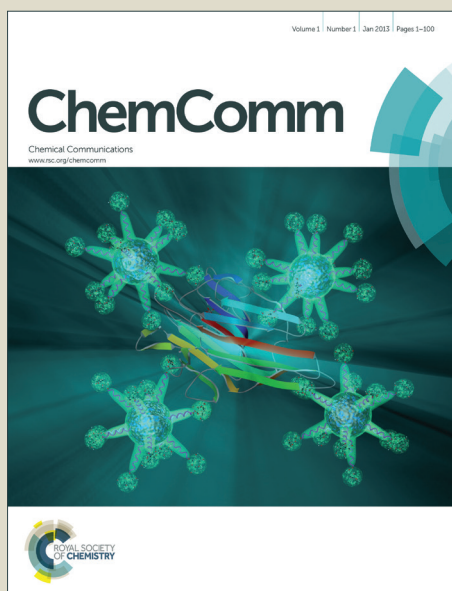


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COMMUNICATION

Synthesis of the first completely spin-compatible N@C₆₀ cyclopropane derivatives by carefully tuning the DBU base catalyst

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Two cyclopropane derivatives of N@C₆₀ were synthesised by well-controlled Bingel reactions, in which 94% of the spin centres were retained, confirmed by a series of quantitative electron spin paramagnetic resonance (EPR) measurements. Further study on the influence of the DBU catalyst base revealed a spin loss mechanism through a fullerene-DBU diradical.

Among different proposals for quantum information processing, nitrogen endohedral fullerenes, such as N@C₆₀, have been regarded as candidate entities to carry qubit information,^{1,2} due to the long decoherence time of their electron spins.³ The chemical functionalization (e.g. dimerization) of these molecules holds great promise^{4, 5, 6, 7} as an approach to fabricate scalable qubits and quantum devices⁸. Benefiting from mild reaction conditions and high yield, the Bingel reaction⁹ was the first chemical reaction performed on N@C₆₀.^{10,11} The most comprehensive previous quantitative analysis of the Bingel reaction⁹ to N@C₆₀ showed a significant electron spin loss (up to 50%) during the synthesis of a fullerene dimer molecule.¹² We have now significantly improved the feasibility of using the Bingel reaction to functionalize N@C₆₀. By controlling the reaction conditions, we have performed two Bingel reactions with minimal spin loss. We propose a possible escape mechanism of the encapsulated nitrogen atom during the reaction, which could explain the spin loss phenomenon observed in previously reported results¹² and guide the synthesis of other N@C₆₀ derivatives in the future.

Crude N@C₆₀ was initially synthesized by ion implantation,¹³ and then purified with the help of high performance liquid chromatography (HPLC),¹⁴ with a final N@C₆₀/C₆₀ molar ratio of 1:700. The concentration was characterized by quantitative EPR and ultraviolet-visible (UV-Vis) spectroscopies, measuring the spin number and the fullerene amount, respectively. With this enriched N@C₆₀ sample, we could acquire an EPR spectrum with excellent signal-to-noise ratio (Fig. 1). The high quality of the EPR spectrum

guarantees the accuracy of spin retention measurements, as the spin number in a sample is proportional to the double integration of the three peaks.

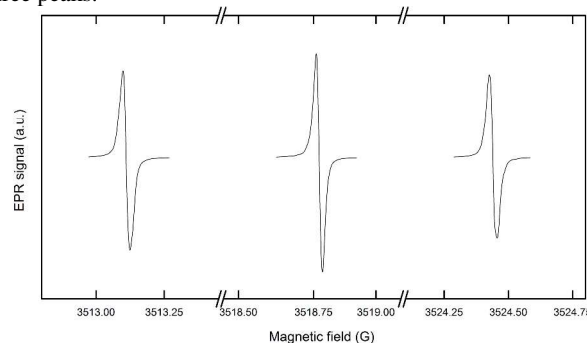
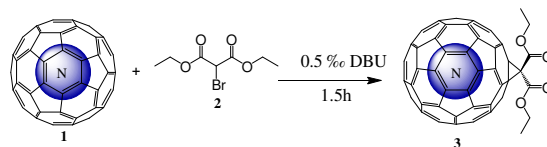
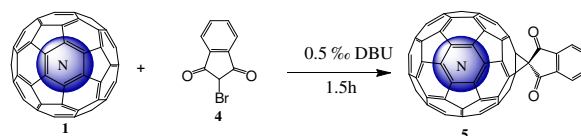


Fig. 1 Quantitative EPR spectrum of N@C₆₀/C₆₀ mixture in toluene solution at 298K (9.862435 GHz frequency, 0.0003170 mW microwave power, 0.0022 G modulation amplitude, 10.00 kHz modulation frequency, 4 scans). In order to demonstrate the line shape of the sharp signal, the field axis is interrupted between the lines.



