

Supplementary Information

**Solution phase synthesis of 1D tubular polymers via
preorganization-polymerization**

Hao Yu, Robert Häner*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012
Bern, Switzerland

*email: robert.haener@dcb.unibe.ch

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1. Materials and methods

1.1. General methods

1.1.1 Synthesis and characterization of compounds

All chemical reagents and solvents were purchased from commercial suppliers (Aldrich, Alfa Aesar or TCI) and used without further purification. Water was obtained from a MilliQ system. The silica gel for the column chromatography had 60 Å pore size, 230 – 400 mesh. Unless otherwise specified, all reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Glasswares were dried in an oven at 110 °C. All synthesized compounds were stored at 0 °C under Ar. NMR spectra were obtained on a Bruker AV 300 (300 MHz) spectrometer at 298 K. Mass data were obtained on Thermo Fisher LTQ Orbitrap XL using Nano Electrospray Ionization.

1.1.2. Solid-phase synthesis

All required reagents and products were purchased from Glen Research (solid support, columns) or Proligo® Reagents (Cap A, Cap B, 0.02 M I₂/THF/Py, TCA deblock, DCI activator).

1.1.3. Spectroscopic measurements

UV-vis spectra were recorded on an optical path of 1 cm over the range of 200 – 800 nm on a Varian Cary-100 Bio-UV/VIS spectrophotometer equipped with a Varian Cary-block temperature controller. Fluorescence data were collected on the Varian Cary Eclipse fluorescence spectrofluorimeter equipped with the Varian Cary-block temperature controller. For the CD measurements a JASCO J-715 spectropolarimeter was used. Unless otherwise mentioned the following settings of the instrument were used: the slit width 5 nm for emission and excitation, medium sensitivity of the detector. The

concentration of monomer **ANT3** was determined using a value of $\varepsilon^{411} = 142800 \text{ dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$ in buffer.

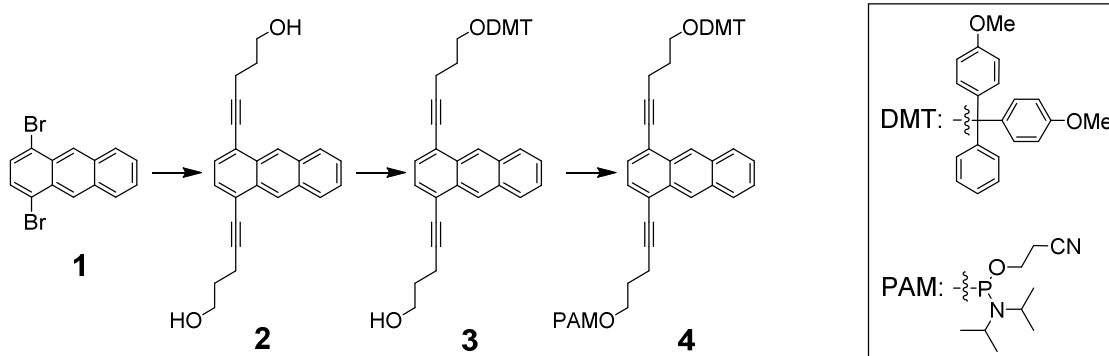
1.1.4. AFM and TEM experiments

AFM measurements. AFM images were obtained under ambient conditions in air with a Nanosurf FlexAFM (Nanosurf AG, Switzerland) instrument using either a $100 \times 100 \mu\text{m}^2$ scanning head. The measurements were carried out in tapping mode employing Tap190Al-G from BudgetSensors (resonance frequency $\sim 190 \text{ kHz}$, force constant 48 N/m). Cantilevers in different batches gave reproducible results. Sample preparation: a $3 \mu\text{L}$ aliquot of **1D-SP** or **1DP** solution in corresponding solvent and concentration was placed on an APTES-modified mica plate ($20 \times 20 \text{ mm}^2$). The mica plates were fixed on a holder and used for AFM studies. After 5 min, the plate was rinsed with Milli-Q water ($0.5 \text{ ml} \times 3$) and dried under a stream of Ar for 10 min.

TEM measurements. Experiments were performed on an FEI Tecnai Spirit device, using an operating voltage of 80 kV. Sample preparation: a $5 \mu\text{L}$ aliquot of the polymer solution in corresponding solvent and concentration was placed on a carbon-coated copper grid (S160-3, 300 mesh Cu, AgarScientific). After 5 min, the remaining solution was blotted with a filter paper and Milli-Q water ($5 \mu\text{L}$) was added. After 1 min, the water was blotted and 0.5 % aqueous uranyl acetate ($5 \mu\text{L}$) was added, which was blotted again after waiting for 5 min. The sample was then used for the measurements.

1.2. Synthesis and characterization

1.2.1. Synthetic procedures for phosphoramidite 4



Scheme S1. Synthetic route to phosphoramidite **4**.

