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Metallofullerenes

$Sc_3N@C_{80}$-Ferrocene Electron-Donor/Acceptor Conjugates as Promising Materials for Photovoltaic Applications**

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Fullerenes and carbon nanotubes show interesting physicochemical and optoelectronic properties, which, in turn, renders them very promising for a wide range of applications.[1] Among fullerenes, endohedral metallofullerenes, which are carbon cages that encapsulate metal atoms, have attracted increasing attention, largely due to their potential relevance in the fields of biomedicine and nanomaterials sciences.[2,3]

Since the discovery of trimetallic nitride template endohedral fullerenes (TNT EMFs) by Dorn and coworkers,[4] their structural, physical, and chemical properties have been explored in great detail.[3] Derivatization of these fullerene species is crucial since it increases their potential applications. So far, however, only a few of the reactions that are very effective on fullerenes and other metallofullerenes (Diels–Alder,[5] 1,3-dipolar cycloaddition,[6] disilirane addition,[7] radical trifluoromethylation,[8] and malonate free radicals[9]) seem to work for these intriguing structures.

A fundamental aspect of $Sc_3N@C_{80}$ chemistry that still awaits exploration is its applicability and performance in electron-donor/acceptor systems.[10] C_{60} and its derivatives exhibit uniquely low reorganization energies in charge-transfer reactions and, simultaneously, show remarkable electron-mobility features, acting as outstanding electron acceptors in different nanoconjugates.[11] None of the trimetallic nitride endohedrals has ever been explored in this context despite the fact that they possess much larger absorptive coefficients than C_{60} in the visible region of the electromagnetic spectrum and a low HOMO–LUMO energy gap while preserving a remarkable electron-accepting ability similar to that of C_{60}.[3]

The recent successful functionalization of $Sc_3N@C_{80}$ based on the 1,3-dipolar cycloaddition of azomethine ylides[6] led us to pursue the covalent linkage of an electron donor, namely ferrocene, to the endohedral C_{80} cage. Herein we report the first photoinduced intramolecular electron-transfer reaction involving an endohedral fullerene from a novel $Sc_3N@C_{80}$-based donor–acceptor dyad.

An isomeric mixture of I_h and D_{5h} $Sc_3N@C_{80}$ was provided by Luna Innovations, Inc., and the I_h-$Sc_3N@C_{80}$ isomer was obtained after chromatographic purification (see the Supporting Information).[12] The pyrrolidinofullerene derivative **1** was prepared by thermal reaction of I_h-$Sc_3N@C_{80}$ with sarcosine and ferrocene carboxaldehyde in a toluene/*o*-dichlorobenzene (*o*-DCB) mixture (Scheme 1). The reaction proceeded smoothly to afford cycloadduct **1** in 44% yield after purification by column chromatography (SiO_2; CS_2/toluene, 1/1). The obtained adduct showed a retention time of 11.53 min. on a buckyclutcher column (toluene; 4 $mL\,min^{-1}$) and the MALDI-TOF mass spectrum of the isolated compound confirmed the formation of the monoadduct (see the Supporting Information).

Two types of $C{=}C$ double bonds are available on the I_h-$Sc_3N@C_{80}$ cage for reaction with the in situ generated azomethine ylide, namely those between two hexagonal rings (6,6-junctions) and those between pentagonal and hexagonal rings (5,6-junctions).[3] The ^1H NMR spectrum of **1** showed the presence of a single regioisomer. This spectrum shows individual resonances for the protons in the Cp ring

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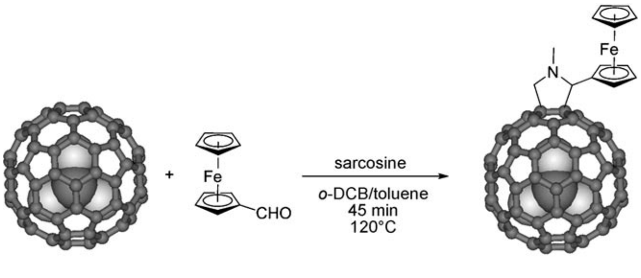
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



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Scheme 1. 1,3-Dipolar cycloaddition reaction of I_h-$Sc_3N@C_{80}$ with ferrocene carboxaldehyde and sarcosine.

