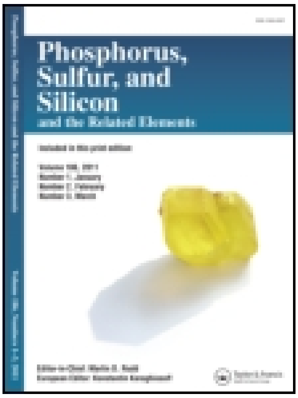

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ORGANOSULFUR-BASED FULLERENE MATERIALS

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Abstract *Chemical functionalizations of an endohedral metallofullerene, $La_2@I_h$-C_{80}, and an empty fullerene, C_{60}, are demonstrated using organosulfur compounds. A novel donor–acceptor system of $La_2@I_h$–C_{80}-exTTF (**3**) synthesized using the Prato reaction shows photo-induced intramolecular charge separation. On the other hand, the photoreaction of C_{60} with N-p-toluenesulfonyl sulfilimine affords N-tosyl-1,2-aziridinofullerene (**5**). The first reversible interconversion of 1,2-aziridinofullerene and 1,6-azafulleroid was found for mono-substituted fullerenes by thermal rearrangement of **5** to **6**. S,S-Diphenylsulfilimines (**7**) with an electron-donating group on the N atom reacts with C_{60} to afford corresponding aziridinofullerenes (**8–10**) regioselectively.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords Aziridinofullerenes; donor–acceptor systems; endohedral metallofullerenes; π-extended tetrathiafulvalene; sulfilimine

INTRODUCTION

Exohedral chemical derivatizations of fullerenes have been developed extensively for examination of their potential usefulness as fullerene-based organic materials.[1] Organosulfur compounds represent a unique feature of materials. We believe that a combination of

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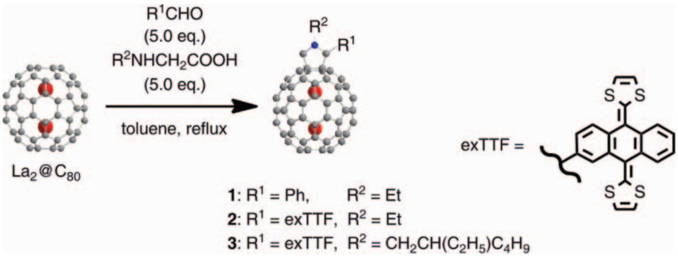
fullerene and organosulfur compounds forms a new class of organic compounds and thereby opens a new field in material science. In this context, here we present novel functionalized fullerenes with organosulfur compounds to afford the corresponding fullerene-based materials, which have important chemical and physical properties.

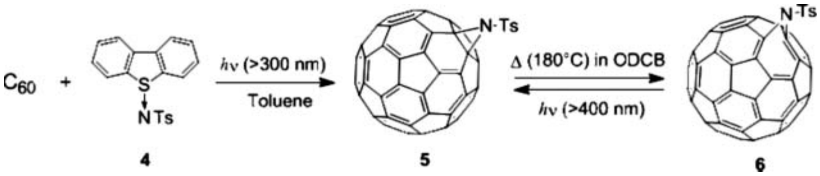
RESULTS AND DISCUSSION

Novel donor–acceptor dyads based on an endohedral metallofullerene, $La_2@I_h$–C_{80}, were synthesized regioselectively using 1,3-dipolar cycloaddition (Prato reaction) of π-extended tetrathiafulvalene (exTTF) containing azomethine ylides regioselectively (Scheme 1).[2] The cyclic voltammetry (CV) of dyad **3** reveals the redox active character of the system attributable to the presence of both donor and acceptor groups (exTTF and $La_2@I_h$–C_{80}, respectively). Despite the proximity between the exTTF and $La_2@I_h$–C_{80}, only a weak electronic interaction was observed in the ground state, as evidenced by absorption spectroscopy and CV measurements of **2** and **3**. On the other hand, transient absorption spectroscopy experiments confirmed the intramolecular interaction of **3** in the excited state. The fast formation of a radical ion pair state (6.0×10^{10} s^{-1}), that is, the reduction of the electron accepting $La_2@C_{80}$ and the oxidation of exTTF, evolves with lifetimes as long as several nanoseconds (3.0×10^8 s^{-1}) in toluene. These rate constants are one tenth of those of a similar system based on C_{60} (exTTF-C_{60}),[3] implying high efficiency of intramolecular electron transfer in exTTF-$La_2@C_{80}$ per unit of time.



