

Supporting Online Material for

A stereoselectively deuterated supramolecular motif to probe the role of solvent during self-assembly processes.

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Contents

<i>Experimental Section</i>	S2
<i>Supporting Data</i>	
Figure S1. UV spectra of (<i>S,S,S</i>)-D-BTA in MCH and heptane	S3
Figure S2. . Normalized UV cooling curves of (<i>S,S,S</i>)-D-BTA and overlays of the UV and CD cooling curves in MCH and heptane.	S4
Figure S3. Fit of the elongation and nucleation regimes for (<i>S,S,S</i>)-D-BTA	S5
Table S1. Thermodynamic parameters of the (<i>S,S,S</i>)-D-BTA self-assembly	S5
Figure S4. CD spectra of (<i>S,S,S</i>)-D-BTA in MCH and heptane at 263 K and 293 K	S6
Figure S5. $\Delta\epsilon$ as a function of temperature for (<i>S,S,S</i>)-D-BTA in heptane	S7
Figure S6. $\Delta\epsilon$ as a function of temperature for (<i>S,S,S</i>)-D-BTA in heptane at varying concentrations.	S8
Figure S7. Normalized absorbance of (<i>S,S,S</i>)-D-BTA UV cooling curves in heptane-MCH mixtures	S9
Figure S8. Interval CD spectra of (<i>S,S,S</i>)-D-BTA in heptane-MCH mixture	S10
Figure S9. $\Delta\epsilon$ as a function of solvent composition in MCH-heptane mixtures.	S11
Figure S10. CD spectra of (<i>S,S,S</i>)-D-BTA in linear alkane solvents	S12
Figure S11. CD spectra of (<i>S,S,S</i>)-D-BTA in decalin, isooctane and cyclohexane	S13
<i>References</i>	S14

Experimental Section

Materials

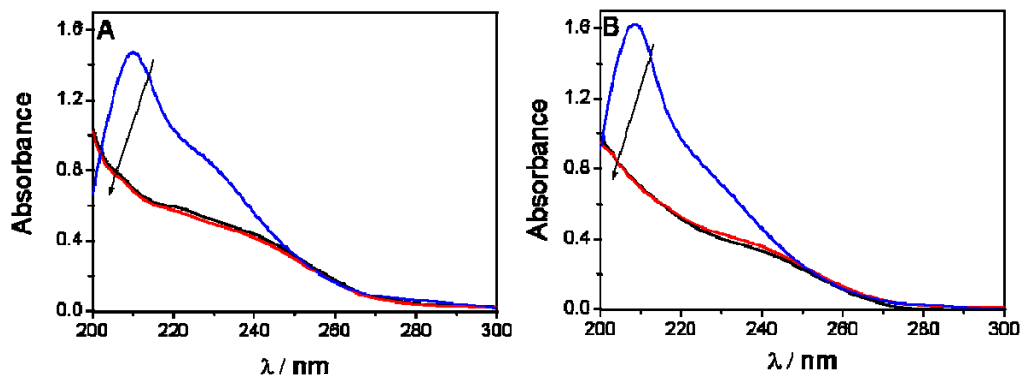
(*S,S,S*)-D-BTA was prepared according to previously described procedures.^[1,2] Heptane (spectrophotometric grade) was purchased from Acros and methylcyclohexane (MCH, spectrophotometric grade) was obtained from Aldrich.

Methods

Ultraviolet (UV) and circular dichroism (CD) measurements were simultaneously performed on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Corresponding temperature-dependent measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope. In all cases, a temperature slope of 1 K min⁻¹ was used. The molar ellipticity $\Delta\epsilon$ was calculated from the CD effect as follows; $\Delta\epsilon = \text{CD effect}/(32980 \cdot c \cdot l)$ where the CD effect is given in mdeg, c is the concentration in mol L⁻¹ and l is the optical path length in cm ($l = 1$ mm or 1 cm). In all experiments, the linear dichroism was measured and in all cases no linear dichroism was observed. Cells with an optical path length of 1 cm or 1 mm were used and spectrophotometric grade MCH and heptane were employed. Solutions were prepared by weighing desired (*S,S,S*)-D-BTA compound (0.14 mg), after which this amount was transferred to a volumetric flask (flasks of 5 mL were employed). Then the flask was filled with the spectrophotometric grade solvent and put in an oscillation bath at 40 °C for 50 min, after which the flask was allowed to cool down. Any loss of solvent was compensated. All fits of the temperature dependent data to obtain the thermodynamic parameters were performed as previously published.^[3,4]

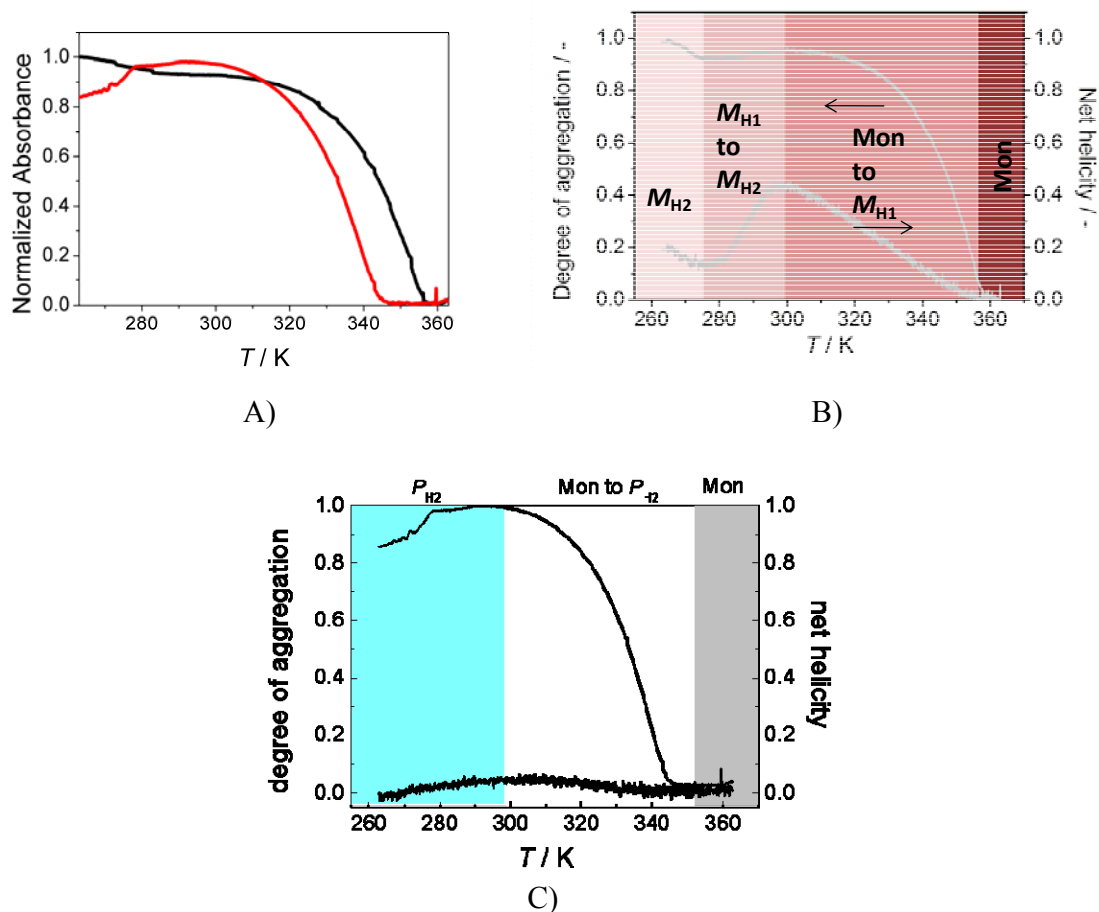
Supporting Data

Figure S1. UV spectra of (*S,S,S*)-D-BTA in MCH and heptane



UV spectra of (*S,S,S*)-D-BTA, $c = 5 \times 10^{-5}$ M at different temperatures. **A)** MCH solution at 90 °C (blue line), 20 °C (red line) and -10 °C (black line). **B)** Heptane solution at 90 °C (blue line), 20 °C (red line) and -10 °C (black line). The arrows show the blue shift upon cooling in the UV spectra, which is indicative for the aggregation behavior of BTAs in solution.

Figure S2. Normalized UV cooling curves of (*S,S,S*)-D-BTA and overlays of the UV and CD cooling curves in MCH and heptane.

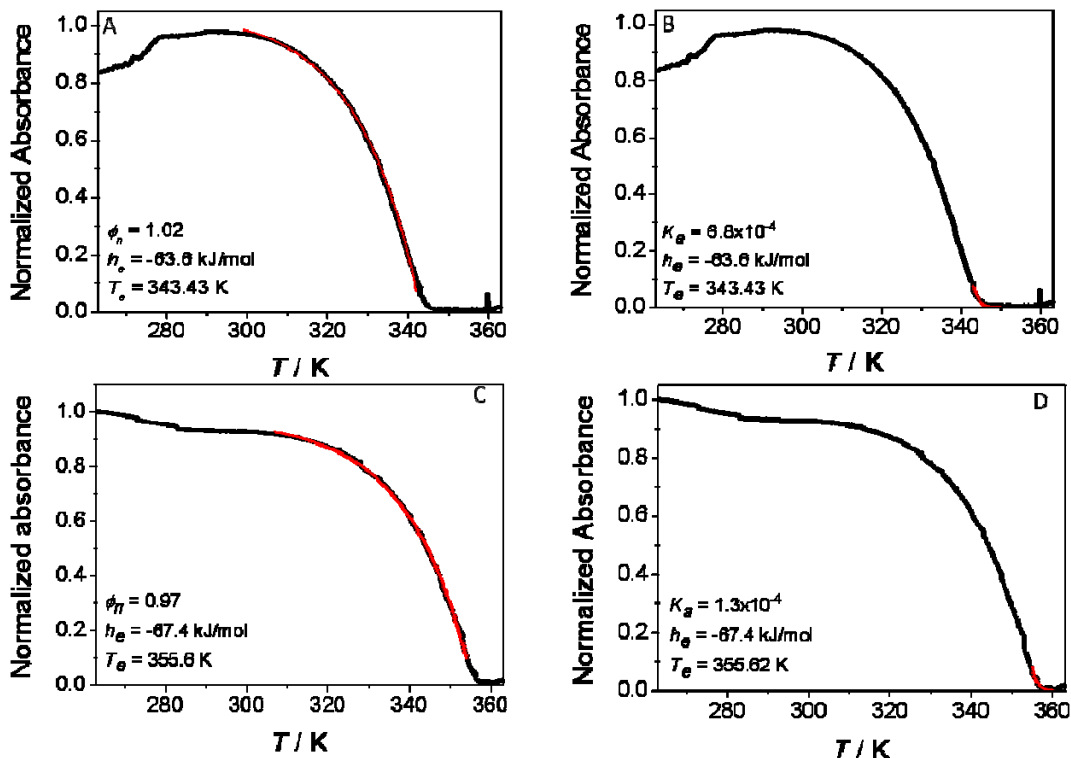


A) Normalized UV cooling curves of (*S,S,S*)-D-BTA in MCH (red) and heptane (black), as a function of temperature, $c = 5 \times 10^{-5}$ M. Monitored at $\lambda = 223$ nm, at a cooling rate of 1 K min^{-1} .

B) Overlay of the net helicity and degree of aggregation of (*S,S,S*)-D-BTA in heptane as a function of temperature. The data is based on the normalized temperature-dependent UV and CD curves, monitored at $\lambda = 223$ nm at a cooling rate of 1 K min^{-1} . Monomers (Mon) form *M* helical supramolecular polymers with a H1 conformation (M_{H1}) in excess in the dark pink region. Below 297 K, in the pink region, the H1 conformation changes into a H2 conformation. In the light pink region, H2 is the most preferred conformation.

