Electronic Supplementary Material (ESI) for Chemical Science.

Arene-Perfluoroarene Interactions Confer Enhanced Mechanical Properties to Synthetic Nanotubes

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A. Materials and Instrumentation

I. Materials.

Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. Anhydrous solvents (toluene, THF, Et_2O, DMF) were obtained from a solvent purification system (JC Meyer System). Poly(ethylene oxide) (PEO) (M_n = 4,000,000 g.mol^{-1}) and 1,4-dioxane (anhydrous >99.8%) were purchased from Sigma-Aldrich.

II. Instruments.

Nuclear Magnetic Resonance (NMR). ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AvanceIII-500 MHz spectrometer with a CryoProbe 5mm DCH w/ Z-Gradient, or on a 400 MHz Agilent DD MR-400 spectrometer using an AutoX 5mm probe w/ Z-Gradient. All spectra were recorded at 25°C. All spectra were calibrated using residual solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.00 for ^{13}C NMR; THF-d_8: 3.58, 1.73 ppm for ^{1}H NMR, 67.57, 25.37 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, dd = doublet of doublets, *br* = broad), coupling constants (Hz), and integration.

Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) Mass Spectrometry. MALDI-TOF mass spectra were recorded on a Bruker AutoFlex III with a 2,5-dihydroxybenzoic acid (DHB) matrix. All measurements were taken in reflectron positive (RP) mode. All data was processed using the corresponding FlexAnalysis software and are presented uncorrected and without any additional calibration. Samples were prepared using a 2,5-dihydroxybenzoic acid (DHB) matrix. To prepare the MALDI samples, macrocycles were dissolved in THF (1 mg mL^{-1}) and combined in equal volume amounts with a saturated solution of DHB in THF. The combined solution was spotted onto the MALDI chip and allowed to dry open to air for 30 minutes before data acquisition.

Size Exclusion Chromatography (SEC). Size Exclusion Chromatography (SEC) was performed in stabilized, HPLC-grade tetrahydrofuran using an Agilent 1200 series with a MALS (18 Angles Dawn Heleos II) detector, and two PolyPore 300x7.5mm columns (Varian p/n 5M-POLY-008-112). All runs were performed at 1.0 mL min^{-1} flow rate and 25°C. All samples were dissolved in THF (1 mg mL^{-1}) and filtered through a 0.2 μm syringe filter (PTFE membrane).

UV-Vis Absorption Spectroscopy. UV-Vis absorption spectra were acquired using a UV-3600 Shimadzu UV-Vis-NIR Spectrophotometer from 600 to 200 nm with a medium scan speed; λ_{max} in nm (ε in L · mol^{-1} · cm^{-1}). All spectra were recorded at room temperature in the presence of air. 1 equivalent of CF_3CO_2H per macrocycle was added to a stock 5mM solution of **MC1**, **MC2** or a 1:1 ratio of **MC1**:**MC2** in 1,4-dioxane. UV-Vis solutions were prepared by taking aliquots of these stock solutions and diluting them down to 5 μM directly before measurement. Three spectra were collected for each solution, one of the neutral MC solutions (pre CF_3CO_2H addition), one directly after the addition of CF_3CO_2H, and then one after one hour of CF_3CO_2H addition.

Fluorescence Spectroscopy. All spectra were recorded at room temperature in the presence of air. 1 equivalent of CF_3CO_2H per macrocycle was added to a stock 5mM solution of **MC1**, **MC2** or a

1:1 ratio of **MC1**:**MC2** in 1,4-dioxane. Fluorescence solutions were taken using the same samples as the UV-Vis data.

Atomic Force Microscopy (AFM). Atomic force microscopy (AFM) was conducted using the facilities at the Northwestern Atomic and Nanoscale Characterization Experiment Center (NUANCE) on a SPID Bruker FastScan AFM under the non-contact mode in air. AFM samples were prepared by taking 5 mM solutions of NTs in 1,4-dioxane, diluting them 10-fold and then drop casting them onto silicon wafers.

***In Solvo* Wide-Angle X-Ray Scattering.** Small- and wide-angle X-ray scattering (SAXS/WAXS) patterns were collected at Argonne National Lab's (ANL) Advanced Photon Source (APS) at both sectors 5-IDD (DND-CAT) and 12-ID-D with a capillary transmission geometry. Experiments conducted at 12-ID-D were collected at a beam energy of 12 keV and experiments conducted at 5-ID-D were collected at a beam energy of 13.3 keV. Individual frames were collected on a set of Pilatus detectors, which were then summed and radially integrated to produce a linear XRD pattern using proprietary software available at the APS. Scattering intensity is reported as a function of the modulus of the scattering vector q, related to the scattering angle 2θ by the equation:

$$q = \frac{4\pi}{\lambda}\sin(\theta)$$

where λ is the X-ray wavelength. The sample-to-detector distance was adjusted to measure across relevant detection ranges. Capillary experiments were conducted using 2.0 mm OD borosilicate capillaries with 0.2 mm wall thicknesses purchased from Hilgenberg GmbH.

Sonication. Sonication was performed with a Branson 3510 ultrasonic cleaner with a power output of 100 W and a frequency of 42 kHz.

Nanofiber Touch-Spinning. Macrocycles along 1 wt/v% Poly(ethylene oxide) (PEO) were touch-spun into fibers at 1000 RPM. The solution was supplied by an automated variable speed syringe pump (Razel Scientific Instruments. R99-E) through a syringe (Hamilton™ 1000 series gastight™ syringe, 1 mL) at a flow rate of 5 $\mu L.min^{-1}$ at room temperature.

Fiber Characterization. Scanning electron microscope (SEM) (Apreo S by ThermoFisher Scientific (formerly FEI)) were used to assess dimensions and alignment of the nanotubes in the fibers. All samples were sputter-coated (Denton Desk V sputter coater) with a 5-nm thick gold film prior to the imaging with SEM. A Fiji software was used to measure diameter of the nanofibers.[1]

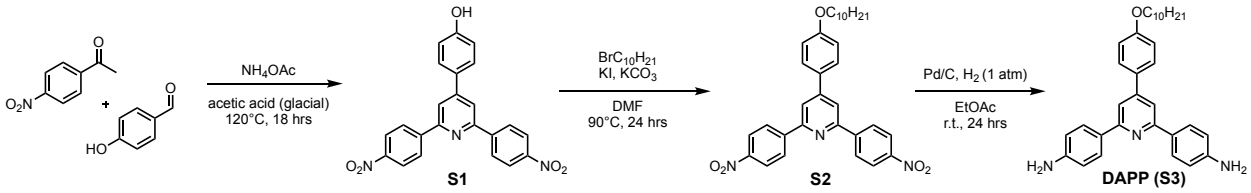
Tensile Testing of Touch-Spun Nanofibers. Uniaxial tensile testing of the fiber samples (n=3 for each fiber group, sample dimensions: 10 mm × 5 mm) was performed using a Test Resources 830LE63 Axial Torsion Test Machine equipped with a 10-lb load cell. The crosshead displacement rate was kept constant at 0.1 mm/s for all the measurements. Elastic modulus was defined as the slope of the linear portion of the stress-strain curve.

B. Synthetic Procedures

Synthesis of monomers.

Terephthalaldehyde (PDA) [Aldrich®] is a commercially available compound that was used without further purification. The diaminophenylpyridine (DAPP) monomer is a previously reported compound that was prepared through a reported three step procedure.[2] Tetrafluoroterephthalaldehyde (F_4-PDA) was prepared in a one-step procedure slightly modified from a reported procedure. [3-4]

Scheme S1: Three step synthesis of DAPP (S3)

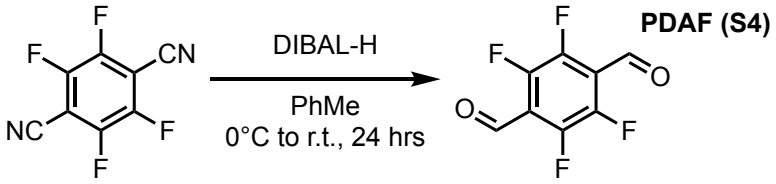


Synthesis of S1: 4-hydroxybenzaldehyde (5.0 g, 41 mmol), 4-nitroacetophenone (13.5 g, 82 mmol) and ammonium acetate (76.5 g, 1.0 mol) were added to a 500 mL round bottom flask equipped with a magnetic stir bar and cold-water condenser and subsequently dissolved in 150 mL of glacial acetic acid. The solution was refluxed and stirred for 18 h. under an N_2 atmosphere. The crude reaction mixture was then cooled, and the precipitate collected *via* vacuum filtration and then washed with methanol (3 × 200 mL) to yield **S1** as a pale-yellow powder (7.68 g, 45.5%). **S1:** ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.64-8.57 (m, 4H), 8.41-8.34 (m, 6H), 8.01-7.91 (m, 2H), 6.97-6.89 (m, 2H). Spectroscopic data is consistent with previous reports.[2]

Synthesis of S2: To a flame dried 40 mL reaction vial equipped with a magnetic stir bar and a pressure rated cap, **S1** (2.0 g, 4.8 mmol), K_2CO_3 (0.84 g, 6.04 mmol, 1.25 equiv), KI (0.40 g, 2.4 mmol, 0.5 equiv), and 1-bromodecane (1.34 g, 6.04 mmol, 1.25 equiv) were added with 20 mL of anhydrous DMF. The solution was then heated to 90°C under an N_2 atmosphere. After 24 h. the reaction was cooled to room temperature and poured into water (200 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were then washed with brine (3 × 100 mL) and dried over $MgSO_4$. The solvent was then removed *in vacuo* to yield **S2** as a tan powder (2.31 g, 86.2%). **S2:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42-8.34 (m, 8H), 8.01 (s, 2H), 7.74-7.69 (m, 2H), 7.11-7.05 (m, 2H), 4.05 (t, *J*= 6.6 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.54 – 1.46 (m, 2H), 1.42 – 1.23 (m, 12H), 0.92 – 0.87 (m, 3H). Spectroscopic data is consistent with previous reports.[2]

Synthesis of DAPP (S3): Palladium on Carbon (0.83 g, 10 wt%) was added to a flame dried round bottom flask equipped with a magnetic stir bar under a stream of N_2. Next, 100 mL of ethyl acetate and **S2** (2.0 g, 3.62 mmol) were added and the reaction was stirred under an atmosphere of H_2 (balloon). After 24 hours the solution was filtered over Celite and the solution was concentrated *in vacuo* to yield **S3** as a yellow powder (1.37 g, 76.6%). **DAPP:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.3 Hz, 4H), 7.70 – 7.62 (m, 4H), 7.05 – 6.98 (m, 2H), 6.79 (d, *J* = 8.5 Hz, 4H), 4.02 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.53 – 1.44 (m, 2H), 1.42 – 1.23 (m, 12H), 0.93 – 0.86 (m, 3H). Spectroscopic data is consistent with previous reports.[2]

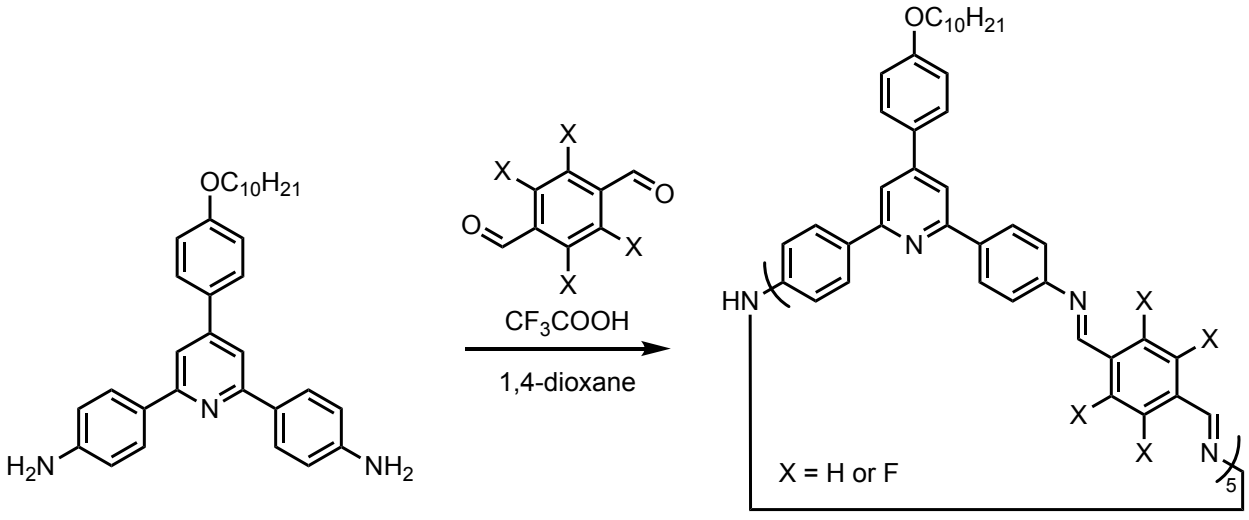
Scheme S2: Synthesis of PDAF (S4)



