

Electronic Supplementary Information

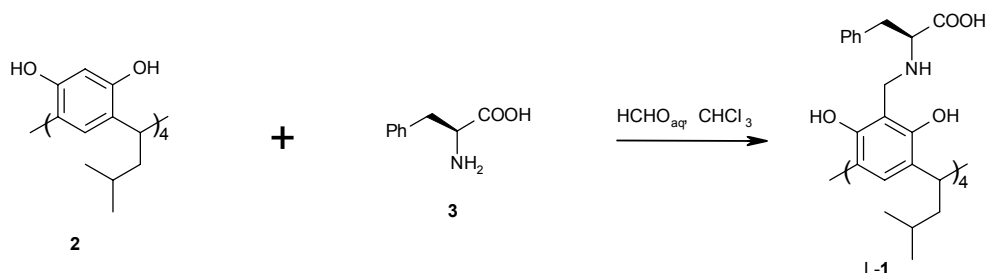
A self-assembled chiral capsule with polar interior

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4. DOSY spectra
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 - Fig. S14. DOSY spectrum of mixture of (**L-1**)₂ and (**L-1**)(**D-1**) in CDCl₃ (C_{(**L-1**)₂} = C_{(**L-1**)(**D-1**)} = 10 mM, 700 MHz, 298K).
5. Crystallographic structure determination

1. Synthesis of L-1:



To the solution of resorcin[4]arene **2** (712 mg, 1 mmol) and L-phenylalanine **3** (744 mg, 4.5 mmol) in CHCl_3 (10 ml) HCHO_{aq} was added (300 μl , 37%, 4 mmol). The reaction was vigorously stirred for 3 days. Then additional portion of CHCl_3 was added (10 ml) and mixture was extracted with citric acid (5% solution in water, 20 ml). The organic layer was separated, filtrated through celite and evaporated. To the resulting residue was suspended in acetonitrile (10 ml) and left overnight with stirring. The resulting precipitate was separated by filtration (1.024 g, 72%)

$[\alpha]_{\text{D}} = -3.1^\circ$ (c 2.07, CHCl_3).

^1H NMR (500 MHz, CDCl_3 , 300 K): δ = 0.934 (d, J = 6.6 Hz, 12 H, H_{a}), 0.939 (d, J = 6.6 Hz, 12 H, H_{a}), 1.412 (heptet, J = 6.6 Hz, 4 H, H_{b}), 2.018 (m, 8 H, H_{c}), 3.297 (dd, J = 7.5 Hz, J = 14.9 Hz, 4 H, H_{h1}), 3.791 (dd, J = 4.8 Hz, J = 14.8 Hz, 4 H, H_{h2}), 3.803 (bm, 4 H, H_{g}), 3.865 (bm, 4 H, H_{f1}), 4.065 (bm, 4 H, H_{f2}), 4.444 (d, J = 8.0 Hz, 4 H, H_{d}), 7.216 (s, 4 H, H_{e}), 7.246-7.280 (m, 4 H, H_{i}), 7.344-7.391 (m, 16 H, H_{i}), 7.516 (bm, 8H, NH_2^+), 10.37 (bs, 4H, OH_1), 11.68 (bs, 4H, OH_2).

^{13}C NMR (125 MHz, CDCl_3 , 300 K): δ = 22.722, 26.847, 26.022, 31.383, 35.060, 42.231, 42.933, 65.188, 105.971, 124.429, 124.893, 125.221, 127.108, 128.862, 129.031, 137.675, 150.958, 151.692, 172.239.

MS (ESI): m/z = 1421.7 [$\text{C}_{84}\text{H}_{100}\text{N}_4\text{O}_{16} + \text{H}$] $^+$, isotope profile agrees.

Elemental analysis: $\text{C}_{84}\text{H}_{100}\text{N}_4\text{O}_{16} \times 0.25 \text{CHCl}_3$ (1451.55): calcd. C 69.71, H 6.96, N 3.86; found C 69.86, H 7.25, N 3.75.

2. NMR spectra of (L-1)₂:

SpinWorks 2.5:

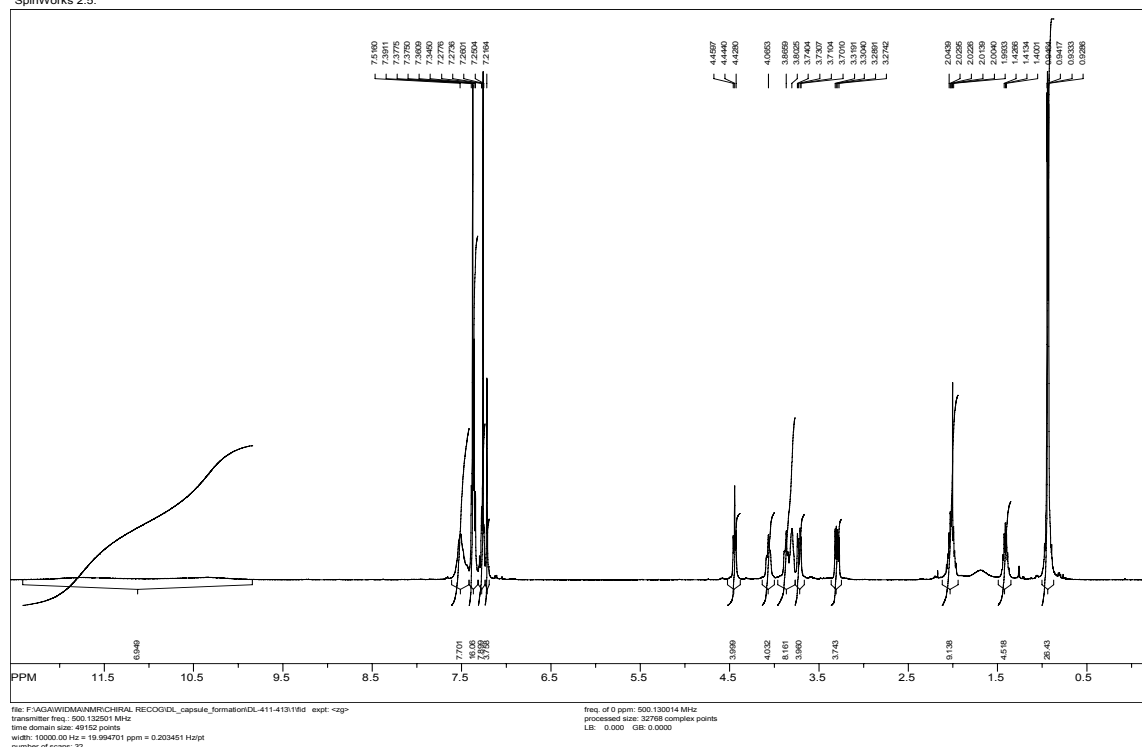


Fig. S1. ¹H NMR spectrum of (L-1)₂ in CDCl₃ (500 MHz, 300K).

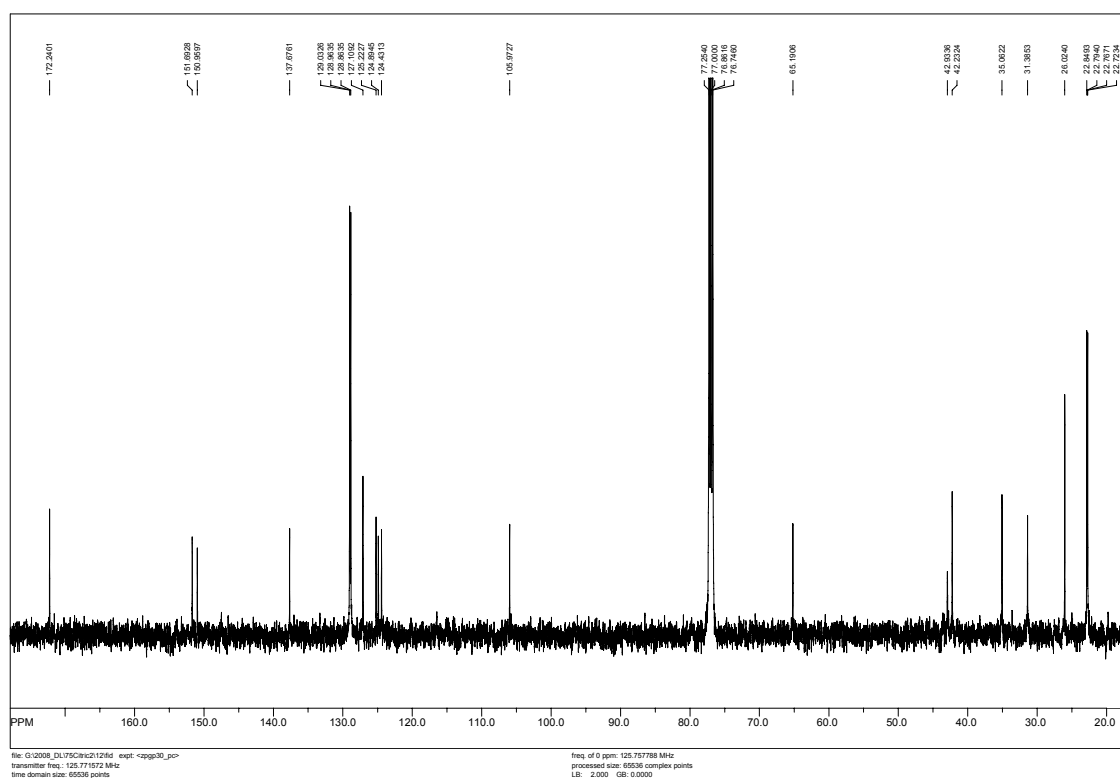


Fig. S2. ¹³C NMR spectrum of (L-1)₂ in CDCl₃ (500 MHz, 300K).