C) Overlay of the net helicity and degree of aggregation of (*S,S,S*)-D-BTA in MCH as a function of temperature ($c = 5 \times 10^{-5}$ M). The data is based on the normalized temperature-dependent UV and CD curves, monitored at $\lambda = 223$ nm at a cooling rate of 1 K min^{-1} . The three colors show three different regions. In the white region, at 343 K, the monomers start forming preferably *P* type helical supramolecular polymers with a H2 type conformation. As the temperature decreases, from 293 K to 263 K, the preference for the helical sense shifts from *P* to *M* (light blue)

Figure S3. Fit of the elongation and nucleation regimes for (S,S,S)-D-BTA

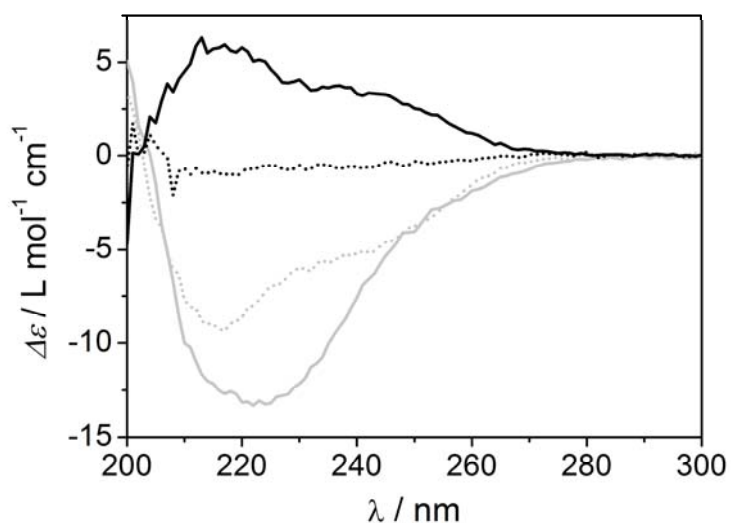


Fit of the elongation and nucleation regimes for (S,S,S)-D-BTA in MCH and heptane ($c = 5 \times 10^{-5}$ M), based on the normalized UV absorption data. The red line corresponds to the fit for the elongation and nucleation regime, respectively. The data were fitted using the nonlinear curve fit option of Origin 8.5 according to previously described references.^[3,4] **A)** Elongation regime in MCH, **B)** Nucleation regime in MCH, **C)** Elongation regime in heptane, **D)** Nucleation regime in heptane.

Table S1. Thermodynamic parameters of the (S,S,S)-D-BTA self-assembly derived from temperature-dependent UV data in heptane and MCH ($c = 5 \times 10^{-5}$ mol L⁻¹) and values for the dielectric constant (ϵ_{sol})^[5].

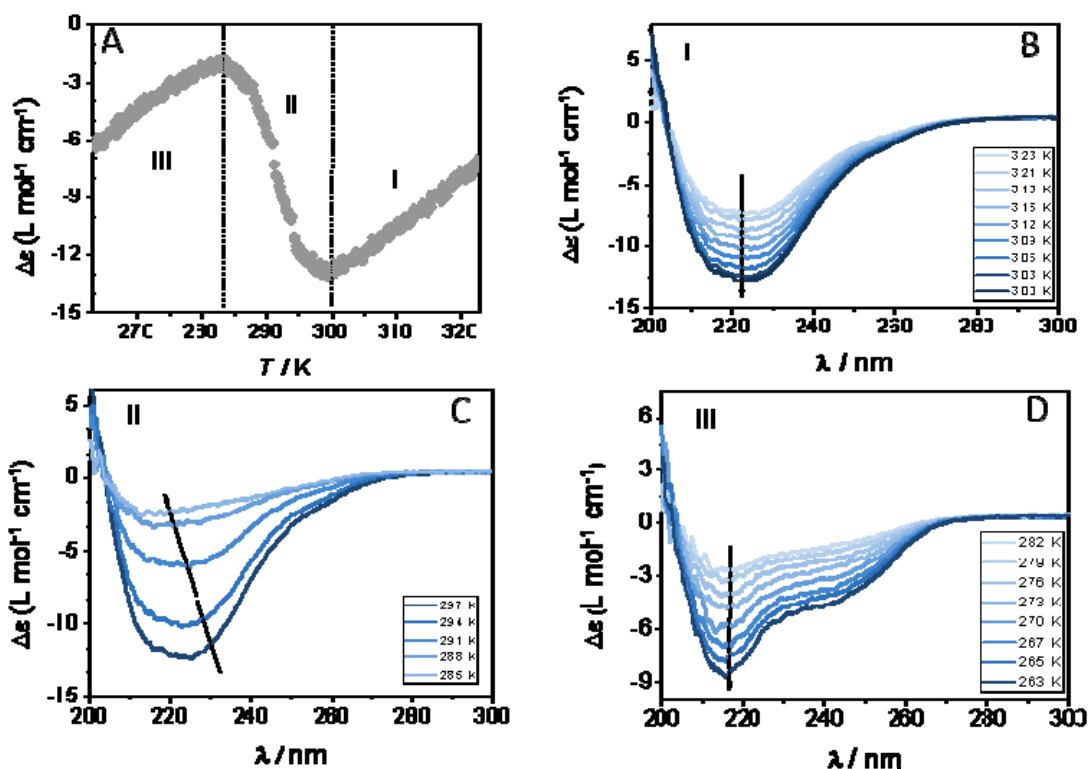
Solvent	ϵ_{sol}	T_e (K)	h_e (kJ/mol)	K_a (-)
heptane	1.92	355.6 ± 0.1	-67.4 ± 0.3	$1.3 \times 10^{-4} \pm 0.3 \times 10^{-4}$
MCH	2.02	343.4 ± 0.1	-63.6 ± 0.3	$6.8 \times 10^{-4} \pm 0.6 \times 10^{-4}$

Figure S4. CD spectra of (*S,S,S*)-D-BTA in MCH and heptane at 263 K and 293 K.



The CD spectra of (*S,S,S*)-D-BTA in MCH ($c = 5 \times 10^{-5} \text{ mol L}^{-1}$) at 293 K (upper black line) and 263 K (lower dotted black line): the shape of the Cotton effect is always double, but the sign changes from positive to negative upon cooling. The CD spectra of (*S,S,S*)-D-BTA in heptane ($c = 5 \times 10^{-5} \text{ mol L}^{-1}$) at 293 K (lower grey line) and 263 K (upper dotted grey line): the shape of the CD spectra changes from single to double upon cooling

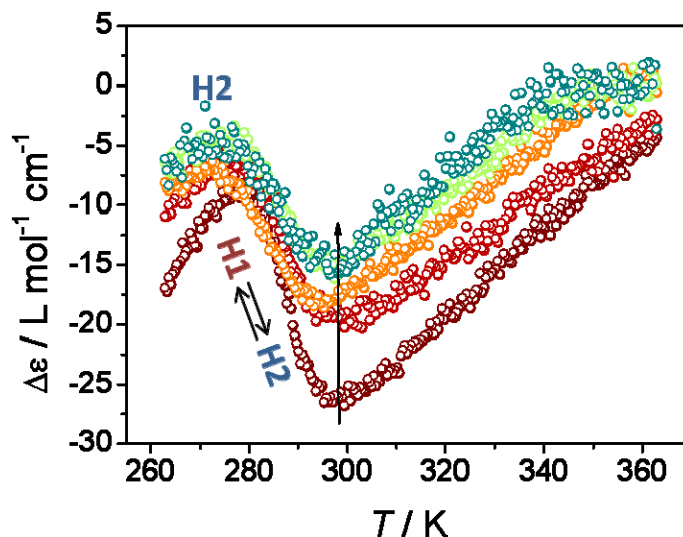
Figure S5. $\Delta\epsilon$ as a function of temperature for (*S,S,S*)-D-BTA in heptane



A) $\Delta\epsilon$ as a function of temperature between 323 K and 263 K, monitored at $\lambda = 223$ nm at a cooling rate of 1 K min^{-1} , for (*S,S,S*)-D-BTA in heptane at $c = 5 \times 10^{-5} \text{ M}$. Three regions are observed upon cooling in which the *intensity* of the Cotton effect changes gradually. The interval CD spectra of (*S,S,S*)-D-BTA in heptane from B) 323 K to 300 K, C) from 297 K to 285 K, D) 282 K to 263 K. As the temperature decreases the shape of the Cotton effect changes from single to double, indicating the change in the conformation of the supramolecular polymer.

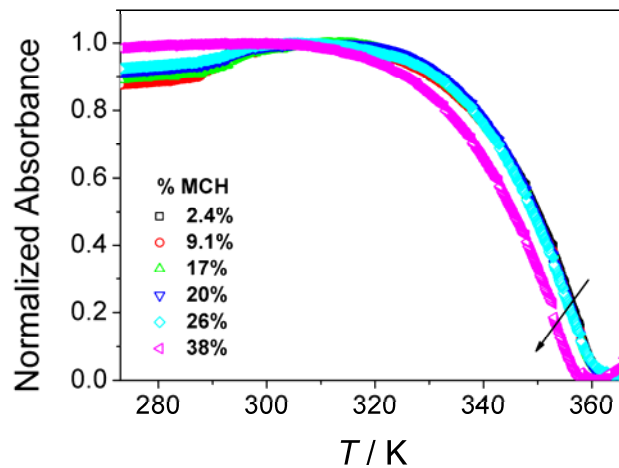
Note: The cooling curves are always probed at $\lambda = 223$ nm. The small shift in λ_{max} from 223 to 215 nm upon switching from H1 to H2 does not noticeably affect the shape of the CD cooling curve.

Figure S6. $\Delta\epsilon$ as a function of temperature for (*S,S,S*)-D-BTA in heptane at varying concentrations.



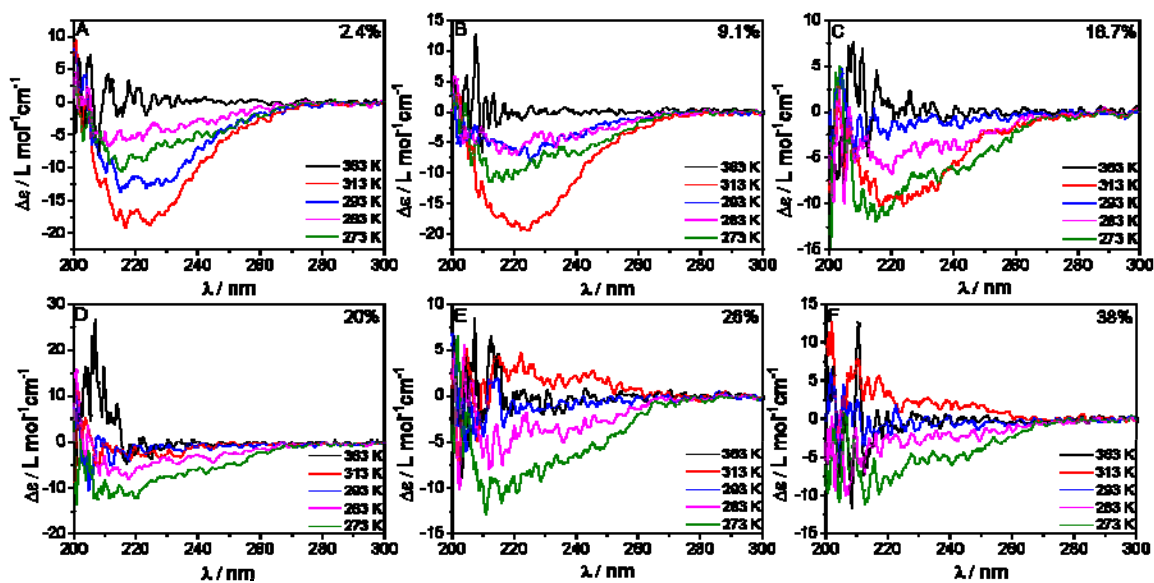
$\Delta\epsilon$ as a function of temperature monitored at $\lambda = 223$ nm at a cooling rate of 1 K min^{-1} , for (*S,S,S*)-D-BTA in heptane at $c = 1.5 \times 10^{-5}$ M (blue), 3.1×10^{-5} M (green), 4.5×10^{-5} M (orange), 2.3×10^{-4} M (red) and 3.5×10^{-4} M (wine-red). The T_e values change as a function of concentration however, the temperature at which the transition between H1 and H2 starts as well as the temperature at which H2 becomes the dominating conformer hardly changes as the concentration changes.

Figure S7. Normalized absorbance of (*S,S,S*)-D-BTA UV cooling curves in heptane-MCH mixtures .



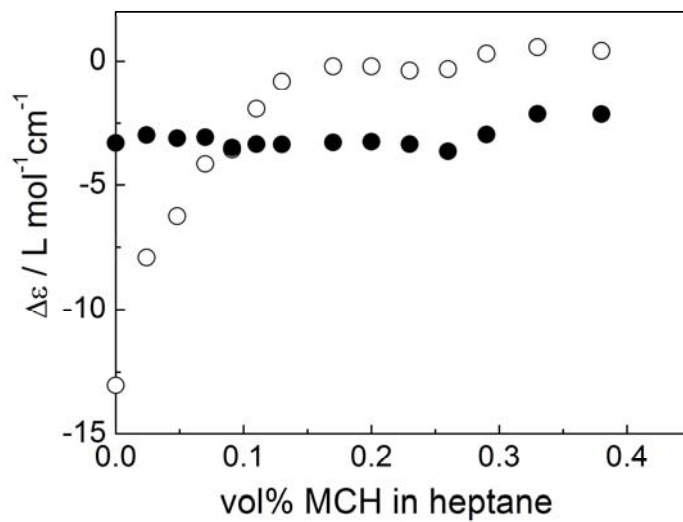
The normalized absorbance of (*S,S,S*)-D-BTA in heptane-MCH mixtures as a function of temperature ($c = 5 \times 10^{-5}$ M). Monitored at $\lambda = 223$ nm, at a cooling rate of 1 K min^{-1} . The ratio of MCH in the mixture varies. The arrow shows the increasing amount of MCH. For clarity, only a few measurements are shown. As the amount of MCH increases, the T_g slightly shifts from 361 K to 358 K which is a result of the increasing polarity of the mixture upon adding more MCH and agrees with the lower T_g found in pure MCH.

