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Nanocarbon Chemistry

Photochemical Addition of Ethers to C_{60}: Synthesis of the Simplest [60]Fullerene/Crown Ether Conjugates**

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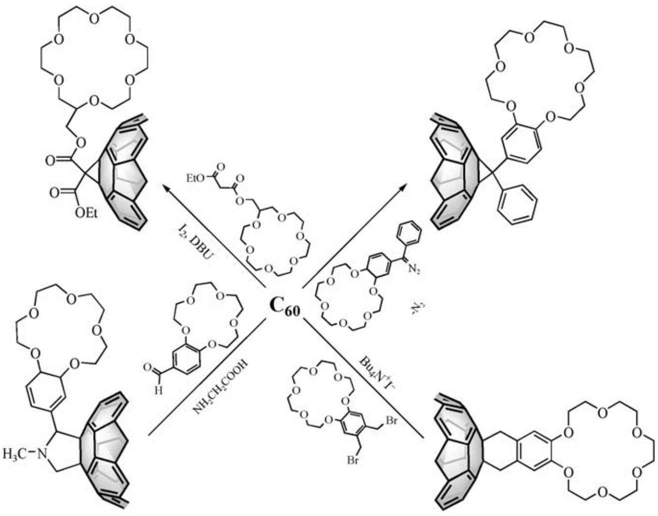
Radical reactions have been widely used for the functionalization of ethers.[1] A growing interest is focused in this area, which stems from the ubiquity of ethers in molecular architecture. However, the direct linkage of ethers and [60]fullerene remains virtually unexplored despite its significant synthetic challenge.

In view of their ability to coordinate selectively alkali metals ions and neutral organic molecules, crown ethers occupy a prominent position in host–guest chemistry. Unambiguously, [60]fullerene/crown ether conjugates represent the most widely studied example of fullerenes integrating an ether moiety. Such arrays display interesting photophysical[2,3] and electrochemical properties[4,5] with broad application potential. For example, it has been shown that the cation-binding-dependant changes in their redox potential and fluorescence quenching may find applications in specific ion sensors and fluorescence switching devices, respectively.[6–9] Furthermore, crown ether tagged fullerenes have been used for exploring the chemistry of C_{60} by electrospray mass spectrometry.[10] More importantly, the covalent linkage of a crown ether moiety on the fullerene core is a unique approach to the construction of functional supramolecular fullerene assemblies,[11] such as exTTF–C_{60} dyads (exTTF = π-extended tetrathiafulvalene),[12] self-assembled carbon nanotube/fullerene donor–acceptor hybrids,[13] fullerene dimers,[14] [60]fullerene-based rotaxanes,[15] fullerene-based thin films formed by self-assembled monolayers (SAMs) of C_{60},[16] as well as Langmuir–Blodgett films.[17] However, the main drawback in these syntheses is the requirement of using an appropriately linker-functionalized crown ether. The linker moiety is used for attaching the crown ether moiety onto the fullerene core through standard reaction protocols, including 1,3-dipolar cycloaddition with azomethine ylides[2,12] or diazomethane derivatives,[10,18] [4+2] cycloaddition with dienes[4] or quinodimethane precursors,[3,7] and the Bingel reaction with malonates (Scheme 1).[6,14] Apparently, the key breakthrough would be the development of methods for the direct functionalization of [60]fullerene with a crown ether through a simple, one-step process, thus reducing both the cost and time of such derivatizations while providing an expedient entry into a novel class of functional fullerenes.



Scheme 1. Representative reactions for the addition of functionalized crown ethers to C_{60}. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Herein, we report an effective free-radical approach for the activation of the otherwise unreactive α-C–H bond in a series of structurally diverse mono- or polyethers and sulfides. This method enables the unprecedented direct covalent functionalization of fullerene C_{60} with crown ethers. A mechanistic explanation for this new reactivity of C_{60} is also provided, based mainly on our analysis of captured intermediates and intermolecular deuterium-isotope-effect studies.

Initially, the photochemical reaction of C_{60} with diethyl ether (**1**) was studied. After screening several sets of reaction conditions, we found that the desired radical addition to C_{60} could be conveniently achieved by irradiating a solution of C_{60} with 200 equivalents of **1**, in the presence of 0.5 equivivalents of tetrabutylammonium decatungstate catalyst (TBADT, $(nBu_4N)_4W_{10}O_{32}$)[19,20] using a 300 W xenon lamp. To our delight, under these conditions ether-functionalized [60]fullerene **1a** was isolated after 20 minutes in 40% yield (Table 1, entry 1). Based on this result, we then investigated the scope of this reaction, under similar conditions, by employing a broad variety of structurally diverse ethers, including cyclic and linear, mono- and polyethers and organic sulfides (Table 1, entries 2–8). Notably, under these conditions the multiple addition of organic free radicals to [60]fullerene[21]—which typically stems from the high reactivity of all thirty double bonds of C_{60} to such species—was suppressed; the

