Supporting Information

We note that the authors have available Excel and text files containing tables of the isomer energies obtained at each addition step as described in the text, as well as .xyz format structure files corresponding to these. The quantity of data was too large to be reasonably included here but the reader is invited to contact the corresponding author for copies of these if of interest.

1. DFT Theoretical Calculations details.
2. Migration Barrier calculations for K within $C_{70}Cl_x$, (x=0-3).
3. Schlegel diagram for K@$C_{70}Cl_{12}$ showing the consecutive addition sites when adding the first chlorine atom at a **d** site
4. Summary of energetics of addition reactions.

1. DFT Theoretical Calculations details.

All structures are geometrically optimised using density functional theory applied to real space clusters under the local density approximation, with the AIMPRO code [1]. Hartwigsen, Goedecker and Hutter pseudopotentials are used for all atoms [2]. Atom-centered Gaussian basis functions are used to construct the many-electron wave function with all angular momenta allowed up to maxima l=2, with 12 contracted functions used to describe carbon (approximately equivalent to 6-31G*), and 40 uncontracted functions for chlorine and potassium. Charge density oscillations in partially-filled degenerated orbitals during the self-consistency cycle were damped using a Fermi occupation function with kT=0.04 eV. All structures are charge neutral. The K diffusion barrier is calculated with the nudged elastic band method using 7 images combined with a climbing algorithm. The method has previously been successfully applied for the modeling of fullerenes in various configurations, notably Fullerene-nanohorn interaction [3], N- and P- doping and oxidation of fullerenes [4], and stability and thermal homolysis of solid hydroazafullerene $C_{59}NH$ [5].

We have not corrected for basis set superposition errors (BSSE) since we are primarily considering energy differences between isomers and hence any BSSE should be approximately equivalent in every case. The only place that BSSE may have an effect is in the absolute binding energies if there is any BSSE correction required for the isolated Cl_2, however an extremely complete basis set was employed for the Cl atoms (40 uncontracted functions including polarisation functions, as compared to typically around 12 for a C-44G* basis set) and hence we do not anticipate significant error from BSSE. Harmonic ro-vibrations will lead to negligible correction in the electronic energies for the fullerene since the moment of inertia incorporates a very large mass (and the R^2 term is also very large). Hence they are only of potential importance for the Cl_2 molecule, where even in this case it will only result in at best an extremely small offset in all the results (i.e. the relative energies will not be affected).

2. Migration Barrier calculations for K within $C_{70}Cl_x$, (x=0-3).

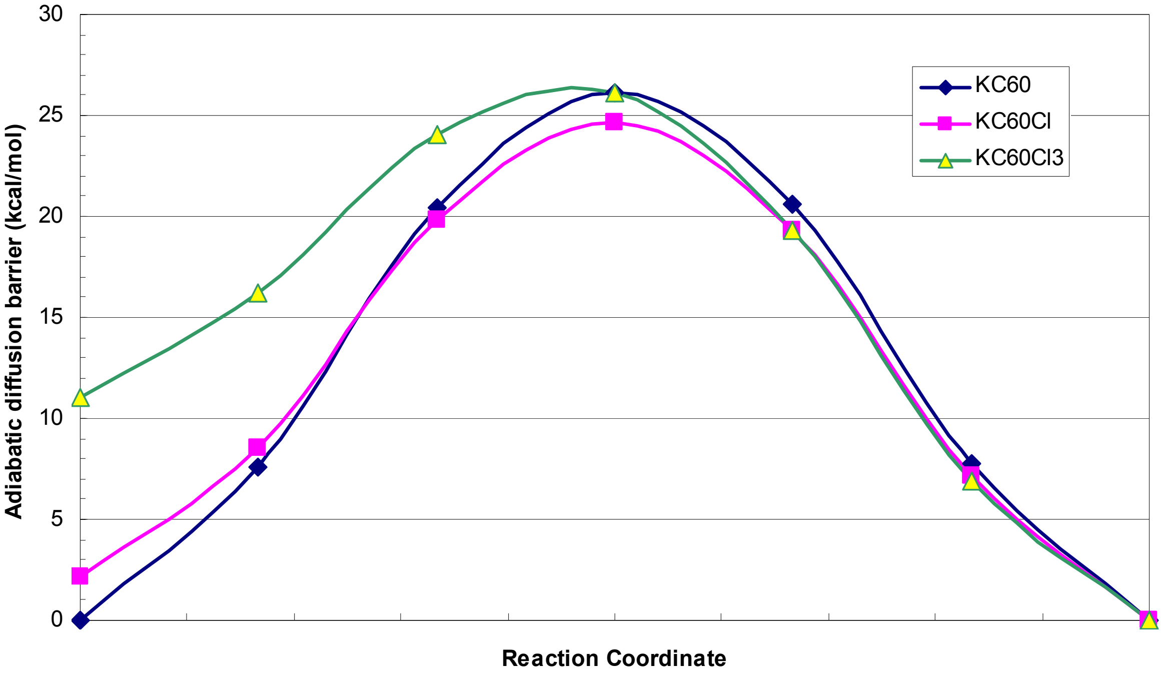

Figure S2. Calculated migration barrier for K within C_{70} between the two off-centre positions, as a function of surface chlorination (following the '**a**' addition route as described in the main text). Barriers have been calculated using the nudged elastic band method combined with a climbing algorithm, showing the barrier for transformation from the $\mathbf{a}^*$-form of $KC_{70}Cl_3$ to the **a** form is only 15.05kcal/mol, as the K site in the $\mathbf{a}^*$ route becomes increasingly unstable with chlorine addition. Lines are simply a guide for the eye.

3. Schlegel diagram for K@$C_{70}Cl_{12}$ site d:

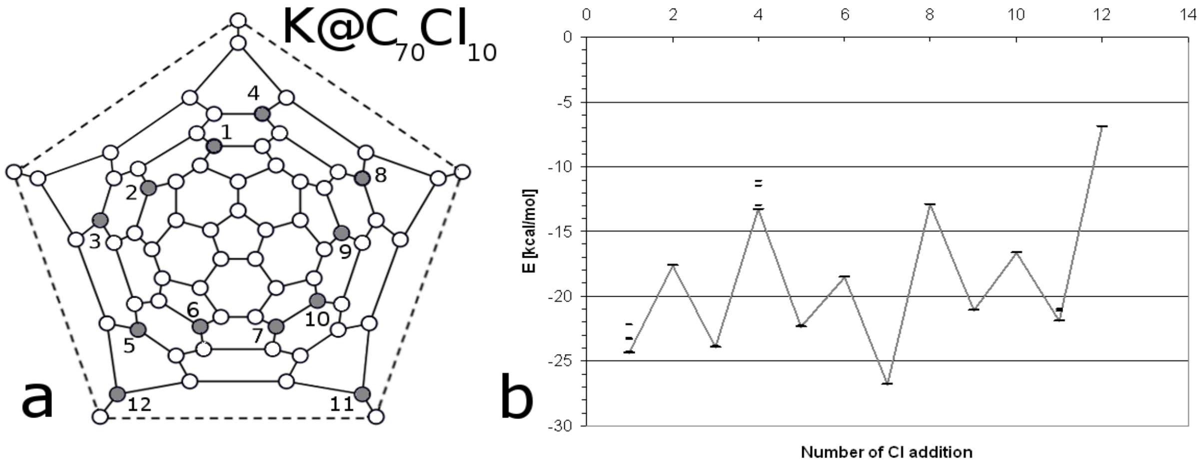

Figure S3. Schlegel diagram for K@$C_{70}Cl_{12}$ showing the consecutive addition sites when adding the first chlorine atom at a **d** site (a) and the corresponding addition energies in kcal/mol (b). The dotted pentagon is the closest to the K atom.

