$) pair.

Evidence for an electron transfer scenario rather than energy transfer came from time-resolved photolysis studies, which were designed to characterize the deactivation processes and, more fundamentally, to identify the transient intermediates evolving from the supposed intramolecular dynamics. Specifically, 355 nm illumination of dyad 7 (absorption ratio of Fc:fullerene = 3:97 at 355 nm)$^{33}$ in benzonitrile (2.0 $\times$ 10$^{-5}$ M) leads to the instantaneous observation of a new absorption (Figure 8a), disclosing characteristics that are absolutely different to those noted for 9 and 10 and for the ferrocene models.$^{34}$

Figure 8. a) Transient absorption spectrum in the visible region recorded with different time delays upon flash photolysis of dyad 7 (2.0 $\times$ 10$^{-5}$ M) at 355 nm in deoxygenated benzonitrile. b) Absorption-decay profile at 600 nm recorded upon flash photolysis of dyad 7 (2.0 $\times$ 10$^{-5}$ M) at 355 nm in deoxygenated benzonitrile.
Despite the unquestionable excitation of the fullerene core, dyad 7 shows no appreciable singlet–singlet absorption in the range 500–960 nm (see Figure 4). The lack of a singlet–singlet absorption, at least within the applied time-resolution of 18 ps, suggests that the transient charge-transfer product (C60N–)(Fc+) stems from a rapid intramolecular electron transfer with a lower limit for $k$ of $5 \times 10^{10}$ s$^{-1}$.

It should be noted that the ferrocene triplet excited state, as a potential product of the rapid fullerene singlet excited-state deactivation, is spectroscopically invisible in the monitored region (500–750 nm, see above). On the contrary, the transient species reveals strong resemblance with the one-electron oxidation product of ferrocene, for which a transient maximum absorption, at least within the applied time-resolution of 18 ps, is markedly accelerated. For example, lifetimes of the charge-transfer absorption decays readily with clean monoexponential dynamics and an underlying lifetime of 0.4 ns for dyad 7.

Considering these spectroscopic and kinetic facts, we reach the important conclusion that, besides the thermodynamically forbidden singlet–singlet transfer, a singlet–triplet energy deactivation of the photoexcited azafullerene. The correspond-ingly accelerated ICT has been observed.

The photophysical measurements reveal an instantaneous deactivation of the photoexcited azafullerene. The corresponding radical pair (C60N–)(Fc+) was found to be the product of a very rapid intramolecular charge transfer process. With reference to the semiclassical Marcus model, we estimated an electronic coupling $V$ of nearly 60 cm$^{-1}$ in benzonitrile and thus corroborate the electrochemical results. Based on these data we demonstrate that the fullerene core in the corresponding azafullerene is quite susceptible to electronic perturbation, despite the extent of delocalization of the carbon network, which is expected to compensate these effects.

### Conclusion

In order to enhance the ground-state intramolecular electronic interactions between the electroactive moieties within fullerene-based dyads, we synthesized the azafullerene–ferrocene hybrid 7 where the two electroactive groups are connected by one o-bond only. The electrochemistry studies clearly show that the redox potentials of both the ferrocenyl and the azafullereryl groups in 7 changed significantly as compared to the appropriate model compounds ferrocene or Fc-Et (oxidation) and 9 or 10 (oxidation and reduction) and showed significant ICT from the covalently bonded electron-donating ferroceny1 to the accepting azafullereryl group at ambient conditions. These changes are much larger than those observed for ferrocenyl fullopyrrolidines,[13] and dimethylaniline-substituted dithienyl-ethyl fullopyrrolidine,[20] in which a small but evident ICT has been observed.

The photophysical measurements reveal an instantaneous deactivation of the photoexcited azafullerene. The corresponding radical pair (C60N–)(Fc+) was found to be the product of a very rapid intramolecular charge transfer process. With reference to the semiclassical Marcus model, we estimated an electronic coupling $V$ of nearly 60 cm$^{-1}$ in benzonitrile and thus corroborate the electrochemical results. Based on these data we demonstrate that the fullerene core in the corresponding azafullerene is quite susceptible to electronic perturbation, despite the extent of delocalization of the carbon network, which is expected to compensate these effects.

### Table 3. Driving-force dependence ($\Delta G_{\text{int}}$, $\Delta G_{\text{adt}}$, $\Delta G_{\text{el}}$, $\Delta G_{\text{m}}$) and thermodynamic parameters ($\lambda$, $\Delta G_{\text{el}}$, $\lambda$) for intramolecular electron-transfer events in dyad 7.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\Delta G_{\text{dt}}$</th>
<th>$\Delta G_{\text{at}}$</th>
<th>$\Delta G_{\text{et}}$</th>
<th>$\lambda$</th>
<th>$\Delta G_{\text{m}}$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>0.21</td>
<td>1.58</td>
<td>0.08</td>
<td>0.34</td>
<td>0.6</td>
<td>0.048</td>
</tr>
<tr>
<td>ODCB</td>
<td>0.26</td>
<td>0.09</td>
<td>0.41</td>
<td>0.76</td>
<td>0.044</td>
<td>0.86</td>
</tr>
<tr>
<td>bcnz</td>
<td>0.34</td>
<td>1.01</td>
<td>0.49</td>
<td>0.86</td>
<td>0.044</td>
<td>58.5</td>
</tr>
</tbody>
</table>

[a] Determined from the relation $\Delta G_{\text{m}} = \frac{e^2}{4\pi\epsilon_{0}\mu} \left(\frac{1}{2R_{n} - R_{p} - R_{c}} - \frac{1}{2R_{c} - R_{p} - R_{n}}\right)$, with $E_{\text{red}}(D^-/D)$ as the oxidation potential of donor (see Table 1), $E_{\text{ox}}(A^-/A^{\bullet+})$ as reduction potential of acceptor (see Table 1), $\lambda$, as radius of donor (3.7 Å), $\lambda$, as radius of acceptor (4.4 Å), $R_{c}$ as solvent dielectric constant (toluene: 2.39; THF: 7.6; ODCB: 9.93; benzonitrile: 24.8), and $R_{n}$ as solvent dielectric constant (9.93).[b] Determined from the relation $\Delta G_{\text{dt}} = E_{\text{red}}(D^-/D) - E_{\text{ox}}(A^-/A^{\bullet+}) + \Delta G_{\text{el}}$. [c] Determined from the relation $\Delta G_{\text{at}} = E_{\text{ox}}(D^-/D) - E_{\text{red}}(A^-/A^{\bullet+}) + \Delta G_{\text{el}}$. [d] Determined from the relation $\Delta G_{\text{et}} = E_{\text{ox}}(D^-/D) - E_{\text{red}}(A^-/A^{\bullet+}) + \Delta G_{\text{el}}$ with $\Delta G_{\text{et}}$ as excited state energy of the chromophore (1.5 eV). [e] Determined from the relation $\lambda = \lambda_{p} + \lambda_{n}$, where $\lambda_{p} = \frac{e^2}{4\pi\epsilon_{0}\mu} \left(\frac{1}{2R_{p} - R_{c} - R_{n}} - \frac{1}{2R_{c} - R_{p} - R_{n}}\right)$, with $\lambda_{p}$ as internal reorganization energy (0.3 eV), $\lambda_{n}$ as solvent reorganization energy, and $\lambda$ as solvent refractive index (toluene: 1.496; THF: 1.407; ODCB: 1.551; benzonitrile: 1.496). [f] Determined from the relation $\Delta G_{\text{el}} = \lambda_{el}$, with $\Delta G_{\text{el}}$ as Gibbs activation energy.
Experimental Section

(C60)2 (1) was prepared according to literature procedures.21 Spectra and instrumentation were as follows: 1H and 13C NMR (JNM EX and JNM GX, Jeol); mass spectra (MAT 311 A, Varian); UV/Vis (UV-3102, Shimadzu); IR (Vector-22, Bruker). HPLC analyses have been carried out on a Cosmosil Buckyprep column (250 × 4.6 mm, Waters) using toluene as eluent. The HPLC purification has been carried out on a Cosmosil Buckyprep column (250 × 20 mm, Waters) using toluene as eluent.

Electrochemistry. Cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) were performed on a PC-driven electrochemical analyzer (BAS 100W, Bioanalytical Systems) at room temperature with a three-electrode configuration in o-dichlorobenzene solution containing the substrate (about 1 mM) and a supporting electrolyte. A gold (21.5 mm), platinum (21.5 mm), or glassy carbon (23 mm) disk served as the working electrode, a platinum wire (21 mm) and a commercial Ag/AgCl aqueous electrode being the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial alumina (No. 1C, Alpha Micropolish, Aldrich; particle size 1.0 µm) prior to use. Tetrabutylammonium hexafluorophosphate (> 99%, Fluka) was recrystallized twice from ethanol and dried in vacuum overnight prior to use and was employed as the supporting electrolyte (0.1 M). Solutions were stirred and deoxygenated by bubbling argon for about 10 minutes prior to each voltammetric or square-wave measurement. Scan rate v was 100 mV/s−1 unless otherwise specified. OSWVs were obtained using a sweep width of 25 mV, a frequency of 15 Hz, a step potential of 4 mV, a square-wave voltammetry (OSWV) was performed on a PC-driven electrochemical analyzer (BAS 100w, Bioanalytical Systems) at room temperature. We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. S.-G.L. and E. greatly appreciate the National Science Foundation, grant CHE-9803088, for generous support of this work. Part of this work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy (contribution No. NDERL-4335 from the Notre Dame Radiation Laboratory).

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References

Pronounced Electronic Coupling in a Fullerene-Ferrocene Dyad


[32] The Born equation is known to overestimate the nonpolarity of toluene.

[33] In the unlikely event of exciting the ferrocene (about 3%), the high-lying nature of the ferrocene singlet excited state (2.46 eV) relative to that of the fullerene singlet excited state (1.5 eV) would result in an even more exothermic intramolecular charge-transfer process than the one evolving from the predominantly excited fullerene (about 97%).

[34] Extending the wavelength region into the near infrared (up to 960 nm) revealed the development of another absorption band similar to that found for the fullerene π-radical anion.


[37] The exact determination of the electron transfer rates was hampered by the instrumental time resolution (18 ps), which led us to apply the rates determined from the emission experiments via Equation (1) in calculating V.


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