

## Supporting Information

### Electronically and geometrically complementary perylene diimides for kinetically controlled supramolecular copolymers

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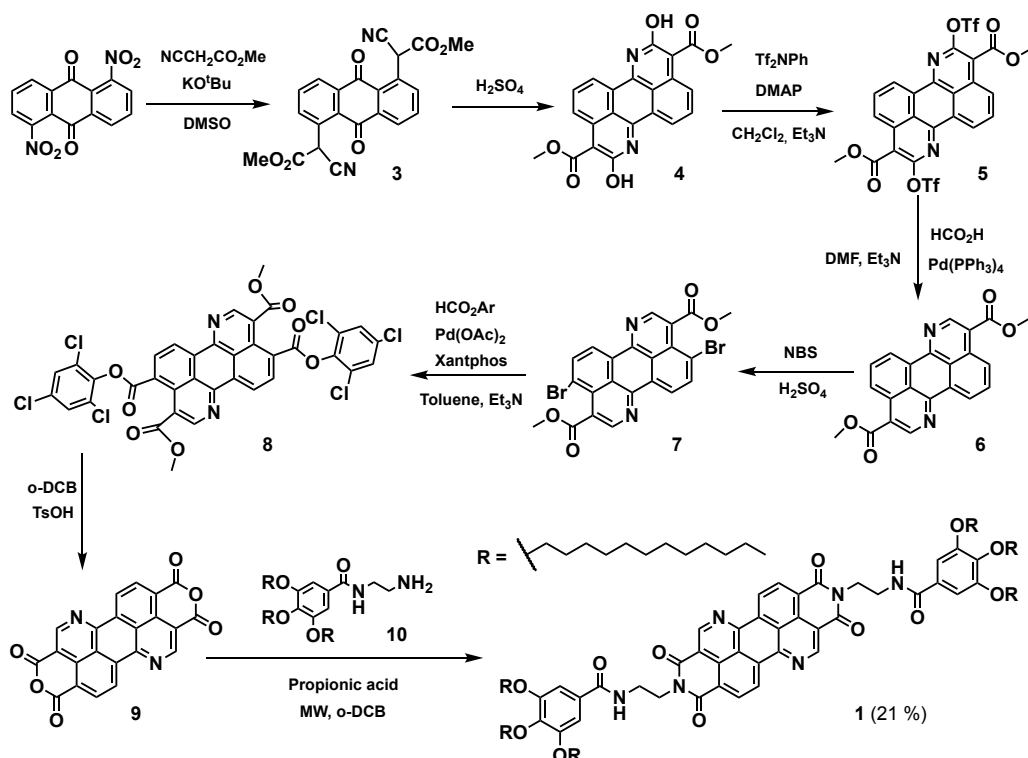
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## 1. Experimental section

**General.** All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 MHz ( $^1\text{H}$ : 300 MHz;  $^{13}\text{C}$ : 75 MHz) spectrometer at 25 °C 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, t = triplet, q = quartet, quin = quintuplet, m = multiplet, br = broad. FTIR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. FTIR spectra in film were recorded on a Jasco FT-IR4600 spectrometer using a  $\text{CaF}_2$  cell with a path length of 0.1 nm. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. All the heating and cooling cycles were performed at 1 °C·min<sup>-1</sup>. The freshly prepared solutions were measured and, after that, the samples were heated up to 90 °C. The samples at 90 °C were registered and cooled to 10 °C. Emission spectra were recorded on a Perkin-Elmer LS55 spectrophotometer. Atomic force microscopy (AFM) images were taken on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a TESPSS tip (Veeco) at a working frequency of ~235 kHz. High-resolution mass spectra (HRMS) were recorded on a MALDI Bruker daltonics Ultraflex TOF/TOF spectrometer.

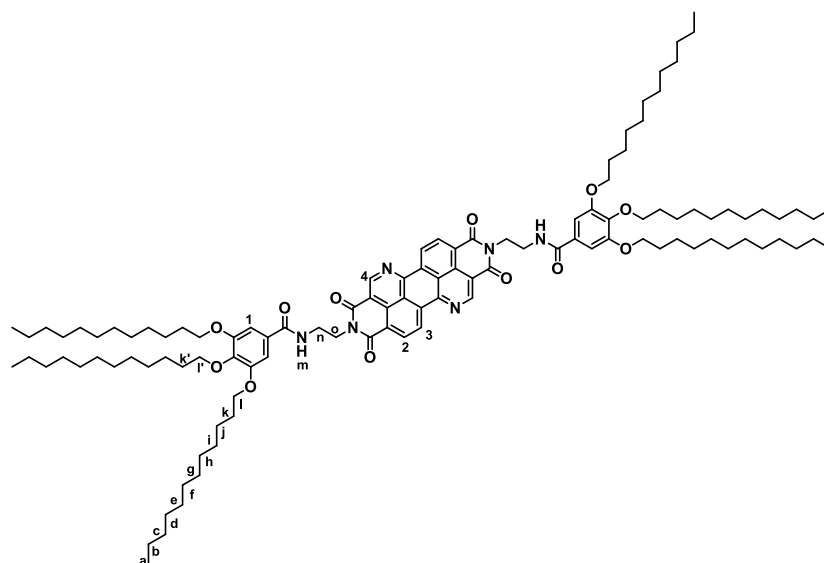
## 2. Synthetic details and characterization



