Directing the Viedma Ripening of Ethylenediammonium Sulfate using "Tailor-made" Chiral Additives

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Supplementary information

The chirality of crystals can be distinguished through circular polarization observed along the optic axis, where the color change on rotating the analyser is opposite for enantiomorph crystals. In 1861, Gladstone stated:\textsuperscript{1}

"If, in order to make these follow in their natural order—red, orange, yellow, green, blue, violet—it is necessary to turn the analyser to the right—that is to say, in the direction of the hands of a watch—the substance is said to exhibit right-handed or positive circular polarization, which is usually indicated by the sign ∨ or +: if, on the contrary, the analyser must be turned to the left to produce the same result, the polarization is left-handed, or negative, and the sign ∧ or − is employed."

The most prominent colors observed for ethylenediammonium sulfate (EDS) crystals when observed between crossed polarizers are amber and blue. Accordingly, our group identifies the chirality of EDS by observing a blue-to-amber-to-clear or an amber-to-blue-to-clear transition on rotating the analyzer clockwise.\textsuperscript{2} The correlation of our method with the ‘natural order’ of light is illustrated for a dextrorotatory and levorotatory crystal in Figure ESI-1 a, b, d, & e. Another method to distinguish the chirality of EDS has been described by Matsumoto, Soai and coworkers, where, starting with crossed polarizers, dextrorotatory crystals decreased in brightness while levorotatory crystals increased in brightness, with clockwise rotation of the analyzer by 45° (Figure ESI-1 c & f).\textsuperscript{3}
Figure ESI-1 a, b & c. Color transitions observed for a dextrorotatory crystal of EDS using polarized light microscopy: (a) blue-to-amber-to-clear when rotating the analyzer clockwise, (b) blue-to-violet-to-red-to-orange-to-clear when rotating the analyzer clockwise and (c) decreasing brightness when rotating the analyzer 45° clockwise (center image: crossed polarizers, left image: 45° counterclockwise and right image: 45° clockwise).

d, e & f: Color transitions observed for a levorotatory crystal of EDS using polarized light microscopy (d) amber-to-blue-to-clear when rotating the analyzer clockwise, (e) yellow-to-orange-to-violet-to-blue-to-clear when rotating the analyzer clockwise and (f) increasing brightness when rotating the analyzer 45° clockwise (center image: crossed polarizers, left image: 45° counterclockwise and right image: 45° clockwise). (Scale bar = 1 mm)
Figure ESI-2. CD spectra of trans-1,2-diphenylethylenediamine in CHCl₃ – Upper spectra: (i) (1R,2R)-1,2-diphenylethylenediamine (3.5 mM) with no EDS (solid line), (ii) (1R,2R)-1,2-diphenylethylenediamine (3 mL, 3.5 mM) shaken with 300 mg l-EDS (106 µm - 150 µm) for 1 hr. and centrifuged for 20 min. (black squares) and (iii) (1R,2R)-1,2-diphenylethylenediamine (3 mL, 3.5 mM) shaken with 300 mg d-EDS (106 µm - 150 µm) for 1 hr. and centrifuged for 20 min. (red squares). Lower spectra: (i) (15,25)-1,2-diphenylethylenediamine (3.5 mM) with no EDS (solid line), (ii) (15,25)-1,2-diphenylethylenediamine (3.5 mM) shaken with 300 mg l-EDS (106 µm - 150 µm) for 1 hr. and centrifuged for 20 min. (black squares) and (iii) (15,25)-1,2-diphenylethylenediamine (3 mL, 3.5 mM) shaken with 300 mg d-EDS (106 µm - 150 µm) for 1 hr. and centrifuged for 20 min. (red squares).

References: