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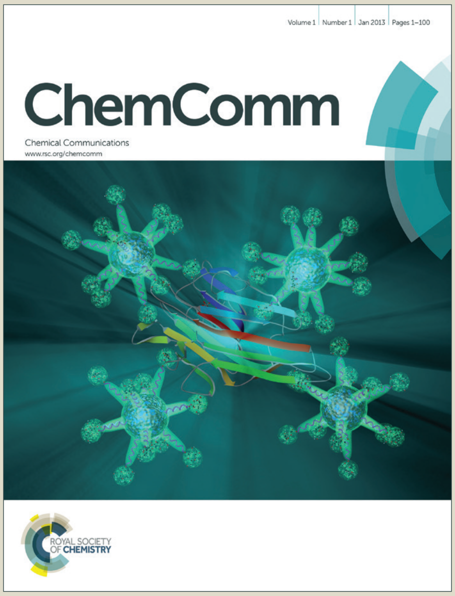

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Synthesis and characterisation of an open-cage fullerene encapsulating hydrogen fluoride†

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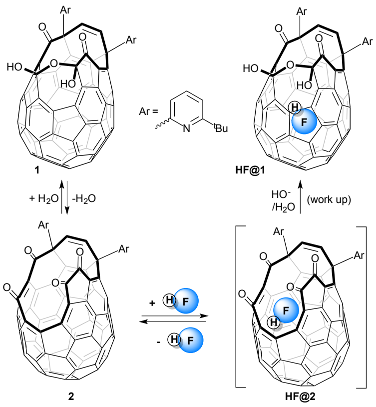
The first encapsulation of hydrogen fluoride in an open-cage fullerene is reported. Solution and solid-state NMR spectra of the novel open-cage endofullerene are described.

Open-cage fullerenes provide the opportunity of trapping atoms and molecules inside an inert three-dimensional environment - a molecular-scale "nanolaboratory".[1-3] Their supramolecular structure makes the study of effectively isolated molecules practically feasible over a wide range of conditions.[4] Physical phenomena such as spin-isomer conversion have been observed inside fullerene cages.[5] The incorporation of the small molecules H_2,[6-10] H_2O,[10-15] N_2,[15,16] CO,[16,17] NH_3,[18] and CH_4,[19] inside the cavity of open-cage fullerenes has been reported. Completion of "Molecular Surgery" to reform the pristine C60 cage has been achieved only for $H_2@C_{60}$,[7,10] and $H_2O@C_{60}$.[10,14] Hydrogen fluoride (HF) is one of the most studied molecules, both theoretically and experimentally.[20] Empirical studies on isolated HF molecules are complicated by its high chemical reactivity and its marked tendency to form aggregates and strong hydrogen-bonds to Lewis bases. Many experiments show the constant presence of oligomers, even in the gas phase.[21] Enclosure in a fullerene would provide a constrained non-coordinating environment for a single molecule of HF and potentially allow novel studies on its spectral properties, particularly at cryogenic temperatures. Although the fully enclosed and symmetric $HF@C_{60}$ structure would be ideal, open-cage fullerene hosts could provide many of the same advantages. Important physical properties such as ferroelectricity have been anticipated for endofullerenes enclosing freely-rotating molecules with an electric dipole moment.[22]

Herein we describe the insertion of HF into the cavity of open-cage fullerene **1**, and the solution and solid-state NMR study of endofullerene **HF@1**.

Density Functional Theory (DFT) calculations gave activation energies of 64.3, 52.2. and 29.8 kJ/mol respectively for the entry of H_2, H_2O and HF into **2**.[23] The lower barrier for the incorporation of H_2O compared to H_2, though surprising, agrees with the experimental evidence[10] (temperatures of 100 and 120 °C are required respectively) and is presumably due to attractive dipolar interactions between the polar molecule and the open fullerene neck. The very low activation energy predicted for the entry of HF into **2** and the possibility of trapping the endohedral HF via hemiacetal formation made **HF@1** a viable target. The calculated binding energy for HF inside **2** (25.9 KJ/mol) and the barrier for the release of HF from **HF@2** (55.7 KJ/mol) suggested that the loss of HF from **HF@2** would be slow at room temperature allowing **HF@1** to form.

