Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tubes or sheets: divergent aggregation pathways of an amphiphilic 2,7-substituted pyrene trimer

M. Vybornyi, Y. Bur-Cecilio Hechevarria, M. Glauser, A.V. Rudnev and R. Häner

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

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1. General methods

1.1 Synthesis and characterization of compounds

All chemical reagents and solvents required for the synthesis have been purchased from commercial suppliers (Aldrich, Alfa Aesar or TCI) and used without further purification. Water was used from a MilliQ system. Analytical thin layer chromatography (TLC) was carried out using aluminium sheets, precoated with silica gel 60 and fluorescent indicator. The silica gel for the column chromatography had 60Å pore size, 230-400 mesh. Air-sensitive reactions and manipulations have been carried out under Ar atmosphere using standard Schlenk technique. Glassware was dried in an oven at 110 °C. All synthesized compounds were stored at 0^0C under Ar. NMR spectra were obtained on a Bruker AV 300 (300 MHz) spectrometer at 298 K. Mass-spectrometric data were obtained on Thermo Fisher LTQ Orbitrap XL using Nano Electrospray Ionization.

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 I_2/THF/py, TCA deblock, DCI activator).

1.3 Spectroscopic measurements

UV/VIS spectra were collected with an optical path of 1 cm over the range of 200-500 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 using. Unless otherwise noted the following settings of the instrument were used: the excitation wavelength 365 nm, the slit width 5 nm for emission and excitation, medium sensitivity of the detector. The concentration of **27Py$_3$** was determined using a value of ε^{273}=34000 dm^3 mole^{-1} cm^{-1} in EtOH for a single pyrene unit.

1.4 AFM and TEM experiments

AFM measurements. AFM imaging was performed under ambient conditions in air with a Nanosurf FlexAFM (Nanosurf AG, Switzerland) instrument using either a 100×100 μm^2 or a 10×10 μm^2 scanning head. The measurements were carried out in tapping mode employing either PPP-NCHR-W cantilevers from Nanosensors (resonance frequency ~280 kHz, tip radius ~10 nm) or Tap190Al-G from BudgetSensors (resonance frequency ~190 kHz, force constant 48 N/m). Both types of cantilevers gave reproducible results. Sample preparation: a 15 µL aliquot of a 5 µM **poly27Py$_3$** solution [mixture of aqueous buffer (10 mM sodium chloride, 10 mM phosphate buffer, pH = 7.2) and ethanol 80/20 v/v] was placed on an APTES-modified mica plate (20 × 20 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 ml total volume) and dried under a stream of Ar for 30 sec.

TEM measurements. Experiments were performed on a FEI Morgagni 268 using an operating voltage of 80 kV. Sample preparation: a 5 µL aliquot of the 2 µM **27Py$_3$** solution obtained by any of the methods described above was placed on a carbon-coated grid (S160-3, 300 mesh Cu, AgarScientific). After 5 min, the remaining solution was blotted with a filter paper and of Milli-Q water (5 µL) was added. After 1 min, the water was blotted and 0.8 % aqueous uranyl acetate (2 µL) was added, which was blotted again after waiting for 30 sec. After repeating the uranyl staining procedure once again, the sample was used for the measurements

2. Experimental procedures

2.1 Synthesis

2.7-Dibromopyrene (**1**) was purchased from TCI

5,5'-(Pyrene-2,7-diyl)bis(pent-4-yn-1-ol) (2):

2.7-Dibromopyrene (**1)** (1.00 g, 2.73 mmol), bis(triphenylphosphine)palladium(II) chloride (45 mg, 0.065 mmol) and copper(I) iodide (7.0 mg, 0.036 mmol) were suspended in THF (20 mL) under argon and heated to 70 °C. After addition of triethylamine (20 mL), 4-pentyn-1-ol (1.00 mL, 11.1 mmol) was added to the mixture, which was stirred at this temperature for 36 h. After cooling to room temperature, the solvents were removed under reduced pressure. The column chromatography (dry deposition, eluent - CH_2Cl_2/PhMe/MeOH 87:10:3) furnished yellow solid **2** (720 mg). Analytical data for **2**: R_f 0.3 (CH_2Cl_2/methanol 97:3); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 4H), 8.16 (s, 4H), 4.59 (t, *J* = 5.2 Hz, 2H), 3.60 (td, *J* = 6.2, 5.1 Hz, 4H), 2.59 (t, *J* = 7.1 Hz, 4H), 1.86 – 1.72 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 130.67, 127.74, 127.59, 122.57, 121.30, 91.55, 80.75, 59.46, 31.58, 15.44. HRMS for $C_{26}H_{22}O_2$ ($M+H^+$): found 367.1693 (calculated 367.1693).

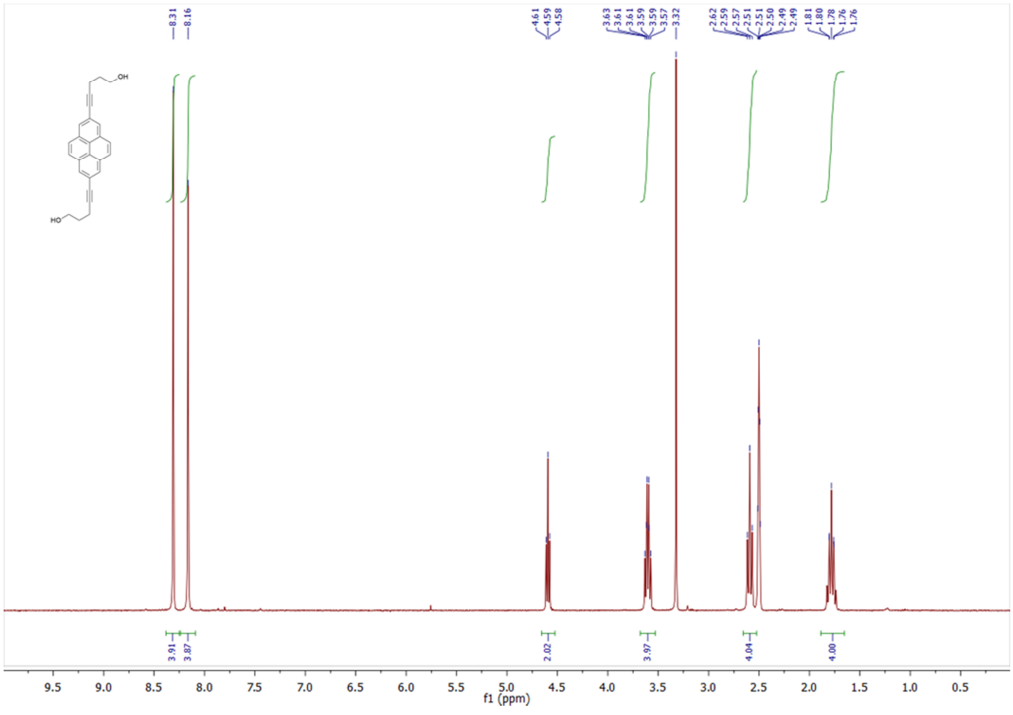
5-(7-(5-(Bis(4-methoxyphenyl)(phenyl)methoxy)pent-1-yn-1-yl)pyren-2-yl)pent-4-yn-1-ol (3):

To a solution of **2** (360 mg, 0.98 mmol) in pyridine (12 mL), a solid 4,4'-dimethoxytrityl chloride (335 mg, 0.98 mmol, 1 eq) was added dropwise. The mixture was stirred for 3 h and evaporated afterwards. The residue was dissolved in a small volume of CH_2Cl_2 and subjected to column chromatography (CH_2Cl_2/MeOH/NEt_3 97/2/1). The fractions containing **3** were collected. This furnished 250 mg (38%) of yellow solid **3.** Analytical data for **3:** R_f=0.55 (CH_2Cl_2/MeOH/NEt_3 97/2/1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 2H), 8.22 – 8.09 (m, 6H), 7.47 – 7.16 (m, 9H), 6.93 – 6.81 (m, 4H), 4.60 (t, *J* = 5.2 Hz, 1H), 3.64 (s, 6H), 3.63 – 3.54 (m, 2H), 3.21 (t, 2H), 2.67 (t, 2H), 2.60 (t, 2H), 1.90 (m, 2H), 1.79 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.93, 145.16, 135.89, 130.66, 130.59, 129.62, 127.75, 127.68, 127.64, 122.56, 121.32, 121.20, 113.09, 91.55, 91.50, 85.29, 81.14, 80.74, 61.35, 59.48, 54.87, 31.59, 28.59, 15.92, 15.42. HRMS for $C_{47}H_{40}O_4$ ($M+Na^+$): found 691.2919 (calculated 691.2817)

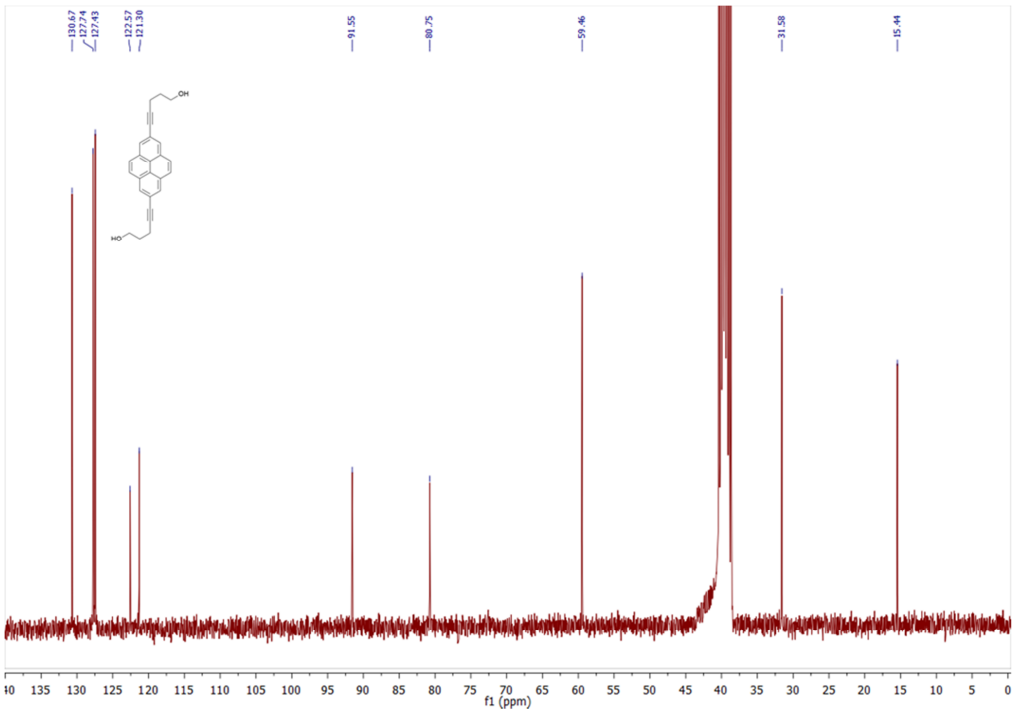
5-(7-(5-(Bis(4-methoxyphenyl)(phenyl)methoxy)pent-1-yn-1-yl)pyren-2-yl)pent-4-yn-1-yl (2-cyanoethyl) diisopropylphosphoramidite (4):

Compound **3** (250 mg, 0.374 mmol) was dissolved in CH_2Cl_2 (10 mL). After addition of DIPEA (193 µL, 1.10 mmol, 3 eq) and 2-cyanoethyl-N,N-diisopropylchlorophosphoramidite (113 mg, 0.487 mmol, 1.3 eq), the mixture was stirred for 5 h. The solution was evaporated and the residue was dissolved in a small volume of hexane/EtOAc/NEt_3 50/49/1 and purified by a flash chromatography (hexane/ EtOAc/NEt_3 50/49/1), furnished 242 mg (75%) **4** as a yellowish solid. Analytical data for **4**: R_f= 0.60 (hexane/ EtOAc/NEt_3 50/49/1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 2H), 8.21 – 8.13 (m, 6H), 7.42 – 7.27 (m, 9H), 6.92 – 6.85 (m, 4H), 3.84 – 3.75 (m, 4H), 3.64 (s, 6H), 3.61 – 3.56 (m, 2H), 3.21 (s, 2H), 2.81 – 2.61 (m, 6H), 1.95 – 1.84 (m, 4H), 1.16 (dd, *J* = 6.8, 4.7 Hz, 12H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.93, 145.16, 135.89, 130.63, 129.63, 128.60, 127.54, 127.42, 126.52, 122.58, 121.21, 118.94, 113.10, 90.98, 85.29, 81.14, 62.47 – 60.51, 58.20, 54.87, 42.47, 30.57, 28.32, 24.36, 19.85, 15.70. ^{31}P NMR (122 MHz, DMSO) δ 146.74. HRMS for $C_{56}H_{57}N_2O_5P$: found 869.4071 (calculated 869.4078)

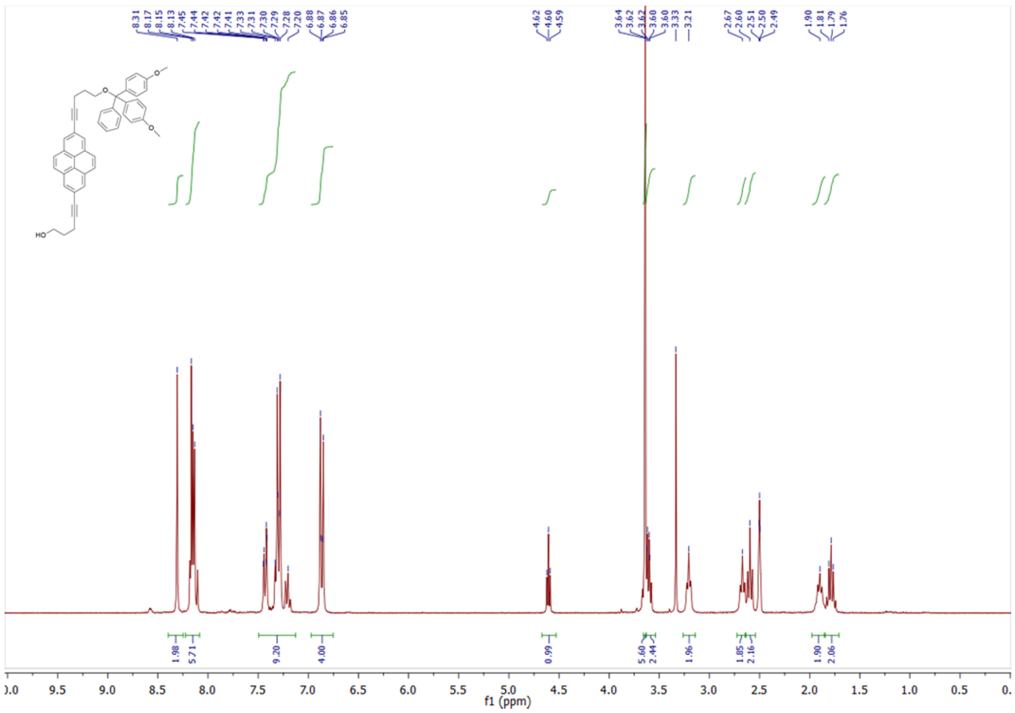
^{1}H NMR (300 MHz, DMSO) of **2**:



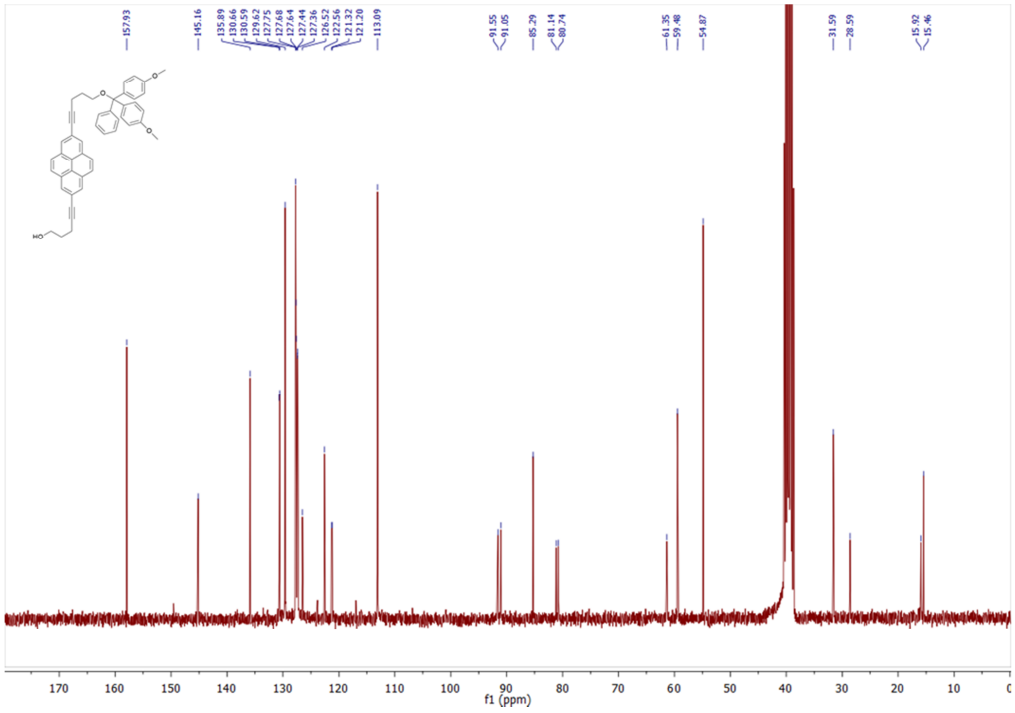
^{13}C NMR (75 MHz, DMSO) of **2**:



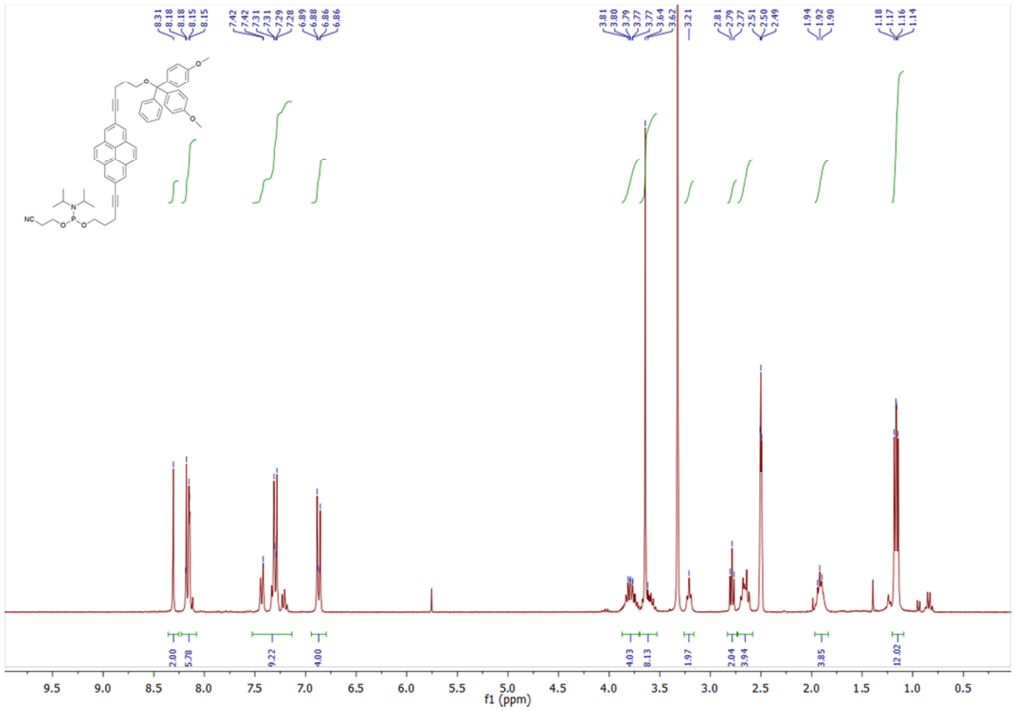
^{1}H NMR (300 MHz, $CDCl_3$) of **3**:



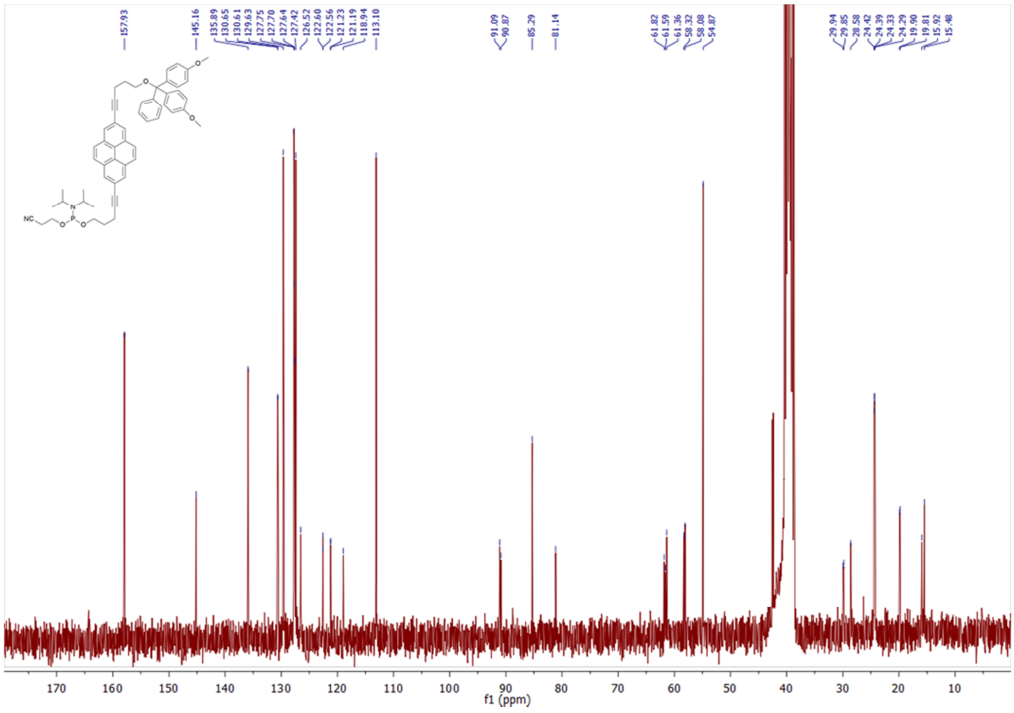
^{13}C NMR (75 MHz, DMSO) of **3**:



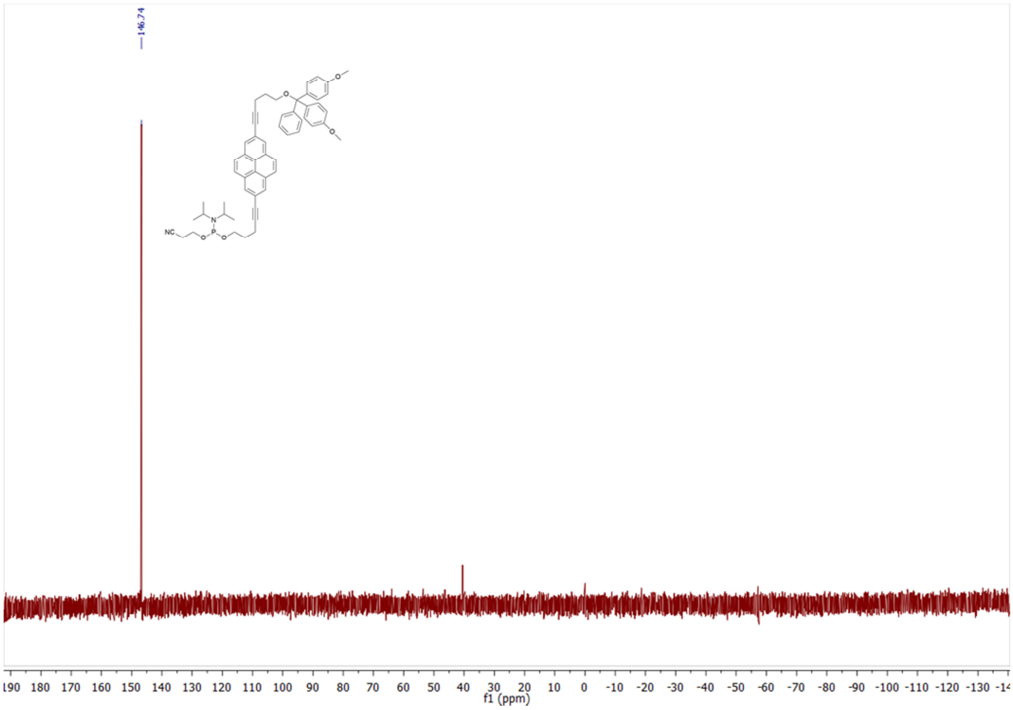
^{1}H NMR (300 MHz, DMSO) of **4**:



^{13}C NMR (75 MHz, DMSO) of **4**:



^{31}P NMR (122 MHz, DMSO) of **4**:



2.2 Solid-phase synthesis of $27Py_3$

Trimer **$27Py_3$** was synthesized on the Applied Biosystems 394 DNA synthesizer using preloaded USIII support. We followed a standard cyanoethyl phosphoramidite coupling protocol for the 1 µmol synthesis ("trityl-off" mode). The coupling yields per single step were ≥95 % (monitoring by "trityl assay"). The cleavage of the **$27Py_3$** from the support was achieved by treatment with 0.8 ml of 2M NH_3/MeOH (Aldrich) for 16 hours at 50^0C in a closed vial. The supernatant was separated from the support by centrifugation. The remained beads were treated with 0.8 ml of 2M NH_3/MeOH two times. All supernatants were collected, and 1 ml of aqueous NH_3 was added. After 30 min of a shaking at the room temperature, the sample was lyophilized. The crude product was purified by reverse-phase HPLC (LiChrospher 100 RP-C8, 5 µm, Merck, Bio-Tek Instruments); eluent A=(Et_3NH)OAc (50 mM, pH 7.0)/CH_3CN in 50/50 v/v; eluent B=CH_3CN; gradient 0–100% B over 14 min, then 100% B over 9 min. Gradient flow 1 ml/min. The pure compound was characterized by mass spectrometry: HRMS for $C_{78}H_{62}O_{10}P_2^{2-}$: found 1220.3852 (calculated 1220.3830)

3. Spectroscopic measurements

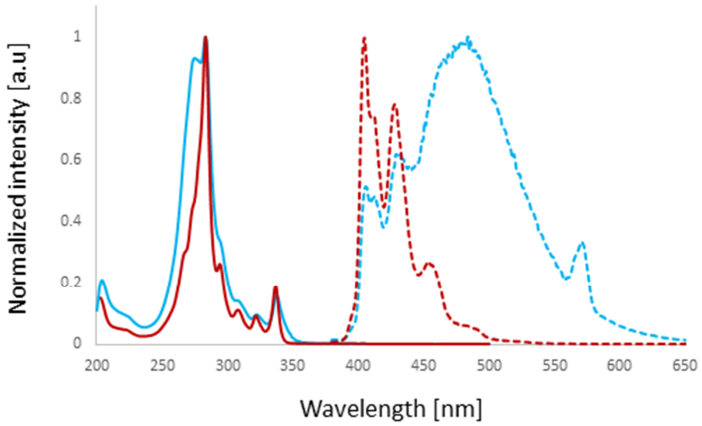


Figure S4. Normalized UV-vis (solid lines) and fluorescence (excitation at 285 nm, dashed) spectra of the 5 µM **27Py$_3$** (blue) and 5 µM **2** (red) in ethanol; band at 570 nm: second order transmission of the monochromator.

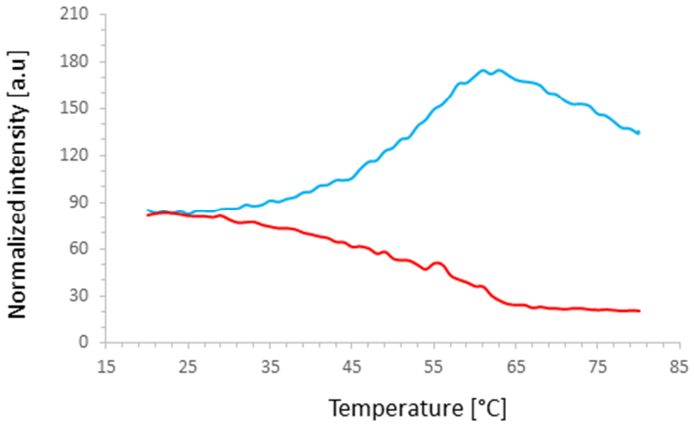


Figure S5. Supramolecular polymer formation curve (cooling rate 0.1°C/min) recorded in aqueous medium (10 mM sodium chloride, 10 mM phosphate buffer, pH = 7.2, ethanol 20% vol.) and monitored at 480 nm emission upon 275 nm (blue) and 352 nm (red) excitation wavelengths.

4. HPLC purification and characterization

The purification method used [eluent A=$(Et_3NH)OAc$ (50 mM, pH 7.0)/CH_3CN in 50/50 v/v; eluent B=CH_3CN]:

Time, min	Eluent A, %	Eluent B, %
0 – 2	100	
2 – 16	0	100
16 – 22	0	100
22 – 24	100	0
24 – 30	100	0

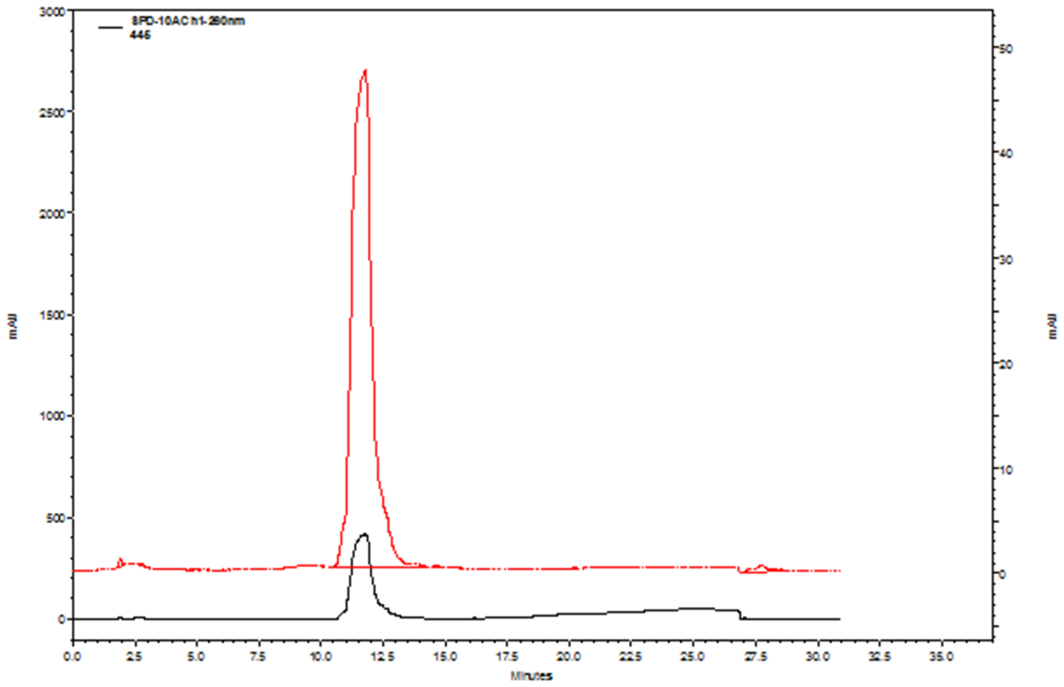


Figure S6. HPLC trace of **27Py$_3$** monitored at 260 nm (red) and 350 nm (black)

5. AFM and TEM images of nanotubes

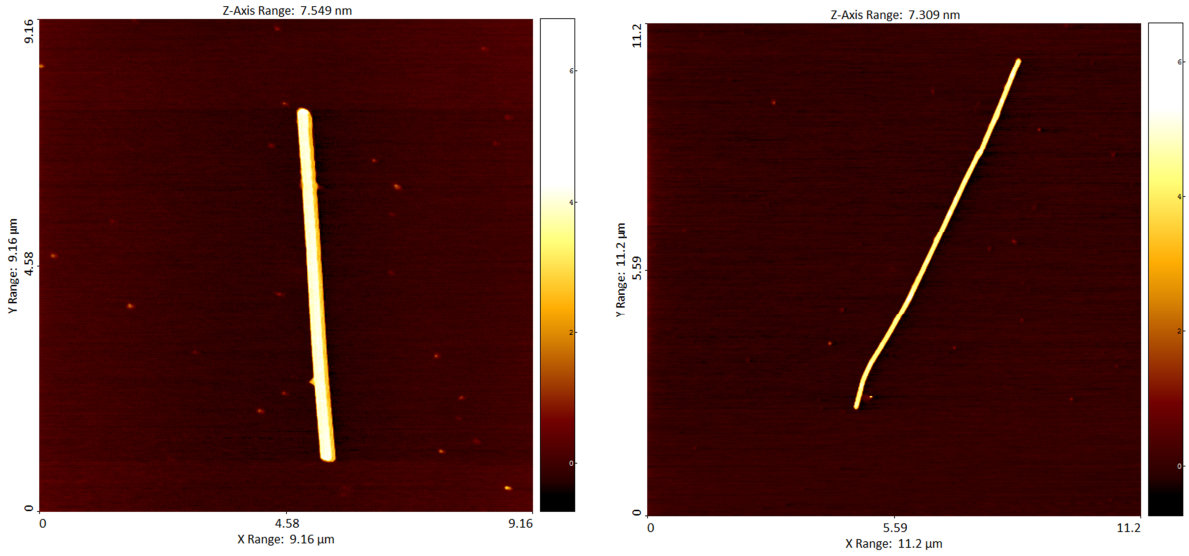


Figure S7. Additional selected AFM images of poly27Py$_3$ nanotubes

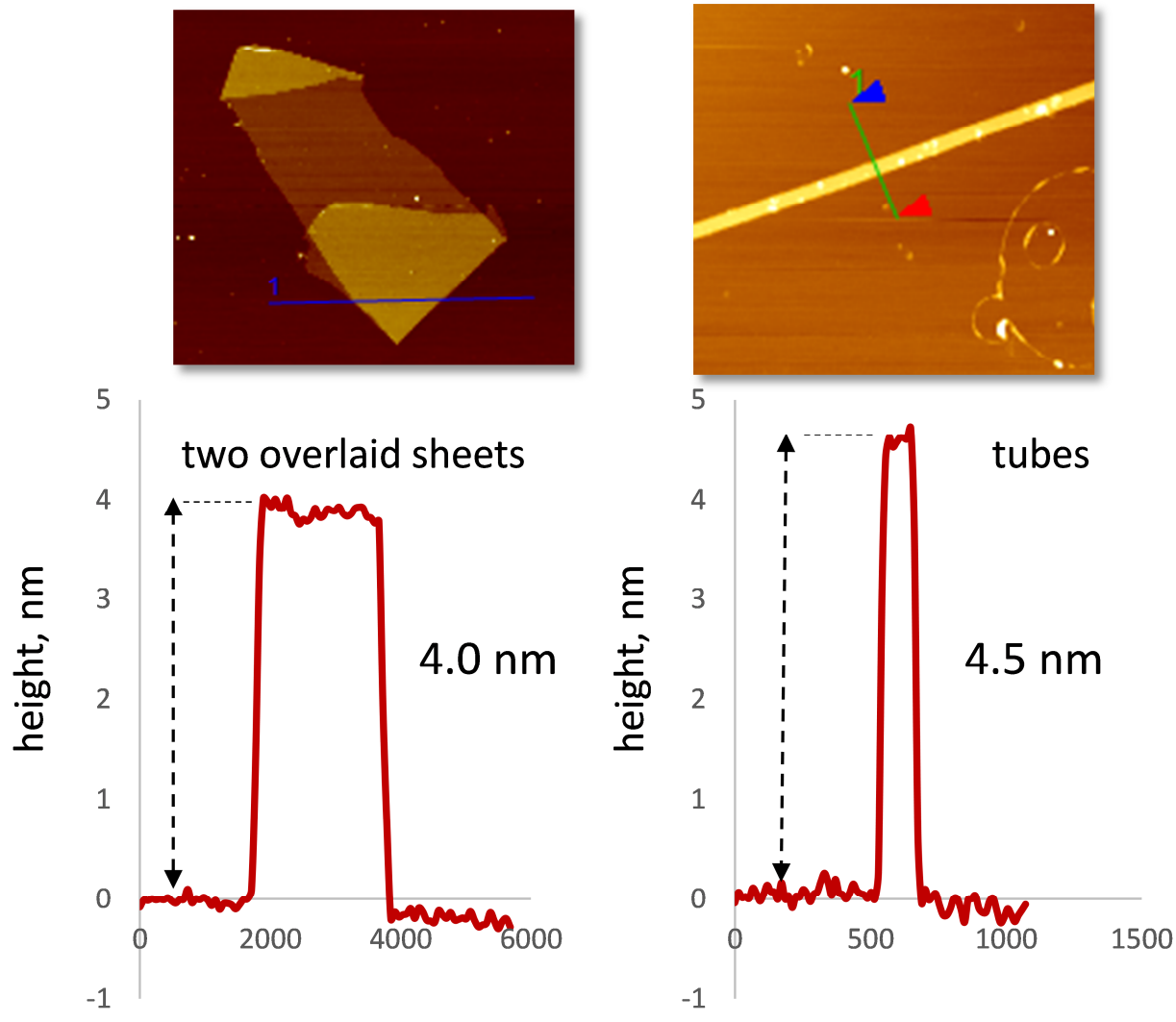
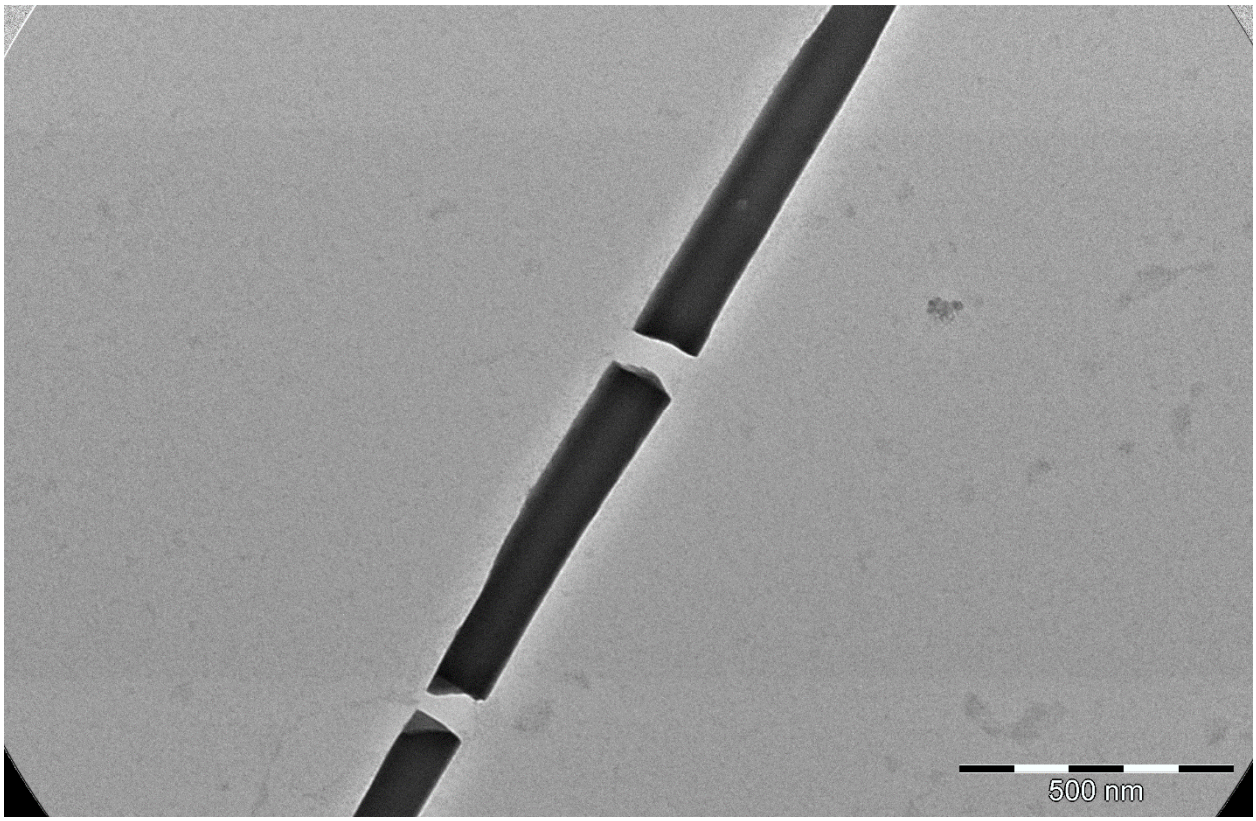
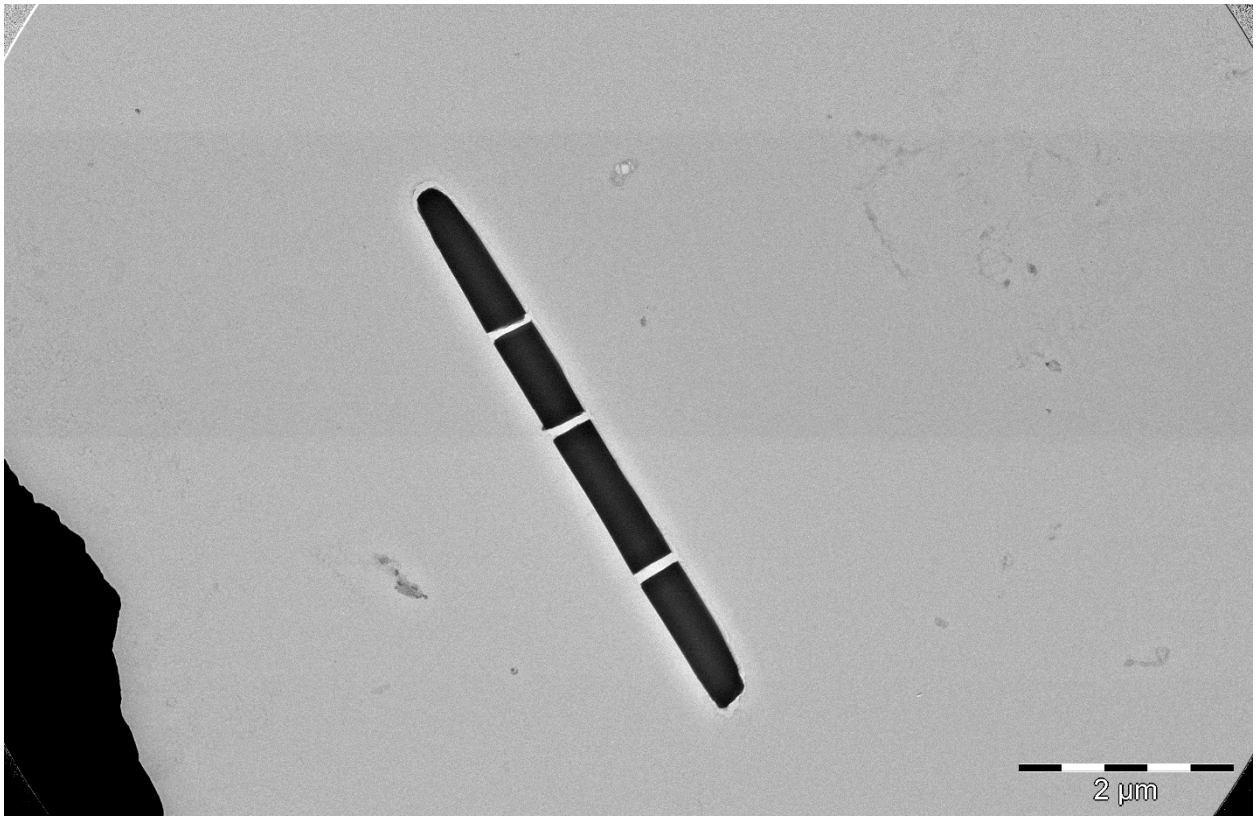


Figure S8. AFM height profiles for two overlaid sheets and a tube


500 nm


2 µm

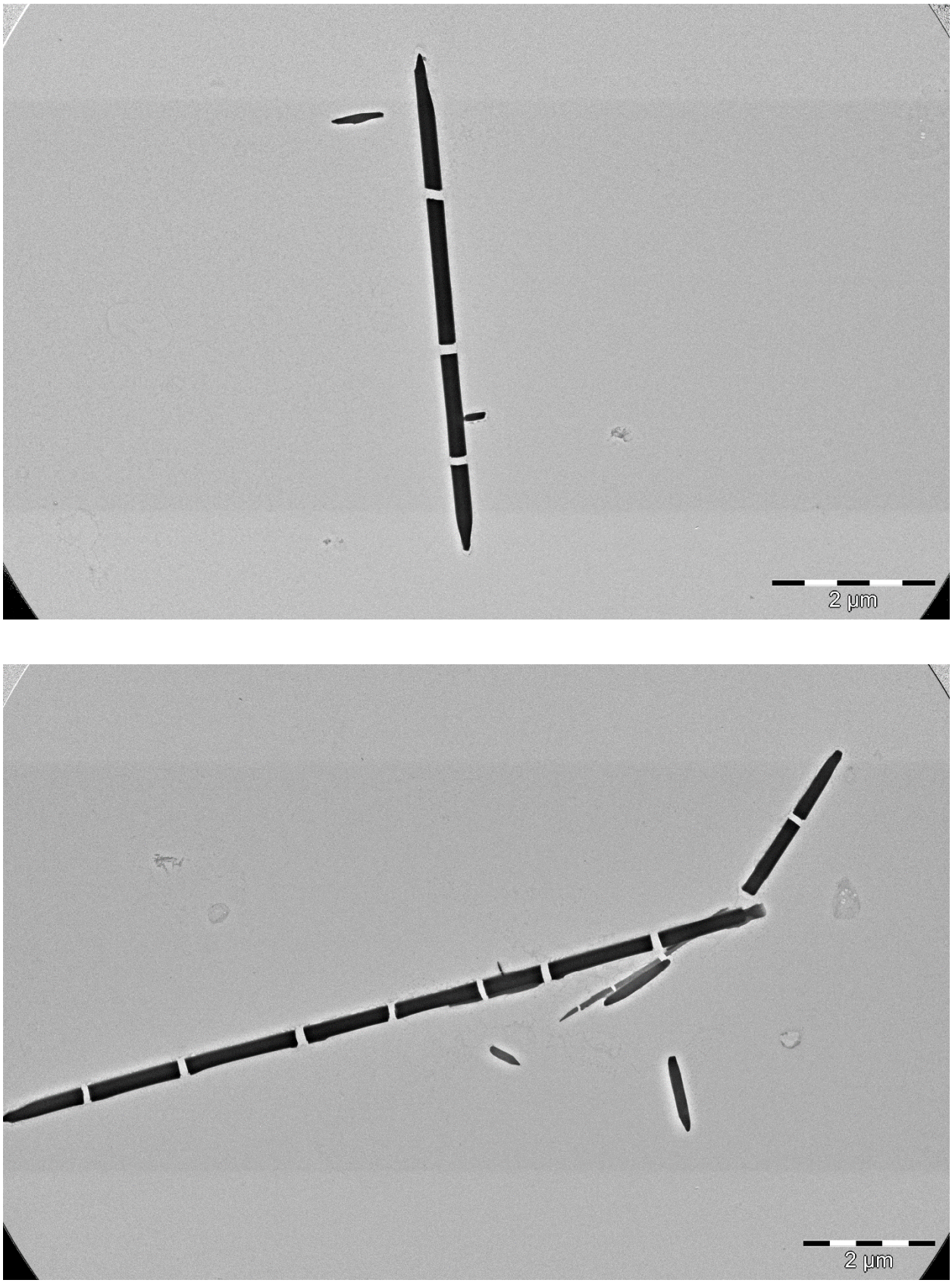


Figure S9. TEM images of poly27Py$_3$ nanotubes