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Nonchromatographic Purification of Fullerenes via Reversible Addition to Silica-Supported Dienes

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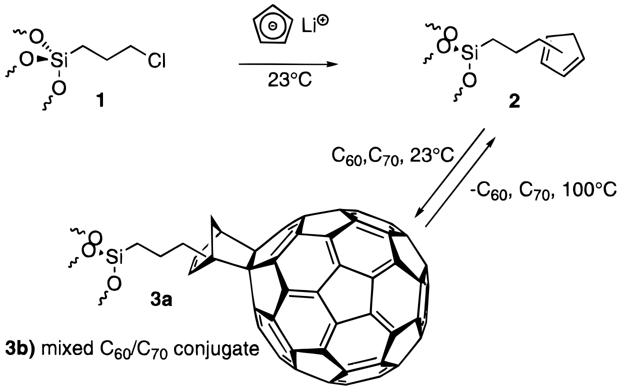
Fullerenes and their derivatives posses a number of potentially useful magnetic,[1] electronic,[2] biological,[3] and chemical properties.[4] One major limit to the exploitation of these properties is the high cost of purification of the fullerenes from each other and from byproducts formed during their synthesis. Current methodologies rely upon chromatographic techniques[5] to purify fullerenes. While these methods are useful for laboratory fullerene production, they are not cost-effective for large scale purification.[6] As an alternative to these procedures, we have examined the use of reversible attachment of fullerenes to solid supports as a means of fullerene purification.

In previous communications, we have demonstrated the reversible Diels−Alder addition of fullerenes with free[7] and polymer-supported dienes.[8] These addition reactions occur at room temperature and are reversible, releasing C_{60} upon heating. To exploit this property for purification of fullerenes, we investigated the use of thermally stable silica-supported dienes. We report here the use of these diene-based materials both to purify C_{60} and C_{70} from other polycyclic aromatics and to provide separation of these individual fullerene species.

Reaction of chloropropyl-functionalized silica gel **1**[9] with lithium cyclopentadienylide provided the cyclopentadiene-functionalized silica gel **2** (Scheme 1). This material reacted rapidly with C_{60} at room temperature (Figure 1) to yield fullerene-substituted material **3a**. Chloropropyl-functionalized silica gel **1**, in contrast, does not absorb C_{60}, ruling out adsorption as the means of C_{60} uptake.[10] Maximal uptake of C_{60} by silica gel **2** was 28 mg of C_{60}/g of silica gel (7.5% of the theoretical maximum).[11] Functionalized silica gel **2** was reacted with C_{60}/C_{70} mixtures in similar fashion (Figure 1) to provide mixed fullerene-functionalized material **3b**: the initial rate of C_{70} uptake was essentially the same as that observed for C_{60} ($k_{C_{60}}/k_{C_{70}} = 1.03$).

Scheme 1



The addition of fullerenes to functionalized silica gel **2** is readily reversible and selective for C_{60}: heating of **3b** in toluene to 100 °C for 5 h releases 93.7% of the bound C_{60} and 41.1% of the bound C_{70} (Figure 2). The release process was fully reproducible, with the fullerenes being completely reabsorbed upon cooling of the solution.[12] The difference in release provides fullerenes significantly enriched in C_{60}: the initial C_{60}/C_{70} ratio was 90:10, the final ratio was 96:4. This selectivity is fully comparable to that observed from a single iteration of the calixarene-based C_{60} purification strategy.[6a]

With reversible binding of C_{60} and C_{70} established, we next examined the application of this process to the purification of fullerenes from other materials. For these studies, we used soot extract from the potentially commercially efficient flame synthesis of fullerenes.[13] Crude soot extract in toluene (Figure 3, trace a) was reacted with functionalized silica gel **2**. The fullerene-containing silica **3b** was washed and resuspended in toluene. Heating of this solution to 100 °C followed by decanting then provided purified fullerene solution, free from non-fulleroid materials (Figure 3, trace b).

