Supporting Information

Chirality inversion in hydrogen-bonded rhodanine-oligothiophene derivatives by solvent and temperature

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1. Materials

All reagents and solvents were obtained from commercial suppliers and purified or dried according to standard procedures. Column chromatography was performed on silica gel (VWR Silica 60, particle size 0.040–0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received. Matrix-assisted laser desorption/ionization-time of flight (MALDI) was performed in a Bruker Daltonics. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer and/or Bruker Avance III HD 500 MHz spectrometer.

UV/Vis measurements were performed in a conventional quartz cell (light pass 1 mm) on a Cary 5000 UV/Vis-NIR spectrophotometer. Circular dichroism spectra were acquired using a 1 mm quartz cell on a Jasco J1700 Spectropolarimeter, with 1 s integrations, 1 accumulation and a step size of 1 nm with a bandwidth of 1 nm over a range of wavelengths from 300 to 800 nm at the indicated temperature in each case (Peltier); samples were freshly prepared and transfer to the CD cell, and the spectra immediately recorded. TEM measurements were done with a Technai G2 (FEI) microscope with an accelerating voltage of 200 kV. 5 μL of the sample solution were deposited onto a freshly glow discharged carbon-covered grid (400 mesh). The suspension was left for 2 min, and then, the grid was negatively stained with 5 μL of uranyl acetate (2% in water) for another 1 min and finally blotted using a filter paper. FTIR spectra were recorded with a Vertex 70 from Bruker Optics, equipped with MCT detector and a black-body source. The solutions were studied in cells from Specac Pike with KBr NaCl windows. The solutions were inserted in a home-made cell between two NaCl windows. The spectra were measured with the built-in MCT detector of the Vertex 70. The spectra were compensated from CO2 and moisture with OPUS from Bruker. The solvent intensities were measured separately and subtracted. Fluorescence spectra were recorded in a Fluoromax-4 using freshly prepared solutions of compound 7b in the indicated solvents. The emission spectra were recorded from 565 nm to 850 nm (slit width = 2 nm) after excitation at 550 nm (slit width = 2 nm). The was collected using an integration time of 0.2 s. The excitation spectra were collected under the same conditions, where the emission wavelength and the collection range were selected according to the emission spectra to observe the desired bands (details in the ESI, Figure S5).

2. Synthesis

The synthetic route for compounds **7a** and **7b** is shown in Schemes 1, 2 and 3.

Synthesis of compound 4 (3,3''',3'''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde)

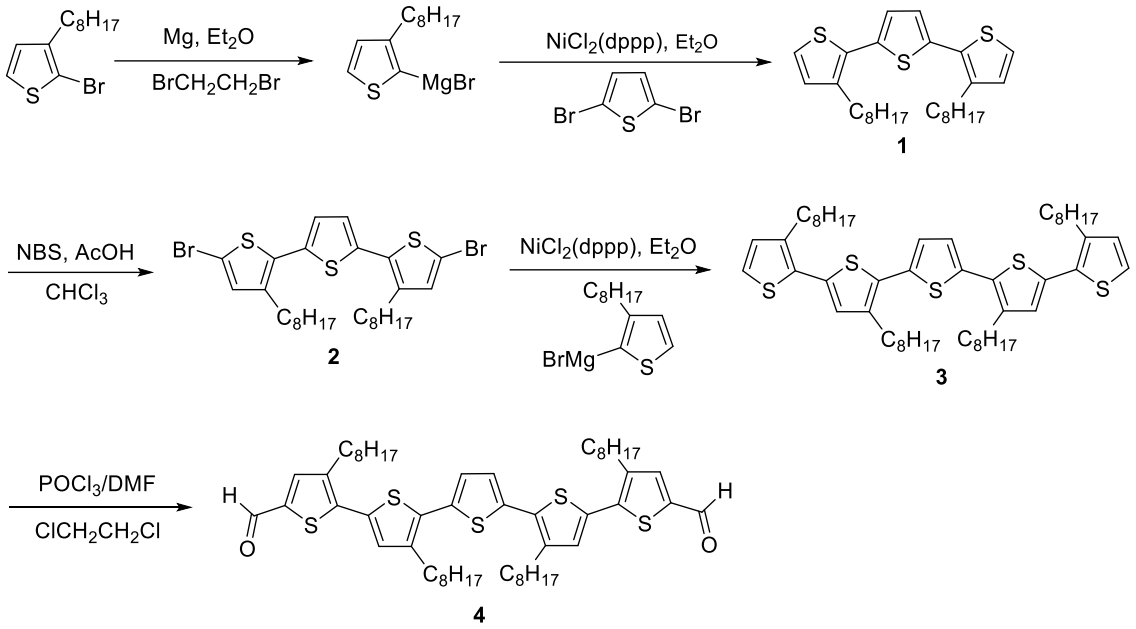
Compound **4** was prepared adapting procedures described in the literature, starting from 3-octyl-2-bromothiophene.[1] Briefly, 3-octyl-2-bromothiophene (6 g, 21.8 mmol, 1 equiv.) was converted in the magnesium bromide analogue using Mg (1.06 g, 43.6 mmol, 2 equiv.) in dried diethyl ether (100 ml) under N_2 atmosphere. 0.3 mL of dibromoethane were added at the beginning to activate the Mg. Once the reaction became greyish, it was stirred at 35 ºC for 1 hour. The Grignard reagent (21.8 mmol, 3 equiv.) was then directly added to a solution of 2,5-dibromothiophene (1.76 g, 7.26 mmol, 1 equiv.) in dried diethyl ether (40 ml) in the presence $NiCl_2$(dppp) (792 mg, 1.46 mmol, 0.2 equiv.), and were stirred overnight at 35 ºC under N_2 atmosphere. The day after, the reaction was poured into a mixture of crushed ice and HCl 2 M (50 mL). The organic layer was separated and then the aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and it was then purified by column chromatography using n-heptane as eluent to obtain compound **1** as a yellow oil (3.10 g, 90 % yield). Then, *N*-bromosuccinimide (2.69 g, 15.1 mmol, 2.3 equiv.) was added in small portions to a solution of compound **1** (6.56 mmol, 1 equiv.) in chloroform and acetic acid (150 mL, 1/1, v/v) at room temperature. The reaction was stirred at room temperature covered with aluminium foil and monitored by ^{1}H-NMR. Once the dibromide derivative was formed, distilled water was added to quenched the reaction and it was extracted with $CHCl_3$ (three times). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under vacuum to yield compound **2** as a yellow solid (4.12 g, quantitative yield). Compound **2** (2.48 g, 3.90 mmol, 1 equiv.) was treated with 2-(3-octylthienyl) magnesium bromide prepared from 2-bromo-3-octylthiophene (3.22 g, 11.7 mmol, 3 equiv.) as described above, in the presence of $NiCl_2$(dppp) (423 mg, 0.78 mmol, 0.2 equiv.), and were stirred overnight at 35 ºC under N_2 atmosphere. The day after, the reaction was quenched with HCl 1 M (10 mL), followed by the addition of water (50 mL). The mixture was extracted with dichloromethane, and washed with brine, water and dried over Na_2SO_4. The residue was then purified by column chromatography in n-heptane/ethyl acetate (10/1) as eluent to yield compound **3** as a yellow oil (2.96 g, 88 % yield). A Vilsmeier reagent was prepared using a mixture of $POCl_3$ (1.59 ml,

17.04 mmol, 6.3 equiv.) and dimethylformamide (1.69 ml, 21.91 mmol, 8.1 equiv.) (ratio $POCl_3$/DMF = 0.8),[2] and heating to 80 ºC for 3 hours (until the mixture became intense orange). The Vilsmeier reagent was added to a solution of compound **3** (2.90 g, 3.37 mmol, 1 equiv.) in 1,2-dichloroethane (45 mL), which became intense red colour. The reaction was stirred overnight at 80 °C. The following day, the mixture was poured into ice water (50 mL), neutralized with a saturated solution of K_2CO_3, and then extracted with dichloromethane. The organic layer was washed with brine and water, and it was dried over Mg_2SO_4. The crude was purified by column chromatography in dichloromethane/cyclohexane (2:3) as eluent to yield dialdehyde **4** as a red solid (2.78 g, 90 % yield).

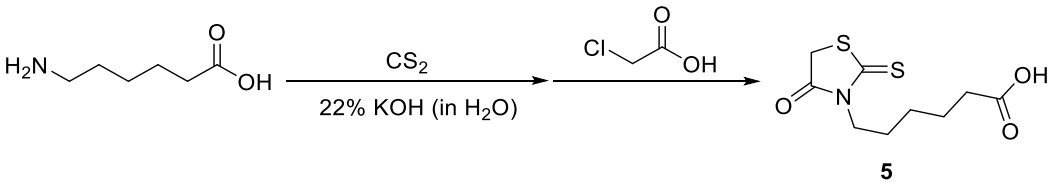
Synthesis of compounds 7a and 7b

Rhodanine **5** was synthesized as previously described in the literature,[3] and it was obtained as a pale-yellow solid (65 % yield). Then, dialdehyde **4** (0.98 mmol, 1 equiv.) rhodanine **5** (3.92 mmol, 4 equiv.) and ammonium acetate (0.98 mmol, 1 equiv.) were mixed in acetic acid (0.3 mL), and the mixture was stirred at 95 ºC overnight.[4] The solvent was evaporated under reduced pressure and the crude was washed with H_2O (three times). The organic phase was dried over $MgSO_4$, and it was purified by dissolving the residue in the minimum amount of $CHCl_3$ and adding cold acetone to precipitate the product. The precipitate obtained was filtered off, washed with acetone and dried under vacuum to yield compound **6** as a black solid (945 mg, 70% yield). Then, compound **6** (250 mg, 1 equiv.), was mixed with the corresponding amine (8 equiv.), $SOCl_2$ (8 equiv.), and triethylamine (24 equiv.) in $CHCl_3$ and stirred at room temperature for 24 hours.[5] The reaction was monitored by TLC, and it showed that the major product was the desired product (although around 7% of monosubstituted product is formed as well). The crude was washed with HCl 1 M, brine and distilled water. The organic phase was dried over $MgSO_4$, and it was purified by column chromatography in a mixture of $CHCl_3$/ethanol, starting from pure chloroform until $CHCl_3$/ethanol (20:1). Then, the fraction obtained from the column was precipitate with cold acetone to obtain the crystalline black solids of the final compounds **7a-b**.

