Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information

Morphological diversity of supramolecular polymers of DNA-containing oligopyrenes – Formation of chiroptically active nanosheets

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MATERIALS AND METHODS

Solvents and chemicals required for the synthesis were purchased from commercial suppliers (Aldrich, Glen Research or TCI) and used without further purification. All dilutions were carried out using MilliQ water. For AFM measurements, mica plates were purchased from Plano GmbH. For TEM measurements, Carbon Films on 300 Mesh Copper Grids from Agar Scientific were used. 5-(6-(5-(Bis(4-methoxyphenyl)(phenyl)methoxy)pent-1-ynyl)pyren-1-yl)pent-4-ynyl-2-cyanoethyl diisopropylphosphoramidite required for the solid-phase synthesis of oligophosphodiesters was prepared as previously reported[1].

Synthesis of oligophosphodiesters OP1-OP20

Oligophosphodiesters **OP1N-OP20** were synthesized on a 1 µmol scale using the standard cyanoethyl phosphoramidite DNA solid phase synthesis approach on an ABI 394 (Applied Biosystems Instruments) automated synthesizer.[1] dG-CPG 500, dC-CPG 500, dG-CPT 500 and dA-CPG 500 were used as a solid support. Cleavage was achieved by treating the support with 0.9 ml of 28% aqueous ammonia (for **OP3**-**OP20**) or 0.9 ml 28% aqueous ammonia and 0.1 ml of ethanol (for **OP1N** and **OP2N**) at 55 °C in a closed vial with vigorous shaking for 16 hours. After cooling, the solid support was separated from the supernatant by centrifugation. The supernatant was lyophilized; remaining solid was dissolved in 2 ml of the mobile phase A, passed through a 0.45 µm membrane filter, and finally HPLC purified on a C_8 column using triethylammonium acetate buffer (TEAA) and acetonitrile as eluents at a flow rate of 1 ml/min at 55 °C. The purity of the oligomers was confirmed by HPLC traces and mass spectrometry.

HPLC Purification

HPLC purification was carried out on a Shimadzu HPLC system using Reprosil 100 C_8 250 x 4 mm column. Mobile phase A: 0.1 M triethylammonium acetate (TEAA) buffer (pH 7.0) and HPLC grade acetonitrile in 80/20 v/v. Mobile phase B: Acetonitrile (HPLC grade). Detection was carried out using a Shimadzu SPD-10A UV/Vis Detector, monitoring the intensity of absorbance at 360 nm.

Sample preparation

Supramolecular polymers from **OP1N-OP20** were prepared according to the following procedure: required aliquots of 100 mM PBS buffer, 5 M sodium chloride and an oligomer were added to a 500 µL cuvette containing a calculated quantity of MilliQ water to achieve desired concentrations of all components. The mixtures were heated to 90 °C in a conventional heating block thermostat and were cooled to 20 °C at a controlled rate of 0.1 °C/min.

Spectroscopic measurements

Absorption spectra were recorded on a Varian Cary-300 Bio-UV/VIS. Fluorescence data were collected on a Varian Cary Eclipse fluorescence spectrofluorometer at an excitation wavelength of 365 nm. For the CD measurements, a JASCO J-715 spectropolarimeter was used. All measurements were performed in quartz cuvettes with an optical path of 1 cm.

Transmission Electron Microscopy (TEM) Measurements

Experiments were performed on an FEI Tecnai Spirit device, using an operating voltage of 80 kV. For sample preparation, a drop (5 µl) of the solution was placed onto a copper grid coated with carbon. After 5 minutes, the grid was washed with a drop of distilled water. Then a drop of aqueous uranyl acetate solution (0.8%) was added onto the copper grid. After 1 min, the excess stain was removed by tapping the grid with filter paper and the grid was dried at room temperature.

Atomic Force Microscopy (AFM) Measurements

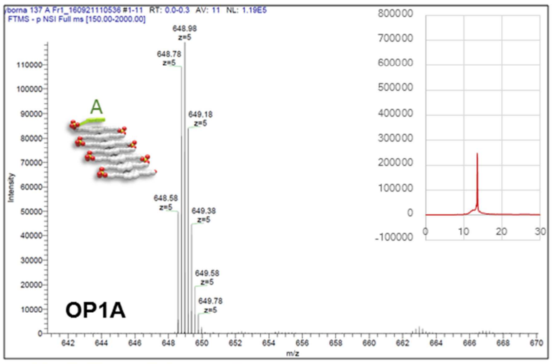
AFM imaging was acquired with a Nanosurf FlexAFM using Tap190Al-G cantilevers from BudgetSensors (resonance frequency ≈ 190 kHz, force constant = 48 N/m). Sample preparation included deposing 20 µl of the supramolecular polymer solution in buffer (10 mM PBS PH 7.0 and oligomer-dependent sodium chloride concentration) onto an APTES-modified mica plate. After 5 min incubation, the samples were rinsed with 5 ml of distilled water. All images were recorded using a soft tapping mode.

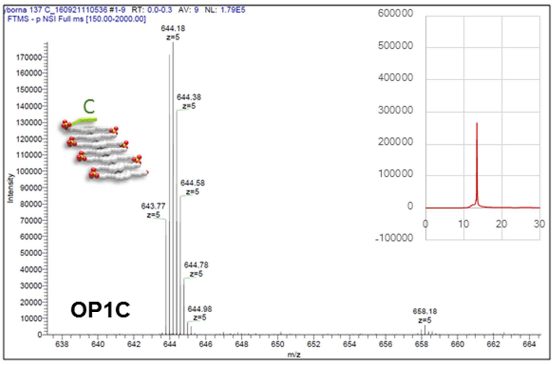
LIST OF SEQUENCES

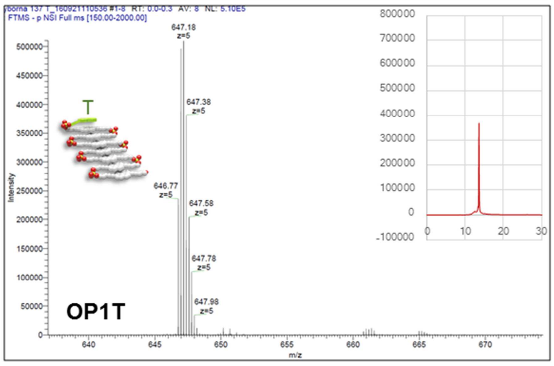
Code	Sequence	Theor. mass	Exp. mass
OP1G	5´-Py_7-G-3´	3263.1	3263.9
OP1A	5´-Py_7-A-3´	3247.1	3247.9
OP1C	5´-Py_7-C-3´	3223.1	3223.8
OP1T	5´-Py_7-T-3´	3238.1	3238.8
OP2G	5´-Py_7-GG-3´	3592.3	3592.9
OP2A	5´-Py_7-AG-3´	3576.3	3576.9
OP2C	5´-Py_7-CG-3´	3552.3	3552.9
OP2T	5´-Py_7-TG-3´	3567.3	3567.9
OP3	5´-Py_7-CTG-3´	3856.5	3856.9
OP4	5´-Py_7-CTTG-3´	4160.7	4161.0
OP5	5´-Py_7-CTT CG-3´	4449.9	4450.0
OP10	5’-Py_7-CTT CCG TGA G - 3’	6014.9	6014.3
OP14	5´-Py_7-CTG T CAC GAG TCA G-3´	7259.7	7258.5
OP20	5’-Py_7-(CTT CCG TGA G)$_2$ - 3’	9095.8	9095.8

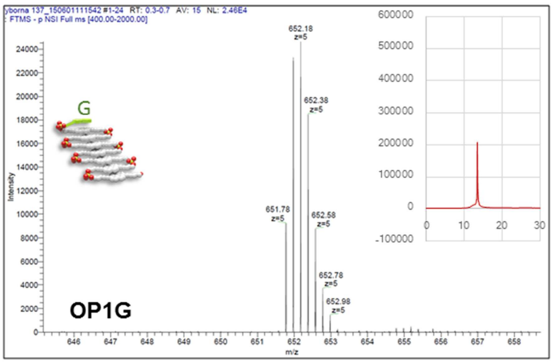
CHARACTERIZATION OF OLIGOMERS

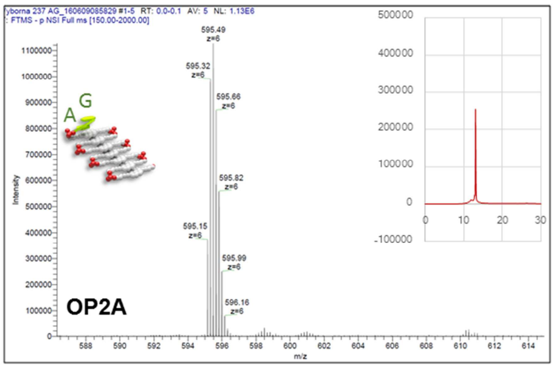
Mass spectrometry and HPLC analysis of the synthesized oligomers

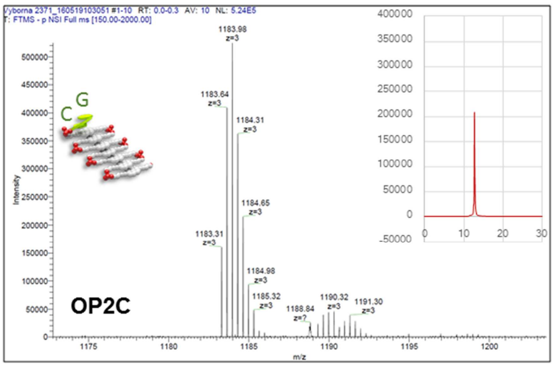


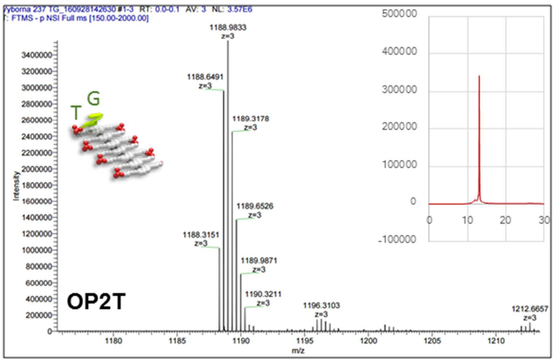


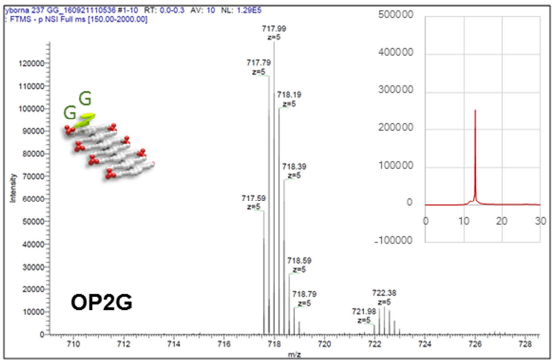


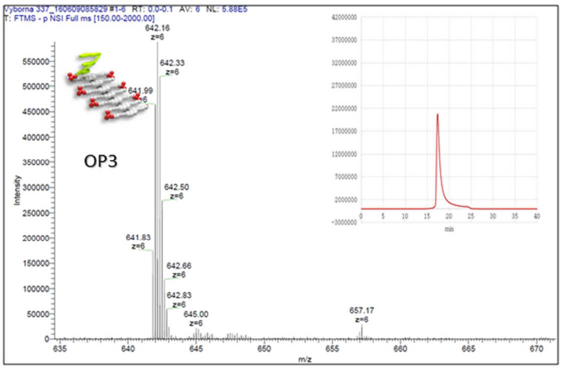








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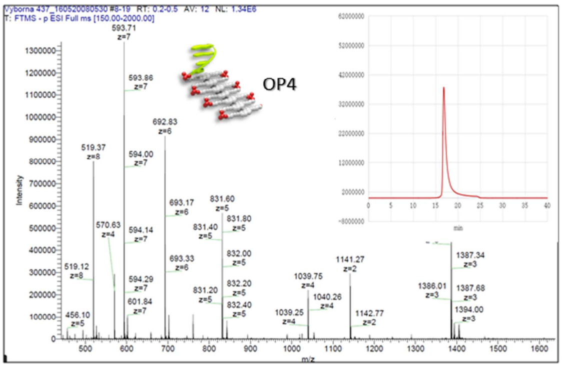
OP3
642.16 z=6
642.33 z=6
641.99 z=6
642.50 z=6
641.83 z=6
642.66 z=6
642.83 z=6
645.00 z=6
657.17 z=6
Intensity
m/z
min


Vyborna 437_160520080530 #8-19 RT: 0.2-0.5 AV: 12 NL: 1.34E6
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OP4
593.71 z=7
593.86 z=7
692.83 z=6
519.37 z=8
594.00 z=7
693.17 z=6
831.60 z=5
831.80 z=5
831.40 z=5
570.63 z=4
594.14 z=7
832.00 z=5
693.33 z=6
1141.27 z=2
1387.34 z=3
519.12 z=8
594.29 z=7
1039.75 z=4
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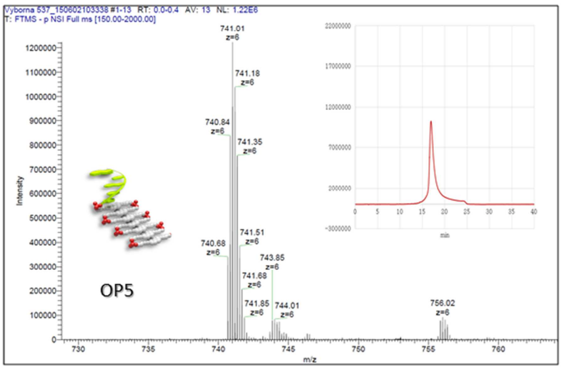
Intensity
m/z
min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OP5
741.01 z=6
741.18 z=6
740.84 z=6
741.35 z=6
741.51 z=6
740.68 z=6
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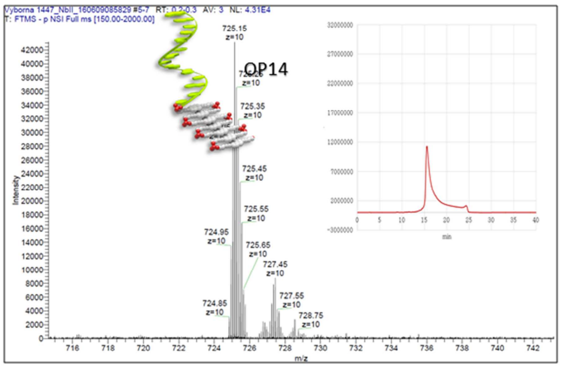
756.02 z=6
Intensity
m/z
min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OP14
725.15 z=10
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725.55 z=10
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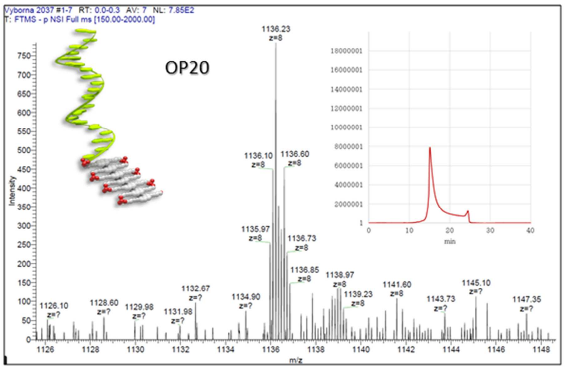
Intensity
m/z
min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OP20
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1135.97 z=8
1136.73 z=8
1136.85 z=8
1138.97 z=8
1139.23 z=8
1141.60 z=8
1145.10 z=?
1143.73 z=?
1147.35 z=?
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1126.10 z=?
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Intensity
m/z
min

