Computational method

The calculations reported here were performed using AIMPRO[1], a spin-polarised local density functional supercell code combining a plane wave charge density description (150Ry cut-off) performing a Bloch sum over lattice vectors with a localised atom-centred Gaussian basis to construct the Kohn-Sham wavefunctions. Nitrogen and hydrogen atoms were described using a basis constructed from four Gaussians, multiplied by spherical harmonics up to a maximum angular momentum of l=2 (nitrogen), and l=1 (hydrogen).

Carbon atoms were treated using a contracted Gaussian basis constructed from similar functions with maximum angular momentum three up to l=1, one up to l=2 (final basis equivalent of C44G*). Hartwigsen – Goedecker - Hütter pseudopotentials are used, with 1s electrons incorporated in the core. Matrix elements of the kinetic energy and the pseudopotentials are found in real space while the Hartree and exchange-correlation energies and potentials are found from a Fourier expansion of the charge density. Large hexagonal cells were used (a=14.28Å, c=12.29Å) in order to ensure that the fullerenes were sufficiently far apart to preclude interaction. Given the large cell size, a single k-point was used. Atomic positions were optimised using a conjugate gradient scheme.

CHOICE OF FUNCTIONAL

[1] "LDA Calculations using a basis of Gaussian orbitals", P. R. Briddon, R. Jones, *Phys. Stat. Sol. (b)*, **217** 1, 131-171 (2000).

Experimental Section.

Materials: Solvents and chemicals were purchased from Aldrich and used as received. Column flash chromatography was performed on Merck silica gel 60 (70-230 mesh). High-pressure liquid chromatography (HPLC) was performed on a recycling JAI LC-9101 instrument.

Synthesis: Hydroazafullerene $C_{59}HN$ was prepared by dissolving in *o*-dichlorobenzene the cluster-opened C[60]-N-MEM ketolactam (MEM: methoxy-ethoxy-methyl),[2] followed by degassing with nitrogen and then refluxing with a large excess of *p*-toluenesulfonic acid (100 equiv.) for 7 minutes (Scheme 1).[15] After that period, the reaction mixture was immediately cooled down to room temperature and passed through a short path of silica gel with toluene as eluent. The hydroazafullerene was isolated in pure form by preparative HPLC (Buckyprep column 20x250 mm, 20 ml/min flow rate, toluene eluent, 335 nm detection, retention time 8.19 min.). A typical chromatograph is shown in the Supporting Information section (Figure S1).

Transmission Electron Microscopy (TEM): One drop of hydroazafullerene $C_{59}HN$ (1 mg) either dissolved in toluene or dispersed in carbon disulfide-diethyl ether was placed onto a copper grid (3 mm, 200 mesh, formvar film coated). After drying in air, TEM images were taken on a Philips TEM 208 at an accelerating voltage of 100 kV.

Electron Paramagnetic Resonance (EPR): 3.7 mg of $C_{59}HN$ powder has been sealed into a standard 4mm quartz tube under the dynamic vacuum ($\sim 10^{-5}$ bar). A Bruker E580 EPR spectrometer has been used in combination with a Varian resonator and a homebuilt high-temperature unit for high-temperature EPR experiments. The thermal stability was better than ±0.5 K over entire temperature range. A standard sample in the second resonator has been used to correct the EPR intensity for the possible changes in the resonator quality factor.