Compound **2**

Compound **1** was synthesized according to reported procedures^{1,2}. To a refluxed solution of **1** (806 mg, 2.40 mmol), Pd(PPh₃)₄ (111 mg, 0.096 mmol), PPh₃ (31 mg, 0.12 mmol), CuI (28 mg, 0.144 mmol) and TEA (2.5 mL) in THF (25 mL) under N₂, was added 4-pentyn-1-ol (505 mg, 6.00 mmol). The reaction mixture was refluxed for 22 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (DCM followed by 5% MeOH/DCM) to afford **2** (500 mg, 61%) as yellow needles.

¹H NMR (300 MHz, CDCl₃) δ : 8.88 (*s*, 2H), 8.06-8.09 (*dd*, *J* = 3.0 Hz, 2H), 7.55 (*s*, 2H), 7.50-7.53 (*dd*, *J* = 3.0 Hz, 2H), 3.92-3.98 (*q*, *J* = 6.0 Hz, 4H), 2.77-2.83 (*t*, *J* = 6.0 Hz, 4H), 1.99-2.08 (*p*, *J* = 6.0 Hz, 4H), 1.50-1.53 (*t*, *J* = 3.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ : 132.23, 131.06, 129.26, 128.58, 126.16, 125.71, 121.77, 96.31, 79.60, 62.05, 31.79, 16.68.

HRMS: *m/z* for C₂₄H₂₂O₂, calcd 342.1614; found 342.1608.

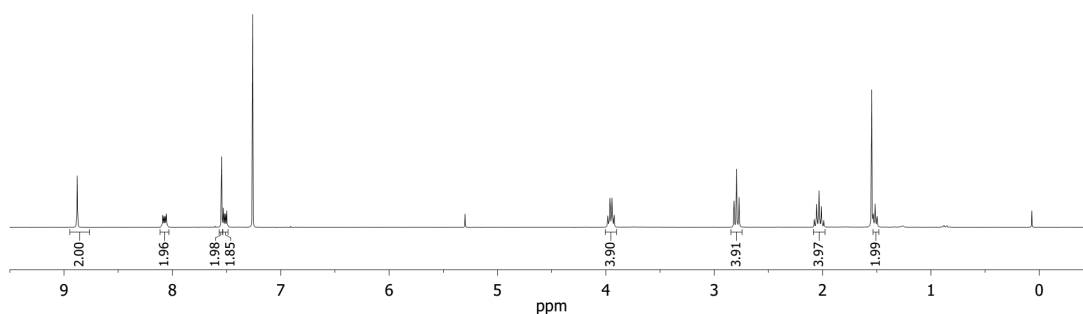


Figure S1. ^1H NMR spectrum of **2** in CDCl_3 at room temperature.

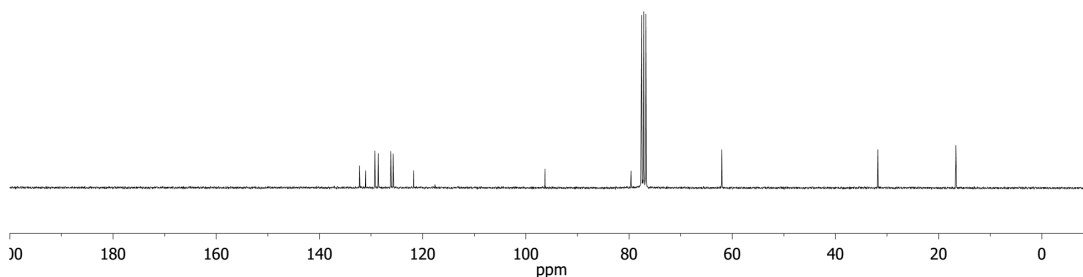


Figure S2. ^{13}C NMR spectrum of **2** in CDCl_3 at room temperature.

Compound **3**

To a solution of **2** (440 mg, 1.28 mmol), DMAP (8 mg, 0.064 mmol) and TEA (2 mL) in dry DCM (15 mL) under N_2 at room temperature, a solution of 4,4'-dimethoxytrityl chloride (653 mg, 1.93 mmol) in dry DCM (5 mL) was added over a period of 50 min. The reaction mixture was stirred for 1 h in total. The solvent was removed at 27°C under reduced pressure. The residue was purified by silica gel column chromatography (1% MeOH/DCM followed by 5% MeOH/DCM, with 1% TEA) to yield **3** (417 mg, 50%) as yellow foams.

^1H NMR (300 MHz, CDCl_3) δ : 8.87 (*s*, 1H), 8.81 (*s*, 1H), 8.05-8.08 (*d*, $J = 9.0$ Hz, 1H), 7.94-7.97 (*d*, $J = 9.0$ Hz, 1H), 7.42-7.53 (*m*, 6H), 7.35-7.38 (*d*, $J = 9.0$ Hz, 4H), 7.11-7.28 (*m*, 3H), 6.75-6.78 (*d*, $J = 9.0$ Hz, 4H), 3.92-3.98 (*q*, $J = 6.0$ Hz, 2H), 3.66 (*s*, 6H), 3.33-

3.37 (*t*, $J = 6.0$ Hz, 2H), 2.77-2.85 (*m*, 4H), 1.99-2.09 (*p*, $J = 6.0$ Hz, 4H).

