Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information for

Length control of supramolecular polymeric nanofibers based on stacked planar platinum(II) complexes by seeded-growth

By

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Experimental Details and Procedures

Equipment and Materials

All reactions were carried out under atmospheres of dry nitrogen using standard Schlenk line techniques. All chemicals were purchased from Aldrich and were used as received unless otherwise stated. The oligo(ethylene glycol) monomethyl ether precursor possessed M_n = 750 g/mol and a distribution of chain lengths with x = 16 as the most significant component. For general synthesis, dry N_2-saturated dichloromethane (DCM) and acetonitrile (MeCN) were obtained from a Grubbs-type solvent system using filtration through an alumina column impregnated with deoxygenated catalysts. Chloroform ($CHCl_3$), MeCN and dimethylformamide (DMF) used in self-assembly experiments were HPLC grade and filtered through a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 µm pore size) before use. NMR spectra were recorded at ambient temperatures on a Varian 400 spectrometer with all resonances referenced to residual NMR solvent resonances (^{1}H and ^{13}C). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of complex **3** was performed using a Bruker Ultraflextreme running in linear mode. Samples were prepared by mixing a solution containing *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2propenylidene]malonitrile matrix (20 mg/mL in tetrahydrofuran) and a solution of **3** (1 mg/mL in tetrahydrofuran) in a 1:9 (v/v) ratio. Approximately 1 µL of the mixed solution was deposited onto a stainless steel sample plate and allowed to dry in air. **1**[1] and 2,6-bis(tetrazol-5-yl)pyridine[2] were synthesized and purified according to literature procedures.

Transmission Electron Microscopy (TEM)

The samples for electron microscopy were prepared by drop-casting one drop (ca. 10 µL) of the colloidal solution onto a carbon coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. No staining of the samples was necessary. Images were analyzed using the ImageJ software package developed at the US National Institute of Health.[3] For the statistical length analysis, 180 - 230 cylinders were carefully traced by hand to determine the contour length. From this data L_n and L_w of each sample of fibers were calculated as shown below (L = length of object, N= number).[4, 5]

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \qquad\qquad L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i\, L_i}$$

The standard deviations (σ) of the measured lengths are related to length dispersity (L_w/L_n) assuming a Gaussian distribution through the following expression.[4, 5]

$$\frac{L_w}{L_n} - 1 = (\frac{\sigma}{L_n})^2$$

Gaussian distribution functions overlaying relevant histograms were plotted according to the probability density function of a normal distribution as shown in the following equation:

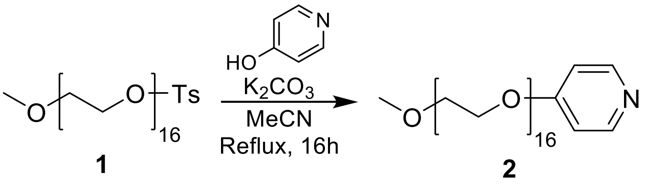
$$f(x|L_n, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-L_n)^2}{2\sigma^2}}$$

Where L_n is the mean contour length of the measured fibers and σ is the standard deviation.

Ultraviolet-visable Absorption (UV-vis)

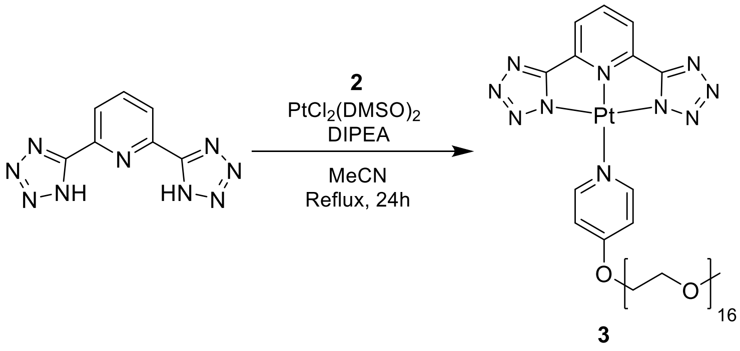
UV-vis absorption spectra were obtained on a Lambda 35 spectrometer employing standard quartz cells (1 cm) from 200 to 800 nm. For varying temperature experiments, a magnetic stirrer for single cell holders was used alongside a Peltier temperature controller accessory.

Synthesis of **2**



1 (1.5 g, 1.6 mmol, 1.0 eq.), K_2CO_3 (0.24 g, 1.8 mmol, 1.1 eq.) and 4-hydroxypyridine (0.16 g, 1.6 mmol, 1.0 eq.) were dissolved in MeCN (100 mL) and refluxed for 16 h. MeCN was removed under vacuum and a mixture of water (50 mL) and DCM (50 mL) was added. The product was extracted into dichloromethane, washed with brine (1 × 50mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography using a 10% methanol in DCM mixture to give a light brown oil (0.67 g, 0.81 mmol, yield = 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 7.18 Hz, 2H), 6.33 (d, *J* = 7.72Hz, 2H), 3.95 (t, J=4.8 Hz, 2H), 3.69 (t, *J* = 4.77 Hz, 2H), 3.63 – 3.47 (m, 58H), 3.45(t, *J* = 4.77, 2H), 3.26 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.1, 118.1, 99.8, 71.9, 70.6, 70.44, 70.0, 59.9; MALDI-TOF: calculated for [M] based on the functionalization of the starting polyethylene glycol with a peak M_W of 737 g/mol (n=16): 814. Found (MALDI-TOF+): 816.

Synthesis of **3**



In an argon atmosphere MBraun MB150B-G glove box, **2** (0.16 g, 0.20 mmol, 1.0 eq.), 2,6-bis(tetrazol-5-yl)pyridine (42 mg, 0.20 mmol, 1.0 eq.), $Pt(DMSO)_2Cl_2$ (84 mg, 0.20 mmol, 1.0 eq.) and diisopropylethylamine (DIPEA) (78 mg, 0.60, 3.0 eq.) were mixed in MeCN. The reaction mixture was sealed, removed from the glove box and sonicated for 15 min to dissolve all the contained solids. After transferring the reaction mixture to a Schlenk line, it was then refluxed for 24 h. MeCN was removed under vacuum and the crude product was purified by silica chromatography using 10% methanol in DCM as eluent to give final product as a yellow solid (0.16 g, 0.13 mmol, yield = 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.32 (d, *J* = 6.7 Hz, 2H), 8.12 (t, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 6.8, 2H), 4.37 (t, *J* = 4.5 Hz, 2H), 3.95 (t, *J* = 4.4 Hz, 2H), 3.77 – 3.55 (m, 58H), 3.53 (t, *J* = 5.13 Hz, 2H), 3.35 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 167.4, 163.8, 155.2, 154.2, 147.0, 143.4, 120.4, 113.2, 72.0, 71.0, 70.6, 69.1, 59.5; MALDI-TOF: calculated [M]: 1222. Found (MALDI-TOF+): 1221.

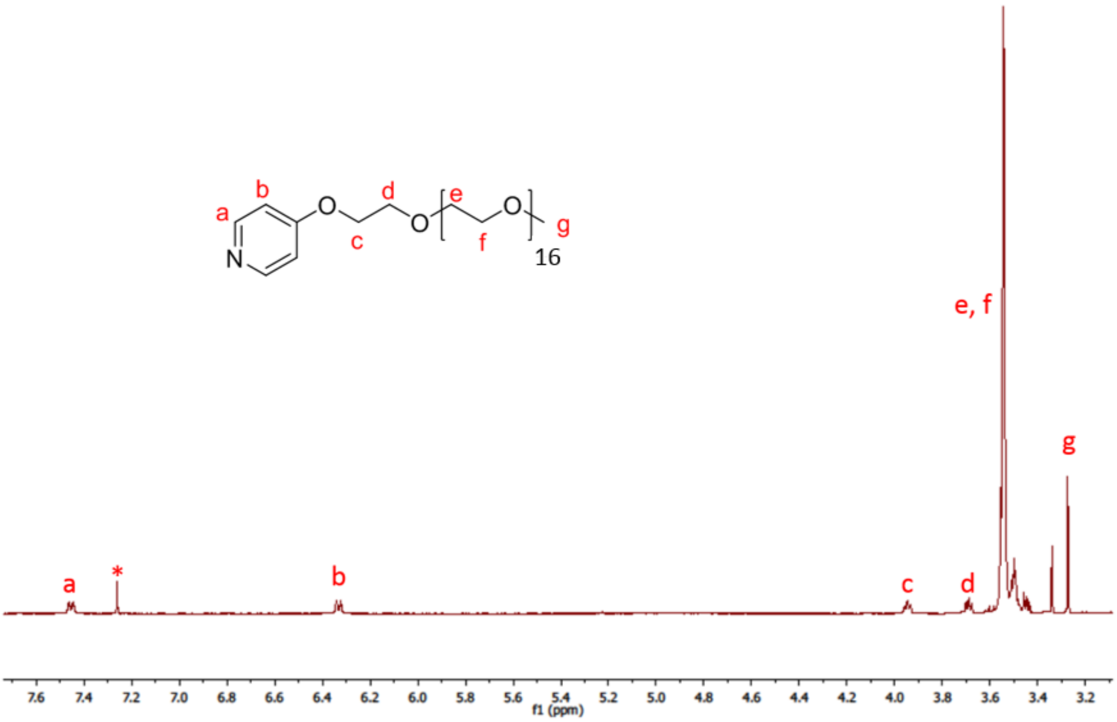


Fig. S1. ^{1}H NMR spectrum for **2** in $CDCl_3$ (asterisk denotes residual solvent signal).

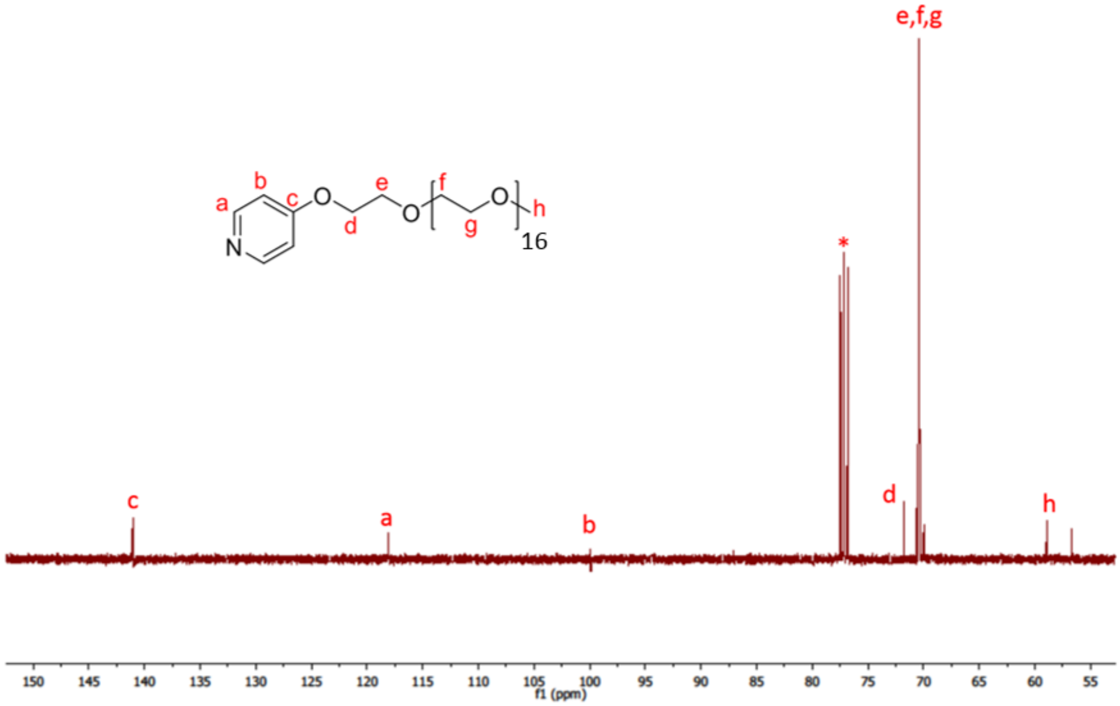


Fig. S2. ^{13}C NMR spectrum for **2** in $CDCl_3$ (asterisk denotes residual solvent signal).

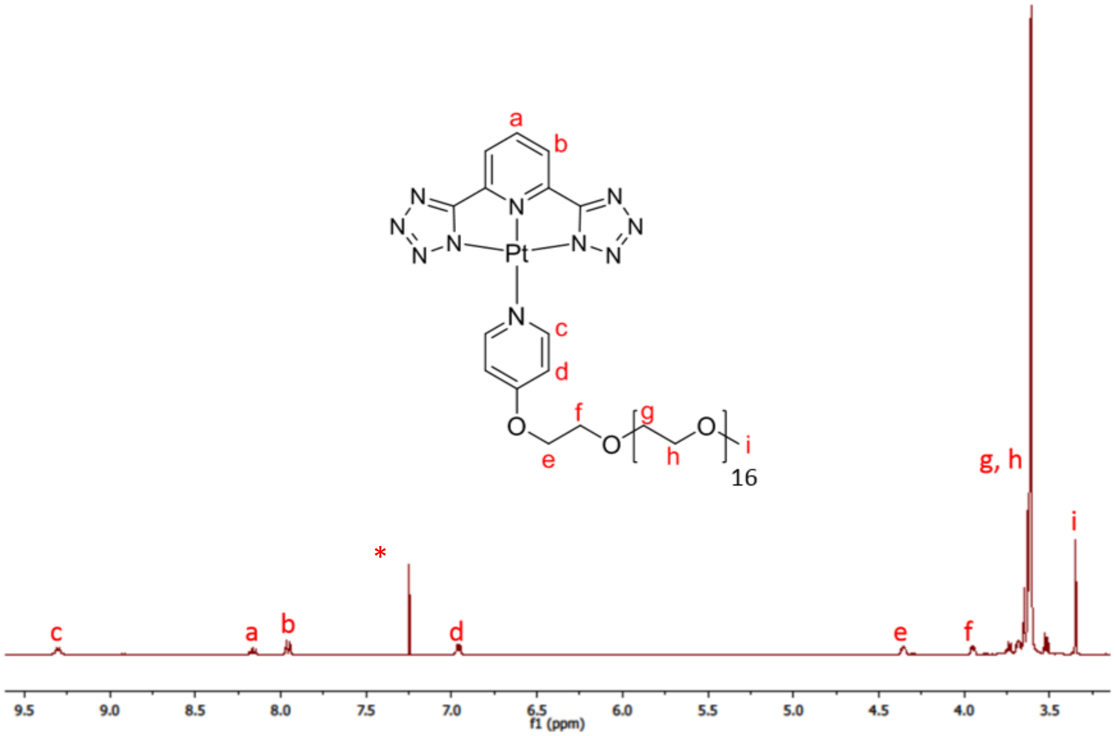


Fig. S3. ^{1}H NMR spectrum for **3** in CDCl$_3$ (asterisk denotes residual solvent signal).

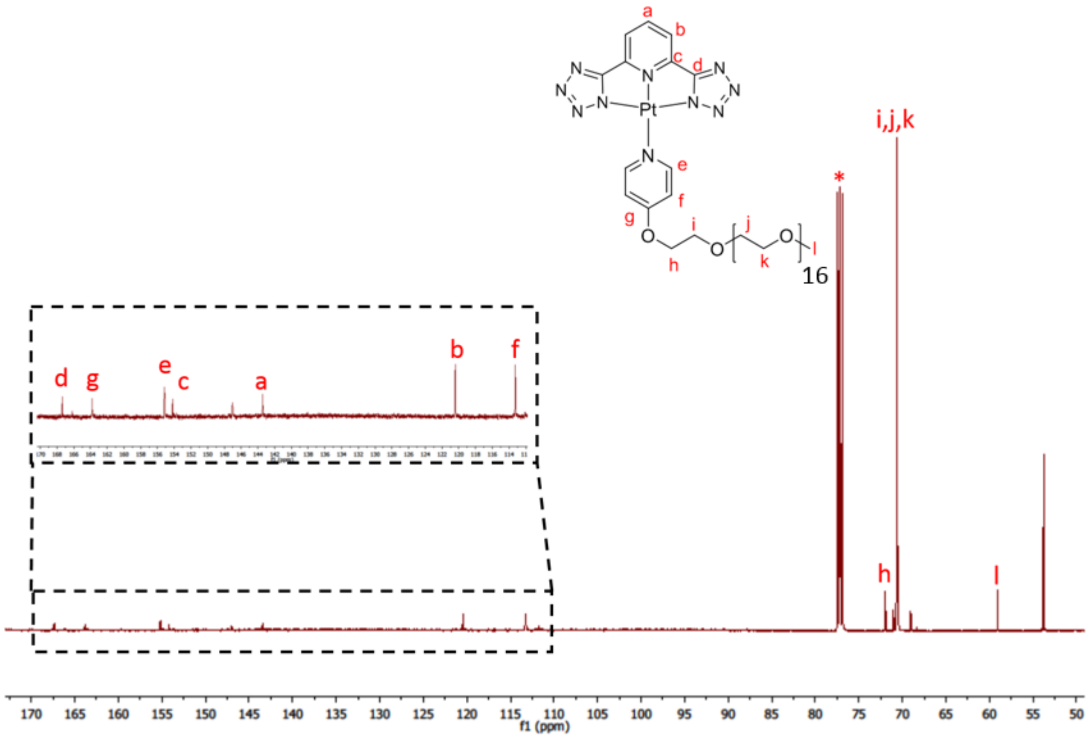


Fig. S4. ^{13}C NMR spectrum for **3** in CDCl$_3$ (asterisk denotes residual solvent signal; the peak at 53.5 ppm corresponds to CH$_2$Cl$_2$).

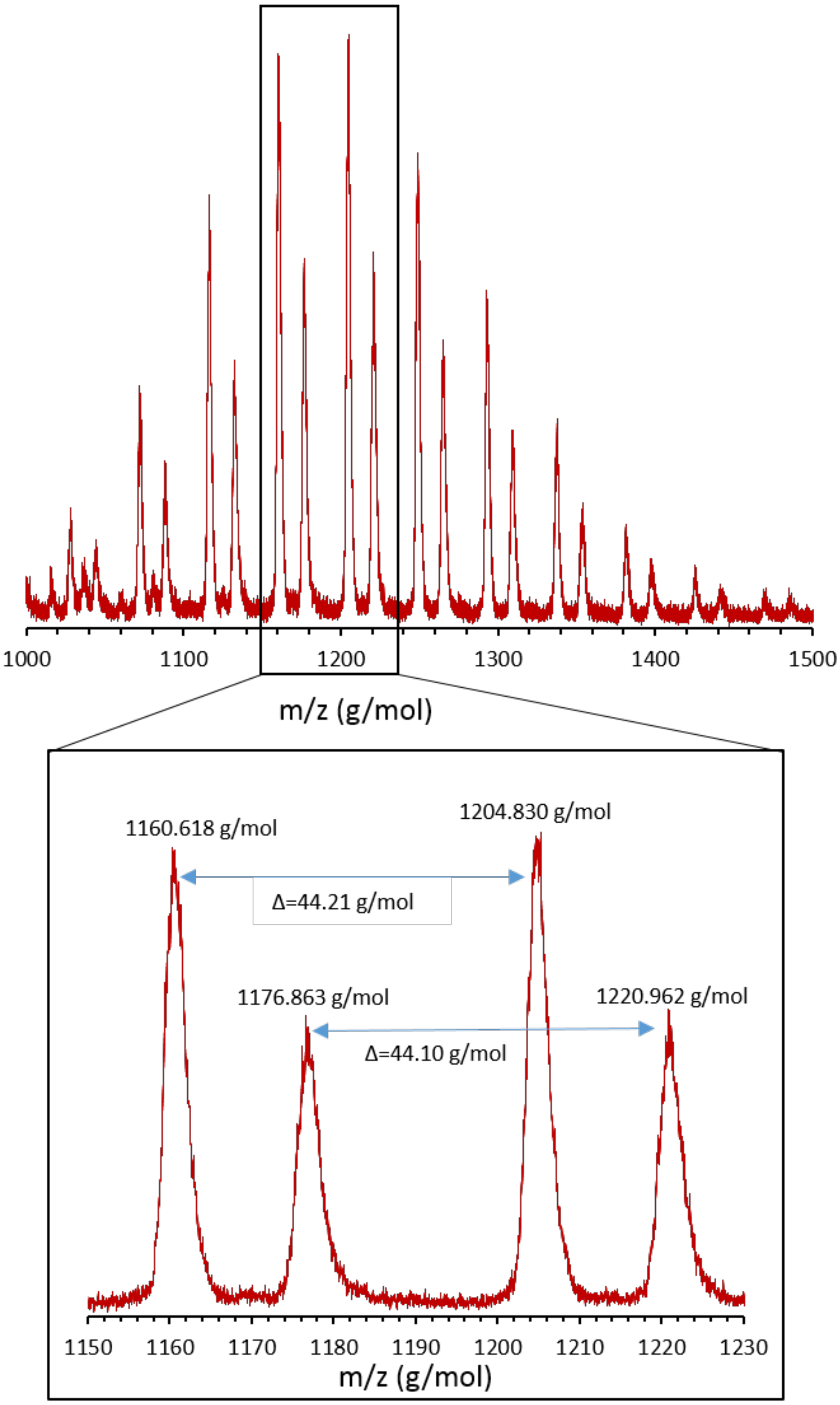


Fig. S5. MALDI-TOF mass spectrum of **3**.

Self-Assembly Experiments and Additional Figures

Self-Assembly of 3

Complex **3** was dissolved in either $CHCl_3$, MeCN or DMF (solvents selective for the oligo(ethylene glycol) substituent) at concentrations between 0.05 – 5 mg/mL. These solutions were clear yellow. After ageing in solution for 24 h at 21 ˚C, 10 μL aliquots were drop cast onto carbon-coated copper grids. Analysis by bright field TEM showed polydisperse length fibers (e.g. in $CHCl_3$, L_n = 206 nm, L_w = 355 nm, L_w/L_n = 1.73, σ/L_n = 0.85) (Fig. S6). The fiber thickness was found to be similar in all three solvents, with the exception of DMF which led to fibers with varying width. Fiber lengths in MeCN and DMF were found over 2 µm, values much larger than those formed in $CHCl_3$.

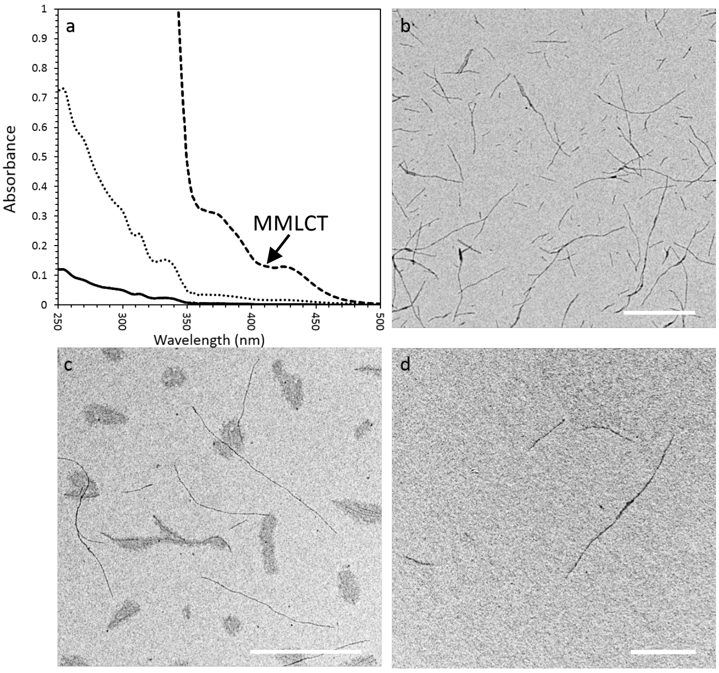


Fig. S6. (a) UV-vis absorption spectra obtained for **3** at room temperature in $CHCl_3$ (solid line: 0.01 mg/mL; dotted line: 0.05 mg/mL; dashed line: 0.1 mg/mL). Bright field TEM images of polydisperse fibers formed at 0.5 mg/mL by spontaneous nucleation in (b) $CHCl_3$, (c) MeCN, and (d) DMF. Scale Bars: 500 nm.

Estimate of Fiber Width

An estimate of the diameter of the fibers' core was calculated from density functional theory (DFT) calculations reported by the De Cola group on a similar pincer ligand.[6] The distance from the N1 on the 2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine pincer ligand to N2 on the pyridiyl ancillary ligand was reported to be 4.408 Å. Combining this with known bond distances, the core size is estimated to be 1.055 nm.

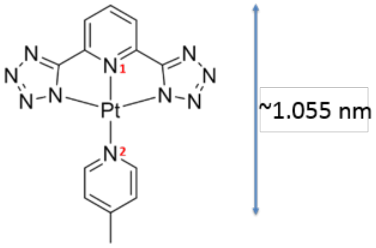


Fig. S7. Estimating the core forming square planar complex size.

Dissolution of Fibers in Hot MeCN

A 0.5 mg/mL solution of polydisperse length fibers of **3** in MeCN was heated to 80 ˚C for 1 h. A TEM grid was then dipped into the solution and then rested on a filter paper to dry. The TEM images captured showed no cylinders present, only dark patches were detected and attributed to a film formed by unimer. UV-vis data for the heated solution also showed a decrease in the metal-metal to ligand charge transfer (MMLCT) band at ~425 nm with increasing temperature (Fig. S8).

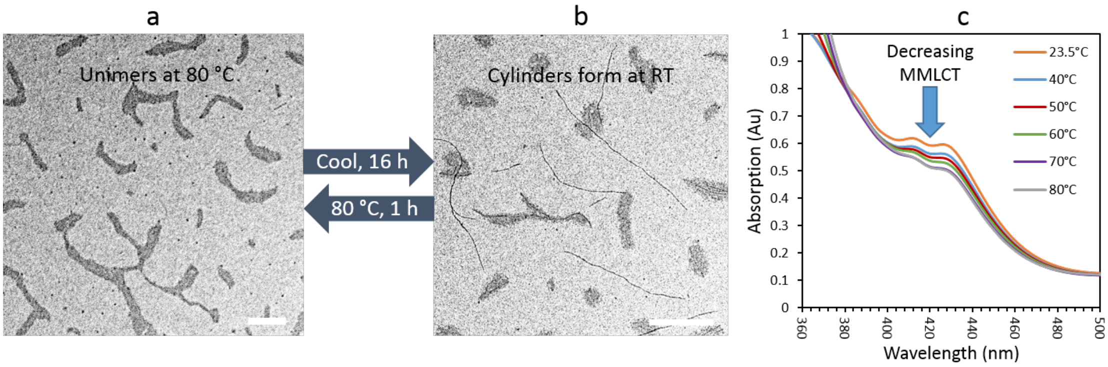


Fig. S8. TEM image fibers after (a) heating to 80 ˚C for 1 h and (b) cooling to room temperature for 16 h. (c) UV-vis absorption spectra of the characteristic MMLCT band exhibited in the aggregated species. Strength of this band decreases with rising temperature – showing dissolution of the fibers at higher temperatures. Scale bars: 500 nm

Preparation of Seed Fibers

A 7 mL vial containing 1 mL of a 0.1 mg/mL solution of colloidal, polydisperse fibers of **3** in $CHCl_3$was capped and sonicated at 0 ˚C for 1 h in a Bandelin Sonorex Digitec ultrasonic bath. TEM micrographs of the fragmented fibers (referred to as seeds) are show in Fig. S9b.

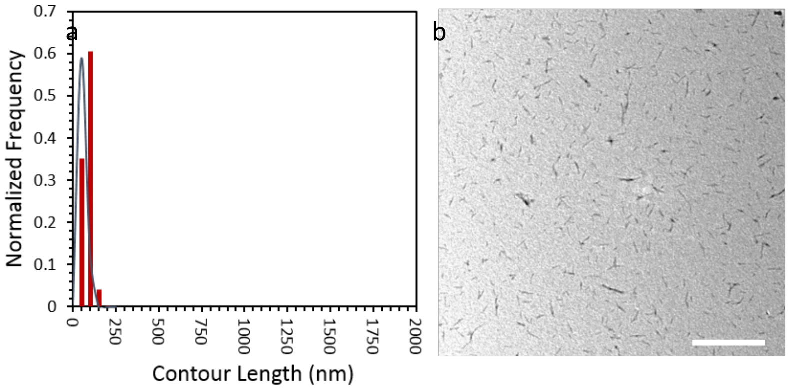


Fig. S9. (a) Bright field TEM image of seeds formed by sonication of polydisperse fibers in $CHCl_3$. (b) Histogram of the contour length distribution of the seeds formed (L_n = 60 nm, L_w = 68 nm, L_w/L_n = 1.14, σ/L_n = 0.35). Scale Bar: 250 nm

Seeded Growth of Fibers of **3**

To 5 separate 1.5 mL screw cap vials was added 200 µL of a 0.1 mg/mL solution of seed fibers (20 µg, L_n = 60 nm, L_w/L_n = 1.14) in $CHCl_3$. To these solutions was added 5 µg, 10 µg, 20 µg, 40 µg and 80 µg of **3** dissolved in hot (80˚C) MeCN at 2 mg/mg. After stirring for 5 s, the solutions were aged for 24 h at 21˚C. Multiple TEM images were obtained and the contour lengths were measured from 180 – 240 fibers (data summarized in Table 1 in the main text).

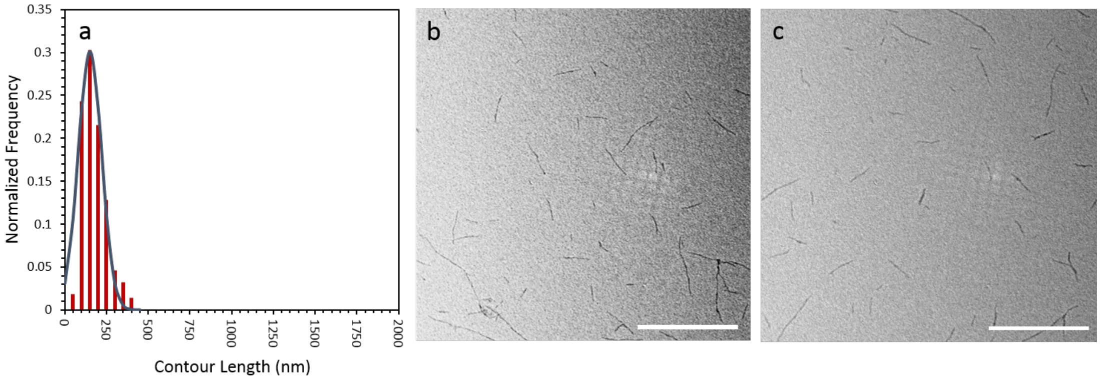


Fig. S10. (a) Length histogram and (b-c) bright field TEM images of fibers formed from the addition of 5 µg of **3** to 20 µg of seeds. Scale Bars: 500 nm

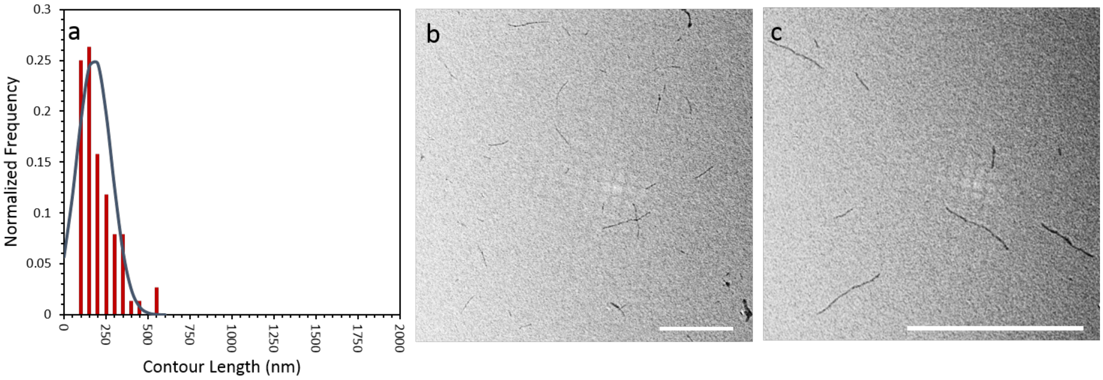


Fig. S11. (a) Length histogram and (b-c) bright field TEM image of fibers formed from the addition of 10 µg of **3** to 20 µg of seeds. Scale Bars: 500 nm

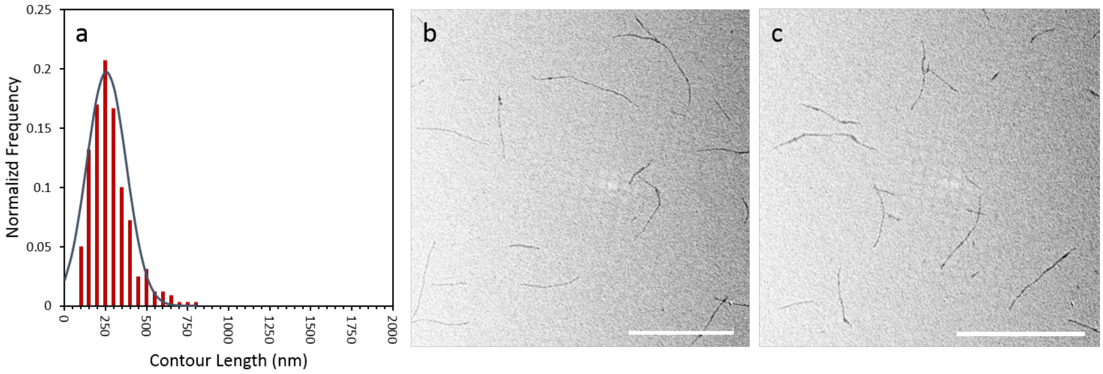


Fig. S12. (a) Length histogram and (b-c) bright field TEM image of fibers formed from the addition of 20 µg of **3** to 20 µg of seeds. Scale Bars: 500 nm

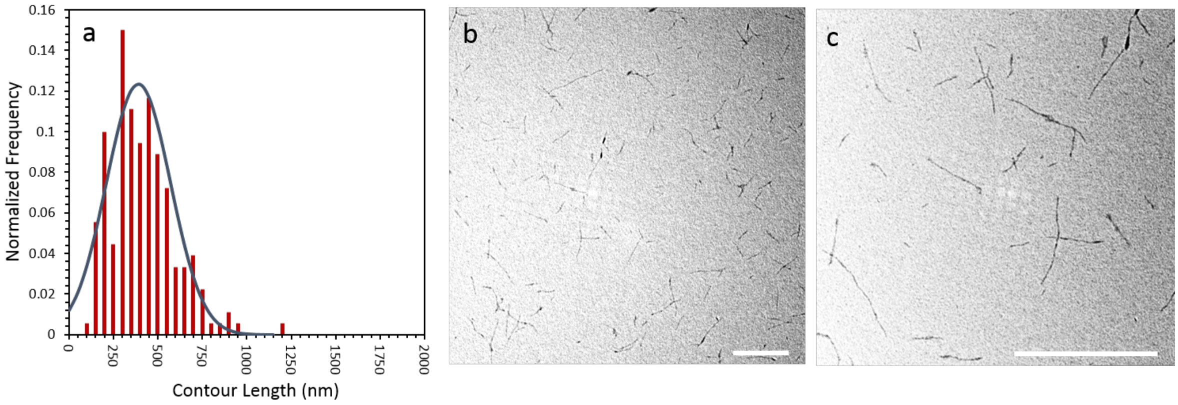


Fig. S13. (a) Length histogram and (b-c) bright field TEM image of fibers formed from the addition of 40 µg of **3** to 20 µg of seeds. Scale Bars: 1000 nm

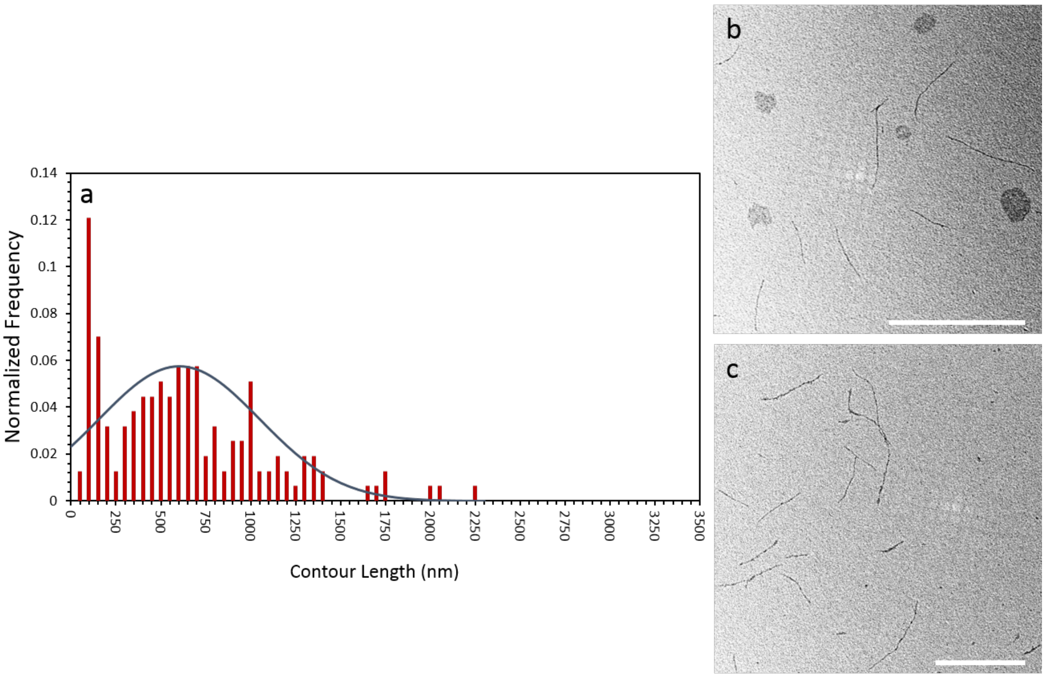


Fig. S14. (a) Length histogram and (b-c) bright field TEM image of fibers formed from the addition of 80 µg of **3** to 20 µg of seeds. Scale Bars: 1000 nm

Uv-vis Absorption Spectra of Fibers of Different Length

Two vials containing 0.1 mg/mL solutions of fibers of **3** in $CHCl_3$ with different lengths (solution 1: L_n = 119 nm, L_w/L_n = 1.17 and solution 2: L_n = 50 nm, L_w/L_n = 1.10) were prepared. Their resulting UV-vis spectra (Fig. S15) showed no significant shift in the characteristic MMLCT absorption band, suggesting the maximum conjugation limit for these structures is shorter than 50 nm.

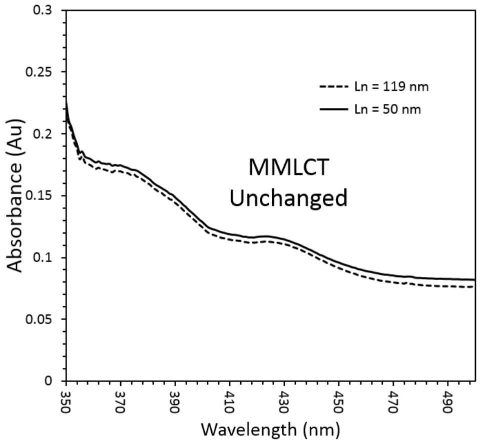


Fig. S15. Uv-vis absorption spectra of the MMLCT band at two different fiber lengths in $CHCl_3$.

Investigation of Potential Dynamic Exchange for Fibers of **3**

A 7 mL vial containing a 0.1mg/mL solution of colloidal fibers of **3** (L_n = 247 nm, L_w/L_n = 1.30) in $CHCl_3$ was capped and sonicated at 0 ˚C for 45 minutes in a Bandelin Sonorex Digitec sonication bath. The solution was then drop cast onto a TEM copper grid after various time intervals (t = 0, 1d, 3d) and imaged. The contour lengths at each of these time points were obtained from counting 220 – 240 fibers (Fig. S16).

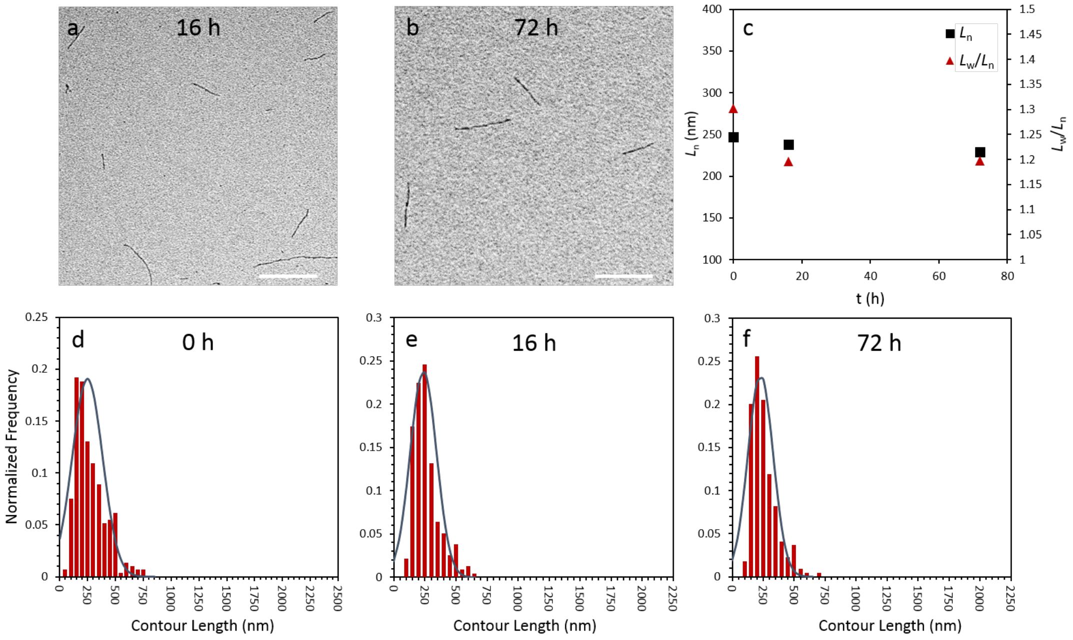


Fig. S16. Monitoring fibers' lengths post sonication for dynamic exchange behavior. Bright field TEM image of fibers after (a) 16 h and (b) 72 h of ageing. (c) Plot of L_n and L_w/L_n as a function of time. Length histograms of fibers after (d) 0 h, (e) 16 h and (f) 72 h of ageing in $CHCl_3$ at 21 °C Scale bars: 250 nm

Long Term Colloidal Stability of the Fibers of **3** in Solution

A 7 mL vial containing a 0.5 mg/mL solution of fibers of **3** (L_n = 206 nm, L_w/L_n = 1.73) in $CHCl_3$ was capped and aged at x21 °C on the benchtop. The solution was drop cast onto a TEM copper grid after 1, 7 and 104 days. After aging, no visible changes were observed in the solutions (i.e. a color change, precipitation, or metallogel formation) and the fibers showed negligible change by TEM analysis (Fig. S17).

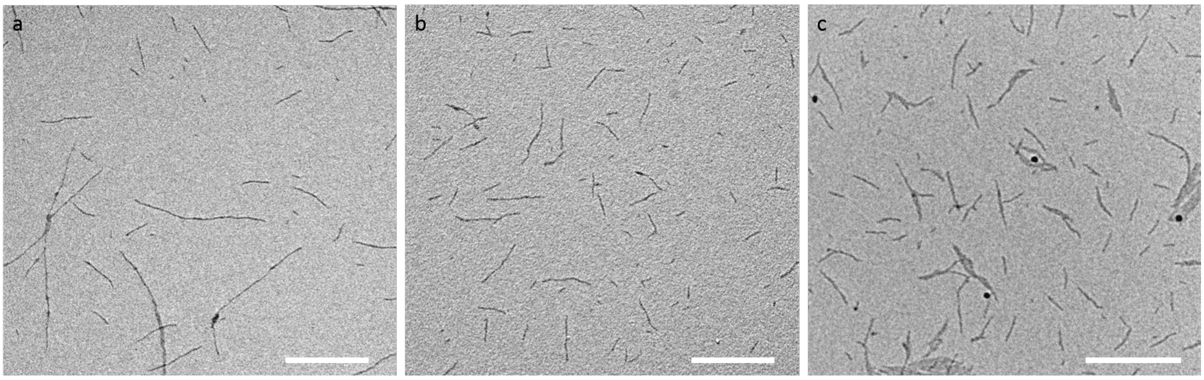


Fig. S17. TEM images of fibers of **3** after aging for (a) 1 d, (b) 7 d, and (c) 104 days in $CHCl_3$. Scale bars: 250 nm.

References

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