4. Summary of energetics of addition:

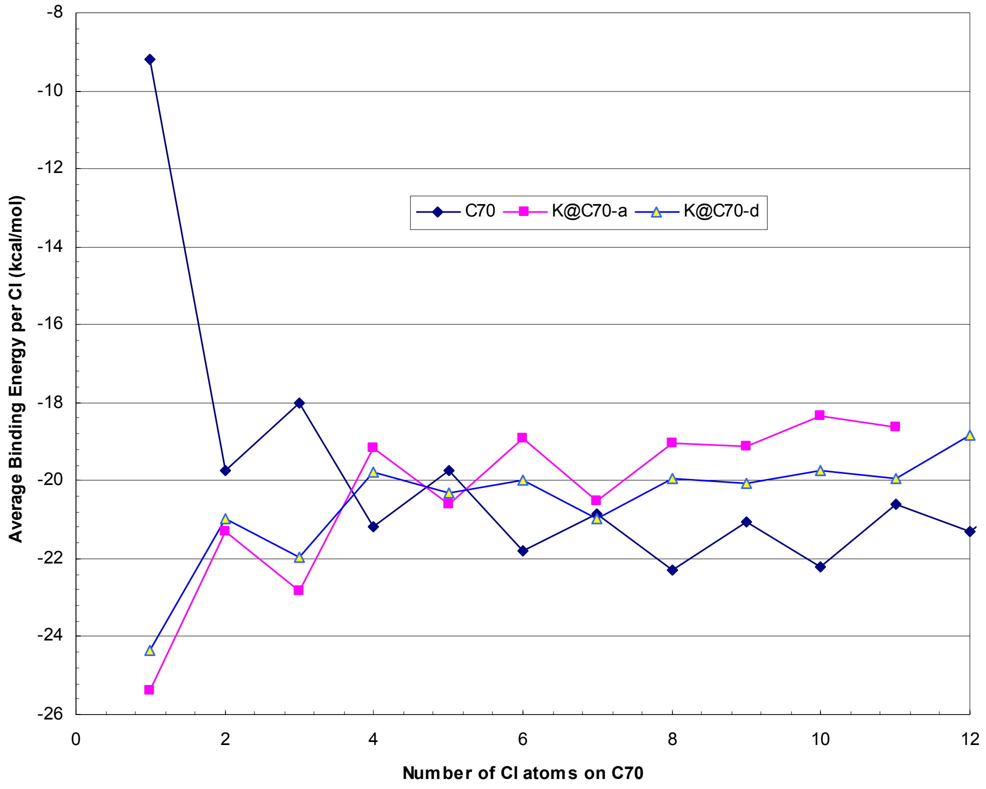

Figure S4. Average binding energy per Cl atom (kcal/mol) for addition to C_{70} and KC_{70} via the a- and d- addition routes. This shows the overall trend that Cl is more stable on C_{70} than KCl_{70}, as well as individual features (such as the inversion in odd/even stability).

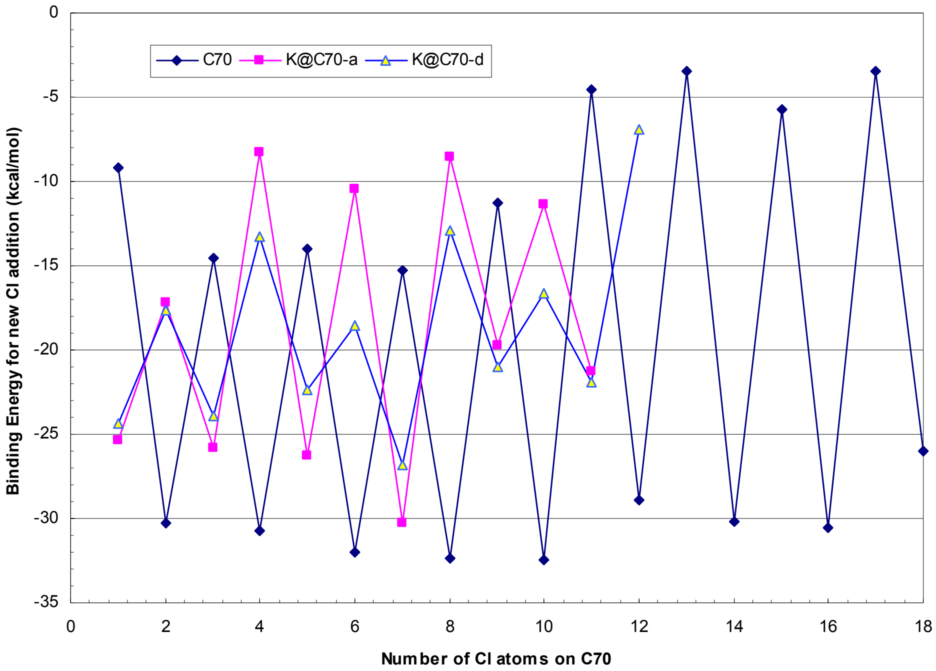

Figure S5. Binding energy for addition of Cl atom Cl_x (kcal/mol) to $C_{70}Cl_{x-1}$ and $KC_{70}Cl_{x-1}$ via the a- and d- addition routes.

References:

1 Rayson, M. H. ; Briddon, P. R. *Comput. Phys. Commun.* **2008**, 178, 128-134

2 Hartwigsen, C.; Goedecker, S.; Hütter, J.; *Phys. Rev. B* **1998**, *58*, 3641.

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4 C. P. Ewels, H. El Cheikh, I. Suarez-Martinez, G. Van Lier*, Phys. Chem. Chem. Phys.* 16, 2145 (2008)

5 D. Arcon, M. Pregelj, P. Cevc, G. Rotas, G. Pagona, N. Tagmatarchis, C. P. Ewels, *Chem. Commun.* 3386 (2007)