Synthesis of PDAF (S4): To a 500 mL round bottom flask equipped with a magnetic stir bar, 2,3,5,6-tetrafluoroterephthalonitrile (10 g, 0.05 mol) and anhydrous toluene (150 mL) were added, and the solution was cooled to 0°C under a N_2 atmosphere. Next, a 1 M solution of diisopropylaluminum hydride (DIBAL-H) in anhydrous toluene (125 mL, 0.125 mol) was added dropwise. The solution was stirred and held at 0°C for 1 hour and then allowed to warm to room temperature overnight. After 24 hour the reaction was quenched with 2 M HCl (400 mL) until the reaction solution reached a pH <2. The solution was then stirred for 1 hr. The precipitate formed was then filtered and washed with CH_2Cl_2 (3 × 50 mL). The aqueous layer was then extracted with an additional CH_2Cl_2 (2 × 50 mL). The combined organic layers were then washed with saturated $NaHCO_3$ (3 × 50 mL) and brine (3 × 50 mL). The solution was dried over $MgSO_4$ and concentrated *in vacuo.* The resulting crude product was then recrystallized from cold CH_2Cl_2 to yield **S4** as a pale yellow crystalline solid (1.0 g, 10%). **PDAF:** ^{19}F NMR (400 MHz, $CDCl_3$): δ -143.71 Hz (s, 4F). Spectroscopic data is consistent with previous reports.[2]

Synthesis of macrocycles. All macrocycles were prepared through previously reported syntheses.[2]

Scheme S3: General Macrocycle Procedure



Synthesis of MC1: To a 1-dram vial, **DAPP** (S3, 36 mg, 0.07 mmol) and terephthalaldehyde (**PDA**, 9.8 mg, 0.07 mmol, 1.0 equiv) were added and then dissolved in 3.65 mL of anhydrous 1,4-dioxane (20 mM with respect to **DAPP**). Next, a 2 M solution of trifluoroacetic acid in 1,4-dioxane (36 µL, 0.07 mmol, 1 equiv) was added to the vial. The vial was then vigorously shaken, and the reaction immediately turned bright orange and began to gel. The vial was then left to sit overnight

on the benchtop. The reaction was then neutralized with triethylamine (0.5 mL) and poured into Et_2O. The resulting precipitate was isolated *via* centrifugation and then rinsed with Et_2O (2 × 5 mL), EtOAc (3 × 5 mL), hexanes (3 × 5 mL), and acetone (3 × 5 mL). The bright yellow solid was then dried under high vacuum to yield the desired macrocycles (35.0 mg, 81%).

Synthesis of MC2: To a 1-dram vial, **DAPP** (S3, 36 mg, 0.07 mmol) and **PDAF** (**S4**, 15.0 mg, 0.07 mmol, 1.0 equiv) were added and then dissolved in 3.65 mL of anhydrous 1,4-dioxane (20 mM with respect to **DAPP**). Next, a 2 M solution of trifluoroacetic acid in 1,4-dioxane (36 µL, 0.07 mmol, 1 equiv) was added to the vial. The vial was then vigorously shaken, and the reaction immediately turned bright yellow and began to gel. The vial was then left to sit overnight on the benchtop. The reaction was then neutralized with triethylamine (0.5 mL) and poured into Et_2O. The resulting precipitate was isolated *via* centrifugation and then rinsed with Et_2O (2 × 5 mL), EtOAc (3 × 5 mL), hexanes (3 × 5 mL), and acetone (3 × 5 mL). The bright yellow solid was then dried under high vacuum to yield the desired macrocycles (39.3 mg, 81%).

Sample Preparation for Touch-Spinning. 5mM solutions of macrocycle were prepared by adding vacuum dried macrocycle to anhydrous 1,4-dioxane and sonicating the solution overnight to break up the solid. After resuspension, 1 equiv of trifluoroacetic acid (with respect the macrocycles) was added to induce assembly into nanotubes. The solutions were left to sit, undisturbed, for 30 min and then 1 wt/v% poly(ethylene oxide) (PEO, M_n = 4,000,000 g·mol^{-1}) was added to each vial.

C. NMR Spectra

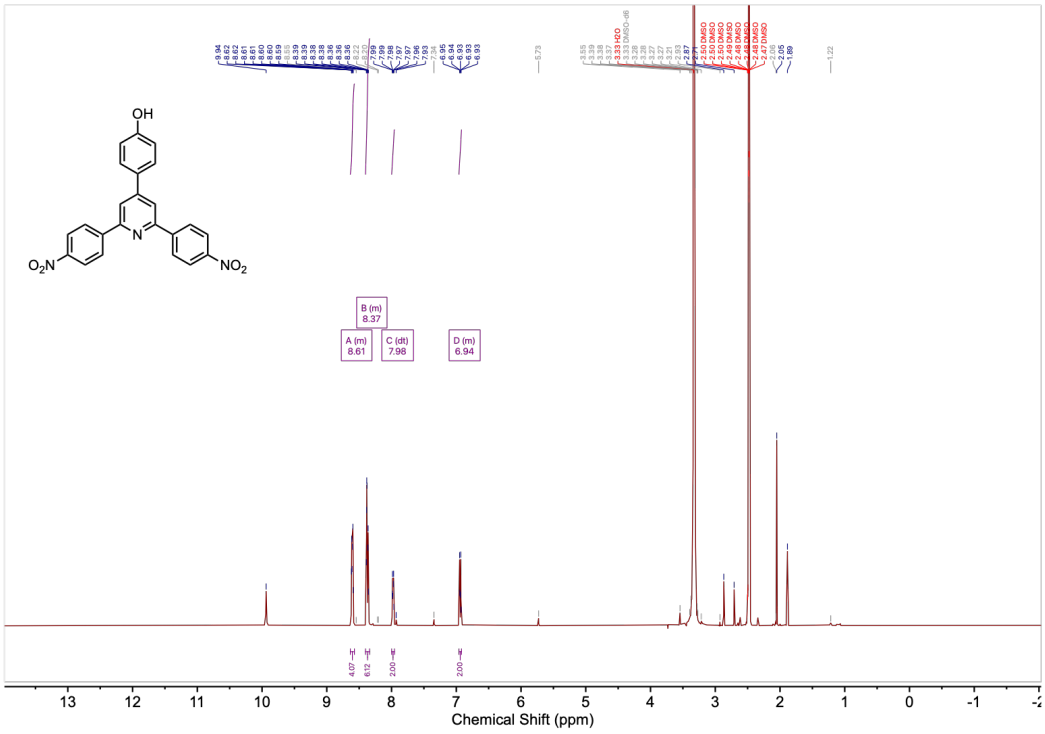


Figure S1. ^{1}H NMR (DMSO-d^6, 500 MHz, 298 K) of **S1**.

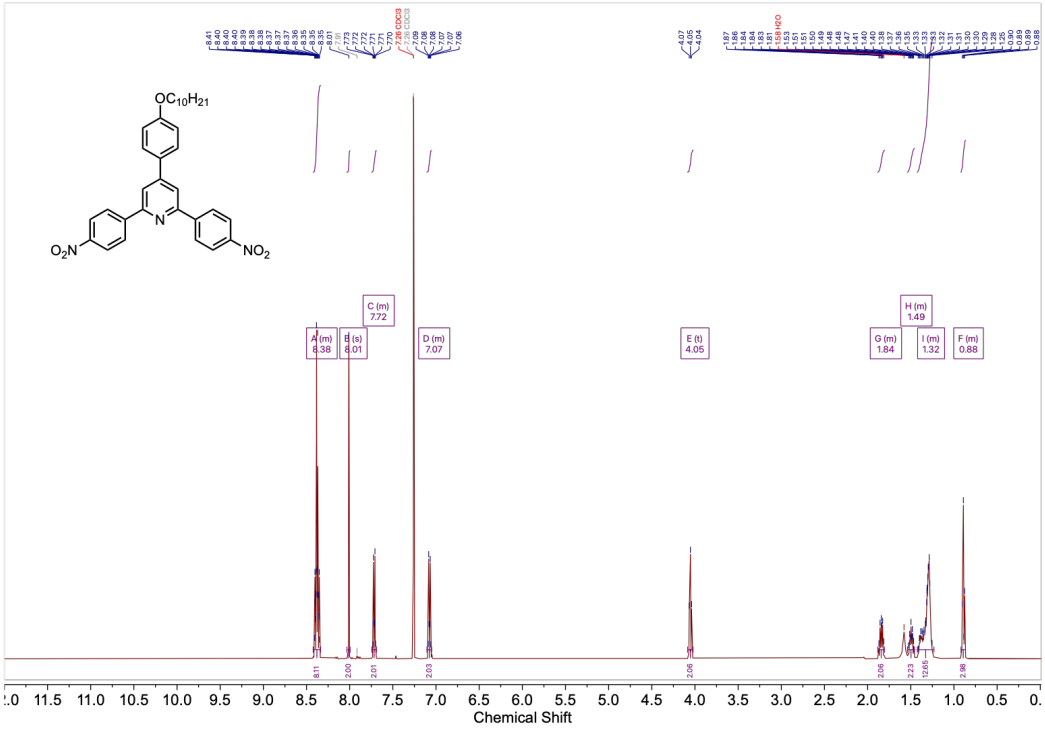


Figure S2. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) of **S2**.

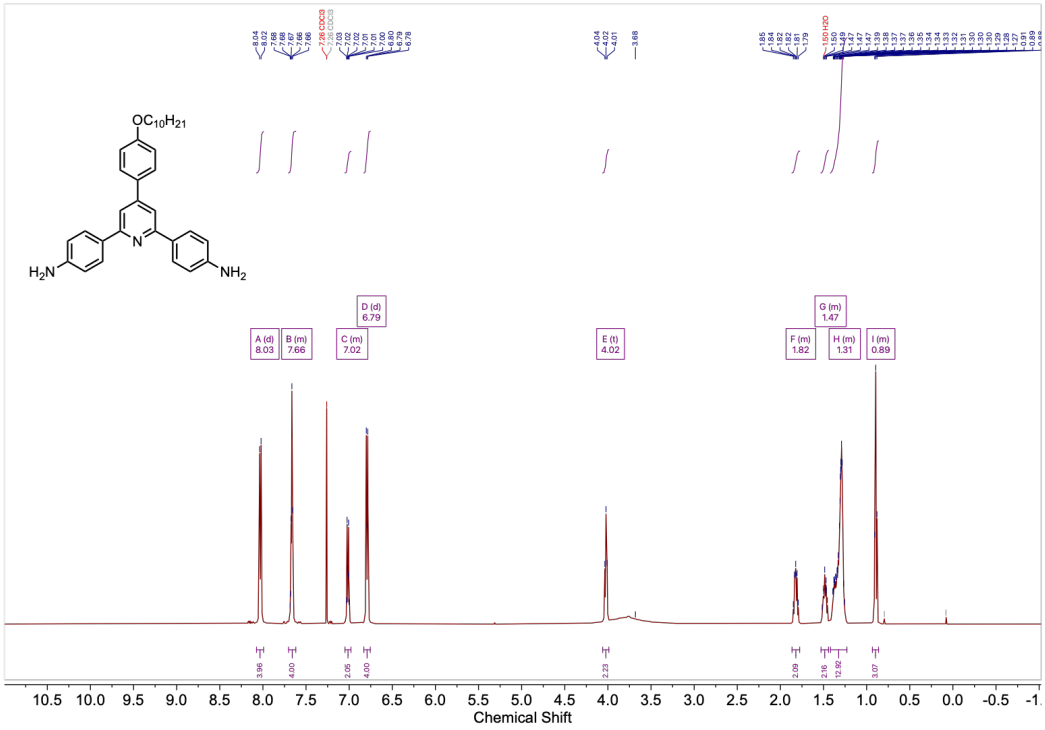


Figure S3. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) of DAPP (**S3**).

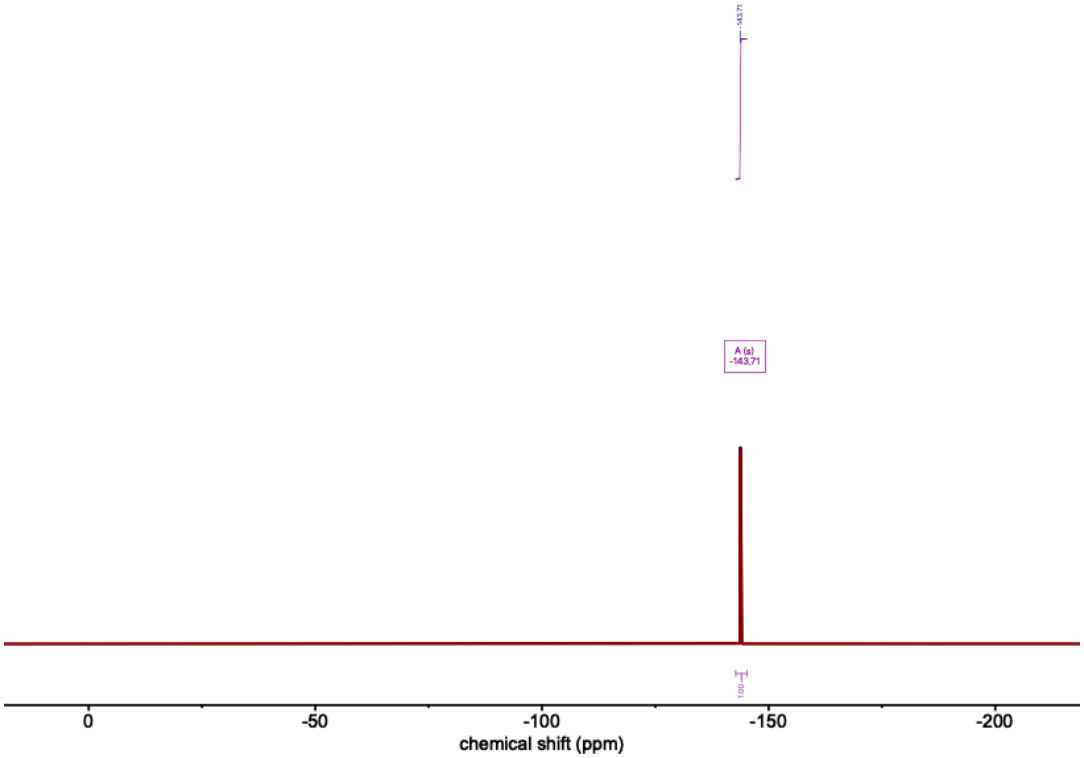


Figure S4. ^{19}F NMR ($CDCl_3$, 500 MHz, 298 K) of PDAF (**S4**).

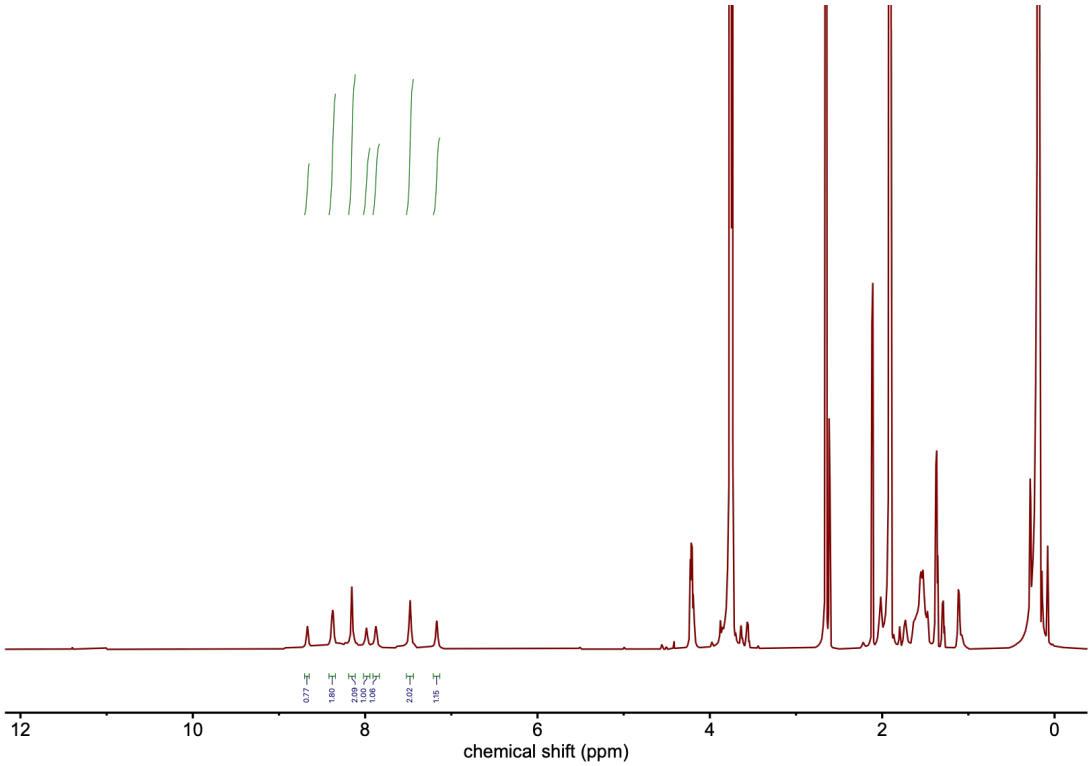


Figure S5. ^{1}H NMR (THF-d^{8}, 500 MHz, 298 K) of PDA-DAPP (**MC1**).

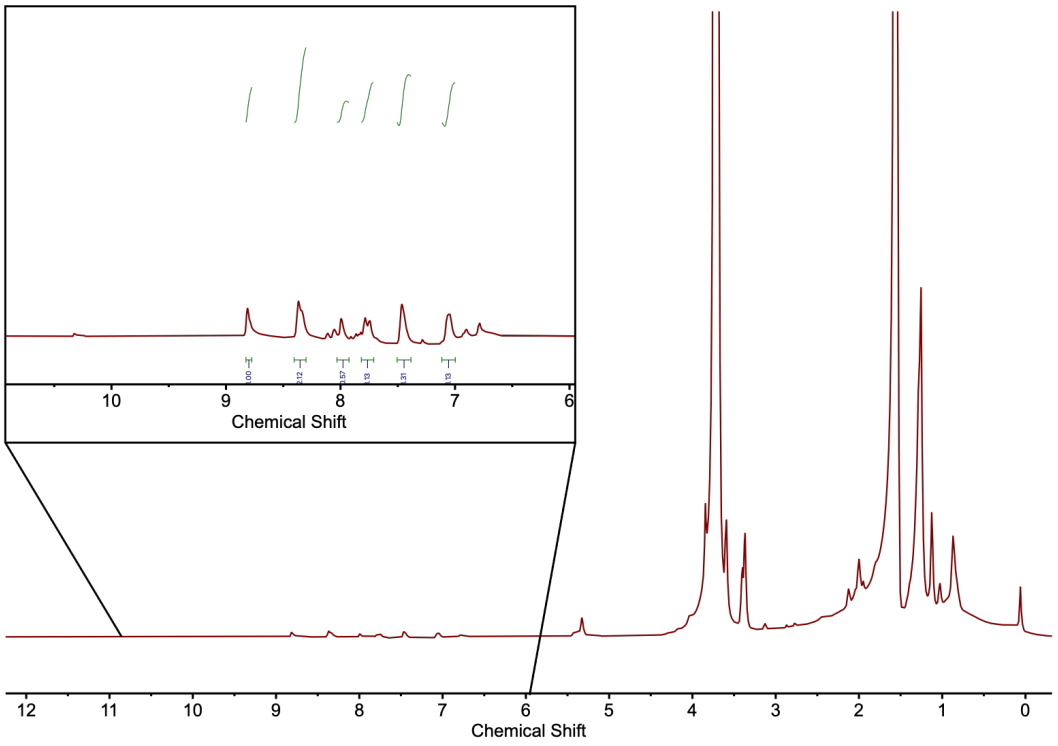


Figure S6. ^{1}H NMR (DCE-d^{4}, 500 MHz, 298 K) of PDAF-DAPP (**MC2**).

D. MALDI-TOF Data

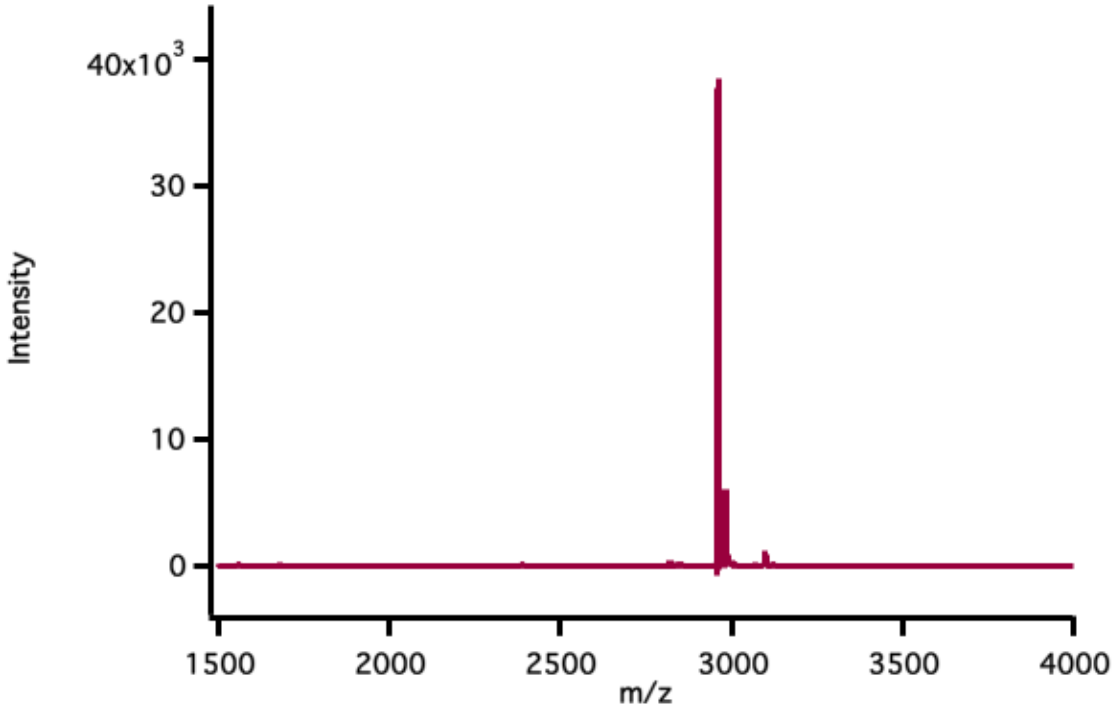


Figure S7. MALDI-TOF spectrum of **MC1** (PDA-DAPP).

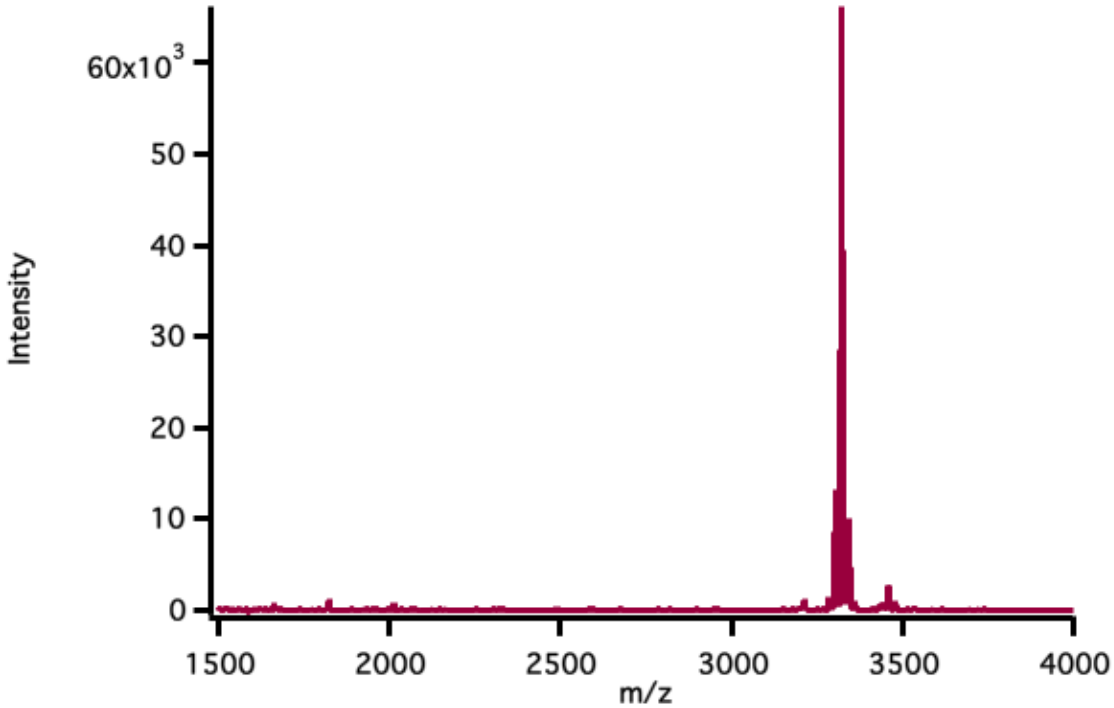


Figure S8. MALDI-TOF spectrum of **MC2** (PDA-DAPP).

