SUPPLEMENTARY INFORMATION

Corannulene and its penta-*tert*-butyl derivative co-crystallize 1:1 with pristine C_{60}-fullerene

by

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X-ray Crystallography Experimental. A crystal of C_{60}:**1** was measured on a Rigaku Saturn 70 with CCD area detector and graphite monochromated Mo-Kα radiation. A crystal of C_{60}:**5** was measured on a three circle Bruker D8 diffractometer with a SMART6000 CCD detector, equipped with a Rigaku Cu rotating anode generator. Structures were solved by direct methods[S1] and expanded using Fourier techniques.[S2] Neutral atom scattering factors were taken from Cromer and Waber.[S3] Anomalous dispersion effects were included in Fcalc[S4]; the values for Δf' and Δf" were those of Creagh and McAuley.[S5] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S6] All calculations were performed using the CrystalStructure[S7,S8] crystallographic software package, except for refinement, which was performed using SHELXL-97.[S1] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced in calculated positions and refined on a riding model. C_{60}:**5** was a non-merohedral twin with twin law [0.085 0.000 -0.915 0.000 -1.000 0.000 -1.085 0.000 -0.085]; BASF refined to 0.478. Refinement details are summarized in Table **S1**.

For C_{60}:**1,** the C_{60} molecule was disordered, and modeled with four different orientations. The major component was located completely from difference maps, and subsequent atom positions for smaller components were determined and refined by first locating the highest peaks from difference maps for the next major disorder component, using Monte Carlo methods to calculate the remaining atom positions, and then refining these positions with a central dummy atom that acted as the pivot. This was repeated for all orientations. The occupancy of each orientation (required to sum to one), was C1-C60 = 0.431(6), C101-C160 = 0.254(7), C201-C260 = 0.169(7) and C301-C360 = 0.148(6). Similarity restraints were applied to all C_{60} components. Refinement values are still high, and reflect the fact that the C_{60} can essentially be considered to have crystallized with no preferred orientation. Another problem lies in that a possible twin law was identified, however, the batch scale factor (BASF) refined to zero. The data was therefore treated as originating from a single component crystal. See Figures S.1 and S.2 for the asymmetric unit and packed unit cell of C_{60}:**1.**

For C_{60}:**5,** the C_{60} molecule was disordered, and modeled with two different orientations that were refined (C1-C60 = 0.602(6): C101-C160 = 0.398(6)). Similarity and distance restraints were applied to these carbon atoms. Two lattice solvent 1,2-dichlorobenzene molecules were present in the asymmetric unit; one was present at 0.5-occupancy, and was disordered about an inversion centre while the second was disordered over two positions (with refined occupancies C307-C312, Cl3, Cl4 = 0.518(6): C313-C318, Cl5, Cl6 = 0.482(6)). Distance and similarity

restraints were applied to the lattice solvent molecules. See Figures S.3, S.4 and S.5 for the asymmetric unit, extended interactions and packed unit cell of C_{60}:**5**.

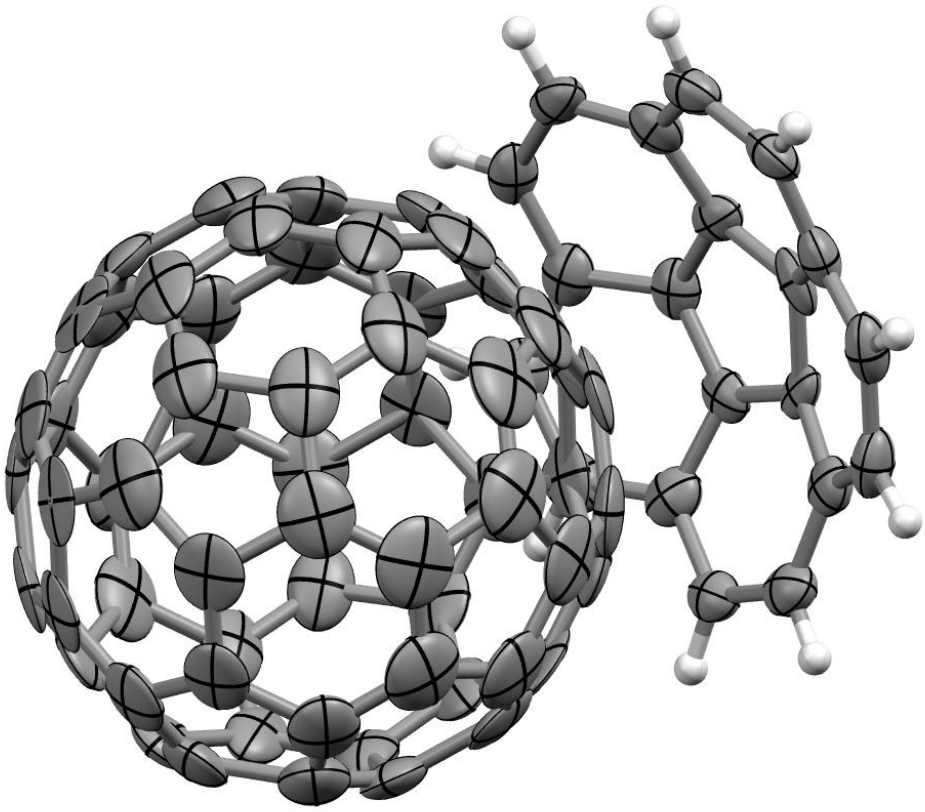

Figure S.1: 50% probability ellipsoid representation of the asymmetric unit of C_{60}:**1**, with the minor disorder components of C_{60} omitted for clarity.

