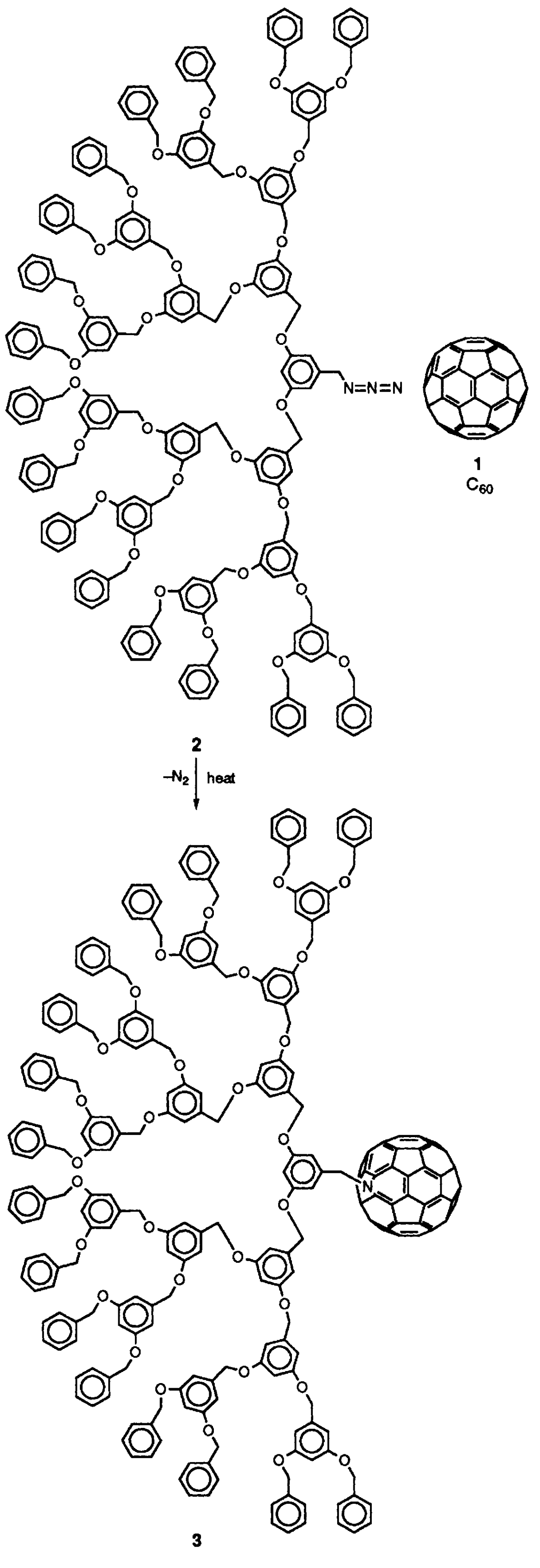
Dendritic Fullerenes; a New Approach to Polymer Modification of C_{60}

Craig J. Hawker,*[a] Karen L. Wooley[b] and Jean M. J. Fréchet[b]

[a] *IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, USA*
[b] *Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York, 14853, USA*

A new route for the preparation of polymer modified fullerenes by the cycloaddition reaction of azides is demonstrated and the physical properties of the dendritic fullerene obtained show influences from both the parent dendrimer and C_{60}.



In the space of three years since the first publication of a method for producing macroscopic quantities of fullerenes an enormous amount of interest has been created in these closed-cage carbon allotropes.[1,2] Recently, study of the chemical reactivity of fullerenes, particularly C_{60}, has grown rapidly. Although a variety of nucleophilic and cycloaddition reactions have been shown to occur,[3] only a limited number of such reactions have been applied to the preparation of polymer modified fullerenes[4–6] even though this may lead to novel materials which are more readily processed and where the fullerene moiety is encapsulated by an insulating polymeric layer. To explore further this concept we report the preparation of fullerenes modified by direct reaction of dendritic macromolecules. Dendritic macromolecules are themselves an area of increasing interest[7] and their choice as the polymeric fragment was due to their globular three-dimensional structure, which may lead to greater encapsulation, and the ability to prepare monofunctional, monodisperse materials of known molecular mass.

Previously, polymer modification of C_{60} has been by the uncontrolled addition of either amino or organolithium functionalized linear polymers[4] to C_{60} or by the reactions of pre-functionalized fulleroids.[5,6] Here we describe the preparation of dendrimer modified C_{60} by the controlled one-step cycloaddition reaction of a dendritic azide with C_{60} **1**. Owing to availability, the dendrimer chosen was the terminally deuteriated fourth generation azide, D_{112}-[G-4]-N_3 **2** (M_r 3429 amu), which was prepared by reaction of the corresponding bromide with sodium azide in dimethylsulfoxide. Under similar conditions to those reported[8] for the reaction of C_{60} with organic azides, the azide **2** was heated at reflux with C_{60} **1** (2 equiv.) in dry chlorobenzene for 24 h. After purification by flash chromatography eluting with toluene followed by dichloromethane the monoaddition product **3** was obtained in a 68% yield (Scheme 1).

