

## Easily characterized systems of C<sub>60</sub> grafted on SiO<sub>2</sub>

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**Abstract**—Fullerenes grafted on silica with cleavable anchors give materials that can be easily characterized after thermal/chemical treatment or use as catalysts. Transesterification of an ester linkage leads to detachment of the fullerene moiety from the silica and permits study with standard spectroscopic methods. In particular, UV–vis spectroscopy was proved to be a valuable tool permitting structure analysis and quantitative determination at the same time.

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Since their discovery fullerenes have been envisaged as potential candidates for a number of applications related to energy transfer<sup>1</sup> or photoinduced electron transfer<sup>2</sup> systems. In the field of catalysis, various kinds of reactions have been successfully catalyzed by fullerenes or fullerene derivatives.<sup>3–5</sup> Interest is not limited to homogeneous catalysis but heterogeneous systems have also been studied.<sup>6</sup> Although, fullerenes anchored on silica by grafting lead to well-dispersed materials, structural characterization as well as quantitative determination has proved complicated because of the presence of the large excess of silica.<sup>7</sup> One major difficulty is the quantitative determination of the intact fullerene structures after thermal or chemical treatment.<sup>7</sup>

In this article a new approach is proposed that simplifies characterization of supported fullerenes through controllable detachment of the fullerene moiety from the silica. Introduction of a labile bond linkage that can be easily and quantitatively cleaved under predetermined conditions permits analysis of the fullerene structure in solution. In this way the advantages of the grafting technique (permanent attachment, catalysts with well-

dispersed fullerene moieties) are preserved while at any stage characterization of the fullerene is highly simplified (absence of silica). Thus, now the fullerene structure can be verified with any of the standard spectroscopic methods. In particular, UV–vis is very attractive since it requires exceedingly small amounts and at the same time (i) provides information related to changes in the fullerene structure and (ii) permits an accurate and quantitative determination of the amount of detached fullerene. Both of these aspects are presented in this article.

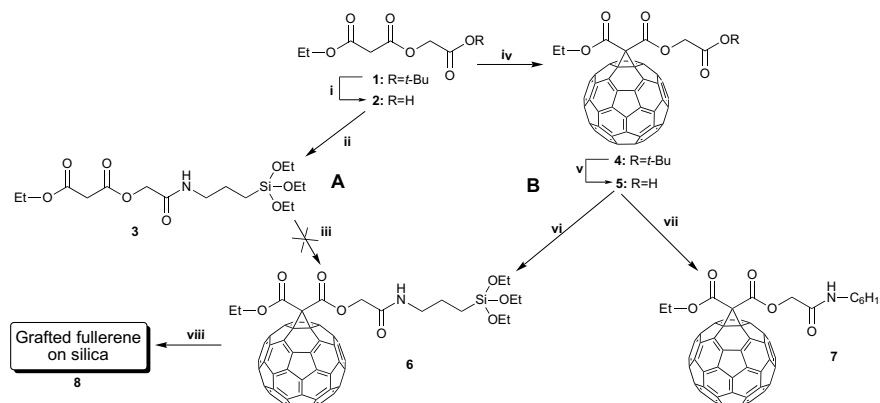
The proposed approach requires that the grafted fullerene should have at least one cleavable linkage. The ester bond was considered as particularly attractive since it can be cleaved under a variety of conditions. However, any protecting group compatible with the fullerene structure can be used for this part. Deprotection will result in cleavage and liberation of the fullerene moiety from the silica. Therefore, the proposed methodology can be easily extended to other systems.

The Bingel reaction was chosen for the functionalization of the fullerene sphere since it is well known<sup>8</sup> and introduces the necessary ester bond in one step. On the other hand, in order to anchor our derivative on silica, we selected the triethoxysilyl group, which has been used in many cases in the past<sup>9</sup> to attach organic molecules (including fullerene derivatives) to silica. The synthetic pathway is shown in Scheme 1.

