

## Supporting Information

### Pyridine-based tricarboxamides: complementary monomers for supramolecular copolymerization with $C_3$ -symmetric oligophenylenetricarboxamides

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## Contents

1. Experimental section	S-2
1.1. Materials and methods	S-2
2. Synthetic details and characterization	S-3
3. Collection of spectra	S-6
4. Supplementary Figures and Tables	S-11
FTIR in solution of <b>(R)-2</b>	S-11
UV-Vis spectra of <b>(R)-2</b> in different solvents	S-11
Modified SaS experiment between <b>a-1</b> and <b>(R)-2</b>	S-11
MRs experiment between <b>(S)-2</b> and <b>(R)-2</b>	S-12
Modified MR experiment by mixing <b>(S)-1</b> and <b>(R)-2</b>	S-12
Average copolymer length and bond fraction derived from the supramolecular copolymerization model	S-13
5. Copolymerization experiments	S-14
5.1.1. Application of the co-polymerization model	S-15
6. References	S-16

## 1. General experimental conditions

### 1.1. Materials & Methods

All solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, chloroform, methanol, MCH and chloroform) as well as standard lab chemicals (TBAF, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, triethylamine, CuI, NaOH, HCl, MgSO<sub>4</sub>, EDC, DMAP) were obtained from Sigma-Aldrich, VWR or Alfa Aesar and used as purchased. THF for air sensitive was distilled in the presence of sodium. Reagents were used as purchased from Sigma-Aldrich. Deuterated solvents were purchased from Sigma-Aldrich. Air-sensitive reactions were carried out under argon atmosphere. Analytical thin layer chromatography (TLC) was performed using aluminum-coated Merck Kieselgel 60 F254 plates.

NMR spectra were recorded on a Bruker Avance 300 or Bruker Avance 700 spectrometer using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, dd= double doublet, t = triplet, q = quadruplet, m = multiplet, br = broad.

FT-IR spectra of bulk compounds were recorded on a Bruker Tensor 27 (ATR device) spectrometer. Solution FTIR spectra were recorded on a JASCO-FT-IR-6800 spectrometer using a CaF<sub>2</sub> cell with a path length of 0.1 mm.

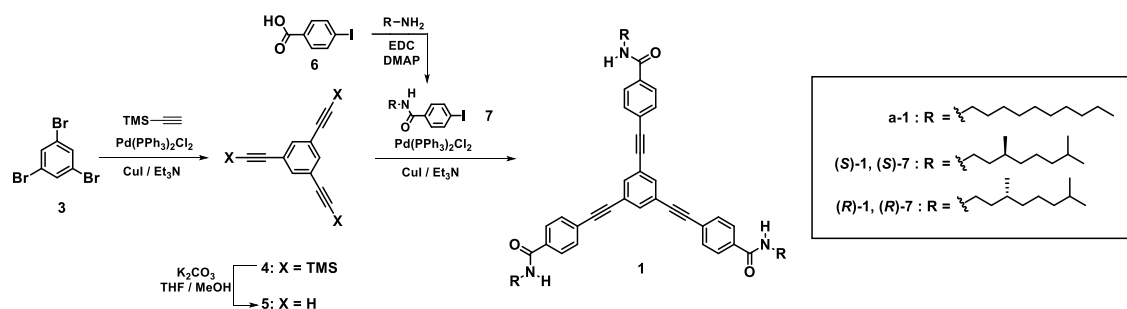
Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer. UV-Vis spectra were recorded on a JASCO V-630 spectrophotometer by using quartz cuvettes (Hellma) with cell path (*l*) of 1 cm.

For the polymerization and co-polymerization experiments, tricarboxamides **1** or/and **2** were first dissolved in CHCl<sub>3</sub>, then, the solvent was evaporated and redissolved in methylcyclohexane. Thermal experiments were performed at constant cooling rates of 1 K·min<sup>-1</sup> from 293 to 363 K. UV-vis experiments were performed on a JASCO V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 500 nm, with a wavelength increment of 0.2 nm, a response time of 1 s, and a bandwidth of 2 nm using a quartz cuvette (Hellma) with cell path (*l*) of 1 cm.

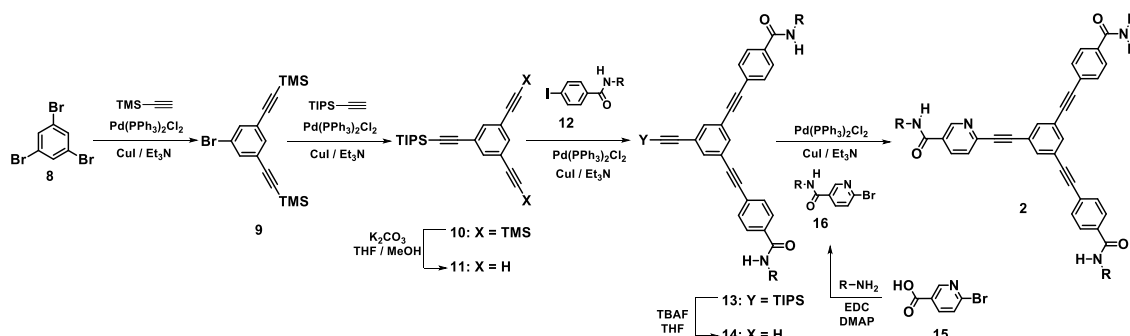
Circular dichroism (CD) measurements were performed on a JASCO-1500 dichrograph equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 500 nm, with a wavelength increment of 0.2 nm, a response time of 1 s, and a bandwidth of 2 nm using a quartz cuvette (Hellma) with cell path (*l*) of 1 cm.

AFM measurements were performed under ambient conditions using a MultiMode 8HR SPM from Bruker operating in tapping mode in air. Silicon cantilevers with a resonance frequency of 300 kHz were used. Solutions were spin-coated onto HOPG.

## 2. Synthetic details and characterization



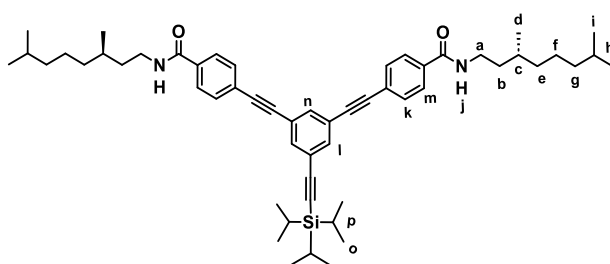
**Scheme S1.** Synthesis of triangular-shaped tricarboxamides **1**.



**Scheme S2.** Synthesis of pyridine tricarboxamides **2**.

The synthesis of tricarboxamides **1**<sup>[1]</sup> and (*S*)-**2**<sup>[2]</sup> and pyridine (*R*)-**16**<sup>[2]</sup> were described in previous contributions.

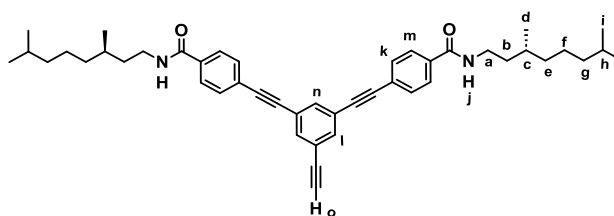
### 4,4'-((5-((triisopropylsilyl)ethynyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(*N*-((*R*)-3,7-dimethyloctyl)benzamide) ((*R*)-**13**)



Compound (*R*)-**12** (1.1 g, 2.82 mmol), CuI (0.007 g, 0.04 mmol), Et<sub>3</sub>N (6 mL) and Pd[(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.13 g, 0.18 mmol) were dissolved in anhydrous THF and deoxygenated by argon/vacuum cycles (x3). Compound **11** (0.35 g, 1.13 mmol) was dissolved in anhydrous THF in a separate flask and deoxygenated by the same procedure. The solution of **11** was transferred to the reaction flask and the reaction mixture was stirred at 60 °C overnight. After this time, the solvent was dried under reduced pressure and the crude was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with HCl 1 M (2x20 mL), NaOH 2 M (2x20 mL) and a saturated solution of NaCl (2x20 mL). After this, the organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent evaporated under reduced pressure. The

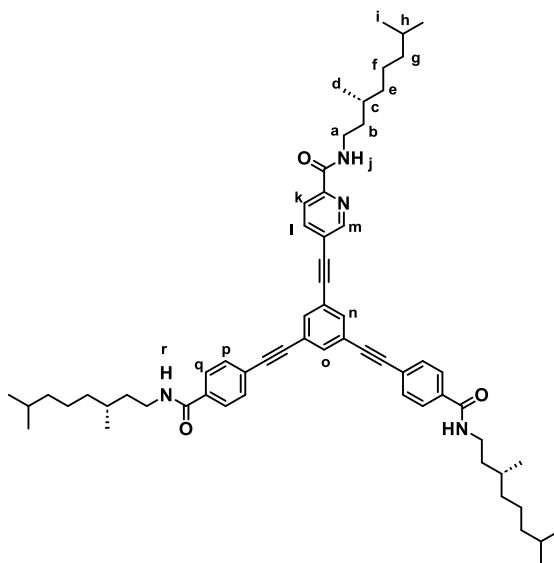
crude product was purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>) yielding **13** as a dark yellow solid (0.28 g, 29%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.76 (4H, H<sub>m</sub>, d, *J* = 8.5 Hz), 7.66 (1H, H<sub>n</sub>, t, *J* = 1.5 Hz), 7.64 (2H, H<sub>l</sub>, d, *J* = 1.5 Hz), 7.57 (4H, H<sub>k</sub>, d, *J* = 8.4 Hz), 6.12 (2H, H<sub>j</sub>, br), 3.45 (4H, H<sub>a</sub>, m), 1.64 (1H, H<sub>h</sub>, m), 1.58 – 1.38 (5H, H<sub>b+p</sub>, m), 1.38 – 1.18 (1H, H<sub>c</sub>, m), 1.22 – 1.05 (6H, H<sub>e+f+g</sub>, m) 1.14 (9H, H<sub>o</sub>, s), 0.95 (3H, H<sub>d</sub>, d, *J* = 6.4 Hz), 0.87 (6H, H<sub>i</sub>, d, *J* = 6.6 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 166.78, 135.00, 134.71, 134.29, 131.93, 127.10, 125.91, 124.57, 123.66, 105.11, 92.81, 89.93, 89.90, 77.36, 39.40, 38.55, 37.28, 36.87, 30.96, 28.10, 24.80, 22.85, 22.74, 19.71, 18.80, 11.41. FT-IR (cm<sup>-1</sup>) 681.20, 770.90, 877.96, 973.89, 1309.99, 1371.85, 1460.77, 1501.78, 1548.10, 1637.35, 2153.38, 2362.66, 2866.81, 2944.74, 3071.35, 3307.97. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>46</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub> [M], 824.5676; found [M+H], 825.5726.

**4,4'-((5-ethynyl-1,3-phenylene)bis(ethyne-2,1-diyl))bis(*N*-((*R*)-3,7-dimethyloctyl)-benzamide) ((*R*)-14)**



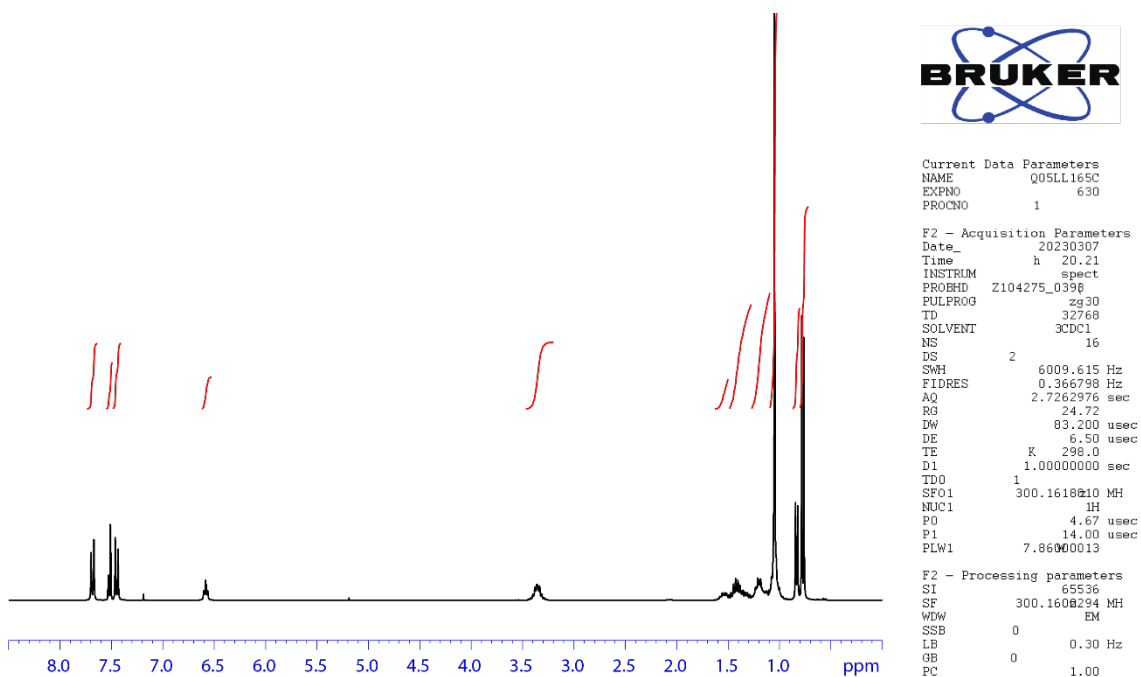
Compound (**R**)-**13** (0.20 g, 0.24 mmol) was dissolved in anhydrous THF under Argon atmosphere. A solution of TBAF 1 M (0.21 mL, 0.46 mmol) in THF was added dropwise. Then, the mixture was stirred at room temperature for 2 hours. After this time, the reaction mixture was washed with a saturated solution of NH<sub>4</sub>Cl (2x20 mL). The product was purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>) yielding (**R**)-**14** as a dark yellow solid (0.16 g, 89%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.75 (4H, H<sub>m</sub>, d, *J* = 8.4 Hz), 7.67 (1H, H<sub>l</sub>, t, *J* = 1.6 Hz), 7.65 (2H, H<sub>n</sub>, d, *J* = 1.5 Hz), 7.59 (4H, H<sub>k</sub>, d, *J* = 8.5 Hz), 6.04 (2H, H<sub>j</sub>, t, *J* = 8.4 Hz), 3.51 (4H, H<sub>a</sub>, m), 3.13 (1H, H<sub>o</sub>, s), 1.64 (1H, H<sub>h</sub>, m), 1.59 – 1.38 (2H, H<sub>b</sub>, m), 1.38 – 1.18 (1H, H<sub>c</sub>, m), 1.22 – 1.05 (6H, H<sub>e+f+g</sub>, m), 0.95 (3H, H<sub>d</sub>, d, *J* = 6.4 Hz), 0.87 (6H, H<sub>i</sub>, d, *J* = 6.4 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 166.77, 135.06, 134.88, 134.80, 131.98, 127.08, 125.86, 123.88, 123.25, 90.05, 89.74, 81.91, 78.83, 77.36, 39.38, 38.52, 37.33, 36.90, 30.97, 28.12, 24.84, 22.85, 22.76, 19.75. FT-IR (cm<sup>-1</sup>): 674.65, 761.14, 850.99, 955.77, 1015.55, 1105.69, 1153.10, 1310.02, 1372.68, 1461.46, 1500.65, 1546.48, 1636.95, 1787.15, 2865.90, 2925.84, 3071.26, 3301.78. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>46</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup>, 668.4342; found [M]<sup>+</sup>, 668.5894.

**4,4'-((5-((6-(((*R*)-3,7-dimethyloctyl)carbamoyl)pyridin-2-yl)ethynyl)-1,3-phenylene)-bis(ethyne-2,1-diyl))bis(*N*-((*R*)-3,7-dimethyloctyl)benzamide) ((*R*)-2)**

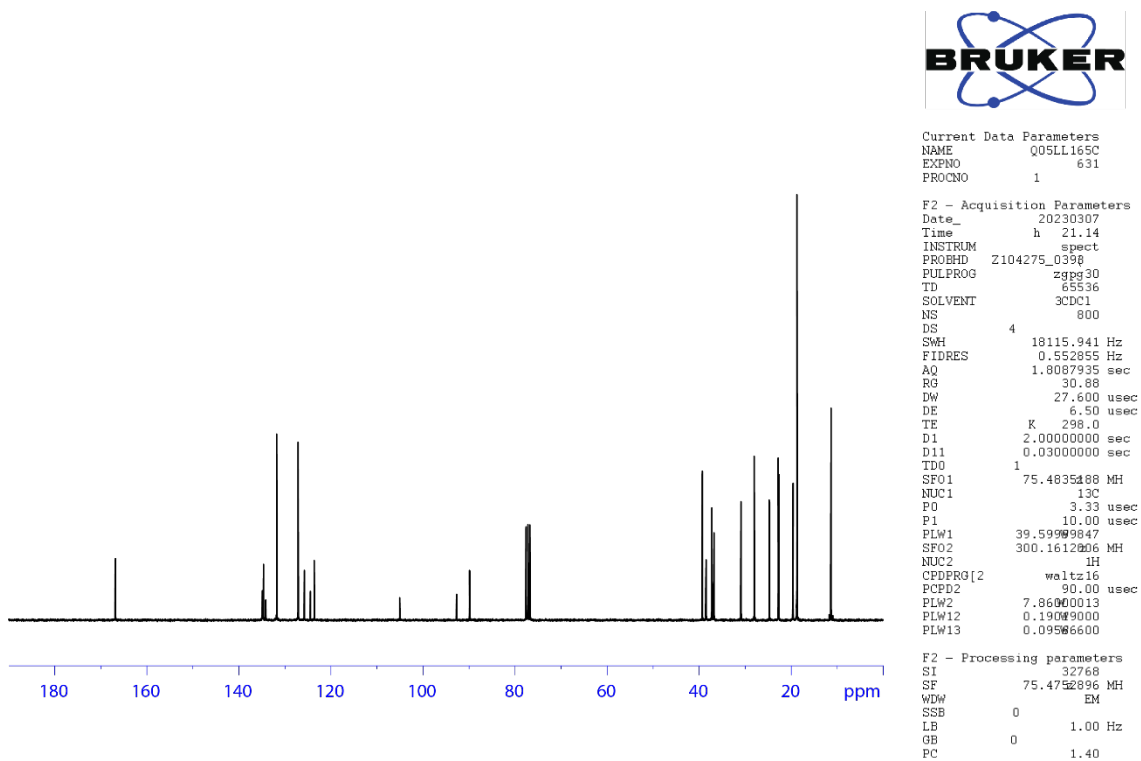


Compound **16** (75 mg, 0.220 mmol), CuI (0.8 mg, 0.004 mmol), Et<sub>3</sub>N (2 mL) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (7 mg, 0.011 mmol) were dissolved in anhydrous THF (5 mL) and subjected to argon/vacuum cycles (×3). In a separate flask compound **13** (134 mg, 0.20 mmol) was dissolved in anhydrous THF (7 mL) and deoxygenated by the same procedure. The solution of **13** was added dropwise to the reaction flask and the mixture was stirred at 60 °C overnight. After this time, the THF was evaporated under reduced pressure, the crude redissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with HCl 1 M (2×20 mL), NaOH 2 M (2×20 mL) and saturated solution of NaCl (2×20 mL). After this, the organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent eliminated under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 99.5/0.5) yielding tricarboxamide (**R**)-**2** as a dark yellow solid (75 mg, 37%). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 8.94 (1H, H<sub>m</sub>, br), 8.11 (1H, H<sub>l</sub>, dd, *J* = 8.36, 1.61 Hz), 7.74 (6H, H<sub>q+n</sub>, m), 7.71 (1H, H<sub>o</sub>, br), 7.57 (5H, H<sub>k+p</sub>, m), 6.17 (1H, H<sub>j</sub>, t, *J* = 5.39 Hz), 6.09 (2H, H<sub>r</sub>, t, *J* = 5.39 Hz), 3.50 (6H, H<sub>a</sub>, m), 1.86 – 1.64 (3H, H<sub>h</sub>, m), 1.53 (6H, H<sub>b</sub>, m), 1.44 – 1.26 (3H, H<sub>c</sub>, m), 1.26 – 1.09 (18H, H<sub>e+f+g</sub>, m), 0.96 (9H, H<sub>d</sub>, m), 0.87 (18H, H<sub>i</sub>, d, *J* = 6.5 Hz). <sup>13</sup>C NMR (700 MHz, 318 K, CDCl<sub>3</sub>) δ 166.53, 164.75, 147.92, 145.09, 135.26, 134.00, 134.67, 134.52, 131.703, 129.22, 128.39, 128.34, 126.87, 126.79, 125.52, 123.77, 122.67, 89.97, 89.35, 89.21, 89.13, 39.11, 38.37, 38.23, 37.00, 36.61, 36.54, 30.68, 29.55, 27.83, 24.55, 22.55, 22.46, 19.41. FT-IR (cm<sup>-1</sup>): 525.48, 542.03, 562.30, 586.79, 637.53, 673.14, 694.77, 722.70, 762.86, 805.22, 849.08, 872.77, 1018.82, 1115.30, 1170.36, 1215.98, 1246.95, 1276.00, 1316.18, 1365.45, 1380.09, 1431.66, 1467.04, 1501.31, 1543.07, 1589.87, 1607.29, 1633.25, 1716.05, 2219.35, 2853.98, 2924.03, 2953.52, 3077.40, 3284.44. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>62</sub>H<sub>80</sub>N<sub>4</sub>O<sub>3</sub> [M+H]<sup>+</sup>, 929.6230; found [M+H]<sup>+</sup>, 929.6297.

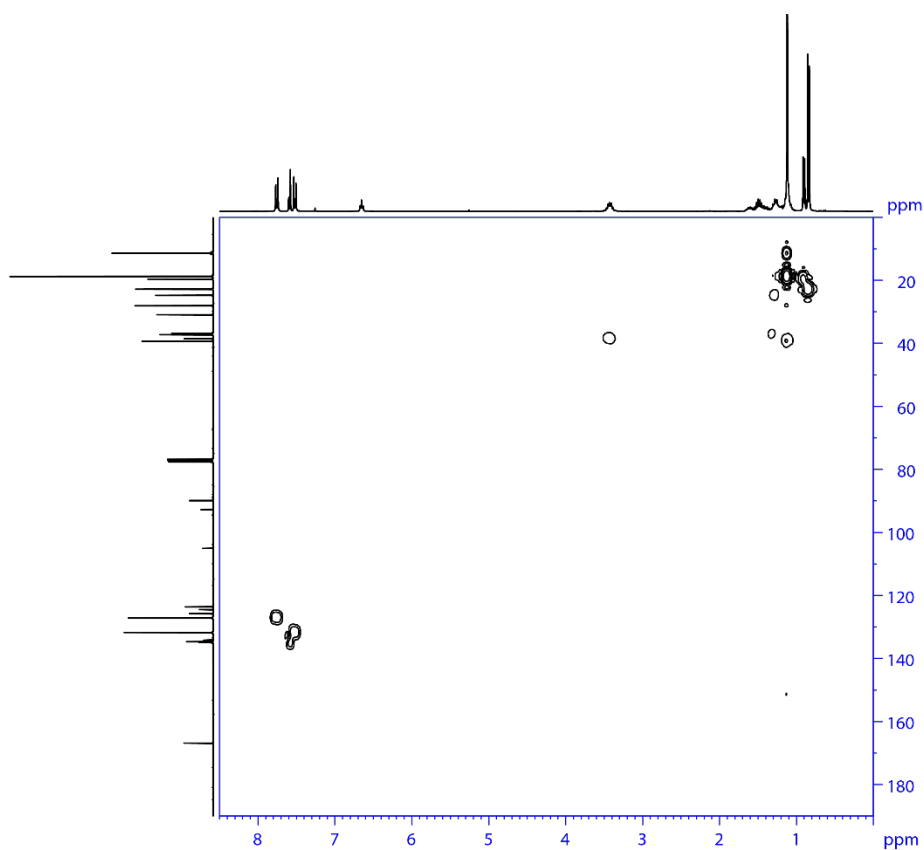
### 3. Collection of spectra



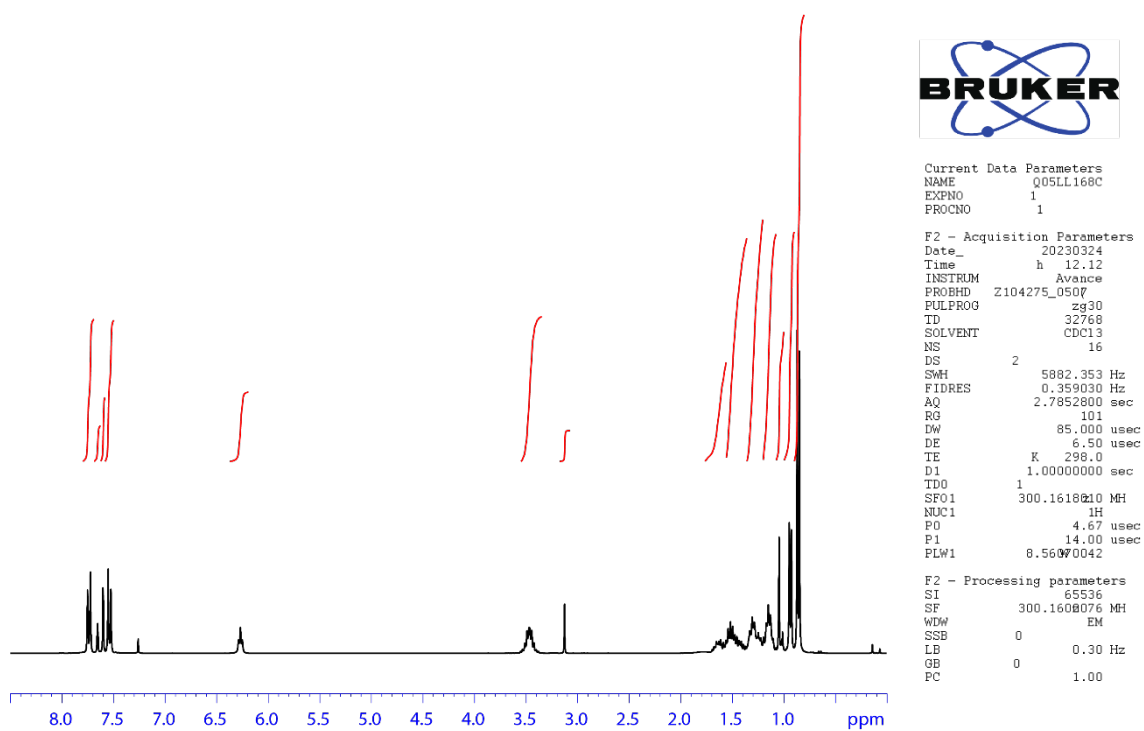
<sup>1</sup>H-NMR spectrum of compound (*R*)-13 (CHCl<sub>3</sub>, 298 K).



<sup>13</sup>C-NMR spectrum of compound (*R*)-13 (CHCl<sub>3</sub>, 298 K).



$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC spectrum of compound (**R**)-13 ( $\text{CHCl}_3$ , 298 K).



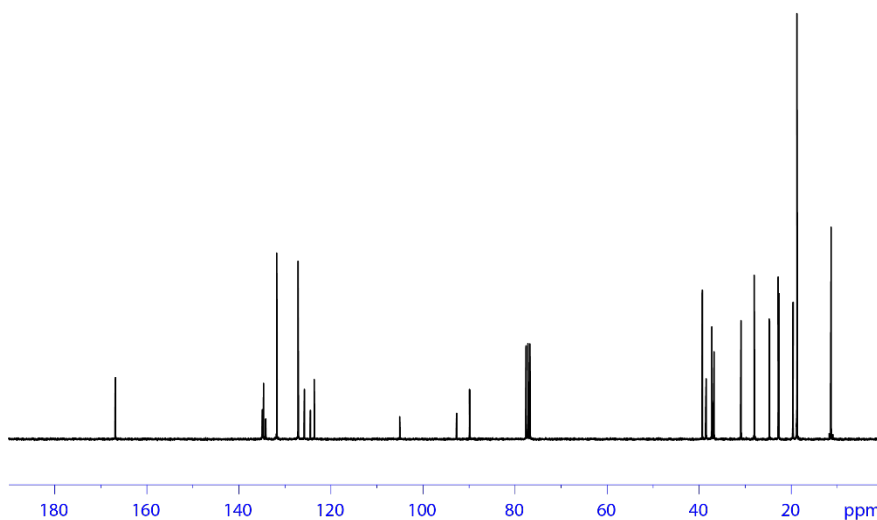
$^1\text{H}$ -NMR spectrum of compound (**R**)-14 ( $\text{CHCl}_3$ , 298 K).



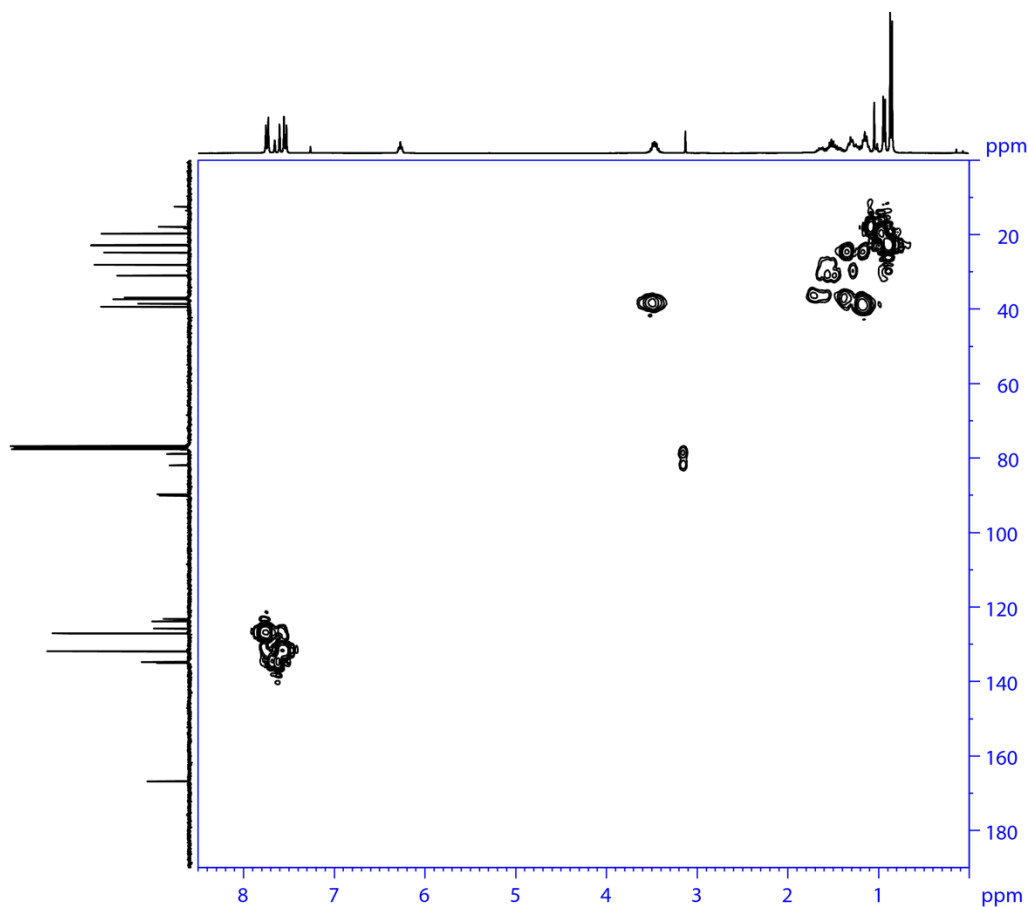
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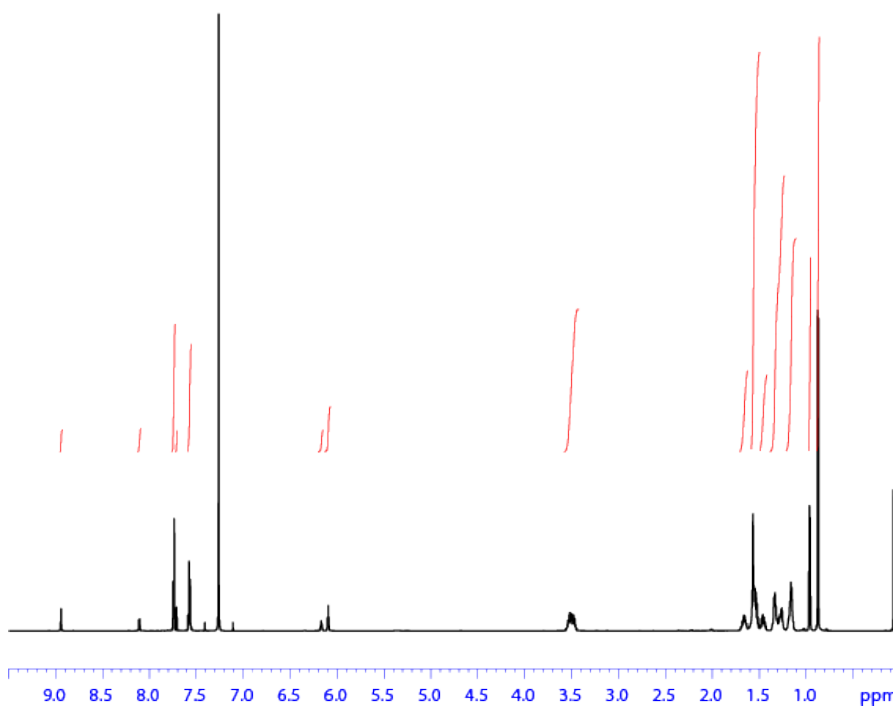


$^{13}\text{C}$ -NMR spectrum of compound (*R*)-14 ( $\text{CHCl}_3$ , 298 K).



$^1\text{H}$ ,  $^{13}\text{C}$ -HMBC spectrum of compound (*R*)-14 ( $\text{CHCl}_3$ , 298 K).



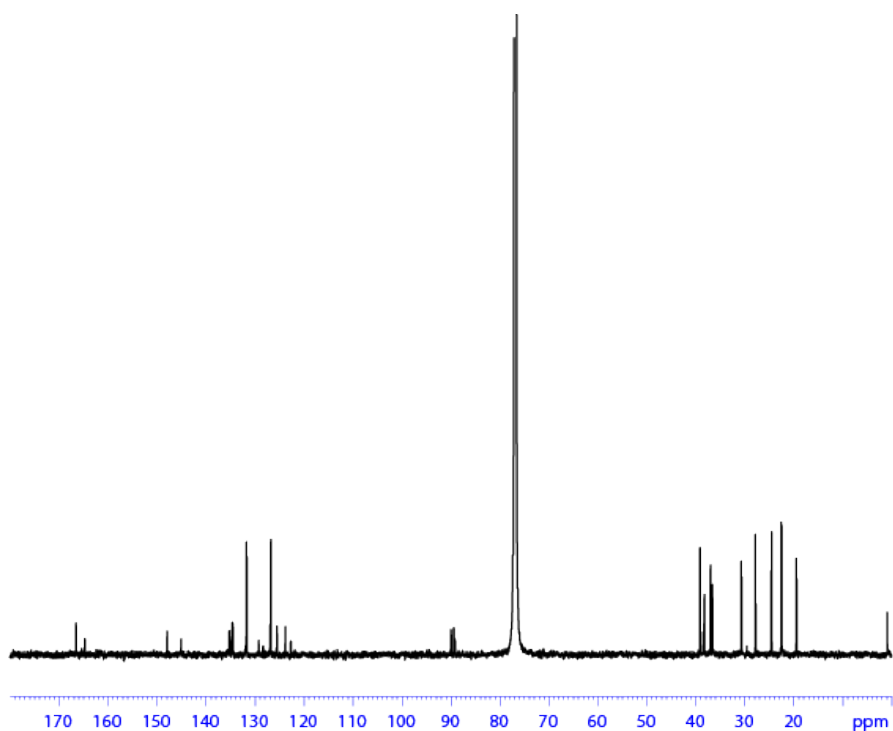


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<sup>1</sup>H-NMR spectrum of compound (**R**)-**2** (CHCl<sub>3</sub>, 298 K).

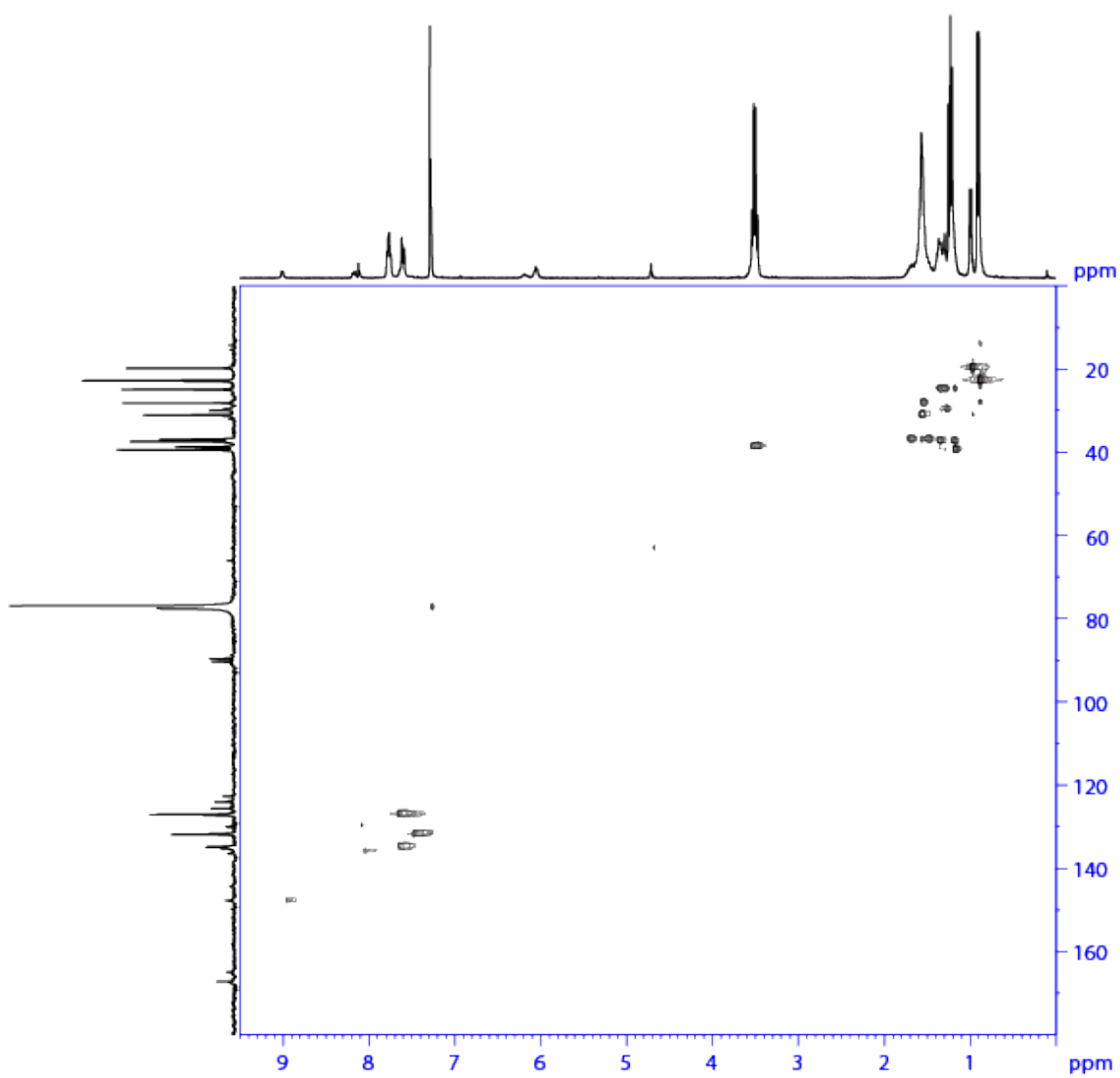


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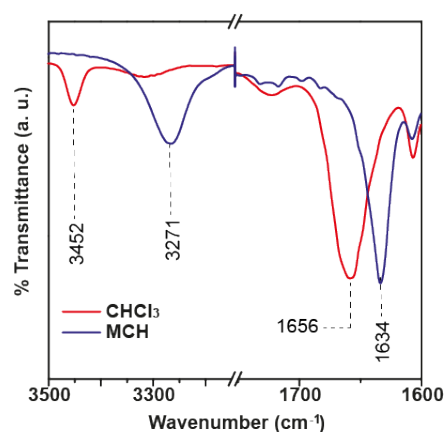
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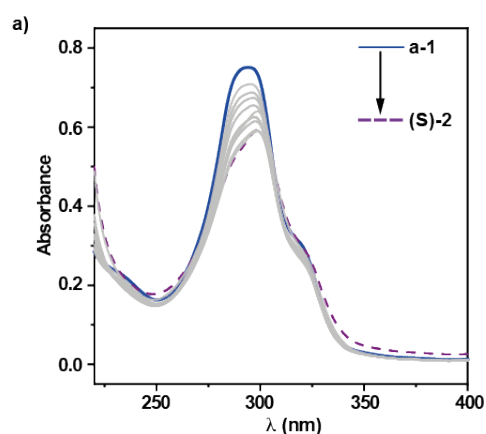


$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC spectrum of compound (**R**)-**2** ( $\text{CHCl}_3$ , 298 K).

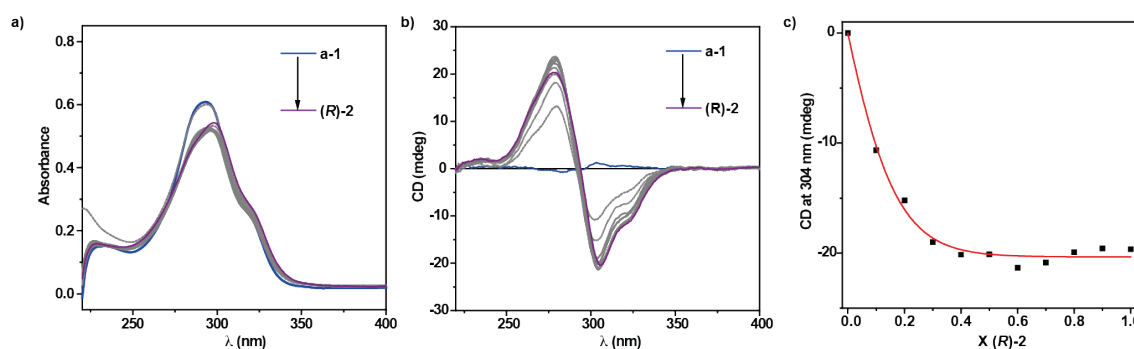
#### 4. Supplementary figures



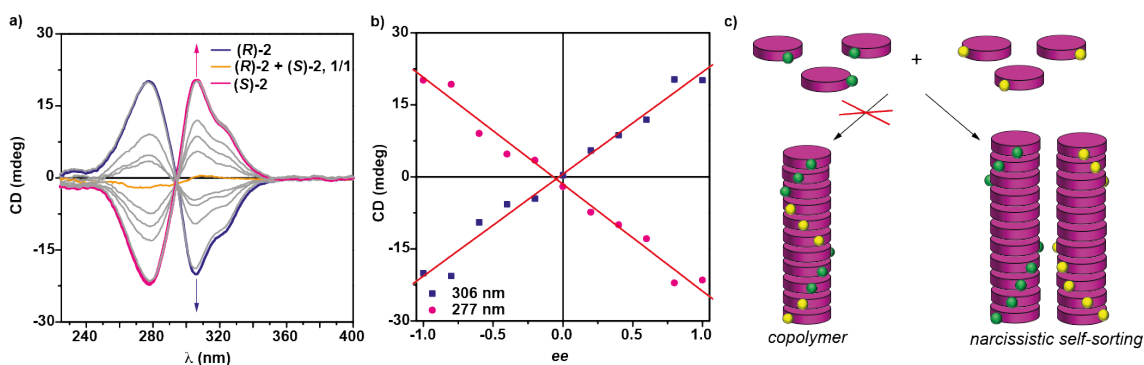
**Figure S1.** Partial FTIR spectra of (*R*)-2 recorded in different solvents ( $c_T = 1$  mM).



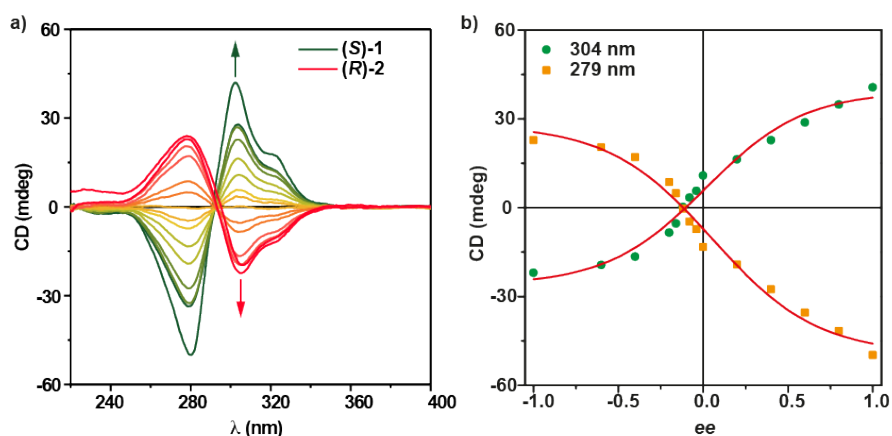
**Figure S2.** UV-Vis spectra of tricarboxamides **1** (blue, solid line), (**S**)-2 (purple, dashed line) and mixtures of both (grey lines) at different ratio. Experimental conditions: MCH as solvent, 20 °C,  $c_T = 10$   $\mu$ M.



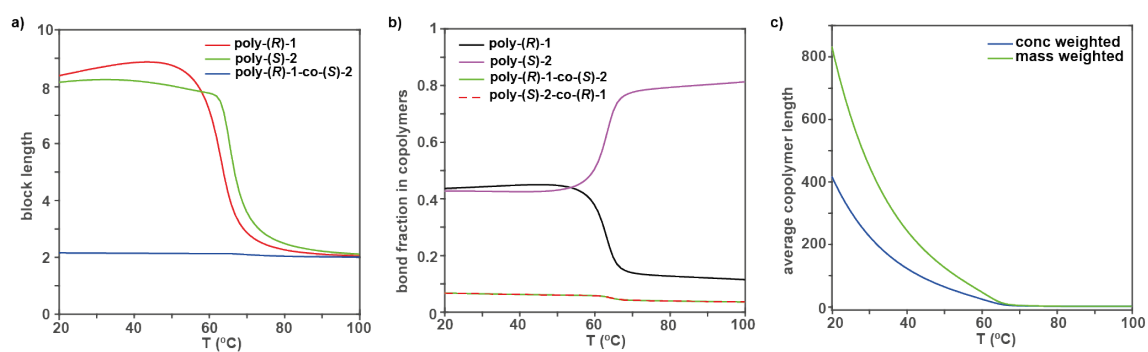
**Figure S3.** SaS experiment between **a-1** and (**R**)-2. UV-vis (a) and CD (b) spectra of mixtures of **a-1** and (**R**)-2 (20 °C, MCH,  $c_T = 10$   $\mu$ M). The arrows indicate the changes upon increasing the ratio of (**S**)-2. c) Changes in the CD intensity at 304 nm against the amount of sergeant (**S**)-2. The red line in panel (c) corresponds to a sigmoidal fit to guide the eye.



**Figure S4.** MRs experiment between **(S)-2** and **(R)-2**. CD (a) spectra of mixtures of **(S)-2** (pink line) and **(R)-2** (blue line) (20 °C, MCH,  $c_T = 10 \mu\text{M}$ ). The pink and blue arrows indicate the changes upon increasing the ratio of **(S)-2** and **(R)-2**, respectively; b) plot of the variation of the dichroic response upon modifying the  $ee$ . ( $ee = 1$  corresponds to pristine **(S)-2** and  $ee = -1$  corresponds to **(R)-2**). The red lines in panel (b) corresponds to a linear fit to guide the eye; schematic representation of the two possible scenarios justifying the lack of amplification of asymmetry in the MRs experiment.



**Figure S5.** Modified MR experiment by mixing **(S)-1** and **(R)-2**; a) CD spectra of pristine **poly-(S)-1** (green line), **poly-(R)-2** (red line) and mixture of both at different ratio (the green and red arrows indicate the changes in the CD spectra upon the addition of increasing amounts of **poly-(S)-1** or **poly-(R)-2**, respectively; b) plot of the variation of the CD response versus the  $ee$  (the red lines correspond to a sigmoidal fitting to guide the eye). Experimental conditions: MCH as solvent; 20 °C;  $c_T = 10 \mu\text{M}$ .



**Figure S6.** a) Variation of the calculated block length of **poly-(R)-1**, **poly-(S)-2** and **poly-(R)-1-(S)-2** versus temperature, obtained by the application of the supramolecular copolymerization model; b, c) Variation of the bond fraction (b) and calculated average copolymer length (c) of **poly-(R)-1**, **poly-(S)-2** and **poly-(R)-1-co-(S)-2** against temperature obtained by the application of the supramolecular copolymerization model.

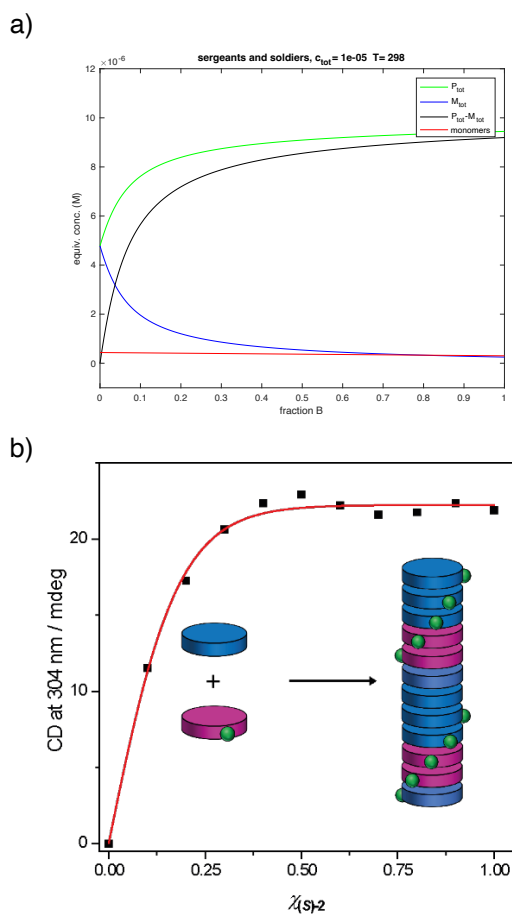
## 5. Copolymerization experiments

### 5.1. SaS between **a-1** and **(S)-2**

Simulation of the copolymerization in the SaS experiments between **a-1** and **(S)-2** for different given values of mismatch penalties (MMP).

The simulated speciation curves were obtained using the MATLAB script provided in ref. 3 for different given values of mismatch penalties (MMP). The total concentration was stated as  $10 \mu\text{M}$ . The given values for the elongation enthalpy and entropy of the homopolymers **a-1**<sup>1</sup> and **(S)-2**<sup>2</sup> used, were reported previously, being:  $\Delta H_e = -78 \text{ kJ mol}^{-1}$ ,  $\Delta S = -0.14 \text{ kJ K}^{-1}\cdot\text{mol}^{-1}$  and nucleation penalty  $\Delta H_n = -27 \text{ kJ mol}^{-1}$  for **a-1**, named as monomer A, and  $\Delta H_e = -64 \text{ kJ mol}^{-1}$ ,  $\Delta S = -0.09 \text{ kJ K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta H_n = -19 \text{ kJ mol}^{-1}$  for **(S)-2**, named as monomer B.

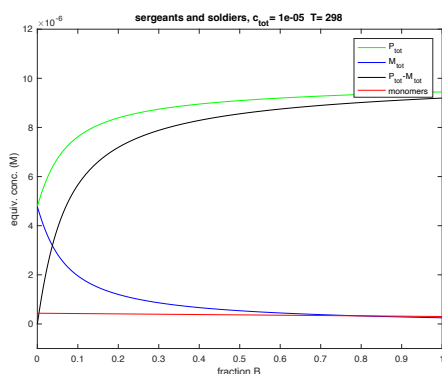
Comparison of the SaS experiments for **a-1** and **(S)-2** shows best matching for MMP value of  $0.05 \text{ kJ mol}^{-1}$ .



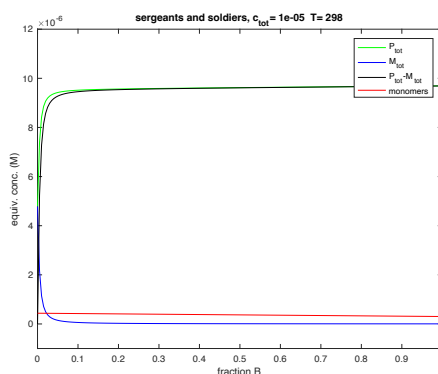
**Figure S7.** Speciation curves of the copolymerization of **a-1** and **(S)-2** for a given MMP  $0.05 \text{ kJ}\cdot\text{mol}^{-1}$ . b) Changes in the CD intensity at 304 nm against the amount of sergeant **(S)-2**. The red line in (b) corresponds to a non-linear fit to a Boltzmann equation ( $20 \text{ }^\circ\text{C}$ , MCH,  $c_T = 10 \mu\text{M}$ ).

### 5.1.1. Simulation of the speciation curves

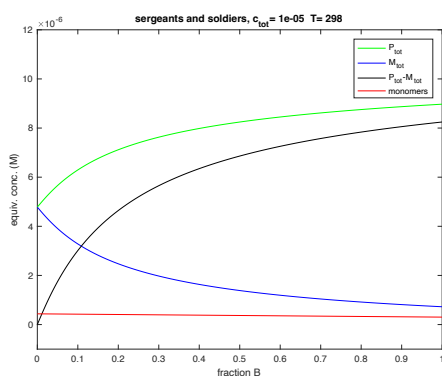
**MMP = 0.05 kJ mol<sup>-1</sup>:**



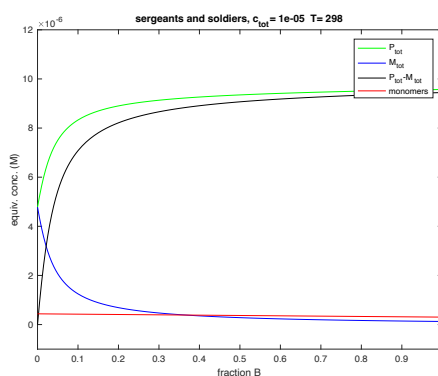
**MMP = 0.5 kJ mol<sup>-1</sup>:**



**MMP = 0.025 kJ mol<sup>-1</sup>:**



**MMP = 0.075 kJ mol<sup>-1</sup>:**



**Figure S8.** Comparison of the simulated speciation plots for the modified SaS experiments performed by mixing **a-1** and **(S)-2** and by considering MMP values of 0.05, 0.5, 0.025 and 0.075 kJ/mol.

## 6. References

- [1] F. García, P. M. Viruela, E. Matesanz, E. Ortí, L. Sánchez, *Chem. Eur. J.*, **2011**, *17*, 7755 – 7759.
- [2] L. López-Gandul, A. Morón-Blanco, F. García, L. Sánchez, *Angew. Chem. Int. Ed.*, **2023**, *62*, 37, e202308749.
- [3] H. M. M. ten Eikelder, B. Adelizzi, A. R. A. Palmans and A. J. Markvoort, *J. Phys. Chem. B*, **2019**, *123*, 6627–6642.