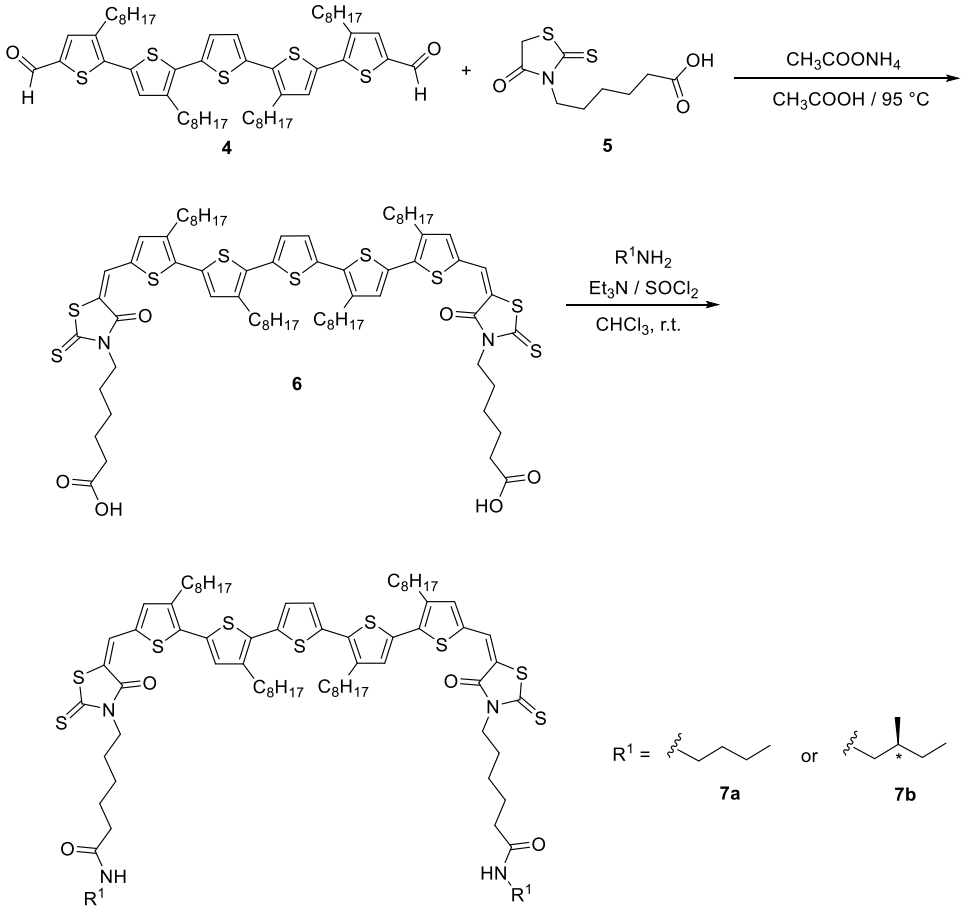
Scheme 1. Synthesis of dialdehyde **4**.



Scheme 2. Synthesis of compound **5** (6-(4-oxo-2-thioxothiazolidin-3-yl) hexanoic acid).

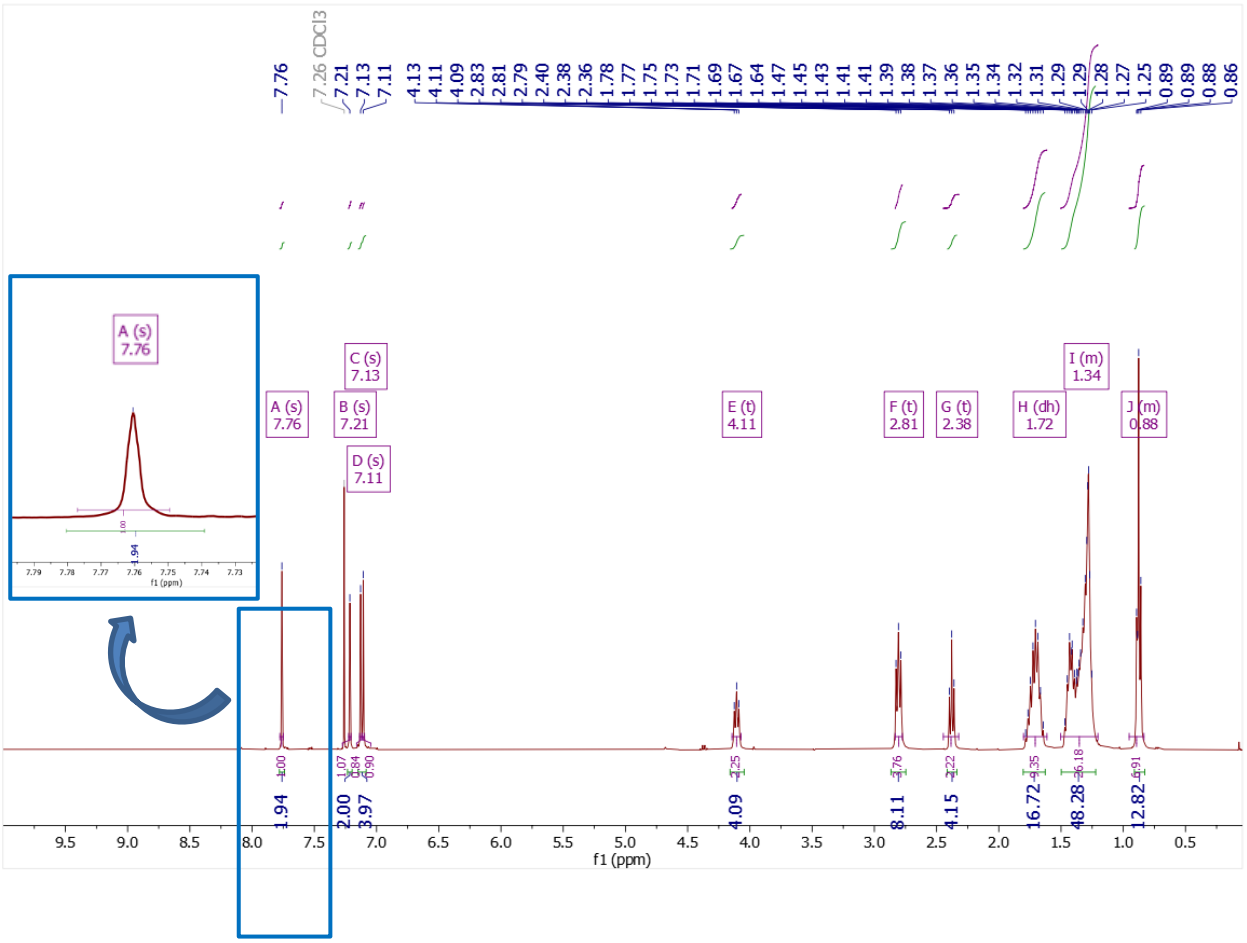


Scheme 3. Synthesis of compound **6** and the final amide-containing compounds **7a-b**.

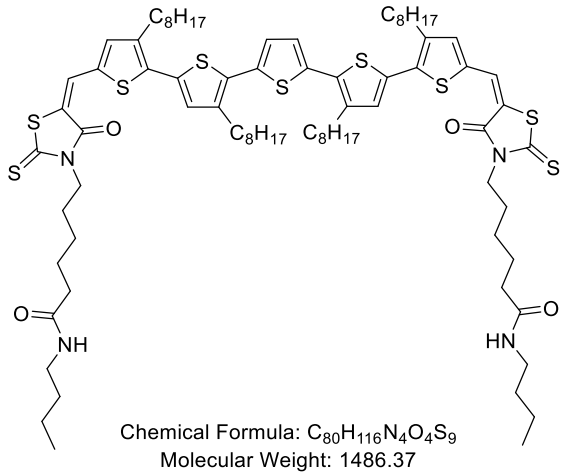


Compound 6: black solid (945 mg, 70% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, 2H, H-double bond), 7.21 (s, 2H, H-thiophene), 7.13 (s, 2H, H-thiophene), 7.11 (s, 2H, H-thiophene), 4.11 (t, *J* = 7.6 Hz, 4H, rhodanine-CH_2), 2.81 (t, *J* = 7.8 Hz, 8H, 4 x CH_2 aliphatic chain thiophenes), 2.38 (t, *J* = 7.4 Hz, 4H, 2 x CH_2-CONH), 1.80 – 1.62 (m, 16H, 4 x CH_2 aliphatic chain rhodanine, 4 x CH_2 aliphatic chain thiophenes), 1.50 – 1.20 (m, 44H, 2 x CH_2 aliphatic chain rhodamine, 20 x CH_2 aliphatic, 0.95 – 0.83 (m, 12H, 4 x CH_3 aliphatic chain thiophenes).

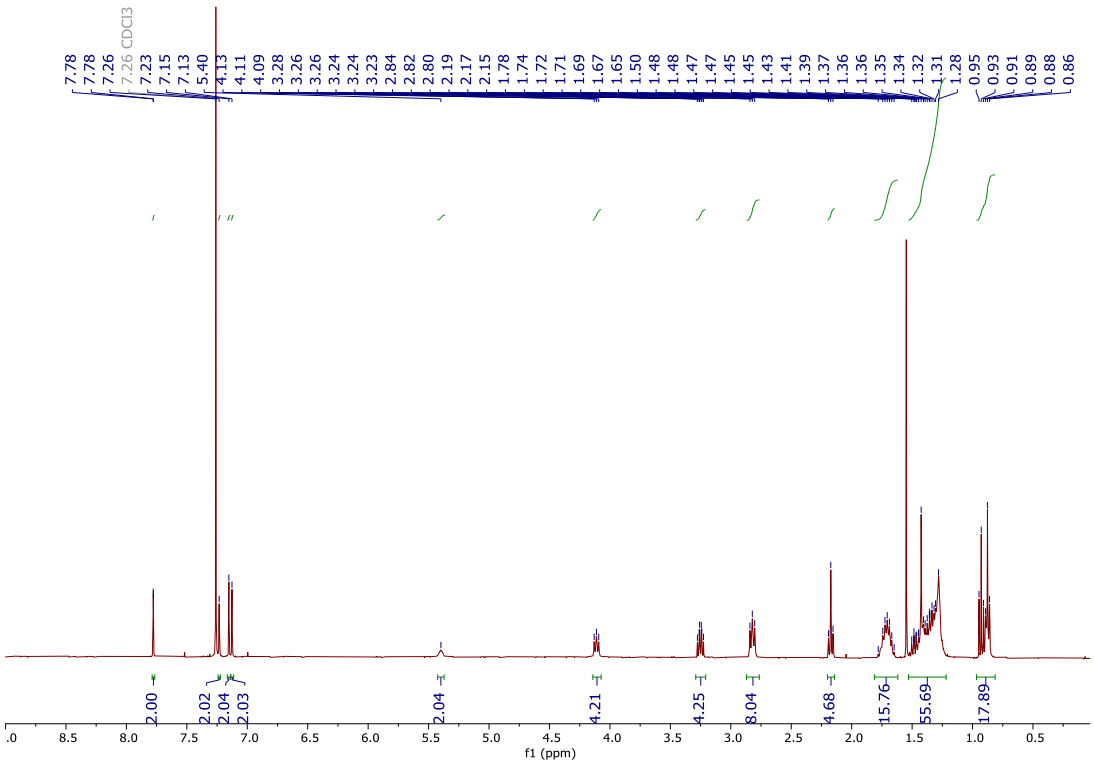


Compound 7a: black solid (127 mg, 35% yield).

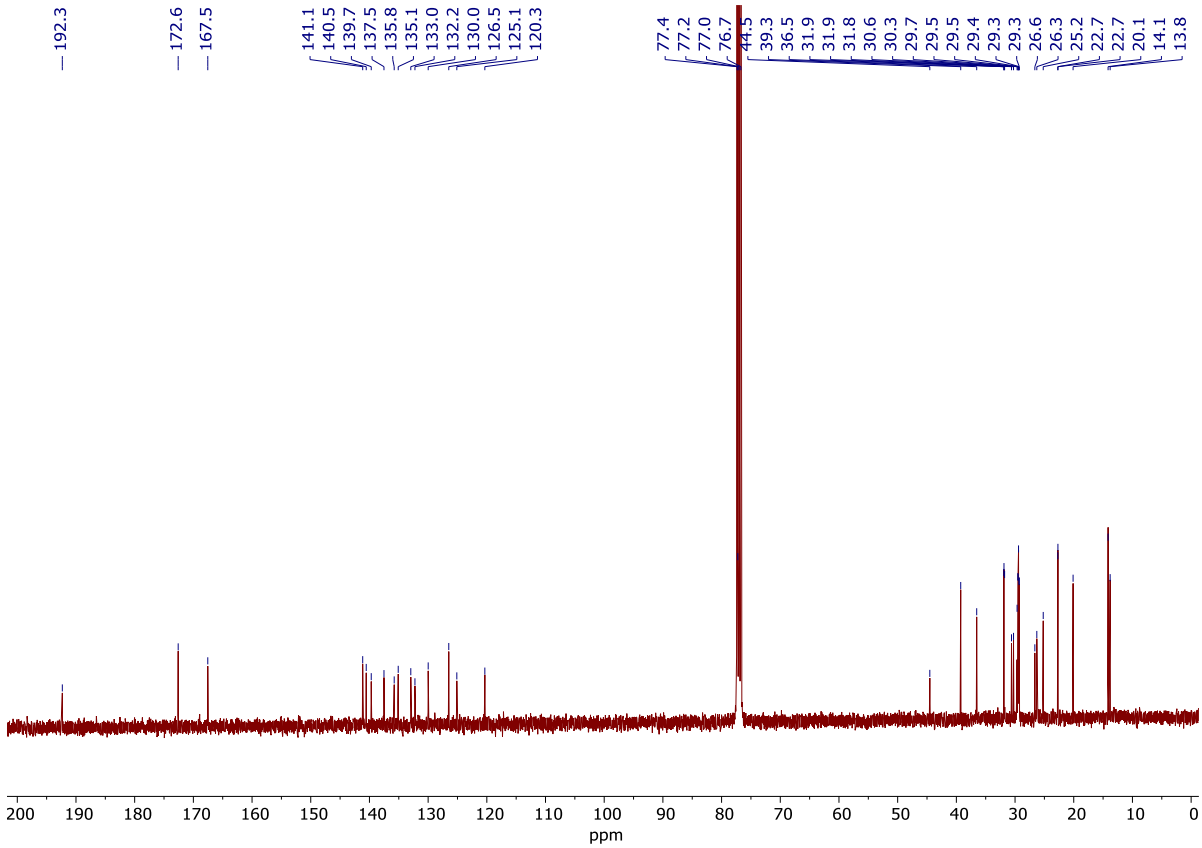


^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.78 (s, 2H, H-double bond), 7.23 (s, 2H, H-thiophene), 7.15 (s, 2H, H-thiophene), 7.13 (s, 2H, H-thiophene), 5.40 (s, 2H, NH amide), 4.11 (t, *J* = 7.6 Hz, 4H, rhodanine-CH_2), 3.25 (td, *J* = 7.2, 5.7 Hz, 4H, CONH-CH_2), 2.89 – 2.74 (m, 8H, 4 x CH_2 aliphatic chain thiophenes), 2.23 – 2.09 (m, 4H, 2 x CH_2 aliphatic chain amine), 1.79 – 1.62 (m, 16H, 4 x CH_2 aliphatic chain amine CH_2, 4 x

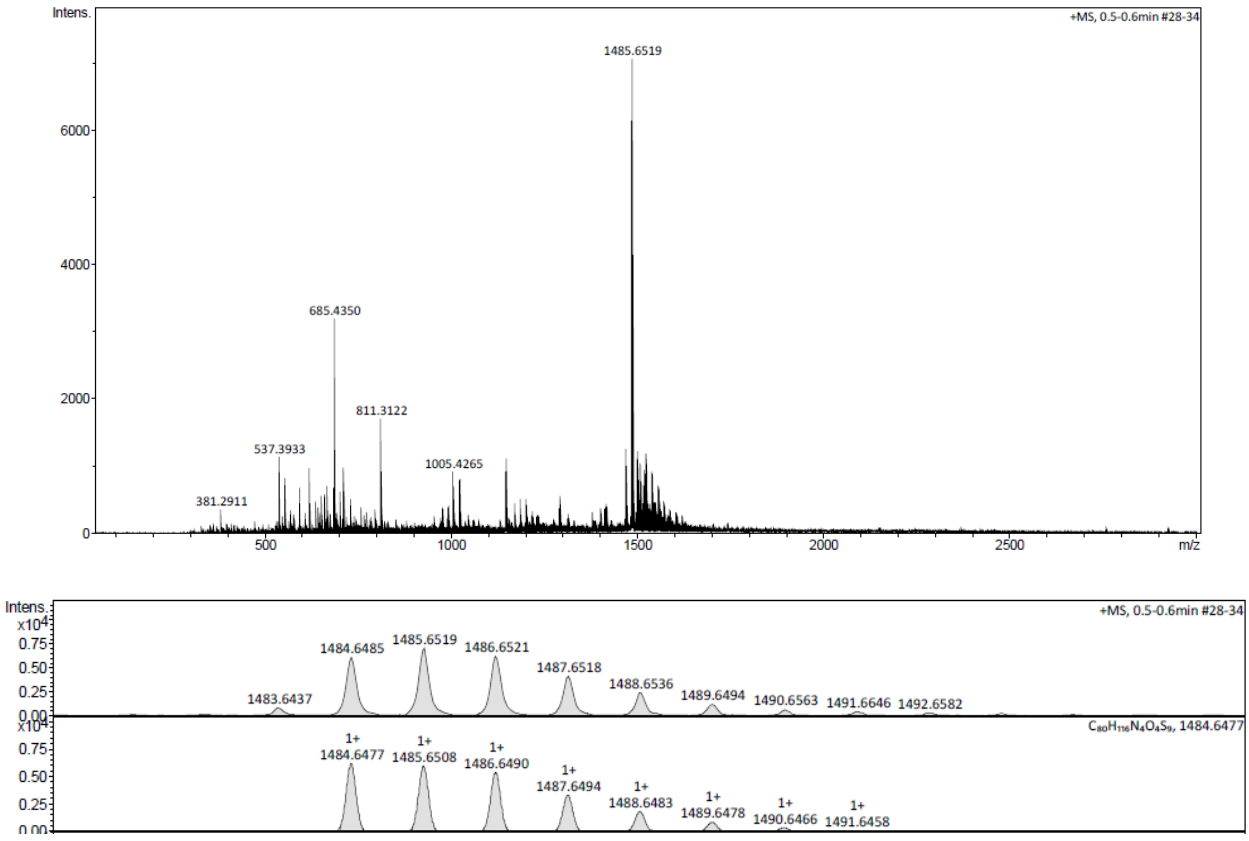
CH_2 aliphatic chain thiophenes), 1.53 – 1.16 (m, 52H, 6 x CH_2 aliphatic chain amine CH_2, 20 x CH_2 aliphatic chain thiophenes), 0.93 (t, J = 7.3 Hz, 6H, 2 x CH_3 aliphatic chain amine), 0.90 – 0.85 (m, 12H, 4 x CH_3 aliphatic chain thiophenes).



