Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for:

The Sergeants-and-Soldiers Effect: Chiral Amplification in Naphthalenediimide Nanotubes

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X-Ray Data[1]

Table S1. Crystal data and structure refinement for $C_{22}H_{14}N_2O_8.3(C_2H_6OS)$, **5**

Identification code	js0810 (**5**)	
CCDC deposition number	743751	
Empirical formula	$C_{22}H_{14}N_2O_8.3(C_2H_6OS)$	
Formula weight	668.74	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.0612(2) Å	α = 90.00°
	b = 11.8489(2) Å	β = 98.513(1)°
	c = 28.6964(5) Å	γ = 90.00°
Volume	3047.05(10) Å^3	
Z	4	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.306 mm^{-1}	
F(000)	1400	
Crystal size	0.35 x 0.23 x 0.12 mm^3	
Theta range for data collection	3.51 to 27.81°	
Index ranges	-11 <= h <= 11, -15 <= k <= 15, -27 <= l <= 37	
Reflections collected	11900	
Independent reflections	6197 [R(int) = 0.0261]	
Completeness to theta = 27.81°	85.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.987 and 0.907	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6197 / 18 / 406	
Goodness-of-fit on F2	1.052	
Final R indices [I>2sigma(I)]	Rl = 0.0631, wR2 = 0.1676	
R indices (all data)	Rl= 0.0721, wR2 = 0.1758	
Largest diff. peak and hole	0.956 and -0.762 e.Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector. **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Mercury ver. 1.4.1 (CCDC) and Ortep-3 for Windows ver. 1.08 (L. J. Farrugia, *J. Appl. Cryst* (1997), **30**, 565). **Special details**: There are two independent molecules of $C_{22}H_{14}N_2O_8$ in this structure: each possesses a strict (crystallographic) centre of symmetry. One of the DMSO molecules is disordered about two sites. Bond length restraints and a common, isotropic displacement parameter for the C and O atoms were assigned to this moiety.

[1] CCDC 743751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

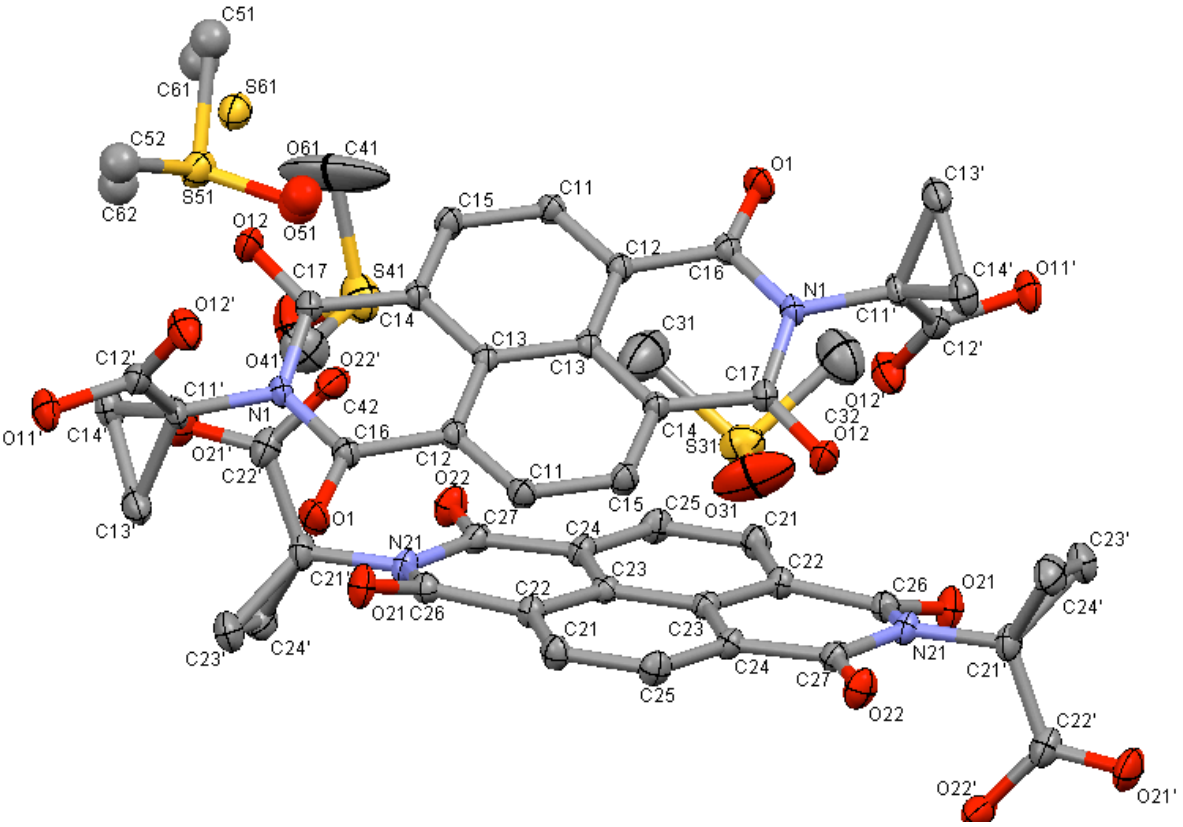

Figure S1. Molecular structure of **5** showing the atom labelling scheme. Hydrogens are not shown for clarity. Single crystals obtained from dimethylsulfoxide solution. Displacement ellipsoids are scaled to the 50% probability level.

