Supporting Information for:

The thermodynamics of the self-assembly of covalently linked oligomeric naphthalenediimides into helical organic nanotubes

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Experimental section

Synthesis: All syntheses were carried out according to published literature protocols.[1]

Analysis: VT NMR experiments were undertaken on a Bruker 400 MHz spectrometer as follows: number of dummy scans = 2; number of scans = 16; equilibration time = 300 s. Where a mixture of solvents was used, TCE was added to the NDI first, followed by the second solvent before sonication. The temperature was regulated by the heating element in the instrument for high temperatures, and with a liquid nitrogen cooling inlet for low temperatures. The experiments were recorded from high temperature to low temperature.

VT CD experiments were undertaken on an Applied Photophysics Chirascan Circular Dichroism Spectrophotometer with the following parameters: monochromator bandwidth = 1 nm; sampling time-per-point = 1 second; number of repeats per scan = 2, scanning increments = 1 nm; temperature equilibration time = 300 s. The spectrum of the control solvent was pre-recorded and auto-subtracted from subsequent scans. The temperature was regulated by a thermoelectric temperature controller using a water-cooling system (maximum temperature = 95°C). The experiments were recorded from high temperature to low temperature.

The fitting to the isodesmic model was carried out using the protocol reported by Sanders *et al.*[2] The plot of the proton peak as a function of temperature was fitted to the isodesmic model using the Boltzmann equation:

$$y = [A_2 + (A_1 - A_2)] / [1 + \exp[(x - x_0)/dx]]$$

Where A_1 = minimum value of physical parameter monitored
A_2 = maximum value of physical parameter monitored
x_0 = Melting temperature (T_m, at which $\phi_{agg} = 0.5$)
dx = characteristic temperature that is related to the slope of the function at the melting temperature (T*).

The thermodynamic parameters were then calculated from these variables, as described by Sanders *et al.*[2]

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[1] Olsen, J.-C.; Batchelder, N. A.; Raney, J. H.; Hansen, D. E. *Supramol. Chem.*, **2012**, *24*, 841-850.

[2] Ponnuswamy, N.; Pantoş, G. D.; Smulders, M. M. J.; Sanders, J. K. M. *J. Am. Chem. Soc.*, **2012**, *134*, 566-573.

Variable Temperature Circular Dichroism (VT CD) data

The raw data for the VT CD experiments are shown below, with the corresponding fitting data adjacent where appropriate.

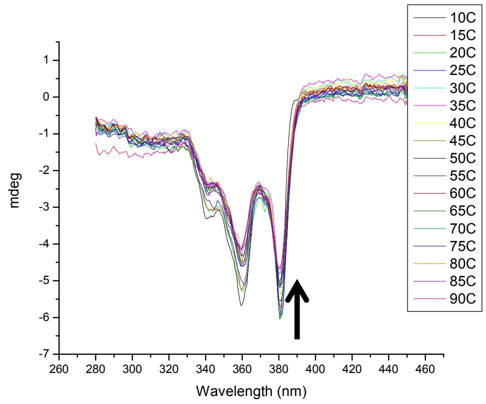


Figure S1. The VT CD traces for **1** in TCE at 4 × 10^{-5} M.

