Electronic Supporting Information for:

Stereoselective Aggregation of Chiral Complexes with Threefold-Symmetric Pendant Carboxyl Groups: An Example of "Perfect" Self-Assembly Not Seen in the Crystalline State?

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1. Materials and methods

Complex synthesis: $[Rh(\mathbf{L})_3]$,[1] $[Rh(\mathbf{L^b})_3]$,[1] and $[Co(\mathbf{L})_3]$[2] were synthesized according to literature procedures. $[Rh(\mathbf{L})_3]$ was resolved into its Δ and Λ enantiomers following the procedure[2] developed for $[Co(\mathbf{L})_3]$.

Preparation of the aggregates: A saturated solution of $[Rh(\mathbf{L})_3]$ was prepared in AR grade methanol via a combination of stirring and sonication. All undissolved material was removed by filtration through a 0.45 μm filter. The concentration of this stock solution was established by UV/vis spectroscopy (typically 3×10^{-4} M), and was diluted with further methanol as necessary. Aggregation was induced by deionised water that had been acidified slightly with HCl (typically 2 − 3 drops of 1 M HCl per 100 mL).

UV/vis Spectroscopy: UV-visible spectra were collected using an Ocean Optics HR400 detector and SpectraSuite software, with illumination from a DT-Mini-2-GS deuterium-halogen light source or using a Cary 100 Bio spectrophotometer. Solutions were placed in 1 cm plastic or quartz cuvettes for measurement.

FT-IR Spectroscopy: All IR spectra were recorded using a Thermo Scientific Nicolet 5700FT-IR spectrophotometer. Unless otherwise stated, FT-IR spectra were measured on solid-state samples using an attenuated total reflection (ATR) module (Ge crystal). Spectra were measured at a resolution of 4 cm^{-1}.

Fluorescence spectra: Emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorimeter running FluorEssence software.

2. Supplementary UV/vis spectra

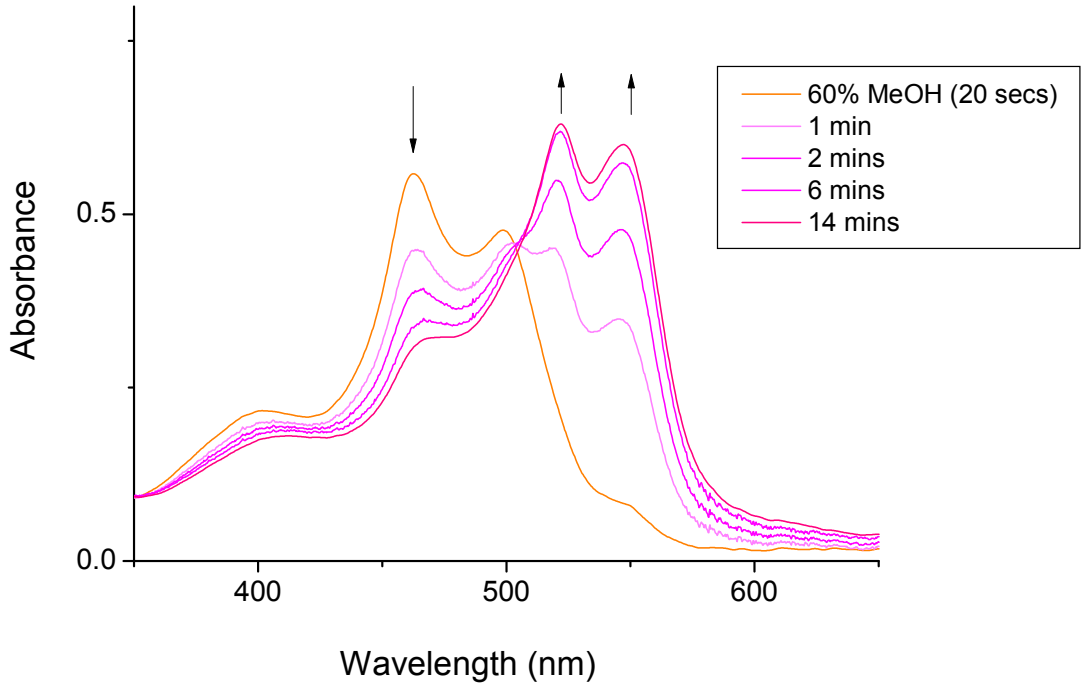

Figure S1. (a) Evolution of the UV/vis spectrum of [Rh(**L**)$_3$] after the addition of water to a methanolic solution of the complex to give a MeOH/H_2O composition of 60/40 v/v. The spectral changes indicate the conversion of form A to form B. Line colours indicate the approximate solution colours.

