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Supporting Information: Enantiopure molecule forms monolayer of cyclic pentamers with no chiral preference

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Pentamer Chirality Analysis

Image analysis methods implemented in Matlab were used to automate the determination of S-ICA pentamer cluster chirality. The analysis procedure received as input the manually determined center positions of each cluster. The angular orientation (δ) of each cluster as a function of distance (r) from the center was then calculated by projecting the image onto $\sin(5\theta)$ and $\cos(5\theta)$ vectors. We found that $\delta(r)$ was roughly linear in the range of 10–30 pixels from the center of the pentamer, with the slope depending on the chirality of the cluster. The data were fit to a line to determine this slope, and thus the cluster chirality.

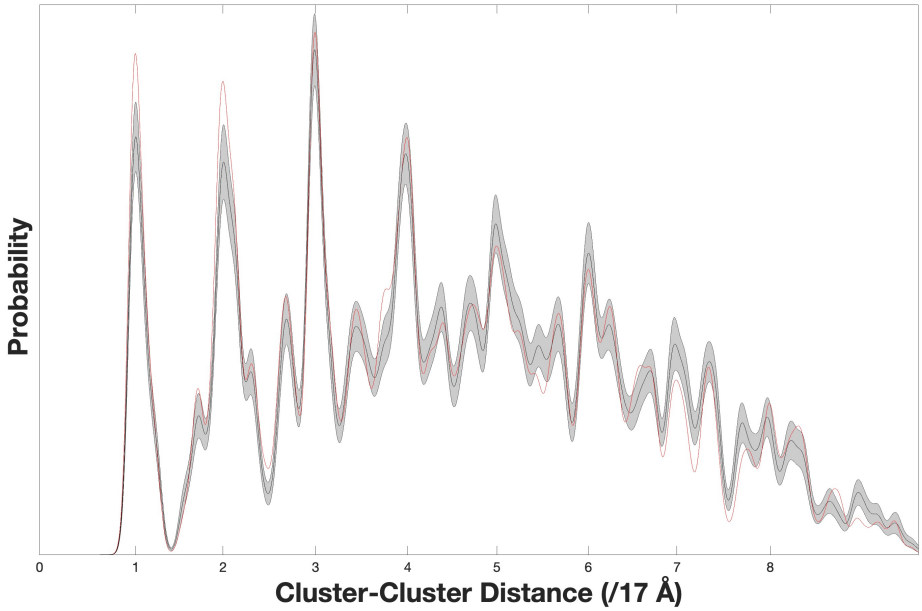

Figure S1: Correlation function showing the probability of two clusters having the same chirality, calculated as a function of their distance. The black line shows the expected correlation for random distribution of chirality, with the standard deviation (1σ) shaded gray. The red trace is the experimental correlation.

The correlation function shown in Figure S1 was computed to determine whether nearby pentamers were likely to have the same chirality; that is, whether homochiral domains are formed. The effect, if it exists at all, is quite weak and limited to near neighbors, as can

be seen by the close overlap between the experimental correlation function (red line) and the correlation function calculated empirically from randomly chosen chirality (black line, gray bounds showing one standard deviation.) Note that the correlation functions are not normalized, and decay at longer distances because of the finite image size.

Crystal Structure Details

S-indoline-2-carboxylic acid (S-ICA) crystallizes as colorless plate-like crystals from an acetonitrile/ diethyl ether solution. There are two molecules of the indole in the unit cell of the primitive, acentric, monoclinic space group $P2_1$. The correct absolute stereochemistry was determined by comparison of the known chirality at C2 (S) with that of the model. This is supported by comparison of intensities of Friedel pairs of reflections yielding a Flack x parameter = 0.2(2) [1] and a Hooft y parameter = 0.19(19). [2] While these values deviate from the ideal value of zero, they are strongly indicative that the enantiomorph of the space group is correct. However, only three atoms are available to contribute to these measurements (nitrogen and two oxygen), thus this is a reasonable result.