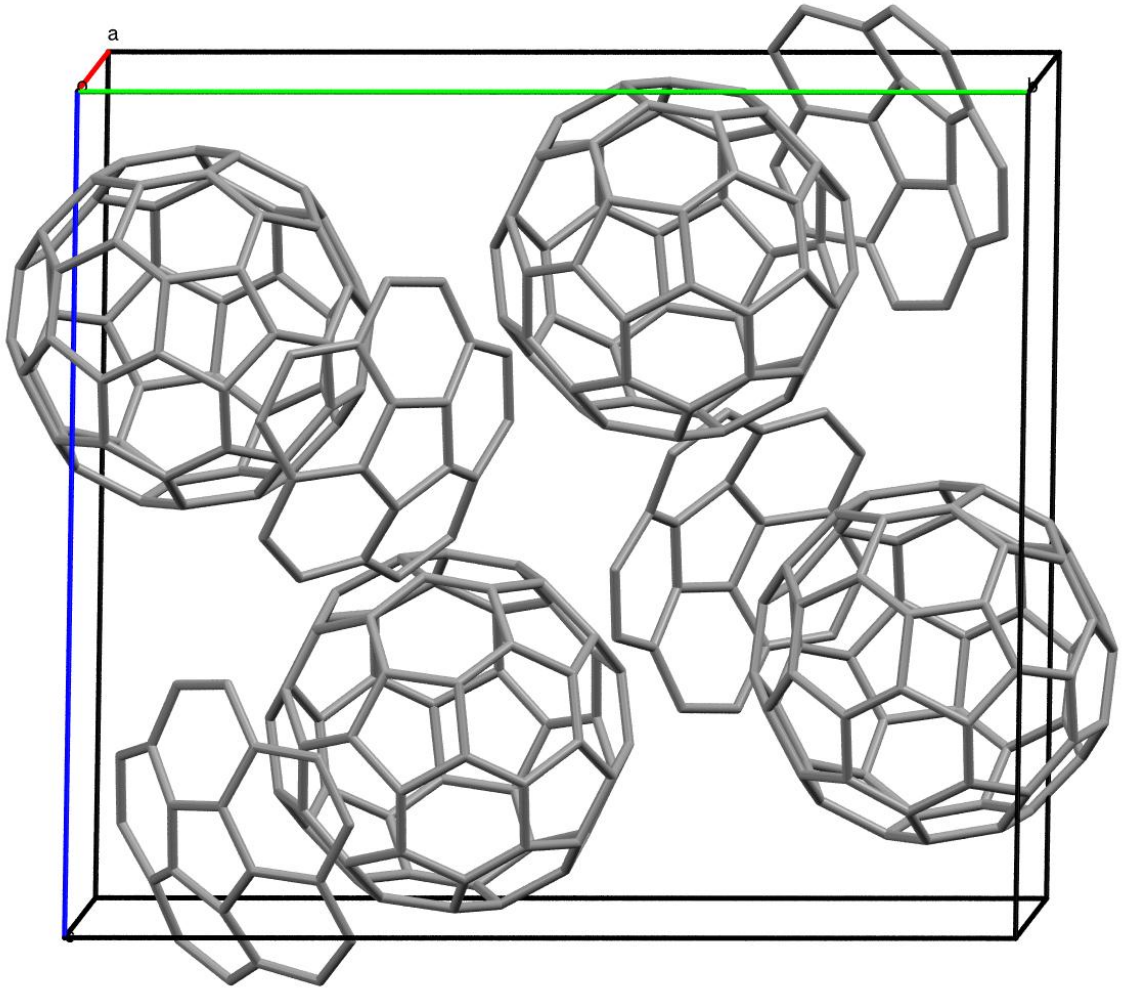

Figure S.2: Capped stick representation of the packed unit cell for C_{60}:**1**, with the minor disorder components of C_{60} omitted for clarity. Symmetry equivalents generated by operators: (i) 1-x, 1-y, 1-z, (ii) ½-x, -½+y, ½-z, (iii) ½+x, 3/2-y, ½+z.

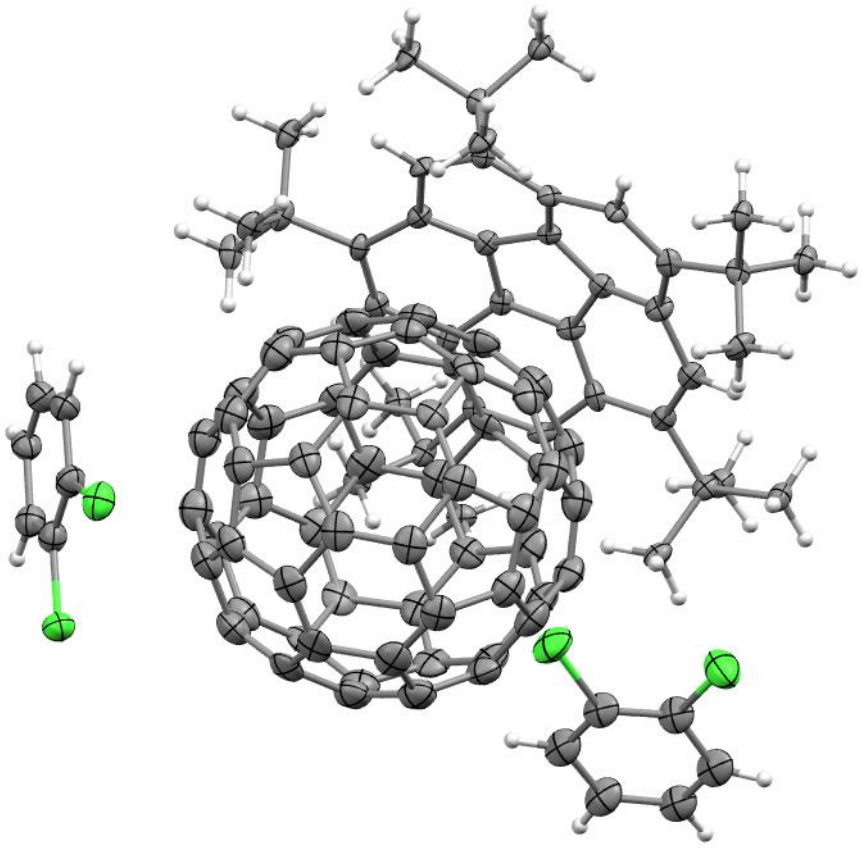

Figure S.3: 50% probability ellipsoid representation of the asymmetric unit for C_{60}:**5**, with the minor disorder components of C_{60} and dichlorobenzene molecules omitted for clarity.

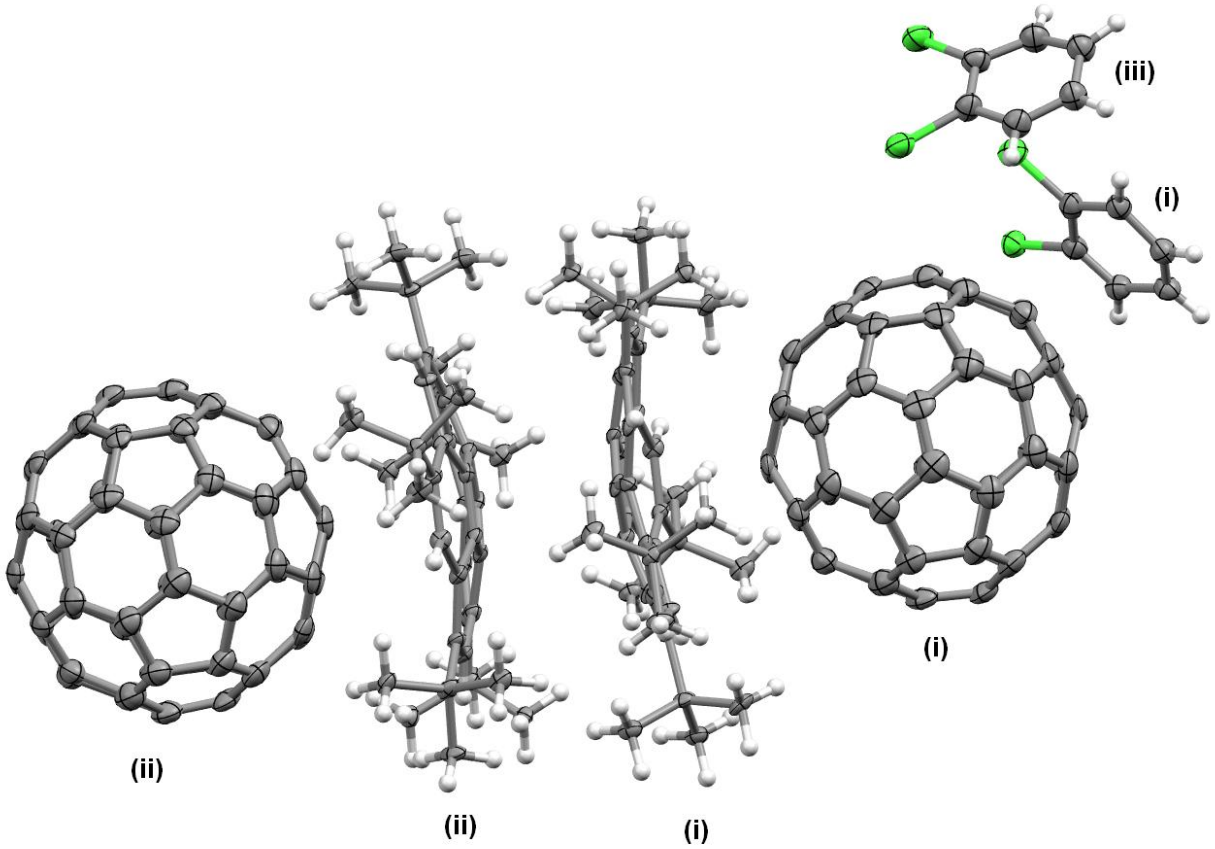

Figure S.4: 30% Probability ellipsoid representation of C_{60}:**5**, with the minor disorder components of C_{60} omitted for clarity. (i) x, y, z (ii) –x, 1-y, -z (iii) ½-x, -½+y, ½-z.

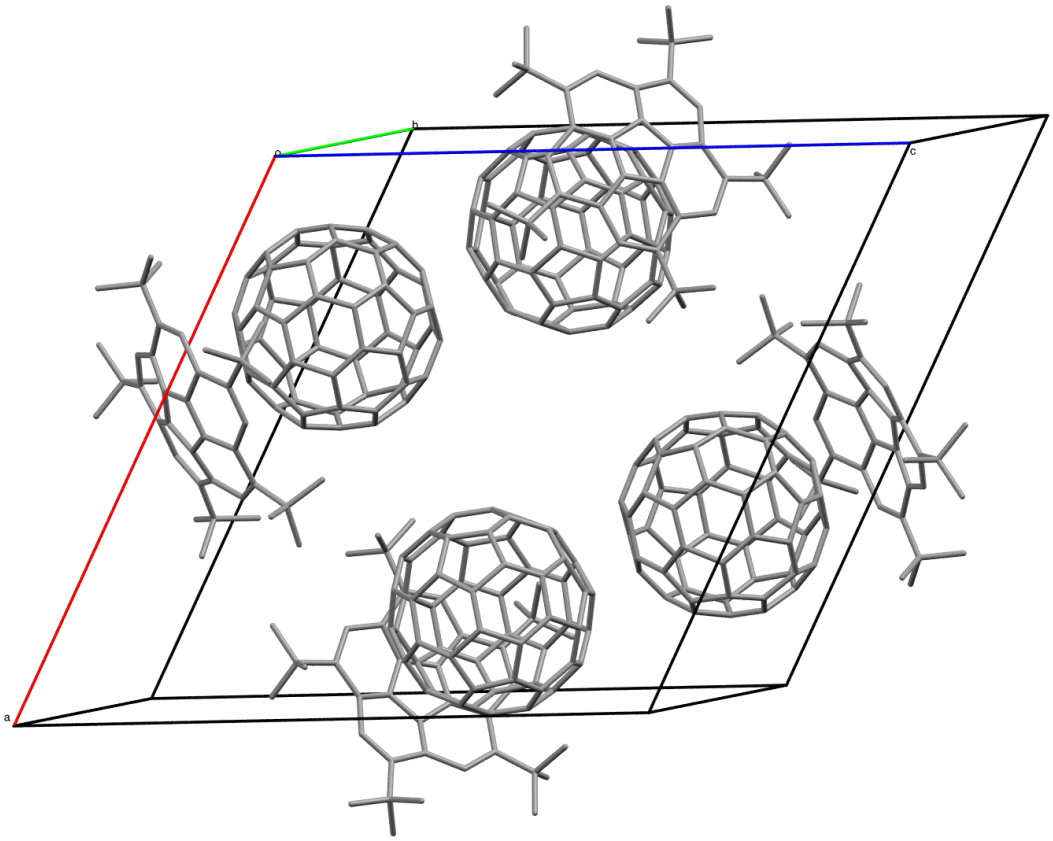

Figure S.4: Capped stick representation of the packed unit cell for C_{60}:**5**, with the minor disorder components of C_{60}, lattice solvent dichlorobenzene and H-atoms omitted for clarity. Symmetry equivalents generated by operators: (i) ½-x, ½+y, ½-z, (ii) 1-x, 1-y, 1-z, (iii) ½+x, ½-y, ½+z.

Table S1 Summary of Crystallographic Data

Compound reference	C_{60}:**1**	C_{60}:**5**
Chemical formula	C_{60}•$C_{20}H_{10}$	C_{60}•$C_{40}H_{50}$• 1.5($C_6H_4Cl_2$)
Formula Mass	970.96	1472.00
Crystal system	Monoclinic	Monoclinic
a/Å	13.0695(10)	21.975(6)
b/Å	18.6034(15)	15.264(4)
c/Å	17.3068(13)	23.000(7)
α/°	90.00	90.00
β/°	110.768(8)	117.783(5)
γ/°	90.00	90.00
Unit cell volume/Å^3	3934.5(5)	6825(3)
Temperature/K	163(2)	100(2)
Space group	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, *Z*	4	4
Radiation type	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	0.094	1.674
No. of reflections measured	35719	35649
No. of independent reflections	7297	14175
R_{int}	0.0537	0.0000
Final R_1 values ($I > 2\sigma(I)$)	0.1551	0.1184
Final $wR(F^2)$ values (all data)	0.4859	0.3355
Goodness of fit on F^2	2.112	1.050

References.

S1. SHELXD: G.M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112-122.

S2. DIRDIF99: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

S3. D.T. Cromer, J.T. Waber, "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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S6. D. C. Creagh, J.H. Hubbell, "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

S7. CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2005). 9009 New Trails Dr. The Woodlands TX 77381 USA.

S8. CRYSTALS Issue 10: D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, Chemical Crystallography Laboratory, Oxford, UK. (1996).