**Scheme S1.** Synthesis of the BQQDI **1**.

Compounds **3-10** were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.<sup>S1,S2</sup>

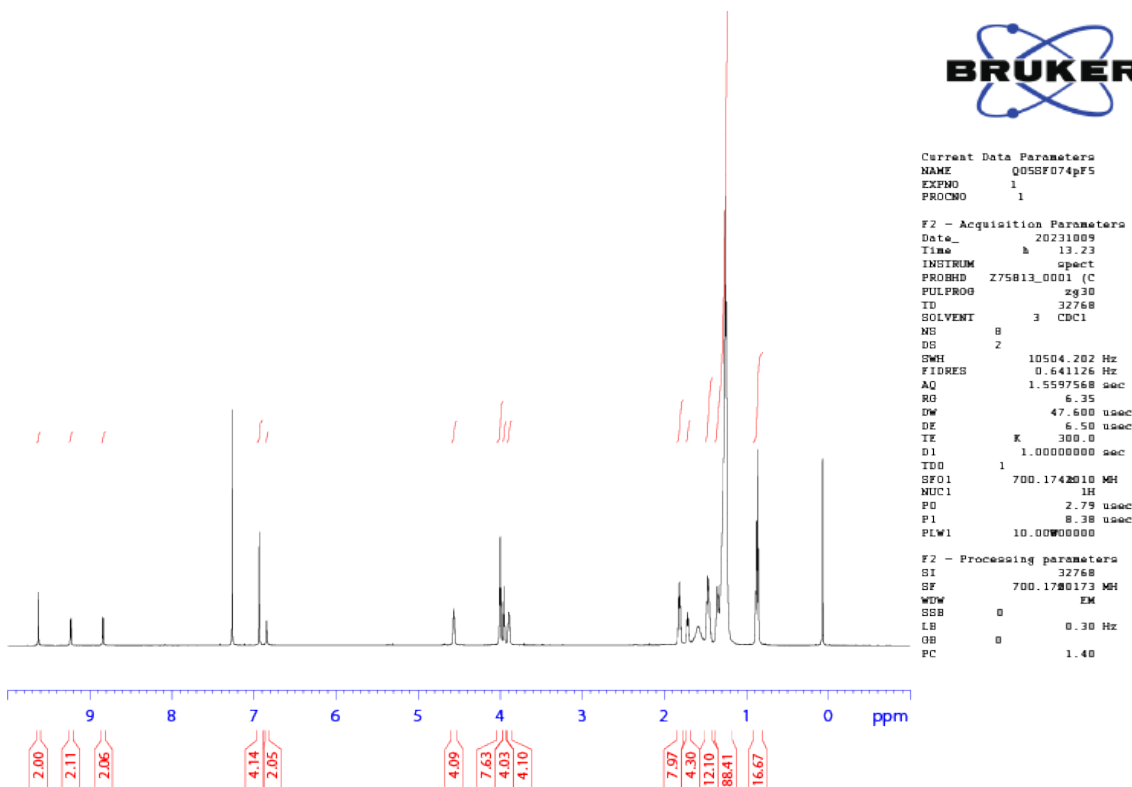
***N,N'*-((1,3,8,10-tetraoxo-1,3,8,10-tetrahydroanthra[9,1,2-*cde*:10,5,6-*c'd'e'*]bis([2,7]naphthyridine)-2,9-diyl)bis(ethane-2,1-diyl)bis(3,4,5-tris(dodecyloxy)benzamide) (**1**)**



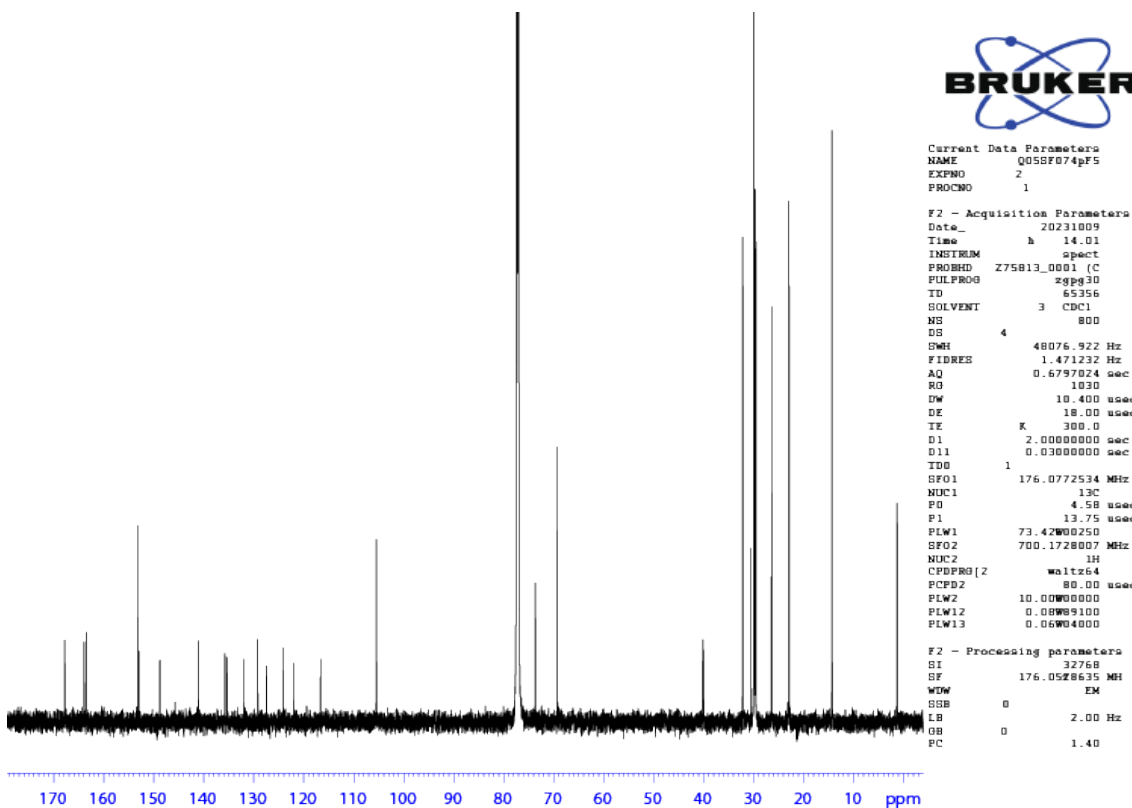
Dianhydride **9** (0.05 g, 0.13 mmol, 1 eq.) and benzamide **11** (0.23 g, 0.32 mmol, 2.5 eq.) were purged with argon in a microwave sealed tube. Then, propionic acid (1.5 mL) and *o*-DCB (3 mL)

were added, and the mixture was reacted in a microwave for 40 minutes at 150°C. The obtained crude was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and all the volatile liquids were evaporated in vacuo. The crude was purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>/THF 99/1) to obtain an orange solid. The product was further purified by centrifugation in methanol (3×8 mL) yielding 47.7 mg of **1**. Yield: 21%. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ: 9.62 (s, 2H, H<sub>4</sub>), 9.23 (d, 2H, H<sub>3</sub>, *J* = 7.7), 8.84 (d, 2H, H<sub>2</sub>, *J* = 7.7), 6.93 (s, 4H, H<sub>1</sub>), 6.84 (t, 2H, H<sub>m</sub>, *J* = 5.1), 4.56 (m, 4H, H<sub>n</sub>), 4.00 (m, 8H, H<sub>l</sub>), 3.95 (m, 4H, H<sub>l</sub>), 3.89 (m, 4H, H<sub>n</sub>), 1.81 (m, 8H, H<sub>k</sub>), 1.71 (m, 4H, H<sub>k</sub>), 1.47 (m, 12H, H<sub>j</sub>), 1.37-1.19 (m, 96H, H<sub>b-i</sub>), 0.86 (m, 18H, H<sub>a</sub>, *J* = 6.3). <sup>13</sup>C RMN (175 MHz, CDCl<sub>3</sub>) δ: 167.8, 163.9, 163.4, 153.1, 152.9, 148.8, 140.9, 135.7, 135.3, 131.9, 129.2, 127.4, 124.1, 122.0, 116.6, 105.4, 77.2, 73.7, 69.3, 40.1, 39.9, 32.1, 32.1, 30.5, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 26.3, 26.2, 22.9, 22.8, 14.3. HRMS-MALDI-TOF *m/z* calculated C<sub>112</sub>H<sub>170</sub>N<sub>6</sub>O<sub>12</sub> [M+2]<sup>+</sup> 1793.3033, found 1793.2935.

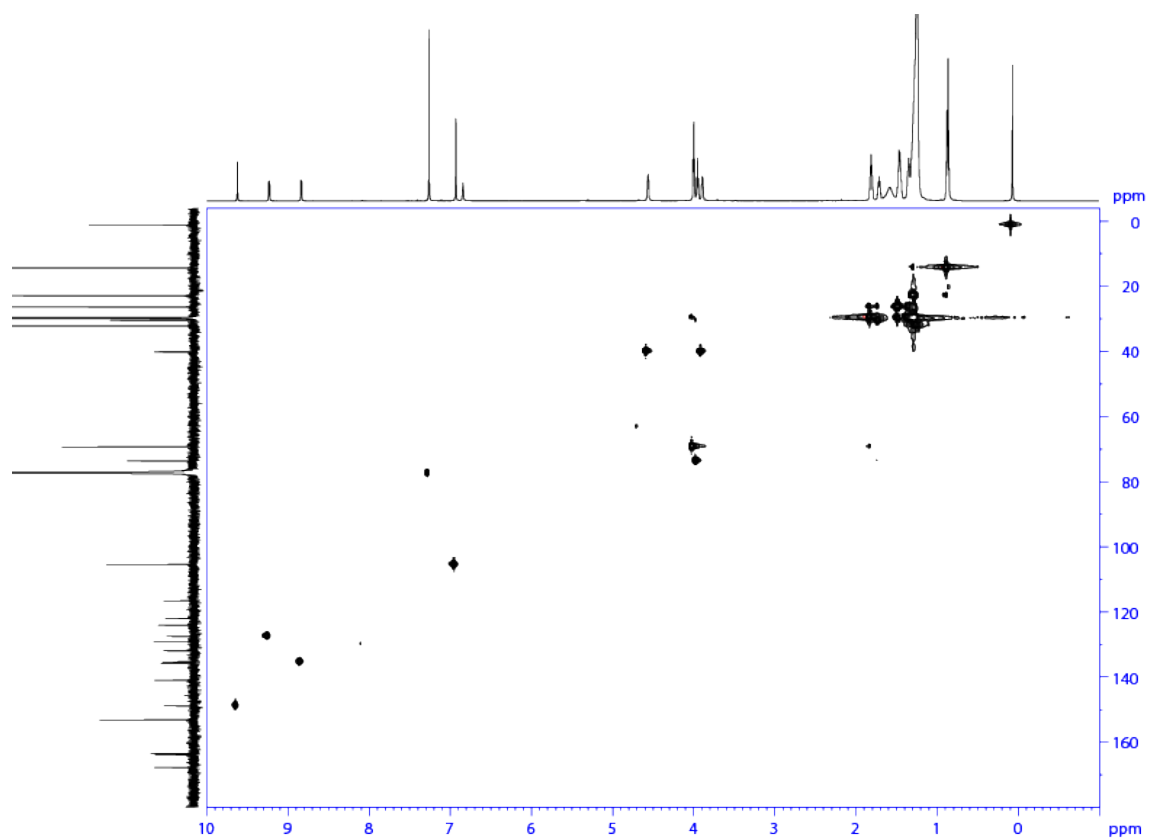
### 3. Collection of spectra



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz, 328 K) of BQQDI 1.

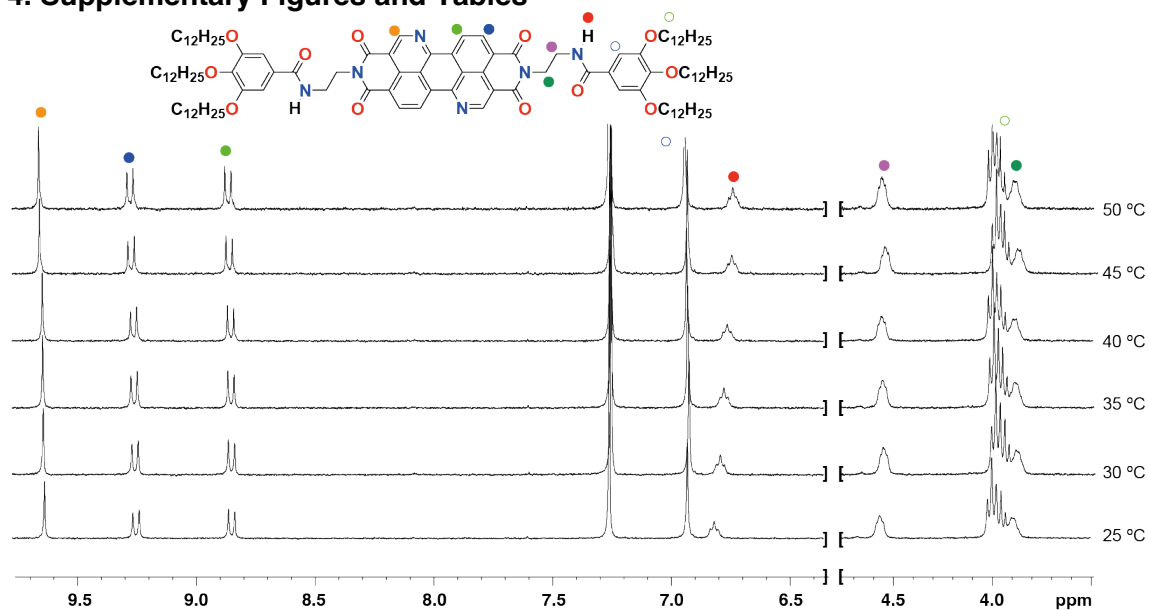


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 328 K) of BQQDI 1.