^{13}C NMR (75 MHz, CDCl_3) δ : 158.51, 145.50, 136.66, 131.06, 130.21, 129.29, 129.21, 128.65, 128.53, 128.36, 127.89, 126.12, 126.07, 122.06, 121.52, 113.18, 96.93, 96.17, 86.05, 79.66, 79.37, 62.08, 55.24, 31.82, 29.68, 17.26, 16.70.

HRMS: m/z for $\text{C}_{24}\text{H}_{22}\text{O}_2$, calcd 644.2921; found 644.2907.

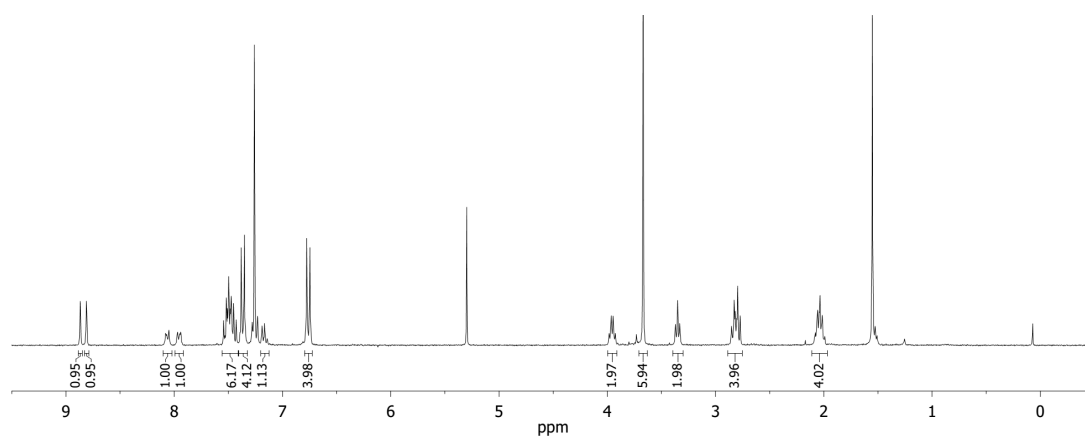


Figure S3. ^1H NMR spectrum of **3** in CDCl_3 at room temperature.

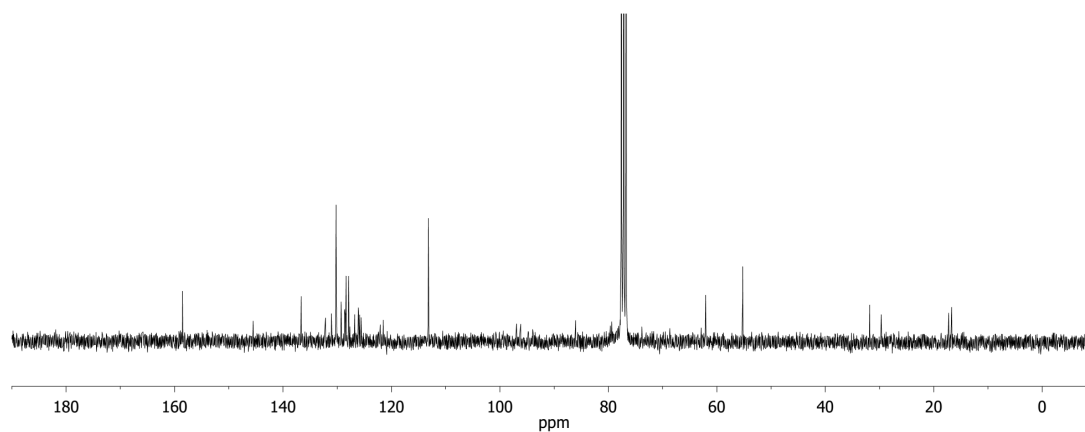


Figure S4. ^{13}C NMR spectrum of **3** in CDCl_3 at room temperature.

Phosphoramidite **4**

To a solution of **3** (226 mg, 0.35 mmol) and DIPEA (0.5 mL) in dry DCM (6 mL) under N₂ at room temperature, 2-cyanoethyl-N,N-diisopropylchlorophosphoramidite (108 mg, 0.46 mmol) was added. The reaction mixture was stirred for 1 h in total. The solvent was removed at 29 °C on under reduced pressure. The residue was purified by silica gel column chromatography (33% EA/hexane, with 1% TEA) to yield **4** as pale yellow foams (220 mg, 74%).

¹H NMR (300 MHz, CDCl₃) δ: 8.87 (*s*, 1H), 8.81 (*s*, 1H), 8.07-8.10 (*d*, *J* = 9.0 Hz, 1H), 7.95-7.98 (*d*, *J* = 9.0 Hz, 1H), 7.42-7.53 (*m*, 7H), 7.35-7.38 (*d*, *J* = 9.0 Hz, 4H), 7.11-7.28 (*m*, 2H), 6.75-6.78 (*d*, *J* = 9.0 Hz, 4H), 3.90-4.00 (*m*, 2H), 3.67 (*m*, 8H), 3.33-3.37 (*t*, *J* = 6.0 Hz, 2H), 2.75-2.83 (*m*, 4H), 2.61-2.66 (*m*, 2H), 1.99-2.09 (*m*, 4H), 1.20-1.22 (*d*, *J* = 6.0, 12H).