Scheme 1. Reaction 1



Scheme 2. Reaction 2

Two separate reactions were then performed with the spin-enriched $N@C_{60}/C_{60}$ mixture (**1**) to synthesise derivatives **3** and **5**. For reaction 1 (**Scheme 1**), 0.34 mg of **2** (diethyl bromomalonate 92%, Sigma-Aldrich) were dissolved with 1 mg of **1** in 2.5 ml of toluene, followed by dropwise addition of 0.42 ml of 0.5% DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene 99.0%, Sigma-Aldrich)-toluene solution. The reaction mixture was left for 1.5 hours under argon at room temperature and isolated from light, giving product **3**. Reaction 2 (**Scheme 2**) was done under the same conditions, replacing reagent **2** with 0.32 mg of **4** (2-Bromo-1,3-indandione 90.0%, Sigma-Aldrich). By ignoring the small difference of molar absorptivity among products and pristine fullerene at 320 nm, the yields for reaction 1 and reaction 2 could be estimated to be 59% and 53%, respectively, according to the integral of the HPLC signal (**Fig. 2**). Product fraction **3** was collected directly at 6.2 minutes; **5** was obtained by locking the HPLC in recycle mode for three passes to completely separate the mono-adduct from the bis-adducts, whose peaks originally overlapped (**Fig. 2b**). Common Bingel reaction adducts, such as **3**, tend to elute before pristine fullerene in reversed phase chromatography due to an increase in their polarity; the delayed retention time for **5** may be caused by the additional interaction between the indene-like addend and the stationary phase.

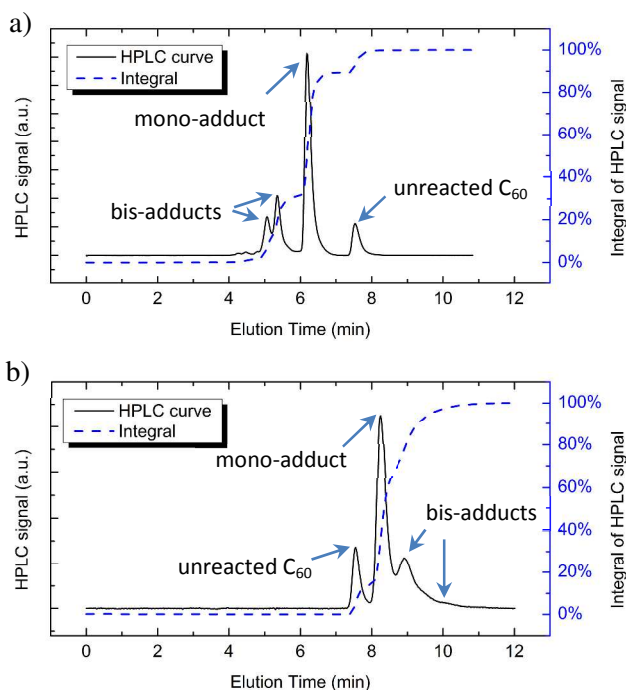


Fig. 2. HPLC charts for the reaction products. Peaks at 6.2 minutes (a) and 8.3 minutes (b) represent the products **3** and **5**, respectively. (toluene, 16 ml/min flow rate, Buckyprep-M 20 mm I.D. x 250 mm column, 312 nm absorption)

The isolated mono-adducts, **3** and **5**, have been characterized by mass spectrometry (MS), UV-Vis spectroscopy and ¹H nuclear magnetic resonance (NMR) spectroscopy and show the expectant structure (see Supporting Information). We further measured the zero-field splitting (ZFS) tensors by fitting the solid state EPR spectra of **3** and **5** in frozen toluene (**Fig. 3**). The ZFS parameters of **3** ($D = 8.4$ MHz, $E = 0.36$ MHz) were consistent with those in a previous work¹⁰. Meanwhile, we report the ZFS parameters ($D = 8.9$ MHz, $E = 0.57$ MHz) for **5**, herein, for the first time. The similar ZFS parameters for **3** and **5** can be attributed to their having the same C_{2v} symmetry and similar functional groups.

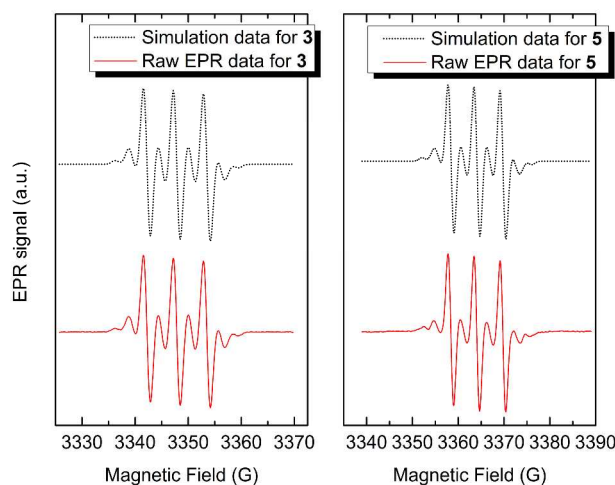


Fig. 3. Left: Solid state EPR spectrum of **3** in frozen toluene (77K, 9.3799 GHz) and its best fit with $D = 8.4$ MHz, $E = 0.36$ MHz; Right: Solid state EPR spectrum of **5** in frozen toluene (77K, 9.4280 GHz) and its best fit with $D = 8.9$ MHz, $E = 0.57$ MHz (Both simulations were done by EasySpin¹⁵)

The spin retention ratio of the reaction is an essential parameter as the loss of the EPR signal represents the escape of the encapsulated nitrogen atom, and the resulting decomposition product can no longer act as a qubit. In order to monitor the loss of EPR signal throughout both reactions, a series of 0.2 ml aliquots were taken from the reaction solutions to perform quantitative EPR analysis at 0, 10, 20, 40 and 80 minutes after the start of the reaction, respectively. All tested samples were injected back into the reaction vessel to minimize the effect on reaction-mixture concentration. Since the reactors are sealed and no solvent evaporated, the volumes of each solution before and after the reaction were found to be equal, meaning all measured samples were of equal concentration and, therefore, directly comparable. According to the spin number evolutions (**Fig. 4a**), nearly all of the spin signal was retained (94%) during both reactions, which substantially surpassed that of the well-reported Prato reaction for the functionalization of $N@C_{60}$ (having a spin retention ratio of 73%¹⁶–79%⁶). Therefore, the Bingel reaction conditions reported in this work are highly suited for the synthesis of $N@C_{60}$ dimers and oligomers for application in scalable quantum information devices.

To further understand the observed high spin retention ratio and possible side-reactions causing spin loss, we investigated the influence of the reaction conditions and found that the spin retention ratio is highly dependent on two parameters. One is the molar ratio between the DBU catalyst base and the halomalonate; the other is the concentration of DBU added. This was confirmed by repeating reaction 1 (**Scheme 1**) with excess DBU and non-diluted DBU, respectively, and comparing their spin number evolutions (**Fig. 4b**). A significant spin loss (60%) appeared on addition of a fourfold excess of DBU, while only 6% of the spin signal was lost under the stoichiometric condition. Furthermore, the decreasing spin signal kept its downward trend after the main reaction finished (80% of the spin was lost 80 minutes after the end of the reaction, see Supporting Information). On the other hand, applying pure DBU led to a more rapid decrease in spin signal at the beginning of the reaction (compared with using 0.5% DBU) resulting in a final spin loss of 18%. The extra spin loss due to using concentrated base catalyst can be related to local excesses of DBU arising from uneven and non-global mixing of the reagents in the beginning of the reaction.

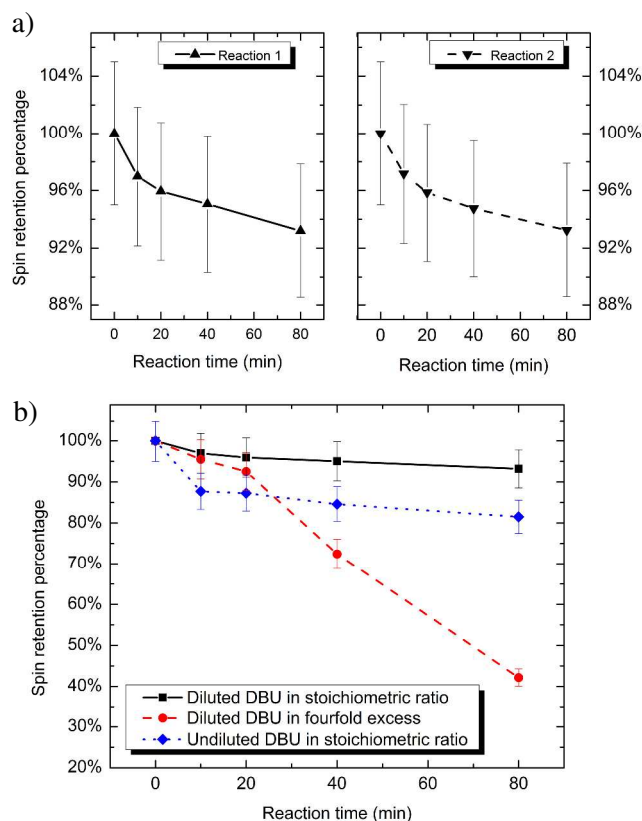


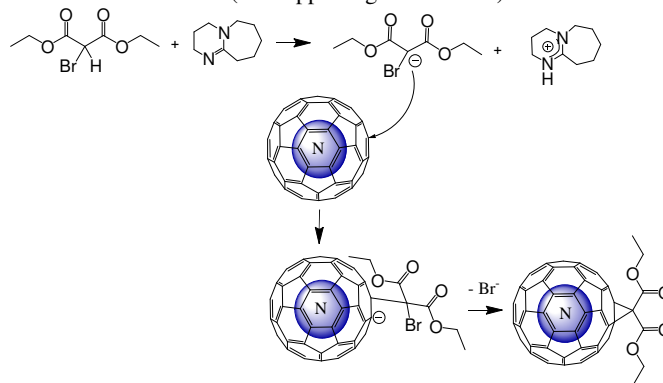
Fig. 4. (a) The spin retention evolutions for reactions 1 and 2, respectively. (b) The spin retention evolution for reaction 1 with differing amounts or concentrations of DBU.

Based on this quantitative analysis, we propose a mechanism to explain the influence of the catalyst on the spin retention. When the molar ratio between the halomalonate and DBU catalyst base is stoichiometric, the reaction proceeds smoothly via the typical Bingel reaction mechanism¹⁷ (Scheme 3), and all DBU converts to its conjugate acid. However, if there is stoichiometrically more DBU than halomalonate (either globally or locally), the excess of base could directly interact with the fullerene or its derivatives to form a dissociated diradical (Scheme 4), which has been reported during a Bingel reaction between empty-cage C_{60} and excess DBU¹⁸, as well as when reacting C_{60} and DBU directly¹⁹. Since the dissociated diradical experiences a long lifetime before finally combining to form a zwitterion and precipitating¹⁹, there is sufficient time for $N@C_{60}$ destabilization to take place during the dissociated diradical stage.

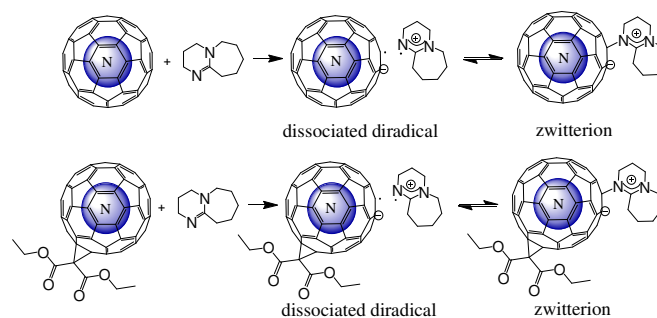
Take the decomposition of $DBU^+-N@C_{60}^-$ diradical as an example (Scheme 5). The procedure is more likely to take place compared to that of pristine $N@C_{60}$, and the reason could be summarized as follows. Firstly, the presence of the dangling bond on the C_{60}^- radical may facilitate the N atom to approach the cage shell from the potential well located in the cage centre²⁰. Secondly, the closed-shell structure of the intermediate for $N@C_{60}^-$ decomposition is electronically more stable than that for pristine $N@C_{60}$. Besides, the smaller steric hindrance during the conformation inversion of the incarcerated N atom²¹ further accelerates its decomposition.

For the DBU⁺-functionalized $N@C_{60}^-$ diradical, we propose that the spin loss mechanism is principally the same, with the functional group having limited influence on the local structure of cage where the decomposition takes place. This similarity could be confirmed by

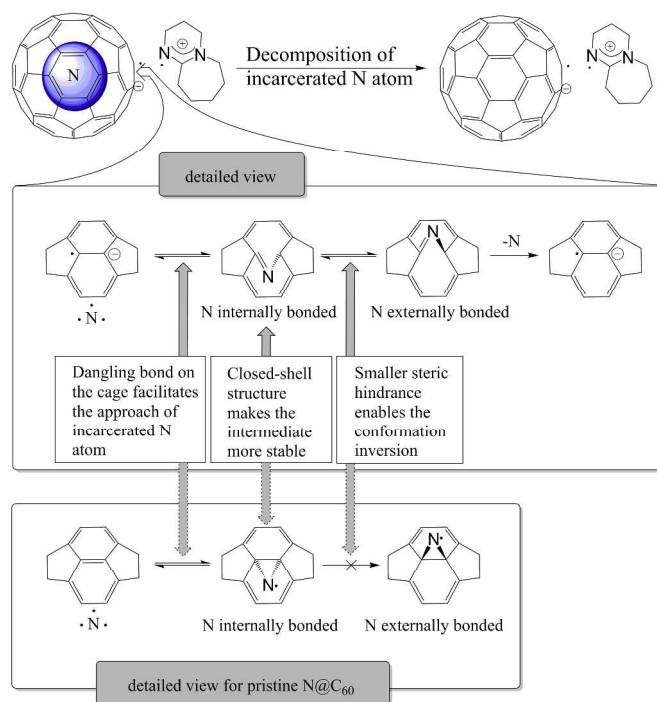
the aforementioned continuous decrease of the spin signal after the main reaction finished (see supporting information).



Scheme 3. The Bingel reaction mechanism involving $N@C_{60}$



Scheme 4. The direct interaction between DBU and $N@C_{60}$ (or its derivatives) forms a dissociated diradical and zwitterion.



Scheme 5. Proposed decomposition pathway for $N@C_{60}^-$ compared with pristine $N@C_{60}$

Hence, we have qualitative proof that the direct interaction between DBU and the nitrogen-containing endohedral fullerene and its

derivatives is the fundamental cause of the spin loss. As **Fig. 5** shows, the typical spin signal of $N@C_{60}$ was completely suppressed by the broad spin signal of the fullerene anion, after direct reaction with sufficient DBU. Moreover, after conversion of the fullerene anion back to a neutral fullerene with acid, almost no spin signal was recovered, which means the endohedral system has decomposed.

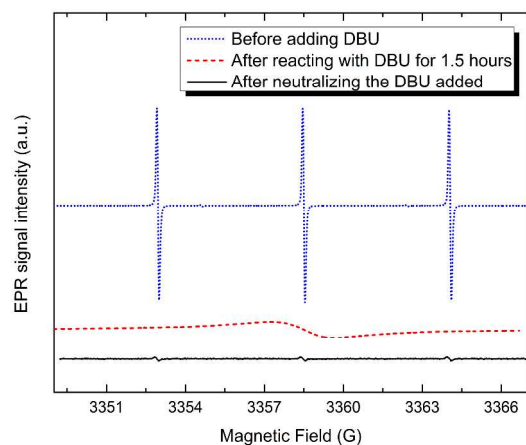


Fig. 5. The significant influence of DBU to the spin signal of $N@C_{60}$.

With the above analysis, the 50% spin loss reported previously during the synthesis of a bisfullerene¹² could now be explained. As the halomalonate was synthesised *in situ* by adding iodine and pristine malonate, the lack of halomalonate at the beginning of the reaction may lead to direct interaction between the catalyst base and endohedral fullerene, thus leading to significant decomposition of the endohedral system.

Conclusions

In summary, we have synthesised two cyclopropane derivatives of $N@C_{60}$ by the Bingel reaction with enriched-purity $N@C_{60}/C_{60}$ starting material. By using diluted and stoichiometric DBU, an electron spin retention ratio of 94% was observed through a series of quantitative EPR measurements for both reactions. This is the highest reported spin retention ratio for any $N@C_{60}$ derivative synthesis to date. Therefore, we believe that the Bingel reaction scheme is a feasible approach to the scaled-up functionalization of $N@C_{60}$. Closer study of the influence of the concentration and amount of DBU used during the reaction suggests a decomposition mechanism for the endohedral system, which explains the spin loss phenomenon observed in the literature and emphasizes the importance of carefully controlling the base catalyst during a Bingel reaction with highly sensitive fullerenes such as $N@C_{60}$.

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Notes and references

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Electronic Supplementary Information (ESI) available: MS, UV-Vis and ¹H-NMR data for products **3** and **5**, the spin number evolution after the end of the main reaction (fourfold excess of DBU catalyst). See

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