In summary, we have demonstrated the reversible attachment of fullerenes to a cyclopentadiene-functionalized silica support. This process has been used to selectively extract fullerenes from extracts of fullerene-containing soot. This material also provides a means of separating individual fullerene species through selective release of C_{60}. Application of this methodology to large scale purification of fullerenes is currently ongoing and will be reported in due course.

Experimental Section

Lithium Cyclopentadienylide. Dicyclopentadiene (6.2 mL, 75 mmol) was heated under argon. Cyclopentadiene was distilled and collected and then added to a flask containing

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(10) Benzyl ether-substituted silica gel (produced via reaction of the sodium salt of benzyl alcohol with chloropropyl-functionalized silica gel **1**) was likewise unreactive toward C_{60}.

(11) The relatively low uptake probably results from cyclopentadiene functions inaccessable to the sterically demanding fullerene reactant.

(12) In contrast to our previously reported polymer, there is no loss of fullerene capacity during repeated use. Additionally, the fullerenes obtained after heating were not contaminated by $C_{60}C_5H_6$. These two observations demonstrate the enhanced stability of the silica gel based material **2** relative to previous polymeric systems.

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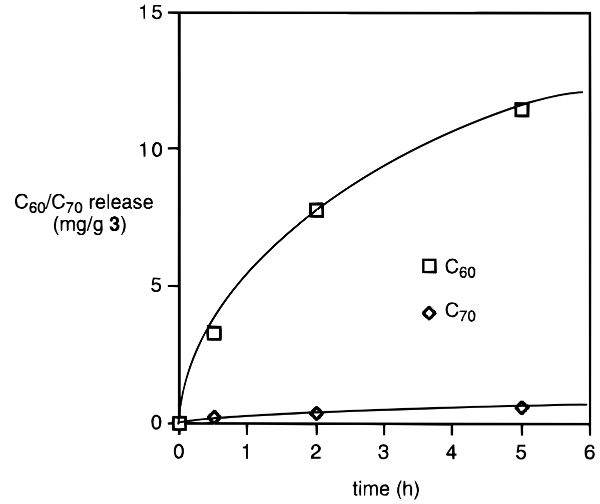

Figure 1. Plot of uptake of C_{60} and C_{70} vs time. Reaction was run at 22 °C in toluene, with gentle agitation. Fullerenes are from a crude extract of fullerene-containing soot: initial concentrations: 1.283 mM C_{60}, 0.136 mM C_{70}; final concentrations 0.861 mM C_{60}, 0.093 mM C_{70}.

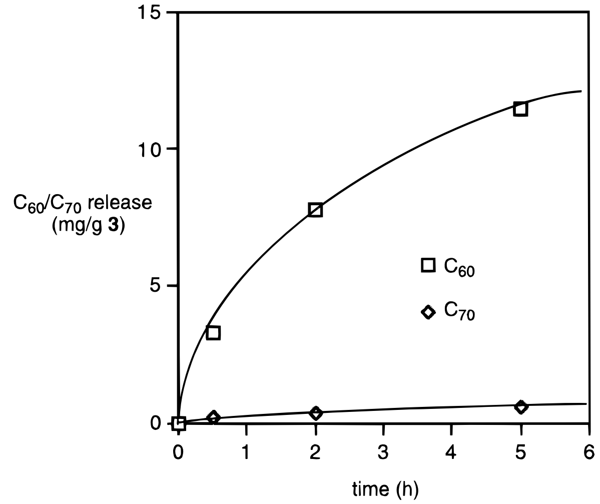

Figure 2. Plot of release of C_{60} and C_{70} vs time from material **3b**. Heating of fullerene-bound material **3b** in toluene at 100 °C for 5 h releases 93.7% of the bound C_{60} and 41.1% of the bound C_{70}.

hexane (120 mL) and a stir bar. *n*-Butyllithium (47.2 mL of a 1.6 M solution in hexanes, 75 mmol) was then added to the resulting solution at room temperature, providing a white inhomogeneous solution. The mixture was stirred at room temperature for 2 h and then filtered through a cannula under vacuum, yielding a white solid. The product was washed with hexane (2 × 100 mL) and then dried *in vacuo* to provide lithium cyclopentadienylide (4.98 g, 92%) as a white solid.

Cyclopentadiene-Substituted Silica Gel 2. 3-Chloropropyl-functionalized silica gel **1** (1.00 g) (C, 3.47; H, 0.82; Cl, 2.28, chloride functionalization of 0.64 mmol/g of silica gel **1**.) was added in one portion to a solution of lithium cyclopentadienylide (720.4 mg, 10 mmol) in THF (100 mL) at room temperature under Ar. The suspension was stirred at 23 °C for 24 h, filtered, and washed with THF (200 mL) to give 1.21 g of a light yellow powder. Elemental analysis of cyclopentadiene-functionalized silica gel **2**: C, 5.68; H, 1.41; Cl, 2.21. When calculated for C_5H_5 content, this indicates 0.37mmol/g, or 57% substitution.

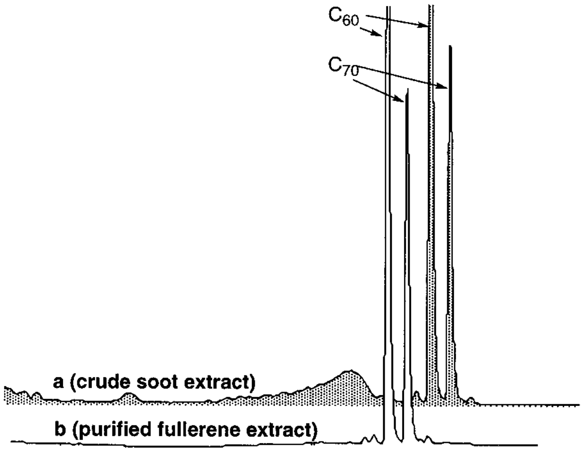

Figure 3. HPLC traces demonstrating purification of fullerene-containing soot. Trace a is the crude soot extract. Trace b is the purified material. The small peaks near the C_{60} and C_{70} peaks are unidentified fulleroids.[13]

C_{60}-Functionalized Silica Gel 3a. Cyclopentadiene-functionalized silica gel **2** (0.200 g) was added to a solution of C_{60} in toluene (10 mL, 1.39 mM). The mixture was gently shaken at room temperature for 24 h, then filtered, and washed with toluene (20 mL) to provide 206 mg of **3a** as a brown solid. Elemental analysis of C_{60} adduct silica gel **3a**: C, 7.69; H, 1.38, indicating 0.028 mmol of C_{60}/g of silica gel **3a**, ~20.1 mg C_{60}/g of **3a**.

Mixed C_{60}/C_{70} Functionalized Silica Gel 3b. In analogous fashion, cyclopentadiene-functionalized silica gel **2** (100 mg) was added to an extract of fullerene-containing soot (MER, Tucson, AZ) in toluene (initial concentrations C_{60}, 1.283 mM, C_{70}, 0.136 mM). The mixture was gently shaken at room temperature for 3.5 h, then filtered, and washed with toluene (20 mL) to provide 102 mg of the mixed C_{60}/C_{70} adduct **3b**.

Kinetics Measurements. Fullerene uptake was determined via HPLC, using a reversed-phase C18 column (Rainin Instruments, Woburn, MA). The fullerenes were eluted using a 70:30 methylene chloride/acetonitrile solvent system and were detected at 265 nm, using pyrene as an internal standard.

HPLC Assay of Soot Purification. Cyclopentadiene-functionalized silica gel (100 mg) was added to an extract of flame-synthesized soot in toluene (5 mL) (initial concentrations C_{60}, 0.201 mM, C_{70}, 0.124 mM). The mixture was gently shaken for 1 h, and the liquid phase was assayed by HPLC 0−99% methanol/methylene chloride gradient. The silica gel was then filtered and repeatedly washed with toluene (100 mL). A portion of this silica gel (65 mg) from above was heated in toluene (2.5 mL) at 100 °C under argon for 1 h, and the liquid phase was assayed by HPLC.

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