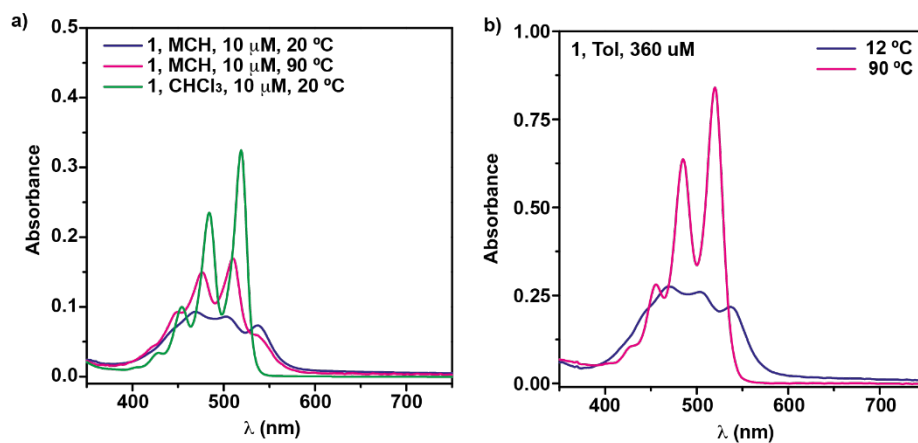


$^1\text{H}$ - $^{13}\text{C}$ -HMQC spectrum ( $\text{CDCl}_3$ , 298 K) of BQQDI 1.

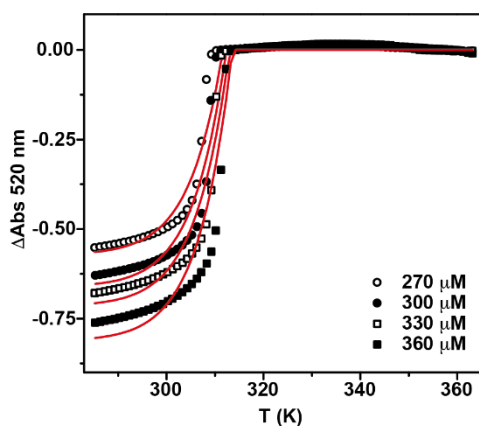
#### 4. Supplementary Figures and Tables



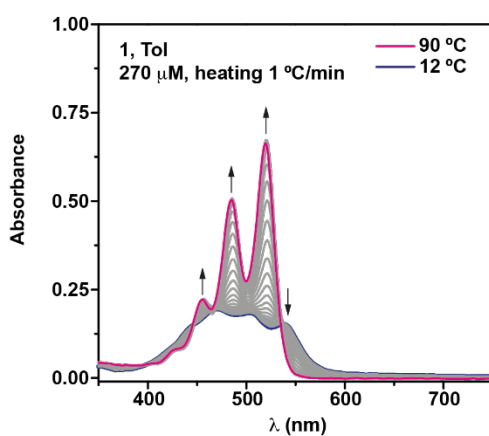
**Figure S1.** Partial  $^1\text{H}$  NMR spectra of **1** recorded at different temperatures showing the aromatic and some of the aliphatic protons ( $c_T = 4$  mM;  $\text{CDCl}_3$ ; 300 MHz).



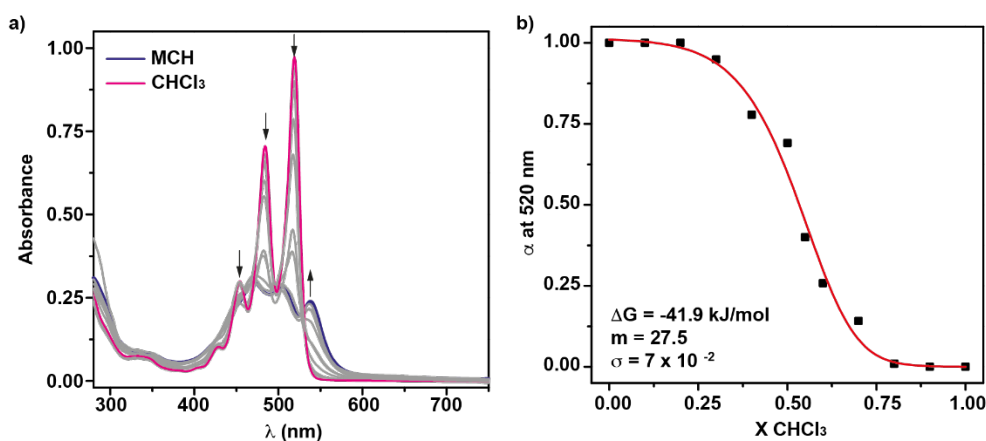
**Figure S2.** UV-Vis spectra of **1** in MCH at different temperatures and in  $\text{CHCl}_3$ ; (a) and in Tol at different temperatures (b).



**Figure S3.** Plot of the variation of the absorbance of **1** at  $\lambda = 520$  nm versus temperature at different concentrations. The red lines depict the fit to the one-component EQ model.

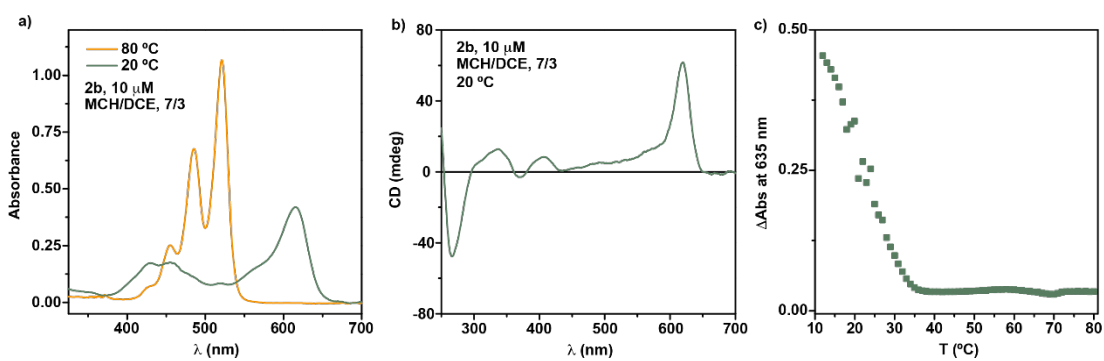


**Figure S4.** UV-Vis spectra of **1** at different temperatures upon heating a solution of **1** in Tol at  $1$  °C/min ( $c_T = 270$   $\mu$ M). Arrows indicate the changes in the absorption pattern upon heating.

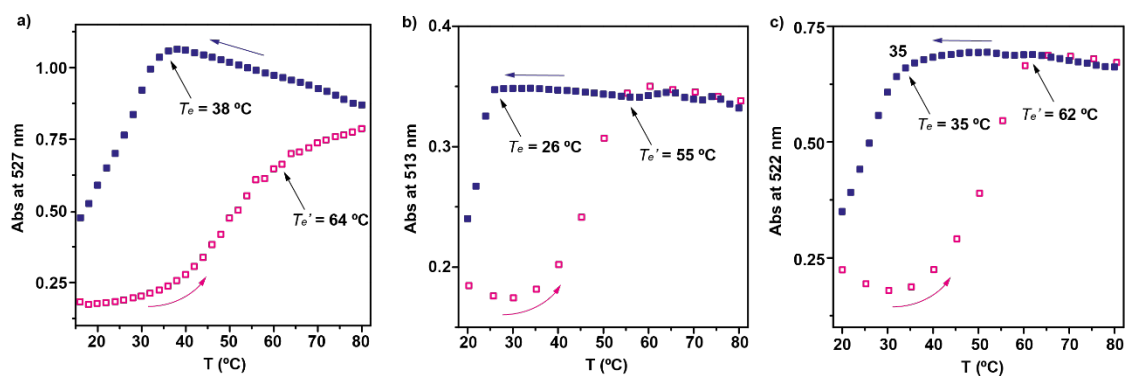


**Figure S5.** (a) UV-Vis spectra of **1** in MCH,  $\text{CHCl}_3$  or in mixtures of these solvents ( $c_T = 30$   $\mu$ M); (b) plot of the variation of  $\alpha$  versus the molar fraction of  $\text{CHCl}_3$ ; the red line in panel (b) depicts the fitting to the SD model. Arrows in panel (a) indicate the spectral changes upon increasing the fraction of MCH.