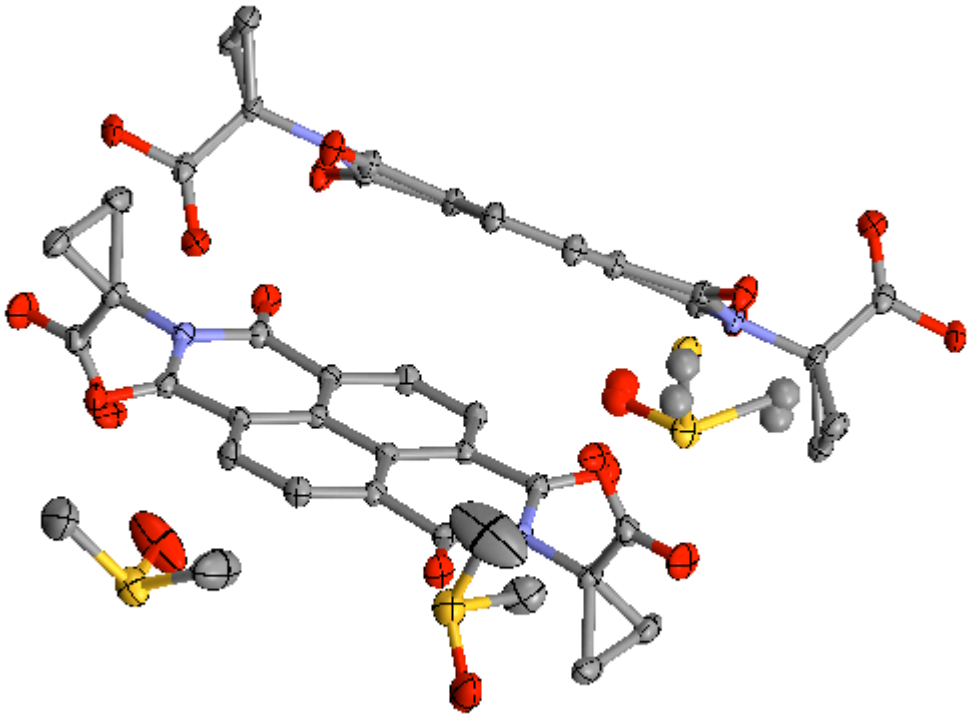

Figure S2. View of the molecular structure of **5**. Hydrogens are not shown for clarity. Single crystals obtained from dimethylsulfoxide solution. Displacement ellipsoids are scaled to the 50% probability level.

Majority Rules Study

Solutions of chiral NDIs L-**1** and D-**1** were made up in tetrachloroethane to an equal concentration (2.5×10^{-5} moldm^{-3}). The L-**1** solution was then titrated with small quantities of the D-**1** solution added and the CD trace recorded for each mixture. Another experiment was performed with the two solutions reversed. CD_{max} points were plotted against percentage of the starting NDI present and the result was an approximately linear trace, suggesting simple dilution with no interaction between the two enantiomers.

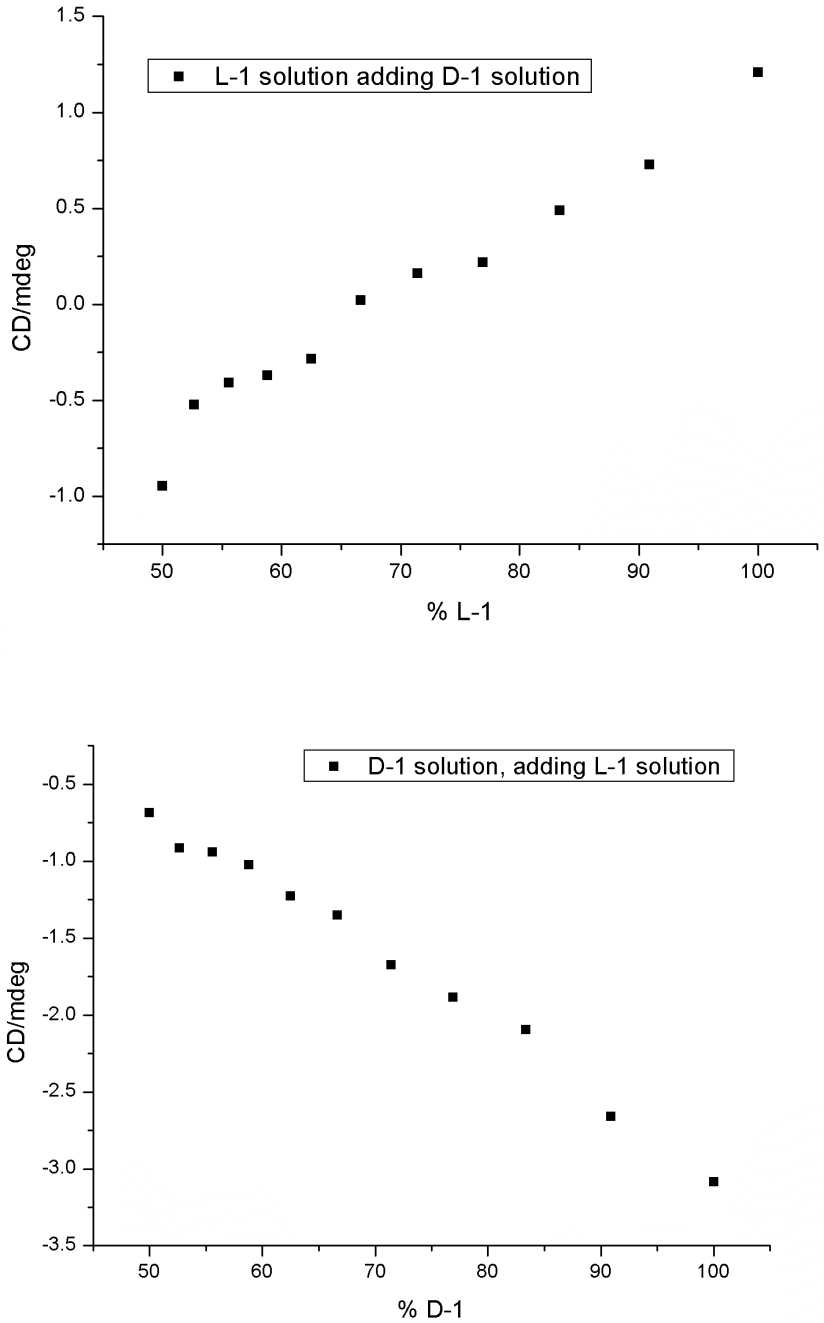

Figure S3. Datasets from majority rules studies involving mixtures of L-**1** and D-**1**.

A second study was performed in which unequal mixed solutions of L-**1** and D-**1** were made up (ratio 70:30 and 30:70 respectively) and small quantities of an equally-concentrated solution of achiral **5** was added, with the CD trace recorded for each mixture. When the CD_{max} points were plotted against percentage chiral NDIs present, the result were essentially horizontal plots. This shows that achiral **5** interacts equally with both chiral enantiomers and does not amplify one over the other, even when they are present in an unequal ratio.