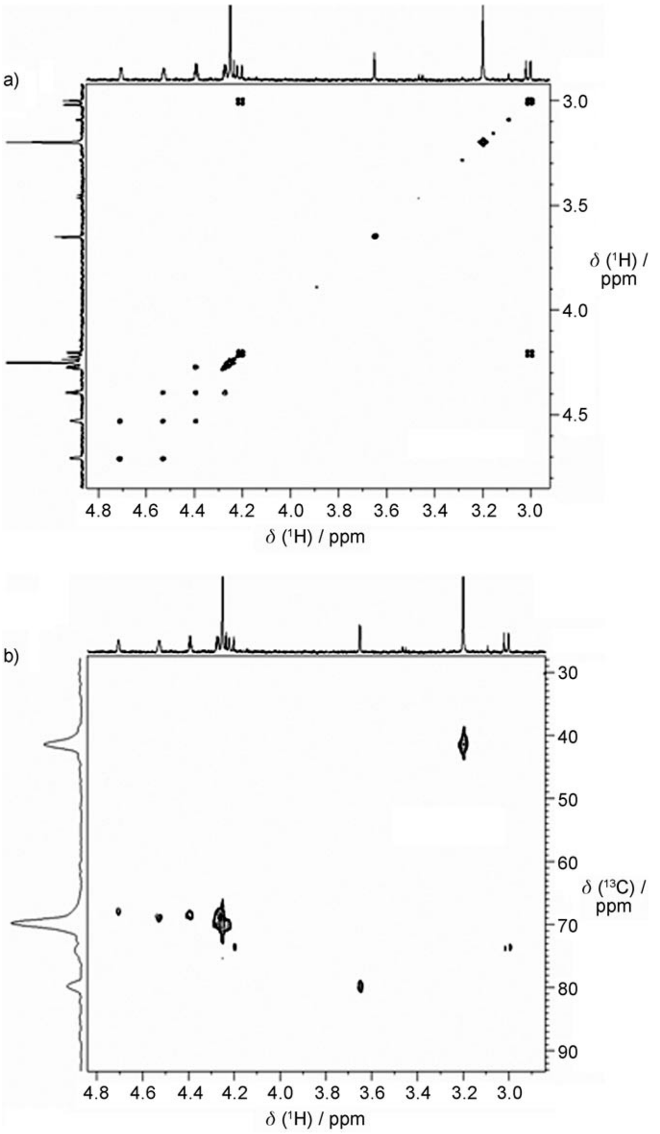

Figure 1. COSY (a) and HMQC (b) spectra of the *N*-methyl-2-ferrocenyl-I_h-[5,6]-$Sc_3N@C_{80}$-fulleropyrrolidine **1**.

attached directly to the pyrrolidine in the region from $\delta = 4.70$ to 4.25 ppm. The coupling between them is evident in the COSY spectrum (Figure 1 a). The protons of the nonsubstituted Cp ring give rise to a singlet at $\delta = 4.25$ ppm. The signals for the pyrrolidine geminal protons are separated by 1.2 ppm and appear as doublets at $\delta = 4.21$ and 3.01 ppm ($J = 9.5$ Hz). The remaining pyrrolidine proton leads to a signal at $\delta = 3.65$ ppm, while for the *N*-methyl group a singlet is observed at $\delta = 3.20$ ppm. The HMQC spectrum (Figure 1 b) obtained at natural abundance allowed us to determine the chemical shifts for the carbon atoms with protons attached to them: the signal for the *N*-methyl carbon appears at $\delta = 41.4$ ppm, all the ferrocenyl signals appear in the range $\delta = 67$–70 ppm, the CH_2 pyrrolidine carbon signals appears at $\delta = 73.5$ ppm, and the signal for the CH carbon linked to the ferrocene appears at $\delta = 80.0$ ppm.

