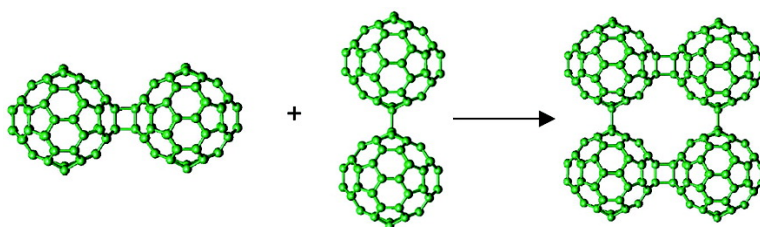


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Li₄C₆₀: A Polymeric Fulleride with a Two-Dimensional Architecture and Mixed Interfullerene Bonding Motifs

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An unexpected discovery in fullerene chemistry has been the ease with which C₆₀ units can covalently bond together to give rise to polymerized fullerene networks with a variety of structural architectures.¹ 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 C₆₀ and in the AC₆₀ (A = K, Rb, Cs) solids arises from [2 + 2] cycloaddition reactions, which result in the formation of four-membered carbon rings (Figure 1a), fusing together adjacent molecules and propagating in one (1D chains) or two (2D layers) dimensions.¹ An alternative bridging mechanism involves the formation of *single* interfullerene C–C covalent bonds (Figure 1b), as encountered in 1D C₆₀³⁻ (Na₂RbC₆₀)² and 2D C₆₀⁴⁻ (Na₄C₆₀)³ fulleride polymers. Recent work on the related fulleride salt, Li₄C₆₀, described its structure as 2D tetragonal with interfullerene bonds formed by [2 + 2] cycloaddition.⁴ Here we report that when we probed the structural properties of Li₄C₆₀ by high-resolution synchrotron X-ray diffraction, we found that it indeed adopts a layered polymeric structure. However, contrary to all other known fullerene polymers, each C₆₀ unit now bonds to its four nearest neighbors in the layers using both the [2 + 2] cycloaddition and the single C–C bridging motifs (Figure 1c), thereby giving rise to two types of differently bonded chains running perpendicular to each other. The resulting 2D fulleride network has neither been observed before experimentally nor been anticipated theoretically.

The synchrotron X-ray powder diffraction profile of Li₄C₆₀⁵ obtained at ambient temperature (Figure 2) revealed that its structure was body-centered monoclinic. Analysis with the LeBail pattern decomposition technique resulted in lattice parameters of $a = 9.3267(3)$ Å, $b = 9.0499(3)$ Å, $c = 15.03289(1)$ Å, and $\beta = 90.949(3)^\circ$ (space group *I2/m*; $R_{wp} = 4.24\%$, $R_{exp} = 1.53\%$). A notable feature of these results is that the structure of Li₄C₆₀ is strongly anisotropic with the closest center-to-center contacts between the C₆₀ units of ~ 9.33 , ~ 9.05 , and ~ 9.95 Å along the a and b axis and the body diagonal, respectively. While the latter contact is comparable to those encountered in monomeric fullerenes and fullerides (~ 10.0 Å), the one along b is reminiscent of that in monoclinic polymerized AC₆₀ (~ 9.11 Å)⁶ in which there are two bridging C–C bonds between C₆₀⁻ ions (Figure 1a). Therefore, the starting structural model used in the Rietveld refinement of the Li₄C₆₀ diffraction data was based on that of RbC₆₀ with linear fulleride chains running along b (Figure 1a). However, the Rietveld refinement did not proceed smoothly within this model with the diffraction profile described poorly ($R_{wp} = 18.6\%$), especially in

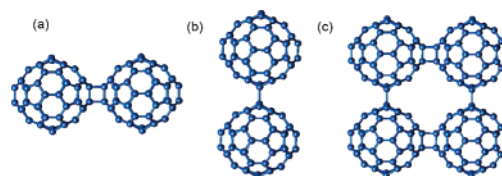


Figure 1. Schematic drawing of the interfullerene C–C bridging structural motifs in polymeric fullerides. (a) [2 + 2] cycloaddition in RbC₆₀, (b) single C–C covalent bonds in Na₂RbC₆₀, and (c) mixed bonding in Li₄C₆₀.

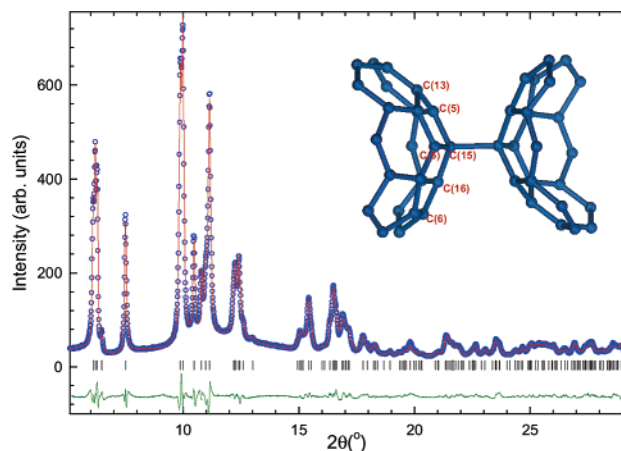


Figure 2. Final observed (○) and calculated (—) synchrotron X-ray diffraction profile for Li₄C₆₀ at 295 K ($a = 9.3264(4)$ Å, $b = 9.0478(4)$ Å, $c = 15.03294(2)$ Å, $\beta = 90.967(3)^\circ$, space group *I2/m*, agreement factors of the Rietveld refinement: $R_{wp} = 5.12\%$, $R_{exp} = 1.53\%$, $R_{F2} = 3.46\%$). The lower solid line shows the difference profile, and the tick marks show the reflection positions. Inset: geometry of the frontier (C(5) and C(16)) and bridging (C(15)) carbon atoms on adjacent fullerenes along the direction (a axis) of single C–C polymerization.

the high 2θ region. At this stage, we note that short C–C contacts are also implied along the a axis, with the interfullerene distances comparing well with earlier observations in fullerides with single C–C interfullerene connections, like the 1D Na₂RbC₆₀ and the 2D Na₄C₆₀ polymers,^{2,3} in which the shortest center-to-center distances are 9.38 and 9.28 Å, respectively.

Thus, starting from the previous model, we performed a search of possible alternative C₆₀ orientations in the ab plane by allowing the two C₆₀ units present in the monoclinic unit cell to rotate about the [010] direction anticlockwise and monitoring the resulting quality-of-fit factors (R_{wp}) of the Rietveld refinements. Figure 1S (Supporting Information) presents the evolution of R_{wp} with the rotation angle, ϕ , which was varied between 0 and 180° in increments of $\delta\phi = 5^\circ$. The refinements were stable throughout the ϕ -range with a single deep minimum in R_{wp} (10.02%) evident at an angle, $\phi = 100^\circ$.⁷ At this angle, it is remarkable that the relative orientation of the molecules is such that pairs of carbon

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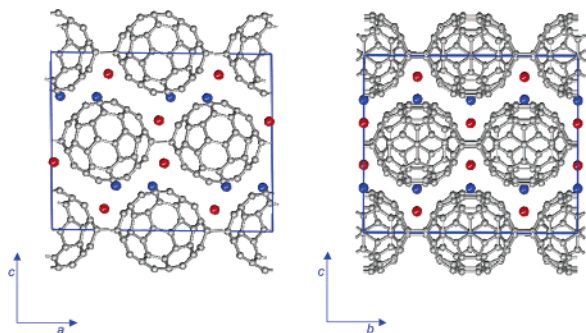


Figure 3. Crystal structure of polymerized Li_4C_{60} , as determined by the present synchrotron X-ray diffraction study: projections on the ac (left) and bc (right) basal planes. Li^+ ions residing in pseudo-tetrahedral and -octahedral holes are depicted as blue and red spheres, respectively.

atoms, located on the a axis, from neighboring fullerenes are brought in proximity (~ 2 Å). Therefore, knowing the orientation of the fullerenes in the lattice determines that they are bonded via $[2 + 2]$ cycloaddition along the b axis and are connected by single C–C bonds along the a axis (Figure 1c). The fit improved significantly in this configuration when we allowed the position of the bonding carbon atom, C(15), to refine. Neighboring C(15) atoms move closer together with the resulting C(15)–C(15) distance of ~ 1.83 Å. Subsequent Rietveld fits were used to refine further the molecular structure of the Li_4C_{60} ground state by employing soft constraints and refining stepwise the fractional coordinates of all C atoms. The minimum in R_{wp} is attained for an interfullerene C(15)–C(15) bond length of $1.75(2)$ Å and an inclination of $\sim 2^\circ$ from the a axis within the ab plane, while the overall C_{60} geometry is maintained with the on-ball C–C distances varying between 1.4 and 1.5 Å. The longest on-ball C–C distances ($1.55(1)$ Å) are between the bonding C(15) atom and its near neighbors, C(5) and C(16) (inset in Figure 2 and Figure 2S of the Supporting Information). The geometry of the bridging four-membered rings along b is in good agreement with that found in the AC_{60} polymer,⁶ with values for the C–C distances of $1.59(2)$ (fusions of adjacent C_{60} units) and $1.47(1)$ Å (on-ball bonds).