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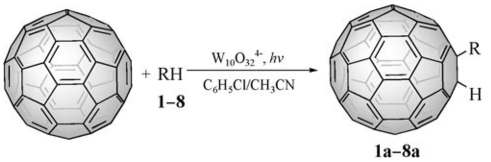
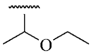
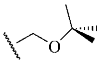
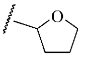
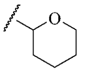
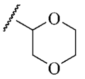
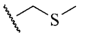
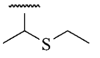
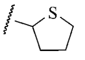
Table 1: TBADT-mediated reaction of ethers **1**–**8** with C_{60}.

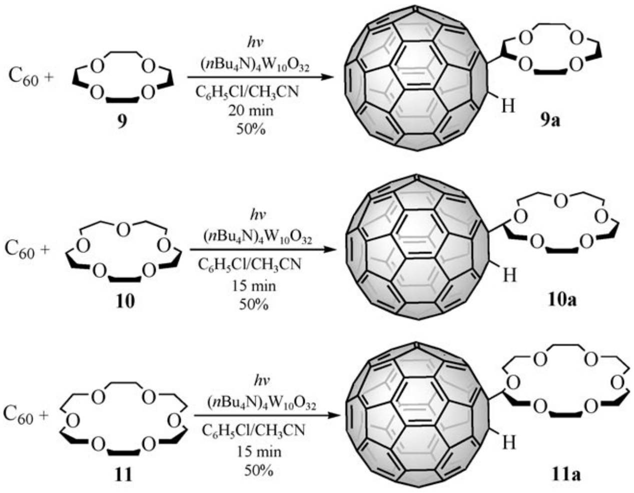


Entry	Substr.	R	t [min]	Yield [%][a]
1	**1**		20	40
2	**2**		90	40
3	**3**		20	40
4	**4**		35	40
5	**5**		80	35
6	**6**		25	50
7	**7**		25	45
8	**8**		20	45

[a] Yield of isolated product.

corresponding monofunctionalized fullerenes **2a**–**8a** were obtained in unexpectedly good yields. Benzophenone, a well-known triplet photosensitizer, similarly catalyzed this reaction but gave much lower yields (see the Supporting Information).

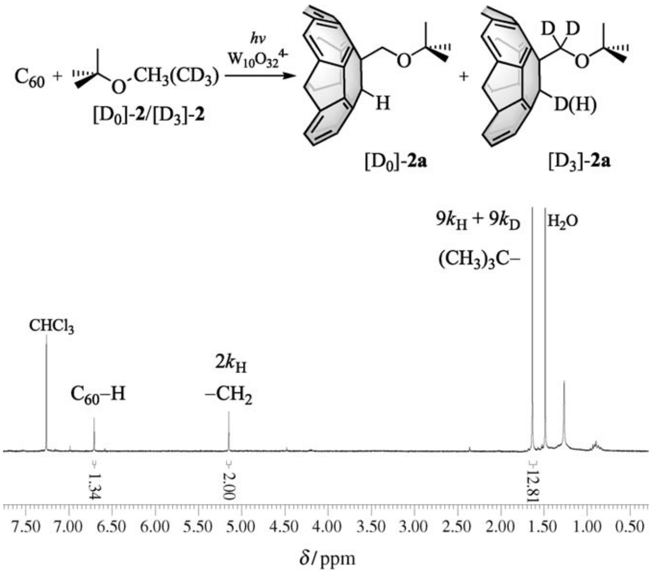
To assess the potential of this novel transformation we studied the addition of crown ethers **9**–**11** to C_{60}. To our delight, this reaction proceeded rapidly (15–20 min) to afford the simplest and hitherto elusive [60]fullerene/crown ether conjugates **9a**–**11a** in good yields, and high regioselectivity and purity (Scheme 2). This reaction, in contrast to the previous methods for the chemical modification of C_{60} with crown ethers, is the first in which a crown ether moiety is covalently attached to the fullerene core through a single σ bond. This implies that the distance between the ionophore moiety and the C_{60} chromophore is the smallest possible, which is a major concern in the design of functional supramolecular systems.



Scheme 2. TBADT-mediated reaction of crown ethers **9**–**11** with C_{60}.

The C_1- or C_s-symmetrical structures of the new fullerene derivatives **1a**–**11a** were unequivocally established by the combined use of $^1H/^{13}C$ NMR, UV/Vis and FTIR spectroscopy, as well as by mass spectrometry (see the Supporting Information). Interestingly, this reaction is highly regioselective; UV/Vis spectroscopic studies revealed the 1,2-addition pattern of all new adducts (the addition has taken place across the one out of thirty [6,6]-ring junctions of C_{60}).

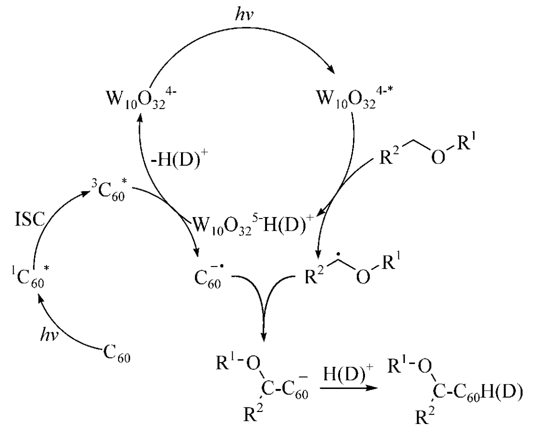
Labeling experiments were then employed to probe the mechanism underlying this reaction. Initially, deuterium-trapping experiments were carried out to determine the origin of the fullerenyl H atom in $RC_{60}H$. For this purpose, the photocatalyzed reaction of **1** with C_{60} was performed in a mixture of either anhydrous C_6H_5Cl/CD_3CN or C_6H_5Cl/CH_3CN containing 1% D_2O. No deuteration observed in the first case, while **1a** was almost quantitatively deuterated on the C_{60} core under the latter set of conditions. Moreover, control experiments excluded the possibility of H/D exchange in **1a** during the reaction under the same experimental conditions (see the Supporting Information). These results suggest, in accordance with our previous studies,[20] the intermediacy of the fullerene anion in the reaction mechanism. To probe this mechanism further and assess the extent of bond making and bond breaking in the transition state, we measured the intermolecular primary kinetic isotope effect (KIE) of this reaction. To this end, we studied the reaction of C_{60} with an equimolar mixture of [D$_0$]-**2**/[D$_3$]-**2** (Scheme 3). The ratio of products [D$_0$]-**2a** and [D$_3$]-**2a**, which is the result of an intermolecular isotopic competition between the CH_3 and CD_3 substituents of [D$_0$]-**2** and [D$_3$]-**2**, respectively, is proportional to the primary isotope effect of k_H/k_D. Integration of the appropriate ^1H NMR signals of both [D$_0$]-**2a** and



Scheme 3. Determination of the intermolecular primary KIE in the reaction of [D$_0$]-**2**/[D$_3$]-**2** with C_{60} by ^1H NMR spectroscopy.

[D_3]-**2a** determined the primary isotope effect $k_H/k_D = 2.36 \pm 0.10$ (Scheme 3). This substantial KIE indicates extensive C–H(D) bond breaking in the transition state of the first slow radical-forming step. Another important finding from this experiment concerns the source of the fullerenyl hydrogen. The adduct [D_3]-**2a** is partially deuterated which indicates, in accordance with the D_2O quenching experiment mentioned above, that the intermediate C_{60} anion is mainly trapped by a proton originated from the residual moisture in the reaction mixture.

Scheme 4 depicts a plausible mechanism consistent with the preceding discussion. Initially, the excited state of decatungstate ($W_{10}O_{32}^{4-*}$), generated upon light excitation, abstracts an α-hydrogen atom from the ether affording the one-electron-reduced form of decatungstate ($W_{10}O_{32}^{5-}$) and the corresponding α-oxy C-centered radical. The triplet excited state of C_{60} ($E_{red} = 1.14$ V vs. SCE), generated upon light excitation followed by an effective intersystem crossing ($\Phi_{ISC} \approx 1$), regenerates $W_{10}O_{32}^{4-}$ ($E_{red} = -1.215$ V vs. SCE) through a single-electron-transfer (SET) process, thus completing the catalytic cycle.[20] Finally, radical coupling followed by protonation of the resulting anion affords the observed fullerene adducts.



Scheme 4. Proposed mechanism for the TBADT-catalyzed reaction of ethers with fullerene C_{60}.

In conclusion, we have developed a novel and facile route towards the hitherto unexplored functionalization of fullerene C_{60} with ethers and thioethers. In essence, this method not only enables direct access to a series of novel fullerene–ionophore assemblies that have great potential as building blocks in supramolecular materials science, but also expands the scope of inorganic catalysis in nanocarbon chemistry. Thus, the diversity of available fullerene-based compounds can be expanded with minimal synthetic effort. Further exploration of the characteristics and scope of this novel reaction is in progress.

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Keywords: C–H activation · crown ethers · fullerenes · photocatalysis · radical reactions

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