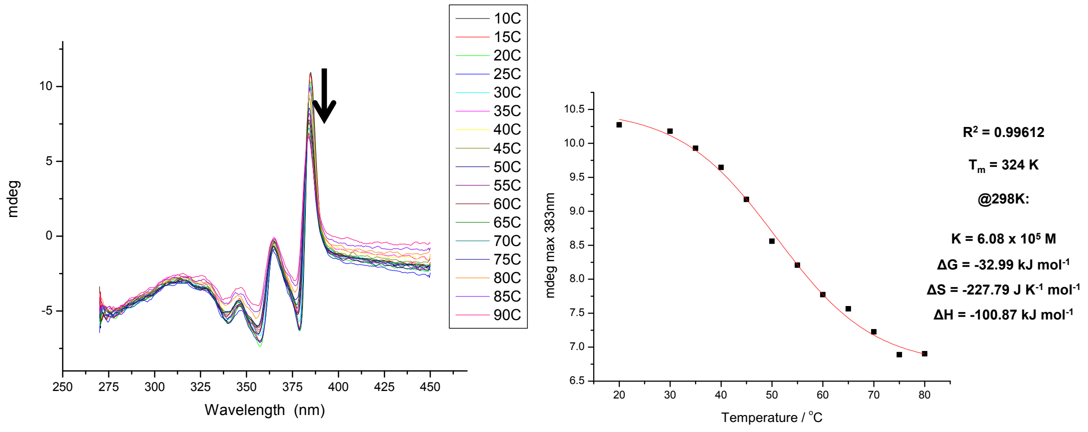


Figure S2. The VT CD traces for **2** in 1% dioxane in TCE at 2 × 10^{-5} M.

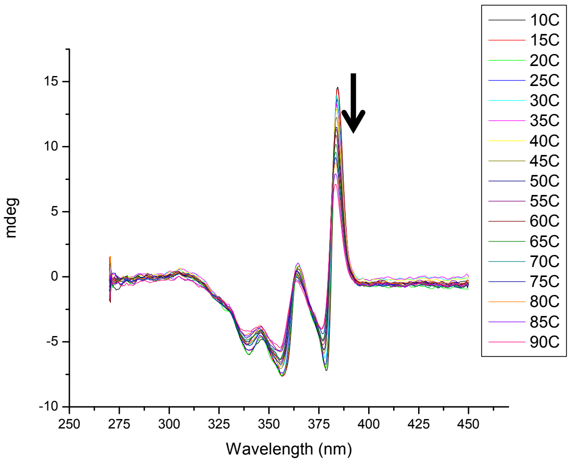
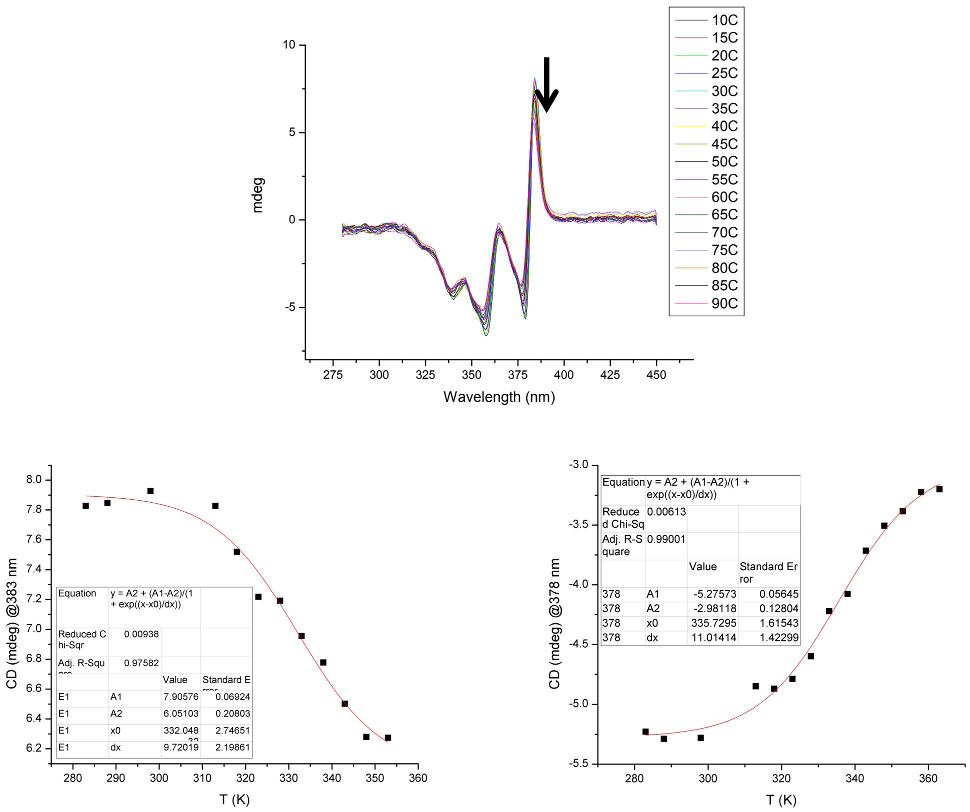


Figure S3. The VT CD traces for **3** 1% dioxane in TCE at 1.4 × 10^{-5} M.

