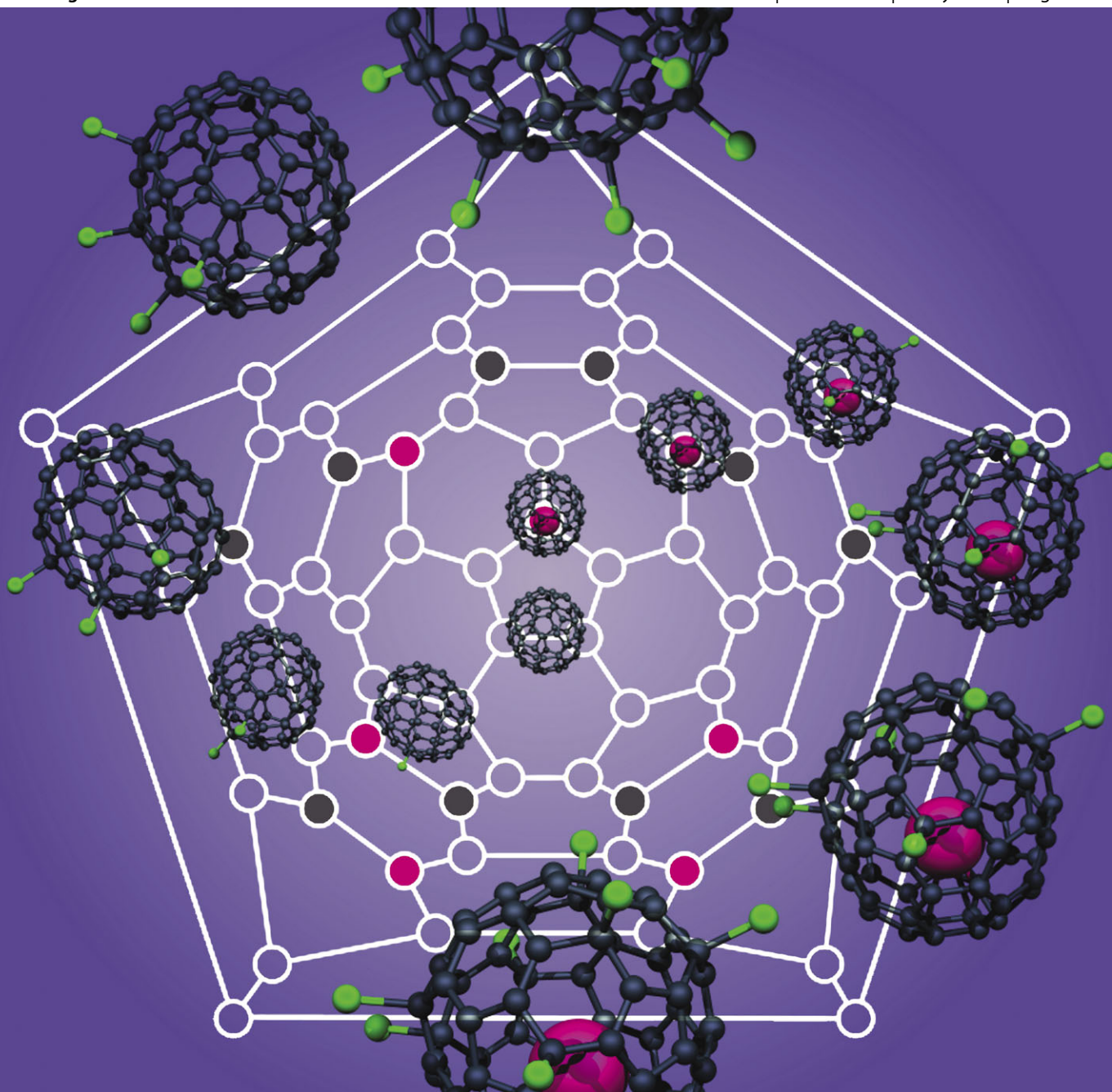


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COMMUNICATION

Controlling fullerene addition sequences, regioselectivity and magic numbers *via* metal encapsulation†Alexis Vlandas,^a Christopher P. Ewels^{*b} and Gregory Van Lier^c

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A systematic density functional study of chlorine addition to C₇₀ up to C₇₀Cl₁₂ confirms experimental observations of regioselectivity and stability of C₇₀Cl₁₀. We show that K@C₇₀ follows an alternative addition sequence with different isomers and magic numbers to C₇₀ such as KC₇₀Cl₃. This prediction is important for controlling functionalisation behaviour *via* encapsulation and endofullerene purification.

Comparative fullerene and endofullerene functionalisation has attracted significant attention in recent years. Studies of the effect of the fullerene cage on the encapsulated species have shown stability increase of LiF inside a C₆₀H₂ cage¹ and a switch from a triplet to quartet ground state of the N atom in N@C₆₀F₂.² Other studies have conversely focused on the impact of the encapsulated species on the chemical reactivity of the fullerene, showing that fullerene reactivity changes upon encapsulation of La₂ and Sc₃N in C₈₀.^{3,4} Changes in the regioselectivity of the first addition reaction for La@C₈₂ with Cp* and AdN₂ have also been studied.⁵ Despite this there are remarkably few theoretical studies available.

Chlorine is recognised as one of the most controllable and versatile fullerene addends, allowing stepwise addition with possibilities of subsequent substitution reactions.^{6,7} A recent detailed experimental study on the chlorination of C₇₀Cl_n⁸ has revealed the existence of $n = 6, 8, 10$ magic numbers and a regioselective addition sequence illustrated by a single, very stable, C₇₀Cl₁₀ isomer. A theoretical study of the sequence of chlorine addition to C₇₀ would be of interest to better understand the synthesis mechanisms of these fullerene adducts. While endofullerene chemistry is expected to be different to that of the parent fullerene, there have been no systematic attempts to quantify this.

Systematic addition pathways for exohedral functionalisation of fullerenes are inherently difficult to tackle theoretically, primarily due to the large number of potential isomers. While mass spectrometry data when functionalising with species *M* can reveal the composition of a given fullerene as C_{*x*}M_{*y*}, assuming a fixed fullerene cage and ignoring symmetry this stoichiometry results in a potential $x!-(x-y)!$ possible isomers. Even reducing this number by symmetry still yields too many isomers, rendering calculations impractical.

The absence of chlorine surface mobility on C₇₀⁸ necessarily implies sequential addition. We recently developed a theoretical approach for systematic analysis of chemical addition (SACHA) especially suitable for studying sequential fullerene functionalisation.^{9–12} In this approach we sequentially chlorinate every available site on the fullerene and take the most stable isomer for subsequent addition. Thus the search is no longer for the total lowest energy isomer of C₇₀Cl_{*n*} but instead the lowest energy isomer that can be formed from chlorination of C₇₀Cl_{*n*–1} which renders the problem tractable using density functional approaches. In this current article we examine the addition sequence of C₇₀Cl_{*n*} chlorinated fullerenes and their related potassium endofullerenes for $n = 1–12$.

All structures are geometrically optimised using density functional theory applied to real space clusters under the local density approximation, using the AIMPRO code.¹³ The method has previously been used successfully to predict amongst other things azafullerene chemistry.¹⁴ Binding energy is defined as the energy difference between the relaxed (K@)C₇₀Cl_{*x*} and the sum of (K@)C₇₀Cl_{*x*–1} and half that of an isolated Cl₂ molecule (see Supplementary Information).

Fig. 1a shows that initial chlorine addition to C₇₀ is favoured at d sites near to the fullerene equator, with binding energy of 9.19 kcal mol^{–1}. The next most stable sites are 2.08 kcal mol^{–1} less stable and are not observed experimentally, and this is thus taken as our cut off energy for regioselectivity.

The Schlegel diagram for subsequent chlorine addition up to $n = 10$ is shown in Fig. 2a, with associated energies up to $n = 12$ in Fig. 3a. The line shows the energetically most favoured path followed by the system. As expected the even numbered additions are significantly more stable than the odd ones due to radical formation for the latter. Chlorine atoms add to d-sites around the circumference in a (1,4) addition sequence until C₇₀Cl₈, at which point the next two

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† Electronic supplementary information (ESI) available: DFT details, second addition pathway Schlegel plot and energetics, magnetisability calculations for C₇₀Cl_{2*x*} ($x = 1–5$), calculated migration barriers for K within KC₇₀Cl_{*x*} ($x = 0–3$), summary fig. showing energetics of Cl addition to C₇₀ and K@C₇₀. See DOI: 10.1039/c1cc11072a

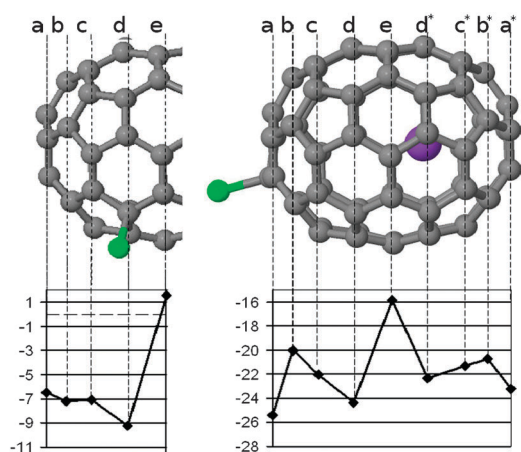


Fig. 1 Addition energies in kcal mol⁻¹ for adding one chlorine atom to C₇₀ (1a) and K@C₇₀ (1b) at all possible symmetry-independent addition sites.

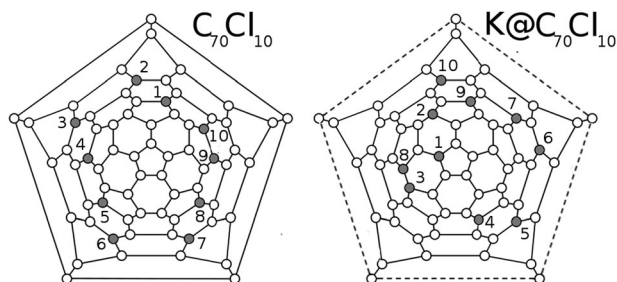


Fig. 2 Schlegel plots of the addition sequence for C₇₀ (a) and K@C₇₀ (b). The dotted pentagon is closest to the K atom.

circumferential d-sites add in a (1,2) pair giving C₇₀Cl₁₀. This sequence matches that proposed experimentally in ref. 15.

Although all (70-*n*) isomers have been calculated at each step we only include in the plot horizontal marks indicating the energy of isomers within 2.08 kcal mol⁻¹ of the most stable form. This shows the extreme regioselectivity of the reaction, since all steps from *n* = 2–10 have no alternative isomers within this energy range. Step *n* = 1 has an alternative isomer at less than this value, but this corresponds only to a change of order in the addition sequence and not to an alternative addition path, as subsequent addition to these brings the system back to the same even numbered isomer as the lowest energy path (see shaded lines for addition 1 in Fig. 3a).

After 10 Cl atom additions the equatorial belt is completed, and the 11th chlorine atom shows significantly weaker binding of only 4.59 kcal mol⁻¹ (since it breaks both symmetry and aromaticity). This suggests that addition will stall at C₇₀Cl₁₀, making this a “magic number” for Cl addition. In addition C₇₀Cl₁₁ has five additional isomers within our energy cut-off. The first of these converges back to the same addition pathway on addition of a 12th Cl atom, but the other four result in new isomer pathways suggesting a loss of regioselectivity at this point in the sequence. Experimentally regioselectivity is seen up to C₇₀Cl₁₀ with further chlorination requiring harsh conditions.⁸ The excellent agreement of our calculations with the detailed experimental observation, showing the same stable isomers and regioselectivity, validates our approach.

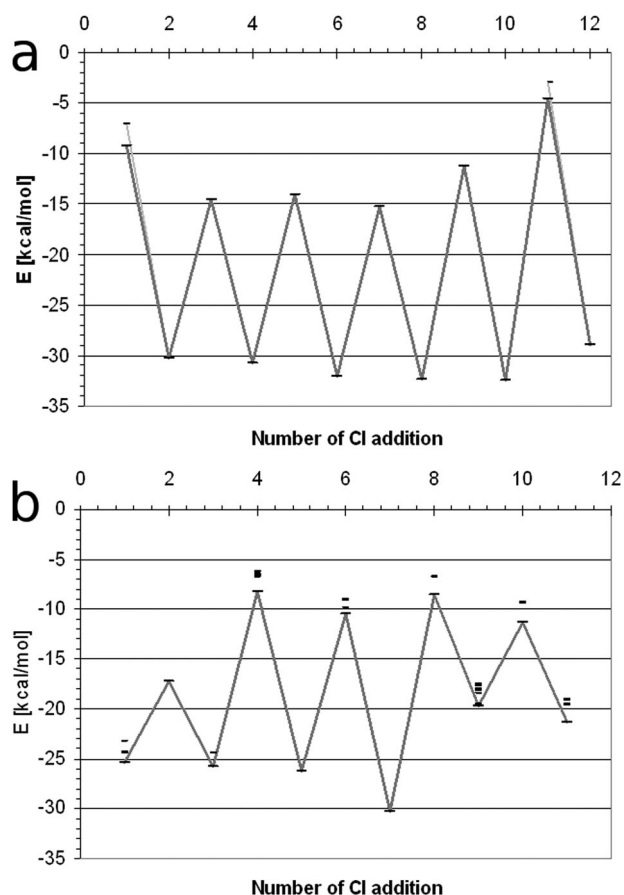


Fig. 3 Energetics of the addition sequences for C₇₀ (a) and K@C₇₀ (b) in kcal mol⁻¹. Shaded lines indicate alternative paths corresponding to a reverse addition order. Horizontal bars indicate energies of all isomers within the 2.08 kcal mol⁻¹ cut-off range.

We now turn our attention to the endofullerene K@C₇₀. After relaxation K sits 1.13 Å off-center along the five-fold fullerene axis. Our nudged elastic band calculations show a surprisingly high barrier of 26.09 kcal mol⁻¹ for the K to switch ends in the fullerene. Mulliken population analysis gives a charge of +0.76 e on the K, the corresponding negative charge distributed over the same end of the C₇₀.

Fig. 1b shows that the K encapsulation breaks the symmetry of the C₇₀, resulting in non-equivalent a,b,c,d positions, now labelled a*,b*,c* and d* on the side of the K atom. The presence of K has a marked effect on the chlorination behaviour of the C₇₀ molecule.

The first difference is that the binding energy of the first Cl atom is 25.39 kcal mol⁻¹, significantly higher than for the parent C₇₀. This is largely due to the electron donation from K, which renders the KC₇₀ cage radical and thus reactive. The result is a parity inversion in the binding energies for the chlorination sequence, with the most stable isomers in the addition sequence now the odd numbered ones (Fig. 3b).

A second difference is the favoured first chlorine addition site is now on the polar pentagon, site a, furthest from the K atom and associated negative charge on the C₇₀. This is a change from the initially favoured position d in the parent fullerene.

Thirdly, there are several isomers within our 2.08 kcal mol⁻¹ cut-off range, suggesting the addition may be less regioselective.

There are 5 equivalent sites, and then only $1.15 \text{ kcal mol}^{-1}$ less stable are the 10 d sites originally favoured for C_{70}Cl . Less stable than the a sites by $2.08 \text{ kcal mol}^{-1}$ are the 5 a* sites, followed by $3.00 \text{ kcal mol}^{-1}$ for the 10 d* star sites. In order to check the addition path regioselectivity we have followed all of these addition sequences.

The addition sequences starting from the less stable d* and a* sites can both be eliminated from further study. The d* sequence converges at $\text{K}@_{\text{C}_{70}\text{Cl}_3}$ onto the same addition sequence as that starting from $\text{K}@_{\text{C}_{70}\text{Cl}}$ at the d-site, and is regioselective to this point. The a* site mirrors that of the a site addition pathway up to $\text{K}@_{\text{C}_{70}\text{Cl}_3}$. This isomer is $11.02 \text{ kcal mol}^{-1}$ less stable than its equivalent 'a' addition path isomer, which can be reached by simply switching the position of the K within the cage. The barrier for this is now only 15 kcal mol^{-1} (see Fig. S2), so we assume the K will switch sites and Cl addition will thereafter follow the a path.

This leaves then two possible addition pathways, commencing either from the a or d site. Following the lowest energy sequence starting from an a-site addition up to $\text{K}@_{\text{C}_{70}\text{Cl}_{10}}$ in Fig. 2b we see that the addition sequence is completely changed as compared to that of the parent C_{70} fullerene. The system tries to balance the conflicting requirements of addition around the equator as for the parent C_{70} with the energetic cost of attaching Cl too close to the excess negative charge on the fullerene near to K.

Addition begins with three (1,4) additions to the fullerene cap, followed by an energetically less favourable ($8.28 \text{ kcal mol}^{-1}$) $n = 4$ addition. It is therefore conceivable that the reaction stops there in mild conditions resulting in a $n = 3$ "magic" number for the endohedral fullerene, $\text{K}@_{\text{C}_{70}\text{Cl}_3}$. This is followed by two pairwise additions at d-sites around the circumference of the cage, for which the binding of the 7th Cl addition is particularly strong ($30.30 \text{ kcal mol}^{-1}$). The 8th Cl is once again much less strongly bound and hence we suggest $\text{K}@_{\text{C}_{70}\text{Cl}_5}$ and $\text{K}@_{\text{C}_{70}\text{Cl}_7}$ should be observable in this addition sequence, with $\text{K}@_{\text{C}_{70}\text{Cl}_7}$ being particularly stable. In general the unstable radical structures (even n for $\text{K}@_{\text{C}_{70}\text{Cl}_n}$) are less stable than their odd alternate equivalents for C_{70} , suggesting addition by this route to $\text{K}@_{\text{C}_{70}}$ will be harder/slower than on the parent fullerene.

The second addition pathway starting from $\text{K}@_{\text{C}_{70}\text{Cl}}$ with Cl attached to a d-site follows that of C_{70}Cl , with occasional alternation in the addition order, and much smaller variation in energy between the even and odd number additions (see Fig. S3). The only exceptions are $\text{K}@_{\text{C}_{70}\text{Cl}_3}$ and $\text{K}@_{\text{C}_{70}\text{Cl}_7}$, which have deeper energy wells and so may be observed experimentally. $\text{K}@_{\text{C}_{70}\text{Cl}_{12}}$ has a Cl binding of only $6.94 \text{ kcal mol}^{-1}$ and hence this addition route for $\text{K}@_{\text{C}_{70}}$ should result in $\text{K}@_{\text{C}_{70}\text{Cl}_{11}}$ as its magic number rather than $\text{C}_{70}\text{Cl}_{10}$ for the parent fullerene. The additional Cl stabilises the radical.

In conclusion, we have systematically studied the addition sequences of chlorine to a C_{70} endofullerene and contrasted it with that of its parent C_{70} . Chlorine addition to $\text{K}@_{\text{C}_{70}}$ is very different to that of C_{70} , the calculations suggesting it will be harder, with different resulting magic numbers and less regioselectivity with at least two competing reaction pathways. The average binding energy per Cl (Fig. S4) to C_{70} starts low

and rapidly increases towards a value oscillating around 21 kcal mol^{-1} , whereas for $\text{K}@_{\text{C}_{70}}$ the trend is reversed, with strongly favoured initial addition, which then tends towards 19 kcal mol^{-1} . Key magic numbers for $\text{K}@_{\text{C}_{70}\text{Cl}_n}$ are $n = 3, 7$ and 11 , whereas for C_{70}Cl_n they are $n = 6, 8$ and 10 .

This approach goes further than simply studying reactivity changes resulting from encapsulation. We are able to show that the initial attachment site of the adduct can be controlled by the encapsulated species. We also predict parity inversion of the stable adduct of $\text{K}@_{\text{C}_{70}\text{Cl}}$ which makes it possible to look for experimental conditions permitting an odd number of adducts to be stably attached to the fullerene. We also give theoretical verification of the recently experimentally observed regioselectivity of C_{70}Cl_n with $n = 1-10$ sequence and the partial loss of this behaviour after K encapsulation.

This study opens up possibilities for new regioselective C_{70} chemistry such as cap vs. equatorial addition or odd vs. even number of adducts by using endohedral relatives of the C_{70} . This could be used as a separation strategy for endohedral fullerenes by providing the ability to separate filled from unfilled just by their addition chemistry.

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