Spectroscopic characterization of the OP1-OP20 supramolecular polymers

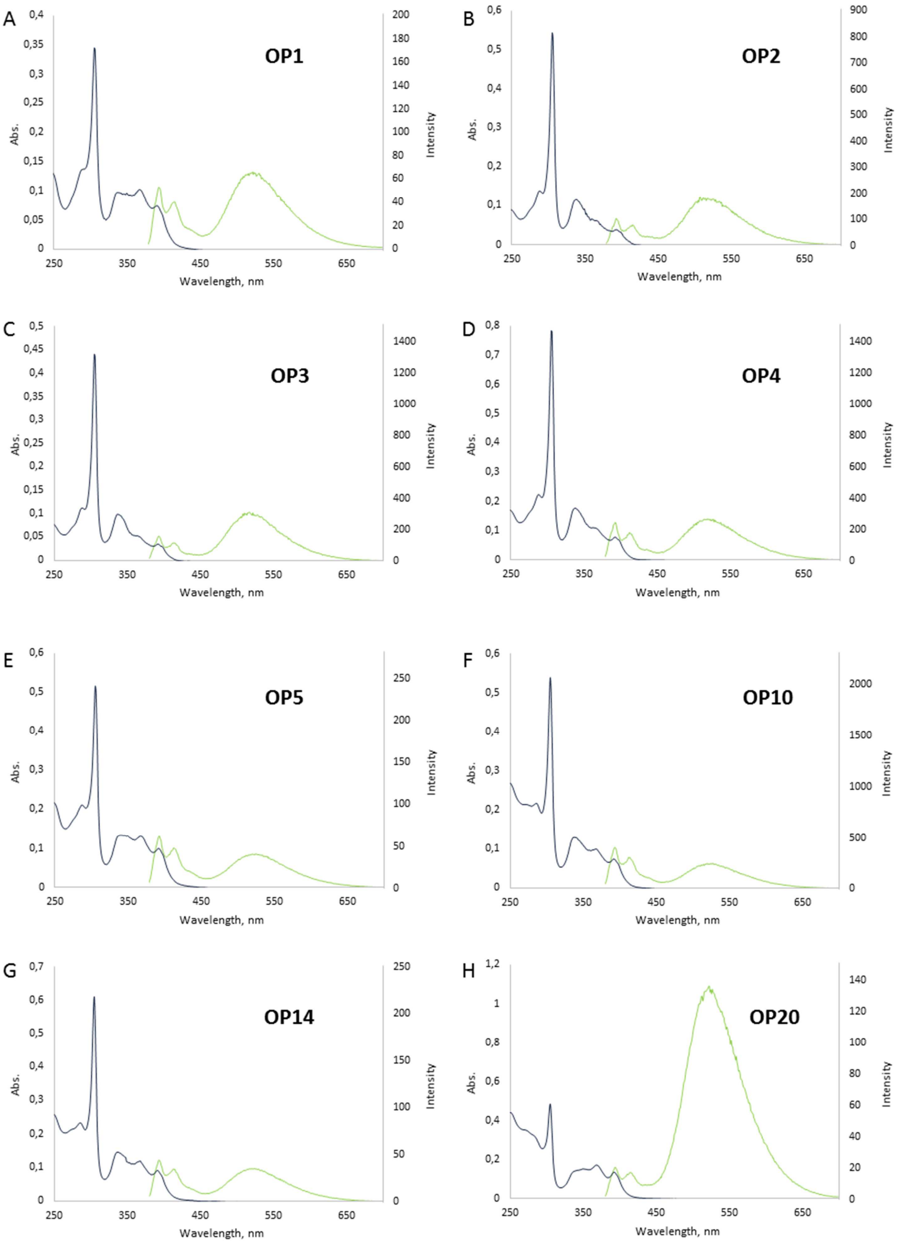
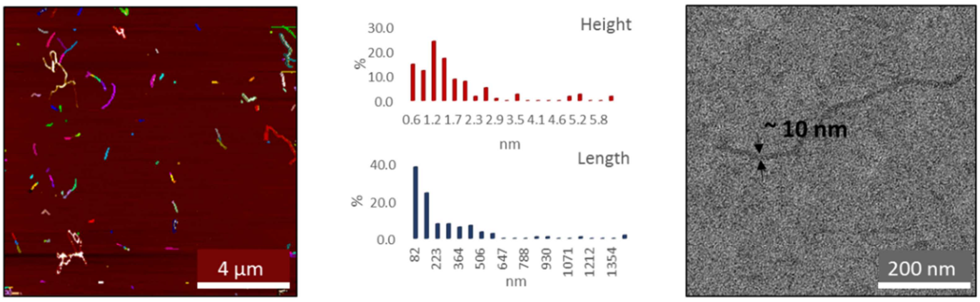


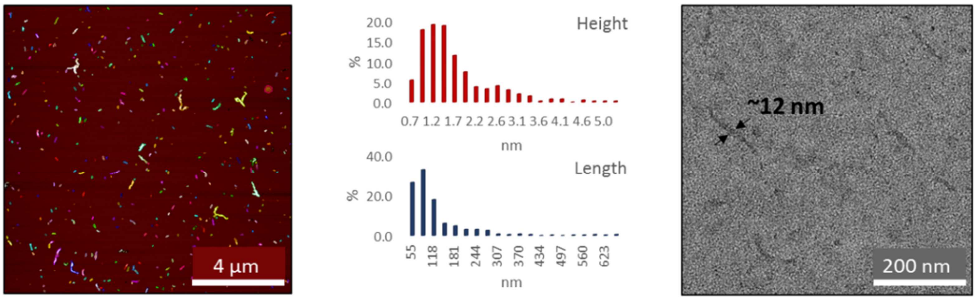
Figure S1. UV/vis absorption (dark blue) and corresponding fluorescence spectra (green) of **OPn** in aqueous media at 20°C (10 mM PBS buffer, pH=7, and variable sodium chloride: 10 mM for **OP1Nb**, 100 mM for **OP2Nb**, 100 for **OP3**, 150 mM for **OP4**, 200 mM for **OP5**, 250 mM for **OP10**, 250 mM for **OP14**, 350 mM for **OP20**).

