

Generalizing the Chiral Self-Assembly of Spheres and Tetrahedra to Non-Spherical and Polydisperse Molecules in $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$

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Abstract

We describe the spontaneous chiral self-assembly of C_{70} with SnI_4 as well as a mixture of C_{60} and C_{70} with SnI_4 . Macroscopic single crystals with the formula $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$ ($x = 0-1$) are reported. C_{60} , which is spherical, and C_{70} , which is ellipsoidal, form a solid solution in these crystals, and the cubic lattice parameter of the chiral phase linearly increases as x grows from 0 to 1 in accordance with Vegard's law. Our results demonstrate that nonspherical particles and polydispersity are not an impediment to the growth of chiral crystals from high-symmetry achiral precursors, providing a route to assemble achiral particles including colloidal nanocrystals and engineered nanostructures into chiral materials without the need to use external templates.

Chiral materials are highly valued in the physical and biological sciences due to their preferential interaction with left- or right-handed circularly polarized light^{1,2} as well as with chiral molecules.³⁻⁵ They can be used in devices that manipulate light,^{6,7} as stereoselective catalysts,⁴ and as sensors for the detection of biomolecules³ and specific enantiomers.⁵ Chiral materials are much more rare than achiral materials, however. Most chiral materials are assembled from molecules with chiral stereocenters, where the chiral molecules themselves are created through stereoselective chemical synthesis.⁸ Chiral materials can also be created through solid-state inorganic materials synthesis as well as through the self-assembly of achiral molecules into chiral crystals.^{2,8} Usually, the achiral molecules that form chiral crystals are floppy or low-symmetry molecules because helical structures need to form through inter- or intramolecular packing arrangements.⁹

We recently reported macroscopic single crystals of the superatomic^{10,11} chiral van der Waals material $C_{60}(SnI_4)_2$, formed by the self-assembly of two very high symmetry molecules: icosahedral C_{60} and tetrahedral SnI_4 .¹² $C_{60}(SnI_4)_2$ is isostructural to $SrSi_2$, and the Sn atoms topologically form a chiral cubic three-connected **srs** net¹³ despite not being chemically bonded to one another. Our discovery demonstrated that high symmetry is not an impediment to 3D chiral self-assembly, creating a new paradigm for chiral materials synthesis.

However, it was unclear whether this chiral self-assembly mechanism would be generalizable to other precursors such as colloidal nanocrystals, or even to other molecules. Unlike C_{60} ,¹⁴ most quasi-spherical molecules and particles cannot be treated like perfect spheres or spherical shells when assembled into solids. For example, while colloidal nanocrystals can appear to be spherical in transmission electron micrographs, they are faceted and their surface is decorated with ligands.¹⁵ In addition, most colloidal nanocrystal syntheses result in a polydisperse collection of nanocrystals,^{15,16} and while “magic-size” nanocrystals are a monodisperse alternative,¹⁷ they are still ligand-capped and non-spherical. Even within the fullerene family, most fullerenes are not spherically symmetric; the second-most common fullerene,

C_{70} , is an elongated ellipsoid with D_{5h} point symmetry.¹⁸ This elongation results in the formation of many different polymorphs of solid C_{70} with differing degrees of orientational order.^{19,20}

Here we demonstrate that elongation of and polydispersity in the “spherical” constituent does not disrupt the chiral self-assembly of quasi-spherical and tetrahedral molecules. Complete replacement of spherical C_{60} in $C_{60}(\text{SnI}_4)_2$ with ellipsoidal C_{70} results in the formation of the isostructural material $C_{70}(\text{SnI}_4)_2$, demonstrating that spherical symmetry is not a prerequisite for this type of chiral self-assembly. We also find that despite their different sizes and shapes, a mixture of C_{60} and C_{70} with SnI_4 self-assembles into a material isostructural to $C_{60}(\text{SnI}_4)_2$. C_{60} and C_{70} do not form an ordered superlattice; instead, they form a molecular solid solution with the formula $(C_{70})_x(C_{60})_{1-x}(\text{SnI}_4)_2$. This discovery indicates that quasi-spherical polydisperse materials with a narrow size distribution, such as colloidal nanocrystals,²¹ can be considered as candidates for chiral self-assembly when combined with appropriately sized tetrahedral structures.²²

Single crystals of $C_{70}(\text{SnI}_4)_2$ are synthesized similarly to $C_{60}(\text{SnI}_4)_2$ (Supporting Information).¹² Like $C_{60}(\text{SnI}_4)_2$, $C_{70}(\text{SnI}_4)_2$ crystallizes in the chiral enantiomorphic space group $P4_132$ (#213) (Table S1), and the Flack parameter of $-0.04(3)$ confirms the single crystal is a single chiral domain and that the absolute configuration (handedness) of the crystal has been successfully resolved.²³ Because neither C_{60} nor SnI_4 contain a stereocenter, it is likely that both left- and right-handed single crystals of $C_{70}(\text{SnI}_4)_2$ will form, so it may also crystallize in the $P4_332$ (#212) space group, which is identical to $P4_132$ except for its handedness. The C_{70} molecule is modeled as a rigid body with six-fold disorder across symmetry elements. The chiral 4_1 screw axis of $C_{70}(\text{SnI}_4)_2$ is shown in Figure 1A with C_{70} disorder omitted; a similar image with disorder is shown in Figure S1, and the asymmetric unit is shown in Figure S2. The structure of $C_{60}(\text{SnI}_4)_2$ is shown in Figure 1B for comparison.¹² Details of the crystal structure refinement are given in Supporting Information. At room temperature, C_{70} is rotating within the crystal, which we observe through a lack of resolved atomicity in the structural model derived from the single crystal diffraction data. Like in $C_{60}(\text{SnI}_4)_2$, the location of individual carbon atoms cannot be resolved.¹² We are not able to determine whether C_{70}

freely rotates or whether it there is some degree of dynamic or static orientational order such that C_{70} preferentially rotates about its long axis.

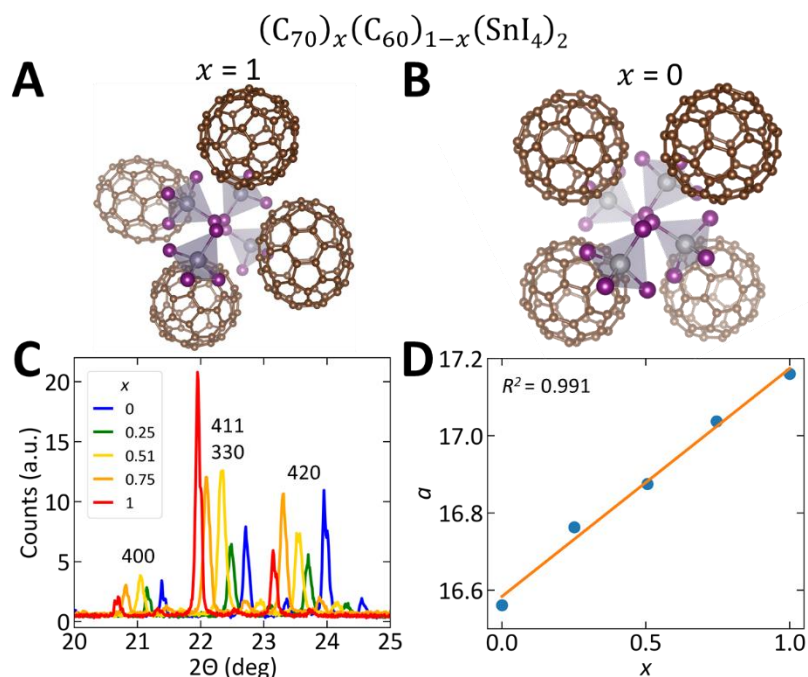


Figure 1: Structure of $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$. A) Depiction of the chiral 4_1 screw axis of $C_{70}(SnI_4)_2$ (disordered carbons omitted) with B) structure of $C_{60}(SnI_4)_2$ for comparison. C) Powder X-ray diffraction pattern of $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$ solid solutions. D) lattice parameter a extracted from Le Bail refinements of powder X-ray diffraction patterns. A linear fit to the observations is shown in orange. B) reprinted from ref 12.

Compared to C_{60} , C_{70} is identical in width but is elongated owing to the addition of five hexagons around its girth.²⁴ There are many polymorphs of solid C_{70} , including a face-centered cubic phase as well as two hexagonally-close-packed phases, one with the long axes of C_{70} aligned and one with random orientations of the molecule.²⁰ In the FCC phase where the C_{70} molecules exhibit full orientational disorder, the lattice constant is 14.96 Å, which indicates that the effective van der Waals radius of C_{70} is 5.29 Å, 5.6% larger than the 5.01 Å radius of C_{60} .¹⁹ Based on the effective radius of SnI_4 of 2.95 Å,¹² the radius ratio γ of $C_{70}(SnI_4)_2$ is 0.56. This ratio is similar to the ratio for $SrSi_2$ ($\gamma = 0.55$) as well as for $C_{60}(SnI_4)_2$ ($\gamma = 0.59$), consistent with these three materials being isostructural and indicating that the larger size of C_{70} compared to C_{60} does not significantly change γ . The fact that $C_{70}(SnI_4)_2$ and $C_{60}(SnI_4)_2$ are both

isostructural to SrSi₂ despite the difference in size and shape of the fullerene supports our previous conclusion that the chirality is templated by SnI₄ and not by the fullerene.¹²

