ELECTRONIC SUPPORTING INFORMATION FOR:

Self-assembly and Luminescence of Pyrazole Supergelators

Sandra Moyano,[a] José Luis Serrano,[a,c] Anabel Elduque*[b] and Raquel Giménez*[a]

[a] *Dpto Química Orgánica. Facultad de Ciencias - Instituto de Ciencia de Materiales de Aragón (ICMA). CSIC - Universidad de Zaragoza. 50009 Zaragoza. Spain. E-mail: rgimenez@unizar.es*

[b] *Dpto Química Inorgánica. Facultad de Ciencias - Instituto de Síntesis Química y Catálisis Homogénea (ISQCH). CSIC - Universidad de Zaragoza. 50009 Zaragoza. Spain. E-mail: anaelduq@unizar.es*

[c] *Instituto de Nanociencia de Aragón, Universidad de Zaragoza. 50018 Zaragoza. Spain.*

CONTENTS (15 pages):

1.- **General methods and materials.**

Starting chemicals and solvents were purchased from commercial sources and used without further purification. All compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy, mass spectrometry and elemental analysis techniques. NMR and experiments were performed on a Bruker ARX 300, Bruker AVANCE 400 and Bruker AVANCE 500 spectrometers operating at 300.13, 400.13 and 500.13 MHz for ^{1}H and 75.46, 100.61, 125.75 MHz for ^{13}C. Chemical shifts are given in ppm relative to TMS, and the solvent residual peak was used as internal standard. Infrared spectra of the compounds were measured in a Nicolet Avatar 360 FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range. Sample preparation was KBr pellets for solids, sandwiched between NaCl windows for gels, or in a solution cell with NaCl windows in case of chloroform solutions. MS analyses were performed using a Bruker Microflex spectrometer. Elemental analyses were performed using a Perkin Elmer 2400 microanalyser. UV-vis and Fluorescence spectra were measured using ATI-Unicam UV4-200 and Perkin-Elmer LS50B spectrophotometers respectively. Temperature dependent circular dichroism spectra were obtained in a Jasco J-810 spectropolarimeter equipped with a Peltier cell holder Jasco CDF-426S, by using a fused silica cell with 100 μm path length.

2.- Synthesis and characterisation.

General procedure for the preparation of compounds 1, 1*S*, 1*R*, 4, 5.

4-(4´-aminophenyl)-3,5-dimethylpyrazol (10 mmol) was dissolved in dry THF under an Ar atmosphere. The solution was cooled down to 0 ºC and then 22 mmol of triethylamine (NEt_3) were added. A THF solution of the acid chloride derived acids (10 mmol in 10 mL) previously prepared from dialkoxy or trialkoxylated benzoic acids[1] was added dropwise. The reaction mixture was stirred for 12 hours at room temperature, after which the solvent was evaporated. The residue was dissolved in ethyl acetate, transferred to a separation funnel, and washed with water. The organic layer was dried with $MgSO_4$, filtered, and the solvent removed under vacuum. The product was obtained as a white solid that was purified by recrystallisation in methanol and dried under vacuum.

1. Yield: 69 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm 7.72 (s, 1H), 7.68-7.65 (m, AA´XX´, 2H), 7.29-7.27 (m, AA´XX´, 2H), 7.06 (s, 2H), 4.06-4.01 (m, 6H), 2,30 (s, 6H), 1.87-1.71 (m, 6H), 1.52-1.43 (m, 6H), 1.27 (m, 36H), 0.88 (t, *J* = 6.5Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ / ppm 165.7, 153.2, 141.6, 136.3, 129.9, 129.7, 129.7, 120.3, 117.8, 105.8, 73.6, 69.5, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 22.7, 14,1, 11.6; FTIR ν / cm^{-1} 3270 (N-H amide), 3151 (N-H pyrazole), 1641 (amide I), 1527 (amide II), 1580, 1497 (arC-C), 1237 (C-O-C); MS (MALDI+, dithranol) m/z 760.7 $[M+H]^+$; Anal. Found C, 75,46; H, 10.11; N, 5.33. Calc for $[C_{48}H_{77}N_3O_4]$: C, 75.84; H, 10.21; N, 5.53 %.

1*S*. Yield: 62 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm 7.86 (s, 1H), 7.68-7.66 (m, AA´XX´, 2H), 7.29-7.27 (m, AA´XX´, 2H), 7.07 (s, 2H), 4.10-4.02 (m, 6H), 2.30 (s, 6H), 1.94-1.79 (m, 3H), 1.71-1.15 (m, 27H), 0.94 (t, *J* = 6.3, 9H), 0.87 (d, *J* = 6.6Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ / ppm 165.7, 153.3, 141.5, 141.5, 136.2, 129.9, 129.9, 120.3, 118.0, 105.8, 71.8,

[1] E. Beltrán, E. Cavero, J. Barberá, J. Serrano, A. Elduque, and R. Giménez, *Chemistry - A European Journal*, 2009, **15**, 9017–9023

67.8, 39.3, 39.3, 37.5, 37.3, 36.4, 29.8, 29.6, 28.0, 24.7, 22.7, 22.6, 22.6, 19.6, 11.6; FTIR ν / cm^{-1} 3296 (N-H amide), 3172 (N-H pyrazole), 1643 (amide I), 1535 (amide II), 1580 (arC-C), 1236 (C-O-C); MS (MALDI+, dithranol) m/z 760.8 $[M+H]^+$; Anal. Found C,7 5.96; H, 10.53; N, 5.38. Calc for $[C_{48}H_{77}N_3O_4]$: C, 75.84; H, 10.21; N, 5.53 %.