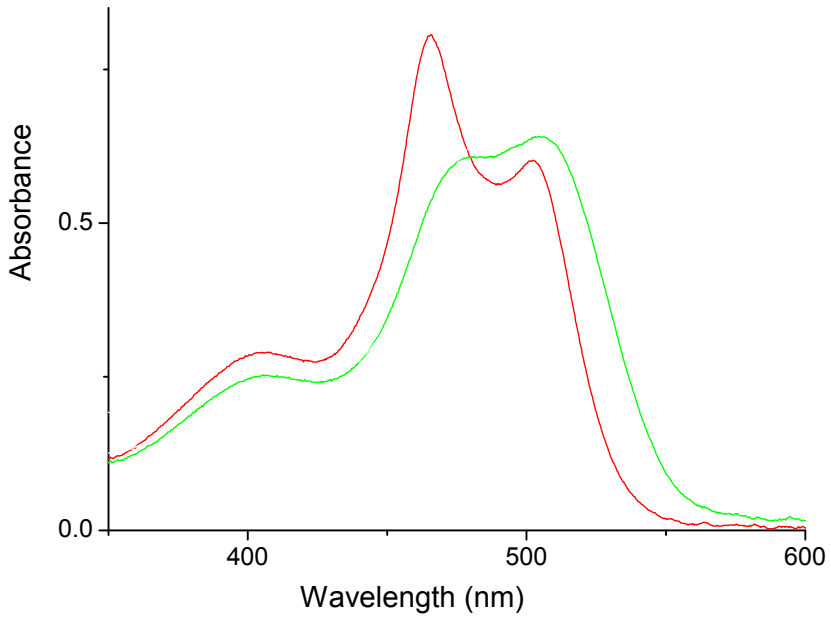

Figure S2. UV-visible absorption spectra of [Rh(**L**)$_3$] in DMSO (red curve) and in DMSO/H_2O 50/50 v/v (green curve).

2. Dynamic light scattering

In DLS experiments, a monochromatic polarized beam of laser light is incident on a sample, which is scattered into a detector placed at a certain angle respecting to the incident beam. Our set-up employs a He-Ne laser (λ= 633 nm) as a light source. A single mode fibre optics beam splitter divides the scattered light into two beams which impinge on two separate photomultiplier tubes (PMTs) allowing the intensity fluctuations to be analysed using cross-correlation. The PMTs are connected to a multiple tau digital correlator (Flex99, www.correlator.com) in order to calculate the correlation functions.

Samples were placed in a 1 cm path length plastic cuvette (Optics Planet). The concentration of the sample was sufficiently dilute that only single scattering takes place. The cuvette was put into a scattering chamber filled with water as a refractive index matching fluid. Measurements were taken at room temperature and the scattered light was detected at an angle of 90° with respect to the direction of the incident beam.

To determine the size distribution of the particles, we used cumulant[3] and contin analysis.[4]

