Synthesis of ethylenediammonium sulfate (EDS)

Ethylenediamine (99%; 178 mL; 2.66 moles) and ethanol (99%; 750 mL) were added slowly to a 4 L beaker cooled in an ice-bath. Concentrated sulfuric acid (96.8%; 145 mL; 2.64 moles) was added dropwise with continuous stirring (Caution! The reaction of ethylenediamine with sulfuric acid is highly exothermic so the reaction must be carried out slowly with continuous ice cooling). Additional ethanol (2 x 250 mL) was added to the reaction mixture during the synthesis as the product formed and the reaction mixture became viscous. Ethylenediammonium sulfate was isolated by vacuum filtration and washed with ethanol (99%; 375 mL) and ether (250 mL). The resulting colorless EDS (320 g, 2.05 mol; 77%) was air-dried and ground into a fine powder with a mortar and pestle prior to use.

Preparation of ethylenediammonium sulfate saturated solution

Ethylenediammonium sulfate (175 g) was slowly dissolved in warm distilled water (0.16 L) in a 250 mL Erlenmeyer flask immersed in a water bath at 60 °C for several hours. The solution was allowed to cool overnight at room temperature and the presence of ethylenediammonium sulfate crystals observed at the bottom of the flask ensured that the solution was saturated. The ethylenediammonium sulfate saturated solution was centrifuged at *ca.* 400 rpm in Fisher Brand 50 mL culture tubes prior to use for seeded crystal growth.

Closed system setup for the abrasion/grinding experiments

(*i*) Abrasion/grinding with glass beads: *ca*. 0.5 g of EDS powder, 1.2 mL of saturated EDS solution, *ca*. 1.0 g of glass beads (3 mm diameter; Fisher Scientific), and a magnetic stir bar (9.85 mm x 6.32 mm) were added to a 5 mL round bottom flask and closed with a glass stopper.

(*ii*) Abrasion/grinding with ceramic beads: *ca*. 0.25 g of EDS powder, 1.0 mL of saturated EDS solution, *ca*. 3.0 g of YTZ® Zirconia grinding media (0.80 mm diameter; Tosoh Corporation), and a magnetic stir bar (9.85 mm x 6.32 mm) were added to a 5 mL round bottom flask and closed with a glass stopper.

The stirring rate of commercial stirrers was verified using a strobe light (Strobotac Stroboscope, type 1538A (General Radio Co., Concord, MA)). The position for steady stirring was determined for each stir plate prior to securing the flask above the stir plate. Corning magnetic stirrer/hotplates (Model PC420) were used for experiments carried out at 480 and 1100 rpm. Specially built stirrers equipped with speed controllers (OE Motor Controller or MSRX Speed Controller (PINE Instrument Company)) were used to control the stirring rate at 2400 rpm and 4800 rpm. A Buchler Instruments' *Evapo-Mix* operating at *ca.* 40 Hz was used for the rotary shaking experiment.

Crystal seeding technique

Ethylenediammonium sulfate crystallites (*ca*. 5 μL) were sampled from the abrasion/grinding mixture at various times using an automatic pipette and transferred to the bottom of a 125 mL Erlenmeyer flask containing about 100 mL of freshly centrifuged ethylenediammonium sulfate saturated solution. The Erlenmeyer flask was then swirled slightly to disperse the crystallites and immediately poured into a crystallizing dish (100 mm diameter, 50 mm height). The crystallizing dish was partially covered with filter paper and allowed to sit undisturbed for crystal growth. After 1 to 2 days individual crystals were collected (*ca.* 150 crystals with average dimensions of *ca.* 1.6 mm x 1.6

mm x 0.3 mm) and analyzed using a polarized light microscope. Although all attempts were made to minimize the possibility of primary nucleation (yielding racemic crystals) during the seeding experiments, one can not exclude this possibility. Primary nucleation would influence the CEE data more significantly as one approaches homochirality.

Determination of EDS crystal chirality using a polarized light microscope

Ethylenediammonium sulfate crystals were placed on a glass support and analyzed using a polarized light microscope (Leitz, Laborlux 11 Pol S) at 50x magnification. The upper polarizing filter was rotated clockwise to determine the optical rotatory dispersion of individual crystals. A color change from clear to blue to amber was observed for *dextrorotatory* crystals and from amber to blue to clear was observed for *levorotatory* crystals. Error bars in the plot of CEE versus time of stirring (Figure 2b) were calculated for each point by pooling 150 crystals into three groups of 50. The number of *dextrorotatory* and *levorotatory* crystals in each pool was used to obtain three values of the crystal enantiomeric excess (CEE) at each time. The average value at each time was used as the data point and the standard deviation of each set was used as the magnitude of the error bars above and below the data point. It was not possible to calculate error bars for Figure 2a since, in our initial experiments, the data was grouped into only one pool. **Figure ESI 1** shows a histogram plot of CEE versus the number of crystals in the sampling pool for 680 crystals grown from racemic seeds (*i.e.* prior to the abrasion/grinding experiment). Each column shows all the calculated CEE values in each pool. Each column represents the same total number of crystals where the number of points in each column is equal to 680/pool size (*N.B.* in many cases there are overlapping points). This plot is meant to illustrate that a sufficiently large number of crystals should be analyzed to account for the error associated with counting random events.[1]

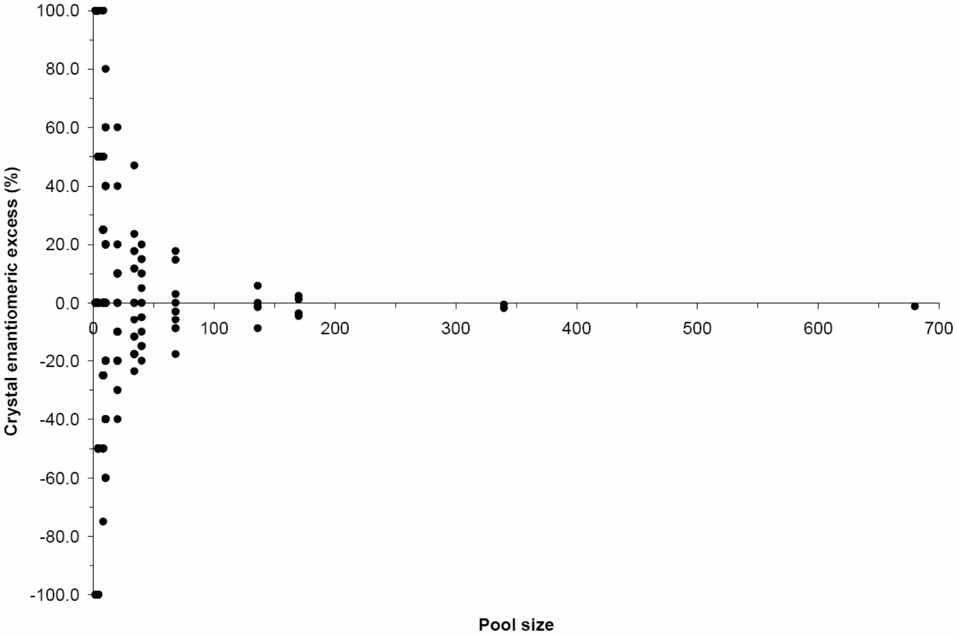

Fig. ESI 1 Histogram plot of CEE *vs.* number of crystals in the sampling pool (N = 680)

References

1. J. S. Siegel, *Chirality*, 1998, **10**, 24-27.