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Crystal engineering a linear polymer of C_{60} fullerene *via* supramolecular pre-organization†

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The action of heat and pressure on a co-crystallate of C_{60} and a calixarene, where the fullerenes are pre-organized in separated linear columns, gives a linear [2 + 2] addition polymer of $(C_{60})_n$ without crosslinking.

Co-crystallizations and supramolecular assemblies are giving rise to an explosion of new crystal structures. Aesthetics, apparent ease of synthesis (self assembly), and the challenge of understanding and manipulating the weak forces that dictate crystal structures are driving this very active field.[1]

Fullerenes have three-dimensional arrays of reactive double bonds that present an unusually difficult problem for controlling the topology of multiple addition reactivity. Solid state pre-organization offers a potential solution. Scattered reports support this hypothesis. An unusual addend transfer reaction, not favored in solution, has been observed in the solid state with a Diels–Alder anthracene/C_{60} adduct.[2] A derivatized fullerene has been shown to assemble spontaneously into macroscopic rods and vesicles.[3] Pressure-induced dimerization of C_{60} to produce C_{120} is more efficient in a co-crystallate than in the bulk.[4] Pressure-induced dimerization of bulk C_{70} is interesting because it leads to selection of a single [2 + 2] addition isomer of C_{140}, even though five equi-energy combinations are possible.[5] Bulk C_{60} can be polymerized under pressure to give, depending on conditions, a variety of [2 + 2] addition polymers, some approaching distinct phases.[6]

Fullerenes are particularly prone to co-crystallization with other molecules[7–10] and under fortunate circumstances, the crystallizing components can become organized in useful ways. One such opportunity is provided by the report that C_{60} co-crystallizes with a calixarene in strictly linear, separated columns.[11] As shown in Fig. 1, the C_{60} molecules are in close van der Waals contact within a column (9.92 Å center-to-center distance) but parallel columnar stacks of calixarenes separate the fullerene columns from each other (12.81 Å center-to-center distance). We reasoned that the action of heat and pressure should lead to strictly linear nanorods of a [2 + 2] addition polymer $(C_{60})_n$ (Fig. 2) and that the calixarenes would prevent crosslinking. The C_{60} molecules in the co-crystallate are known to be freely rotating at room temperature[12] so the pre-positioned fullerenes can readily adopt the required orientation of bonds[13,14] for mutual [2 + 2] addition.

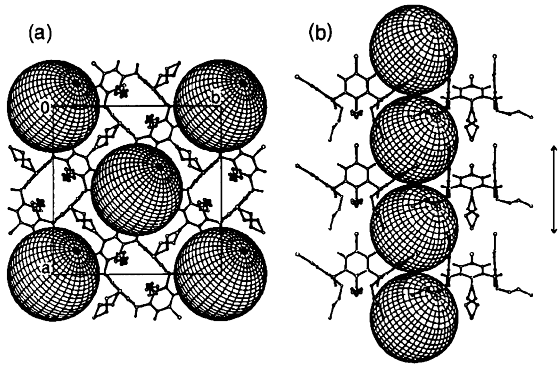

Fig. 1 Two views of the crystal packing of C_{60} and calixarene molecules (a) looking down the columns and (b) side-on. Reproduced with permission from ref. 11.

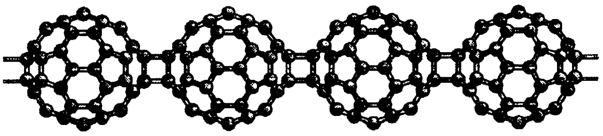

Fig. 2 Schematic depiction of the strictly linear [2 + 2] addition polymer of C_{60}.