Figure S8. Interval CD spectra of (*S,S,S*)-D-BTA in heptane-MCH mixtures



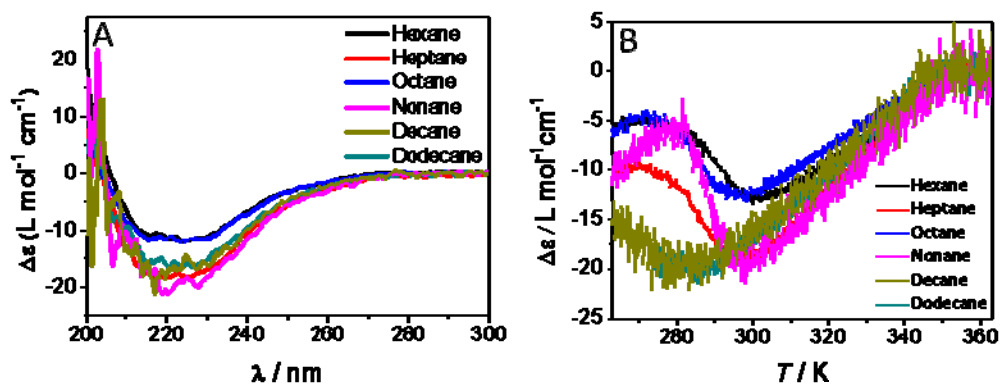
The interval CD spectra of (*S,S,S*)-D-BTA in heptane-MCH mixtures at temperatures: 95 °C, 40 °C, 20 °C, 10 °C, 0 °C. The amount of MCH increases in each run, for clarity only a few measurements are shown. A) 2.4% MCH, B) 9.1% MCH, C) 16.7% MCH, D) 20% MCH, E) 26% MCH, F) 38% MCH. Above 9.1% MCH in the mixture, the shape of the Cotton effect is double independent of the temperature.

Figure S9. $\Delta\epsilon$ as a function of solvent composition in MCH-heptane mixtures.



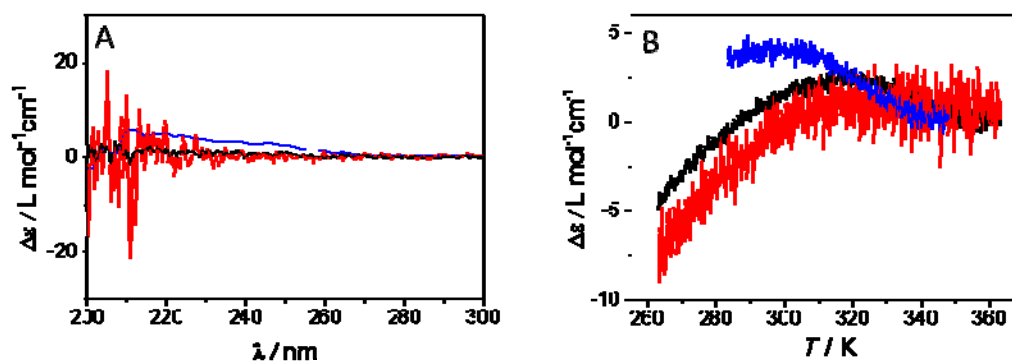
Molar ellipticity $\Delta\epsilon$ as a function of the solvent composition in MCH/heptane mixtures at 293 K (open circles) and 278 K (closed circles) ($c = 50 \mu\text{M}$, $\lambda = 223 \text{ nm}$).

Figure S10. CD spectra of (*S,S,S*)-D-BTA in linear alkane solvents



A) An overlay of the CD spectra of (*S,S,S*)-D-BTA in linear alkane solvents, $c = 5 \times 10^{-5}$ M, $T = 20$ °C. The *sign* and *shape* of the Cotton effect is similar in each case, although the $\Delta\epsilon$ values change slightly. **B)** An overlay of the CD cooling curves of (*S,S,S*)-D-BTA in linear alkane solvents as a function of temperature ($c = 5 \times 10^{-5}$ M). Monitored at $\lambda = 223$ nm, at a cooling rate of 1 K min^{-1}

Figure S11. CD spectra of (*S,S,S*)-D-BTA in decalin, isooctane and cyclohexane.



A) An overlay of the CD spectra of (*S,S,S*)-D-BTA in decalin (red line), isooctane (black line) and cyclohexane (blue line). $c = 5 \times 10^{-5}$ M, $T = 20$ °C. The *intensity* of the Cotton effect is much lower than that observed in linear alkanes. **B)** An overlay of the CD spectra of (*S,S,S*)-D-BTA in decalin (red line), isooctane (black line) and cyclohexane (blue line) as a function of temperature ($c = 5 \times 10^{-5}$ M). Monitored at $\lambda = 223$ nm, at a cooling rate of 1 K min^{-1}

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