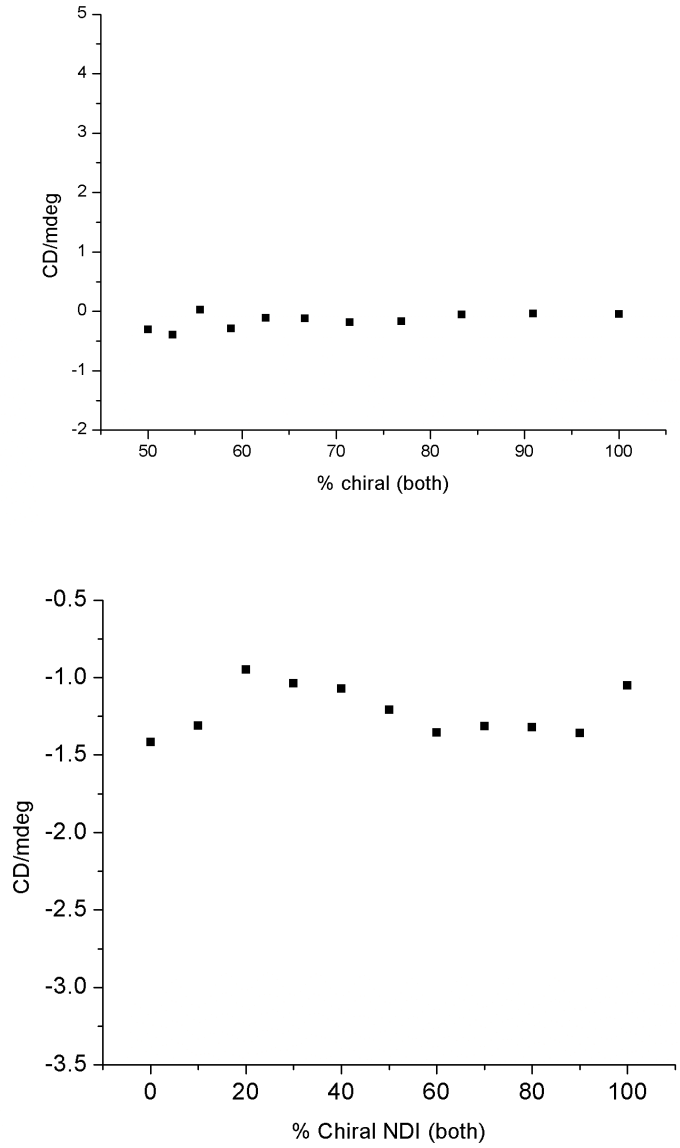

Figure S4. Datasets from studies in which achiral NDI **5** solution was added to mixtures of L-**1** and D-**1** in the ratio 70:30 (top) and 30:70 (bottom).

*Achiral NDI **6***

The CD experimental procedure described in the experimental section of the paper was employed, using **6** as the achiral NDI. L-**1** was used as the chiral sergeant. All solutions were made up in tetrachloroethane to a concentration of 2.1×10^{-4} moldm^{-3}. When the CD_{max} points were plotted against percentage chiral NDI present, they were found to lie almost exactly on the control dataset using ester L-**3**. In other words, **6** interacts with L-**1** to the same degree as L-**3** does – zero.

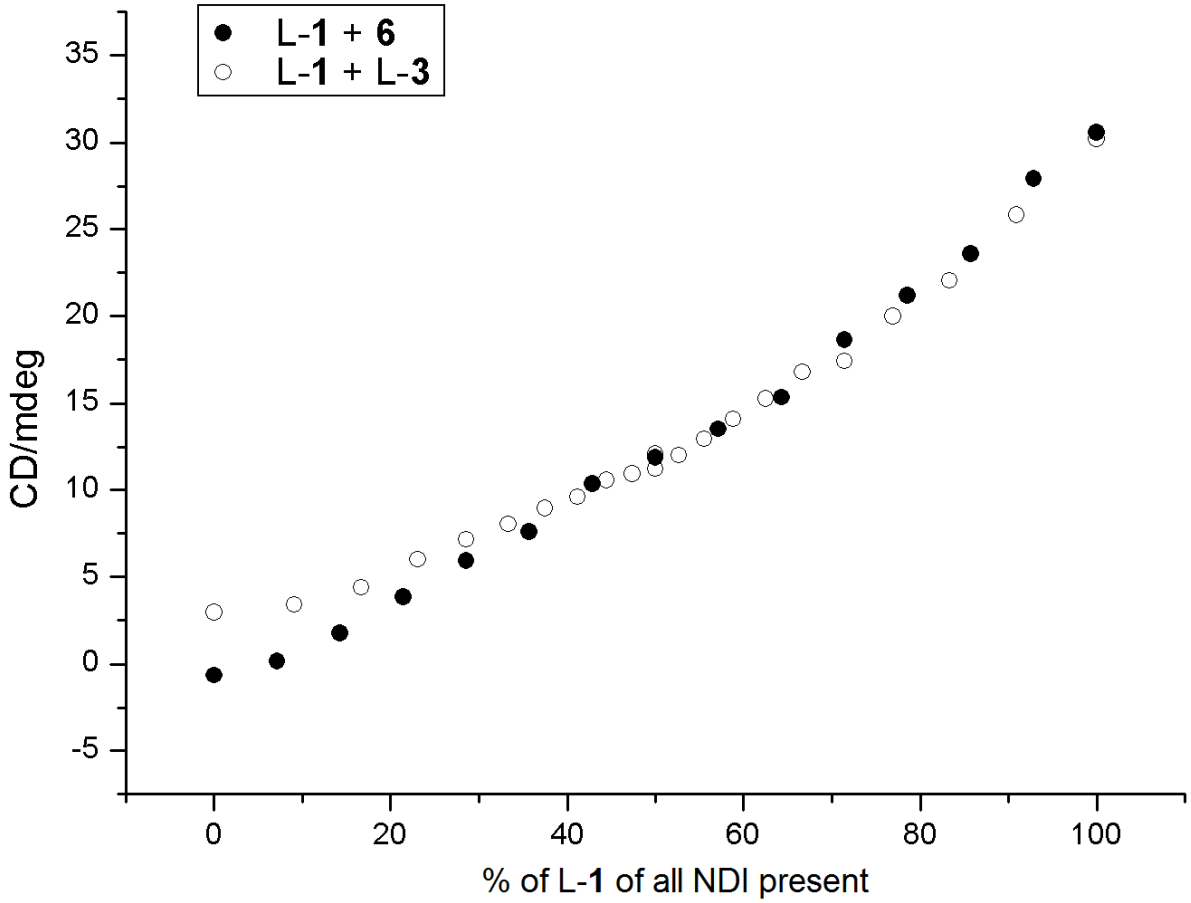

Figure S5. CD_{max} points of L-**1** + **6** mixtures (solid points) plotted against percentage L-**1** present and compared to the control dataset of L-**1** + L-**3** mixtures (hollow points).