¹³C NMR (75 MHz, CDCl₃) δ: 158.52, 145.50, 136.66, 132.20, 132.15, 131.08, 131.05, 130.22, 129.30, 129.24, 128.66, 128.53, 128.37, 127.89, 126.78, 126.09, 122.21, 121.96, 113.18, 96.89, 96.24, 86.05, 79.52, 79.38, 62.69, 62.05, 58.69, 5.24, 43.39, 43.22, 30.74, 29.69, 24.87, 24.76, 20.60, 20.51, 17.27, 16.82.

³¹P NMR (122 MHz, CDCl₃) δ: 148.02.

HRMS: *m/z* for C₅₄H₅₈N₂O₅P, calcd 845.4078; found 845.4077.

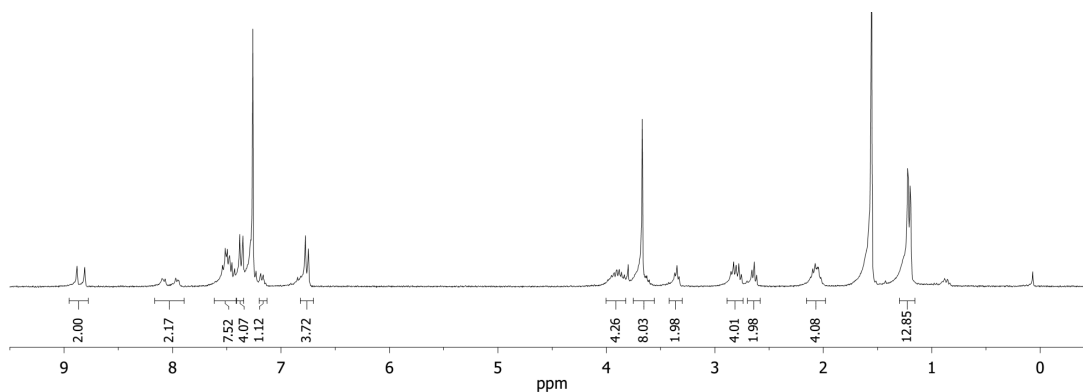


Figure S5. ¹H NMR spectrum of **4** in CDCl₃ at room temperature.

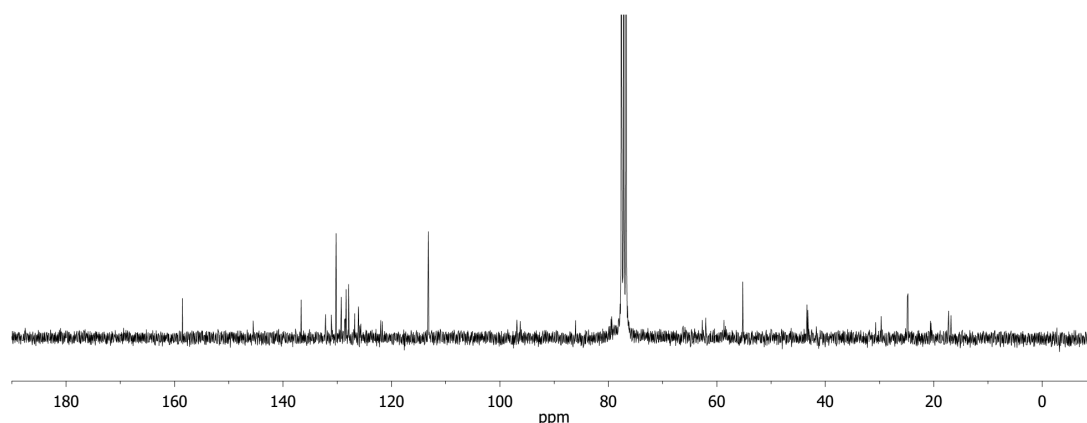


Figure S6. ^{13}C NMR spectrum of **4** in CDCl_3 at room temperature.

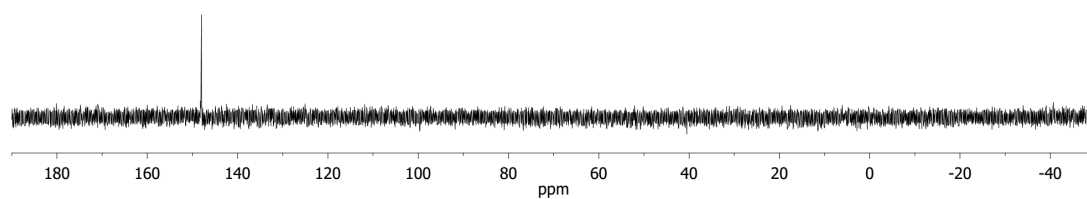


Figure S7. ^{31}P NMR spectrum of **4** in CDCl_3 at room temperature.