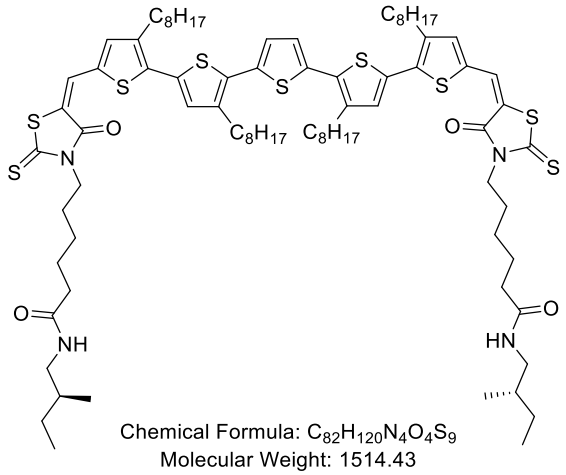
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 192.3, 172.6, 167.5, 141.2, 140.6, 139.7, 137.5, 135.8, 135.1, 133.0, 132.3, 130.0, 126.5, 125.1, 120.3, 44.5, 39.3, 36.5, 31.9, 31.9, 31.8, 30.6, 30.3, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.6, 26.3, 25.2, 22.7, 22.7, 20.1, 14.2, 13.8.



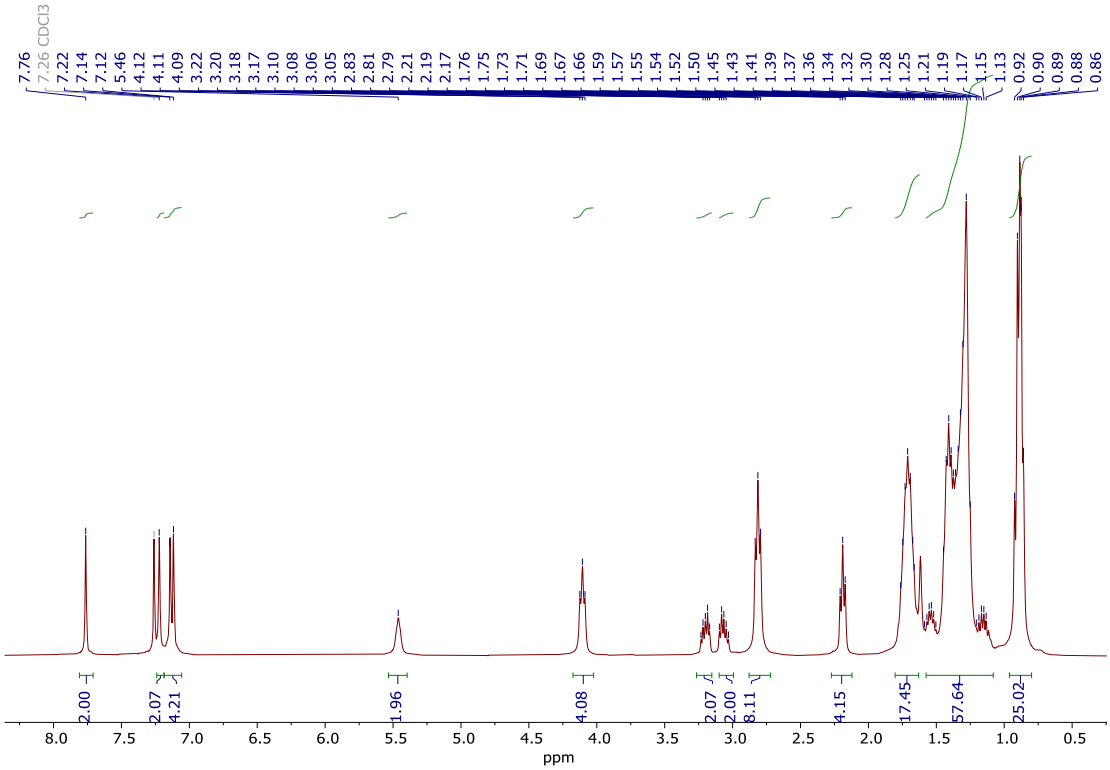
HRMS (ESI+) m/z: 1484.6477 (MH+) ($C_{80}H_{116}N_4O_4S_9$ requires 1484.6483)



Compound 7b: black solid (240 mg, 45% yield).

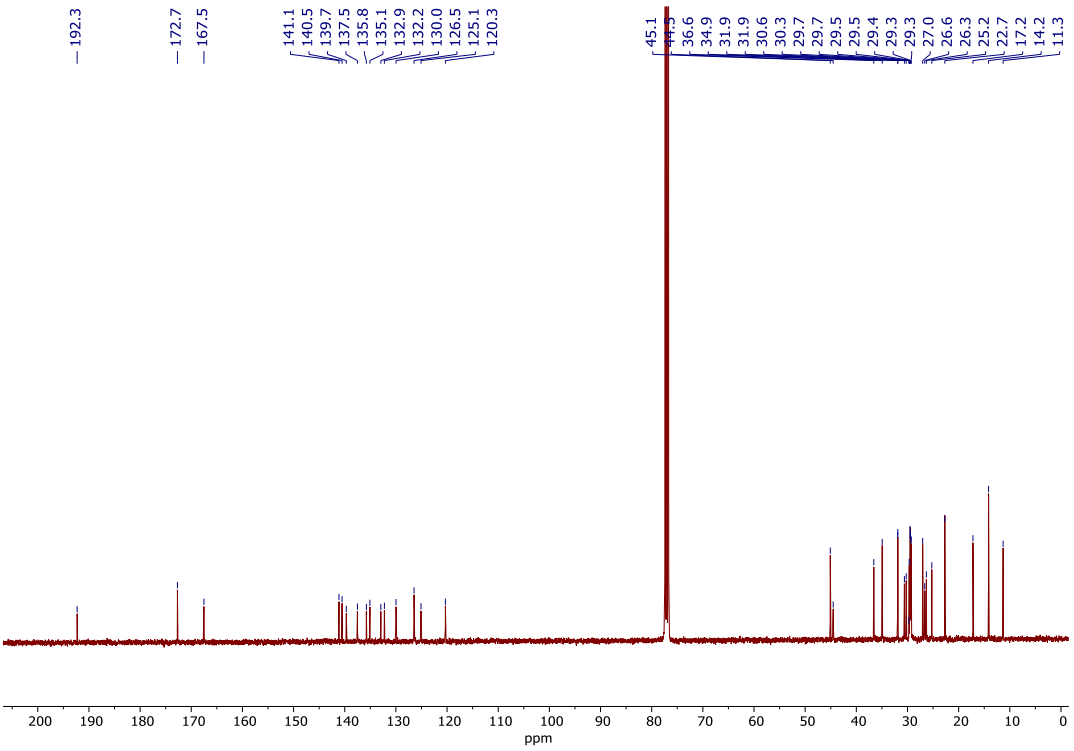


^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, 2H, H-double bond), 7.22 (s, 2H, H-thiophene), 7.14 (s, 2H, H-thiophene), 7.12 (s, 2H, H-thiophene), 5.46 (s, 2H, NH amide), 4.11 (t, *J* = 7.6 Hz, 4H, rhodanine-CH_2), 3.20 (dt, *J* = 13.0, 6.4 Hz, 2H, CONH-CH_2), 3.06 (dt, *J* = 13.0, 6.4 Hz, 2H, CONH-CH_2), 2.81 (t, *J* = 7.9 Hz, 8H, 4 x CH_2 aliphatic chain thiophenes), 2.19 (t, *J* = 7.5 Hz, 4H, CH_2-CONH), 1.83 – 1.07 (m, 76H, aliphatic chain amine CH_2, aliphatic chain thiophenes), 0.97 – 0.81 (m, 24H, 4 x CH_3 aliphatic chain amine, 4 x CH_3 aliphatic chain thiophenes).

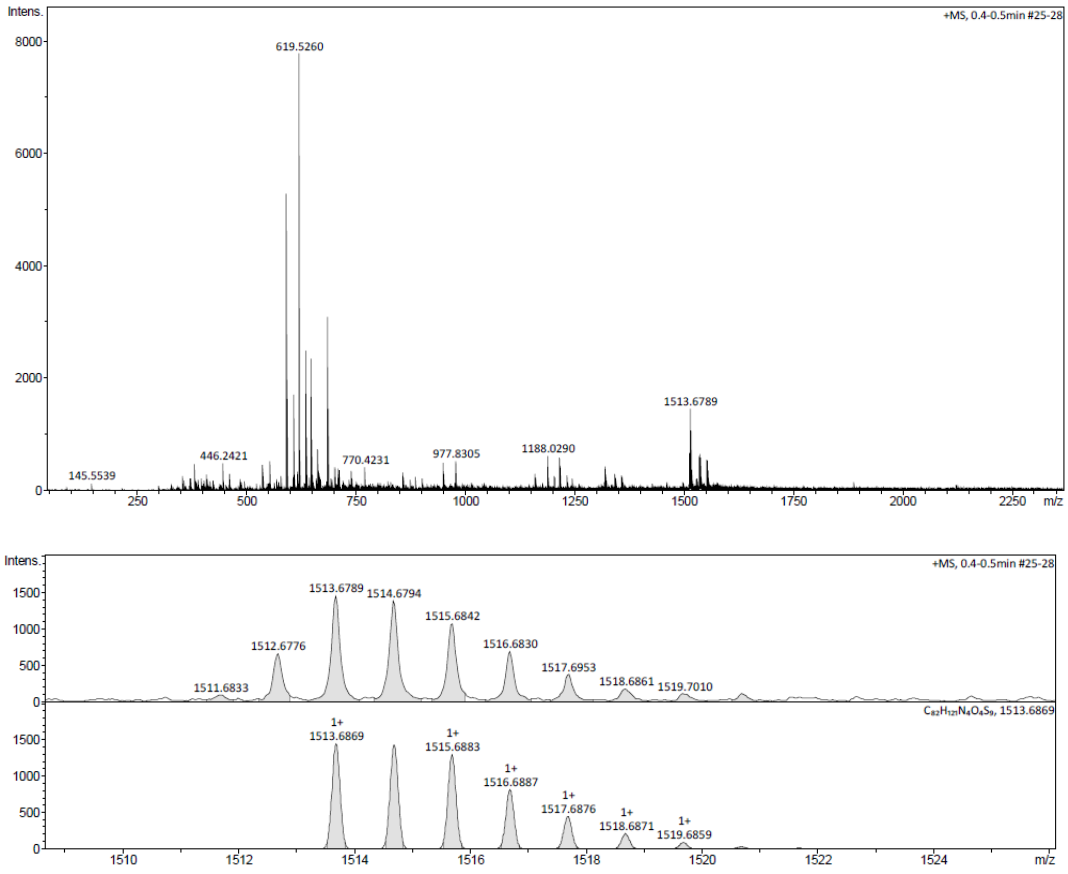


^{13}C-NMR (100 MHz, $CDCl_3$) δ: 192.3, 172.7, 167.5, 141.1, 140.5, 139.7, 137.5, 135.8, 135.1, 132.9, 132.3, 130.0, 126.5, 125.1, 120.3, 45.1, 44.5, 36.6, 34.9, 31.9, 31.9, 30.6, 30.3, 29.7, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 27.0, 26.6, 26.3, 25.3, 22.7, 17.2, 14.2, 11.3.

^{13}C-NMR (100 MHz, $CDCl_3$)



HRMS (ESI+) m/z: 1513.6789 (MH+) ($C_{80}H_{116}N_4O_4S_9$ requires 1513.6796)



3. Spectroscopic measurements

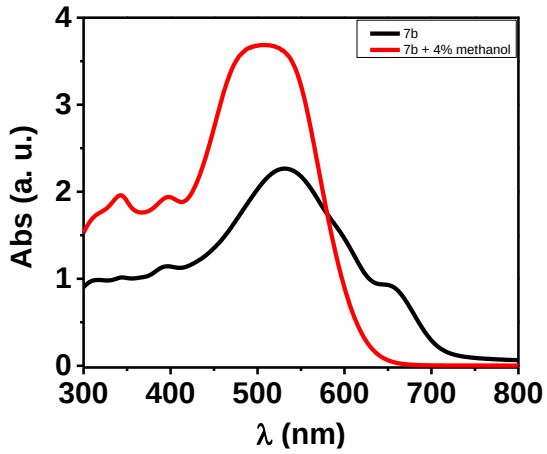


Figure S1. Absorption spectra of **7b** in chlorobenzene after addition of 4% volume of methanol.

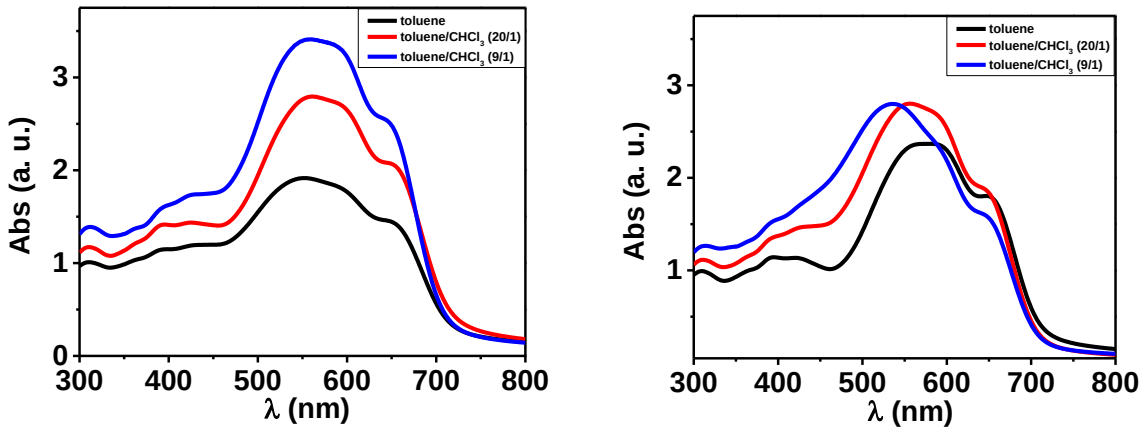


Figure S2. Absorption spectra for **7a** (left) and **7b** (right) in mixtures of toluene and chloroform (c = 0.83 mg/ml for toluene and c = 1.25 mg/ml for the mixtures).

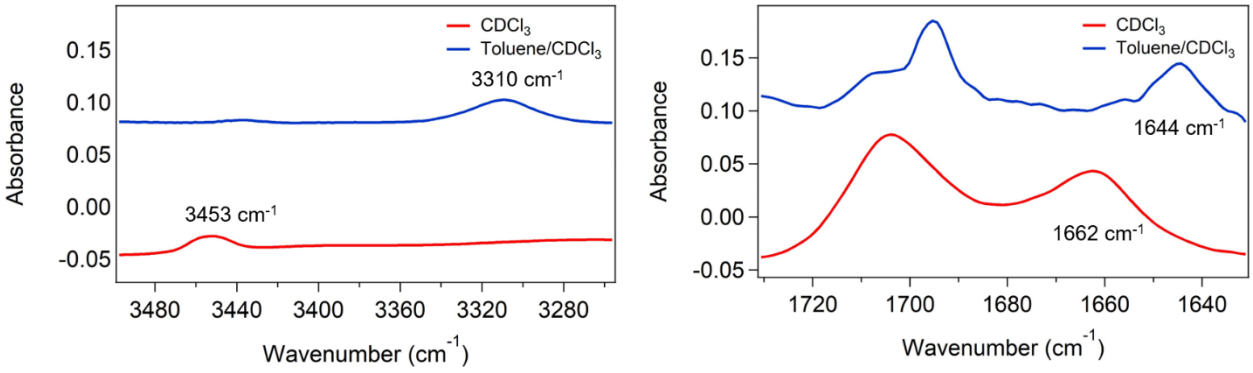


Figure S3. FT-IR spectra in chloroform and toluene/chloroform (9/1). Left side: amide A region; right side: amide I region.

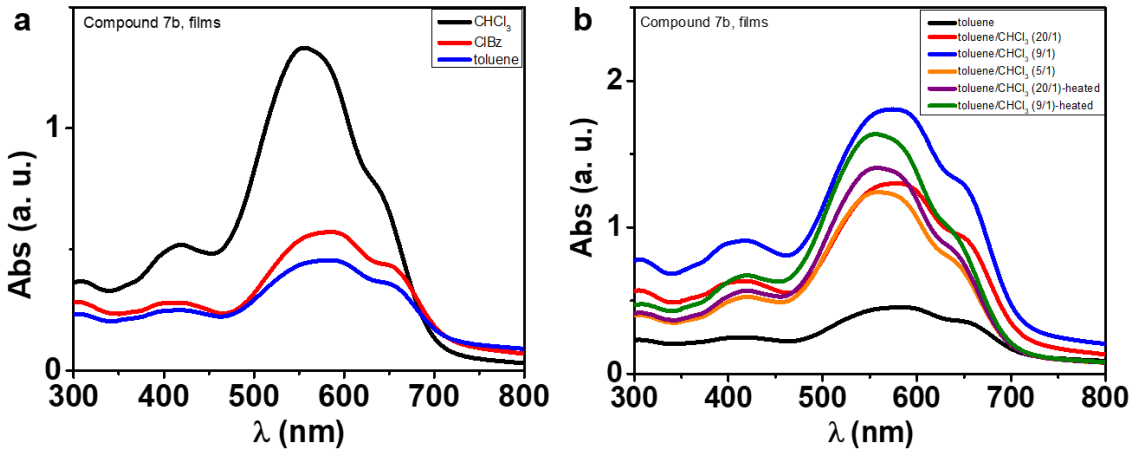


Figure S4. Absorption spectra obtained from drop cast films prepared from solutions of compound **7b** in: a) toluene, chlorobenzene and chloroform; b) different mixtures of toluene/chloroform.

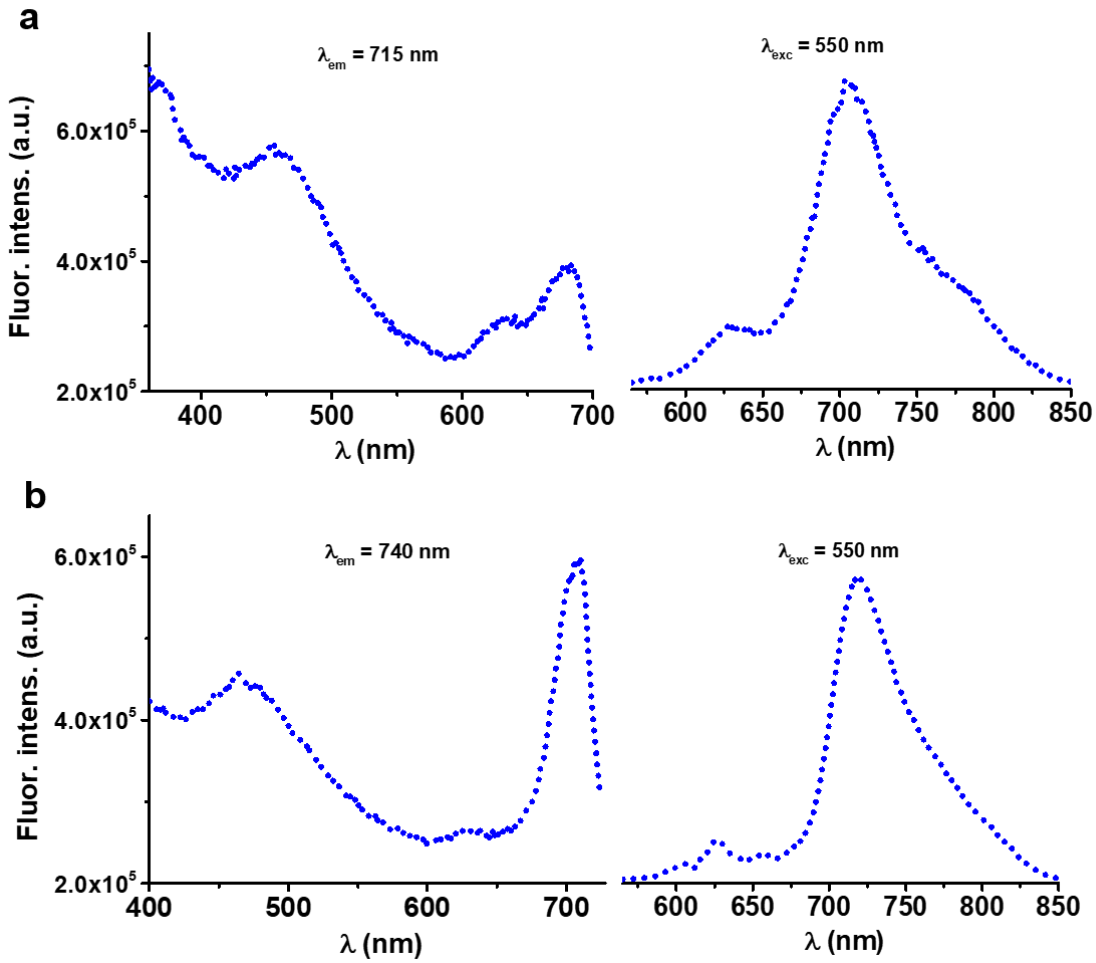


Figure S5. Fluorescence spectra for freshly prepared solutions of compound 7b in a) toluene (c = 0.2075 mg/ml) and b) toluene/chloroform (9/1) (c= 0.625 mg/ml).

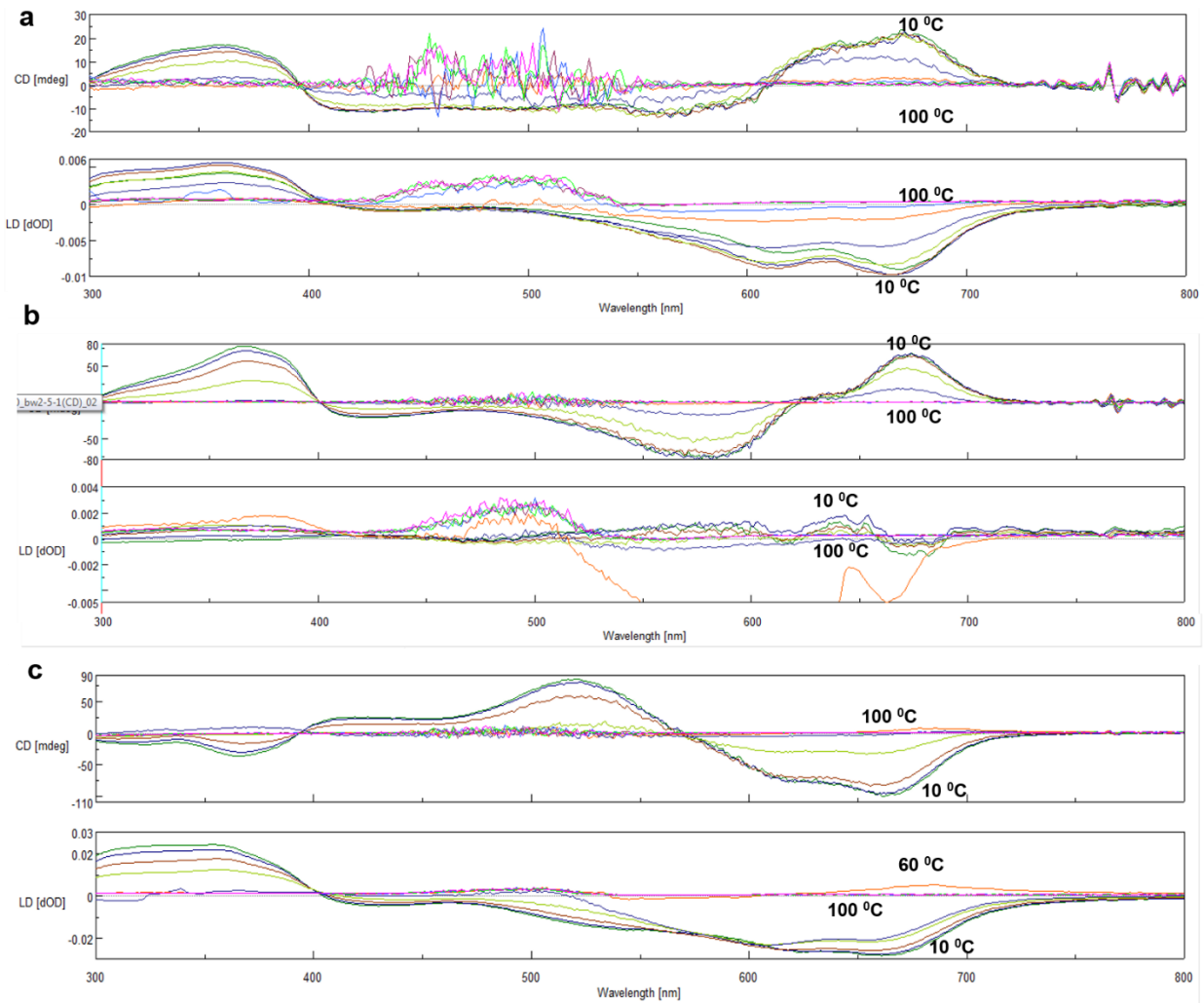


Figure S6. Temperature-dependent CD and LD spectra for 7b in: a) toluene; b) toluene/chloroform (20/1) and c) toluene/chloroform (9/1) . All the samples were analysed at c = 1.25 mg/ml.

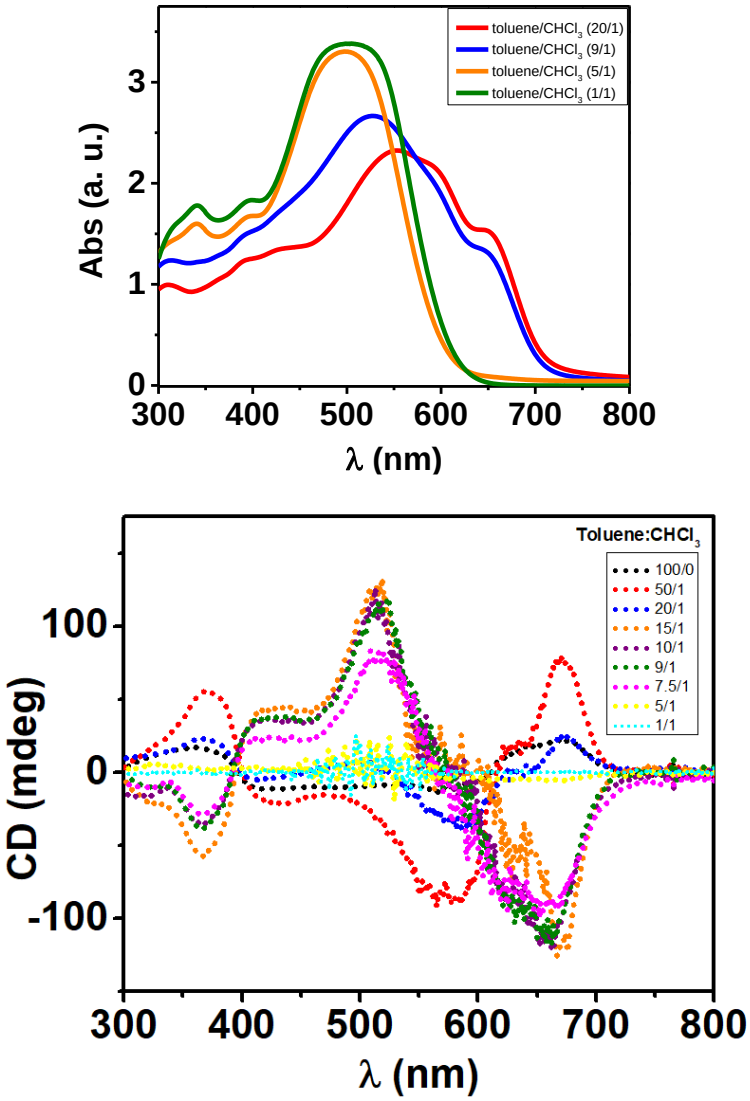


Figure S7. Absorption and CD spectra for **7b** in mixtures of toluene and chloroform (c = 1.25 mg/ml).

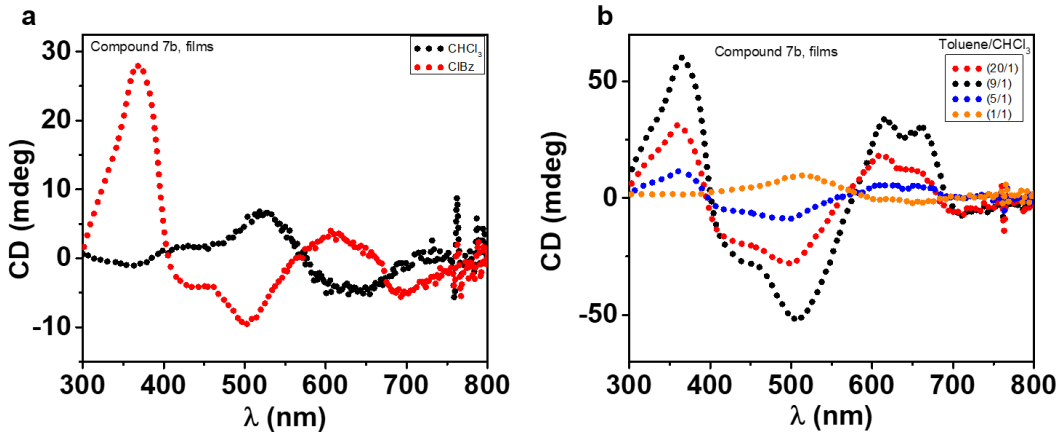


Figure S8. CD spectra obtained from drop cast films prepared from solutions of compound **7b** in: a) chlorobenzene and chloroform; b) different mixtures of toluene/chloroform.

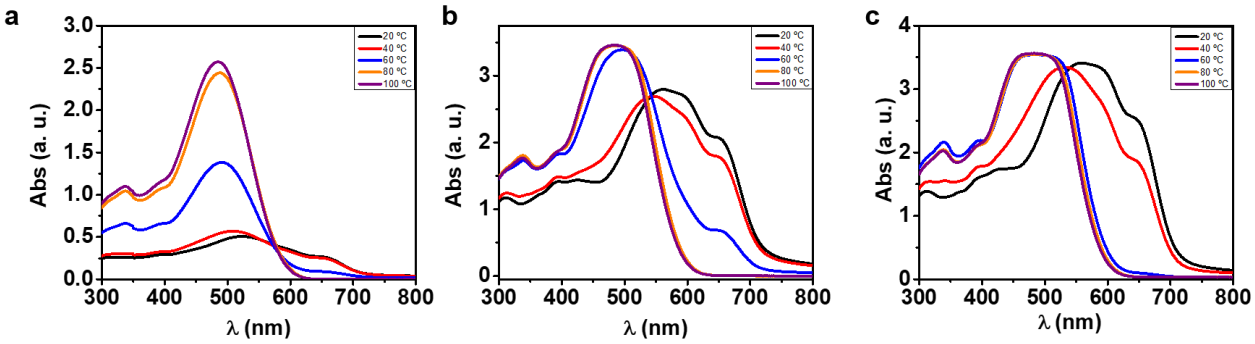


Figure S9. Absorption spectra at different temperatures for **7a** in: a) toluene (c = 0.83 mg/ml), b) toluene/chloroform (20/1) and c) toluene/chloroform (9/1) (c = 1.25 mg/ml).

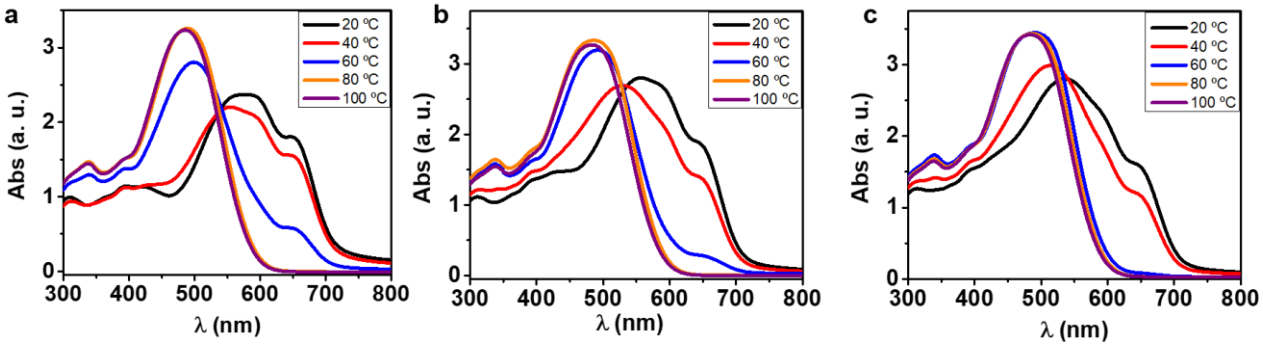


Figure S10. Absorption spectra at different temperatures for **7b** in: a) toluene (c = 0.83 mg/ml), b) toluene/chloroform (20/1) and c) toluene/chloroform (9/1) (c = 1.25 mg/ml).

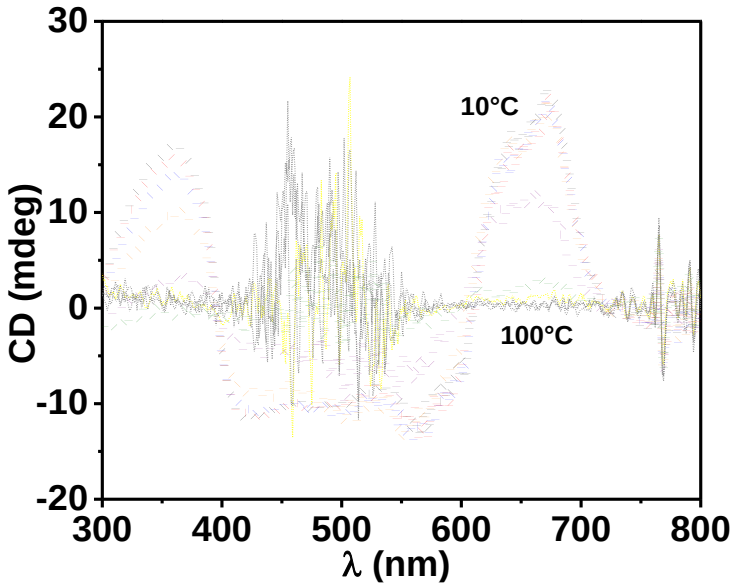


Figure S11. Temperature-dependent CD spectra in toluene at 1.25 mg/ml.

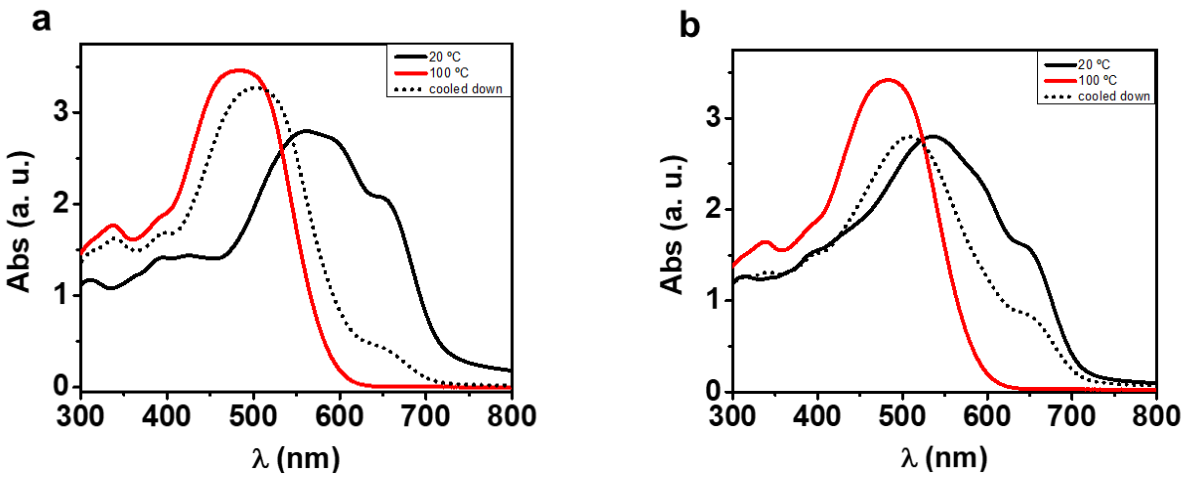


Figure S12. Absorption spectra for at 20 ºC, after heating at 100 ºC and once cooled down at 20 ºC (spectra acquired after 60 min) for a) **7a** in toluene/chloroform (20:1) and b) **7b** in toluene/chloroform (9:1). Concentration is 1.25 mg/ml in both cases.

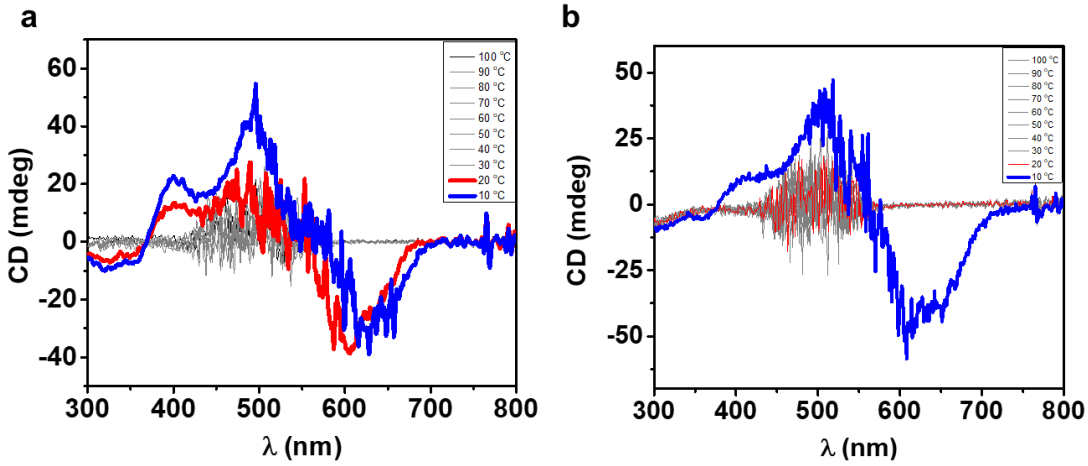


Figure S13. CD spectra of compound **7b** in a) toluene and b) toluene/chloroform (9/1) when cooling down from 100 ºC to 10 ºC at 1 ºC/min. Previously, samples were heated from 10 ºC to 100 ºC under the same conditions. Concentration is 1.25 mg/ml in both cases.