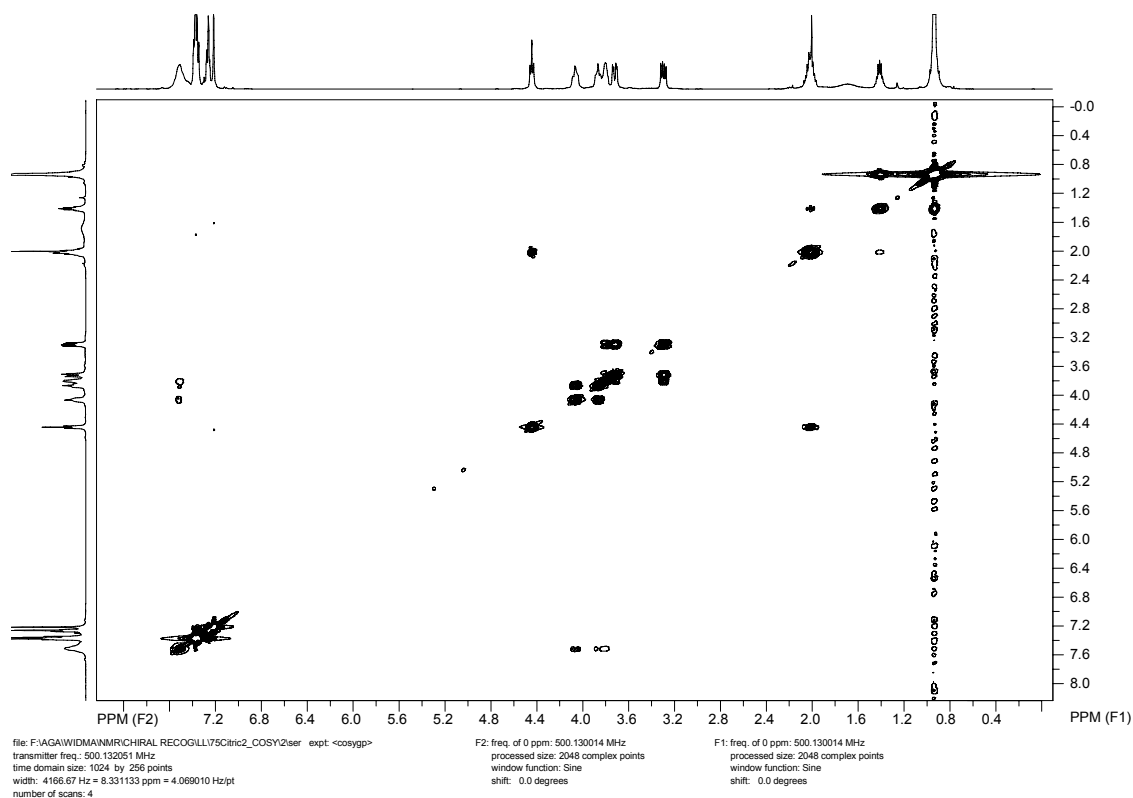


Fig. S3. COSY spectrum of (L-1)₂ in CDCl₃ (500 MHz, 300K).

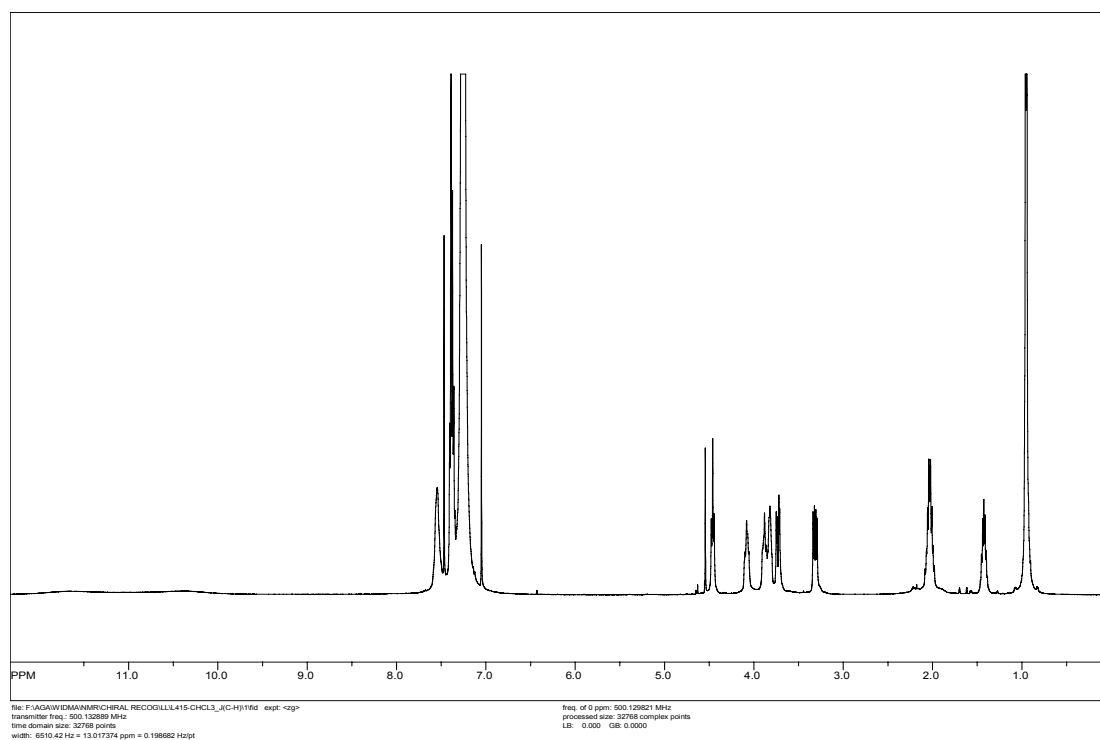


Fig. S4. ^1H NMR spectrum of $(\text{L-1})_2$ in CHCl_3 (500 MHz, 300K).

