Self-Inclusion of Proline-Functionalised Calix[4]arene Leads to Hydrogelation

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Supplementary Information

General

The D-proline calix[4]arene D-**1** was prepared by the same method that was used to prepare the L-proline calix[4]arene L-**1**.[1] ^{1}H NMR spectra were recorded on a Bruker Avance 400N (400.1 MHz for ^{1}H) spectrometer.

Gel-sol transition temperature experiments

The gel-sol transition temperature ($T_{gel\text{-}sol}$) was determined by the dropping-ball method (modified from the method of de Loos[2]), with each system determined in duplicate. Gels were prepared in a glass vial (7 mL, outer diameter 2 cm). Steel balls (110 mg, 30 mm diameter) were carefully placed on top of the gel to avoid disturbing the surface. The vials were then placed in a thermostated water bath (17 cm evaporating dish) heated on a Torrey Pines Scientific hot plate stirrer (model HS30-2) at 10 °C/hour from room temp to a maximum of 60 °C. The temperature at which the steel balls fall through the gels was recorded.

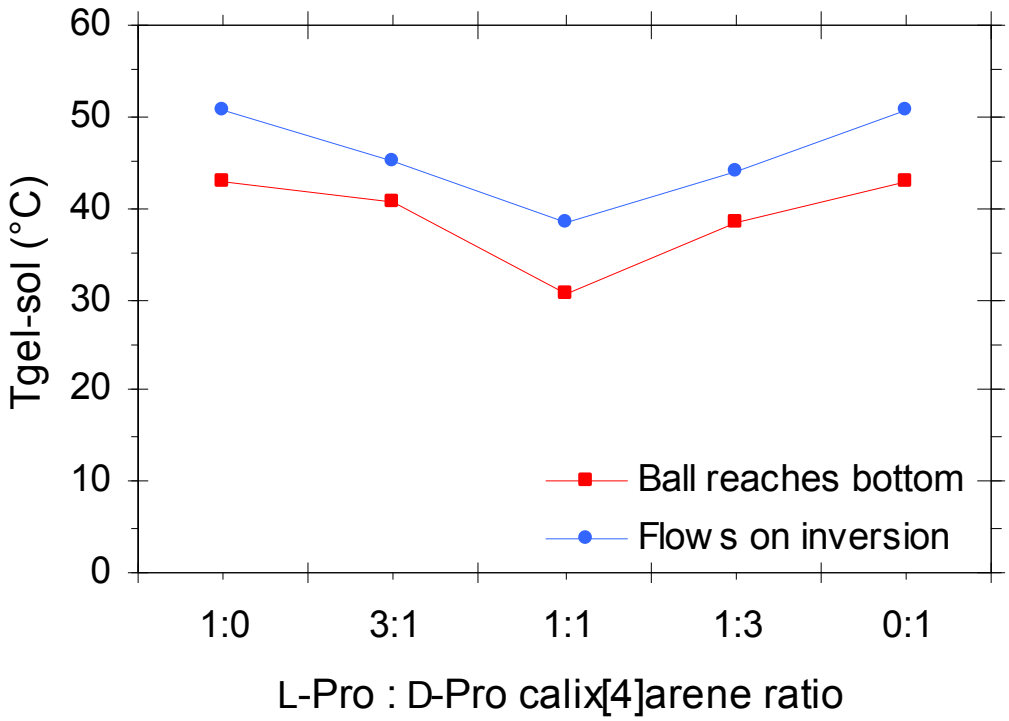


Figure S1: $T_{gel–sol}$ determined for mixtures of L-proline calix[4]arene L-**1** and D-proline calix[4]arene D-**1** hydrogels. Proline calix[4]arene (10 mM) and $La(NO_3)_3$ (20 mM) in water.

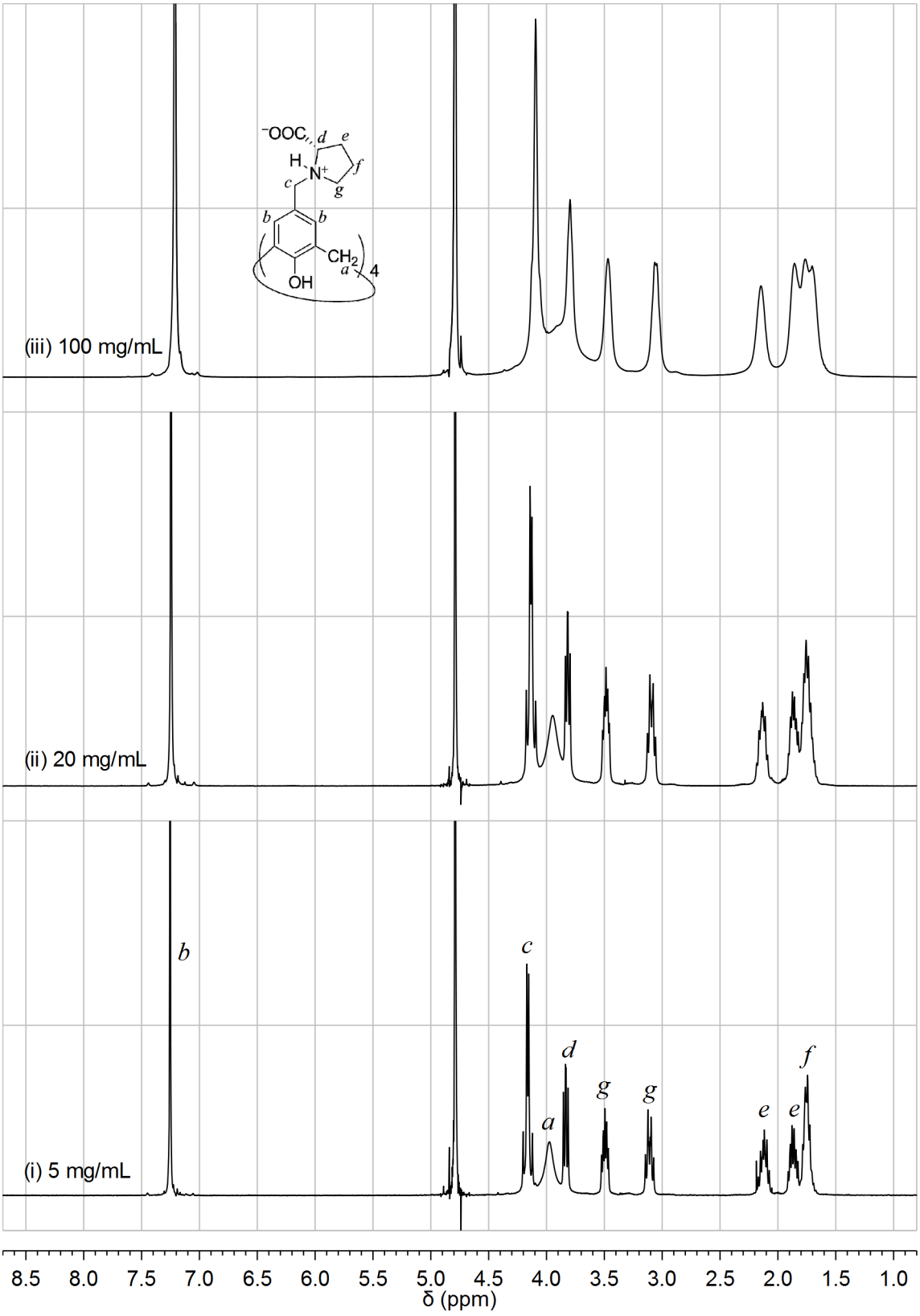
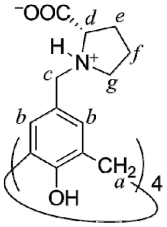


Figure S2: L-Proline calix[4]arene L-**1** at different concentrations in D_2O.



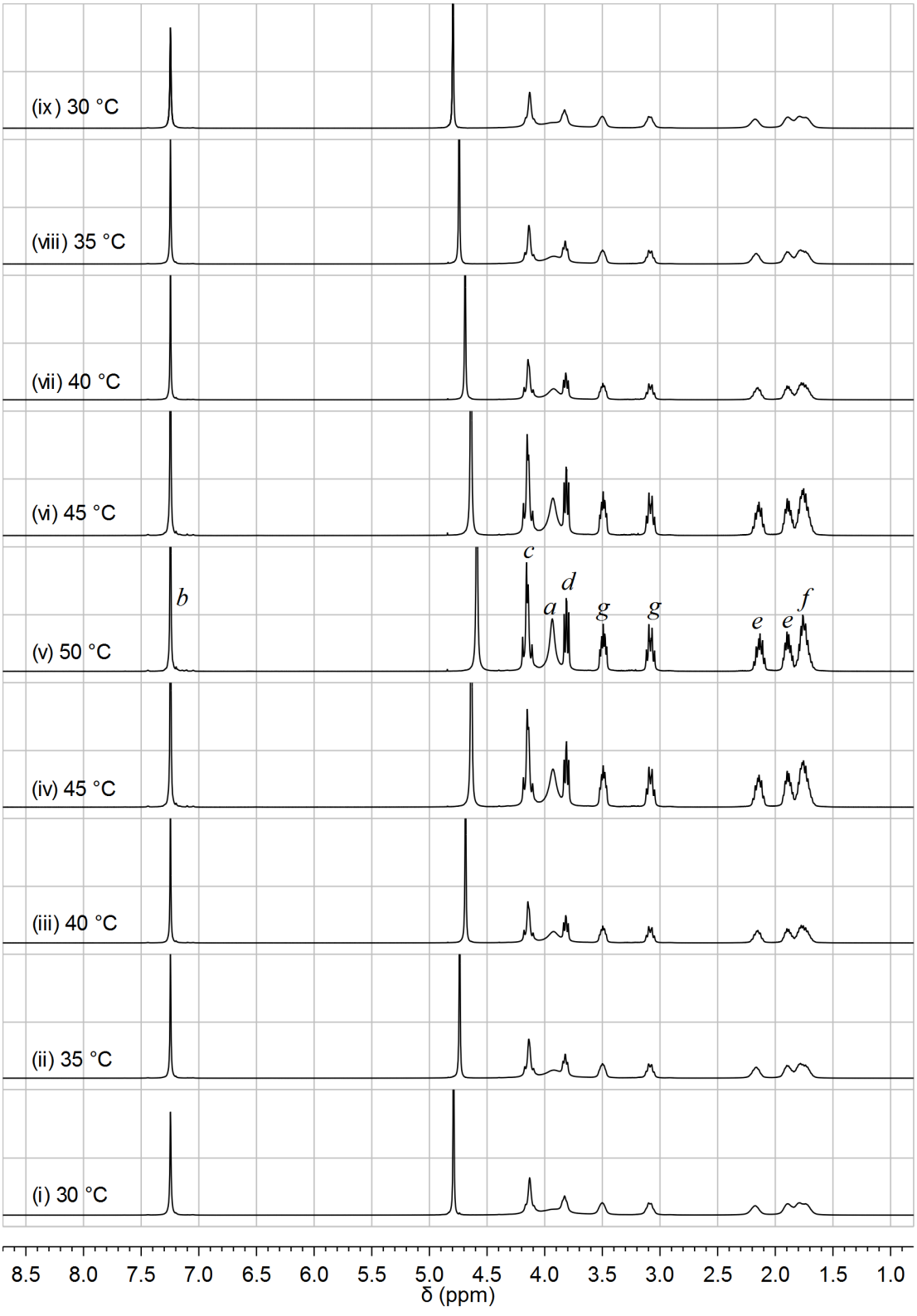


Figure S3: Variable-temperature ^{1}H NMR experiments for L-proline calix[4]arene (100 mg/mL) in D_2O. Sample was heated (i–v) and then cooled (vi–ix).

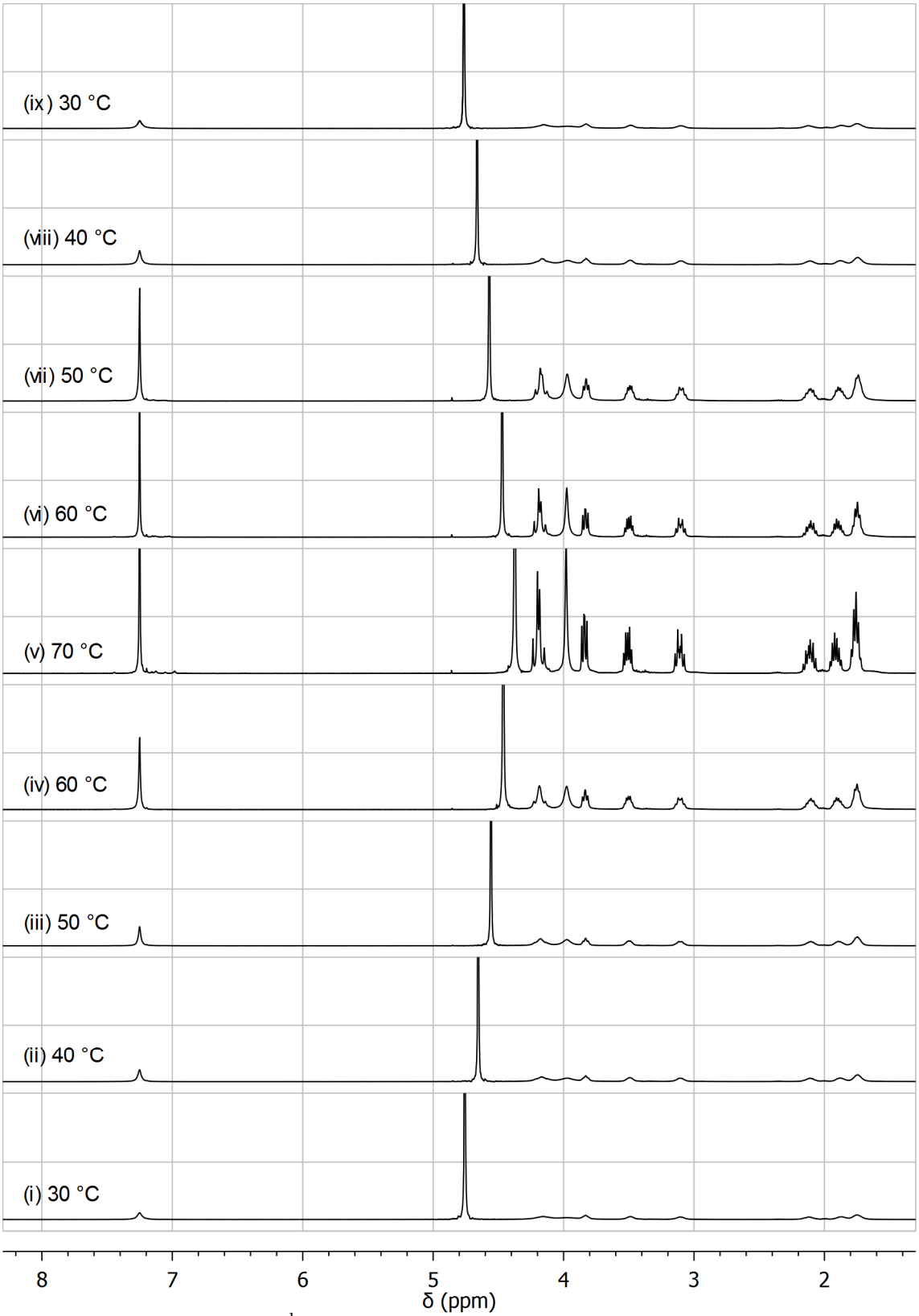


Figure S4: Variable-temperature ^{1}H NMR experiments for L-proline calix[4]arene (20 mg/mL) in D_2O with 30 mol% $La(NO_3)_3$. The integration of the calixarene signals on the cooling cycle (v) → (ix) decreases significantly (>70%), suggesting at room temperature the majority of the calixarene is in a rigid, solid-like phase with a relaxation that makes the material 'NMR silent' under these conditions.[3]

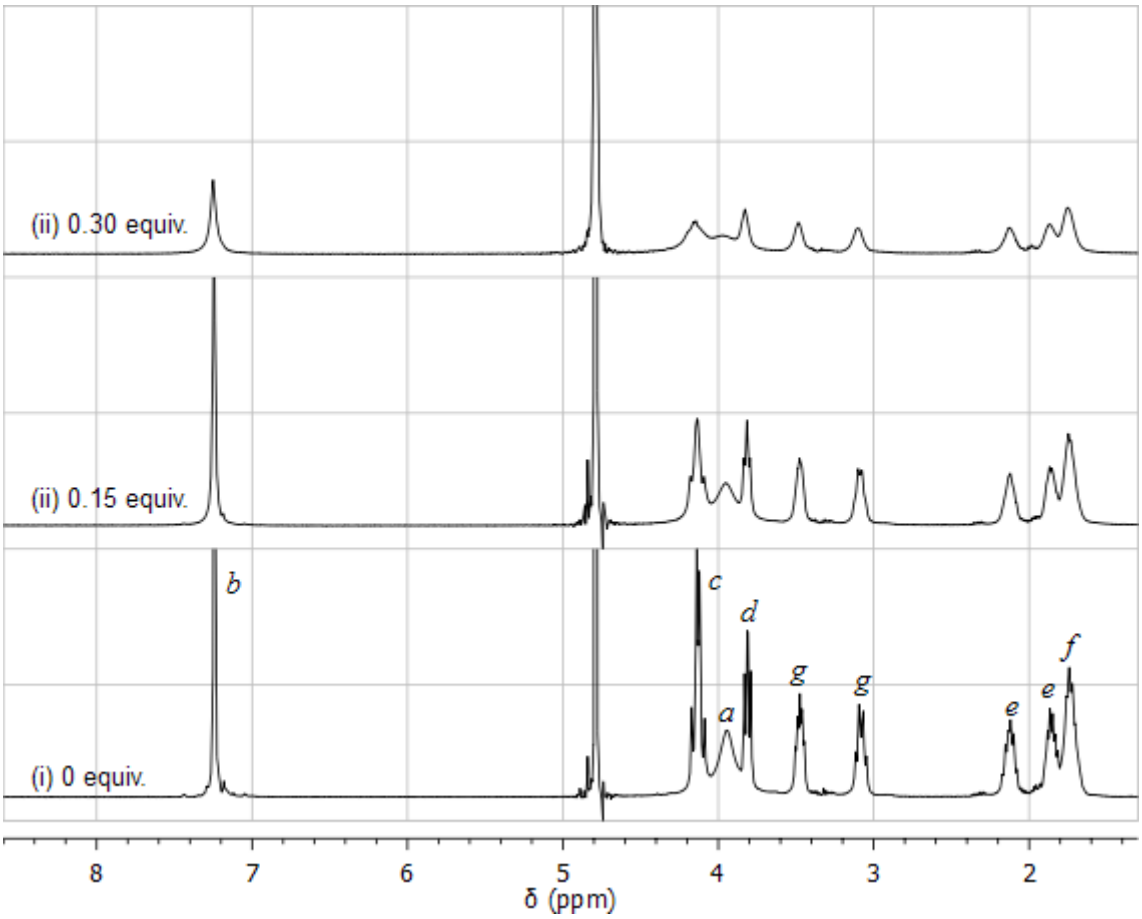


Figure S5: The comparison of ^{1}H NMR spectra (recorded at 300 K) for solutions of: (i) L-proline calix[4]arene (20 mg/mL) in D_2O; (ii) after the addition of 0.15 equivalents of $La(NO_3)_3$; and (iii) after the addition of 0.30 equivalents of $La(NO_3)_3$.

Table S1. Crystal data and structure refinement for mmcy08.

Identification code	mmcy08
Empirical formula	$C_{52}\ H_{73.60}\ La_{0.40}\ N_4\ O_{18.80}$
Formula weight	1111.11
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 35.5856(13) Å
	b = 9.6028(3) Å
	c = 35.8812(9) Å
	β= 99.056(3)°
Volume	12108.5(7) $Å^3$
Z	8
Density (calculated)	1.219 Mg/m^3
Absorption coefficient	0.363 mm^{-1}
F(000)	4694
Crystal size	0.32 x 0.15 x 0.07 mm^3
θ range for data collection	1.50 to 25.00°.
Index ranges	-41<=h<=42, -11<=k<=11, -41<=l<=42
Reflections collected	22605
Independent reflections	10435 [R(int) = 0.0502]
Completeness to θ = 25.00°	97.7 %
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.00/0.81
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10435 / 199 / 701
Goodness-of-fit on F^2	1.101
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1120, wR_2 = 0.3427
R indices (all data)	R_1 = 0.1864, wR_2 = 0.3743
Largest diff. peak and hole†	1.624 and -0.690 e.$Å^{-3}$

† If the largest peak is refined as the missing 0.1 La, the resulting U(eq) is unacceptably high. If La1 was refined with a constrained occupancy of 0.5, the final R-factors were significantly higher: R1= 0.136 and wR2 = 0.396.

Table S2. Selected bond lengths [Å] and angles [°] for mmcy08.

La(1)-O(1)	2.729(17)
La(1)-O(242)	2.578(7)
La(1)-O(2)	2.633(15)
La(1)-O(241)	2.651(6)
La(1)-O(241)[1]	2.691(6)
La(1)-O(242)[1]	2.823(7)
La(1)-O(141)[2]	2.834(9)
O(241)-La(1)-O(1)	97.3(4)
O(242)-La(1)-O(1)	66.3(4)
O(242)-La(1)-O(2)	137.4(3)
O(242)-La(1)-O(241)	49.9(2)
O(2)-La(1)-O(241)	135.2(4)
O(242)-La(1)-O(241)[1]	125.28(19)
O(2)-La(1)-O(241)[1]	72.4(3)
O(241)-La(1)-O(241)[1]	148.36(8)
O(242)-La(1)-O(242)[1]	149.13(9)
O(2)-La(1)-O(242)[1]	72.9(3)
O(241)-La(1)-O(242)[1]	117.46(19)
O(241)1-La(1)-O(242)[1]	47.07(19)
O(242)-La(1)-O(141)[2]	66.6(2)
O(2)-La(1)-O(141)[2]	77.3(3)
O(241)-La(1)-O(141)[2]	69.7(2)
O(241)1-La(1)-O(141)[2]	141.3(2)
O(242)1-La(1)-O(141)[2]	141.3(2)
O(1)-La(1)-O(2)	127.1(5)
O(1)-La(1)-O(141)[2]	126.5(4)
O(1)-La(1)-O(241)[1]	61.1(4)
O(1)-La(1)-O(242)[1]	91.4(4)
C(146)-O(141)-La(1)[3]	137.2(9)
C(246)-O(241)-La(1)	88.3(5)
C(246)-O(241)-La(1)[1]	97.5(5)
C(246)-O(242)-La(1)	90.1(5)
C(246)-O(242)-La(1)[1]	89.4(5)

Symmetry transformations used to generate equivalent atoms:

[1] 1-x,2-y,1-z; [2] x,y+1,z; [3] x,y-1,z

1. T. Becker, C. Y. Goh, F. Jones, M. J. McIldowie, M. Mocerino and M. I. Ogden, *Chem. Commun.*, 2008, 3900.

2. de Loos, M. Hydrogen-bonded low molecular weight gelators. Dissertation, University of Groningen, Groningen, Netherlands, 2005.

3. A. R. Hirst, I. A. Coates, T. R. Boucheteau, J. F. Miravet, B. Escuder, V. Castelletto, I. W. Hamley, and D. K. Smith, *J. Am. Chem. Soc.*, 2008, 130, 9113