Achiral NDI 7

In addition to the single dataset shown in the paper (Figure 10), achiral NDI **7** was also tested as a sergeant with chiral soldiers L-**2** and D-**2**. The resulting datasets were then plotted against a control set along with the existing data for those two sergeants with **5** as a soldier (Figure 7). It was found that **7** also acts as a soldier, but an inferior one to **5**, with both L-**2** and D-**2**. Furthermore, as expected and like **5**, NDI **7** interacts equally with both of them (Figure S6).

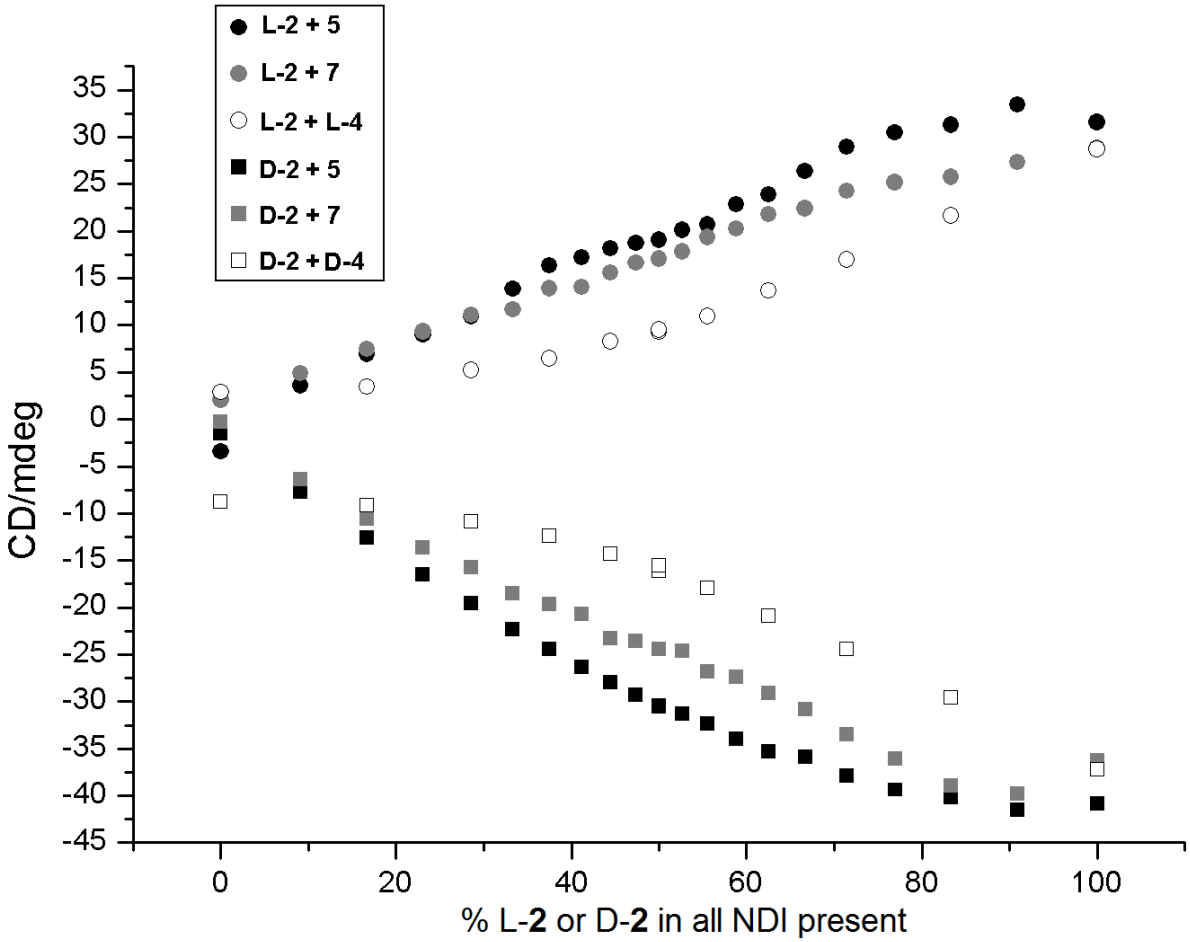

Figure S6. CD_{max} points plotted against percentage chirality for: mixtures of L-**2** with **5** (black circular points), L-**2** with **7** (grey circular points), L-**2** with L-**4** control ester (white circular points), D-**2** with **5** (black square points), D-**2** with **7** (grey square points) and D-**2** with D-**4** control ester (white square points).

Raw CD Data

Raw data plots for the various CD plots shown in the paper and in this Supporting Information are given below. All CD traces for a given experiment are shown with CD plotted against wavelength. The data is shown as recorded, before any corrections were applied. The scan region is either 270-400 or 300-400 nm, constrained at the lower end by the fact that tetrachloroethane absorbs around 250 nm.