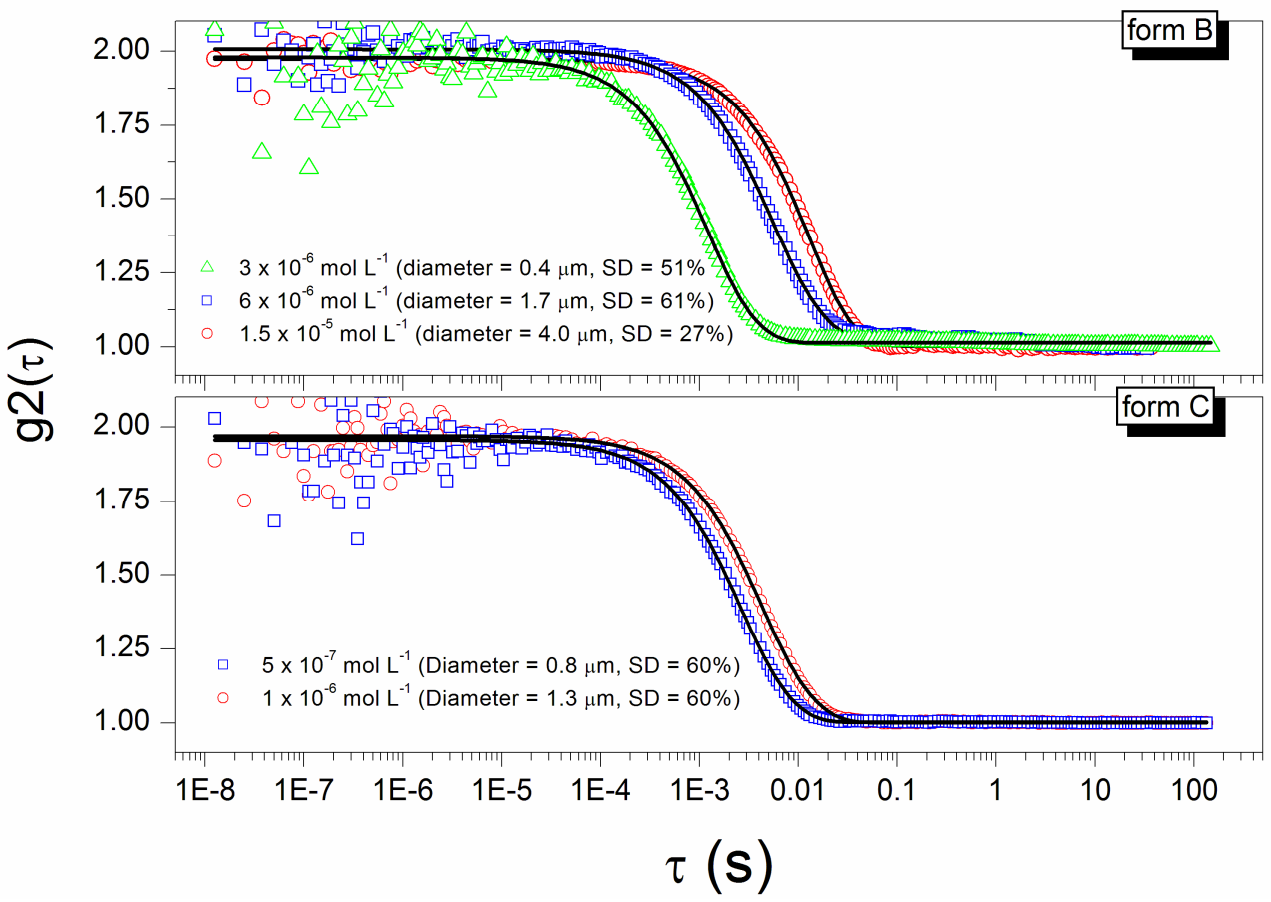

Figure S3. Data of intensity-intensity correlation function ($g^2(\tau)$) for forms B and C of [Rh(**L**)$_3$]. The lines indicate the cumulant fits to the data.