1*R*. Yield: 60 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm 7.75 (s, 1H), 7.68-7.65 (m, AA´XX´, 2H), 7.30-7.27 (m, AA´XX´, 2H), 7.07 (s, 2H), 4.10-4.02 (m, 6H), 2.30 (s, 6H), 1.94-1.79 (m, 3H), 1.71-1.15 (m, 27H), 0.94 (t, *J* = 6.3 Hz, 9H), 0.87 (d, *J* = 6.6Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ / ppm 165.7, 153.3, 141.6, 136.2, 129.9, 129.9, 129.8, 120.3, 118.0, 105.8, 71.8, 67.8, 39.4, 39.3, 37.5, 37.3, 36.4, 29.8, 28.0, 24.7, 22.7, 22.6, 19.6, 11.7; FTIR ν / cm^{-1} 3278 (N-H amide), 3198 (N-H pyrazole), 1645 (amide I), 1529 (amide II), 1581 (arC-C), 1237 (C-O-C); MS (MALDI+, dithranol) m/z 760.6 $[M+H]^+$; Anal. Found C, 75.85; H, 10.26; N, 5.42. Calc for $[C_{48}H_{77}N_3O_4]$: C, 75.84; H, 10.21; N, 5.53 %.

4. Yield: 73 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm 7.81 (s, 1H), 7.69-7.66 (m, AA´XX´, 2H), 7.49-7.48 (d, *J*=2.0Hz, 1H), 7.40-7.36 (dd, *J*=2.0 Hz, *J*=8.4Hz, 1H), 7.29-7.26 (m, AA´XX´, 2H), 6.93-6.90 (d, *J*=8.4Hz, 1H), 4.09-4.04 (m, 4H), 2.30 (s, 6H), 1.89-1.79 (m, 4H), 1.52-1.45 (m, 4H), 1.27 (m, 24H), 0.90-0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ / ppm 165.4, 152.3, 151.9, 149.1, 136.6, 129.8, 127.2, 120.21, 119.5, 118.2, 112.8, 112.2, 69.4, 69.1, 31.9, 29.6, 29.6, 29.6, 29.4, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1, 11.6; FTIR ν / cm^{-1} 3267 (N-H amide), 3174 (N-H pyrazole), 1638 (amide I), 1508 (arC-C), 1271 (C-O-C); MS (MALDI+, dithranol) m/z 604.5 $[M+H]^+$; Anal. Found C, 75,21; H, 9.43; N, 6.61. Calc for $[C_{38}H_{57}N_3O_3]$: C, 75.58; H, 9.51; N, 6.96 %.

5. Yield: 76 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm 7.79 (s, 1H), 7.68-7.66 (m, AA´XX´, 2H), 7.29-7.27 (m, AA´XX´, 2H), 6.98-6.97 (d, *J* = 1.9Hz, 2H), 6.62 (t, *J* = 1.8Hz, 1H), 4.00 (t, *J* = 6.5Hz, 4H), 2.30 (s, 6H), 1.82-1.75 (m, 4H), 1.49-1.42 (m, 4H), 1.27 (m, 14H), 0.88 (t, *J* = 6.7Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ / ppm 165.7, 160.6, 141.93, 137.0, 136.2,

130.0, 129.9, 120.2, 117.9, 105.4, 104.7, 68.4, 31.9, 29.6, 29.6, 29.4, 29.4, 29.2, 26.1, 22.7, 14.2, 11.6; FTIR ν / cm^{-1} 3284 (N-H amide), 3180 (N-H pyrazole), 1650 (amide I), 1530 (amide II), 1591, (arC-C), 1248 (C-O-C); MS (MALDI+, dithranol) m/z 604.5 $[M+H]^+$; Anal. Found C, 75,63; H, 9.46; N, 6.84. Calc for $[C_{38}H_{57}N_3O_3]$: C, 75.58; H, 9.51; N, 6.96 %.

Synthesis and characterisation of compound 2.

4-(4´-hydroxyphenyl)-3,5-dimethylpyrazole (2.65 mmol, 0.5 g) 3,4,5-tridecyloxybenzoic acid (2.92 mmol, 2.25 g.) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) (1.33 mmol, 0.391 g.) were dissolved in dry dichloromethane (25 mL) under an Ar atmosphere and cooled at 0ºC. Afterwards, a solution of dicylohexylcarbodiimide (DCC) (3.32 mmol, 0.685 g.) in dichloromethane (10 mL) was added dropwise. The mixture was stirred at room temperature for 24 hours. A precipitate appeared that was filtered out and the solution was evaporated. The product was purified by column chromatography (silica gel, Hexane: Ethyl acetate, 8:2 as eluent) to give a white solid. Yield: 25 %; R_f = 0.3 (CH_2Cl_2:Hexane 7:3, silica gel TLC plates, UV at 254 nm). ^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm 7.43 (s, 2H), 7.34-7.31 (m, AA´XX´, 2H), 7.26-7.23 (m, AA´XX´, 2H), 4.09-4.04 (m, 6H), 2.31 (s, 6H), 1.88-1.73 (m, 6H), 1.54-1.45 (m, 6H), 1.28 (m, 36H), 0.88 (t, *J* = 5.6Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ / ppm 165.1, 152.9, 149.4, 143.0, 142.1, 131.4, 130.3, 123.9, 121.7, 117.8, 108.6, 73.6, 69.3, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1, 11.6; FTIR ν / cm^{-1} 3191 (N-H pyrazole), 1732 (C=O), 1587 (arC-C), 1273 (C-O-C), 1194 (C-O); MS (MALDI+, dithranol) m/z 783.6 $[M+Na]^+$; Anal. Found C, 75.96; H, 10.04; N, 3.72. Calc for $[C_{48}H_{76}N_2O_5]$: C, 75.74; H, 10.06; N, 3.68 %.

Synthesis and characterisation of compound 3.

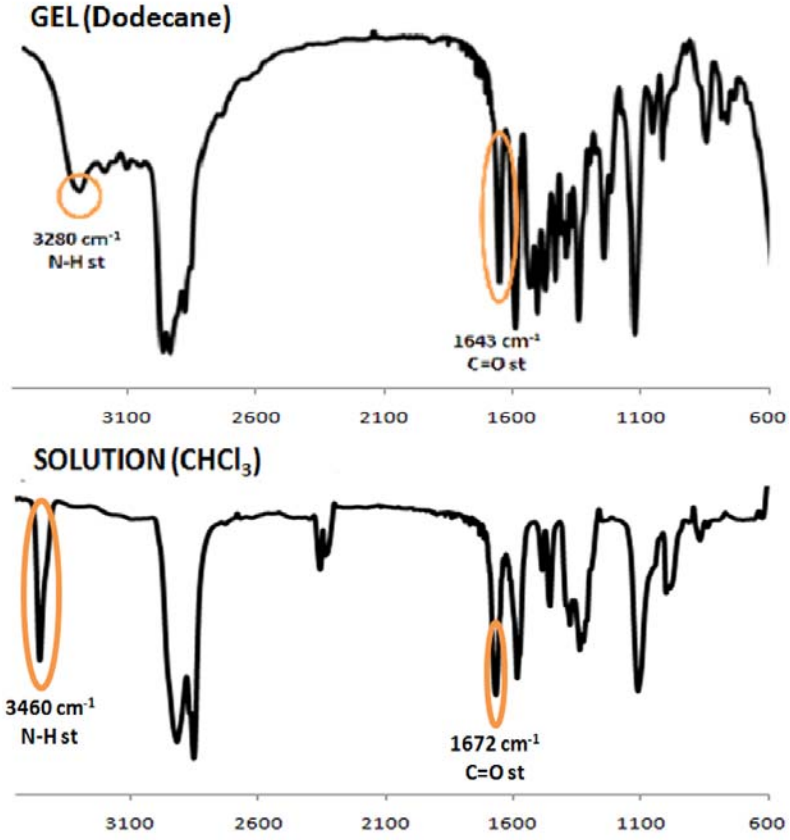
0.06 mmol (50 mg) of **1** were dissolved in acetone (10 mL) and KOH (0.08 mmol, 3.7 mg, dissolved in 5 mL of methanol) was added to the solution. To this solution 0.08 mmol (11.67 mg) of iodomethane were added. The solution was stirred at room temperature for 2 hours. Once the reaction had finished the solvent was evaporated and a white solid was obtained. The product was purified by recrystallisation in methanol. Yield: 58 %; R_f = 0.5 (EtOAc, silica gel TLC plates, UV at 254 nm). ^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm 7.71 (s, 1H), 7.66-7.64 (m, AA´XX´, 2H), 7.26-7.24 (m, AA´XX´, 2H), 7.06 (s, 2H), 4.06-4.00 (m, 6H), 3.78 (s, 3H), 2,25 (s, 3H), 2.24 (s, 3H) 1.85-1.74 (m, 6H), 1.48-1.46 (m, 6H), 1.27 (m, 36H), 0.90-0.86 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm 165.6, 153.3, 145.0, 141.6, 136.1, 130.5, 130.0, 129.9, 120.2, 118.6, 105.9, 73.6, 69.51 36.0, 31.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3, 26.1, 22.17 14.1, 12.5, 10.2; FTIR ν / cm^{-1} 3270 (N-H amide), 3265 (N-H amide), 1653 (amide I), 1558, (arC-C), 1527 (amide II), 1235 (C-O-C); MS (MALDI+, dithranol) m/z 796.6 $[M+Na]^+$; Anal. Found C, 75.99; H, 10.49; N, 5.10. Calc for $[C_{48}H_{77}N_3O_4]$: C, 76.02; H, 10.29; N, 5.43 %.

3.- Table S1. UV-vis absorption and emission data

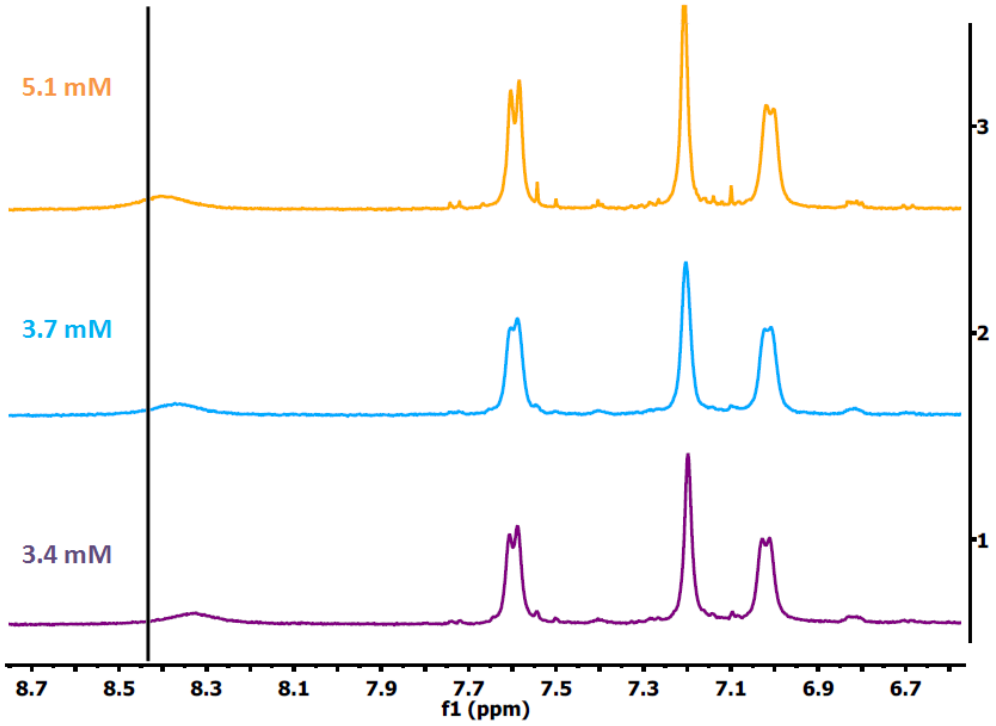
Compd	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)	λ_{em} (nm)	λ_{em} (nm)	λ_{em} (nm)	λ_{em} (nm)	λ_{em} (nm)
	THF[a]	THF[b]	dod[c]	gel[d]	sol[e]	THF[a]	THF[b]	dod[c]	gel[d]	sol[e]
1	292	290	281	287	287	358	415	330	440	440
1*S*	295	290	281	280	287	345	407	328	440	440
1*R*	295	290	281	280	287	345	407	328	440	440

[a] 20ºC, THF, 10^{-5} M. [b] 20ºC, THF, 0.5 % wt. [c] 20ºC, dodecane, 10^{-5} M. [d] 20ºC, dodecane gel, 0.5 % wt. [e] 90ºC, dodecane sol, 0.5 % wt.

4.- Figure S1. FTIR spectra of 1 in dodecane gel (0.5 % wt) and chloroform solution.

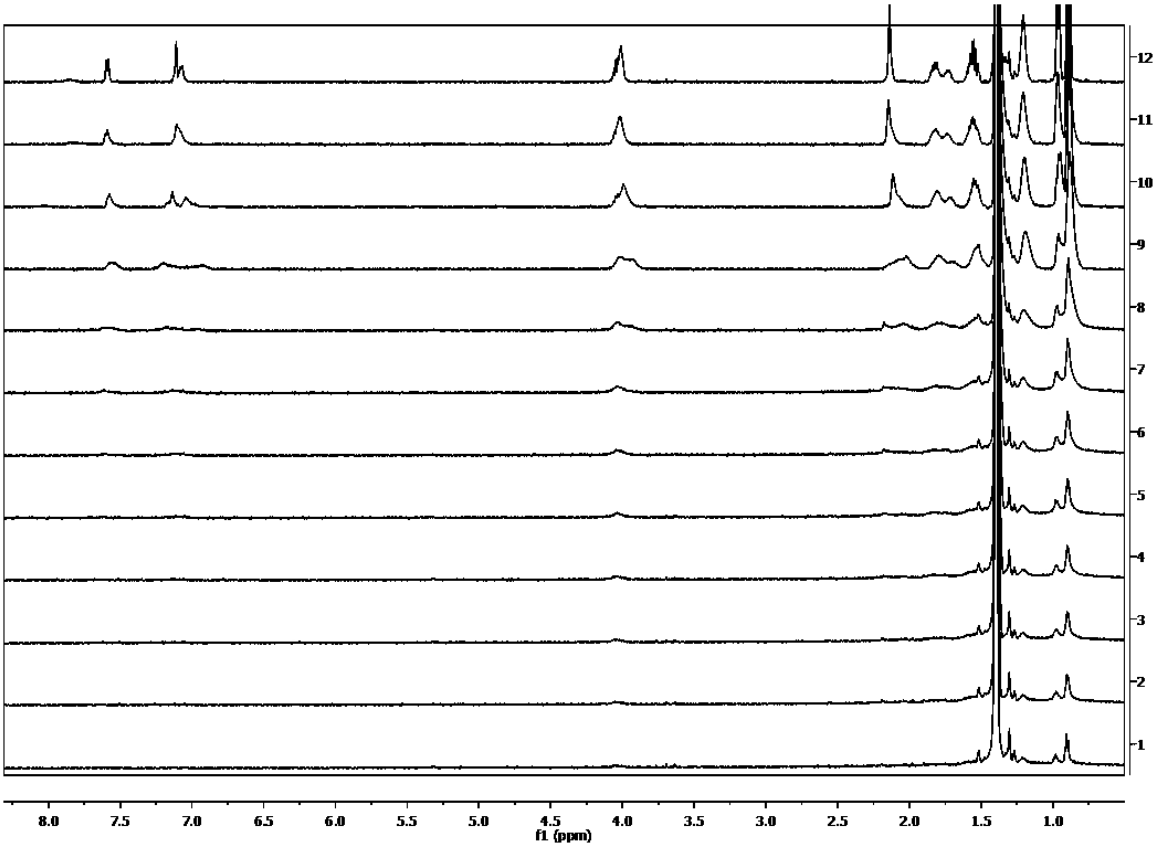


5.- Figure S2. Concentration dependent ^{1}H NMR spectra of compound **1*R*** in cyclohexane-d_{12}



6.- Figure S3. Temperature dependent ^{1}H NMR spectra of compound 1*R* in cyclohexane-d_{12}.

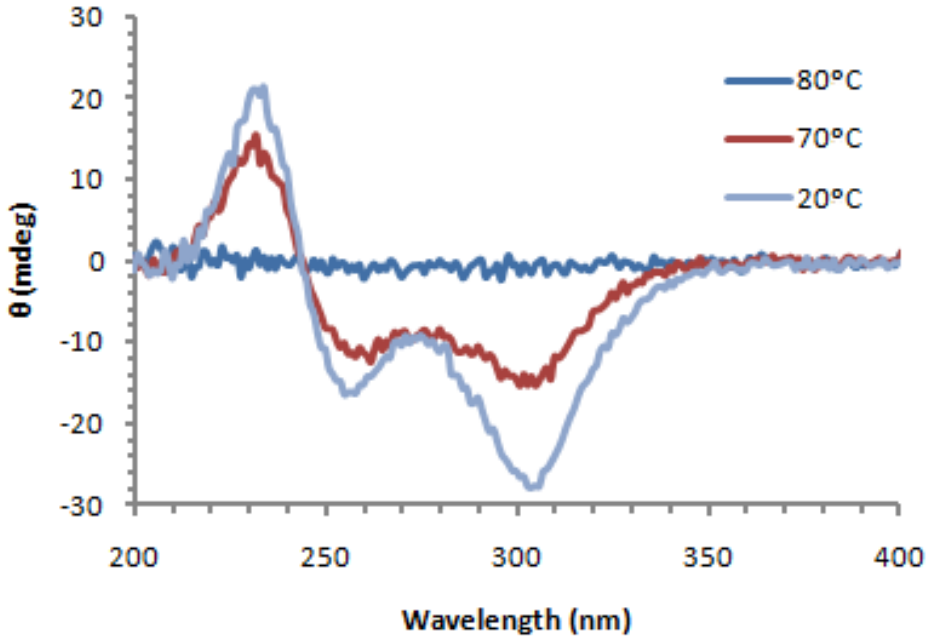
Temperature range: from 298K (down) to 348K (up) in 5K intervals.



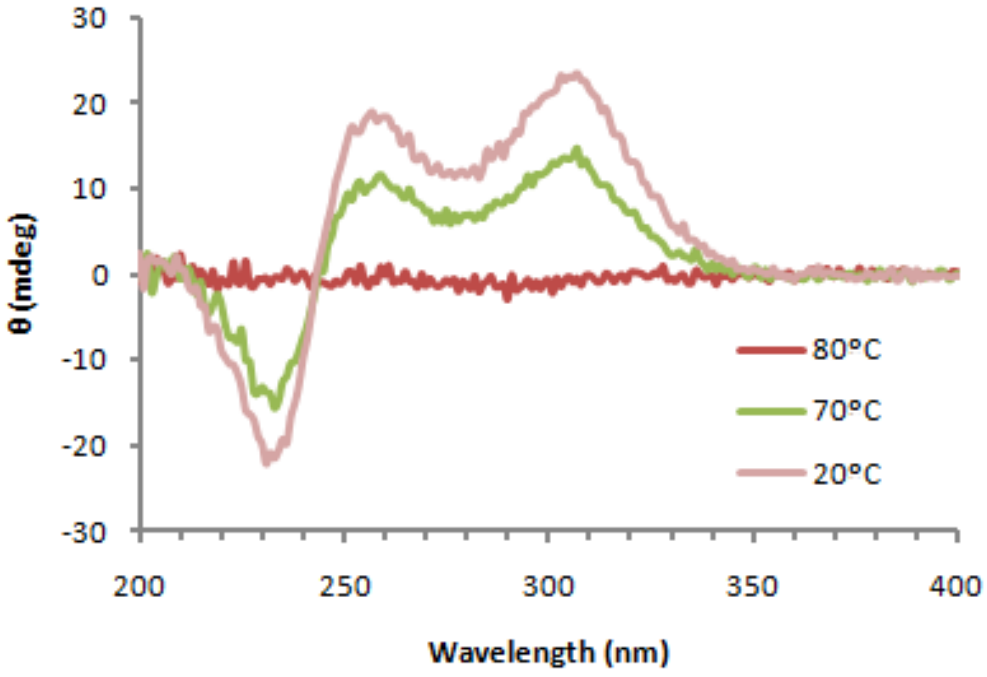
7.- Circular Dichroism spectra

Gels in dodecane (0.5% wt) at 80, 70 and 20ºC.

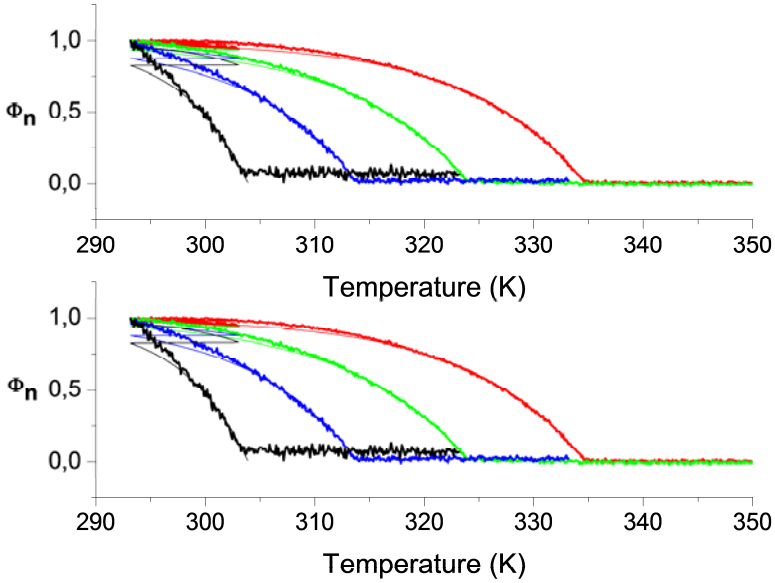
1*S*



1*R*



8.- Figure S4. Normalised CD data monitored at 305 nm in dodecane at different concentrations. **1*R*** (up) Red: 5,2 10^{-4} M, Green: 2,4 10^{-4} M, Blue: 9,8 10^{-5} M, Black: 4,9 10^{-5} M, **1*S*** (down) Red: 4.9 10^{-4} M, Green: 2.5 10^{-4} M, Blue: 9.9 10^{-5} M, Black: 5.1 10^{-5} M; and fitting to equation 1.



9. Fluorescence change with temperature and UV-vis absorption and luminescence spectra of **1*S*** (Figure S5**), 1*R*** (Figure S6) and **1** (Figure S7).

1*S* in the gel state (dodecane, 0.5 % wt). Fluorescence change with temperature on heating.

