Supporting Information: 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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Experimental

1. Synthesis

$C_{70}(SnI_4)_2$ was synthesized by dissolving 50.15 mg C_{70} (99%, Proactive Molecular Research) and 2506.86 mg SnI_4 (95%, Alfa-Aesar) in a mixture of 50 mL toluene (ACS, Sigma-Aldrich) and 60 mL 1,2-dichlorobenzene (99%, Acros Organics) using sonication. 25 mL of benzene followed by ~400 mL pentane (98%, Sigma-Aldrich) were layered on top of the dichlorobenzene-toluene solution and left undisturbed so the solution would mix. Two phases of crystals grew: dull black hexagonally shaped crystals of $C_{70}(SnI_4)_2$ as well as shiny black rectangular crystals of another phase that we hypothesize is a C_{70}-pentane intercalation compound.

$(C_{70})_{0.75}(C_{60})_{0.25}(SnI_4)_2$ was synthesized by dissolving 2.57 mg C_{60} (99.5%, Proactive Molecular Research), 8.80 mg C_{70}, and 504.0 mg SnI_4 in a mixture of 10 mL toluene and 10 mL 1,2-dichlorobenzene using sonication. ~90 mL pentane was layered on top, and the solution was placed in a 4 °C refrigerator and left undisturbed while the solutions mixed. Dull black crystals of $(C_{70})_{0.75}(C_{60})_{0.25}(SnI_4)_2$ were the only phase that formed.

$(C_{70})_{0.5}(C_{60})_{0.5}(SnI_4)_2$ was synthesized by dissolving 5.12 mg C_{60}, 6.11 mg C_{70}, and 503.1 mg SnI_4 in a mixture of 10 mL toluene and 10 mL 1,2-dichlorobenzene using sonication. ~90 mL pentane was layered on top, and the solution was placed in a 4 °C refrigerator and left undisturbed while the solutions mixed. Dull black crystals of $(C_{70})_{0.5}(C_{60})_{0.5}(SnI_4)_2$ were the only phase that formed.

$(C_{70})_{0.25}(C_{60})_{0.75}(SnI_4)_2$ was synthesized by dissolving 7.47 mg C_{60}, 2.93 mg C_{70}, and 504.0 mg SnI_4 in a mixture of 16 mL toluene and 8 mL 1,2-dichlorobenzene using sonication. ~85 mL pentane was layered on top, and the solution was placed in a 4 °C refrigerator and left

undisturbed while the solutions mixed. Dull black crystals of $(C_{70})_{0.25}(C_{60})_{0.75}(SnI_4)_2$ were the only phase that formed.

2. Characterization

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance Eco diffractometer using Cu kα radiation (λ = 1.5406 Å). To prepare the powder, several crystals of $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$ were placed on a Bruker miscut Si low background slide and crushed. Lattice parameters were extracted using Le Bail refinements performed with TOPAS.[1]

Single crystal X-ray diffraction data were collected on a Bruker APEX-II Duo CCD diffractometer or a Bruker D8 Venture diffractometer with a Photon III detector, both using Mo kα (λ = 0.7107 Å) radiation. Crystals were mounted with Parabar 10312 oil (Hampton Scientific) on Kapton loops (MiTiGen). The data are integrated using SAINT (Bruker AXS) and scaled with a multiscan absorption correction using SADABS (Bruker AXS). The $P4_332$ (#212) or $P4_132$ (#213) space groups were identified through systematic absences using XPREP (Bruker AXS). The initial solution was found using the intrinsic phasing method of the SHELXT program[2] and the structure was refined using the least squares algorithm of the SHELXL program[3] in the OLEX2 GUI.[4] The absolute configuration (handedness) of the crystal was resolved using the anomalous dispersion of X-rays, and the correct enantiomer was identified by a Flack parameter of approximately zero.[5]

To refine the single crystal structure for $C_{70}(SnI_4)_2$, a C_{70} molecule was imported from ref 6 (ICSD collection code 75506) using the *importfrag* command in OLEX2 and refined as a rigid body. The coordinates of the C atoms were restrained using an AFIX 9 instruction in SHELXL, which allows the C_{70} molecule to uniformly grow or shrink but fixes the relative position of the C atoms. The occupancy of each C atom was fixed at 1/6 to account for disorder about symmetry

elements. Anisotropic thermal parameters were used for the Sn and I atoms. The C atoms were refined isotropically. Every C atom is restrained to have identical thermal parameters using the EADP instruction in SHELXL.