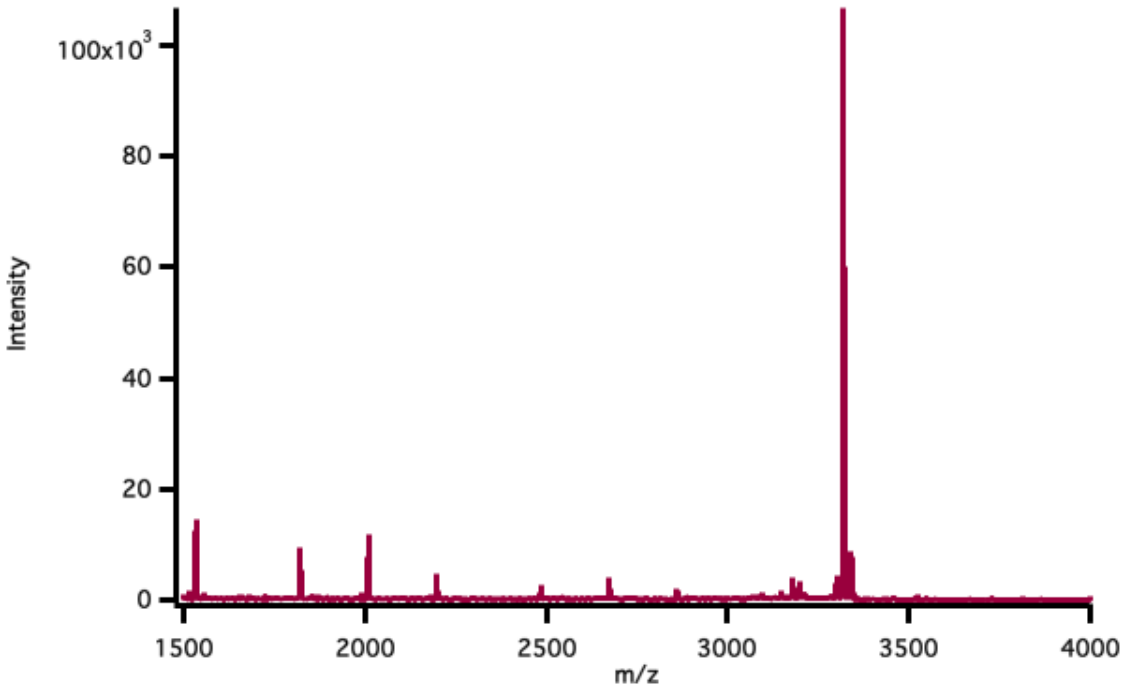


Figure S9. MALDI-TOF spectrum of **MC2** after ^{1}H NMR analysis

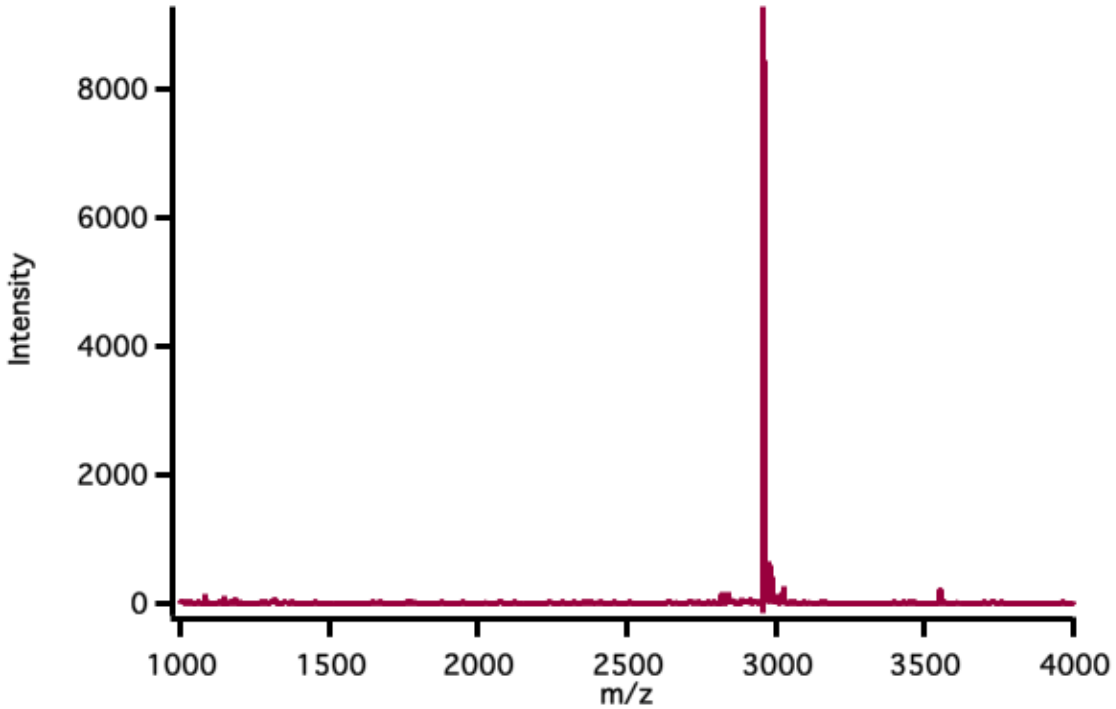


Figure S10. MALDI-TOF spectrum of fiber degradation on touch spun fibers from **NT1**.

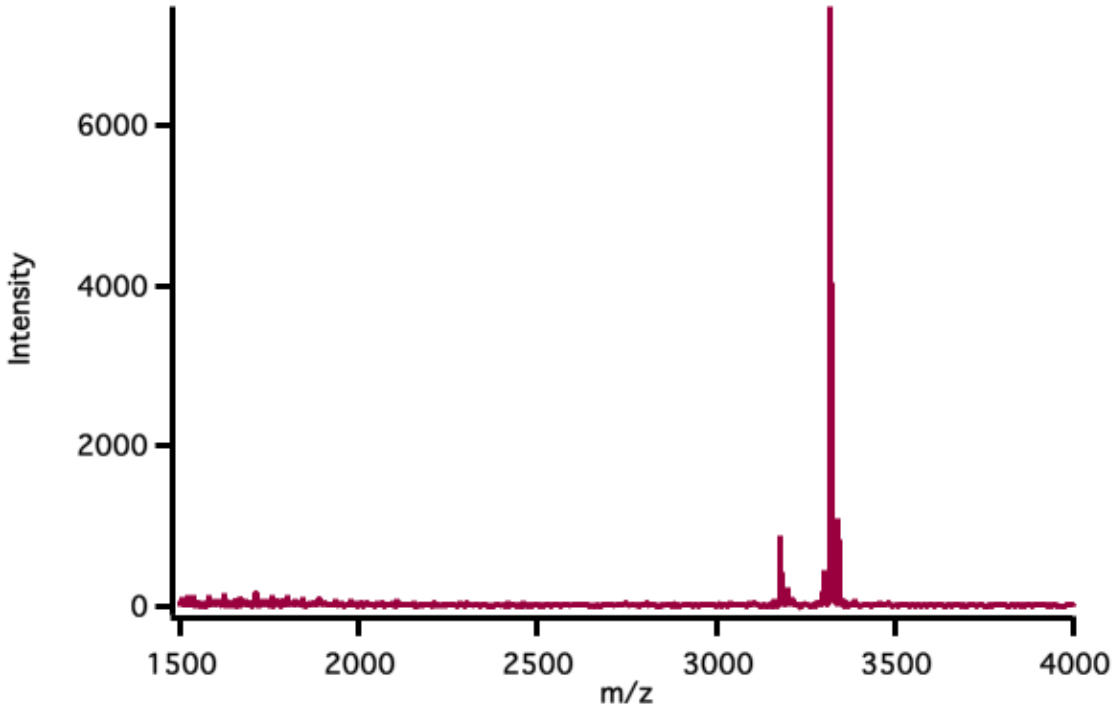


Figure S11. MALDI-TOF spectrum of fiber degradation on touch spun fibers from **NT2**.

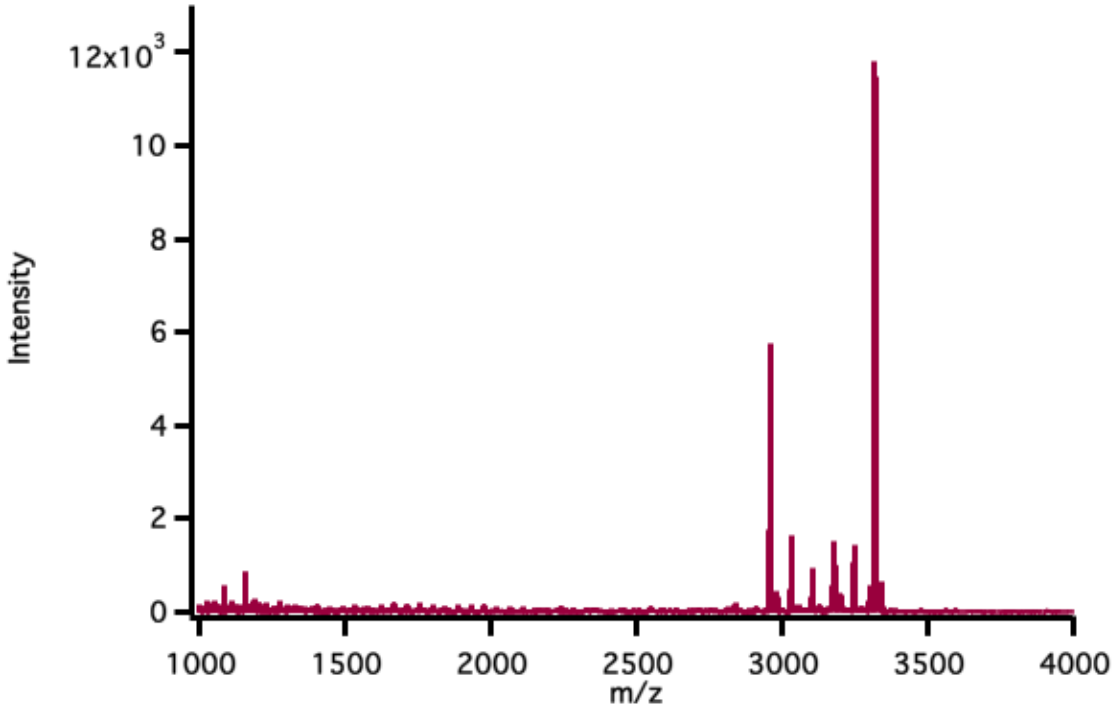


Figure S12. MALDI-TOF spectrum of fiber degradation on touch spun fibers from **NT3**.

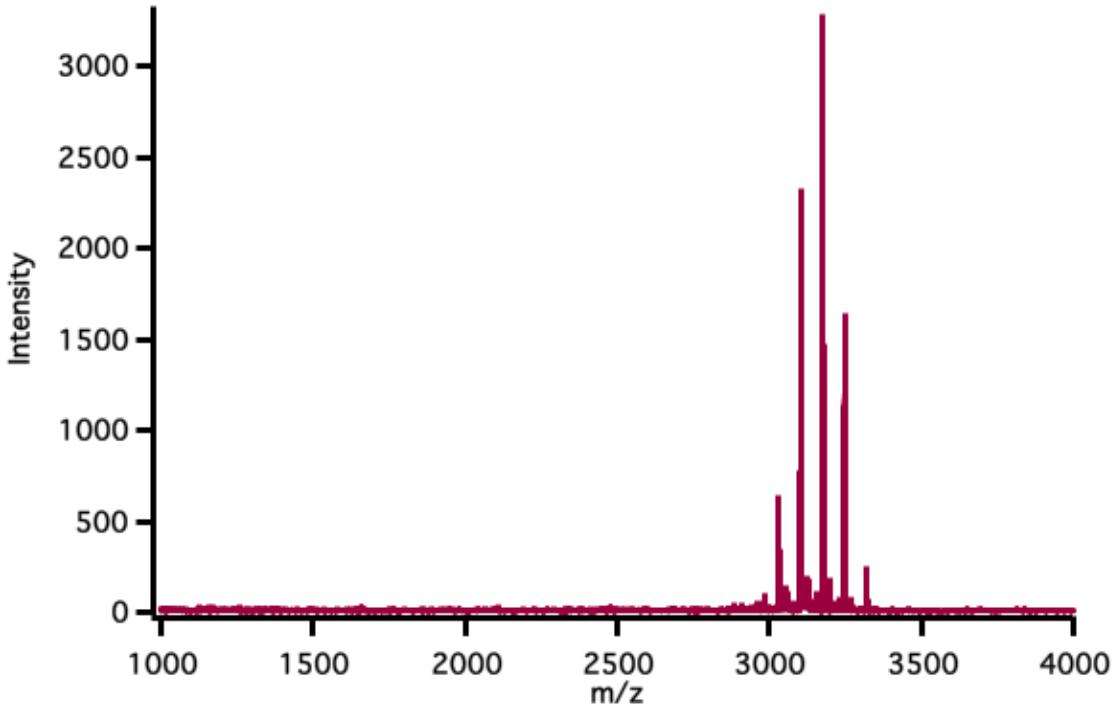


Figure S13. MALDI-TOF spectrum of fiber degradation on touch spun fibers from **NT3** with increased acid loadings to promote scrambling.

E. SEC Data

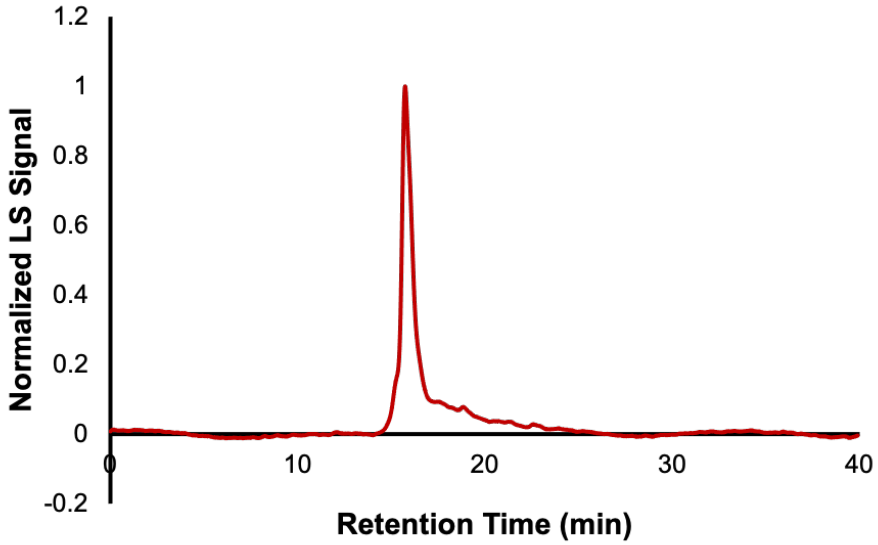


Figure S14. Size exclusion chromatograph of **MC1** using a MALS detector

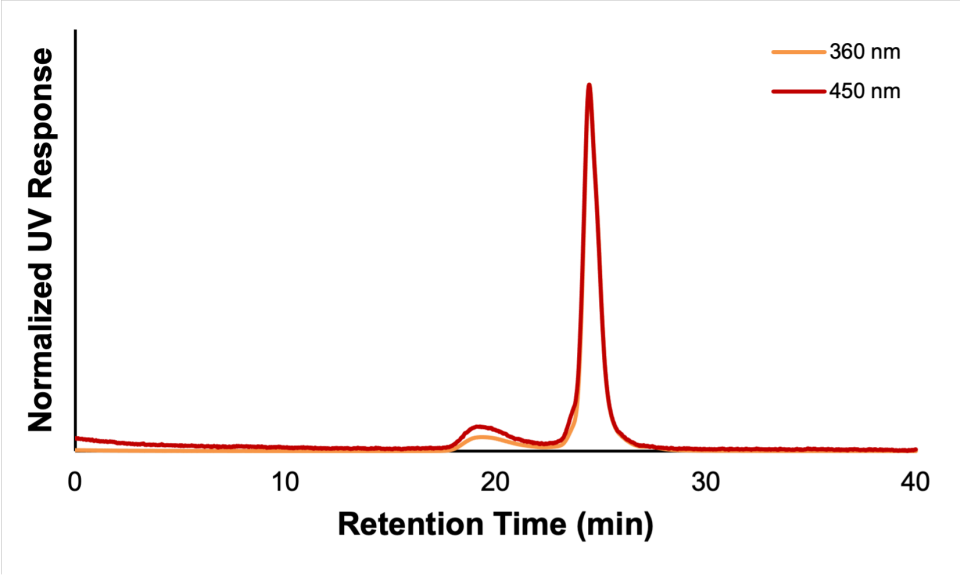


Figure S15. Size exclusion chromatograph of **MC1** using a UV detector. A different instrument was used for this quantitative detection, explaining the difference in elution time from Figure S14. We believe the peak at 20 min could be due to small amounts of aggregation as no peak is observed with the MALS detector.