The above calculations prompted us to attempt the filling of **2** with HF. Gaseous hydrogen fluoride forms relatively stable polymeric adducts with several organic bases;[24] therefore we selected such compounds as a convenient source of anhydrous hydrogen fluoride. When a solution of tetra-ketone **2** or of its hydrate **1** was treated with a large excess of 70% w/w hydrogen fluoride in pyridine (HF-Py), **HF@1** was isolated after basic work-up and chromatography (Scheme 1).



Scheme 1: Generation of **HF@1** from compound **1**

The filling factor of **HF@1** was established by ^{1}H NMR spectroscopy, comparing the integral values of the endohedral HF proton with the protons on the exohedral groups. The highest filling factor (50%) was achieved by equilibrating a solution of **1** or **2** in dichloromethane with an excess (200 eq HF) of HF-Py at room temperature. In these conditions the equilibrium was reached within 24 hours and prolonged reaction time did not afford a higher filling factor; 50% filled **HF@1** was isolated after work up and chromatography in 89% yield. A larger excess (300 eq HF) of HF-pyr did not increase the filling factor, but a lower excess (100 eq HF) gave only 40% filled **HF@1**. Both compounds **1** and **2** can be used as substrate, as the acidic reaction medium is evidently able to afford the dehydration of **1** to form **2**. The filling at 4 °C proceeded at a much slower rate (~6 days) and did not improve the filling factor. At 80 °C a lower filling factor was obtained, as would be expected for an entropically disfavoured process, and decomposition of the substrate occurred giving 30% filled **HF@1** in slightly lower isolated yield (80%). When the filling was carried out in non-chlorinated solvents such as benzene a biphasic system was formed and the substrate was quantitatively extracted into the HF-Py layer. After work-up and chromatography, 50% filled **HF@1** was isolated in very good yield (88%). The ESI+ MS spectrum of the isolated compounds displays signals at *m/z* 1121 and 1141 respectively for the molecular ions [**1**+H]$^+$ and [**HF@1**+H]$^+$.

Solution state NMR typically reveals unusual chemical shifts for the endohedral nuclei due to the strong magnetic shielding effect of the fullerene cage.[4,25] Indeed the ^{1}H signal from the HF molecule in **HF@1** appears as a doublet centred at δ= -6.55 ppm with a J_{HF} of 508 Hz (Figure 1). This chemical shift is similar to those reported for the endohedral protons of **H_2@1** and **H_2O@1** which resonate at δ -7.17 and -9.84 ppm respectively.[10,14] The large J_{HF} value is comparable to that reported for HF in the gas phase.[26]

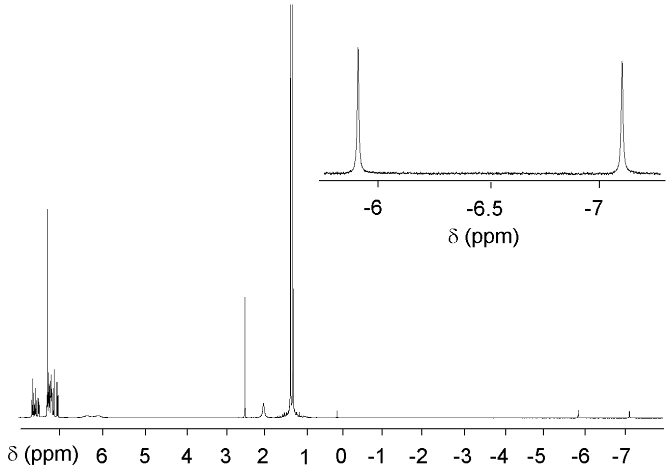


Figure 1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **HF@1**. The δ scale is referenced to $CHCl_3$.

A doublet with a J_{HF} of 508 Hz is present in the ^{19}F NMR at δ -223.91 ppm (Figure 2); the two lines coalesce into a singlet in the proton decoupled spectrum.

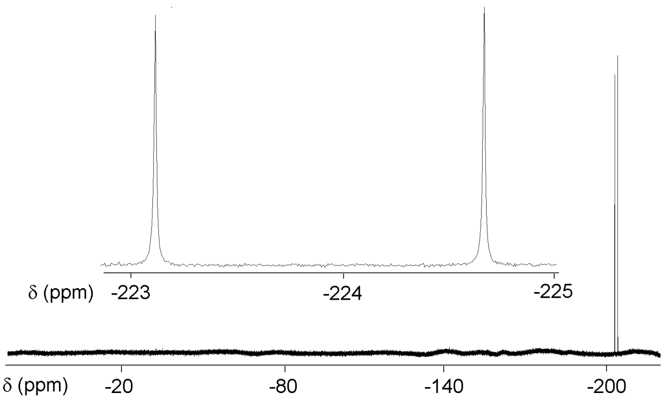


Figure 2: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **HF@1**. The δ scale is referenced to $CFCl_3$.

Solid-state NMR has been used for the characterization of molecular endofullerenes.[25,27,28] The benefits of solid-state NMR include a much larger temperature range, even descending into the cryogenic regime[5] and also the preservation of anisotropic interactions, which are averaged out in solution state NMR, but which contain information on the local structure, dynamics and symmetry. In the case of **HF@1**, the relevant anisotropic nuclear interactions include the chemical shift anisotropy (CSA), which reflects the electronic environment, and the dipole-dipole interaction between the ^{1}H and ^{19}F nuclei of the endohedral molecule.

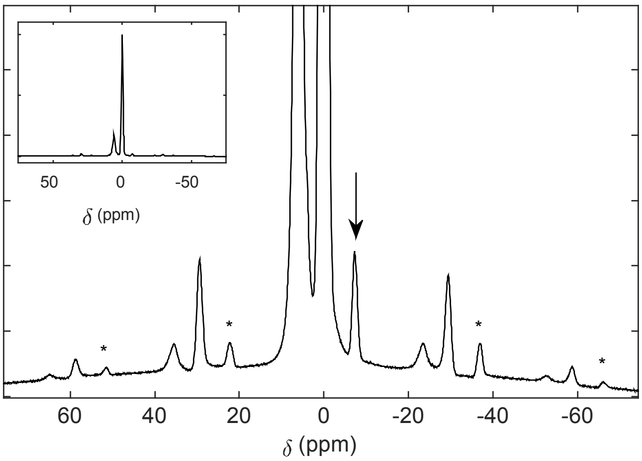


Figure 3: ^{1}H NMR spectrum of **HF@1** recorded at 850 MHz (19.96 T) and a temperature of 263 K. The spinning frequency was 20 kHz. The -7 ppm centre band of the HF resonance is shown by the arrow. The spinning side bands are marked with asterisks.

Magic angle spinning (MAS) may be used to partly average out anisotropic interactions and produce high resolution spectra,[29] which may still reveal the presence of significant anisotropies through spinning sidebands, which appear at multiples of the spinning frequency, and whose intensities are characteristic of the anisotropic interaction parameters.

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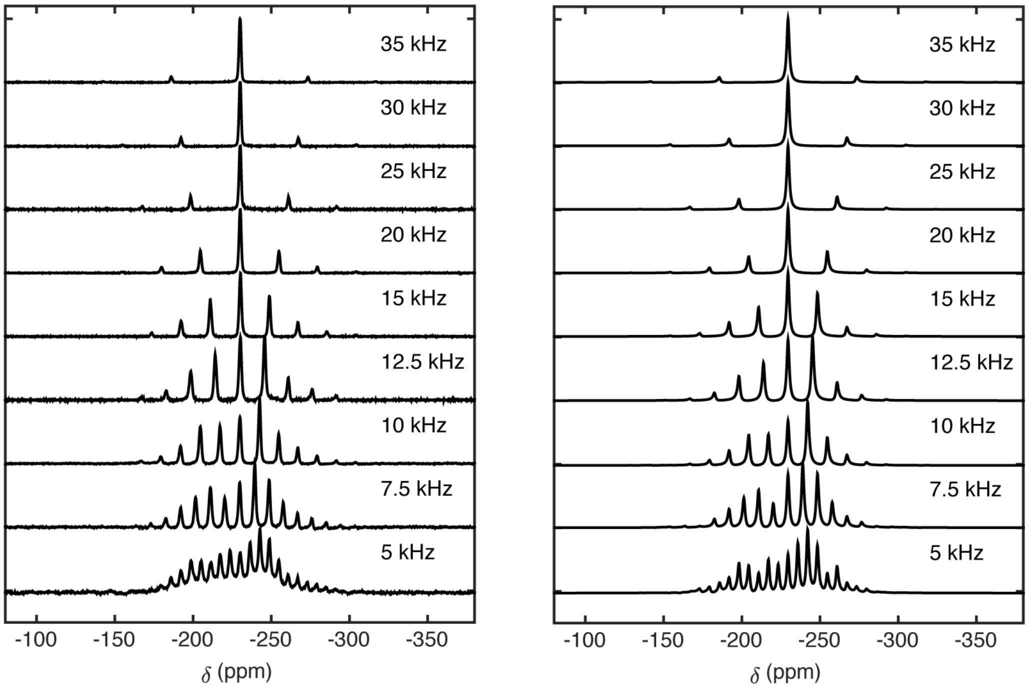