The co-crystallate of *p*-bromocalix(4)arene propyl ether and C_{60} **1**, was prepared by the published method.[11] The identity of the product was checked by single-crystal X-ray determination. Sample homogeneity was checked by consistency of size, shape and color (dark red) under a microscope. Samples (*ca.* 20 mg) were packed in octahedrally shaped MgO containers, wrapped with Re foil for heating, fitted with a thermocouple, and pressed hydrostatically in a cube anvil. The pressure was increased gradually to the desired value (5 GPa) over a 30 min period followed by 1 h of heating at 200 °C. Samples were allowed to cool prior to the release of pressure since heat without pressure causes depolymerization. The polymerized product **2** had a black obsidian-like appearance. Bulk C_{60} was polymerized in a similar manner at 5 GPa and 200 °C to produce a 'crosslinked' material **3**, and at 1.5 GPa and 400 °C to produce an 'orthorhombic phase' **4**.[6]

Energy dispersive X-ray spectroscopy showed that the atomic composition of co-crystallate **1** and its polymerized product **2** were identical. The IR spectrum of **1** is a simple composite of its constituents: C_{60} and calixarene [Fig. 3(a) and (b)]. After pressure/heat treatment to produce **2**, bands due to the calixarene (1600–800 cm^{-1}) are unchanged, indicating that the calixarene component has not undergone chemical reaction [Fig. 3(c)]. On the other hand, several new bands appear in the 'fingerprint' region for fullerene derivatization (800–500 cm^{-1}) indicative of symmetry-lowering reactivity of C_{60}. Comparison of **2** with pressure/heat-treated pristine C_{60} samples **3** and **4** [Fig. 3(d) and (e)]† reveals a very close similarity to the orthorhombic phase **4** of polymerized C_{60}, but not to the crosslinked phase **3**. The Raman spectra of **2** and **4** are also very similar, in both the high and low energy regions (Fig. 4).† This indicates that the detailed mode of polymerization in **2** and in the orthorhombic phase of C_{60} is the same. Since there is growing consensus that the structure of **4** is a linear [2 + 2] addition polymer,[6] and since it is difficult to understand how **2** could be anything but a linear [2 + 2] addition polymer, the spectral consistency of **2** and **4** supports a correct structural assignment in both (Fig. 2).

Partial polymerization of **1** at 1.5 GPa and 150 °C gives a product from which C_{60}, C_{120}[15] and a presumably linear isomer of C_{180} can be separated by HPLC from the sonicated 1-chloronapthalene extract. The evidence for the linear isomer

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† Electronic supplementary information (ESI) available: enlarged copies of Figs. 3 and 4 showing peak frequencies. See http://www.rsc.org/suppdata/cc/b0/b007116l/

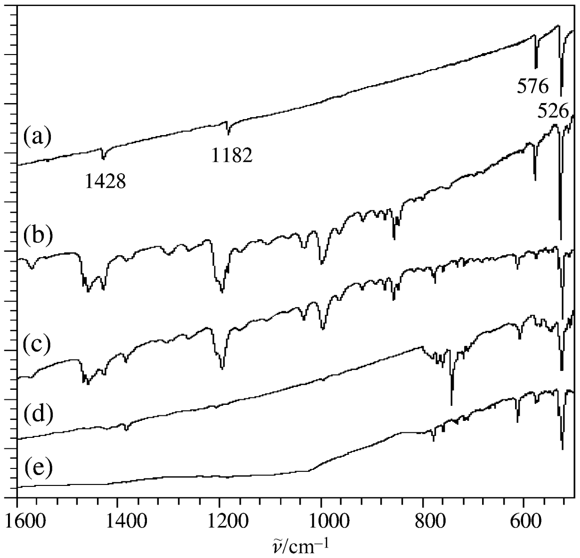

Fig. 3 IR spectra (KBr disk) of (a) C_{60}; (b) co-crystallate of C_{60} and calixarene, **1**; (c) polymerized cocrystallate, **2**; (d) crosslinked $(C_{60})_n$, **3**; and (e) orthorhombic $(C_{60})_n$, **4**. An enlarged copy of this figure which includes peak frequencies is available as ESI.†