Figure S1

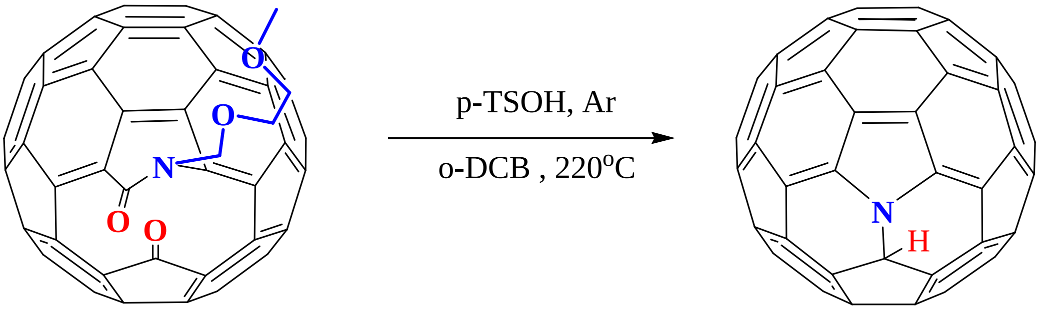


Figure S2

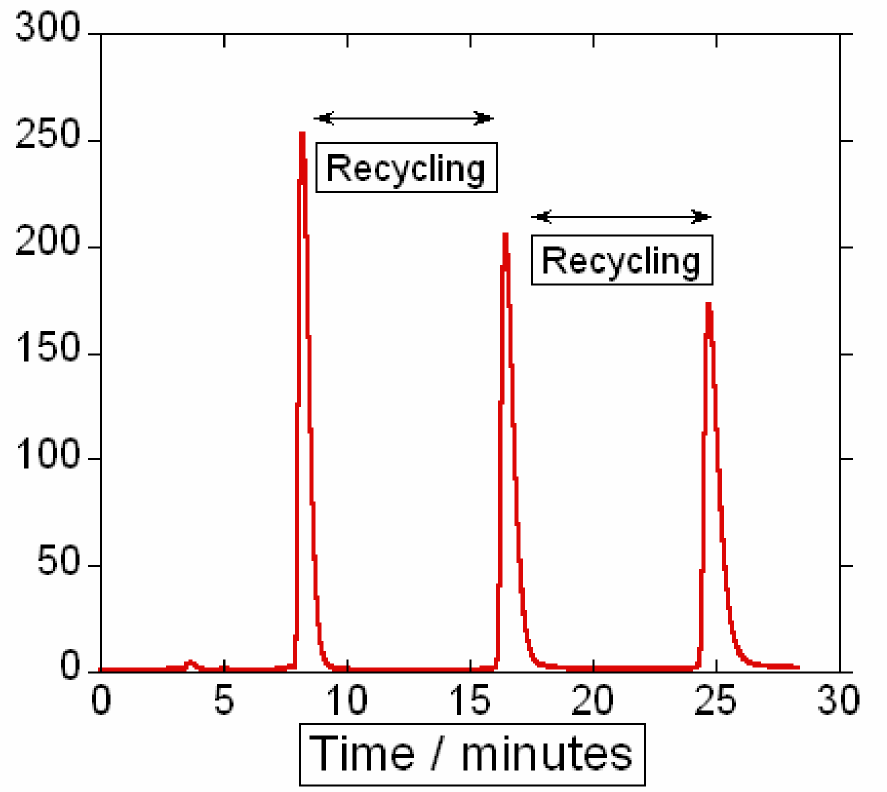
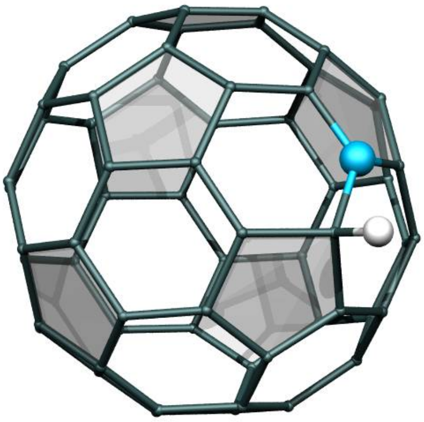
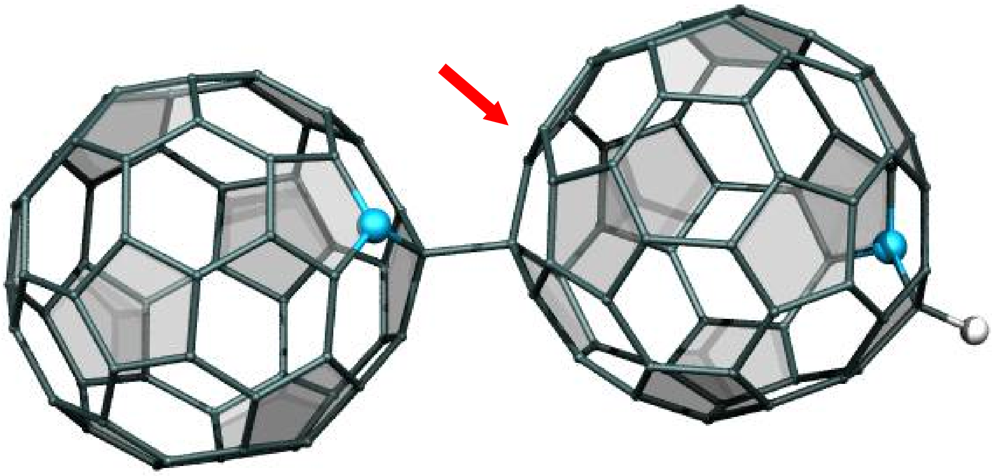