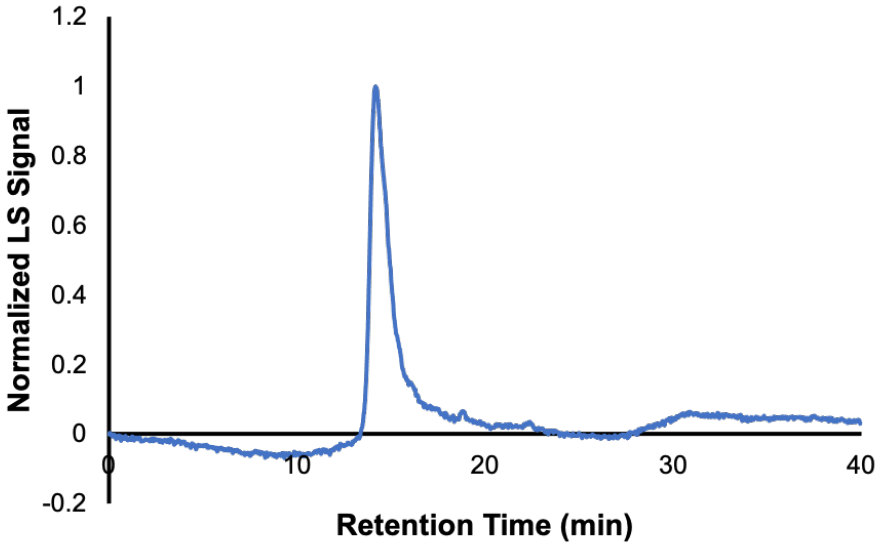


Figure S16. Size exclusion chromatograph of **MC2** using a MALS detector

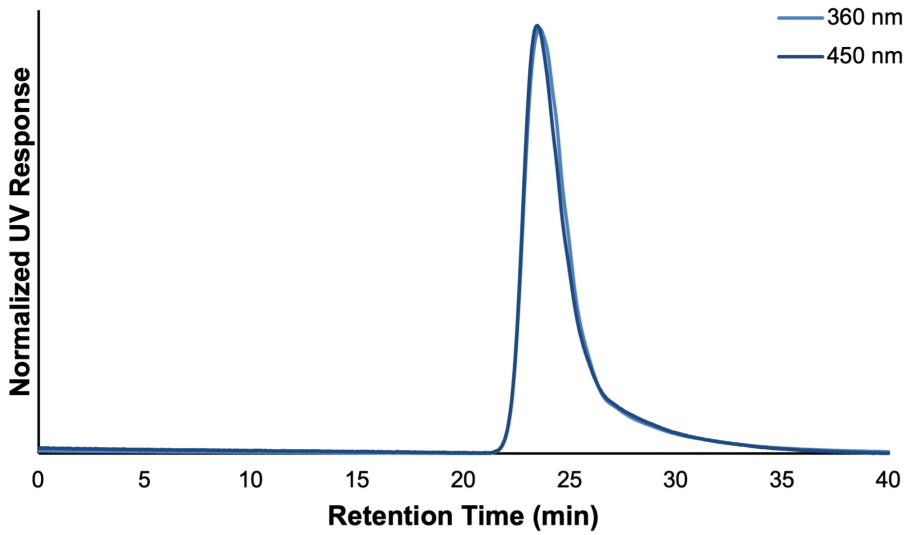


Figure S17. Size exclusion chromatograph of **MC2** using a UV detector. A different instrument was used for this quantitative detection, explaining the difference in elution time from Figure S16.

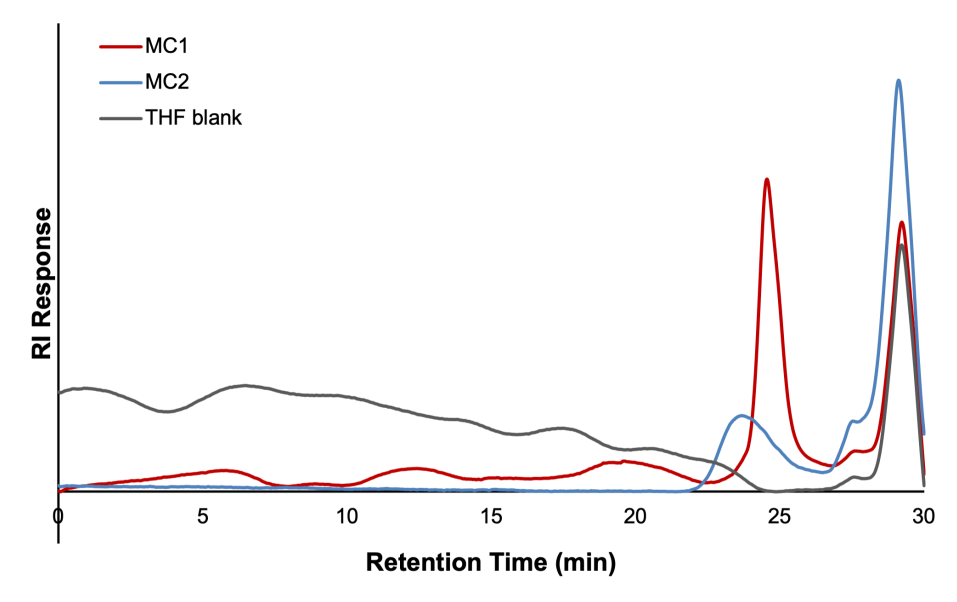


Figure S18. Size exclusion chromatograph of **MC1** and **MC2** using a Refractive Index (RI) detector. The instrument used produced a feature around 28 min that is not indicative of any of the MC samples as it also appears in a blank THF run. The retention times corresponding to both **MC1** and **MC2** agree with the reported UV traces in Figures S15 and S17.

F. UV-Vis Data

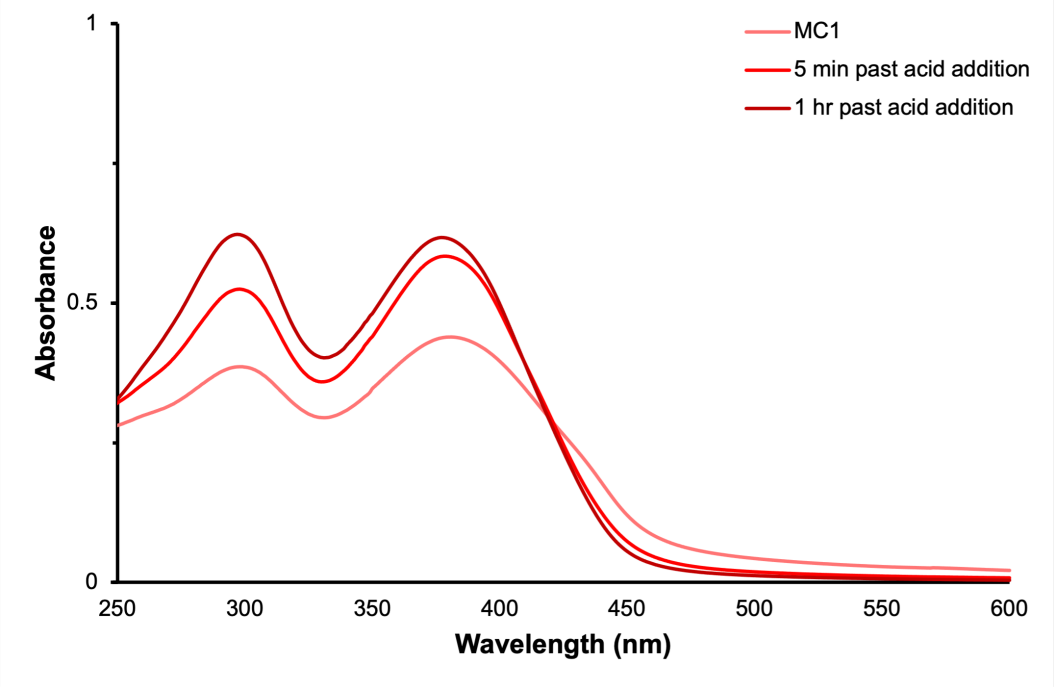


Figure S19. UV-Vis spectra monitoring the assembly of **NT1** upon addition of 1 equiv of CF_3CO_2H per macrocycle

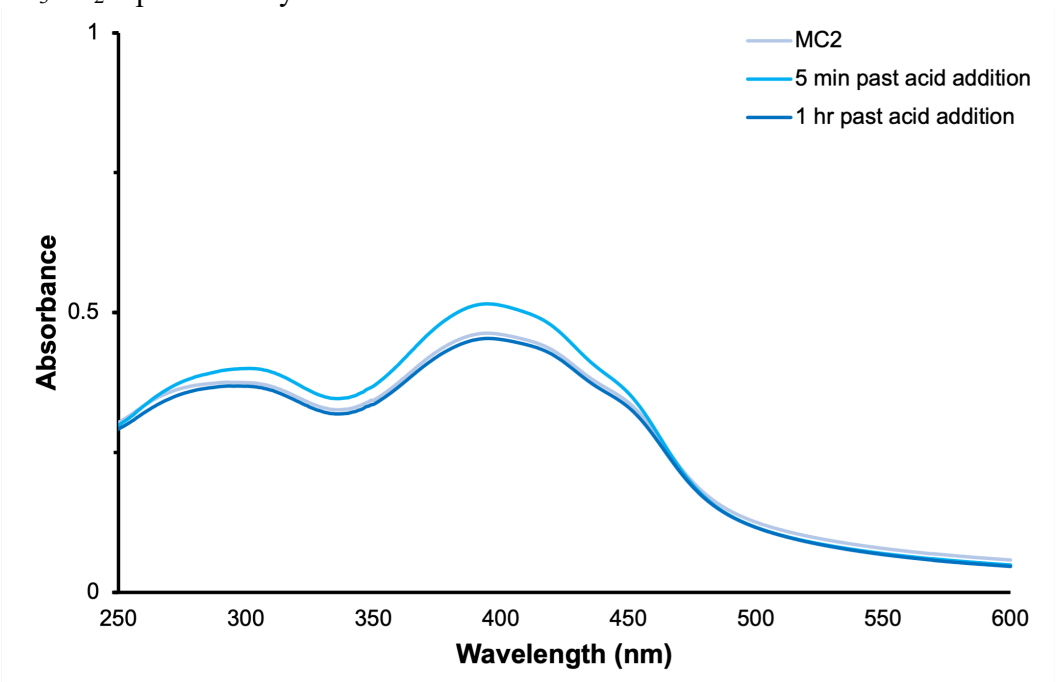


Figure S20. UV-Vis spectra monitoring the assembly of **NT2** upon addition of 1 equiv of CF_3CO_2H per macrocycle.

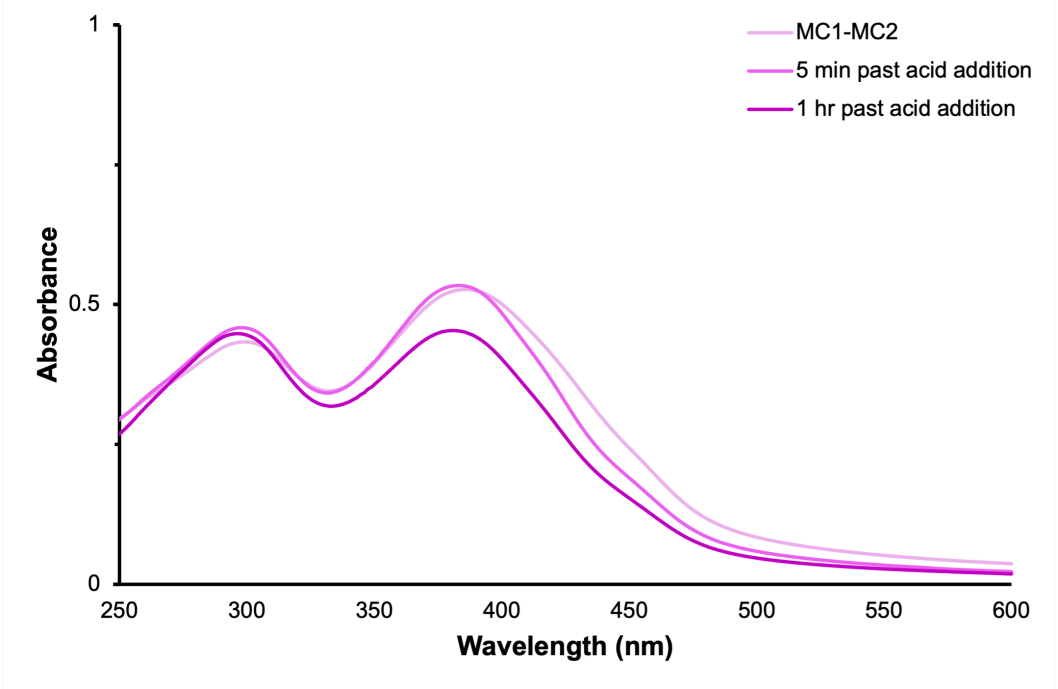


Figure S21. UV-Vis spectra monitoring the assembly of **NT3** upon addition of 1 equiv of CF_3CO_2H per macrocycle.

G. Fluorescence Data

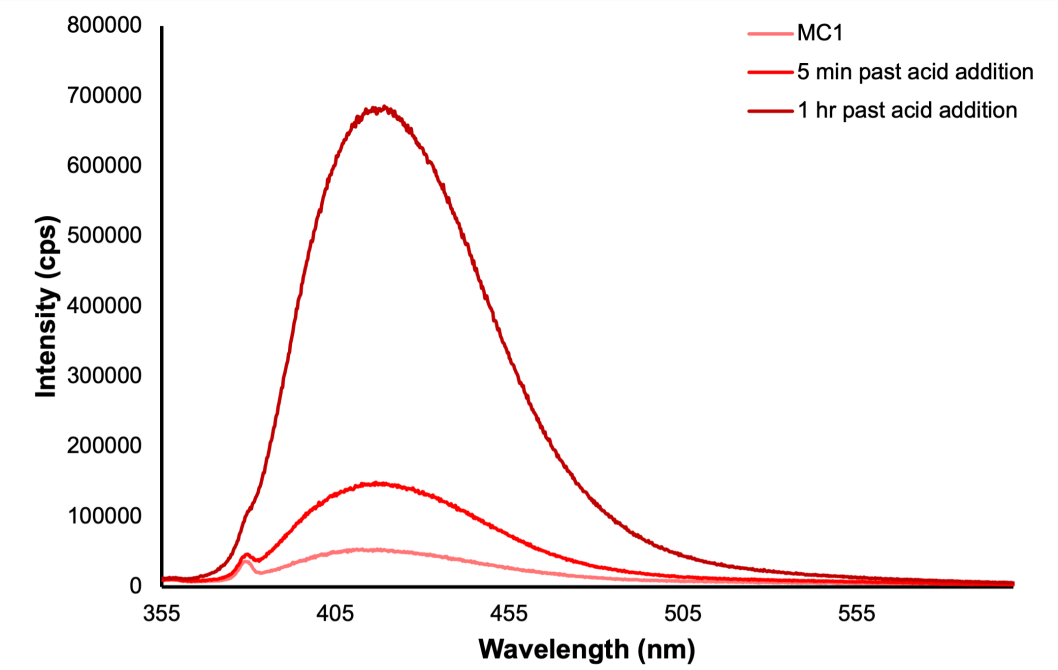


Figure S22. Fluorescence spectra monitoring the assembly of **NT1** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

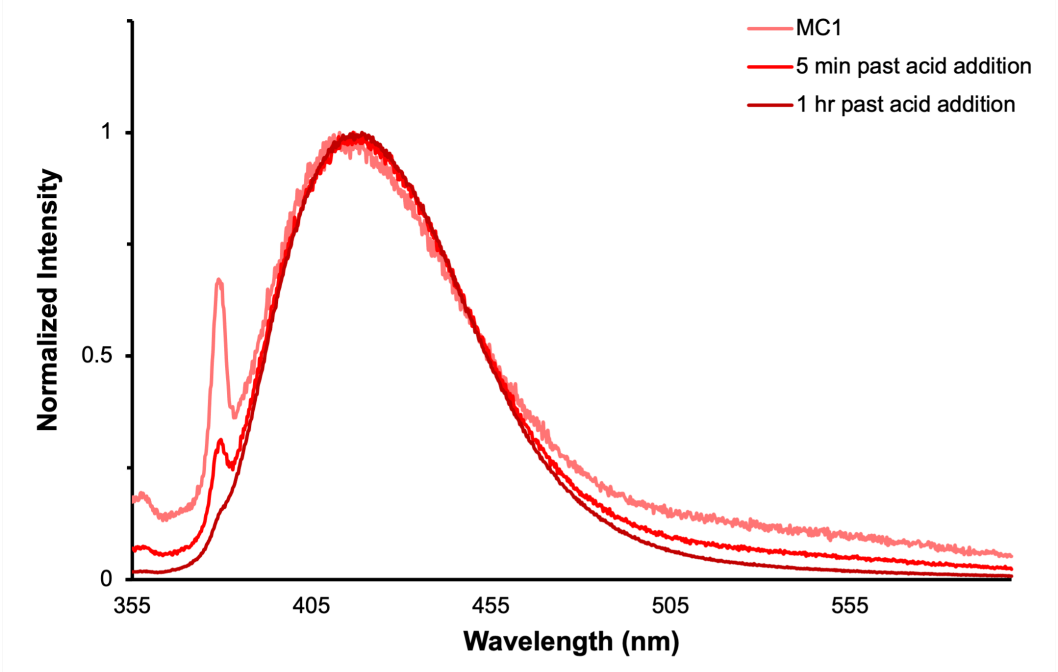


Figure S23. Normalized fluorescence spectra monitoring the assembly of **NT1** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

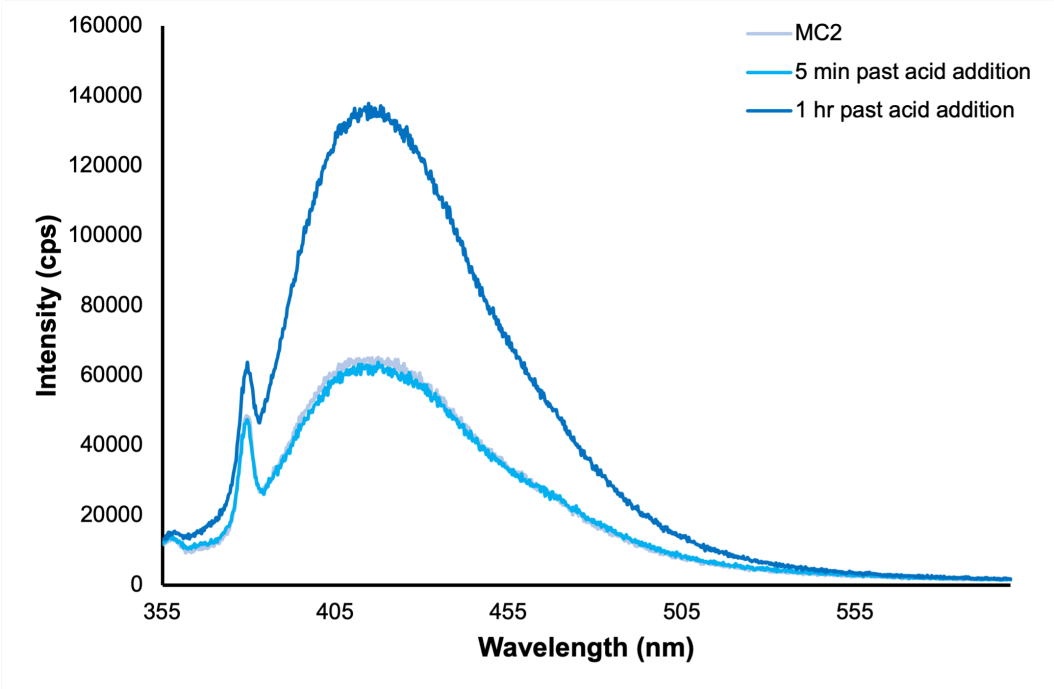


Figure S24. Fluorescence spectra monitoring the assembly of **NT2** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

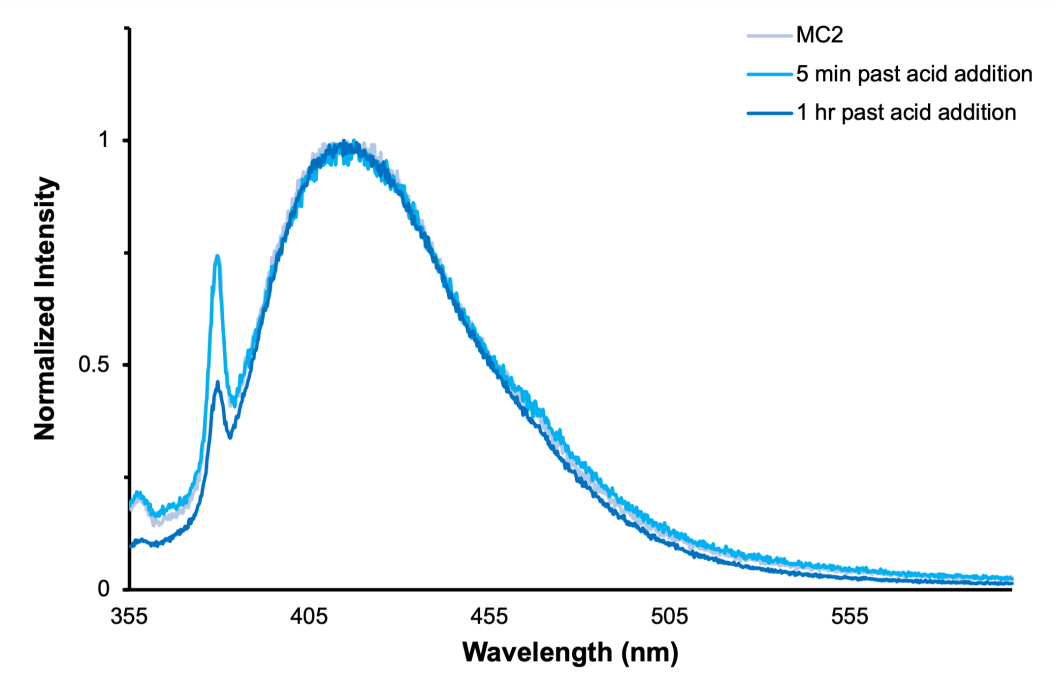


Figure S25. Normalized fluorescence spectra monitoring the assembly of **NT2** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

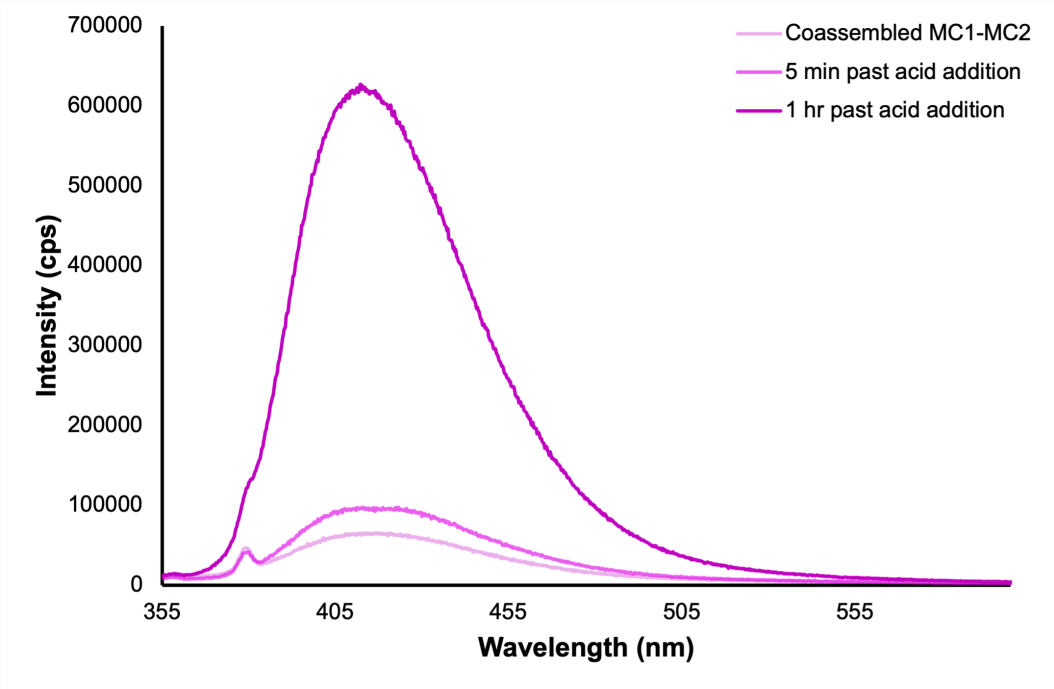


Figure S26. Fluorescence spectra monitoring the assembly of **NT3** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

