Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

The influence of π-conjugated moieties on the thermodynamics of cooperatively self-assembling tricarboxamides

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1.- Materials and Methods section

Synthesis

The oligo(phenylene ethynylene) tricarboxamides **1**, **(*S*)-2** and **(*R*)-3**; *N,N',N''*-tris[(S)-3,7-dimethyloctyl]benzene-1,3,5-carboxamide (**(*S*)-4**) and *N*,*N*',*N*''- tris[(S)-3,7-dimethyloctyl]benzene-1,3,5-tris(carbothioamide) (**BTTA**) were synthesized and characterized in accordance with published procedures.[S-1] The solvent, MCH, was obtained from Aldrich in spectrophotometric grade (99%) and used as received.

Optical spectroscopy

UV-vis and Circular Dichroism measurements were 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 a cooling rate of 60 K/min. In all experiments the linear dichroism was also measured and in all cases no linear dichroism was observed.

S-1 (a) F. García, P. M. Viruela, E. Matesanz, E. Ortí, and L. Sánchez, *Chem. Eur. J.* 2011, **17**, 7755; (b) M. M. J. Smulders, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.* 2008, **130**, 606; (c) T. Mes, S. Cantekin, D. W. R. Balkenende, M. M. M. Frissen, M. A. J. Gillissen, B. F. M. de Waal, I. K. Voets, E. W. Meijer and A. R. A. Palmans, *Chem. Eur. J.* 2013, *DOI: 10.1002/chem.201204273.*

2.- Supplementary Figures and Tables

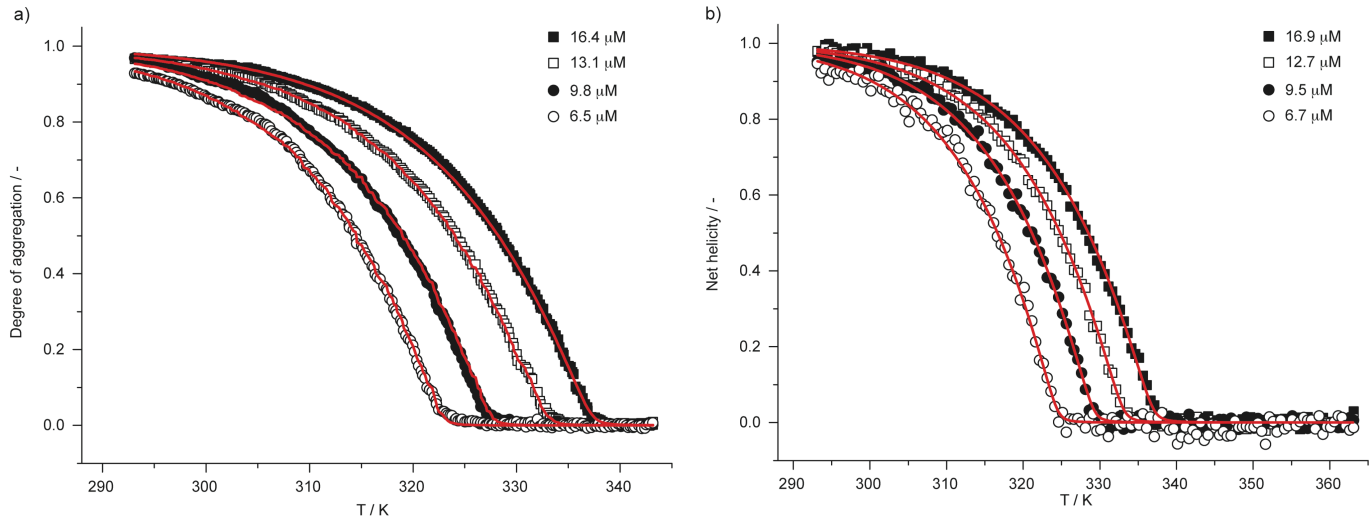

Figure S1. UV-Vis and CD cooling curves of compounds **1** measured at 315 nm (a), and ***(R)-3*** measured at 301 nm (b) in MCH. The red lines in (a) and (b) correspond to the fit to the one-component EQ model reported in reference 4a.

Van't Hoff analysis

Plotting the $1/T_e$ versus the natural logarithm of the concentration allows the construction of a van't Hoff plot. From the linear regression of the data, the enthalpy ΔH and entropy ΔS associated with the self-assembly process can be determined, and the free energy ΔG and the corresponding equilibrium constant K can be calculated (Figure S2).[S-1b] The results are summarised in Table S1.

Table S1. Temperatures of elongation T_e and thermodynamic parameters obtained from the van't Hoff plot for compounds 1-4 in MCH.