SpinWorks 2.5:

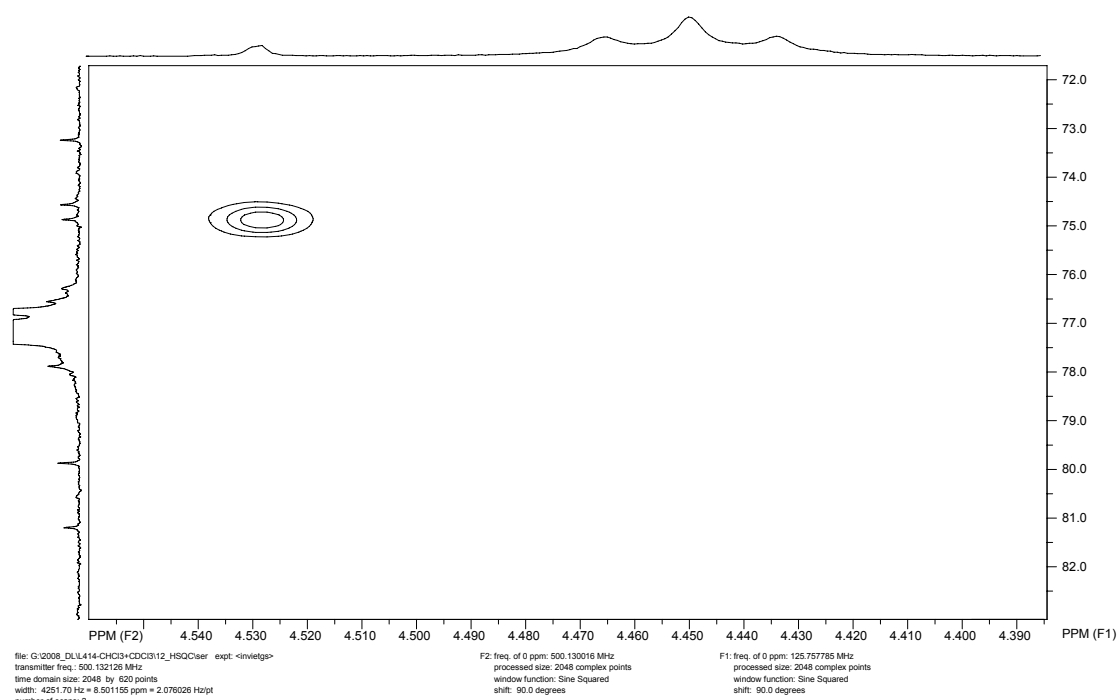


Fig. S5. Part of the HSQC spectrum (^1H - ^{13}C correlation) of $(\text{L-1})_2$ in CHCl_3 , showing correlation for encapsulated CHCl_3 molecule.

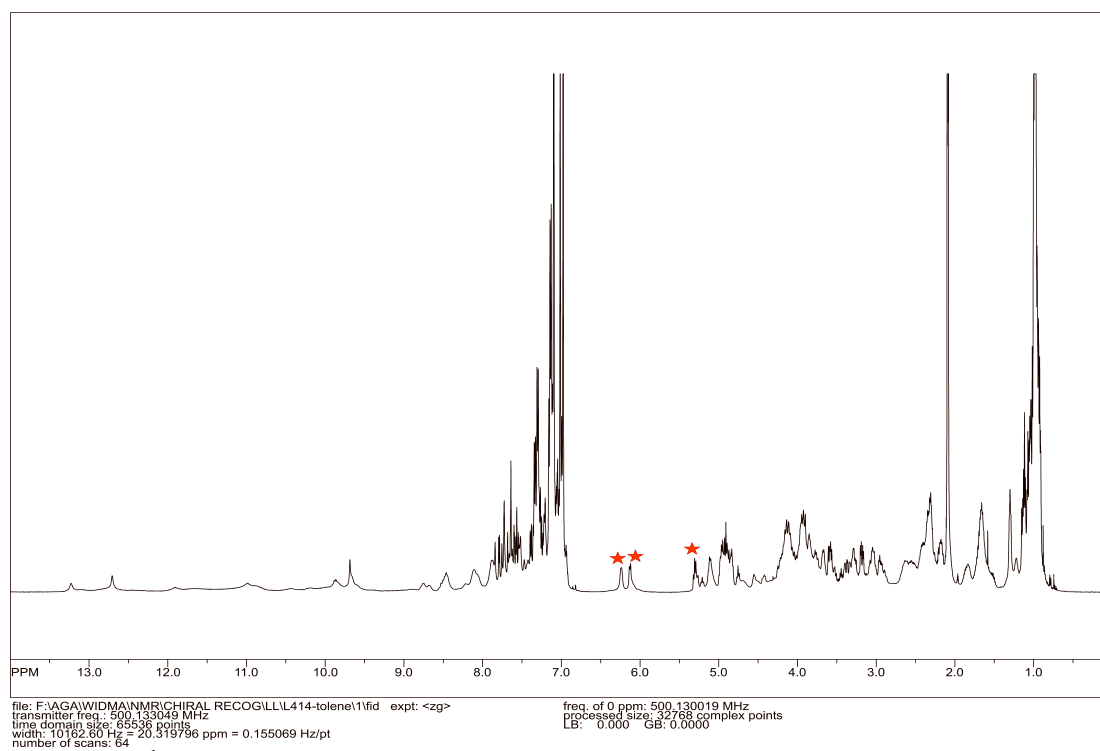


Fig. S6. ^1H NMR spectrum of $(\text{L-1})_2$ in toluene- d_8 (500 MHz, 300K). * denotes encapsulated phenylalanine side chain.