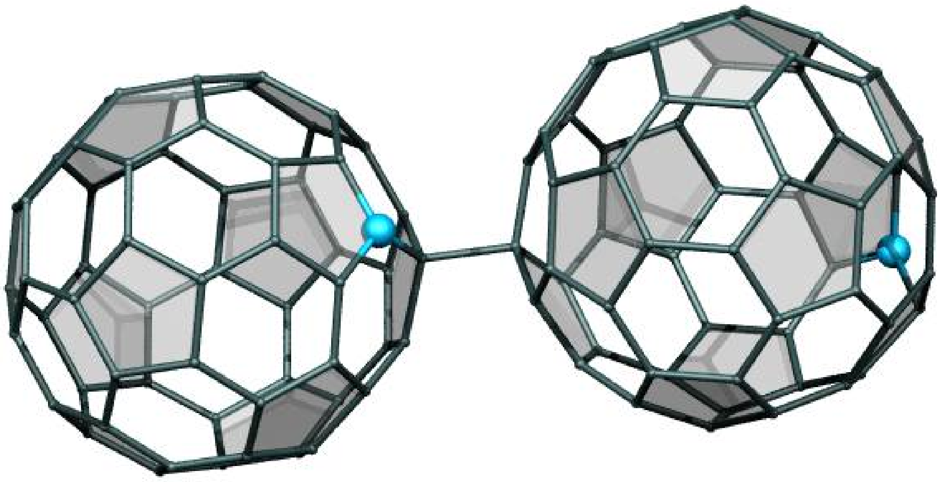
Figure S3



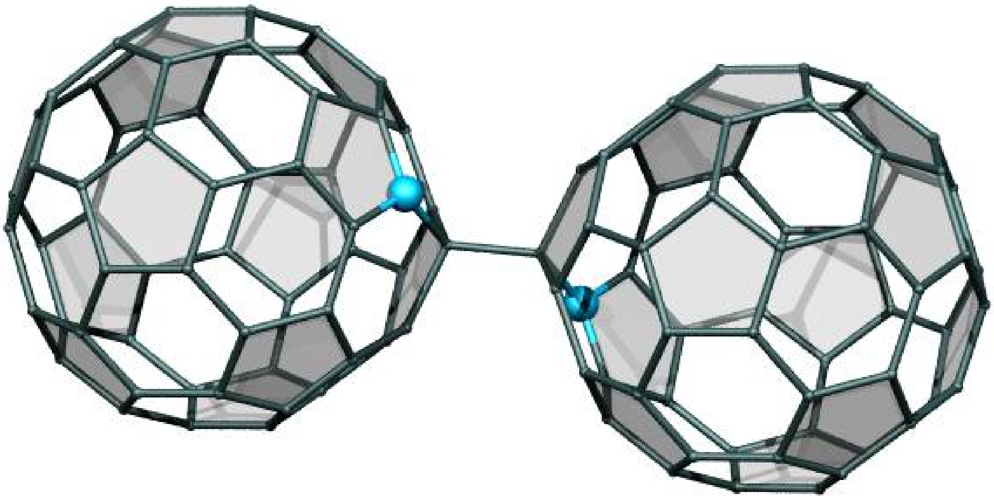
(a) $C_{59}HN$. The nitrogen atom is shown in blue, hydrogen atom in white, pentagons are shaded. The associated radical $C_{59}N$, has the same structure without the hydrogen atom, with the resultant unpaired spin primarily located on the carbon atom currently bonded to the hydrogen.



(b) $C_{59}N$-$C_{59}HN$. When (a) $C_{59}HN$ loses a single H atom, the resultant $C_{59}N$ radical bonds to a neighbouring $C_{59}HN$ fullerene. The unpaired spin is primarily localised on the carbon atom indicated by a red arrow.