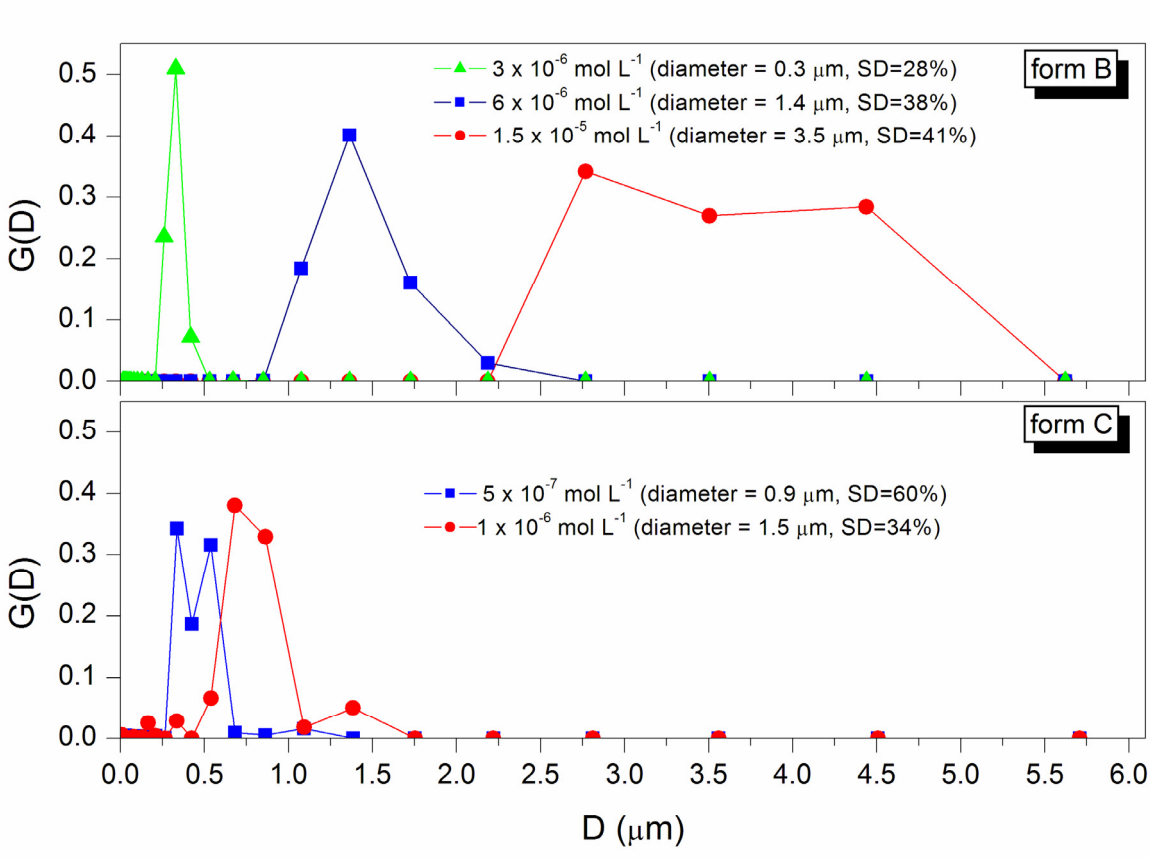

Figure S4. Size distribution of form B (upper) and form C (lower) aggregates of [Rh(**L**)$_3$] extracted from DLS data using contin analysis.

3. Transmission electron microscopy (TEM)

Transmission electron micrographs (TEMs) were recorded on a Philips CM10 Transmission Electron Microscope. Samples were adhered to Formvar-coated copper grids

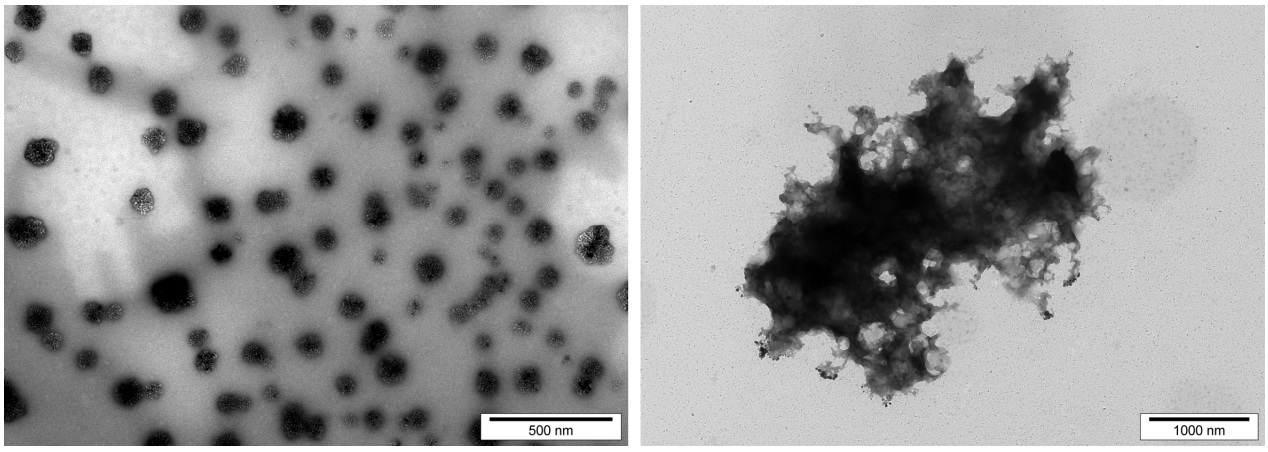

Figure S5. Representative TEM images of form C of [Rh(**L**)$_3$].