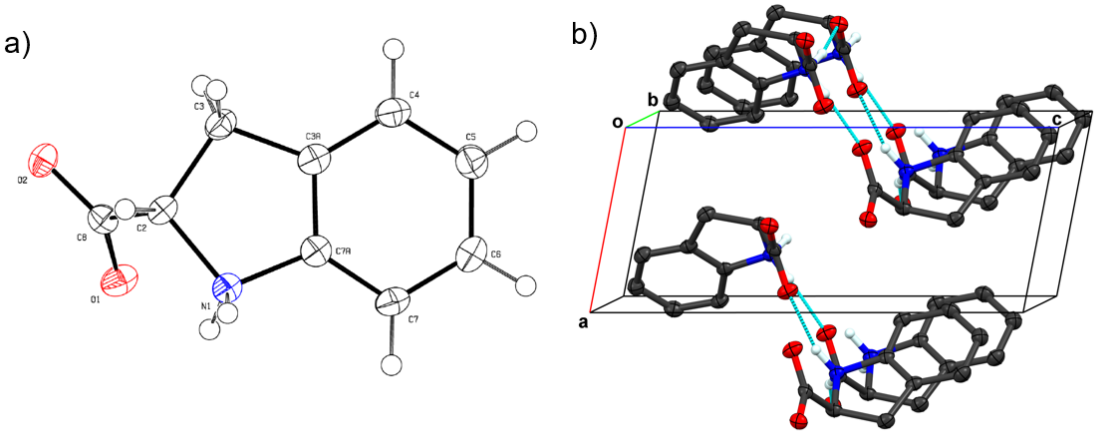

Figure S2: (a) ORTEP diagram of S-ICA, showing ellipsoids at 50% probability level. (b) Unit cell packing showing probable $NH_2^+ \cdots COO^-$ electrostatic interactions.

The structure of the compound reveals that the indole carboxylic acid has adopted a zwitterionic form (see Figure S2). The indole nitrogen bonds two hydrogen atoms and there is a lack of presence of hydrogen atoms on the carboxyl oxygen atoms (Figure S2a). The hydrogen atoms bonded to the indole nitrogen atom were located from a difference Fourier map and refined freely. The C—O bond distances are nearly equal, supporting this claim (Table S4). These hydrogen atoms form hydrogen bonds to neighboring carboxylate oxygen atoms, to O1 related by the crystallographic screw axis and to O2 by translation along the b-axis (see Table S7 for details). There is an additional, intramolecular hydrogen-bond reported in Table S7 that can be ignored (first entry) because the O–H$\cdots$O angle is strained at 114 Å and is not a favorable interaction.

An arbitrary sphere of data was collected on a colorless plate-like crystal, having approximate dimensions of 0.118×0.091×0.019 mm, on a Bruker PHOTON-II diffractometer using a combination of ω- and ϕ-scans of 0.5 Å [1]. Data were corrected for absorption and polarization effects and analyzed for space group determination.[3] The structure was solved by dual-space methods and expanded routinely.[4] The model was refined by full-matrix least-squares analysis of F2 against all reflections.[5] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded (Uiso(H) = 1.5U_{eq}(C) for methyl, 1.2U_{eq}(C) for all others).

The anisotropic displacement parameters are shown in Table S3. The anisotropic displacement factor exponent takes the form: -2π^2 (h2a*2U_{11} + ... + 2hka*b*U_{12})

Table S1: Crystal Summary

Chemical Formula	$C_9H_9NO_2$
M_r	163.17
Crystal color, habit	colorless, plate
Crystal size	$0.118 \times 0.091 \times 0.019$ mm^3
Crystal system	Monoclinic
Space group	$P2_1$
a,b,c (Å)	5.3771(2), 5.7567(2), 12.4675(5)
α, β, γ (Å)	90, 101.824(3), 90
Volume (Å^3)	377.74(2)
Z	2
Temperature (K)	120
λ(Cu–Kα) (Å)	1.54178
μ (mm^{-1})	0.845
d_{calc}	1.435 g/cm^{-3}
No. reflections	5982
No unique reflections	1419
R_{int}	0.0594
Completeness to Θ = 67.679 Å	99.6 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 0.8311
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1419 / 1 / 117
Goodness-of-fit on F^2	1.091
Final R indices [I>2σ(I)]	$R_1 = 0.0408$, $wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0464$, $wR_2 = 0.1000$
Absolute structure parameter	0.2(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.277 and -0.195 e$^-$ Å^3