Particle analysis of the supramolecular polymers

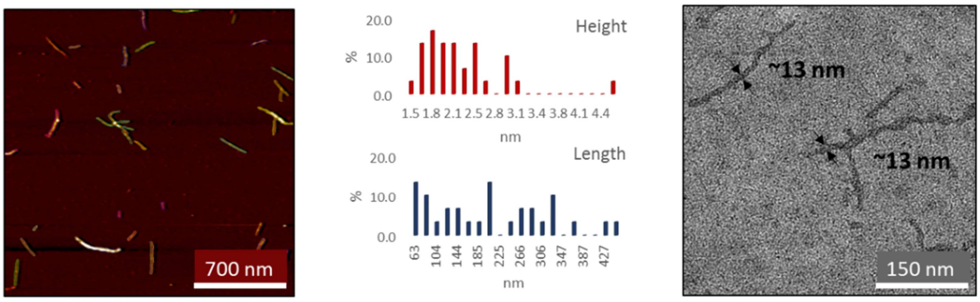
OP2



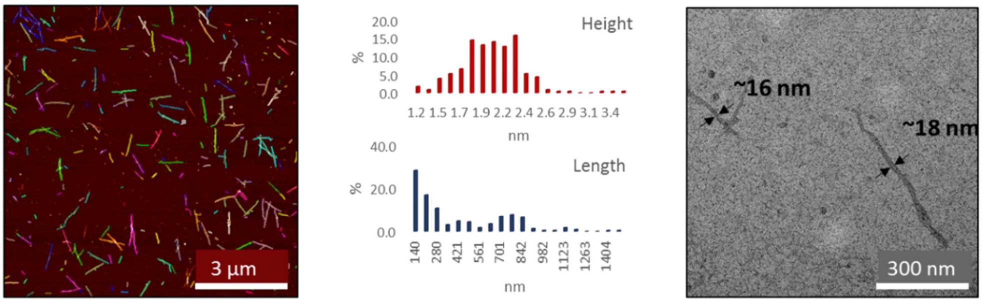
OP3



OP4



OP5



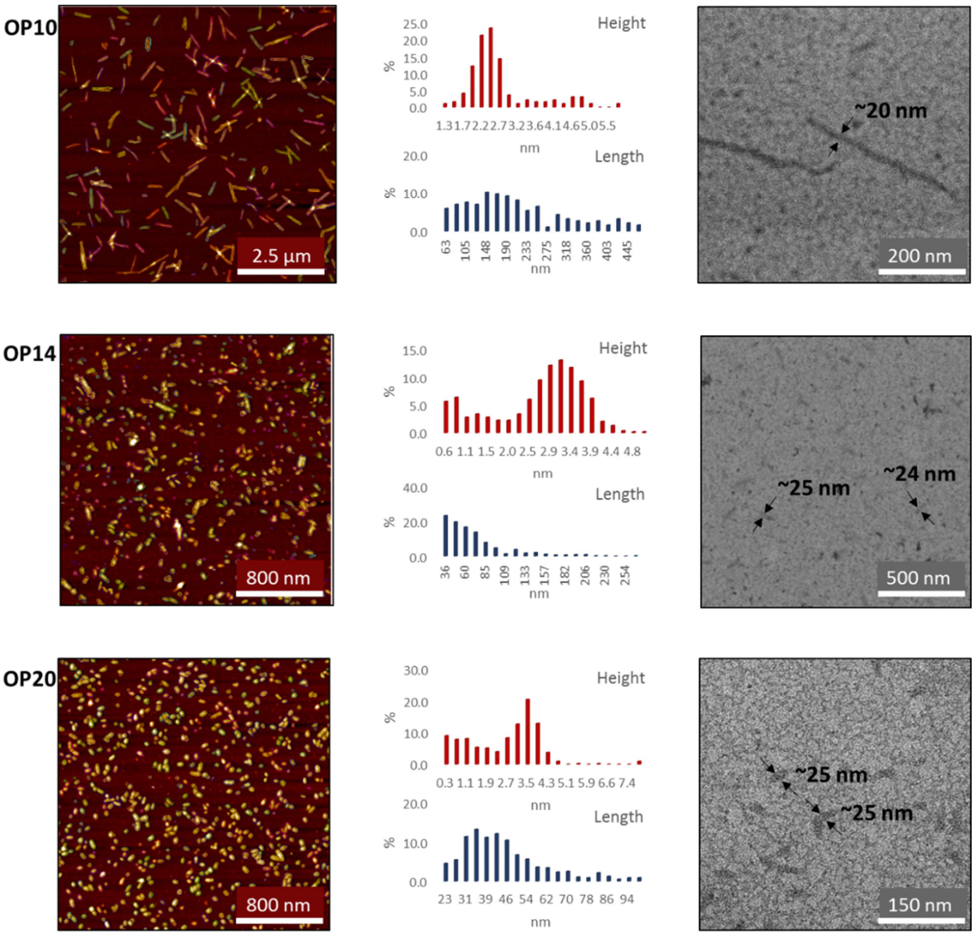


Figure S2. AFM images (left), corresponding height and length analysis (middle) and TEM images (right) for the supramolecular polymers

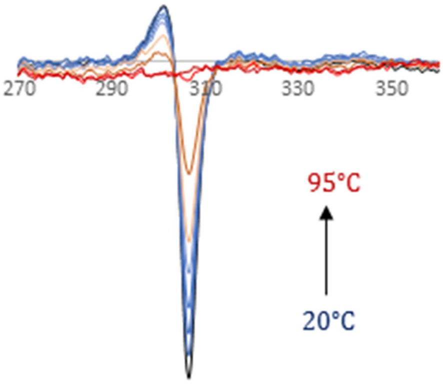


Figure S3. Temperature-dependent CD spectra for 2µM **OP1G** upon heating from 20 °C (black) to 95 °C (red) in 10 °C steps. Conditions: 10 mM PBS, pH=7, 10 mM sodium chloride.

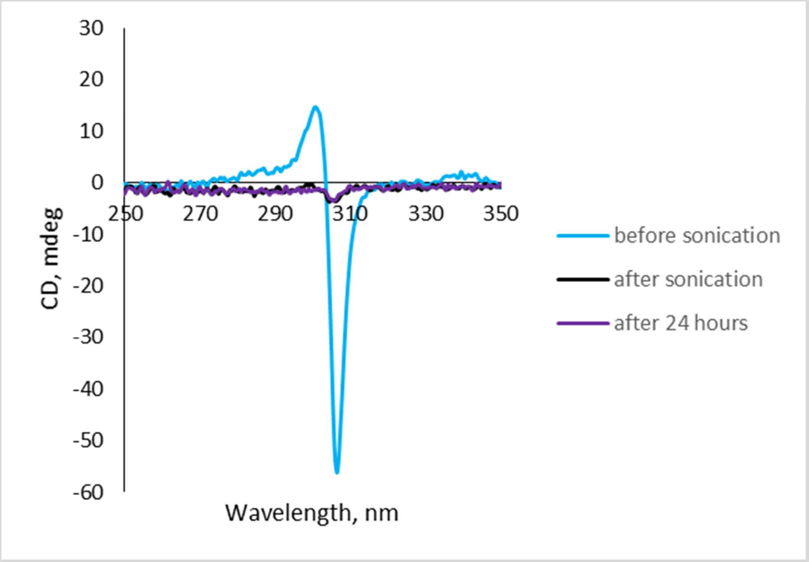


Figure S4. Effect of sonication (Elmasonic S30; 30 min treatment at room temperature) on the CD spectrum of Temperature-dependent CD spectra for 2µM **OP1G**. Conditions: 10 mM PBS, pH=7, 10 mM sodium chloride.

(1) Vybornyi, M.; Rudnev, A. V.; Langenegger, S. M.; Wandlowski, T.; Calzaferri, G.; Häner, R. *Angew. Chemie - Int. Ed.* **2013**, *52* (44), 11488.