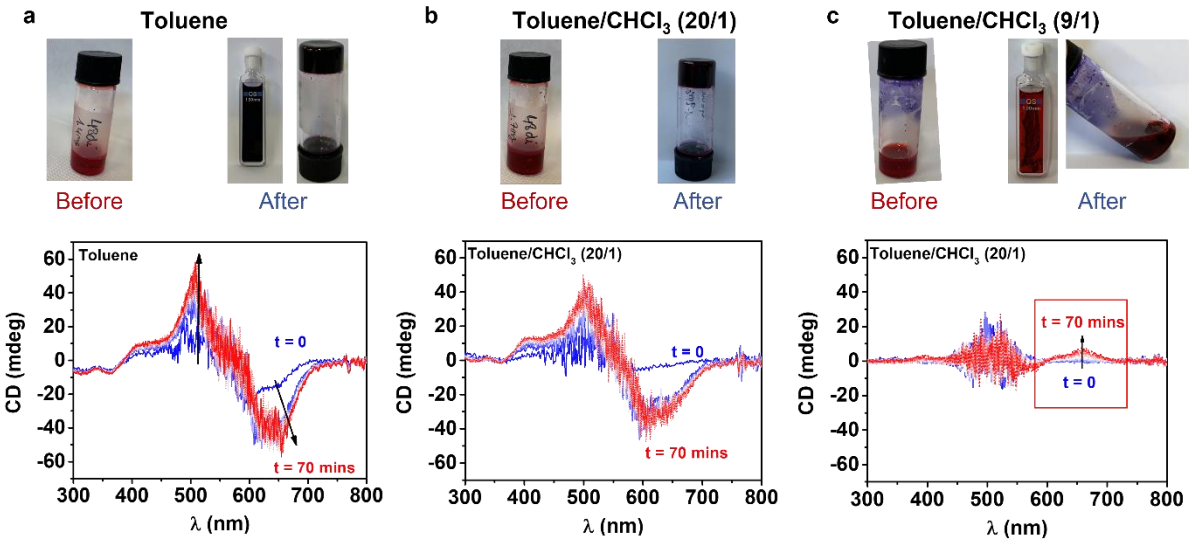


Figure S14. CD spectra of compound **7b** in a) toluene, b) toluene/chloroform (20/1) and c) toluene/chloroform (9/1) when sample where initially prepared by heating to start from the molecularly dissolved state (before picture). Spectra were recorded every 5 minutes for 70 minutes at room temperature. Concentration is 1.25 mg/ml in all the cases.

4. TEM

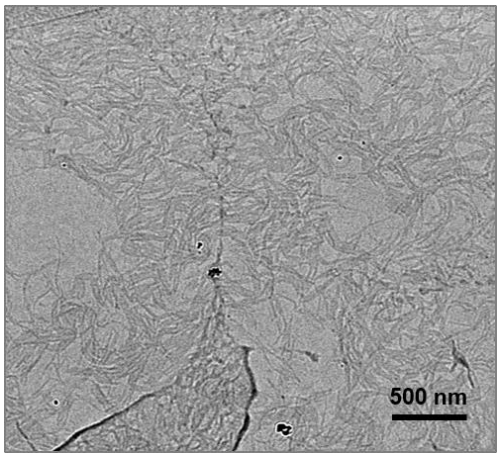


Figure S15. TEM micrographs of derivative **7b** freshly prepared in chloroform.

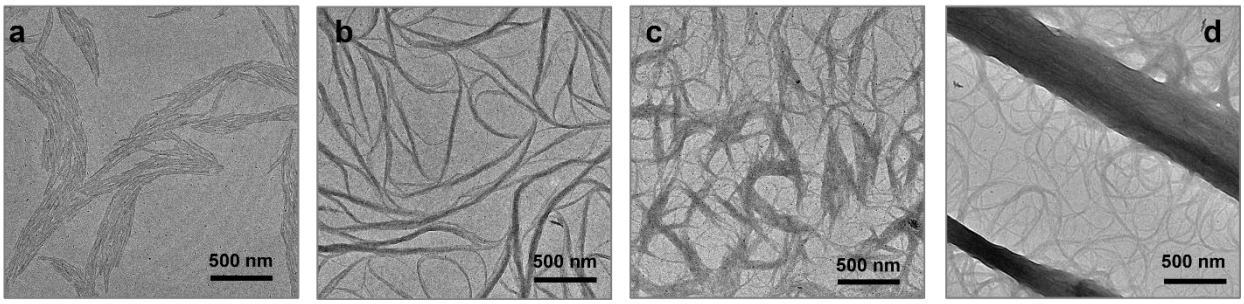


Figure S16. TEM micrographs of derivative **7a** freshly prepared in a) chloroform, b) chlorobenzene and c,d) toluene.

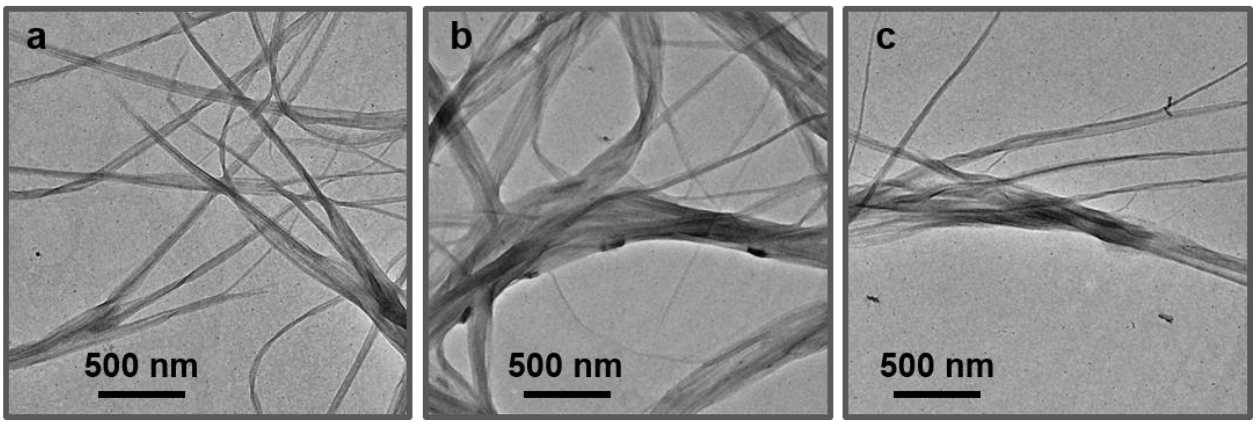


Figure S17. TEM micrographs of derivative **7b** freshly prepared in toluene.

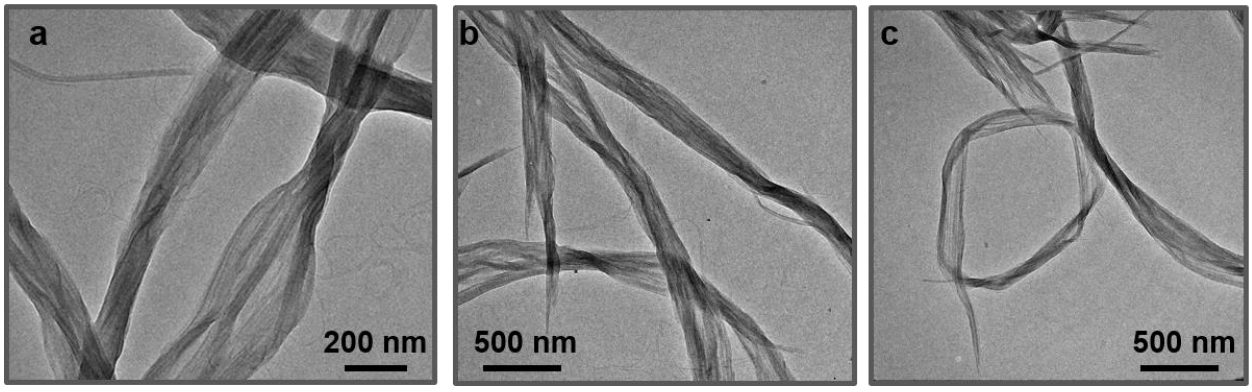


Figure S18. TEM micrographs of derivative **7b** freshly prepared in toluene/chloroform (20/1).

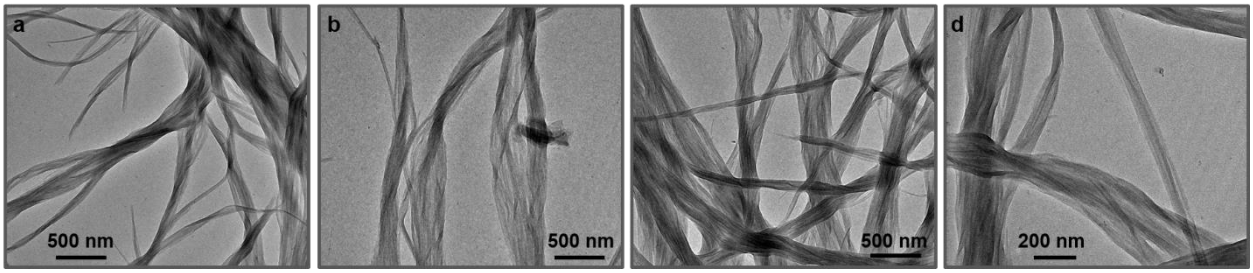


Figure S19. TEM micrographs of derivative **7b** freshly prepared in toluene/chloroform (9/1).

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