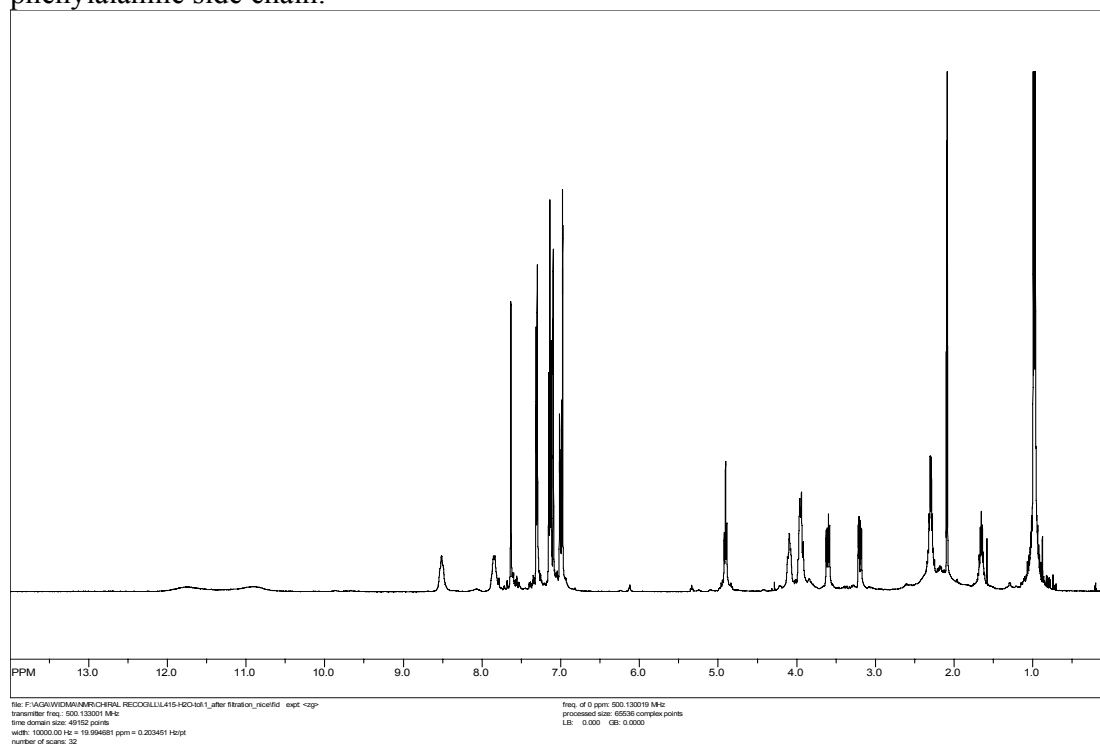


Fig. S7. ^1H NMR spectrum of $(\text{L-1})_2$ in toluene- d_8 equilibrated with H_2O (500 MHz, 300K).

SpinWorks 2.5: sample jaskk in cdcl3

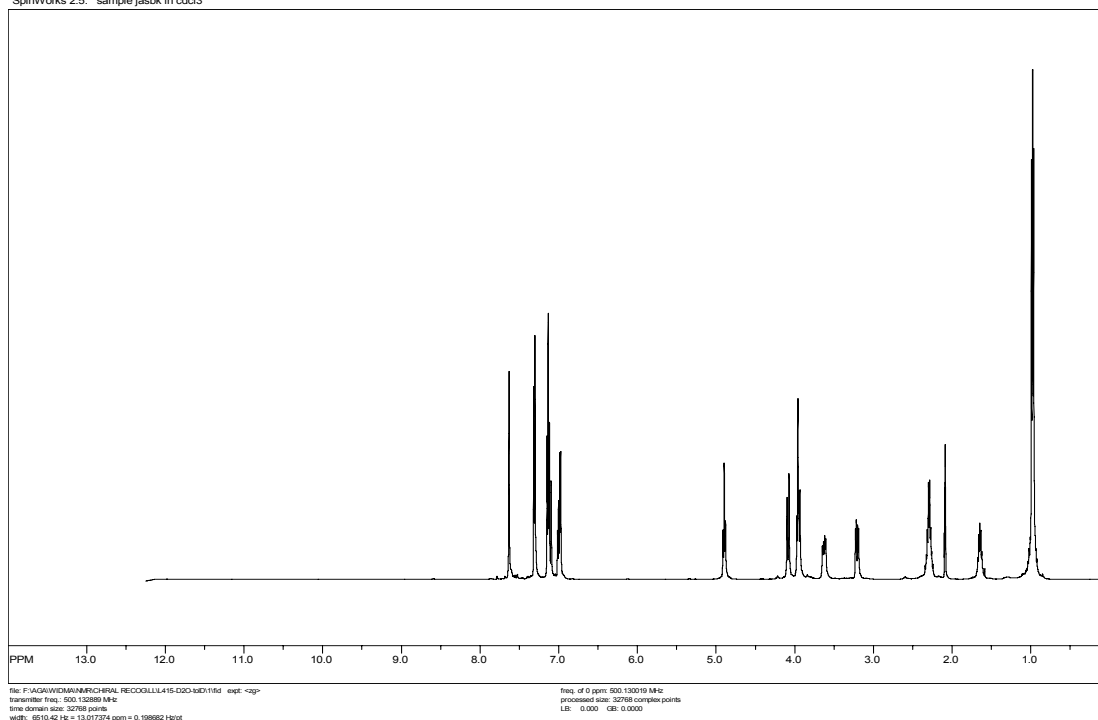


Fig. S8. ^1H NMR spectrum of $(\text{L-1})_2$ in toluene- d_8 equilibrated with D_2O (500 MHz, 300K).