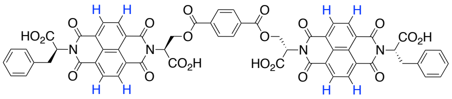


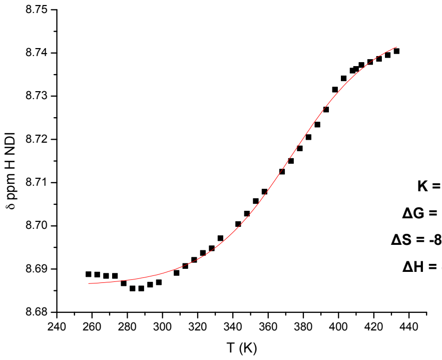
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	0.00938		
Adj. R-Square	0.97582		
		Value	Standard Error
E1	A1	7.90576	0.06924
E1	A2	6.05103	0.20803
E1	x0	332.04832	2.74651
E1	dx	9.72019	2.19861

Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sq	0.00613		
Adj. R-Square	0.99001		
		Value	Standard Error
378	A1	-5.27573	0.05645
378	A2	-2.98118	0.12804
378	x0	335.7295	1.61543
378	dx	11.01414	1.42299

Figure S4. The VT CD traces for **3** in 3% dioxane in TCE at 1.4 × 10^{-5} M.

Variable Temperature NMR Data





R^2 = 0.99599

T_m = 373K

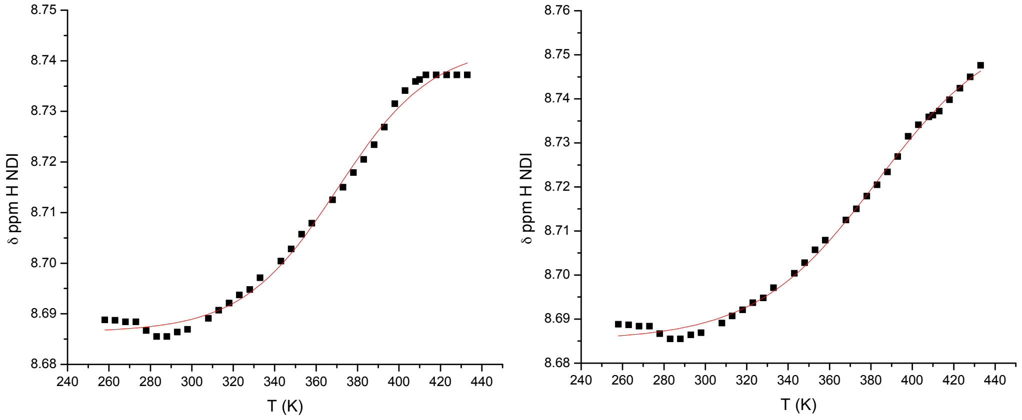
@298K:

K = 3.51 ± 0.01 x 10^4 M

ΔG = -25.93 ± 0.01 kJ mol^{-1}

ΔS = -86.97 ± 14.37 J K^{-1} mol^{-1}

ΔH = -51.85 ± 4.28 kJ mol^{-1}



R^2 = 0.99453

T_m = 370K

@298K:

K = 3.84 x 10^4 M

ΔG = -26.48 kJ mol^{-1}

ΔS = -93.38 J K^{-1} mol^{-1}

ΔH = -54.54 kJ mol^{-1}

R^2 = 0.99658

T_m = 383K

@298K:

K = 2.94 x 10^4 M

ΔG = -25.50 kJ mol^{-1}

ΔS = -89.96 J K^{-1} mol^{-1}

ΔH = -45.68 kJ mol^{-1}

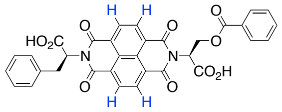
Fig. S5 Top: The isodesmic fitting and thermodynamic parameters for the NDI proton of **2** in 2% THF in TCE at 5 × 10^{-4} M. Data points from 418 – 433 K have been added in from simulated data to enable fitting. Bottom: the two hypothetical extreme scenarios for the simulated data points, showing the range of thermodynamic parameters for the two scenarios.