The single crystal structures of $(C_{70})_x(C_{60})_{1-x}(SnI_4)_2$ (x = 0.25, 0.5, 0.75) were refined similarly to that of $C_{70}(SnI_4)_2$. The C_{70} molecule was refined as a rigid body using the AFIX 9 instruction, with the occupancy of each C atom in C_{70} set to $x/6$ to account for disorder about symmetry elements where x is the nominal fraction of C_{70} (for instance, the occupancy is set to 1/24 for x = 0.25). To account for the presence of C_{60}, the structure of the C_{60} molecule was taken from the Idealized Molecular Geometry Library.[7] The thermal parameters of each C atom in C_{70} were restrained to be identical to one another using the EADP instruction. Like C_{70}, the C_{60} molecule was refined as a rigid body using the AFIX 9 instruction. The occupancy of each C atom in C_{60} was fixed as $(1 - x)/6$ to account for disorder about symmetry elements (for instance, the occupancy is set to 3/24 for x = 0.25). The thermal parameters of each C atom in C_{60} were restrained to be identical to one another using the EADP instruction. In the x = 0.25 and x = .5 structures, one of the two symmetry distinct I atoms resolved with disorder, and the occupancies of the two sites were constrained to sum to unity.

Crystal structure images are visualized using VESTA.[8] Asymmetric units in Figures S2-S5 are visualized using OLEX2.[4]

Additional Figures

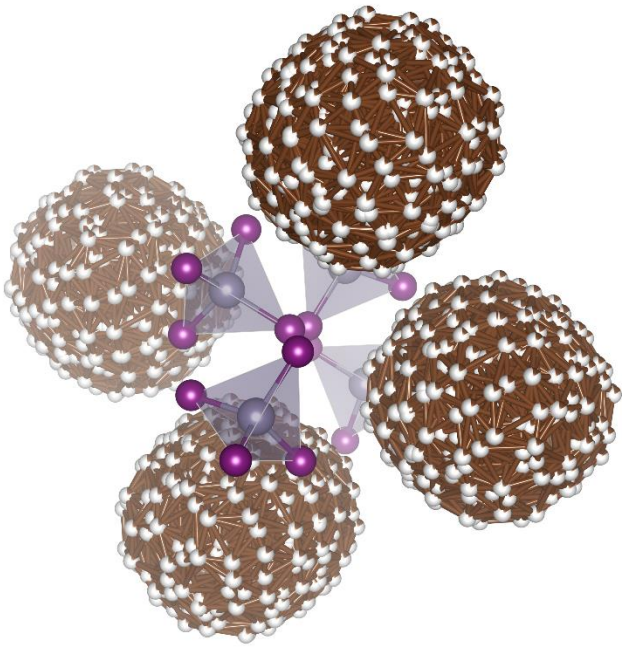

Figure S1: Depiction of 4_1 screw axis in $C_{70}(SnI_4)_2$ with disordered C_{70} molecules shown.

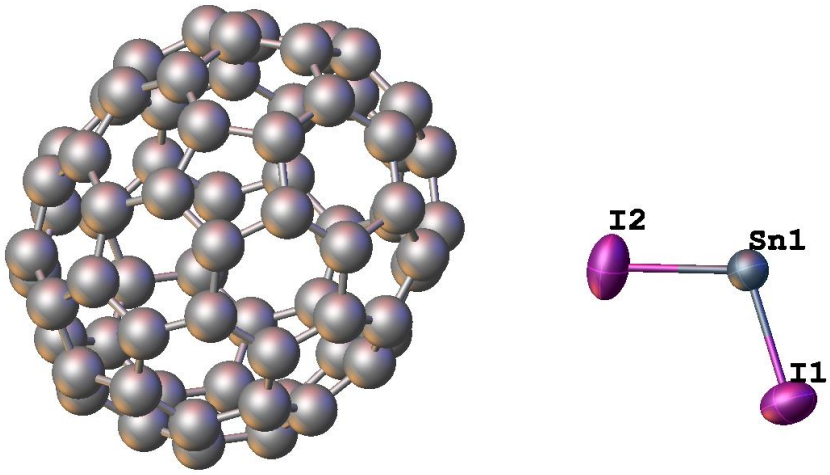

Figure S2: Asymmetric unit for single crystal structure of $C_{70}(SnI_4)_2$. Atoms are represented as 50% probability thermal displacement parameters.