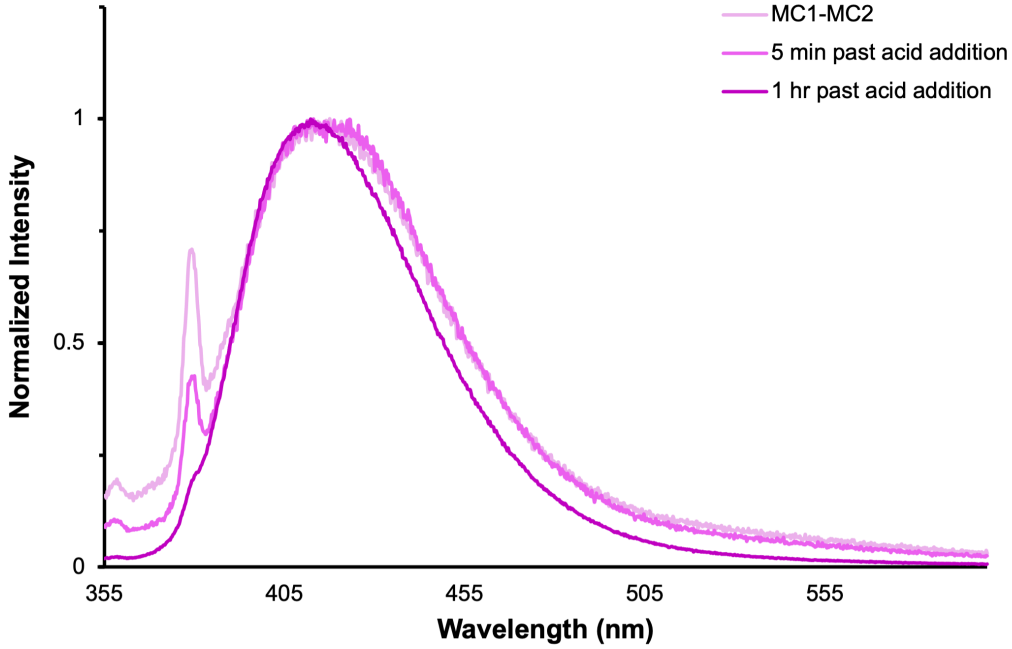


Figure S27. Normalized fluorescence spectra monitoring the assembly of **NT3** upon addition of 1 equiv of CF_3CO_2H per macrocycle (λ_{ex} = 340 nm).

H. Atomic Force Microscopy (AFM) Images

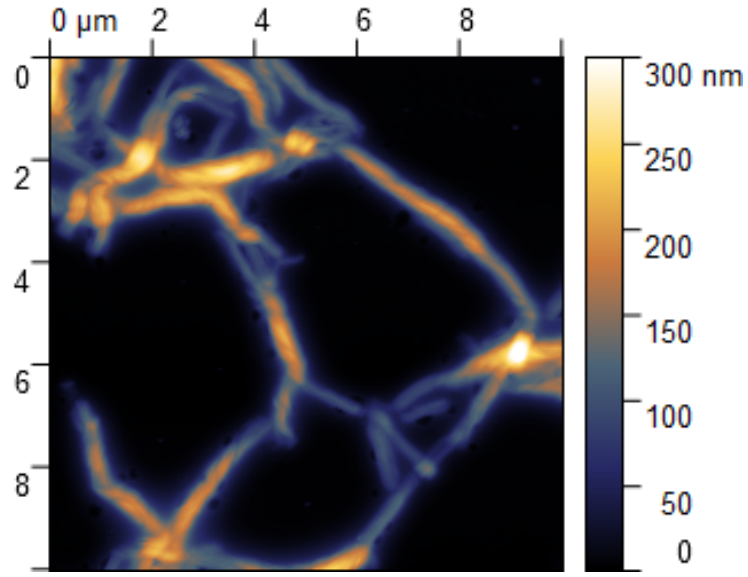


Figure S28. AFM image of as synthesized NT1

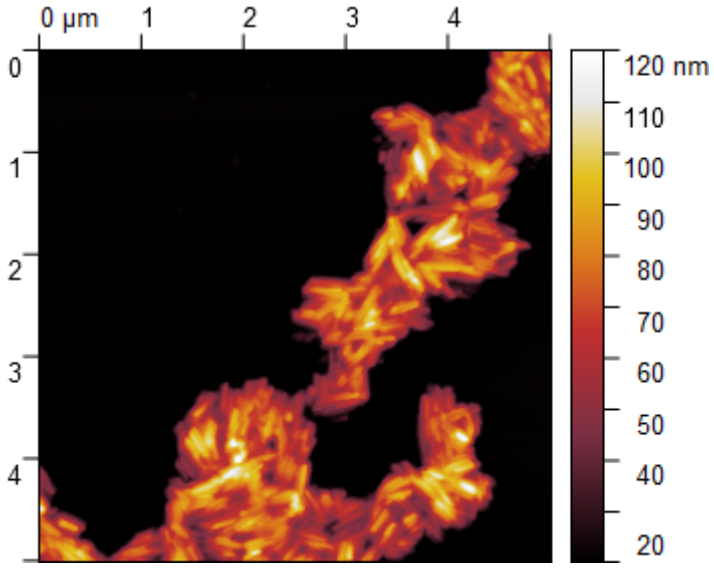


Figure S29. AFM image of NT1 30 min after purification, suspension in 1,4-dioxane, and acidification with CF_3CO_2H (1 equiv per macrocycle)

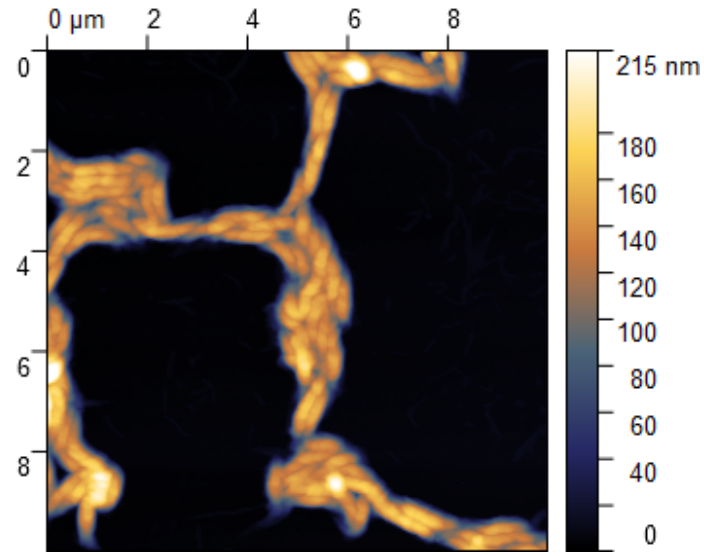


Figure S30. AFM image of as synthesized NT2

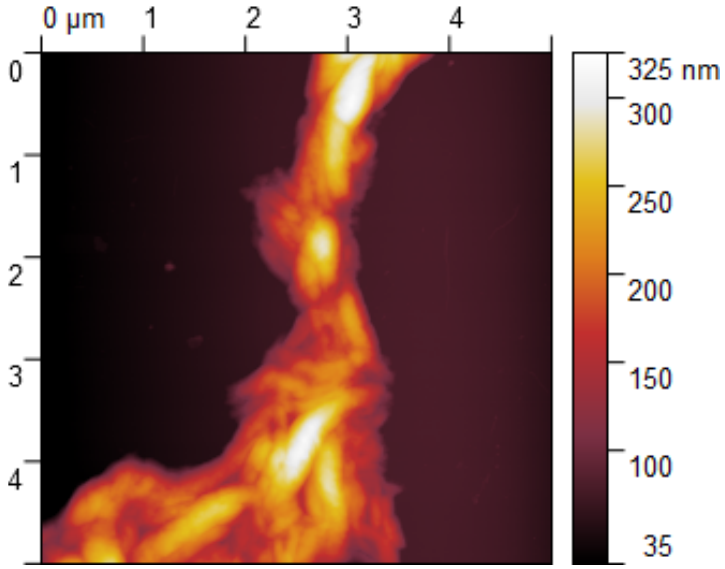


Figure S31. AFM image of NT2 30 min after purification, suspension in 1,4-dioxane, and acidification with CF_3CO_2H (1 equiv per macrocycle)

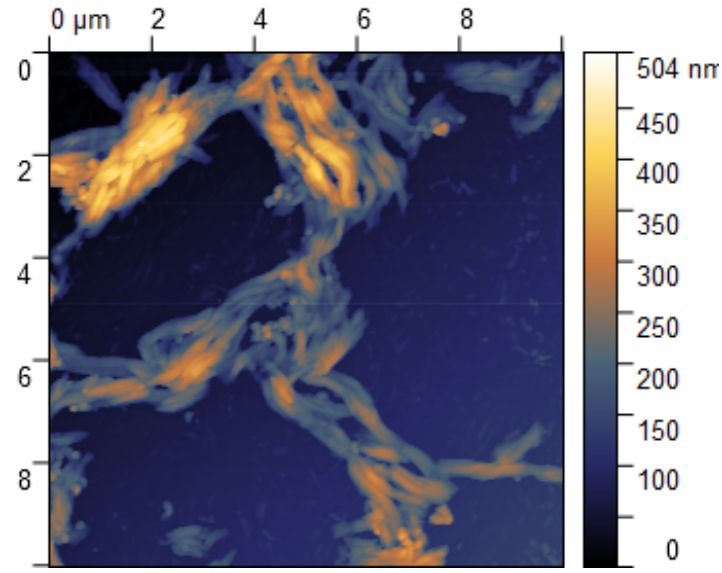


Figure S32. AFM image of NT3 1 week after suspension and acidification with CF_3CO_2H (1 equiv per macrocycle)

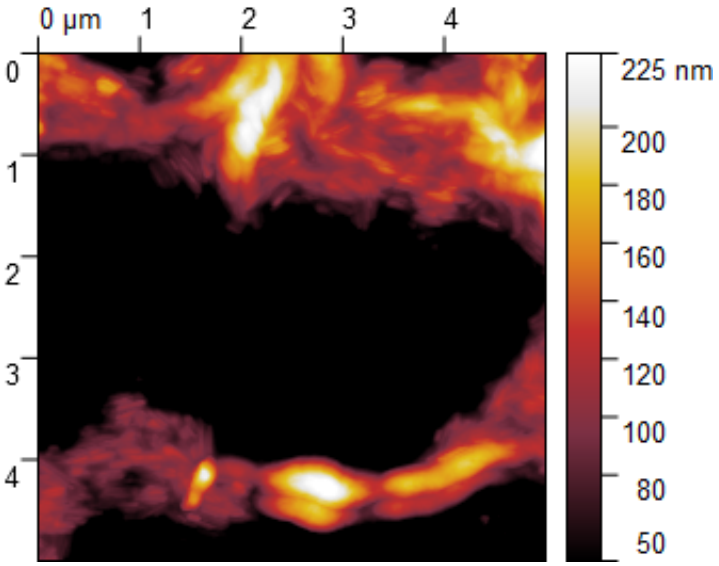


Figure S33. AFM image of NT3 30 min after suspension and acidification with CF_3CO_2H (1 equiv per macrocycle)

I. Scanning Electron Microscopy (SEM) Images

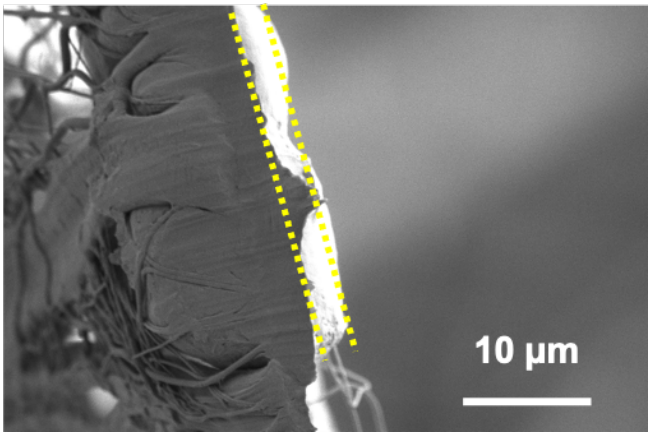


Figure S34. SEM image of a cross section of a bundle of touch spun fibers from a **PEO** solution. The cross section is 5.4 ± 0.73 µm.

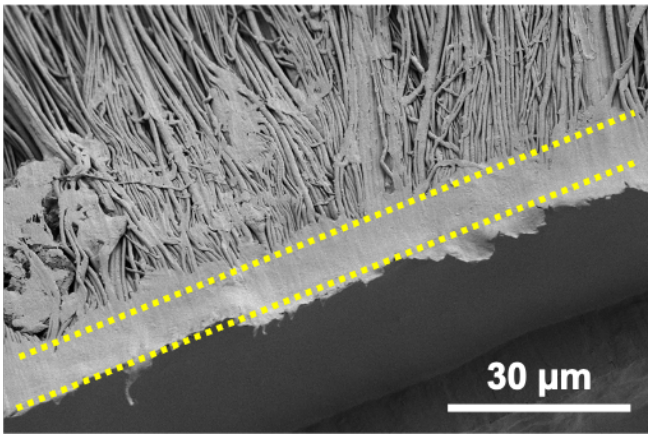


Figure S35. SEM image of a cross section of a bundle of touch spun fibers from **NT1** solution formed from low acid loadings. The cross section is 8.8 ± 0.6 µm.