4. Supplementary structural models

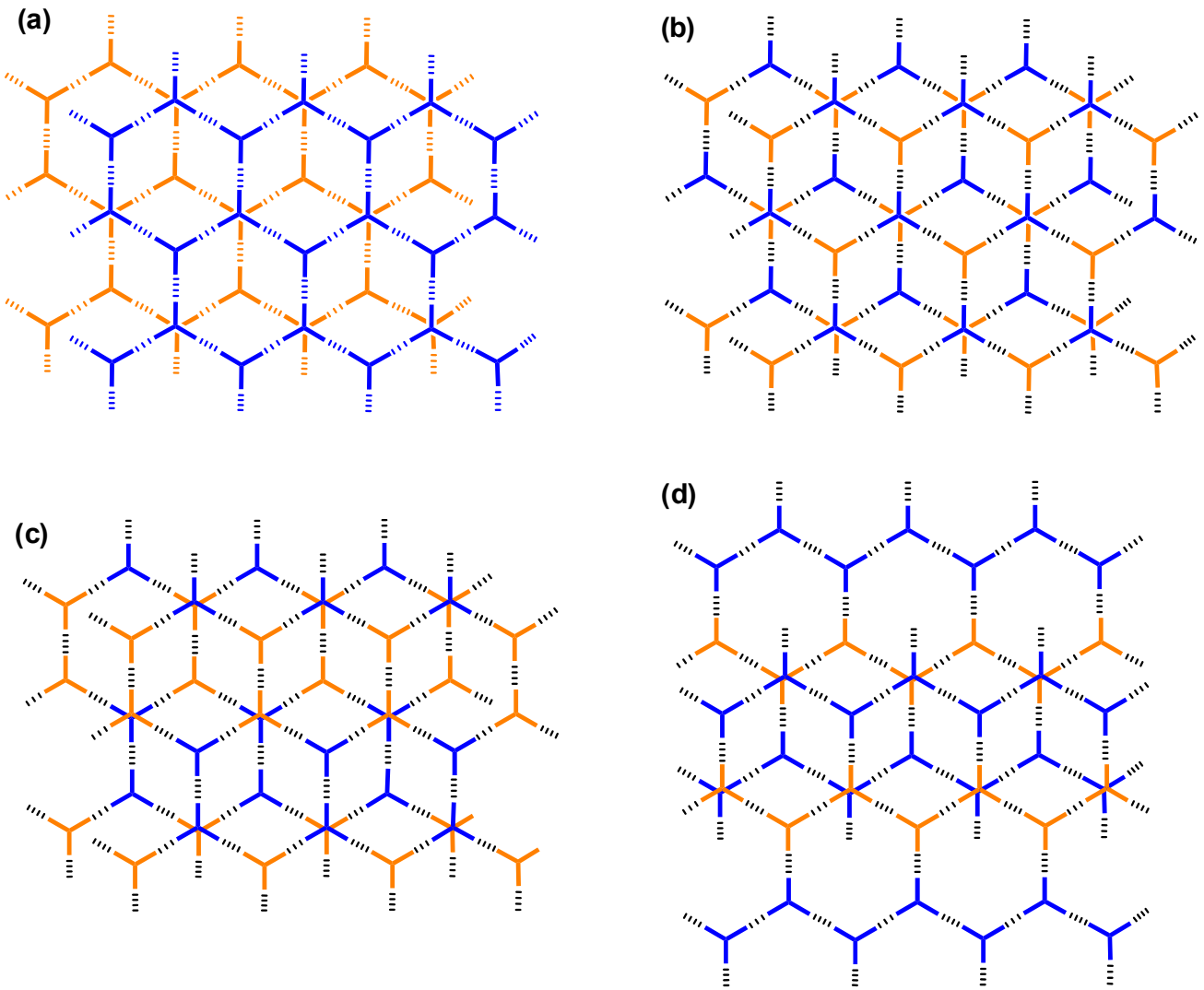

Figure S6. Stacking of variously-structured layers into sheets with an offset interlayer registry. In all cases, close interlayer contacts between Δ and Λ building blocks are possible.

References

1. J. D. Hall, T. M. McLean, S. J. Smalley, M. R. Waterland and S. G. Telfer, *Dalton Trans.*, 2010, **39**, 437-445.
2. S. G. Telfer and J. D. Wuest, *Chem. Commun.*, 2007, 3166-3168.
3. B. J. Frisken, *Appl. Opt.*, 2001, **40**, 4087-4091.
4. S. Provencher, *Comp. Phys. Comm.*, 1982, **27**, 229-242; S. Provencher, *Comp. Phys. Comm.*, 1982, **27**, 213-227.