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A comparison of the photochemical reactivity of N@C_{60} and C_{60}: photolysis with disilirane†

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N@C_{60} has a lower photochemical reactivity toward disilirane than C_{60}, although N@C_{60} does not differ from C_{60} in its thermal reactivity; theoretical calculations reveal that N@C_{60} and C_{60} have the same orbital levels and that N@$^3C_{60}$* has a shorter lifetime than $^3C_{60}$*.

In 1996, Weidinger and co-workers reported the first synthesis and characterization of N@C_{60}.[1,2] It is particularly surprising that the encapsulated nitrogen exists as a single atom in the quartet ground state. Current synthetic methods have typical yields of less than 10^{-2} moles,[3,4] but EPR is sensitive enough to detect these paramagnetic species at a low concentration. Since the N atom is located on average at the center of C_{60}, an EPR spectrum that consists of three sharp hyperfine peaks is observed.[1] The spin density is exclusively localized in the neighborhood of the N atom.[5] No charge transfer from N to C_{60} is observed in N@C_{60} because of the high ionization potential of the N atom, as in the He@C_{60} case.[6]

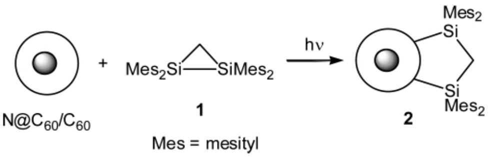
Hirsch and co-workers reported that the nucleophilic cyclopropanation of N@C_{60} with diethyl bromomalonate affords the exohedral mono-adduct, N@C_{61}(COOEt)$_2$, using the Bingel–Hirsch reaction.[7] EPR investigations showed that the hyperfine constant and electronic *g*-factor are equal to those of the unmodified N@C_{60} within experimental error. These results demonstrated that the average position of the N atom is still on-center in N@C_{61}(COOEt)$_2$. They also reported that the thermal reactivity of N@C_{60} is indistinguishable from that of C_{60} during nucleophilic cyclopropanation.[7]

In our series of studies on the chemical functionalization of fullerenes with organosilicon compounds, we have reported the photochemical bis-silylation of C_{60},[8] higher fullerenes,[9] and endohedral metallofullerenes[10] with disilirane. In this context, it is worth noting that disilirane can act as a mechanistic probe to clarify the electronic and chemical characteristics of fullerenes. We now report the bis-silylation of N@C_{60} with disilirane to clarify the photochemical reactivity of N@C_{60} compared with C_{60}.

The photoirradiation (>400 nm) of a toluene solution of 1,1,2,2-tetramesityl-1,2-disilirane **1** (1.8 mg, 1.4×10^{-3} M) and a N@C_{60}–C_{60}[11] mixture (2.3 mg, 1.4×10^{-3} M) gave a mixture of 1,1,3,3-tetramesityl-1,3-disilolane **2** and unreacted N@C_{60}–C_{60} (Scheme 1). The reaction mixture was injected into a JAI Gel 1H + 2H column, and **2** (63%) and unreacted N@C_{60}–C_{60} (32%) were recovered. The mono-adduct **2** was fully characterized by UV-vis, ^{1}H NMR, and LD-TOF mass spectroscopies.[8]

Fig. 1(a) shows the EPR spectrum of **2** in CS_2 at 293 K. The atomic character of the encapsulated nitrogen is preserved in **2** as well as during the reaction and work up steps. The hyperfine constant and electronic *g*-factor of **2** are within experimental uncertainty equal to the values for the unmodified N@C_{60}. This indicates that the average position of the N atom is still on-center in **2**. At 80 K, the EPR spectrum of **2** in CS_2 shows a new feature (Fig. 2(b)), which reveals the actual formation of the N@C_{60} adduct. This low-temperature EPR measurement also confirmed the Bingel–Hirsch cyclopropanation of N@C_{60}.[7]

Interestingly, the signal intensity of **2** is obviously smaller than that of N@C_{60} used in this reaction. This indicates that N@C_{60} has a lower photochemical reactivity than the empty C_{60}. This is a remarkable difference as N@C_{60} does not differ from C_{60} in its thermal reactivity.[7] We determined the concentration of N@C_{60} in the recovered N@C_{60}–C_{60} by EPR measurement. The ratio of N@C_{60} and C_{60} in the starting and recovered N@C_{60}–C_{60} is about 1 : 1.6. We have obtained the