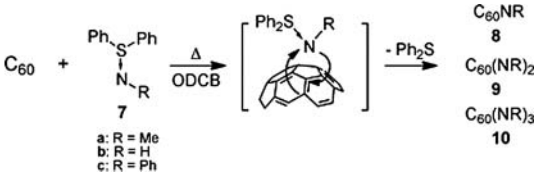
Scheme 1 (Color figure is available online.)

Sulfilimine has been known to generate an *N*-substituted nitrene in thermal or photochemical reactions. It has been reported that *N*-sulfenyl sulfilimine generates a sulfenylnitrene under mild conditions. Nitrenes react easily with alkenes to afford the corresponding three-membered aziridines. In this context, a nitrene is expected to be a key intermediate for aziridination of fullerene instead of azide, which presents crucial difficulties related to toxicity and explosivity. We conducted photoreaction of C_{60} with *N*-*p*-toluenesulfonyl (*N*-tosyl) sulfilimine (**4**) having a dibenzothiophene (DBT) structure to accomplish the regioselective synthesis of *N*-tosyl 1,2-aziridinofullerene ([6,6]-closed C_{60}NTs, **5**) (Scheme 2). Results



Scheme 2

show that **5** thermally rearranges to the 1,6-azafulleroid (**6**) and that the photochemical ring-closure of **6** takes place to afford **5**. This is the first reported reversible interconversion of 1,2-aziridinofullerene and 1,6-azafulleroid for mono-substituted fullerenes. The structures of **5** and **6** were characterized using NMR spectra and X-ray crystallographic analyses.[4]



Scheme 3

Sulfilimines with an electron-donating group on the N atom are well known to undergo Michael-type reactions, followed by concomitant elimination of sulfide to afford the corresponding aziridines. In these reactions, sulfilimines act as a nucleophile to the electrophilic olefins. Furthermore, C_{60} has a characteristic feature—its low LUMO level and electron-accepting property—acting as an electrophilic olefin. In this context, sulfilimines might react with C_{60} to afford corresponding aziridinofullerenes. We have studied the thermal reaction of *S*,*S*-diphenylsulfilimines (**7**) with C_{60} and regioselectively synthesized a bis-aziridinated fullerene and a tris-aziridinated fullerene (Scheme 3). These structures (**8a**, **8b**, **8c**, **9a**, **9b**, **10b**) were determined through spectroscopic analyses. Among these, the structure of bis-aziridinated[60]fullerene, $C_{60}(NCH_3)_2$ (**9a**), was determined using single-crystal X-ray analysis (Figure 1). Results show that the multi-aziridination occurs exclusively at the same six-membered ring of C_{60} to afford one isomer of the bis-adduct and tris-adduct.[5]

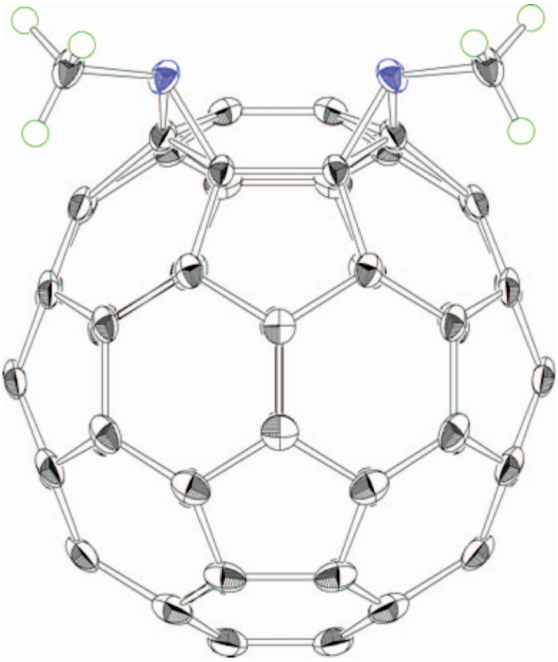


Figure 1 ORTEP drawing of **9a** showing thermal ellipsoids at a 50% probability level. (Color figure is available online.)

EXPERIMENTAL

See Supplemental Materials (available online).

CONCLUSION

Several novel derivatives based on fullerenes and organosulfur compounds were synthesized and then characterized using spectroscopic measurements. The combination of organosulfur and fullerenes is expected to enhance electronic and physical properties of carbon allotropes.

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