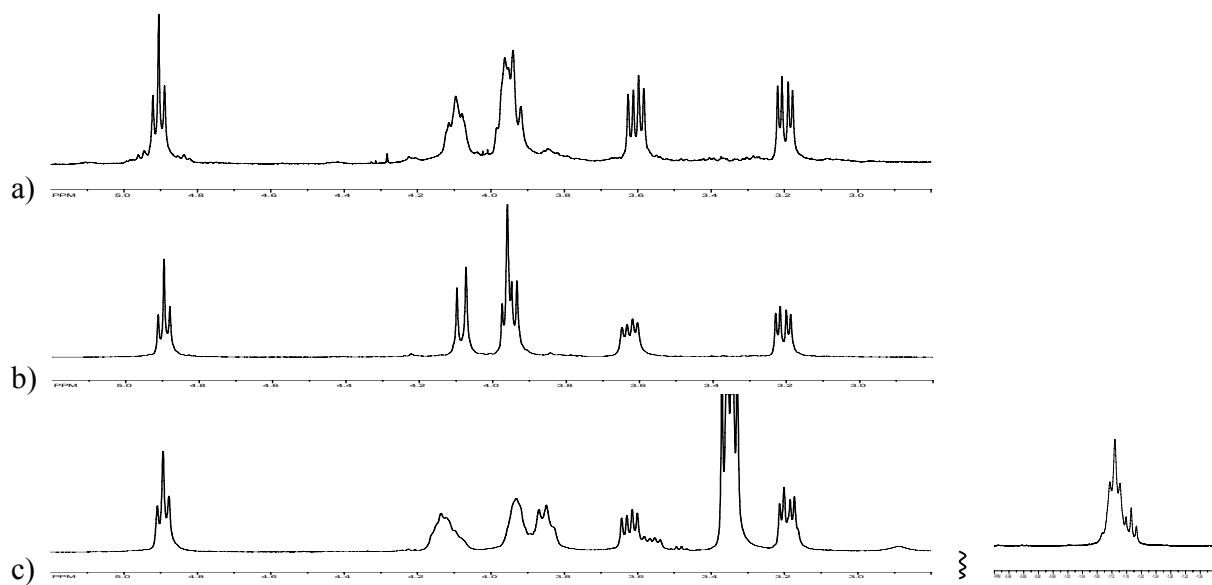


Fig. S9. Comparison of the parts of ^1H NMR spectra of $(\text{L-1})_2$ in toluene-d_8 ($C_{(\text{L-1})_2} = 10\text{mM}$, 500 MHz, 300K): a) equilibrated with H_2O ; b) equilibrated with D_2O ; c) + EtOH (170 mM).

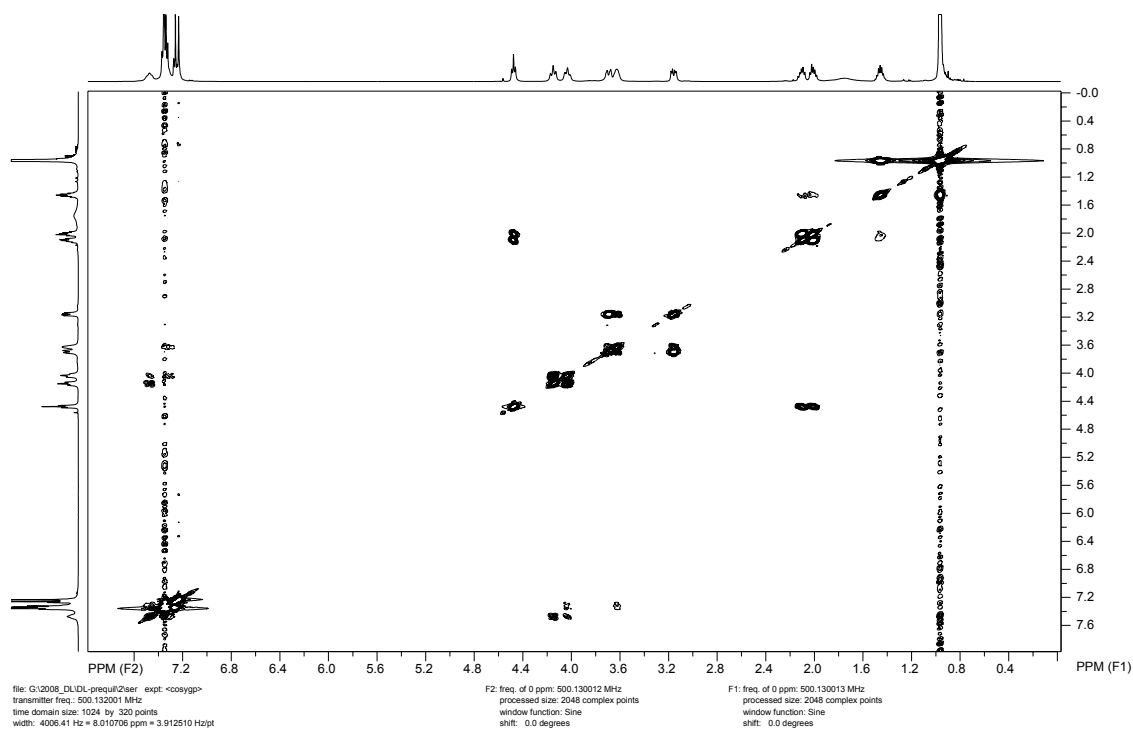


Fig. S12. COSY spectrum of (L-1)(D-1) in CDCl₃ (500 MHz, 300K).

4. DOSY spectra

Diffusion experiments were performed on Varian Direct Drive 700 MHz spectrometer in 298K. A standard stimulated echo sequence with self-compensating gradient schemes and convection compensation was employed. In all measurements following parameters were used: ^1H $\pi/2$ pulse of 6.2 μs , diffusion delay of 50 ms, gradient length of 2 ms with strength increasing in 15 increments from 0.019 to 0.467 T/m. 16 scans were coherently added with relaxation delay of 2s.

DOSY spectra were measured for $(\text{L-1})_2$ and $(\text{D-1})(\text{L-1})$ separately and for the sample containing both capsules.

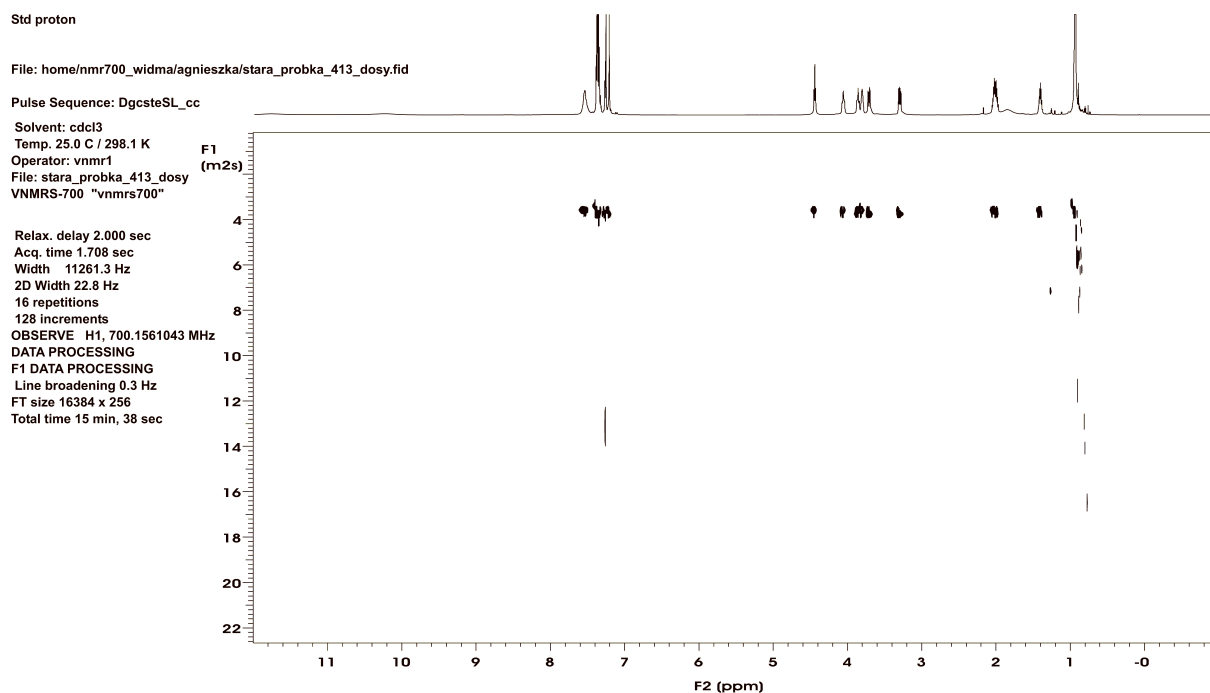


Fig. S13. DOSY spectrum of $(L-1)_2$ in $CDCl_3$ ($C_{(L-1)_2} = 10$ mM, 700 MHz, 298K).

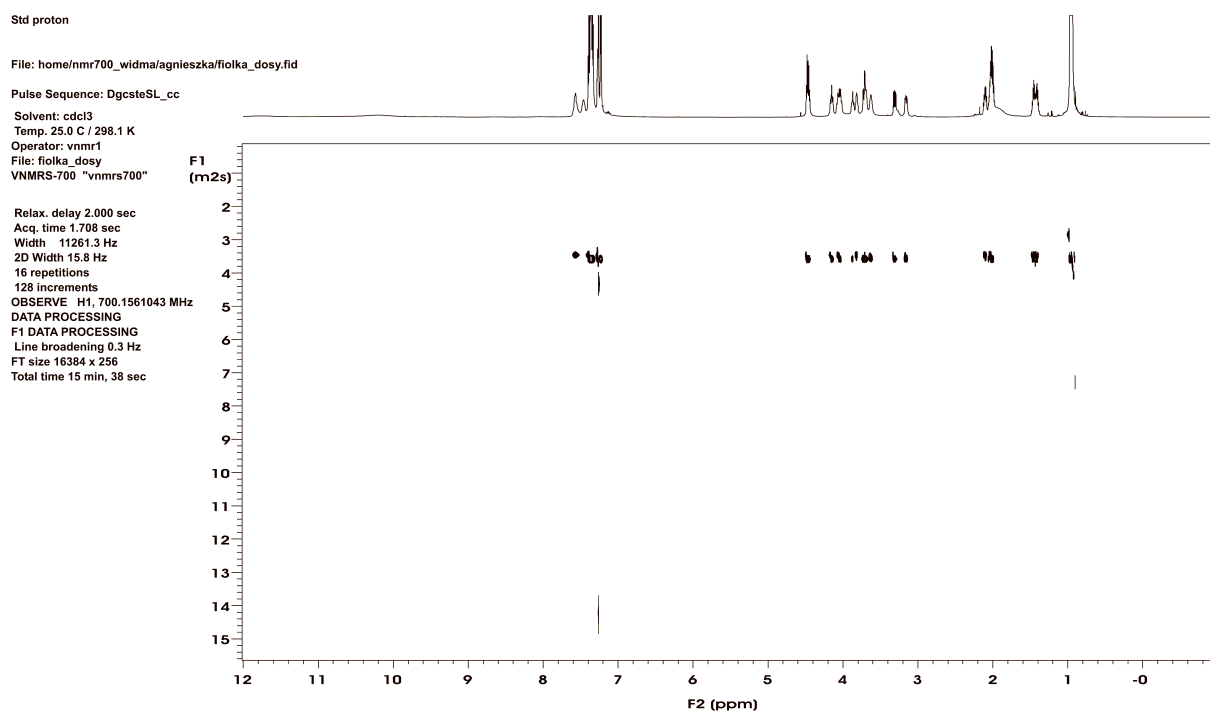


Fig. S14. DOSY spectrum of mixture of $(L-1)_2$ and $(L-1)(D-1)$ in $CDCl_3$ ($C_{(L-1)_2} = C_{(L-1)(D-1)} = 10$ mM, 700 MHz, 298K).

5. Crystallographic structure determination

The diffraction quality crystals of (L-1)₂ were grown from nitromethane/CHCl₃ solution. After removal from the mother liquid the crystal was immediately covered with an immersion oil and frozen at 153 K. However, it should be noted that the solved crystal is one of the three polymorphs that have been obtained from that mixture and measured. Due to twinning problems (orthorhombic space group emulating tetragonal) and disorder at special positions none of the previous two cases two could be satisfactory refined.

The measurement was performed with a KM4CCD j-axis diffractometer with graphite-monochromated Mo-*K*α radiation. The crystal was positioned at 62 mm from the CCD camera. 1500 Frames were measured at 0.5° intervals with a counting time of 20 s. The data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Oxford Diffraction programs. The structure was solved with DIRDIF¹ by using the modeled structure as a starting structure for ORIENT. The structure was refined by using SHELXL (X-Seed interface).² The refinement was based on *F*² for all reflections except those with very negative *F*². Weighted R factors *wR* and all goodness-of-fit *S* values are based on *F*². The non-hydrogen atoms, except for disordered ones, were refined with anisotropic thermal parameters, All H atoms were positioned geometrically. The geometrical restraints were applied for disordered atoms.

The structure contains many disordered solvent molecules (see below). Each of them have been carefully checked with regard to chemical sense and by removal test. In all cases the removal of the given atom the resulted in the appearance of the electron density peak at its place that was considerably higher than background even after many cycles (>20).

Crystal data: (L-1)₂ × (CH₃NO₂)₁₀ × (H₂O)_{4.5}, C₁₇₈H₂₃₉N₁₈O_{56.50}, *M* = 3534.87, monoclinic, space group *C*2, *a* = 30.0262(11), *b* = 18.6448(6), *c* = 33.9434(9) Å, β = 103.348(3)°, *V* = 18489.3(10) Å³, *Z* = 4, *D*_c = 1.270 g/cm³, *F*₀₀₀ = 7540, MoKα, λ = 0.71073 Å, *T* = 173(2)K, 2θ_{max} = 57.3°, 174687 reflections collected, 23415 unique (*R*_{int} = 0.0628). Final *Goof* = 0.957, *R*1 = 0.0692, *wR*2 = 0.1712, *R* indices based on 11769 reflections with *I* > 2σ(*I*) (refinement on *F*²), 2262 parameters, 4 restraints. *Lp* and absorption corrections applied, μ = 0.095 mm⁻¹.

DISORDER MODELS:

1. Disordered phenylalanine aromatic rings (over two positions, rings fixed to be hexagonal: AFIX 66):
 - a) C16A-C21A and C16B-C21B occupancy 0.5:0.5
 - b) C136-C141 and C36B-C41B occupancy 0.73348: 0.26652

AFIX 5 C142

2. Fixed geometry for disordered and purely located nitromethane molecules (AFIX 6 – molecules are allowed to move freely as entities, without changes in internal geometry)
 - a) O305-C308 (occupancy 0.73819)
 - b) O325-C328 (occupancy 0.25)
 - c) O35D-C38D (occupancy 0.25)

¹ P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, *The DIRDIF-99 Program System*, Crystallography Laboratory, University of Nijmegen, The Netherlands; b) V. Parthasarathi, P. T. Beurskens, H. J. Bruins Slot, *Acta Crystallogr., Sect. A* **1983**, 39, 860–864.

² L. J. Barbour, *J. Supramol. Chem.* **2001**, 1, 189–191.

- d) O329-C332 (occupancy 0.71061)
- e) O333-C336 (occupancy 0.28939)
- f) O342-C345 (occupancy 0.40375)
- g) O359-C363 (occupancy 0.27053)
- h) O366-C369 (occupancy 0.26652)
- i) O370-C374 (occupancy 0.72947)