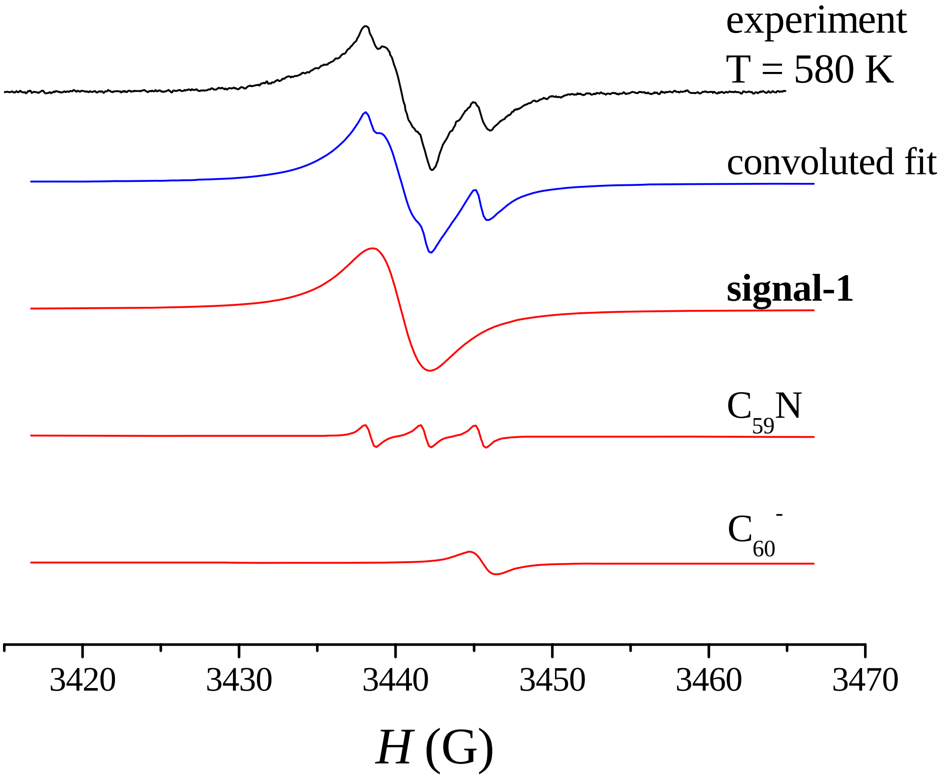


(c) Metastable form of $C_{59}N$-$C_{59}N$. When (b) loses its remaining hydrogen atom.



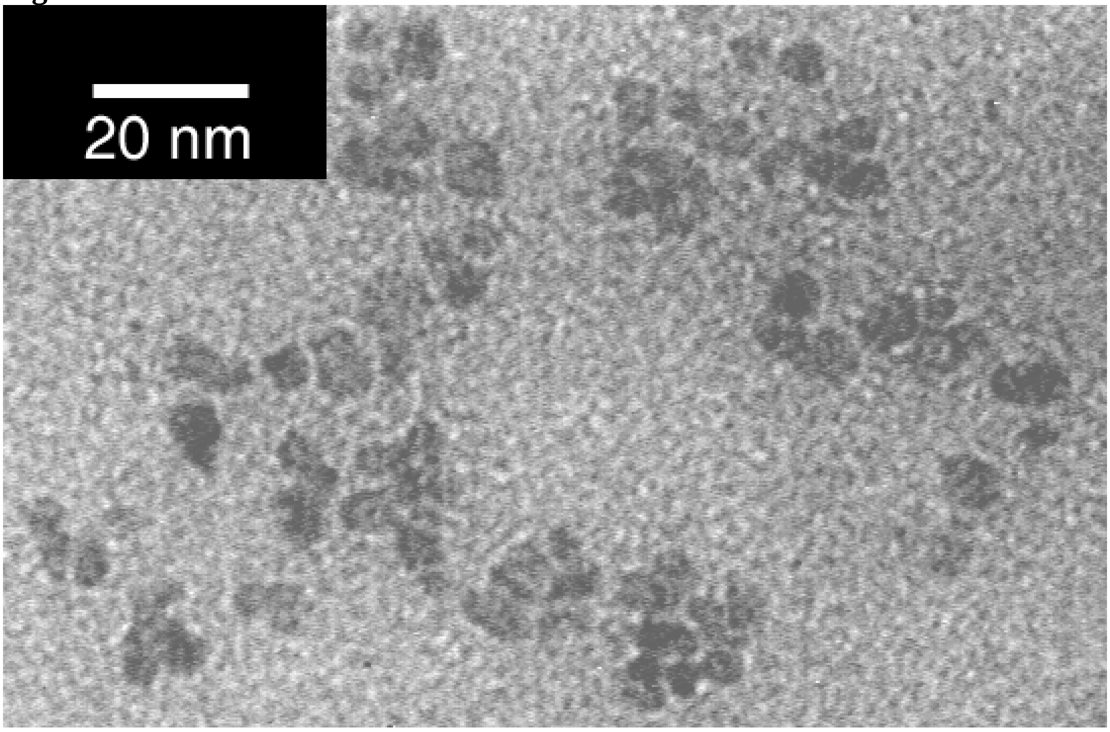
(d) Stable form of the bisazafullerene $C_{59}N$-$C_{59}N$ dimer, 6.7 kcal/mol more stable than (c).

Figure S4.



Representative experimental EPR spectrum measured at 580 K, a fit of the spectrum, and the three components, i.e. **signal-1**, $C_{59}N$ signal and C_{60}^{-} used for the spectral fitting.

Figure S5.



Representative TEM image of hydroazafullerene $C_{59}HN$ material from a toluene solution showing the self-assembled formation of well ordered spherical aggregates.