1.2.2. Solid-phase synthesis of monomer ANT3

Synthesis

Monomer **ANT3** was synthesized on the Applied Biosystems 394 DNA synthesizer using preloaded support (Universal III CPG 1000). We followed a standard cyanoethyl phosphoramidite coupling protocol for the 1 μmol synthesis (“trityl-off” mode). The coupling yields per single step were $\geq 90\%$ (monitoring by “trityl assay”). The cleavage of monomer **ANT3** from the support was achieved by treatment with 1 ml of 2 M NH_3 (Aldrich) for 16 hours at 55 $^\circ\text{C}$ in a closed vial. The supernatant was separated from the support by centrifugation. The remained support were washed 3 times with 1 ml MeOH. All supernatants were collected and lyophilized.

Purification

The crude product was purified by reverse-phase HPLC (column: ResproSil 100 RP-C8, 5 μ m, Dr. Masch GmbH; HPLC: Shimadzu Schweiz GmbH); eluent A = Et₃NHOAc (100 mM, pH 7.2, with 10% MeOH); eluent B = CH₃CN; gradient 0 – 50% B over 2 min, 50 – 67% B over 5 min, then 67 – 100% B over 1 min. Gradient flow 1 ml/min. The pure compound was characterized by mass spectrometry.

HRMS: m/z for C₇₂H₆₂O₁₀P₂²⁻, calcd 574.1915; found 574.1916.

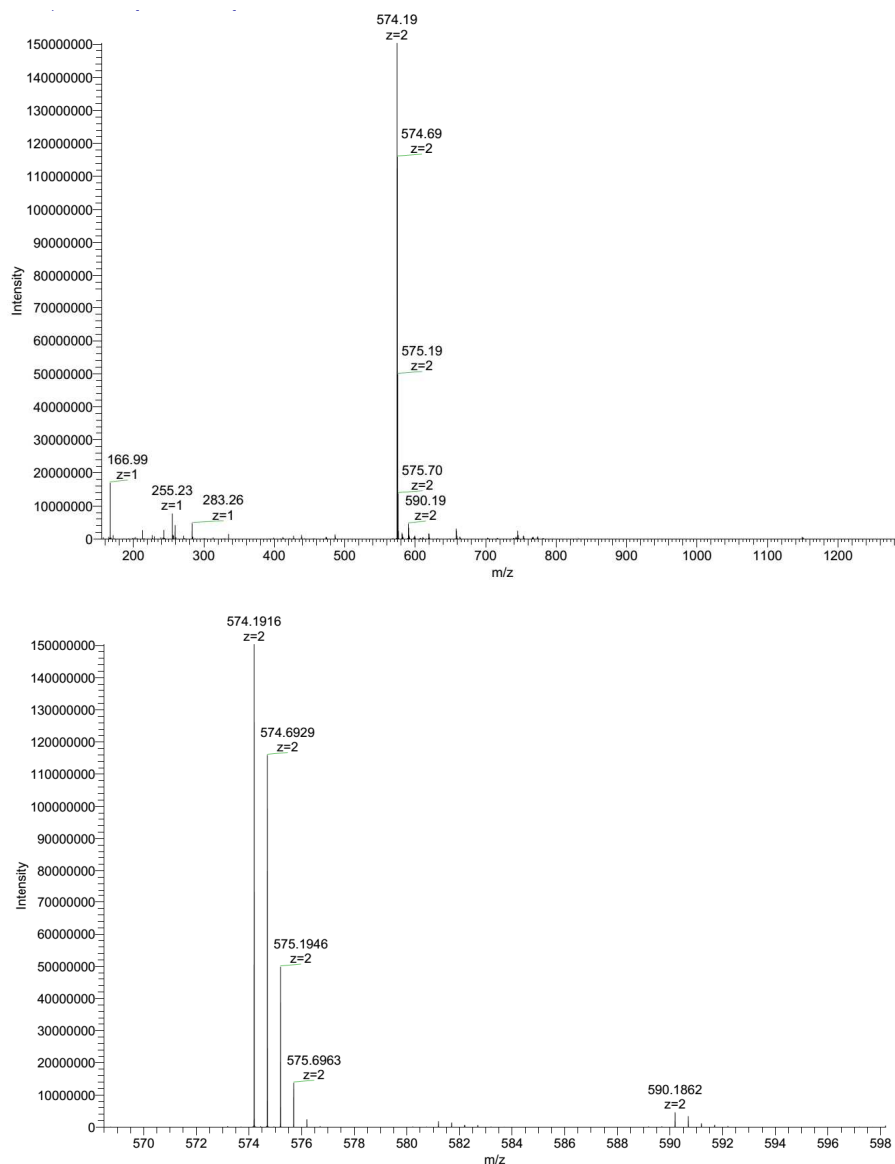


Figure S8. HRMS spectra of monomer ANT3.

Time (min)	Eluent A (%)	Eluent B (%)
0	100	0
2	50	50
7	33	67
8	0	100
11	0	100
12	50	50
16	50	50

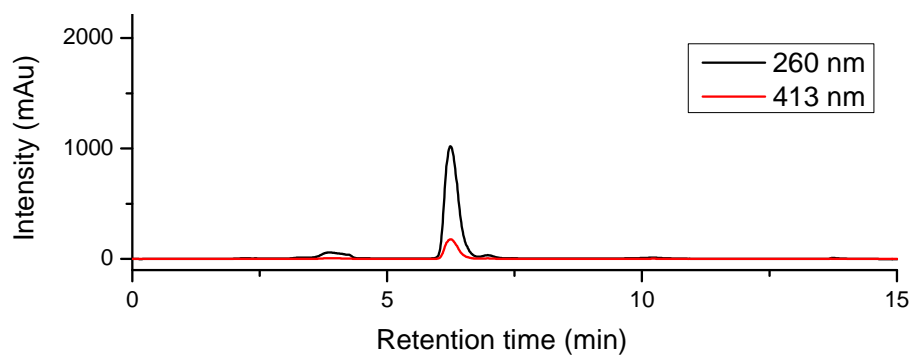


Figure S9. HPLC gradient table and HPLC analytical trace of purified monomer **ANT3**.

1.3. UV-vis and fluorescence spectra of 1D-SP

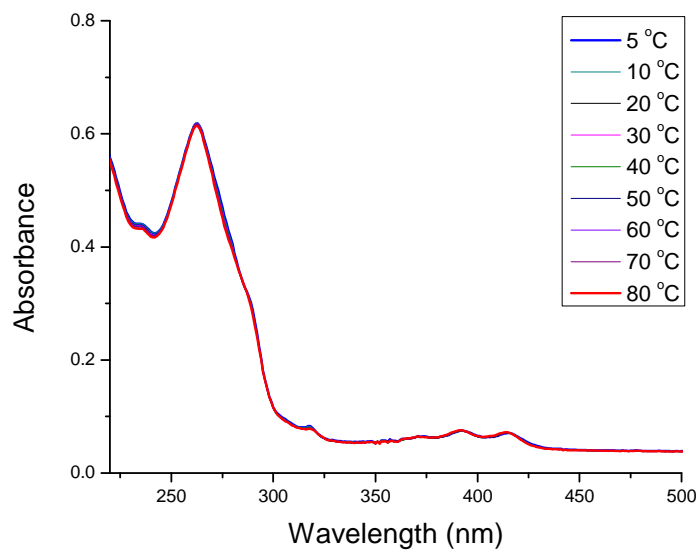


Figure S10. Temperature-variable UV-vis spectra of **1D-SP**. Conditions: 10 mM NaCl, 10 mM sodium phosphate buffer, pH 7.2, [ANT3] = 1 μ M.

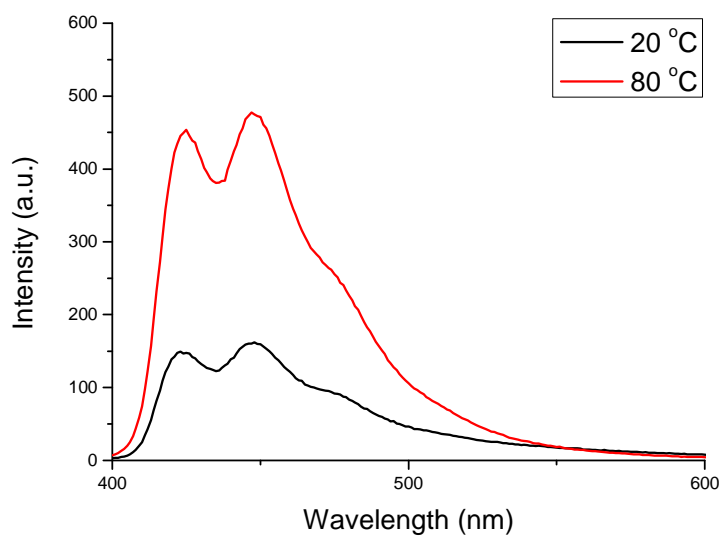


Figure S11. Emission (excited at 390 nm, measured at 20 °C and 80 °C) spectra of **1D-SP**. Conditions: 10 mM NaCl, 10 mM sodium phosphate buffer, pH 7.2, [ANT3] = 1 μ M.

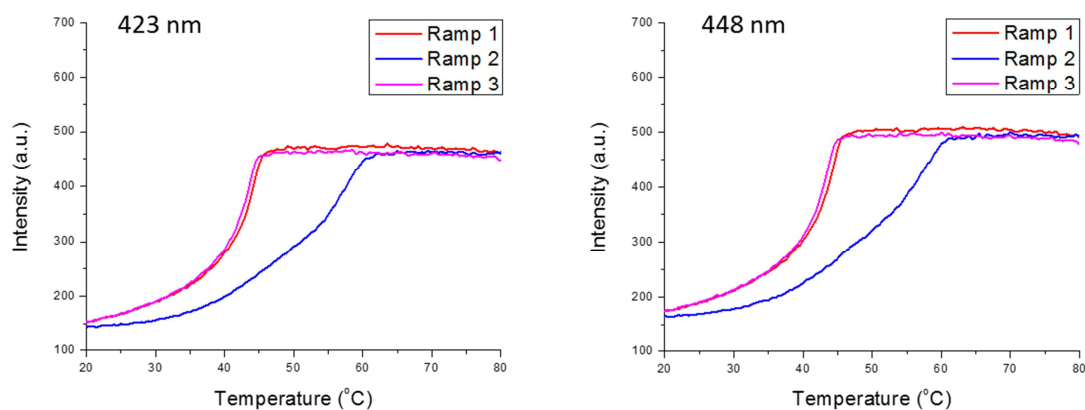


Figure S12. The fluorescence melting curves (monitored at 423 nm and 448 nm) of **1D-SP**. Ramp 1: 80 – 20 °C, 0.5 °C/min; Ramp 2: 20 – 80 °C, 0.5 °C/min; Ramp 3: 80 – 20 °C, 0.5 °C/min. Conditions: 10 mM NaCl, 10 mM sodium phosphate buffer, pH 7.2, [ANT3] = 1 μ M.

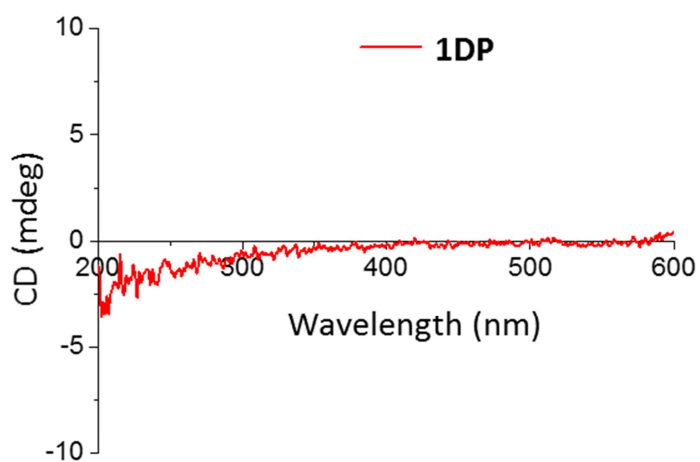


Figure S13. CD spectrum of **1DP**. Conditions: 10 mM NaCl, 10 mM sodium phosphate buffer, pH 7.2, [ANT3] = 1 μ M.

1.4. UV irradiation experiment setup

The solution of **1D-SP** in buffer was transferred into a fluorescence cuvette (1 cm) and carefully deoxygenated by bubbling Ar through the solution over 10 min. The irradiation experiment was performed under a UV lamp (8 W, CAMAG UV lamp, 12VDC/VAC) at 366 nm. For every 10 min, the reaction mixture was monitored by UV-vis spectroscopy. The experiment setup is shown below:

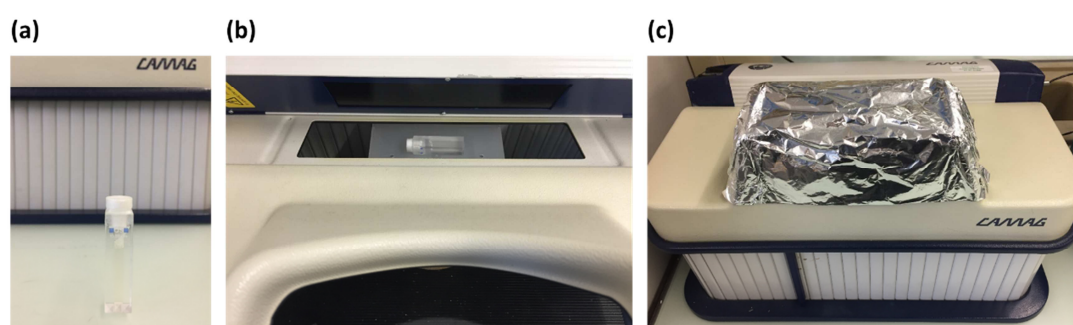


Figure S14. UV irradiation experiment setup. **a**, **1D-SP** solution in 1 cm fluorescence cuvette. **b**, The cuvette was placed under the UV lamp as close as possible to the bulb. **c**, The irradiation experiment was in process.

2. Supplementary AFM and TEM images

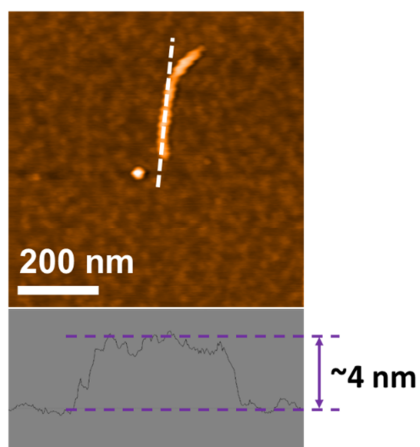


Figure S15. AFM image of one single chain of **1D-SP** in water. The cross-sectional height profile along the contour surface is shown at the bottom.

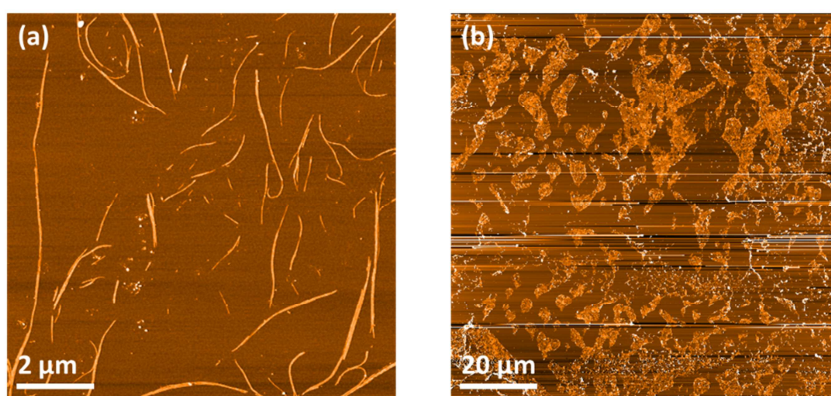


Figure S16. (a): AFM overview image of **1D-SP** in water. (b): AFM overview image of **1DP** in ethanol.

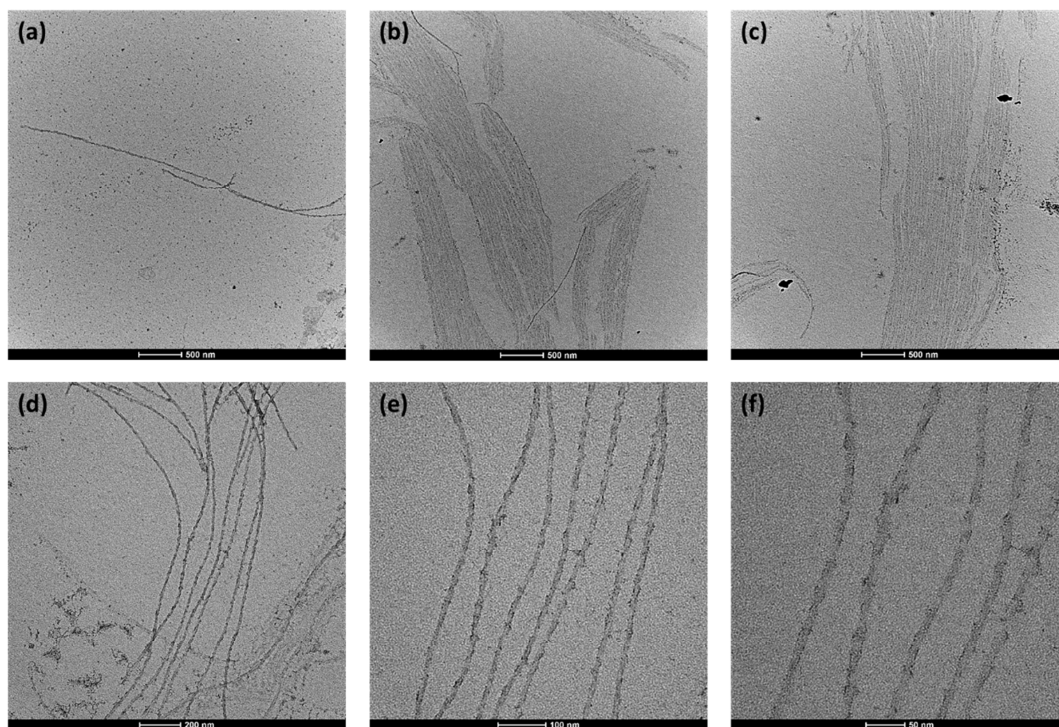


Figure S17. (a)-(c): TEM images of **1D-SP** in water. (d)-(f): TEM images of **1DP** in water.

3. Repeat unit number calculation

Definitions:

w : width of the flattened tubular polymers

p : perimeter of the tubular polymers

l : distance between interdigitated anthracenes in the tubular polymers

n : number of **ANT3** in one turn of the tubular polymers

h : pitch for one turn of the tubular polymers

N : number of **ANT3** in 1 μm long tubular polymers

Assuming $l \approx 3.5 \text{ \AA}$ and taking $w = 12.5 \text{ nm}$, n is calculated as below:

$$n = \frac{p}{l} = \frac{2w}{l} = \frac{25}{0.35} = 25$$

Assuming $h = 1 \text{ nm}$ (this value is assumed on the basis of the long axis of anthracene = $\sim 7 \text{ \AA}$ and describes the approximate 'thickness' of a polymer chain), N is calculated as below:

$$N = n \times \frac{1 \mu\text{m}}{h} = 2.5 \times 10^4$$

4. Supplementary references

1. VanVeller, B.; Robinson, D.; Swager, T. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 1182.
2. Wheeler, S. E.; McNei, A. J.; Müller, P.; Swager, T. M.; Houk, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 3304.