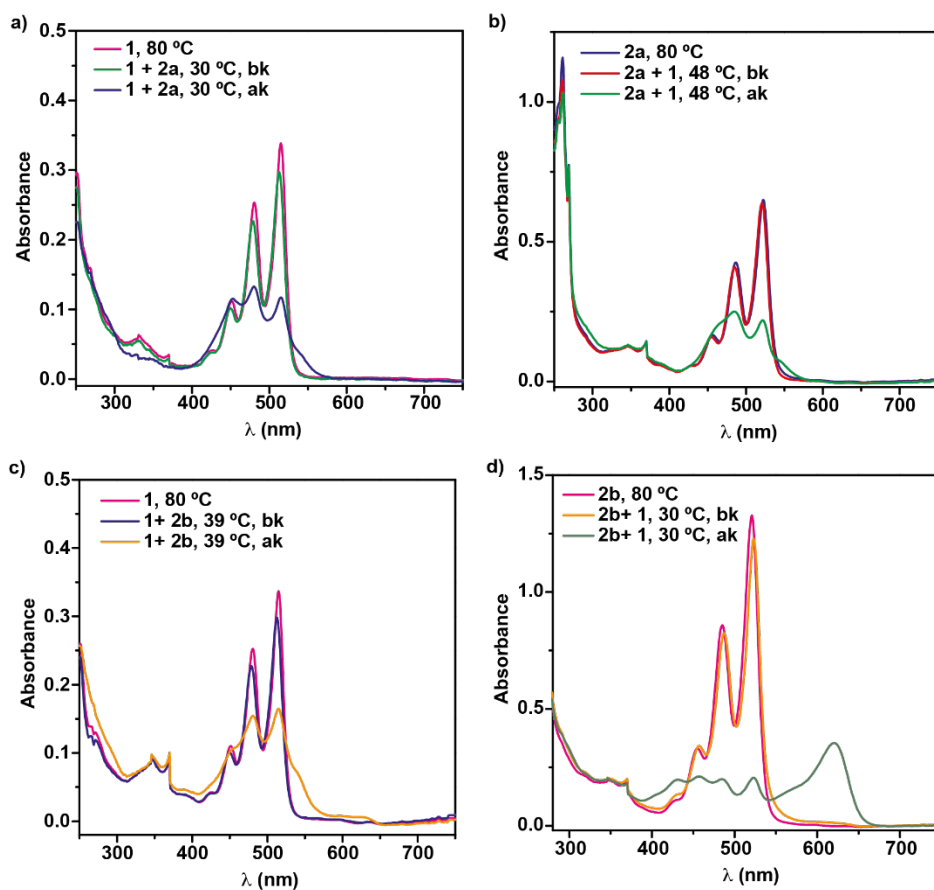




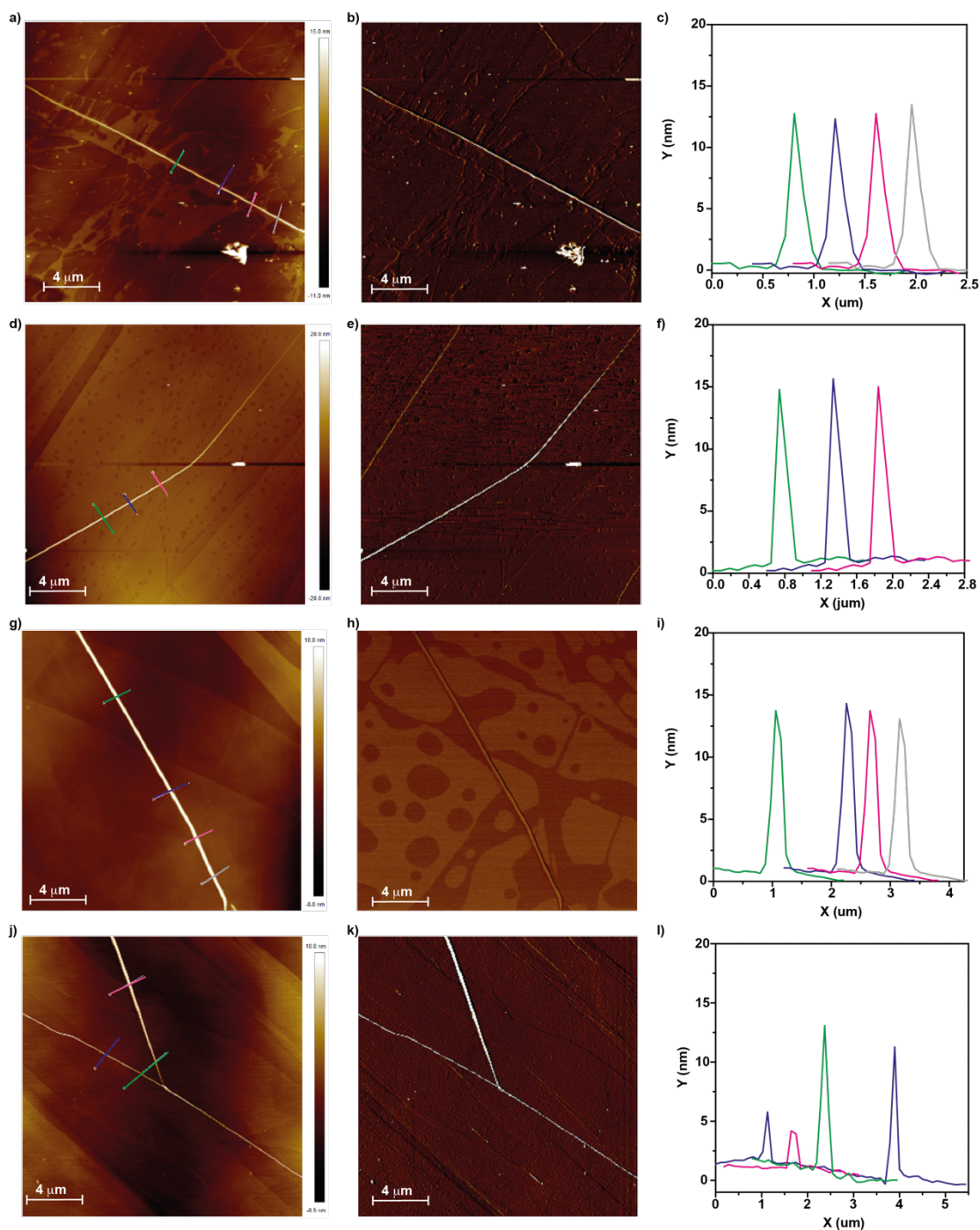
**Figure S6.** UV-Vis spectra (a) and CD spectrum (b) of **2b** in MCH/DCE 7/3 ( $c_T = 10 \mu\text{M}$ ); (c) plot of the variation of the absorbance of **2b** at  $\lambda = 635$  nm versus temperature in MCH/DCE 7/3 ( $c_T = 10 \mu\text{M}$ )