Figure 4: (left) ^{19}F spectra of **HF@1** recorded at 19.96 T and a temperature of 263 K, at the indicated spinning frequencies. The ^{19}F chemical shift scale is referenced to β-Polyvinylidene fluoride (PVDF); (right) Simulated spectra with parameters determined from best fit to experiment. We used SPINACH[30] and SIMPSON[31] for simulations. Details of simulations can be found in supplementary information.

The ^{1}H solid-state MAS spectrum (Figure 3), collected in a magnetic field of 19.96 T (850 MHz for ^{1}H) at a spinning frequency of 20 kHz, displays an intense signal arising from the numerous exohedral protons and narrow peaks from the endohedral HF, reflecting the relatively isolated magnetic environment of the endohedral molecule and its rapid molecular motion inside the cage. This is in agreement with studies on other open-cage endofullerenes.[28]

The ^{1}H chemical shift is -7 ppm in the solid-state NMR spectrum, which is similar to the liquid-state value. The J_{HF} coupling is not resolved in the solid-state NMR spectrum. Spinning sidebands can be seen at multiples of the spinning frequency, 20 kHz.

Magic-angle-spinning ^{19}F spectra of **HF@1** are shown in Figure 4 for a set of spinning speeds. The ^{19}F isotropic chemical shift is observed at –230 ppm.

There are two anisotropic interactions that contribute to the generation of sidebands at low spinning frequencies, namely the dipole-dipole ^{1}H-^{19}F interaction and the ^{19}F CSA. Numerical simulations of the NMR spectra were generated for combinations of isotropic chemical shift, asymmetry parameter, chemical shift anisotropy and the dipolar interaction using both SPINACH[30] and SIMPSON.[31] The direct dipolar interaction was determined to be -7.5 ± 2.5 kHz and the ^{19}F chemical shift anisotropy as 44.1 ppm ± 1.7 ppm, with the biaxiality determined to be 0.6 ± 0.05. The ^{19}F CSA tensor is found to be orientated at (α, β, γ) = (0, 90°, 0) with respect to the dipolar coupling tensor.

The direct dipolar coupling constant for an immobile ^{1}H-^{19}F pair separated by 0.91Å would be -150 kHz. The small value of the observed dipolar coupling therefore indicates that the HF molecule rotates rapidly and almost isotropically inside the open fullerene cage. The second-rank order parameter of the HF molecule, indicating the degree of anisotropy of its rotational motion, is only ~5%.

Conclusions

In this article we report the first HF-endofullerene and its study by solution and solid-state NMR. The solution NMR data shows a large ^{1}H-^{19}F J-coupling of 508 Hz, similar to that obtained for HF in the gas phase. The solid-state NMR spectra indicate that the HF molecule rotates rapidly and almost isotropically in the supramolecular complex. Unfortunately attempts to close the cage to give HF@C60 as reported for H2O@C60[10] resulted in complete loss of HF.

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Notes and references

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† Electronic supplementary information (ESI) available: Experimental procedures, compound characterization data and details of calculations. See DOI: See DOI: 10.1039/c000000x/

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