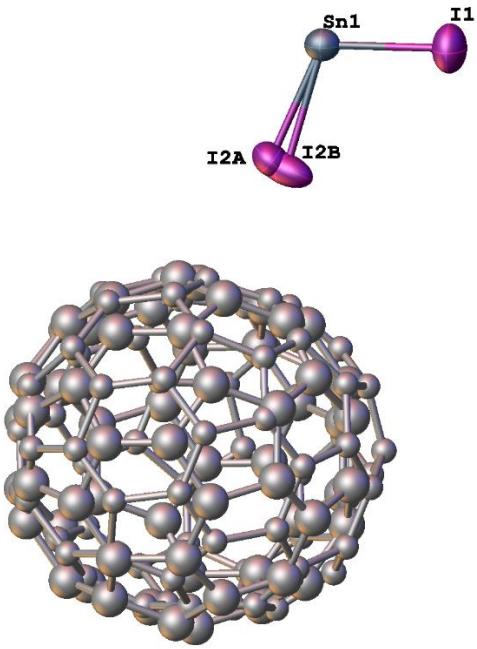

Figure S3: Asymmetric unit for single crystal structure of $(C_{70})_{0.25}(C_{60})_{0.75}(SnI_4)_2$. Atoms are represented as 50% probability thermal displacement parameters.

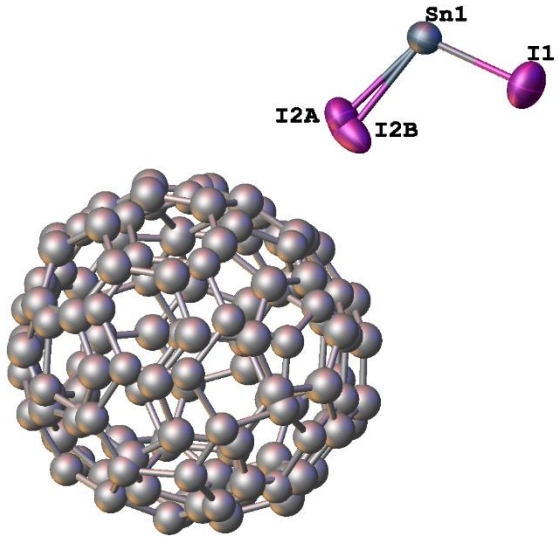

Figure S4: Asymmetric unit for single crystal structure of $(C_{70})_{0.5}(C_{60})_{0.5}(SnI_4)_2$. Atoms are represented as 50% probability thermal displacement parameters.

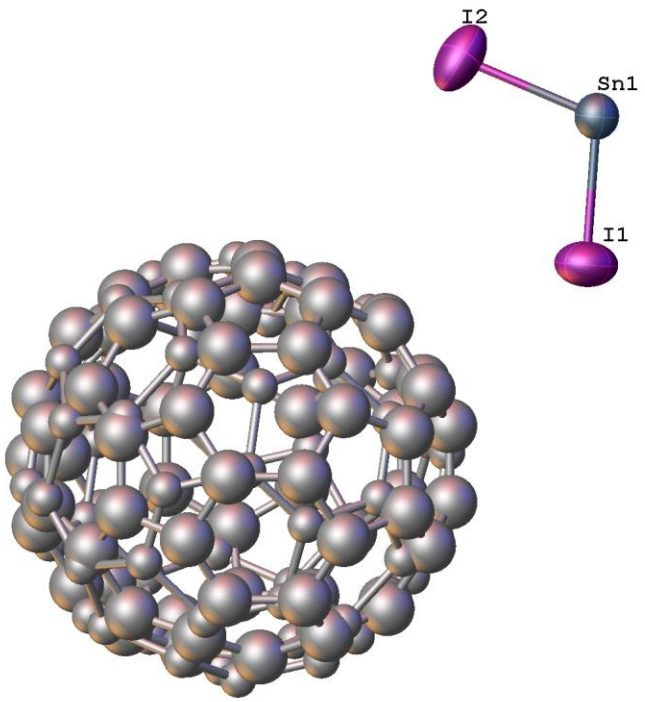

Figure S5: Asymmetric unit for single crystal structure of $(C_{70})_{0.75}(C_{60})_{0.25}(SnI_4)_2$. Atoms are represented as 50% probability thermal displacement parameters.

Additional Tables

Table S1: Crystal data and structure refinement for $C_{70}(SnI_4)_2$.

Empirical formula	$C_{70}I_8Sn_2$
Formula weight	2093.31
Temperature/K	294.99
Crystal system	cubic
Space group	$P4_132$
a/Å	17.1493(7)
Volume/Å^3	5043.6(6)
Z	4
ρ_{calc}g/cm^3	2.757
μ/mm^{-1}	5.937
F(000)	3776.0
Crystal size/mm^3	0.568 × 0.536 × 0.284
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.114 to 57.396
Index ranges	$-21 \leq h \leq 12$, $-23 \leq k \leq 22$, $-23 \leq l \leq 11$
Reflections collected	20622
Independent reflections	2189 [R_{int} = 0.0310, R_{sigma} = 0.0158]
Data/restraints/parameters	2189/0/24
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0679, wR_2 = 0.1910
Final R indexes [all data]	R_1 = 0.0911, wR_2 = 0.2144
Largest diff. peak/hole / e Å^{-3}	0.93/-0.72
Flack parameter	-0.04(3)

Table S2: Crystal data and structure refinement for $(C_{70})_{0.25}(C_{60})_{0.75}(SnI_4)_2$.

Empirical formula	$C_{62.5}I_8Sn_2$
Formula weight	2003.23
Temperature/K	295
Crystal system	cubic
Space group	$P4_332$
a/Å	16.7390(13)
Volume/Å^3	4690.2(11)
Z	4
ρ_{calc}g/cm^3	2.837
μ/mm^{-1}	6.377
F(000)	3596.0
Crystal size/mm^3	0.467 × 0.308 × 0.266
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.44 to 58.274
Index ranges	$-20 \le h \le 22$, $-22 \le k \le 22$, $-8 \le l \le 22$
Reflections collected	18754
Independent reflections	2127 [R_{int} = 0.0585, R_{sigma} = 0.0367]
Data/restraints/parameters	2127/0/42
Goodness-of-fit on F^2	1.163
Final R indexes [I>=2σ (I)]	R_1 = 0.0759, wR_2 = 0.1507
Final R indexes [all data]	R_1 = 0.1277, wR_2 = 0.1725
Largest diff. peak/hole / e Å^{-3}	0.90/-0.81
Flack parameter	-0.08(2)

Table S3: Crystal data and structure refinement for $(C_{70})_{0.5}(C_{60})_{0.5}(SnI_4)_2$.

Empirical formula	$C_{65}I_8Sn_2$
Formula weight	2033.23
Temperature/K	295.01
Crystal system	cubic
Space group	$P4_332$
a/Å	16.8763(13)
Volume/Å^3	4806.5(11)
Z	4
ρ_{calc}g/cm^3	2.810
μ/mm^{-1}	6.225
F(000)	3656.0
Crystal size/mm^3	0.421 × 0.382 × 0.303
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.412 to 57.394
Index ranges	$-22 \leq h \leq 21$, $-22 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	19074
Independent reflections	2081 [R_{int} = 0.0387, R_{sigma} = 0.0239]
Data/restraints/parameters	2081/0/42
Goodness-of-fit on F^2	1.188
Final R indexes [I>=2σ (I)]	R_1 = 0.0794, wR_2 = 0.1478
Final R indexes [all data]	R_1 = 0.1241, wR_2 = 0.1714
Largest diff. peak/hole / e Å^{-3}	1.03/-1.13
Flack parameter	-0.10(2)

Table S4: Crystal data and structure refinement for $(C_{70})_{0.75}(C_{60})_{0.25}(SnI_4)_2$.

Empirical formula	$C_{67.5}I_8Sn_2$
Formula weight	2063.25
Temperature/K	295
Crystal system	cubic
Space group	$P4_332$
a/Å	17.0312(3)
Volume/Å^3	4940.1(3)
Z	4
ρ_{calc}g/cm^3	2.774
μ/mm^{-1}	6.059
F(000)	3716.0
Crystal size/mm^3	0.279 × 0.268 × 0.186
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.348 to 59.06
Index ranges	$-17 \leq h \leq 22$, $-23 \leq k \leq 23$, $-14 \leq l \leq 23$
Reflections collected	27967
Independent reflections	2323 [R_{int} = 0.0568, R_{sigma} = 0.0223]
Data/restraints/parameters	2323/0/32
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1532
Final R indexes [all data]	R_1 = 0.0823, wR_2 = 0.1761
Largest diff. peak/hole / e Å^{-3}	0.70/-0.79
Flack parameter	-0.06(3)

References

(1) Coelho, A. A. TOPAS and TOPAS-Academic : an optimization program integrating computer algebra and crystallographic objects written in C++. *J. Appl. Crystallogr.* **2018**, *51*, 210–218.

(2) Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.

(3) Sheldrick, G. M. Crystal structure refinement with SHELXL . *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

(4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2 : a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(5) Flack, H. D. On enantiomorph-polarity estimation. *Acta Crystallogr. Sect. A Found. Crystallogr.* **1983**, *39*, 876–881.

(6) van Smaalen, S.; Petricek, V.; de Boer, J. L.; Dusek, M.; Verheijen, M. A.; Meijer, G. Low-temperature structure of solid C70. *Chem. Phys. Lett.* **1994**, *223*, 323–328.

(7) Guzei, I. A. An idealized molecular geometry library for refinement of poorly behaved molecular fragments with constraints. *J. Appl. Crystallogr.* **2014**, *47*, 806–809.

(8) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.