For the synthesis of the key molecule **6** our efforts focused initially on the pathway **A** (Scheme 1) where, in

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**Scheme 1.** Synthesis of **6**. Reagents and conditions: (i)  $\text{CF}_3\text{COOH}$ ,  $\text{CH}_2\text{Cl}_2$  (yield 75%), rt; (ii) and (vi)  $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , 1,3-dicyclohexylcarbodiimide (DCC), hydroxy-1,2,3-benzotriazole (BtOH),  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C} \rightarrow \text{rt}$  (yields 41% and 69%, respectively); (iii) and (iv)  $\text{C}_{60}$ , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),  $\text{I}_2$ , PhMe (yield of **4** 65%); (v) *p*-toluenesulfonic acid monohydrate ( $\text{TsOH}\cdot\text{H}_2\text{O}$ ), PhMe, reflux (yield 88%); (vii)  $n\text{-C}_6\text{H}_{13}\text{NH}_2$ , DCC, BtOH,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C} \rightarrow \text{rt}$  (yield 62%); (viii) silica, toluene reflux.

comparison to pathway B, the expensive fullerene is introduced at the final step of a series of reactions. In addition, synthetic difficulties due to the limited solubility of some intermediate fullerene derivatives<sup>10,11</sup> are eliminated. Starting from compound **1**<sup>10,11</sup> intermediates **2** and **3** were obtained in 75% and 41% yields, respectively. Unfortunately, it was found that compound **3** could, under none of the conditions tested, give the target molecule **6**; a mixture of unknown products was obtained instead. It is probable that the triethoxysilyl group is not stable under the coupling conditions.

In the alternative pathway B intermediate **1** was attached to fullerene, followed by removal of the protective *tert*-butyl group.<sup>10,11</sup> Thus, compound **5** was isolated as a brown solid in 57% overall yield. Coupling compound **5** with  $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  in dichloromethane successfully gave molecule **6** as a reddish solid in 69% yield. The  $^1\text{H}$  NMR of compound **6** in  $\text{CDCl}_3$  is shown in Figure 1.

Refluxing compound **6** in toluene for 5 h with dry silica, then washing with toluene, THF, 1,2-dichlorobenzene/methanol 2:1 (v/v) and finally diethyl ether gave the target grafted fullerene  $\text{C}_{60}/\text{SiO}_2$  **8**. This procedure leads to grafted material only, excluding the presence of any

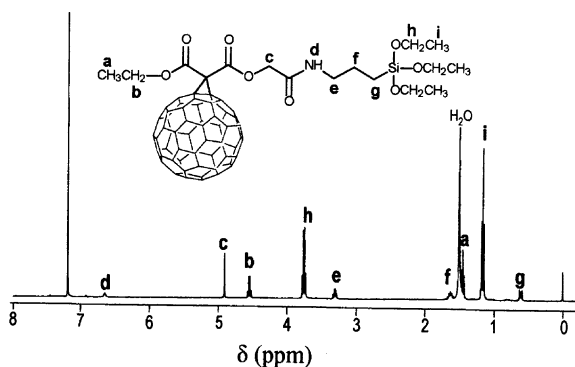
absorbed compound **6** as was confirmed by control experiments with intermediate **4** and model compound **7**. Although, these two compounds contain most of the groups present in compound **6** they can only be absorbed onto silica since the triethoxysilyl group is absent. Their treatment with silica in a similar manner to that of **6** gave brown-red colored silica, as in the case of molecule **6**. However, in contrast to **6**, washing this material with the above solvents quantitatively removed both **4** and **7**.

The grafted fullerene  $\text{C}_{60}/\text{SiO}_2$  was characterized by diffuse reflectance spectroscopy (DRS). The spectrum of grafted material in the area 380–600 nm shows the monosubstituted nature of the grafted fullerene. Indeed, the material synthesized absorbs at 416–430 nm and around 490 nm. Fullerene absorbs<sup>1</sup> at 400–415 nm and around 540 nm, while its monosubstituted derivatives absorb at 420–430 nm and around 490 nm.

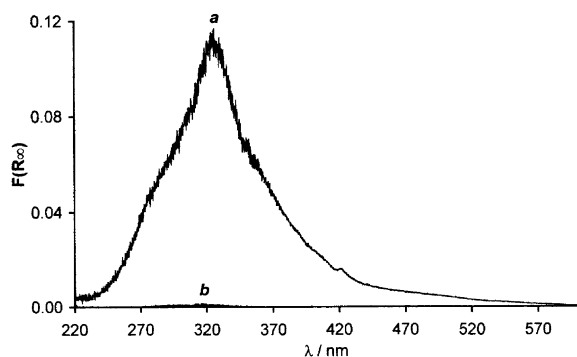
As previously mentioned, the aim of this work was to prepare a grafted material where the fullerene moiety could be cleaved from the silica through a transesterification reaction. In order to test this, a sample of the grafted material was refluxed in methanol with  $\text{H}_2\text{SO}_4$  as catalyst, for 10 h. This period of time was sufficient for complete detachment of the fullerene as depicted in Figure 2.

After reflux a brownish suspension (silica plus precipitated detached fullerene) was obtained, which was filtered and washed repeatedly with methanol to remove the solvent and traces of sulfuric acid. Next, the filtrate receiver was replaced and separation of the detached fullerene derivative was achieved by trituration with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  2:1 (v/v).

Evaporation of the filtrate gave a red film that was characterized by  $^1\text{H}$  NMR and UV–vis spectroscopy. Although  $^1\text{H}$  NMR is of small value in determining changes in the fullerene moiety since the fullerene contains no hydrogen atoms, such measurements can pro-



**Figure 1.**  $^1\text{H}$  NMR spectrum of compound **6** in  $\text{CDCl}_3$ .



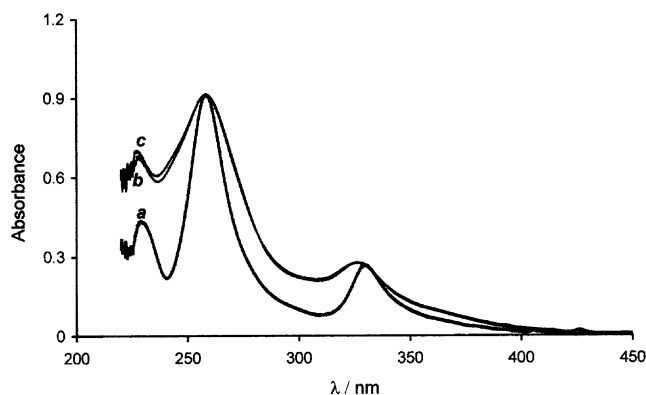
**Figure 2.** DR spectrum of grafted compound **6** on silica, (a) before and (b) after the detachment reaction.

vide information relative to the structure of the organic part after detachment. It was found that apart from the singlet expected for the dimethyl ester of the fullerene derivative of the malonic acid, precipitation immediately after detachment left some ethyl groups present.

UV–vis spectroscopy proved to be far more informative since it can provide information for (i) the monosubstituted character of the fullerene; (ii) the presence of any ‘open’ fullerene structures formed after thermal or chemical treatment since it is known<sup>1,12</sup> that ‘open’ and ‘closed’ fullerene structures show differences in their UV–vis spectra and (iii) the amount of detached fullerene and consequently the percentage of catalyst still present on silica after any treatment. All this information is very important in catalysis and difficult if not impossible to obtain when a large excess of silica is present in the grafted material. In addition, UV–vis spectroscopy requires only a very small amount of compound and so for each analysis only a small quantity of the grafted material is consumed.

In our case, as expected, the UV–vis spectrum of the detached compound was similar to that of a monosubstituted fullerene and different from that of unsubstituted C<sub>60</sub> (Fig. 3).

Also, concentration versus absorption calibration curves acquired by irradiation of solutions of **4** at the two main



**Figure 3.** UV–vis spectra in CH<sub>2</sub>Cl<sub>2</sub> of: (a) fullerene, (b) ester **4** and (c) detached fullerene.

**Table 1.** Linear regression values for curves of compound **4** in CH<sub>2</sub>Cl<sub>2</sub> and molar absorption co-efficients  $\epsilon$

Wavelength (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	[ <b>4</b> ] × 10 <sup>6</sup> (mol L <sup>-1</sup> )	R Value
257	110,500 ± 1000	1.5–8.0	0.99990
326	33,700 ± 200	5.0–28	0.99997

maxima (257 and 326 nm) showed excellent linearity (Table 1). Therefore, the actual amount of the fullerene present was easily and accurately determined to 0.3%.

The catalytic efficiency of the synthesized supported fullerene and analysis results of the fullerene content after a number of catalytic cycles will be published in a forthcoming paper.

In conclusion, in this work a new methodology for the analysis of grafted fullerenes on silica was successfully developed. Its main advantage is that fullerene characterization is simplified through its controlled removal from the silica surface and by solution studies.

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