Confirmation of the hybrid dendrimer–fullerene structure of **3** was by a variety of techniques. Size exclusion chromatography gave a single peak at essentially the same elution volume as the starting dendrimer **2**, however, **3** was easily distinguished from **2** by TLC. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectroscopy showed the disappearance of resonances for the benzyl azide group at the focal point and the appearance of peaks at δ 4.59 and 54.57, respectively (CH_2N) as well as a set of 32 peaks in the aromatic region between δ 133 and 148 (fullerene nucleus) (Fig. 1). No relaxation agents were used in either the ^1H or ^{13}C NMR experiments. These peaks correspond to the open annulene structure of a monosubstituted C_{60} azafulleroid and agree closely with the results of Prato and Wudl.[8] Further confirmation of the hybrid dendrimer–fullerene structure was obtained from the IR and UV–VIS spectra of **3** which were found to contain absorbances due to both the dendrimer and fullerene fragments. As expected the multi reduction pattern of a fullerene was observed, however, the first three reduction waves in the cyclic voltammogram of **3** occurred at lower values than those reported[5,9] ($E_{1/2} = -0.65$, -1.05 and -1.50 V *vs.* Ag/AgCl/3.8 mol dm^{-3} KCl) and may reflect the insulating influence of the globular dendritic macromolecule (Fig. 2). The dendritic fullerene **3** proved to be extremely soluble in a variety of organic solvents, unlike C_{60},[10] and was found to have a glass transition temperature of 325 K, 13 K

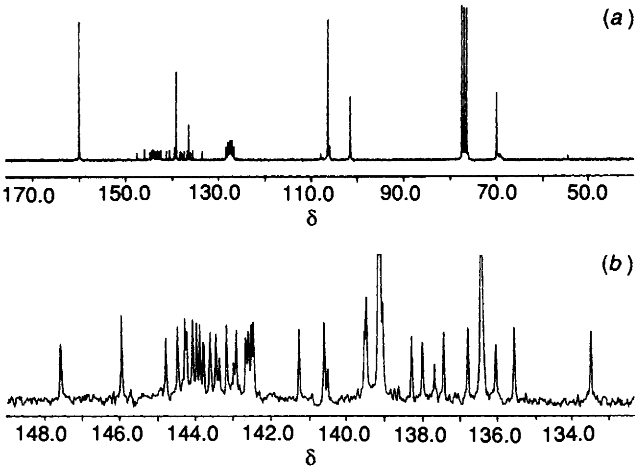


Fig. 1 ^{13}C NMR spectrum of the dendritic fullerene **3** (*a*) with expanded section (δ 133–149) showing resonances due to the fullerene moiety (*b*)

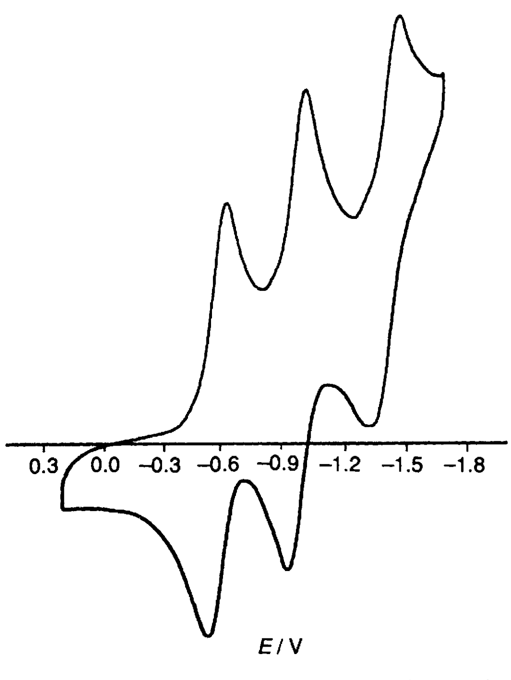


Fig. 2 Cyclic voltammetry response of dendritic fullerene **3** in CH_2Cl_2 with 0.1 mol dm^{-3} $TBABF_4$ as supporting electrolyte: Pt working and Au counter electrodes; Ag/AgCl, reference electrode; scan rate, 100 mV s^{-1}

higher than the starting dendrimer,[11] indicating the dramatic influence that the dendrimer and fullerene portions have on the overall properties of the hybrid molecule **3**. Thermal stability of **3** was however similar to both the starting dendrimer and C_{60} with 10% mass loss at 425 °C.

The use of dendrimers also allowed the question of multiaddition to be easily explored by size exclusion chromatography since the molecular mass increases by *ca.* 3400 for each dendrimer addition. In the above case the crude reaction mixture contained essentially only the monoaddition product **3** with very little di-addition (*ca.* 5%) and no observable amounts of higher addition products. Significantly, when six equivalents of **2** were used per C_{60} the mono- and di-addition compounds were again the major products (2:3 ratio) with little or no observable higher addition products. This inability to obtain significant tri- or higher-substitution may be due to steric hindrance around the C_{60} nucleus and/or unfavourable electronic considerations after di-addition.

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