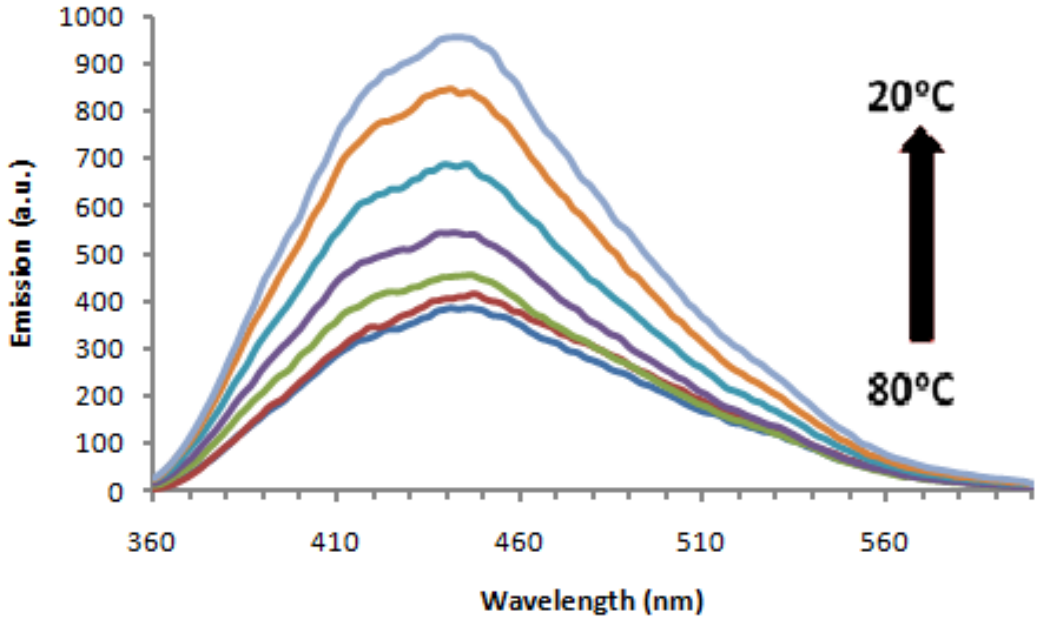
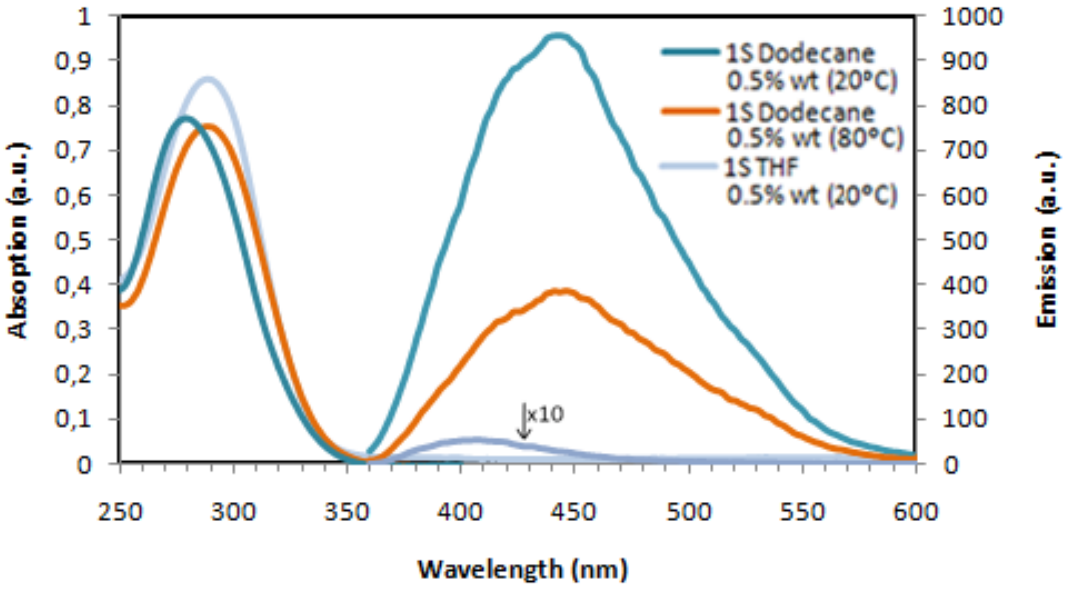


Figure S5. UV-Vis absorption and emission spectra of **1*S*** in THF (light blue); in dodecane in the gel state (dark blue) and in the sol state (orange) at 0.5 % wt.



1*R* in the gel state (dodecane, 0.5 % wt). Fluorescence change with temperature on heating.

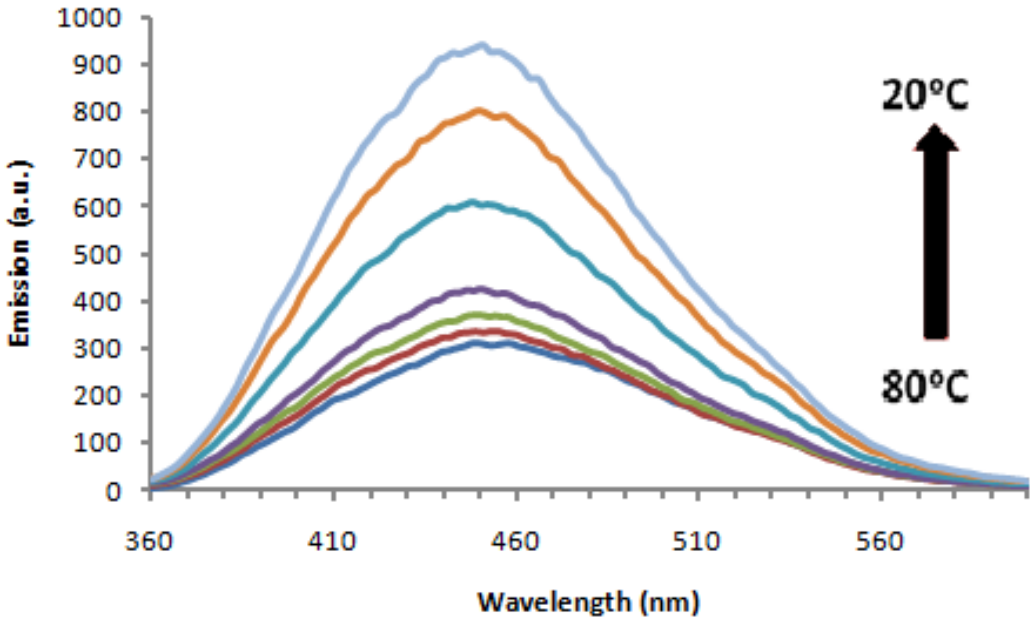
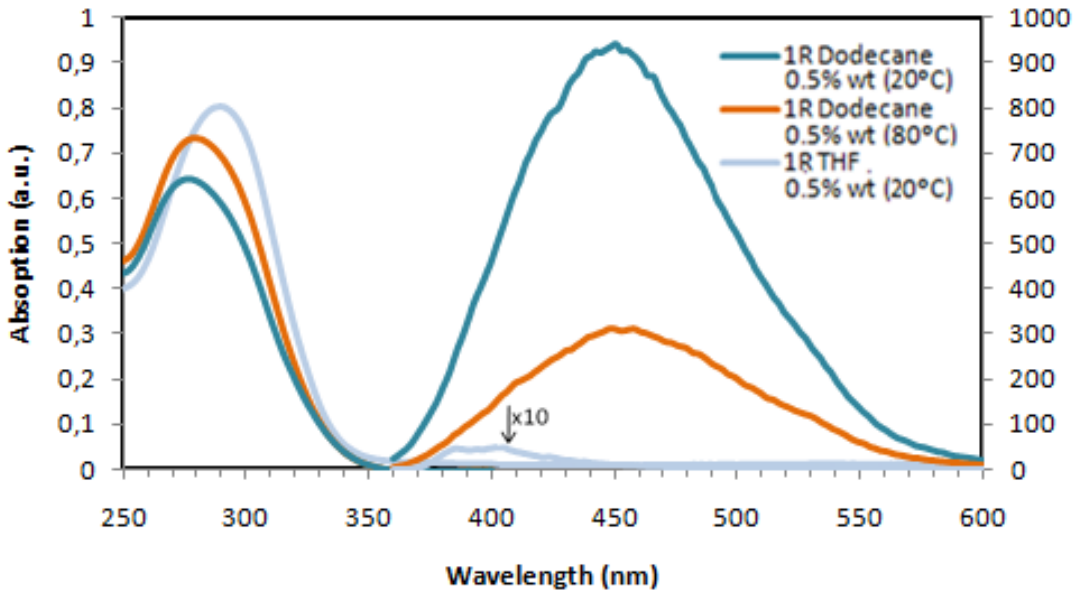


Figure S6. UV-Vis absorption and emission spectra of **1*S*** in THF (light blue); in dodecane in the gel state (dark blue) and in the sol state (orange) at 0.5 % wt.



1 in the gel state (dodecane, 0.5 % wt). Fluorescence change with temperature on heating.

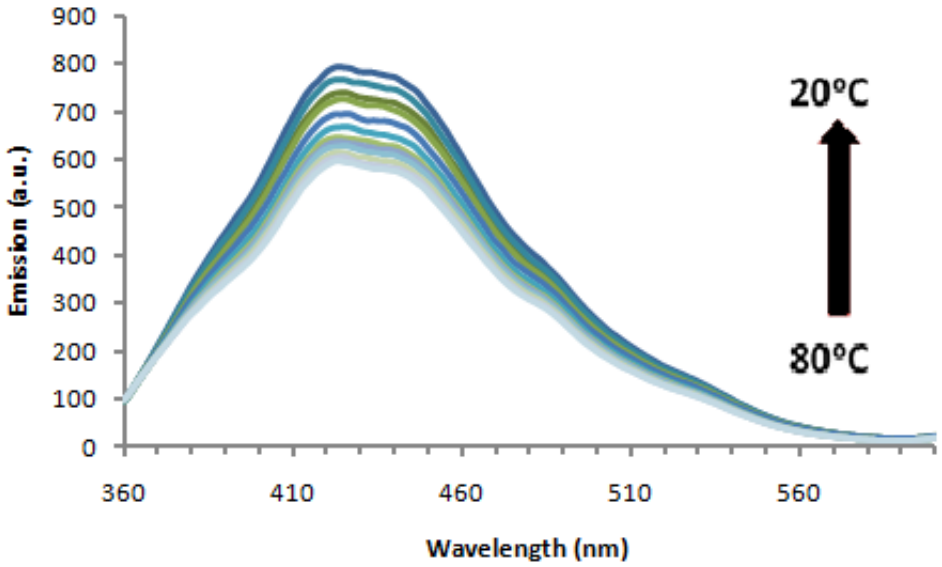


Figure S7. UV-Vis absorption and emission spectra of **1** in THF (light blue); in dodecane in the gel state (dark blue) and in the sol state (orange) at 0.5 % wt.