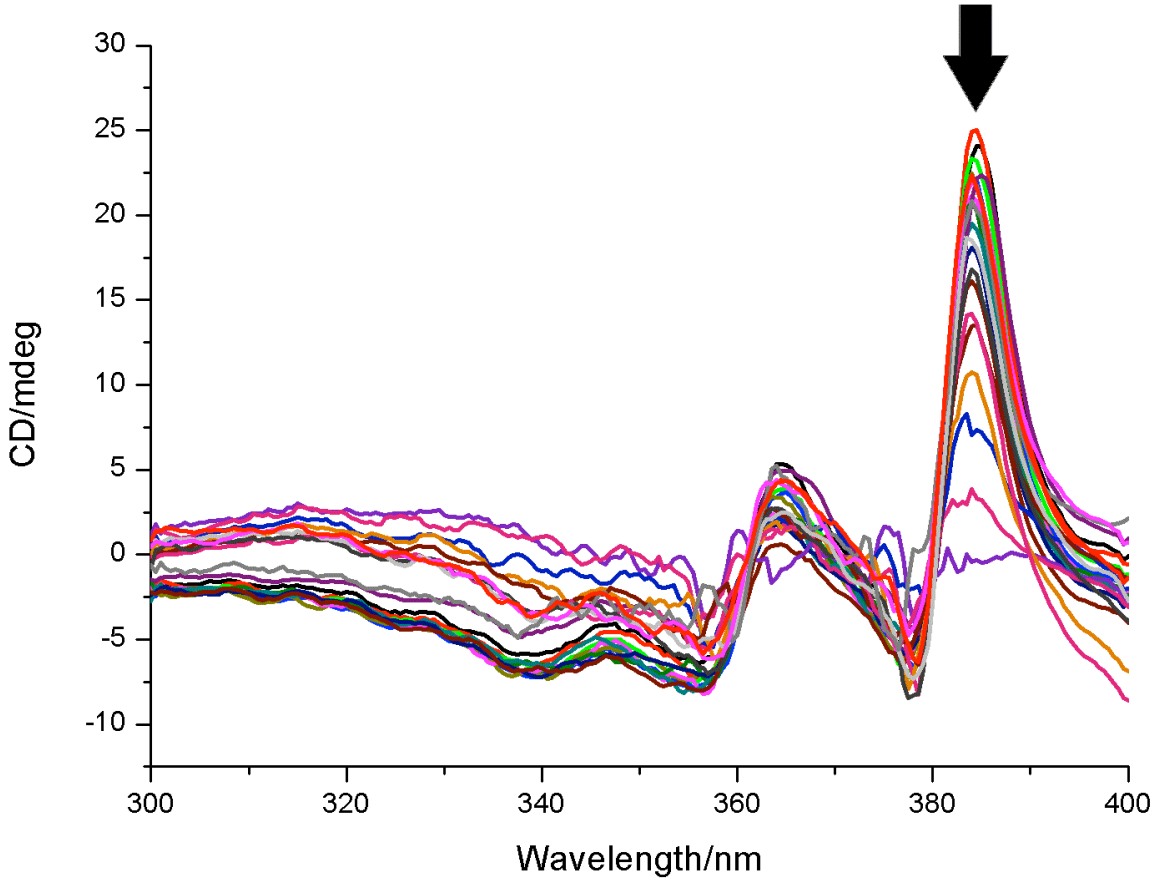

Figure S7. One of the three datasets that were averaged to produce the L-**1** + **5** data from which the CD_{max} points for Figure 6b were derived. The traces cover concentrations from 0% to 100% chiral and overall NDI concentration was constant at 2.1×10^{-4} moldm^{-3}. The CD_{max} is indicated with an arrow.

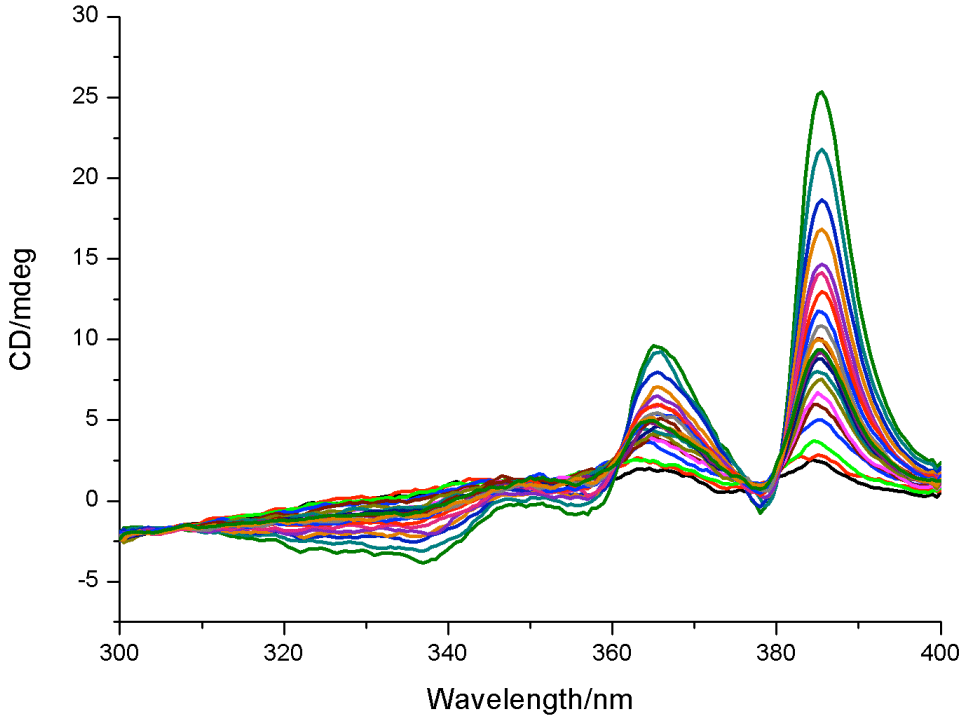

Figure S8. Traces for the control data used with L-**1** for Figures 6b and 10, consisting of mixtures of L-**1** and L-**3** ester.

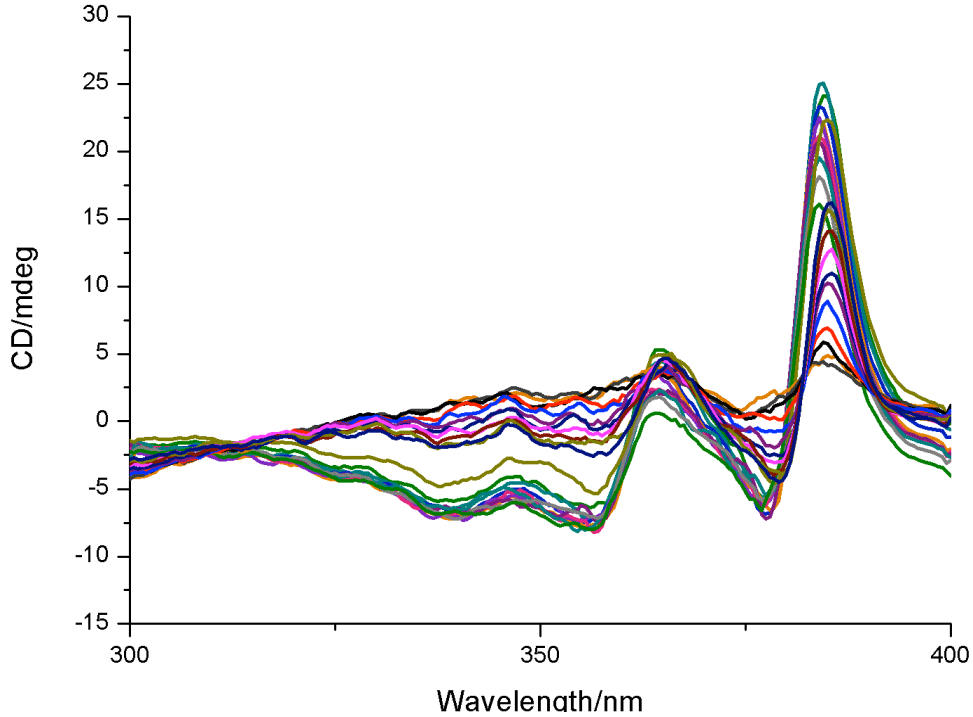

Figure S9. Traces for the L-**2** + **5** dataset in Figures 7 and S6. Note that due to an equipment error the wavelength of the CDmax changed slightly between the two experiments making up the 50-100% and 0-50% chiral parts of the run, meaning that a correction was later applied.

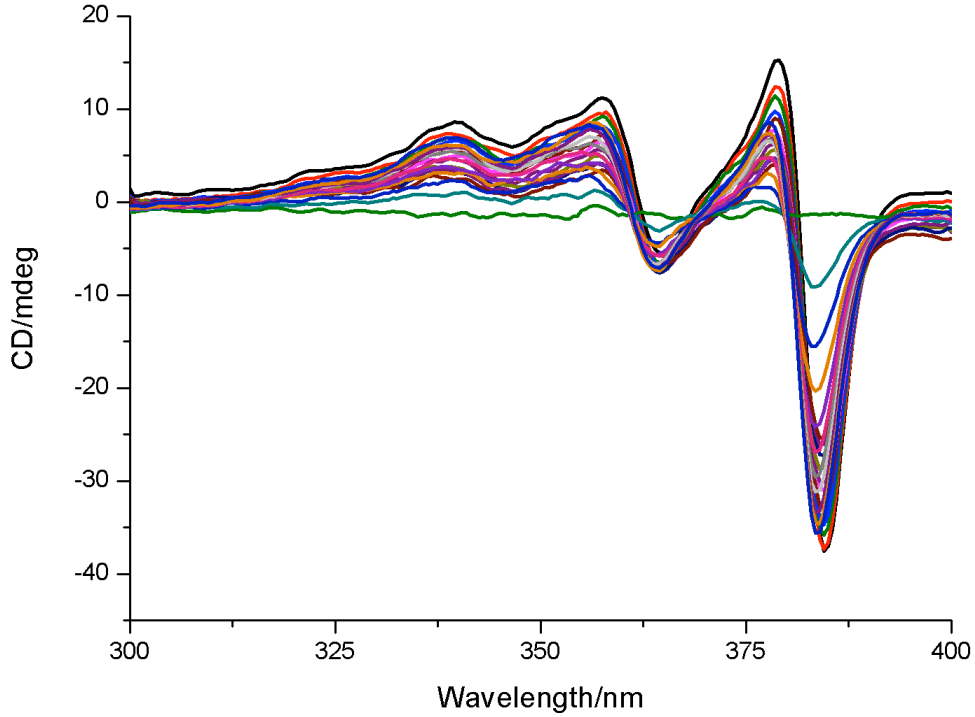

Figure S10. Traces for the D-**2** + **5** dataset in Figures 7 and S6.

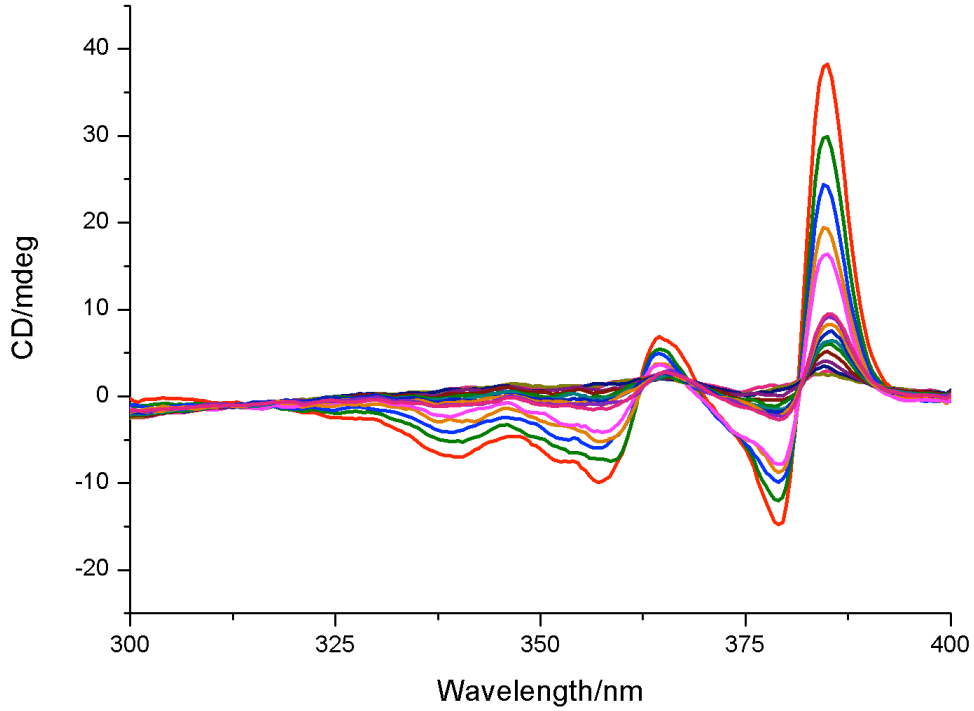

Figure S11. Control data using L-**2** + L-**4** ester, used in Figures 7 and S6. Note a smaller number of datapoints were taken as for the experimental run with **5**, but still covering the same range of ratios.

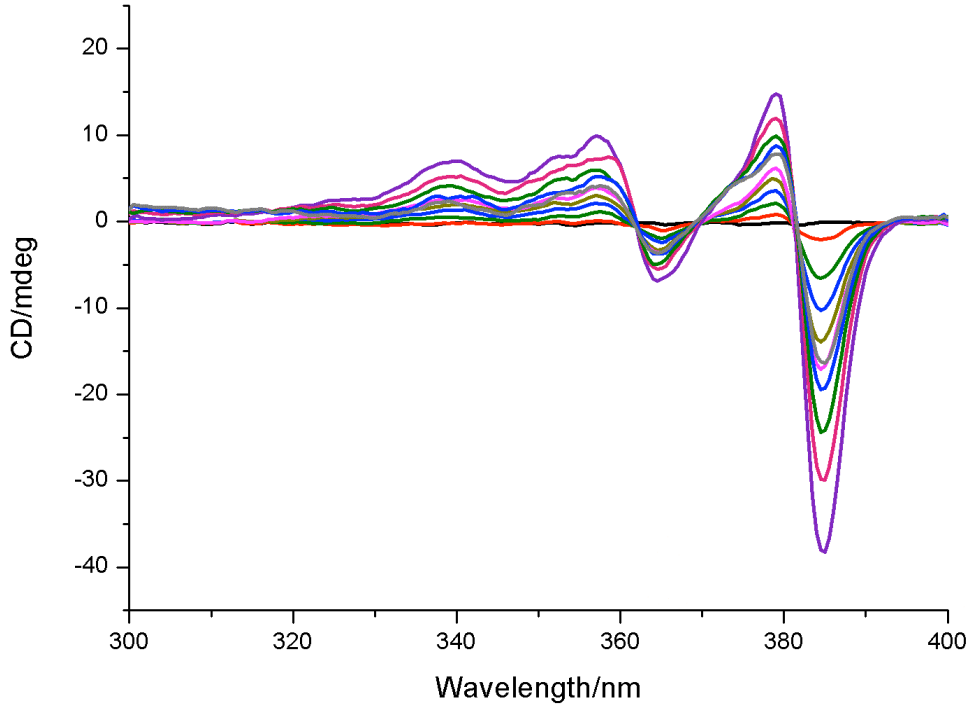

Figure S12. Control data using D-**2** + D-**4** ester, used in Figures 7 and S6. A smaller number of datapoints were taken as for the experimental run with **5**, but still covering the same range of ratios.

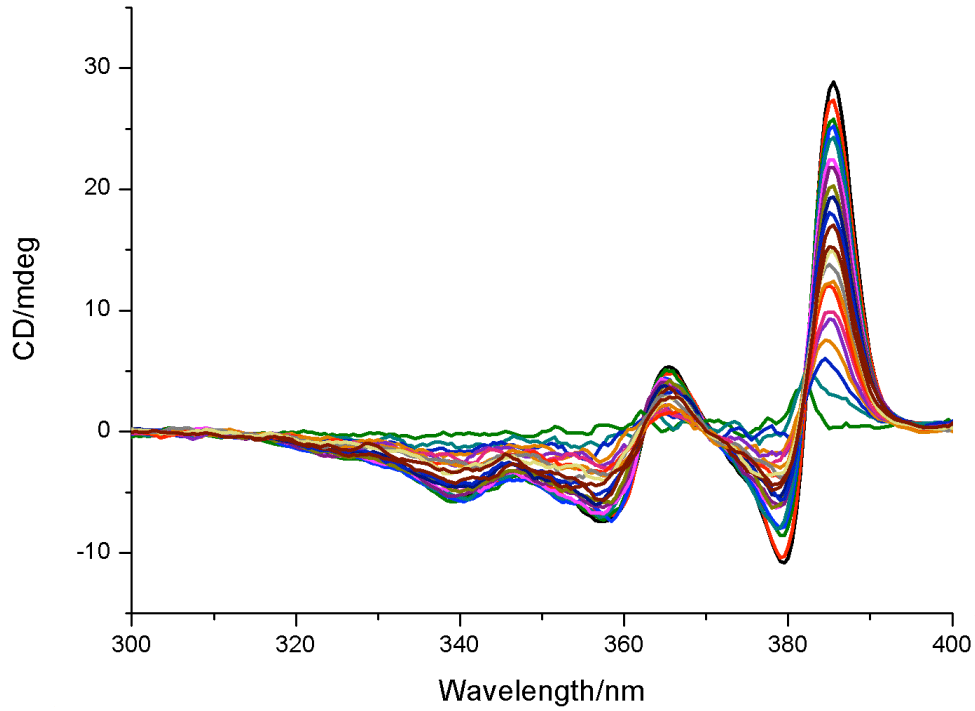

Figure S13. L-**2** with **6** data runs, as seen in Figure S6.

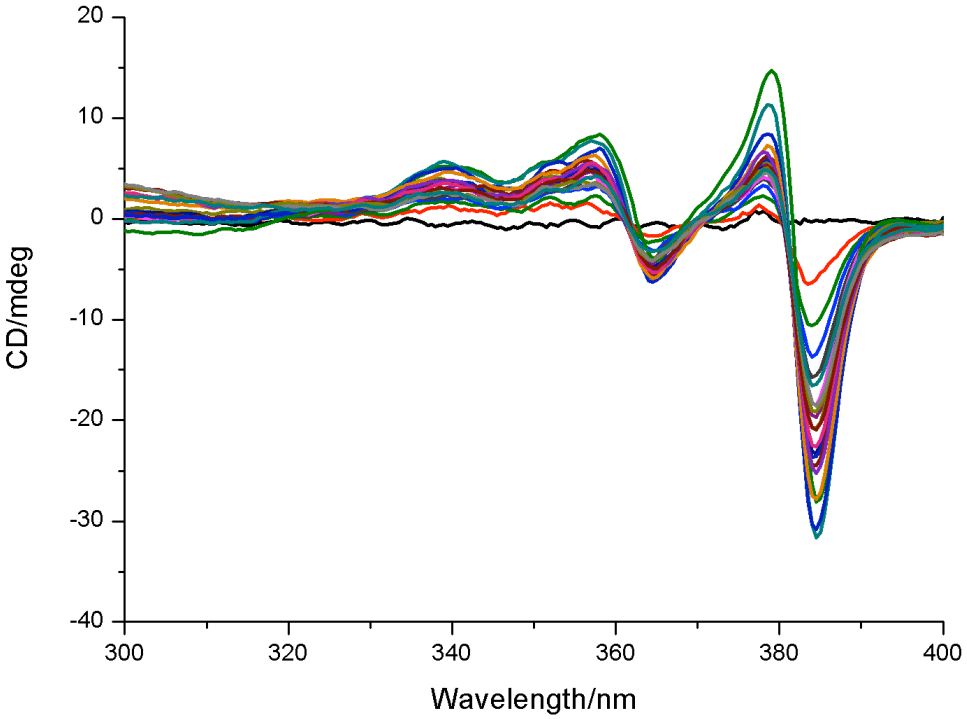

Figure S14. D-**2** with **6** data runs, as seen in Figure S6.

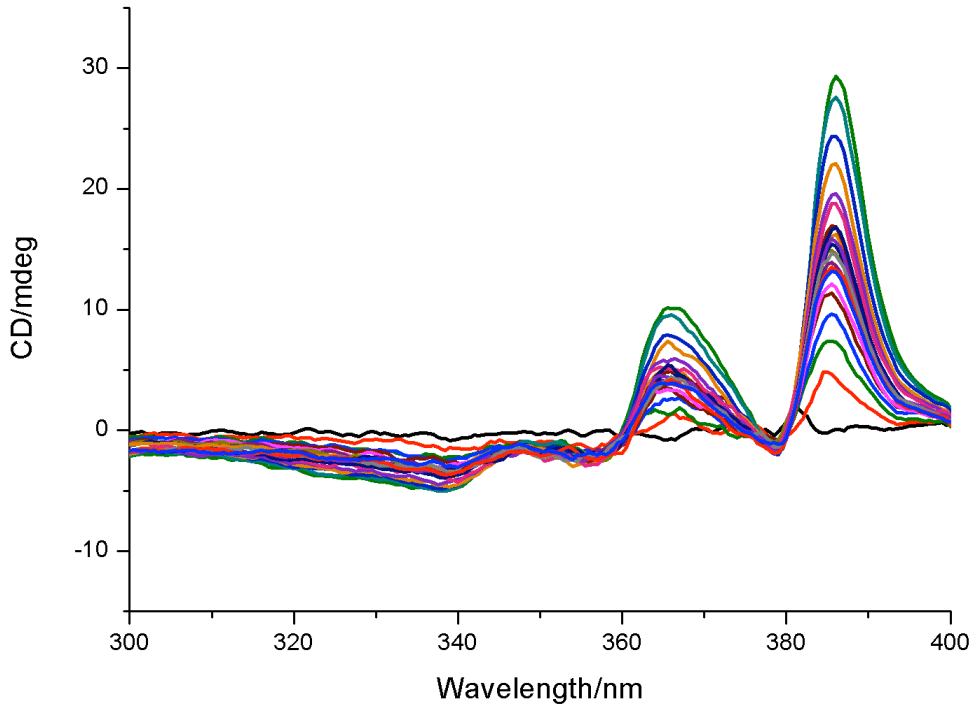

Figure S15. L-1 with **6** data runs, as seen in Figure 10.

NMR Data

The experiments with C_{60} using mixtures of L-**1** and **5** (Figure 8) were repeated using the same procedure but with **7** replacing **5**. Quantities were altered in accordance with the slightly greater molecular mass of **7**. The results (Figure S16) displayed similar behaviour as with the initial **5** studies, though the two are not directly comparable due to the slightly different ratios caused by precipitation. Like **5**, NDI **7** does not significantly affect the C_{60} signal when added alone to C_{60}.

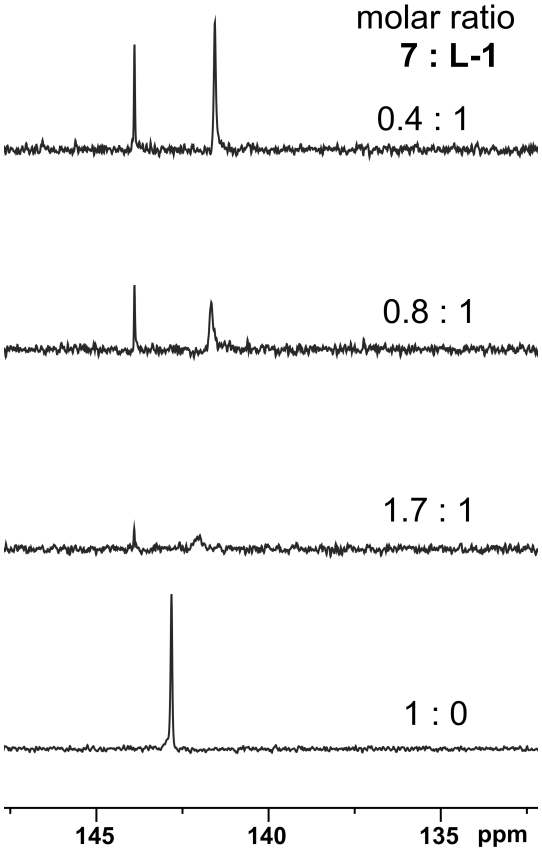

Figure S16. ^{13}C NMR data for mixtures of achiral NDI **7** and chiral NDI L-**1** taking up C_{60}. The peak on the left is one of the naphthyl carbons of L-**1**, showing the traces are aligned. The peak on the right is C_{60} and shows its progressively decreasing shielding as the percentage of achiral **7** in the mixture increases.