By mixing C₇₀ and C₆₀ in the precursor solution and varying the fraction x of C₇₀, we synthesize single crystals of the mixed fullerene variant (C₇₀) _{x} (C₆₀)_{1- x} (SnI₄)₂ ($x = 0-1$), which is isostructural to both C₆₀(SnI₄)₂ and C₇₀(SnI₄)₂. Asymmetric units of the single crystal structures are shown in Figures S3-5, and refinement statistics are given in Tables S2-4. As x increases from 0 to 1, the cubic lattice constant a linearly increases from that of C₆₀(SnI₄)₂ to that of C₇₀(SnI₄)₂ (Figure 1C-D), demonstrated by the shift of reflections in the X-ray diffraction patterns to lower angle. This indicates that (C₇₀) _{x} (C₆₀)_{1- x} (SnI₄)₂ forms a solid solution where C₆₀ and C₇₀ partially occupy the same crystallographic site in a random fashion.²⁵ (At a given site, the probability of finding C₇₀ is x and C₆₀ is $1-x$, and there is no long-range ordering of C₆₀ and C₇₀.) The lattice parameter of the resulting material varies linearly with composition, in accordance with Vegard's law for solid solutions.²⁶ Synthesized precession images of the $hk0$ plane from single crystal X-ray diffraction measurements reveal that there are no superlattice reflections in our solid solutions (Figure 2), confirming that C₆₀ and C₇₀ form a molecular solid solution in (C₇₀) _{x} (C₆₀)_{1- x} (SnI₄)₂.

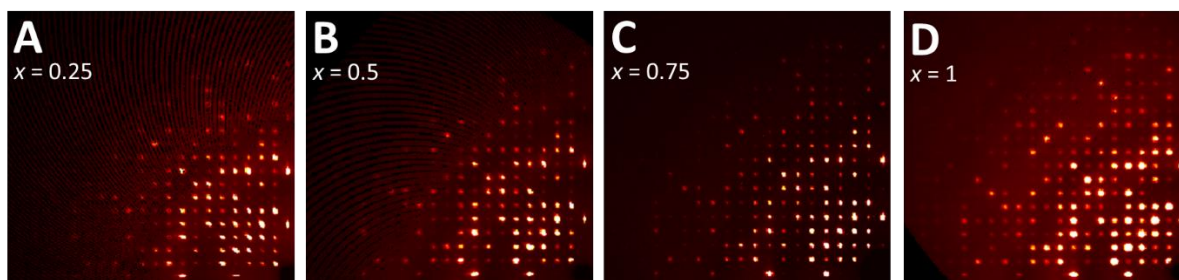


Figure 2: Single-crystal diffraction. Synthesized single crystal X-ray diffraction precession images of one quadrant of the $hk0$ plane for crystals of (C₇₀) _{x} (C₆₀)_{1- x} (SnI₄)₂ with A) $x = 0.25$, B) $x = 0.5$, C) $x = 0.75$, and D) $x = 1$.

In conclusion, the synthesis of C₇₀(SnI₄)₂ demonstrates that a perfect sphere is not needed for the chiral self-assembly of quasi-spherical and tetrahedral molecules into macroscopic single crystals. Furthermore, the polydispersity of C₆₀ and C₇₀ in the (C₇₀) _{x} (C₆₀)_{1- x} (SnI₄)₂ solid solution does not disrupt

this chiral self-assembly mechanism, despite the 5.6% size difference between C₆₀ and C₇₀. These results confirm our hypothesis that the tetrahedral shape of SnI₄ is responsible for templating the chiral structure because the assembly process is insensitive to the ellipsoidal particles and polydispersity. Our results demonstrate that the spontaneous chiral self-assembly of polydisperse and imperfect particles such as colloidal nanocrystals²¹ and engineered nanostructures²⁷ should be possible when paired with an appropriately sized tetrahedral co-crystallizer.

Supporting Information

Methods, additional depictions of crystal structures (Figures S1-S5), tabulated crystal data and structure refinement details (Tables S1-S4). (PDF)

Single crystal X-ray diffraction structures and structure factors have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 2072467-2072470 and are accessible at <https://www.ccdc.cam.ac.uk/structures/> as well as in the Supporting Information.

Crystal structure of C₇₀(SnI₄)₂ (CIF)

Crystal structure of (C₇₀)_{0.25}(C₆₀)_{0.75}(SnI₄)₂ (CIF)

Crystal structure of (C₇₀)_{0.5}(C₆₀)_{0.5}(SnI₄)₂ (CIF)

Crystal structure of (C₇₀)_{0.75}(C₆₀)_{0.25}(SnI₄)₂ (CIF)

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Notes

The authors declare no competing financial interest.

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