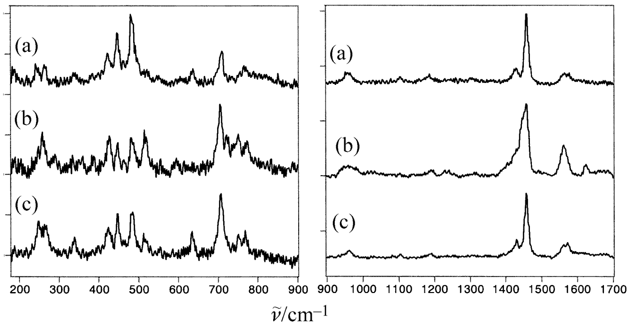

Fig. 4 Raman spectral comparison of [60]-fullerene polymers: (a) polymerized co-crystallate **2**; (b) crosslinked $(C_{60})_n$, **3**; and (c) orthorhombic (linear) $(C_{60})_n$, **4**. Spectra were recorded for samples as 5% KBr pellets with 514 nm Ar laser excitation. An enlarged copy of this figure which includes peak frequencies is available as ESI.†

of C_{180} includes (i) an HPLC retention time [Buckyprep(toluene–1,2-dichlorobenzene (1 : 1)] of 5.3 min compared to C_{60} (4.0 min) and C_{120} (4.6 min), (ii) a *single* HPLC peak rather than *four* that are observed in the low pressure trimerization of bulk C_{60},[16] (iii) an IR spectrum quite different from that of the proposed *triangular* isomer of C_{180},[16] (iv) a fullerene-like UV–VIS spectrum (λ_{max} = 327, 710 nm), and (v) photodegradation to C_{60} and C_{120}. The extremely low solubility and light sensitivity of this material has thwarted attempts to isolate it in significant amounts.

There has been significant effort put into the characterization of photo-[17] and pressure/heat-polymerized[18] C_{60}, partly justified on the basis of potential applications as conductors or nanowires.[6] In order to test the nanowire hypothesis we have subjected the linear polymer to a number of physical and chemical stability tests.

Of potential utility is the observation that it is insoluble in all common solvents and thermally stable at reasonable temperatures. Differential scanning calorimetry at 4 °C min^{-1} heating rate shows an irreversible endothermic process in the range 185–295 °C, consistent with thermal depolymerization at higher temperatures to give C_{60}. This is confirmed by subsequent solubility in organic solvents and UV-VIS identification of C_{60}. HPLC analysis showed traces of C_{120} were also present.

To model charge carrying, the polymer was exposed to reducing agents such as Na/THF or Hg/$R_4N^+Br^-$/THF. In both cases, complete dissolution of the polymer occurred and discrete C_{60}^- ions were detected (λ_{max} = 1075 nm). When smeared onto a platinum electrode and subjected to cyclic voltammetry, cathodic sweep peaks led to the production of C_{60}^- and C_{60}^{2-} in solution. Presumably reduction of the polymer causes monomers to dissociate from the surface like pearls dropping off a necklace. Dimeric C_{120} is known to dissociate immediately upon reduction.[15] In a comparable test for positive hole carrying, the polymer was exposed to oxidizing agents and anodic current. It is stable to aqueous $KMnO_4$ and HNO_3 but a moderate excess of bromine gradually produces $C_{60}Br_8$ (identified by isolation and IR spectroscopy).[19] On a platinum electrode, an irreversible anodic wave was observed at the same potential as C_{60} (*ca.* 1.4 V *vs.* Fc/Fc$^+$) suggesting irreversible decomposition. Although C_{60}^+ is now known as a stable entity,[20] it reacts instantly with errant nucleophiles in the solvent and supporting electrolyte.

In summary, this work shows how crystal engineering can be used fruitfully in fullerene polymer chemistry.[21] With its symmetrical [2 + 2] addition linkages, linear $(C_{60})_n$ is a chemically elegant polymer. One would like it to have a useful application. However, the present work suggests this will not be found as a nanowire. Rather, an analogy can be made to a nano*fuse*. Isolated single chains are unlikely to carry any current at all and bundles of chains are likely to be fragile. We note, however, that the proposed linear-chain isomer of KC_{60} is a metal[22] so stoichiometric intercalation of small cations can stabilize a lattice.

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