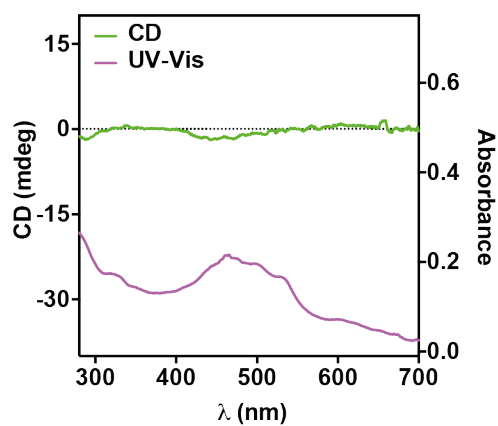
**Figure S7.** Cooling (blue squares and blue arrow) and heating (purple squares and purple arrows) curves obtained by plotting the variation of absorbance versus temperature for **2a** (a), **1** (b) and **2a** (c) in MCH/DCE 7/3 and at  $c_T = 10 \mu\text{M}$ .



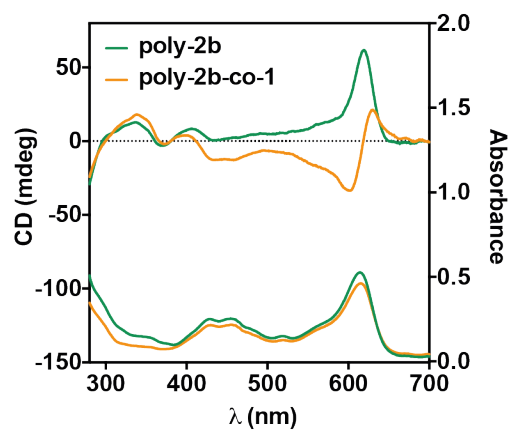
**Figure S8.** (a) UV-Vis spectra of the seeded heteropolymerization to achieve **poly-1-co-2a**, **poly-2a-co-1**, **poly-1-co-2b** and **poly-2b-co-1** in MCH/DCE 7/3 at  $c_T = 10 \mu\text{M}$  (bk = before kinetics; ak = after kinetics)



**Figure S9.** Height (a, d, g, j) and phase (b, e, h, k) AFM images of the heteropolymers **poly-1-co-2a** (a, b), **poly-2a-co-1** (d, e), **poly-1-co-2b** (g, h) and **poly-2b-co-1** (j, k) onto HOPG. Panels (c, f, i, l) show the height profiles of the heteropolymers along the coloured lines in panels (a, d, g, j) (experimental conditions: MCH/DCE 7/3 as solvent,  $c_T = 10 \mu\text{M}$ ).



**Figure S10.** CD (upper panel) and UV-Vis (bottom panel) spectra of **poly-1-co-2a** (experimental conditions: MCH/DCE 7/3 as solvent,  $c_T = 10 \mu\text{M}$ ).



**Figure S11.** CD (upper panel) and UV-Vis (bottom panel) spectra of **poly-2b** and **poly-2b-co-1** (experimental conditions: MCH/DCE 7/3 as solvent,  $c_T = 10 \mu\text{M}$ ).

## 6. References

(S1) T. Okamoto, S. Kumagai, E. Fukuzaki, H. Ishii, G. Watanabe, N. Niitsu, T. Annaka, M. Yamagishi, Y. Tani, H. Sugiura, T. Watanabe, S. Watanabe, J. Takeya, *Sci. Adv.* 2020, **6**, eaaz0632

(S2) S. Ghosh, X.-Q. Li, V. Stepanenko and F. Würthner, *Chem. Eur. J.*, 2008, **14**, 11343.