The last set of Rietveld refinements focused on the search for the precise location of the intercalated Li^+ ions. In cubic A_3C_{60} fullerides, one alkali cation per fullerene occupies the large octahedral site at $(0,0,1/2)$, and two occupy the smaller tetrahedral site at $(3/4,3/4,3/4)$. The holes in the Li_4C_{60} structure corresponding to the tetrahedral and octahedral interstices of the cubic parent structure are at $(1/2,0,3/4)$ and $(0,0,1/2)$, respectively. A difference Fourier analysis of the Li_4C_{60} diffraction data clearly revealed the existence of scattered intensity in the vicinity of the tetrahedral site at $(0.416,0,0.748)$, accounting for two of the Li^+ ions per fullerene. In addition, the Fourier maps showed that while the octahedral site was empty, scattered intensity was now present at positions $(0.023,0,0.380)$ and $(-0.023,0,0.620)$, symmetrically displaced on either side of the center of the hole along the c axis. Splitting of the octahedral interstice and occupation of the two resulting positions account for the additional two Li^+ ions per fullerene. The results of the final Rietveld refinements after allowing the positional parameters and occupation numbers of the Li^+ ions to vary are shown in Figure 2 with the fitted parameters summarized in Table 1S of the Supporting Information.

Perspective views of the refined structure of Li_4C_{60} on the ac and bc basal planes are shown in Figure 3. The origin of the different structures adopted by Li_4C_{60} and the related polymeric fullerides, $\text{Na}_2\text{RbC}_{60}$ (chains bridged by one C–C bond) and Na_4C_{60} (layers bridged by four C–C bonds), is of considerable interest. The stability of polymeric fulleride structures is strongly associated

with the charged state of the fulleride ions and the steric influence of the alkali ions.⁸ The small size of Li^+ (0.60 Å) is of paramount importance in minimizing steric crowding and allowing the incorporation of two Li^+ ions in the space surrounding the pseudo-octahedral site. The closest Li^+ – Li^+ distance in the octahedral interstice is $3.65(14)$ Å, larger than that in Li metal (3.04 Å). Finally, examination of the Li^+ – C_{60} contacts reveals the shortest distances of $2.42(5)$ and $2.54(6)$ Å in the tetrahedral and octahedral sites, respectively. These are larger than the sum of the ionic radius of Li^+ and the van der Waals radius of C. If $\text{Na}_2\text{RbC}_{60}$ or Na_4C_{60} were to adopt structures similar to that of the Li_4C_{60} polymer, severe steric hindrance would be encountered. The Rietveld refinements are also consistent with a Li doping level of $x = 3.49(7)$. Considering the usual behavior of Li for partial electron donation to the fullerene units,⁹ a formal charge smaller than -4 is expected for the C_{60}^{n-} anions. This is again inconsistent with the adoption of the 2D Na_4C_{60} structure, favored for $n \approx -4$.

In conclusion, we have shown that the Li_4C_{60} fulleride adopts a 2D monoclinic polymer structure, comprising two types of differently bonded fullerene chains running perpendicular to each other in the ab basal plane. This structure is the first example of a fullerene polymer with a mixed mode of interfullerene bridging via both *single* C–C bonds and $[2 + 2]$ cycloaddition. The bridging C–C bond distances refine to $1.75(2)$ and $1.59(2)$ Å, which are somewhat longer than typical covalent single bonds, but still consistent with bonding interactions between neighboring fulleride units. No anomalous close contacts between either the alkali ions or between Li^+ and the C_{60} units are encountered. Work is currently in progress to determine the electronic and conducting properties of the Li_4C_{60} polymer.

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Supporting Information Available: Plots of R_{wp} versus rotation angle and C_{60} bridging geometry and a table of the extracted structural parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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