Compound	Concentration [μM]	T_e [K]	ΔH [kJ/mol]	ΔS [kJ/mol.K]	ΔG^a [kJ/mol]
1	16.40 13.12 9.85 6.56	336.8 331.7 326.8 322.4	-56.4	-0.076	-33.6
(*S*)-2	15.20 12.60 9.12 6.08	341.4 337.7 334.6 328.2	-66.4	-0.102	-35.9
(*R*)-3	16.90 12.70 9.50 6.75	336.5 332.6 328.8 324.1	-67.0	-0.108	-34.9
(*S*)-4	41.0 27.0 25.0 14.0 12.0	342.8 337.0 335.7 328.2 327.6	-73.0	-0.129	-34.5

a: determined at 298 K

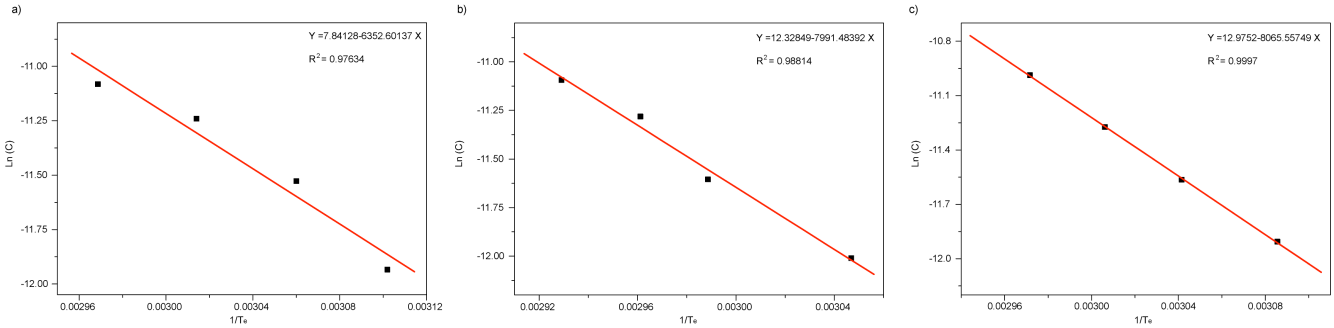

Fig. S2. van't Hoff plots of **1** (a), ***(S)*-2** (b), ***(R)*-3** (c) and the linear fits to obtain the thermodynamic parameters.

Majority Rules experiments

To perform the MR experiment, we mix **(*S*)-2** and **(*R*)-3** in different ratios at a constant total concentration of 12 μM in MCH at 293 K. The resulting CD values in the two maxima of the bisignated Cotton effect, at 280 nm and 304 nm, display a non-linear dependence on the enantiomeric excess, *ee*. Beyond a value of *ee* = 30%, the net helicity is dominated by the major enantiomer.

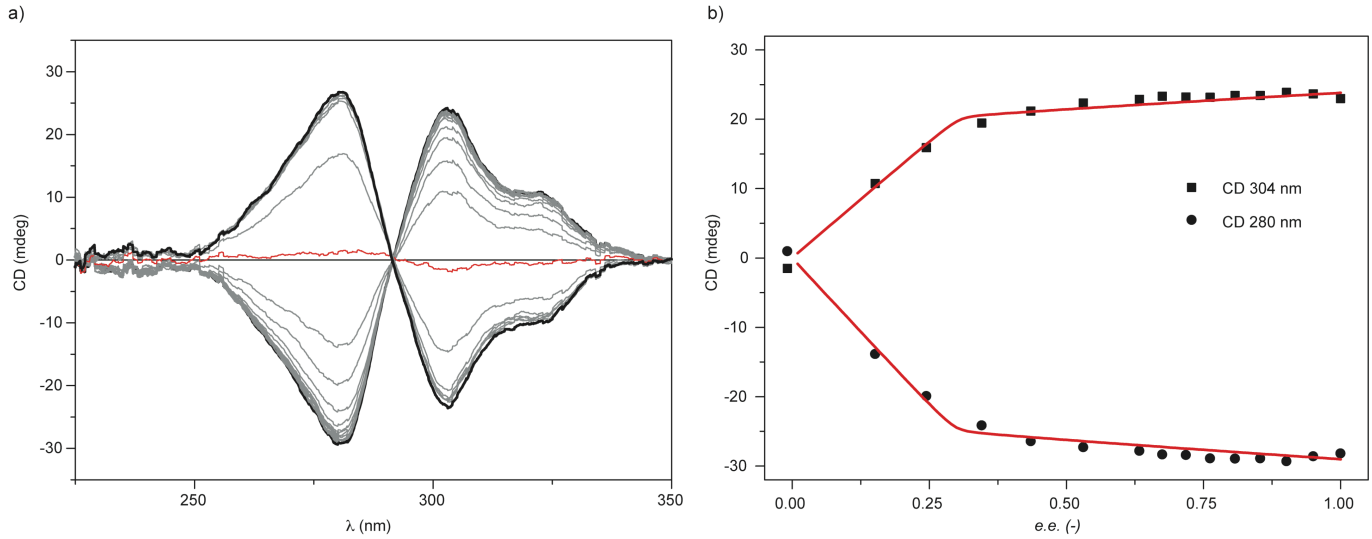

Fig. S3 (a) CD spectra of mixtures of ***(S)-2*** (b) and ***(R)-3*** (MCH, 293 K, 1.2 x 10^{-5} M). (b) Changes in the CD intensity against the *e.e.* observed upon adding increasing aliquots of ***(S)-2*** to a solution of ***(R)-3*** (MCH, 293 K, total concentration = 1.2 x 10^{-5} M). The red lines represent the fitting to the EQ model.