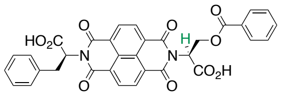
Comparison of the NDI vs. α proton plots for all VT NMR experiments

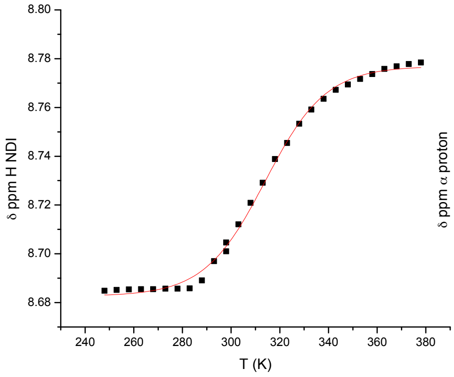
The VT NMR plots for both the NDI and α proton plots in every solvent system reported in the thesis is presented side-by-side for comparison purposes.

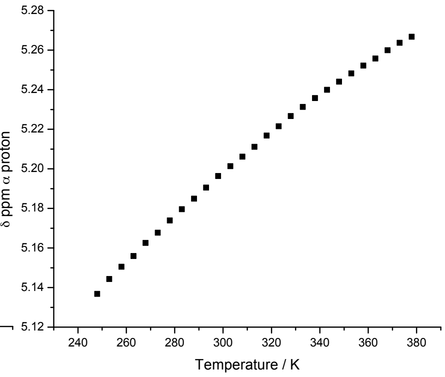
Monomeric NDI **1:**

Monomer **1** in TCE at 1 × 10^{-3} M:

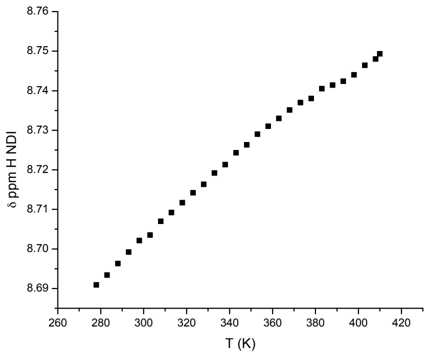


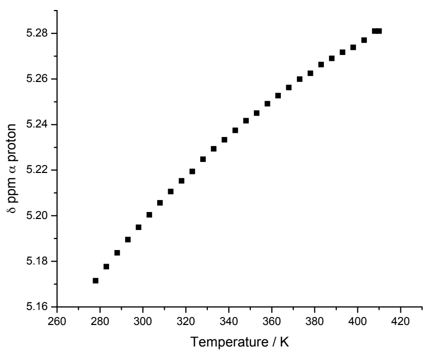




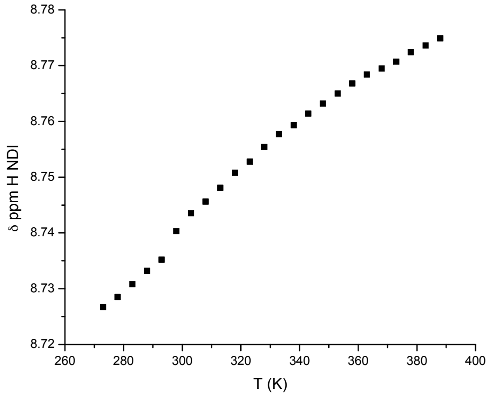


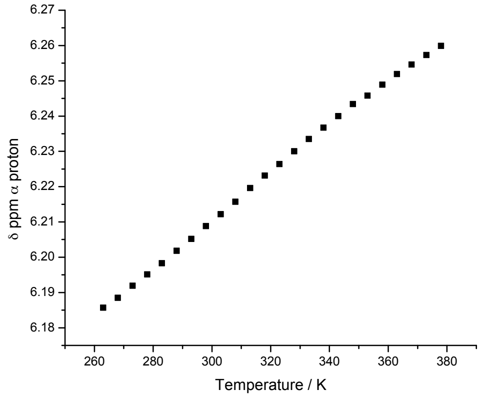
1 in 2% THF in TCE at 1 × 10^{-3} M:



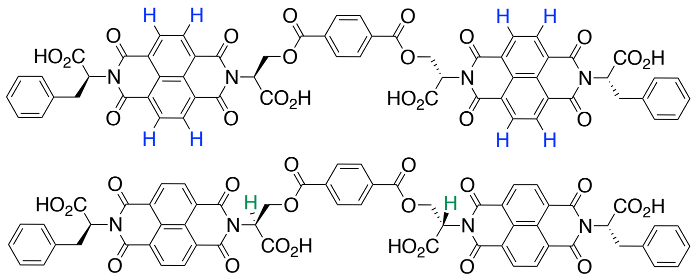


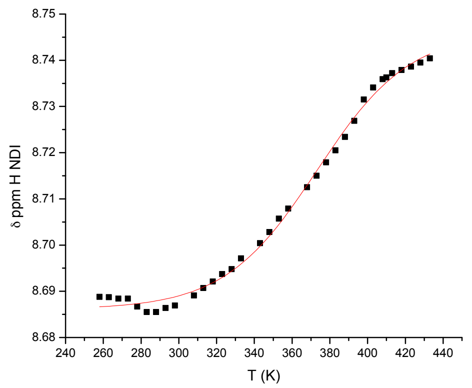
1 in 1% dioxane in TCE at 1 × 10^{-3} M:

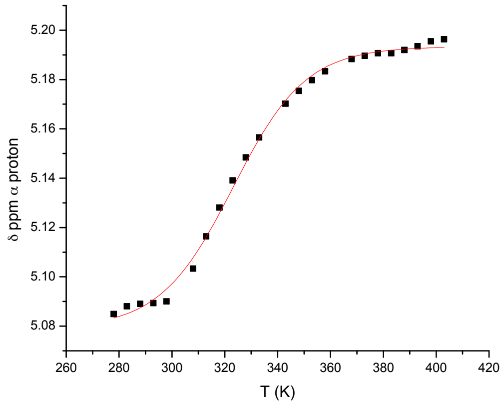




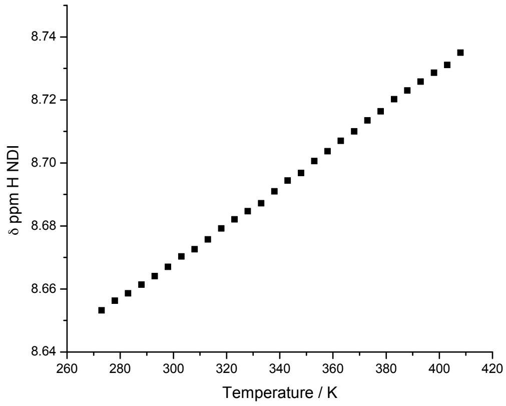
2 in 2% THF in TCE at 5 × 10^{-4} M:

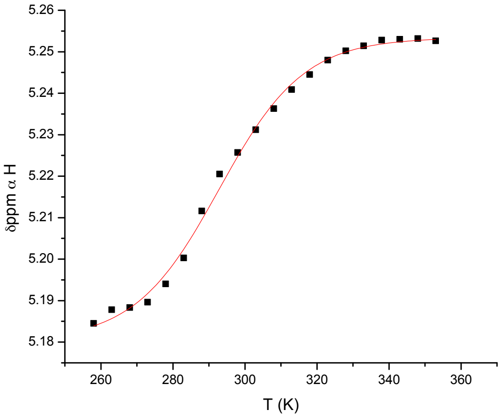




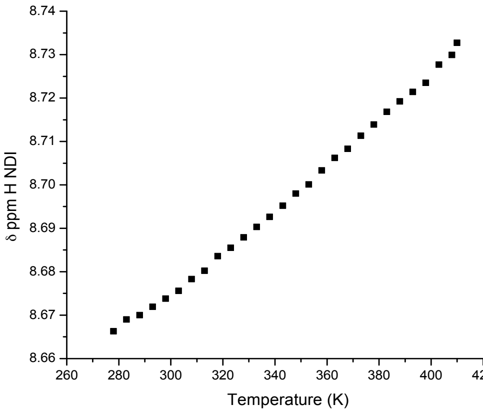


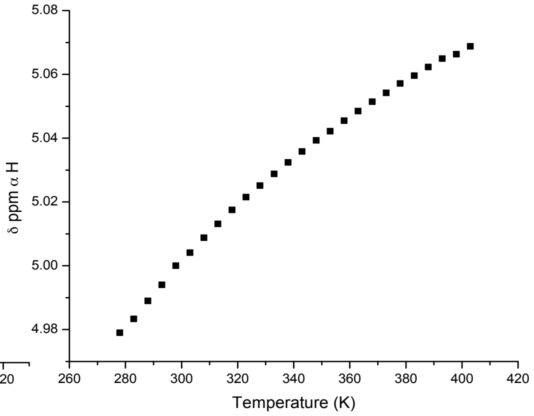
2 in 1% dioxane in TCE at 5 × 10^{-4} M:



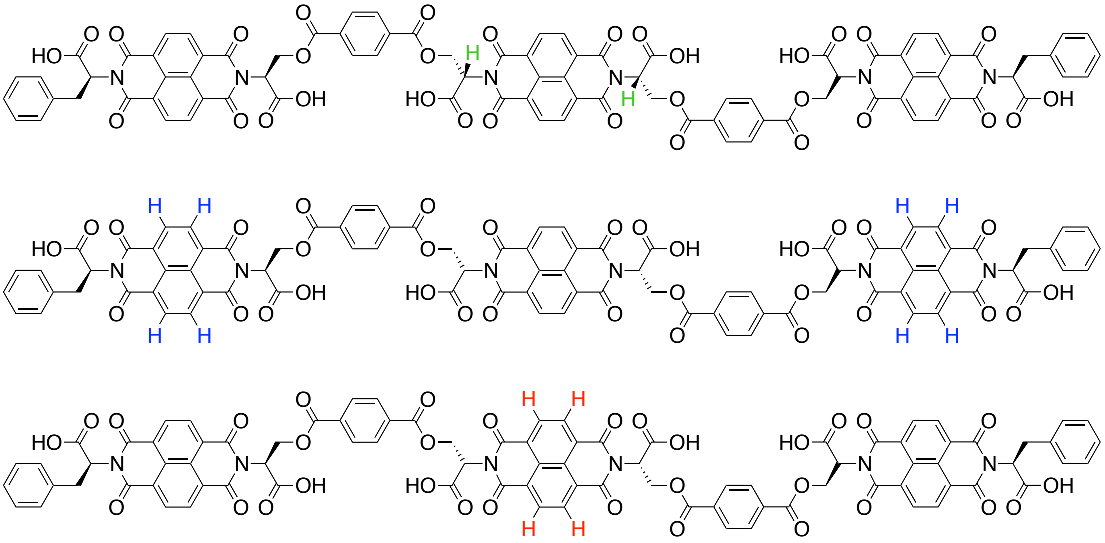


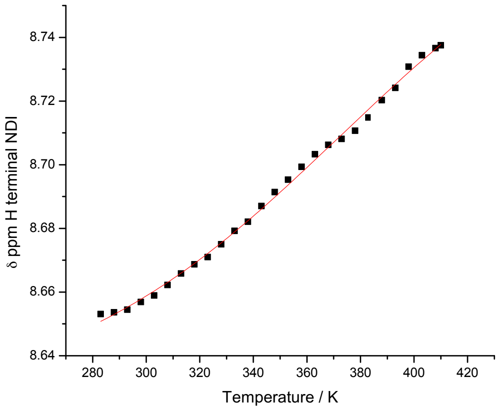
2 in 3% dioxane in TCE at 5 × 10^{-4} M:

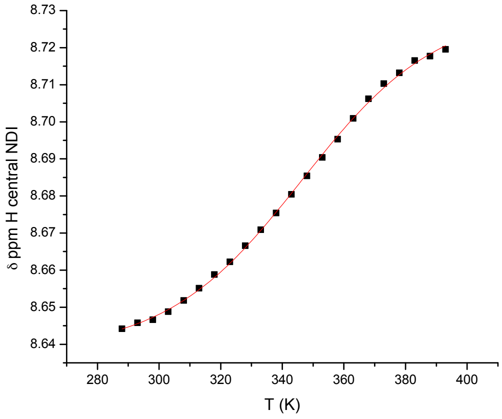




3 in 1% dioxane in TCE at 3.3 × 10^{-4} M:







(The α protons of **3** in this solvent system could not be resolved.)

3 in 3% dioxane in TCE at 3.3×10^{-4} M: