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Mixed Interfullerene Bonding Motifs in C_{60} based polymers

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An unexpected discovery in fullerene chemistry has been the ease with which C_{60} units can covalently bond together to give rise to polymerized fullerene networks with a variety of structural architectures. Such fullerene-bridged arrays display varying dimensionality and interesting electronic (metallic behavior) and magnetic (ferromagnetism above room temperature) properties. The predominant C-C bridging structural motif, encountered in photo- and pressure-polymerized neutral C_{60} and in the AC_{60} (A = K, Rb, Cs) solids arises from [2+2] cycloaddition reactions, which result in the formation of 4-membered carbon rings, fusing together adjacent molecules and propagating in one (1D chains) or two (2D layers) dimensions (Fig. 1a). An alternative bridging mechanism involves the formation of *single* interfullerene C-C covalent bonds, as encountered in 1D C_{60}^{3-} (Na_2RbC_{60}) [1] (Fig. 1b) and 2D C_{60}^{4-} (Na_4C_{60})^3 [2] fulleride polymers. We have recently started working on the related fulleride salt, Li_4C_{60} and its structural properties were probed by X-ray powder diffraction as a function of temperature between ambient conditions and 450(C. Very surprisingly we found that at room temperature the ground state of Li_4C_{60} is a two-dimensional polymer with monoclinic crystal symmetry and an unprecedented architecture, combining both [2+2] cycloaddition and single C-C bridging motifs [3,4] (Fig. 1c). This structure is the first example of a fullerene polymer with a mixed mode of interfullerene bridging and opens the way for the synthesis and study of new C_{60}-based 1D, 2D and 3D polymers. Increasing the temperature leads to the disruption of the bridging motifs and to the simultaneous formation of a *fcc* monomeric phase.

Figure 1. Schematic drawing of the interfullerene C-C bridging structural motifs in polymeric fullerides. (a) [2+2] cycloaddition in AC_{60}, (b) single C-C covalent bonds in Na_2RbC_{60}, and (c) mixed bonding in Li_4C_{60}
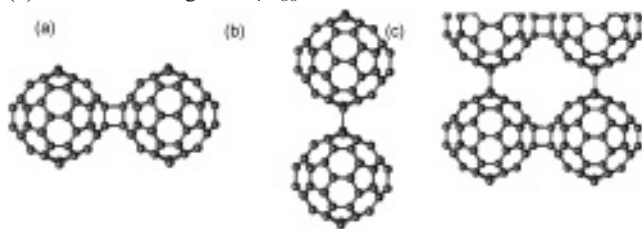
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Nanotube field of C_{60} and C_{70} molecules in carbon nanotubes

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We present calculations of the interaction energy of C_{60} fullerene molecules encapsulated in single-walled carbon nanotubes (SWCNTs), systems known as peapods [1]. We focus on the dependence on the molecular orientations by taking the molecular structure fully into account. First, we approximate the SWCNT as a homogenous cylindrical distribution of carbon atoms, hence keeping the tube's radius R as a single tube-characteristic parameter rather than the two chiral indices n and m [2]. For molecules aligned on the tube axis, we find three different preferential molecular orientations for tube radii in the range 6.5 Å < R < 8.5 Å. We also consider the possibility of having off-centre molecular positions and provide a theoretical description of $(C_{60})_n$@SWCNT peapods as one-dimensional systems. Then, we test our homogenous-tube approximation by calculating the same C_{60}-tube interaction for several actual SWCNTs having tube radii in the same range and investigate its validity [3]. We apply the same approximation to $(C_{70})_n$@SWCNT peapods. Again, for molecules positioned centrally in the tube, we obtain radius-dependent preferential orientations. "Lying" orientations (long molecular axis coinciding with the tube axis) occur at the lower radii, higher radii yield "standing" orientations (long molecular axis *perpendicular to the tube* axis), consistent with experimental electron diffraction results [4].

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