The observation of only two different pyrrolidine carbons suggests the presence of either an enantiomeric mixture of the [5,6] regioisomer or only one pair of enantiomers out of the two possible ones for the [6,6] regioisomers. The fact that no isomerization was observed after prolonged heating suggests the presence of the thermodynamic product, which in this case is the [5,6] regioisomer.[5,6]

Further confirmation of the [5,6] structure for monoadduct **1** was obtained after investigation of its solution electrochemistry. It has recently been demonstrated that the general electrochemical behavior of trimetallic nitride derivatives can be employed to easily differentiate between the two regioisomers formed at [5,6] and [6,6] bonds.[13] Thus, reversible reductive electrochemical behavior has been observed for [5,6] monoadducts whereas the corresponding [6,6] monoadducts exhibit irreversible behavior similar to that of the parent endofullerenes.[13]

The cyclic voltammograms of *N*-methyl-2-ferrocenyl-I_h-[5,6]-$Sc_3N@C_{80}$-fulleropyrrolidine (**1**) and I_h-$Sc_3N@C_{80}$ (for comparison purposes)[12,14] are shown in Figure 2. Three one-electron reversible reductions at −1.14, −1.53, and −2.25 V (vs. Fc/Fc^+) are observed for **1** (Figure 2, trace b), and this reversible electrochemical behavior is consistent with the formation of a ferrocenyl [5,6]-pyrrolidine derivative of $Sc_3N@C_{80}$.[13] Additionally, three oxidations are observed at +0.15, +0.61, and +1.09 V (vs. Fc/Fc^+) in the positive potential range. The first process at +0.15 V (vs. Fc/Fc^+) corresponds to the oxidation of the ferrocenyl moiety and the processes at +0.61 and +1.09 V (vs. Fc/Fc^+) to the oxidations of the fullerene cage.

Before testing electron-transfer interactions in photoexcited I_h-$Sc_3N@C_{80}$-ferrocene dyads, the ground-state features were analyzed as these provide insights into the optical HOMO–LUMO gap of the $Sc_3N@C_{80}$ core. In particular, an absorption around 950 nm relates to an energy of 1.3 eV.

Next we turned to time-resolved transient absorption spectroscopy. Upon photoexciting **1**, the $Sc_3N@C_{80}$ centered singlet excited state decays rapidly. In fact, a singlet excited state lifetime of only 5 ps—a value that is well in line with a close donor–acceptor separation—was determined for $Sc_3N@C_{80}$-Fc. It should be noted that this lifetime is approximately 10 times shorter than in the corresponding reference systems (pristine $Sc_3N@C_{80}$; 48 ps). Moreover, the fast decay is associated with marked changes in the differential absorption spectrum. As Figure 3 illustrates, the singlet excited state

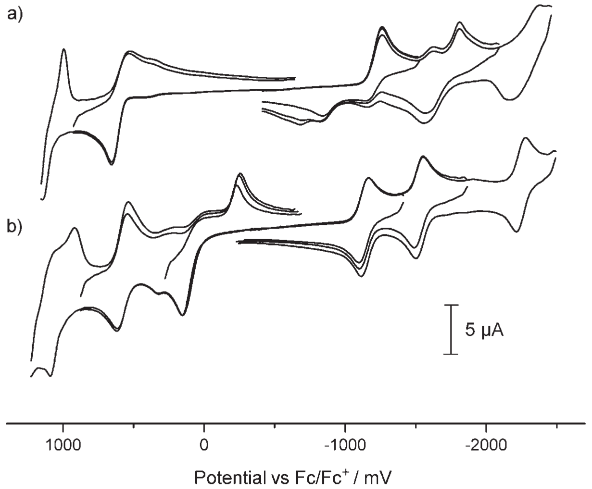

Figure 2. Cyclic voltammograms of a) I_h-$Sc_3N@C_{80}$ and b) *N*-methyl-2-ferrocenyl-I_h-[5,6]-$Sc_3N@C_{80}$-fulleropyrrolidine **1** in nBu_4NPF_6/*o*-DCB. Scan rate: 100 mV s^{-1}.

features (i.e., maxima at 550 and 870 nm) transform over the course of 5 ps into a new set of maxima, which evolve in the visible (i.e., 530 and 626 nm) as well as in the near-infrared region (i.e., 830 and 1120 nm). The close resemblance of the near-infrared part with the radiolytically and spectroelectrochemically generated spectrum of the one-electron reduced $Sc_3N@C_{80}$ radical anion (see the Supporting Information) is of particular importance. In the visible region, features of the one-electron oxidized ferrocenium ion evolve around 680 nm. Taking this into consideration, we conclude the successful formation of the radical ion pair state. An energy of approximately 1.29 eV was estimated based on the electrochemically determined redox potentials. In other words, the formation of this radical ion pair state starting from the $Sc_3N@C_{80}$ singlet excited state (1.50 eV as taken from fluorescence spectra recorded for pristine $Sc_3N@C_{80}$) is thermodynamically feasible. The time vs. absorption profiles in Figure 3 also corroborate that the radical ion pair state is metastable as it decays with a lifetime of 128 ps in carbon disulfide and 84 ps in *o*-DCB.

To shed light onto this particular lifetime value, we complemented our work with measurements with the exact C_{60}-ferrocene analogue[15] in different solvents (CS_2, THF, and benzonitrile). In these solvents we see that the initially formed C_{60} singlet excited state, which appears as a transient maximum at 950 nm, rapidly transforms (4.8 ps in THF) into the radical ion pair state. Maxima at 490 and 1010 nm are unequivocal attributes of the one-electron-reduced C_{60} moiety, while the general signature of the one-electron-oxidized ferrocene is seen around 680 nm. An illustration of this is given in the Supporting Information. The corresponding lifetimes are 46 ps in CS_2, 49 ps in THF, and 27 ps in benzonitrile.

In summary, the ferrocenylpyrrolidine adduct of I_h-$Sc_3N@C_{80}$ has been successfully synthesized and characterized and formation of the [5,6]-regioisomer unambiguously determined by NMR spectroscopy and electrochemistry. Besides being the first covalent donor/acceptor dyad prepared containing an I_h-$Sc_3N@C_{80}$ cage, we have also succeeded, for the first time, in confirming photoinduced electron transfer within this novel system. Most remarkably, a significant stabilization of the radical ion pair state is seen when compared to an analogous C_{60}-ferrocene conjugate. These results appear particularly promising in light of further developments in metal nitride cluster fullerene-based dyads as new and promising materials for solar-energy conversion applications.

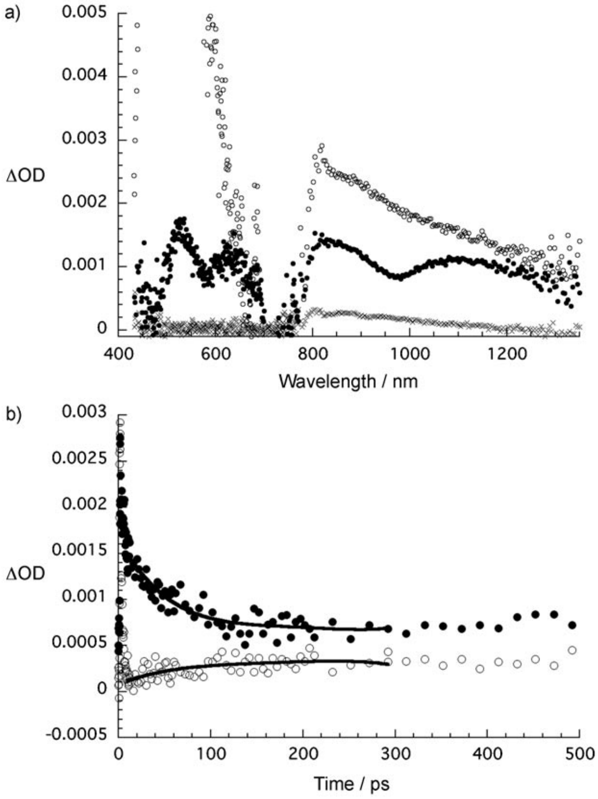

Figure 3. a) Differential absorption spectra obtained upon femtosecond flash photolysis (388 nm, 150 nJ) of **1** in CS_2 with time delays of between 0 and 5 ps at room temperature; ○ 2 ps, ● 10 ps, and × 200 ps. b) Time-absorption profile of the spectra shown above at 625 nm (●) and 1000 nm (○), reflecting the charge-separation and charge-recombination dynamics.

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