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Synthesis of Ar@C_{60} using molecular surgery†

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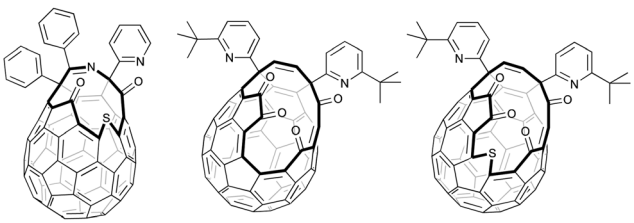
Synthesis of Ar@C_{60} is described, using a route in which high-pressure argon filling of an open-fullerene and photochemical desulfinylation are the key steps for >95% encapsulation of the noble gas. Enrichment by recycling HPLC leads to quantitative incorporation of argon in the product endofullerene, with a mass recovery of tens of milligrams, allowing the first characterisation of fine structure in the solution ^{13}C NMR spectrum.

Endohedral fullerenes (endofullerenes) are substances whose molecules consist of closed fullerene cages (for example C_{60} or C_{70}), each encapsulating a single atom or small molecule.[1] The C_{60} cavity is able to accommodate the noble gas atoms from helium to xenon,[2,3] and the existence of a noble gas endofullerene was first demonstrated when encapsulation of ^{4}He in C_{60} (denoted ^{4}He@C_{60}) was detected from gas-phase neutralisation of $^4HeC_{60}^{+\bullet}$, obtained by collision of accelerated $C_{60}^{+\bullet}$ with helium gas.[4]

Naturally occurring noble gas endofullerenes of extraterrestrial origin have since been detected in meteor deposits.[5] They are materials of great interest for study of their non-bonding intermolecular interactions and the quantum energy level structure of the isolated atom. Encapsulation of the larger noble gas atoms argon, krypton, and xenon leads to electronic and structural distortions of the C_{60} cage – determined by powder diffraction,[6] NMR,[7] IR, Raman and X-ray spectroscopy,[8] variance in the critical temperature of superconducting alkali-doped endofullerenes,[9] exohedral reactivity,[7] and theoretical studies.[8a,10,11] Samples of Ar@C_{60}, Kr@C_{60} and Xe@C_{60} are, so far, obtained from C_{60} by direct encapsulation of the noble gas atom under high temperature and pressure, and typically only 0.2–0.4% incorporation is possible using this method.[3,12] Subsequent removal of empty C_{60} using preparative, recycling HPLC leads to enrichment of the sample (for example, approx. 1.3 mg of Ar@C_{60} has been prepared with >98% purity in several batches with overall yield of <0.1% from C_{60}).[6,9] Although evidence for improved 18% direct encapsulation of argon by laser-vaporisation of C_{60} in the presence of the gas has been reported,[13] there remains no synthetic method to obtain more than ~1 mg of pure Ar@C_{60}, Kr@C_{60} or Xe@C_{60}.

In contrast, larger scale synthesis of ^{4}He@C_{60} (38 mg with 30% ^{4}He filling, enriched to a sample with >95% filling) has been achieved by Komatsu and Murata using multi-step 'molecular surgery', in which an atom or small molecule enters the cavity of an open-cage fullerene whose opening is then sutured to restore the carbon cage around the trapped endohedral species. In their pioneering work, synthesis of H_2@C_{60} as well as ^{4}He@C_{60} was accomplished from open fullerene **1**, by insertion of H_2 directly into **1** and of ^{4}He into the sulfoxide derivative, under high pressure (Fig. 1).[14] The same authors also pioneered the synthesis and orifice-suture of open-cage fullerene **2** in the first reported synthesis of H_2O@C_{60},[15] and we have adapted these procedures for preparation of H_2@C_{60},[16] and HF@C_{60}[17] from **2**.

The orifice of **2** is too small to accommodate argon, but the bigger opening of fullerene **3** permits entry of large guests including methane,[18] and we recently described >95% filling of **3** with CH_4 under >1500 atm of methane at 190 °C, followed



1 2 3

Fig. 1 Open-cage fullerenes **1–3** are key intermediates in the synthesis of He@C_{60} and H_2@C_{60} (from **1**); H_2O@C_{60}, H_2@C_{60} and HF@C_{60} (from **2**); and CH_4@C_{60} (from **3**).

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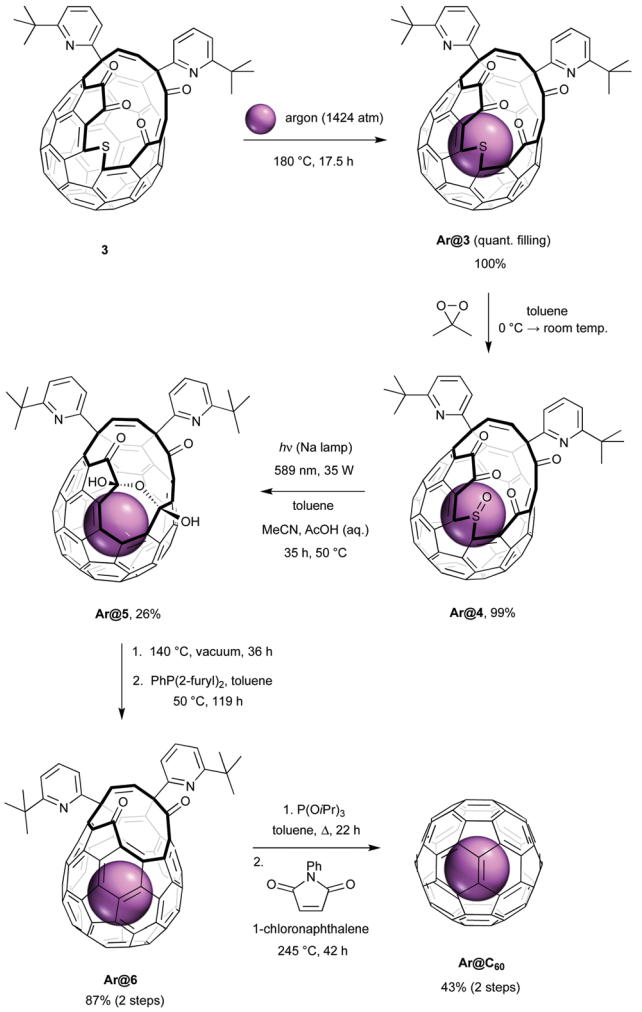

Scheme 1 Synthesis of Ar@C_{60}.

by closure of the orifice of CH_4@**3** to obtain CH_4@C_{60}.[19] Herein, we report that high encapsulation of argon by **3** can be achieved under similar conditions, and closure allows synthesis of Ar@C_{60} with a step-change improvement in argon incorporation, mass recovery and yield when compared to the direct encapsulation method.

Synthesis of Ar@C_{60} was carried out according to the procedures shown in Scheme 1. Fullerene **3** was prepared according to the method reported by Murata, by insertion of sulfur into **2** in the presence of tetrakis(dimethylamino)ethylene.[20] In order to estimate conditions for argon filling, the activation energy for entry of argon into the cavity of **3** was calculated by density functional theory[21] and compared with that of methane. We found a lower barrier to argon entry ($\Delta H^{\ddagger}_{entry}$(Ar) = 55 kJ mol^{-1}; $\Delta H^{\ddagger}_{entry}$($CH_4$) = 86 kJ mol^{-1}) with similar binding enthalpies (ΔH^{bind}(Ar) = −46 kJ mol^{-1}; ΔH^{bind}(CH_4) = −50 kJ mol^{-1}) and anticipated quantitative incorporation of argon under conditions similar to those which gave >95% CH_4 encapsulation. Accordingly, heating powdered **3** at 180 °C under approx. 1400 atm of argon for 17.5 h[22] gave quantitative recovery of Ar@**3**, with argon filling of >99% estimated from the ^{1}H NMR and positive ion ESI mass spectra. Empty open-fullerene **3** is known to rapidly take up water at room temperature[23,24] (endohedral H_2O δ_H = −11.50 ppm in **3**, 300 MHz, $CDCl_3$)[20] yet no resonance corresponding to endohedral water is seen in the ^{1}H NMR spectrum of Ar@**3** in wet $CDCl_3$. Furthermore, no peaks corresponding to empty **3**, or H_2O@**3**, were observed in the high resolution ESI$^+$ mass spectrum of Ar@**3** (ESI†).

Clean and high-yielding oxidation of Ar@**3** with dimethyldioxirane gave the sulfoxide Ar@**4**, and we now applied conditions for photochemical desulfinylation of Ar@**4** that were developed for our synthesis of CH_4@C_{60}.[19] Desulfinylation is the first of the 'closure' steps that suture the orifice of the open-cage fullerene and a similar photochemical ring-contraction by removal of the sulfinyl group (SO) of other sulfoxide open-cage endofullerenes has been reported, using visible-light irradiation in toluene or benzene.[14,25] Photochemical desulfinylative ring-contraction of sulfoxide **4** re-forms fullerene **2** which is unstable under the reaction conditions, but using a vigorously stirred two-phase mixed solvent system of toluene, acetonitrile and acetic acid (10% v/v aqueous) allows *in situ* trapping of **2** as the more stable bis(hemiketal) **5**. Upon irradiation of Ar@**4** for 35 h under these conditions, at 50 °C using a low-pressure sodium lamp, the bis(hemiketal) Ar@**5** was obtained in 26% yield of isolated product. Our previously reported photochemical desulfinylation of CH_4@**4** led to the corresponding bis(hemiketal) CH_4@**5** in only 13% yield under the same conditions,[19] indicating that contraction of the cage-opening is less inhibited by argon, the smaller endohedral species.

Under the mixed (part aqueous) conditions of the photochemical desulfinylation step, the empty open fullerene **4** present in <1% is expected to encapsulate water. In order to avoid contamination of the eventual Ar@C_{60} product with trace H_2O@C_{60}, Ar@**5** was now heated at 140 °C under dynamic vacuum for 36 h. This achieves both dehydration of the bis(hemiketal) to form Ar@**2**, and removal of any endohedral water from the small portion of the material that is not argon-filled. Reduction of Ar@**2** using di-(2-furyl)phenylphosphine was next carried out at 50 °C, a temperature too low for re-entry of water to occur, to give Ar@**6** in 87% yield. Argon filling of >95% was estimated from the high resolution ESI$^+$ mass spectrum of Ar@**6** by comparison of peak intensity for the filled and empty species, m/z = 1111.1691, $[^{12}C_{82}H_{27}ArN_2O_2]^+$ and m/z = 1071.2081, $[^{12}C_{82}H_{27}N_2O_2]^+$. No evidence of H_2O@**6** was found. We assume that the lower argon filling of >95% in Ar@**6** (*cf.* >99% for Ar@**4**) and presence of 3–4% of empty **6** arises from some escape of argon from **4** under the conditions of the desulfinylation, something we did not observe for CH_4@**4**, and reflects the calculated lower barrier to argon loss from **4** ($\Delta H^{\ddagger}_{exit}$(Ar) = 110 kJ mol^{-1}; $\Delta H^{\ddagger}_{exit}$($CH_4$) = 150 kJ mol^{-1}). Loss of argon from **2** in the dehydration step is unlikely ($\Delta H^{\ddagger}_{exit}$(Ar) = 216 kJ mol^{-1}; $\Delta H^{\ddagger}_{exit}$($H_2O$) = 100 kJ mol^{-1}).[21]

Finally, the opening of Ar@**6** was closed under conditions previously reported for the synthesis of H_2O@C_{60},[16] and Ar@C_{60} was obtained with 94.7% filling. Removal of the 5.3% contaminant C_{60} was achieved by recycling preparative HPLC,[6,9,26] to give Ar@C_{60} with 100% incorporation of the noble gas. In this way, we

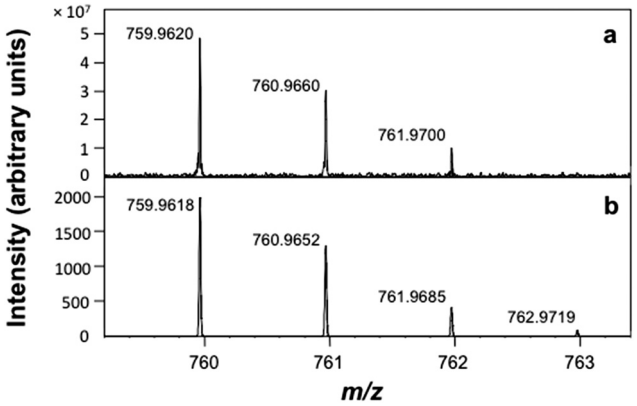

Fig. 2 Positive-ion APPI mass spectrum of Ar@C_{60}. (a) Experimental data and (b) calculated isotope pattern, error −0.2 ppm.

were able to prepare 20 mg of pure Ar@C_{60} in 9.6% yield from fullerene **3**. In our hands, fullerene **3** is obtained from C_{60} in 29–30% using the reported procedures,[15,20,27] so an overall yield of >2.7% Ar@C_{60} is achieved.

The positive-ion atmospheric pressure photoionization (APPI) mass spectrum of Ar@C_{60} is in agreement with the calculated isotope pattern (Fig. 2).

The ^{13}C NMR resonance of Ar@C_{60} was measured with a chemical shift of δ_C = 142.98 ppm in 1,2-dichlorobenzene-d_4 at 298 K, deshielded by $\Delta\delta$ = +0.18 ppm relative to empty C_{60} (δ_C = 142.80 ppm). Dragoe and colleagues have reported a comparable value in benzene-d_6 of $\Delta\delta$ = +0.17 ppm [6,9] and, in the noble gas@C_{60} series, deshielding of the cage ^{13}C NMR resonance with respect to empty C_{60} increases with the van der Waals radius of the enclosed atom: He@C_{60}, $\Delta\delta$ = +0.02 ppm;[14b] Ar@C_{60}, $\Delta\delta$ = +0.18 ppm; Kr@C_{60}, $\Delta\delta$ = +0.39 ppm;[12d] Xe@C_{60}, $\Delta\delta$ = +0.96 ppm.[28] A pair of small side peaks with intensity ratio 2 : 1 is also observed in the ^{13}C NMR spectrum, shifted by −12.50 ppb and −19.86 ppb with respect to the main fullerene resonance (Fig. 3). These peaks are assigned to minor isotopomers of Ar@C_{60} that contain a pair of neighbouring ^{13}C nuclei separated by one bond, and two peaks are observed since there are two types of carbon–carbon bond in C_{60}, either a hexagon–pentagon (HP) or shorter hexagon–hexagon (HH) shared edge, present in a 2 : 1 ratio respectively. The shifts of the side peaks relative to the main peak correspond to one-bond secondary isotope shifts ($^1\Delta_C$ = 12.50 ± 0.01 ppb for the inner HP peak, and $^1\Delta_C$ = 19.86 ± 0.02 ppb for the outer HH peak). These values are slightly smaller in magnitude than those found for empty C_{60} ($^1\Delta_C$ = 12.56 ± 0.01 ppb and $^1\Delta_C$ = 19.98 ± 0.02 ppb for HP and HH peaks respectively) and lie between the values observed for H_2@C_{60} and H_2O@C_{60}.[29]

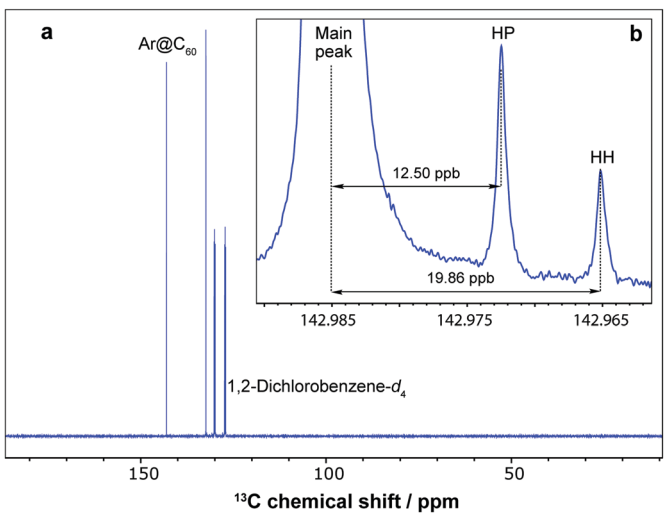

Fig. 3 (a) ^{13}C NMR spectrum of Ar@C_{60} (100% argon filling), 24 mM solution in degassed 1,2-dichlorobenzene-d_4 at a field of 176 MHz and 298 K, acquired with 32 transients. (b) Expanded view of the base of the Ar@C_{60} resonance, acquired at 298 K with 848 transients, to show side peaks arising from minor isotopomers with two adjacent ^{13}C nuclei that share either a hexagon–pentagon (HP) or hexagon–hexagon (HH) edge.

The room temperature infrared and UV spectra of Ar@C_{60} showed no changes in the positions of peaks, compared with C_{60}.

In conclusion we have reported the first synthesis of Ar@C_{60} using molecular surgery, in which high-pressure filling of an open-fullerene and photochemical desulfinylation are the key steps for >95% encapsulation of the noble gas. Further enrichment by recycling HPLC has enabled recovery of the product with quantitative incorporation of endohedral argon, on a scale of tens of milligrams. Our method overcomes the limitation of low mass recovery in the earlier direct encapsulation method and will allow measurement of the energies of the quantised translational modes of the argon atom using IR, THz and inelastic neutron scattering spectroscopy – a sensitive test of current theoretical models of dispersive interactions. The availability of Ar@C_{60} will also facilitate studies of the influence of the endohedral atom upon exohedral reactivity of the fullerene.

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Conflicts of interest

There are no conflicts to declare.

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