Table S2: Atomic coordinates and equivalent isotropic displacement parameters (Å2) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
O(1)	0.1350(4)	0.2671(4)	0.53624(19)	0.026(1)
O(2)	0.5056(4)	0.0830(4)	0.59513(18)	0.022(1)
N(1)	0.2973(5)	0.6747(4)	0.6205(2)	0.019(1)
C(2)	0.4813(5)	0.4733(5)	0.6449(2)	0.019(1)
C(3)	0.5362(6)	0.4410(5)	0.7708(3)	0.023(1)
C(3A)	0.3474(5)	0.5991(5)	0.8084(2)	0.021(1)
C(4)	0.2997(6)	0.6315(5)	0.9128(3)	0.025(1)
C(5)	0.1144(6)	0.7936(6)	0.9257(3)	0.027(1)
C(6)	-0.0177(6)	0.9178(5)	0.8376(3)	0.027(1)
C(7)	0.0288(6)	0.8864(5)	0.7327(3)	0.023(1)
C(7A)	0.2137(5)	0.7259(5)	0.7228(2)	0.020(1)
C(8)	0.3592(5)	0.2555(5)	0.5854(2)	0.019(1)
H(1NA)	0.170(7)	0.634(7)	0.565(3)	0.018(8)
H(1NB)	0.371(8)	0.798(8)	0.600(3)	0.028(10)
H(2)	0.64217	0.51136	0.62022	0.023
H(3A)	0.50982	0.27752	0.79048	0.028
H(3B)	0.7126	0.48707	0.80394	0.028
H(4)	0.39036	0.54605	0.97354	0.031
H(5)	0.07891	0.81869	0.99641	0.032
H(6)	-0.1427	1.02667	0.8487	0.032
H(7)	-0.0616	0.97072	0.67149	0.028

Table S3: Anisotropic displacement parameters ($Å^2$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0237(11)	0.0177(11)	0.0320(12)	-0.0009(9)	-0.0022(9)	-0.0009(9)
O(2)	0.0220(10)	0.0169(10)	0.0281(11)	-0.0025(8)	0.0060(8)	0.0006(8)
N(1)	0.0182(13)	0.0173(13)	0.0212(12)	-0.0008(10)	0.0028(10)	-0.0015(10)
C(2)	0.0168(14)	0.0166(14)	0.0243(15)	0.0009(12)	0.0035(11)	0.0018(11)
C(3)	0.0226(15)	0.0189(16)	0.0266(16)	-0.0021(12)	0.0009(11)	0.0031(11)
C(3A)	0.0190(13)	0.0175(15)	0.0257(15)	-0.0007(12)	0.0008(11)	-0.0030(12)
C(4)	0.0259(16)	0.0231(17)	0.0254(16)	0.0028(13)	0.0003(12)	0.0023(13)
C(5)	0.0282(17)	0.0278(18)	0.0243(15)	-0.0019(12)	0.0056(12)	0.0001(13)
C(6)	0.0240(16)	0.0238(18)	0.0331(17)	-0.0017(13)	0.0079(13)	0.0035(12)
C(7)	0.0206(15)	0.0197(15)	0.0263(16)	0.0018(13)	-0.0007(11)	0.0009(12)
C(7A)	0.0183(14)	0.0170(16)	0.0231(14)	-0.0024(11)	0.0023(11)	-0.0050(11)
C(8)	0.0205(14)	0.0186(14)	0.0191(13)	0.0019(12)	0.0056(10)	-0.0032(13)

Table S4: Bond lengths (Å) for S-ICA

atom-atom	distance
O(1)-C(8)	1.237(4)
O(2)-C(8)	1.258(4)
N(1)-C(7A)	1.466(4)
N(1)-C(2)	1.514(4)
N(1)-H(1NA)	0.90(4)
N(1)-H(1NB)	0.88(5)
C(2)-C(8)	1.534(4)
C(2)-C(3)	1.548(4)
C(2)-H(2)	1.0000
C(3)-C(3A)	1.507(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3A)-C(7A)	1.369(4)
C(3A)-C(4)	1.390(5)
C(4)-C(5)	1.399(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.379(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.392(5)
C(6)-H(6)	0.9500
C(7)-C(7A)	1.382(4)
C(7)-H(7)	0.9500

Table S5: Bond angles for S-ICA

atom-atom-atom	angle
C(7A)-N(1)-C(2)	106.5(2)
C(7A)-N(1)-H(1NA)	114(2)
C(2)-N(1)-H(1NA)	109(2)
C(7A)-N(1)-H(1NB)	109(3
C(2)-N(1)-H(1NB)	111(3)
H(1NA)-N(1)-H(1NB)	108(4)
N(1)-C(2)-C(8)	109.4(2)
N(1)-C(2)-C(3)	106.0(2)
C(8)-C(2)-C(3)	111.5(2)
N(1)-C(2)-H(2)	110.0
C(8)-C(2)-H(2)	110.0
C(3)-C(2)-H(2)	110.0
C(3A)-C(3)-C(2)	104.0(2)
C(3A)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3A)	111.0
C(3A)-C(3)-H(3B)	111.0
C(2)-C(3)-H(3B)	111.0
H(3A)-C(3)-H(3B)	109.0
C(7A)-C(3A)-C(4)	119.4(3)
C(7A)-C(3A)-C(3)	111.1(3)
C(4)-C(3A)-C(3)	129.6(3)
C(3A)-C(4)-C(5)	118.1(3)
C(3A)-C(4)-H(4)	121.0
C(5)-C(4)-H(4)	121.0
C(6)-C(5)-C(4)	121.1(3)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(7)	121.3(3)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(7A)-C(7)-C(6)	116.2(3)
C(7A)-C(7)-H(7)	121.9
C(6)-C(7)-H(7)	121.9
C(3A)-C(7A)-C(7)	124.0(3)
C(3A)-C(7A)-N(1)	111.4(3)
C(7)-C(7A)-N(1)	124.6(3)
O(1)-C(8)-O(2)	128.1(3)
O(1)-C(8)-C(2)	118.2(3)
O(2)-C(8)-C(2)	113.7(2)

Table S6: Torsion angles

atom-atom-atom-atom	angle
C(7A)-N(1)-C(2)-C(8)	110.3(2)
C(7A)-N(1)-C(2)-C(3)	-10.0(3)
N(1)-C(2)-C(3)-C(3A)	9.1(3)
C(8)-C(2)-C(3)-C(3A)	-109.8(3)
C(2)-C(3)-C(3A)-C(7A)	-5.0(3)
C(2)-C(3)-C(3A)-C(4)	176.1(3)
C(7A)-C(3A)-C(4)-C(5)	0.2(4)
C(3)-C(3A)-C(4)-C(5)	179.0(3)
C(3A)-C(4)-C(5)-C(6)	0.1(5)
C(4)-C(5)-C(6)-C(7)	-0.1(5)
C(5)-C(6)-C(7)-C(7A)	-0.2(5)
C(4)-C(3A)-C(7A)-C(7)	-0.5(5)
C(3)-C(3A)-C(7A)-C(7)	-179.6(3)
C(4)-C(3A)-C(7A)-N(1)	177.7(3)
C(3)-C(3A)-C(7A)-N(1)	-1.3(3)
C(6)-C(7)-C(7A)-C(3A)	0.5(4)
C(6)-C(7)-C(7A)-N(1)	-177.5(3)
C(2)-N(1)-C(7A)-C(3A)	7.3(3)
C(2)-N(1)-C(7A)-C(7)	-174.5(3)
N(1)-C(2)-C(8)-O(1)	-5.5(4)
C(3)-C(2)-C(8)-O(1)	111.4(3)
N(1)-C(2)-C(8)-O(2)	175.5(2)
C(3)-C(2)-C(8)-O(2)	-67.6(3)

Table S7: Intermolecular Interactions

D–H$\cdots$A	d(D–H)	d(H$\cdots$A)	d(D$\cdots$A)	<(DHA)
N(1)-H(1NA)...O(1)	0.90(4)	2.14(4)	2.645(3)	114(3)
N(1)-H(1NA)...O(1) #1	0.90(4)	2.00(4)	2.765(3)	141(3)
N(1)-H(1NB)...O(2) #2	0.88(5)	1.80(5)	2.650(3)	163(4)

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