Scheme 1

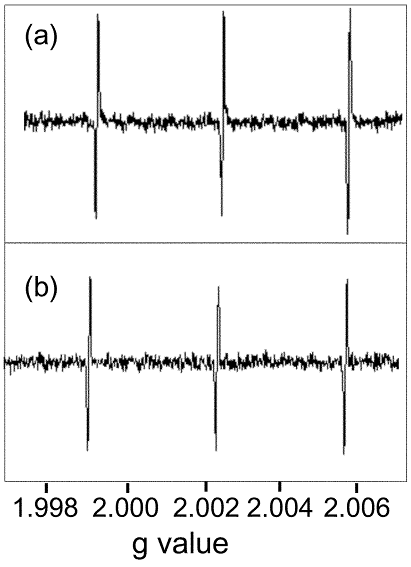


Fig. 1 EPR spectra of (a) the mono-adduct (**2**) in CS_2 and (b) N@C_{60} in toluene at 293 K.

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† Electronic supplementary information (ESI) available: experimental results. See http://www.rsc.org/suppdata/cc/b3/b309470g/

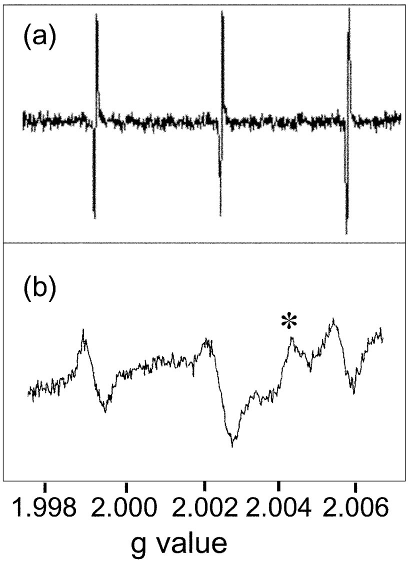

Fig. 2 EPR spectra of the mono-adduct (**2**) in CS_2 (a) at 293 K and (b) at 80 K. * = impurity.

relative reactivity of N@C_{60}–C_{60} by the following calculation: $[100 - (32 \times 1.6)]\%/(100–32)\% = 0.7$.

Up to now, based on control experiments and laser flash photolysis, it has been believed that the bis-silylation reaction of C_{60} with disilirane **1** proceeds by electron transfer from **1** to $^3C_{60}$* *via* an exciplex.[13] The significant difference in the photochemical reactivity of N@C_{60} and C_{60} may be ascribed to (i) the different excitation energies of N@C_{60} and C_{60} or (ii) the faster quenching of N@$^3C_{60}$*. Theoretical calculations reveal that N@C_{60} and C_{60} have the same orbital levels, as shown in Fig. 3, and that the N atom does not move to an off-center position to obtain stronger interactions, even in N@$^3C_{60}$*.[14] It is likely that the three parallel spins on the N atom play an important role in the decay of N@$^3C_{60}$*. In fact, preliminary calculations of spin orbit interactions show that the spin orbit coupling between the excited Ψ(N@$^3C_{60}$*) and ground Ψ(N@C_{60}) states is larger than the corresponding coupling between $\Psi(^3C_{60}*)$ and $\Psi(C_{60})$,[15] which suggests that N@$^3C_{60}$* has a shorter lifetime than $^3C_{60}$*.

Bis-silylated N@C_{60} has been successfully prepared and characterized. Even in an electron-rich fullerene cage, the N atom is located on average at the center of C_{60}. A notable finding is that N@C_{60} has a lower photochemical reactivity toward disilirane than C_{60}. In this context, detailed photophysical kinetic studies of absorption and fluorescence processes would help to make possible a comprehensive understanding of the photochemical reactivity of N@C_{60}.[16]

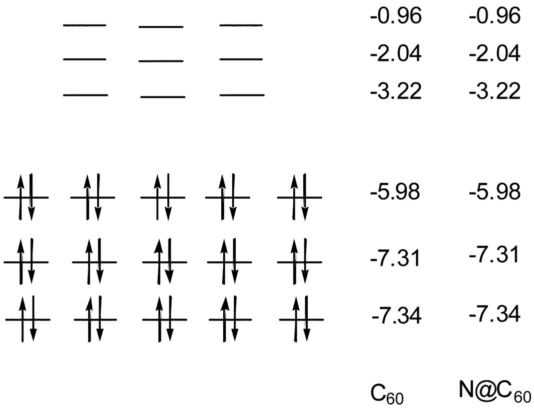

Fig. 3 Orbital energies of N@C_{60} and C_{60} calculated at the B3LYP/6-31G* level in eV.

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