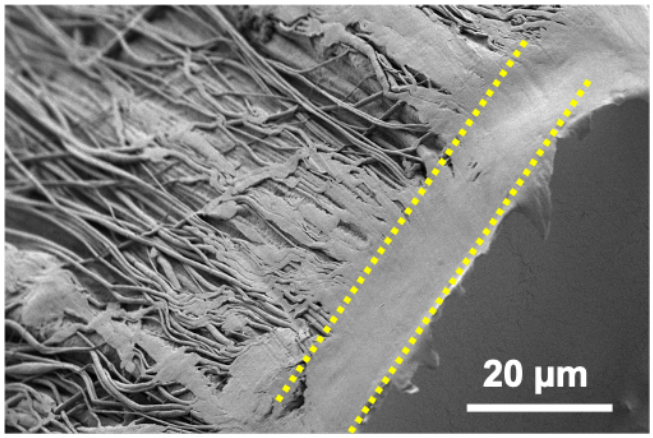


Figure S36. SEM image of a cross section of a bundle of touch spun fibers from **NT2** solution formed from low acid loadings. The cross section is 14 ± 1.3 µm.

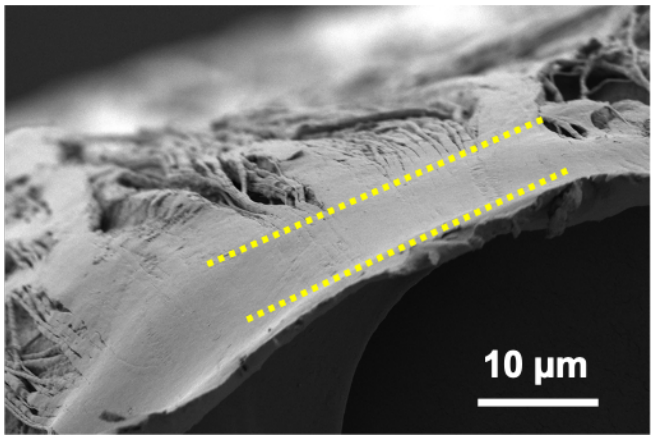


Figure S37. SEM image of a cross section of a bundle of touch spun fibers from **NT3** solution formed from low acid loadings. The cross section is 3.7 ± 0.3 µm.

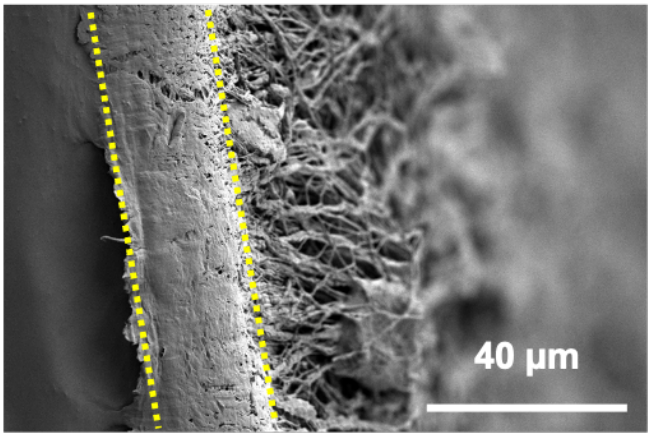


Figure S38. SEM image of a cross section of a bundle of touch spun fibers from a crude **NT1** solution formed from high acid loadings. The cross section is 16 ± 4.2 µm.

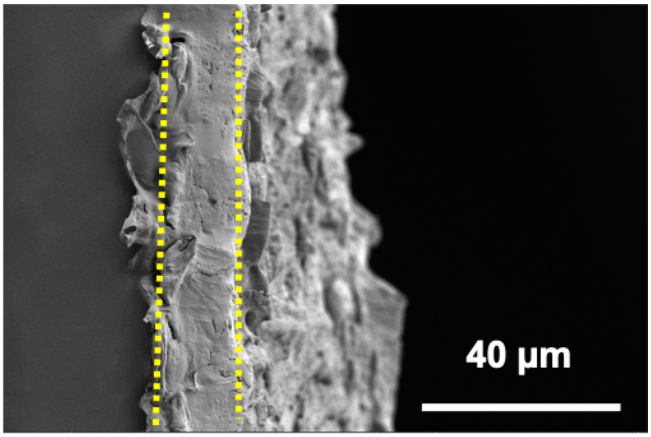


Figure S39. SEM image of a cross section of a bundle of touch spun fibers from a crude **NT2** solution formed from high acid loadings. The cross section is 18 ± 3.5 µm.

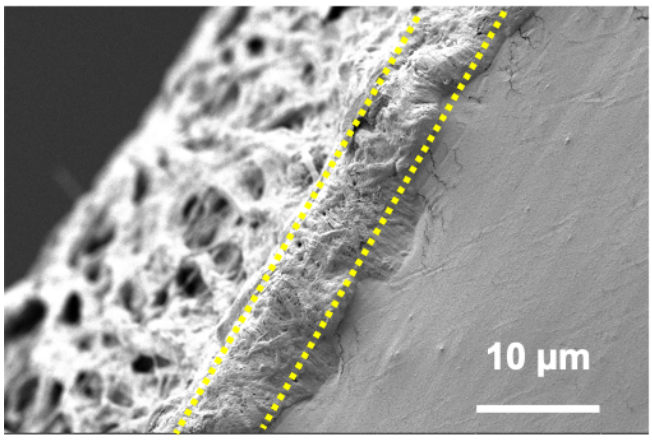


Figure S40. SEM image of a cross section of a bundle of touch spun fibers from a crude **NT3** solution formed from high acid loadings. The cross section is 8.2 ± 2.3 µm.

J. Tensile Testing

Table S1. Results of Tensile Testing for touch spun fibers from nanotube solutions with low and high levels of scrambling.

Fibers	Young's Modulus (MPa) High Acid Loading	Young's Modulus (MPa) Low Acid Loading
PEO (control sample)	211 ± 31	211 ± 31
NT1	420 ± 36	1086 ± 63
NT2	295 ± 36	488 ± 60
NT3	1093 ± 50	2096 ± 380

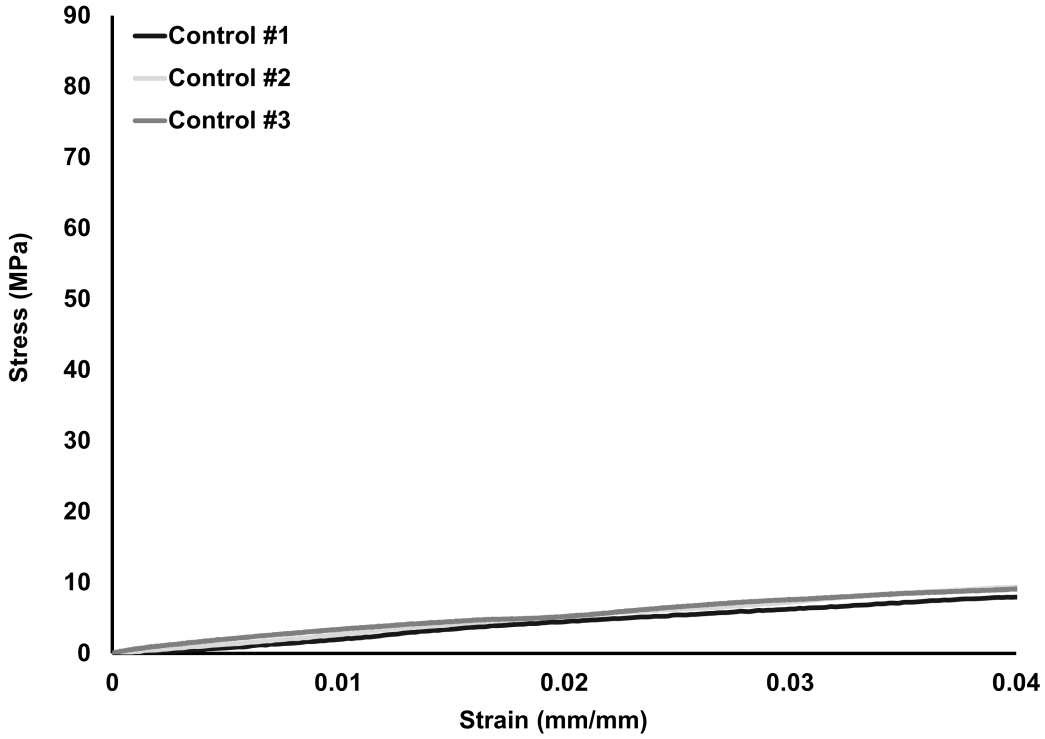


Figure S41. Tensile tests of touch-spun PEO fibers.

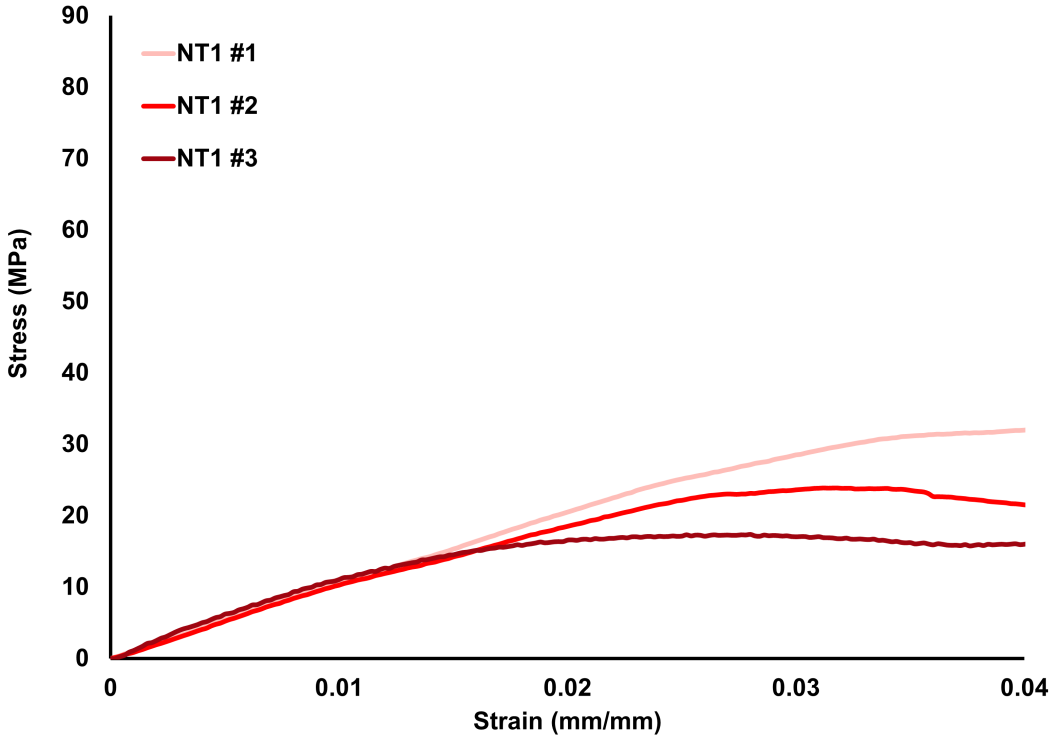


Figure S42. Tensile tests of touch spun **NT1** nanofibers.

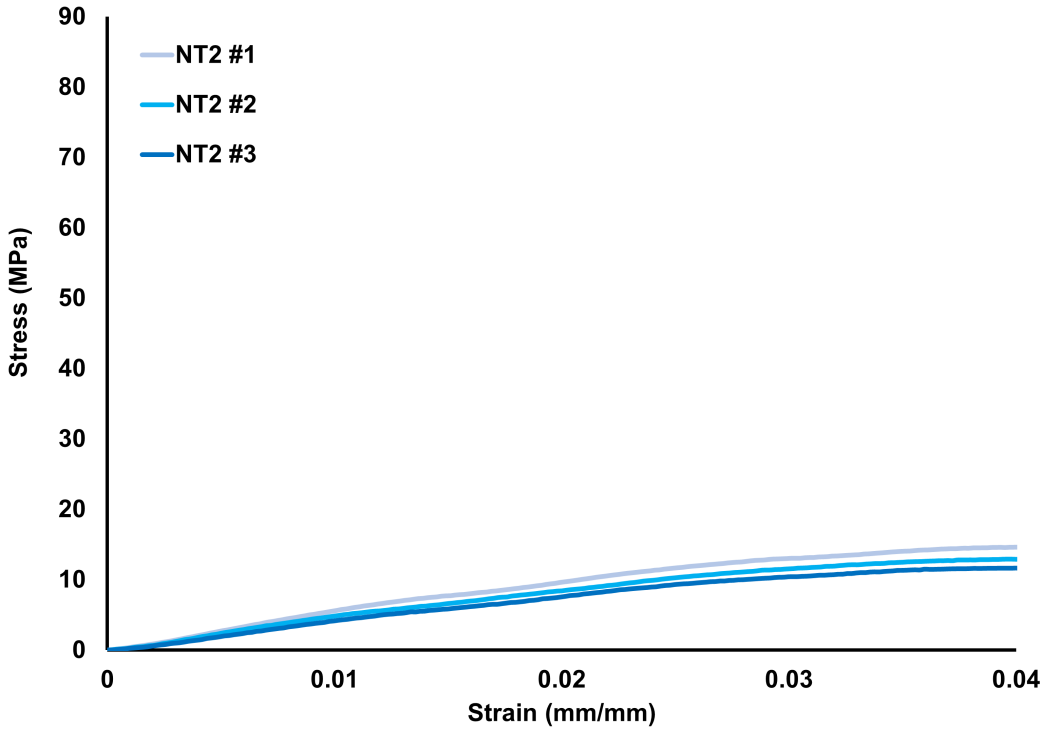


Figure S43. Tensile tests of touch spun **NT2** nanofibers.

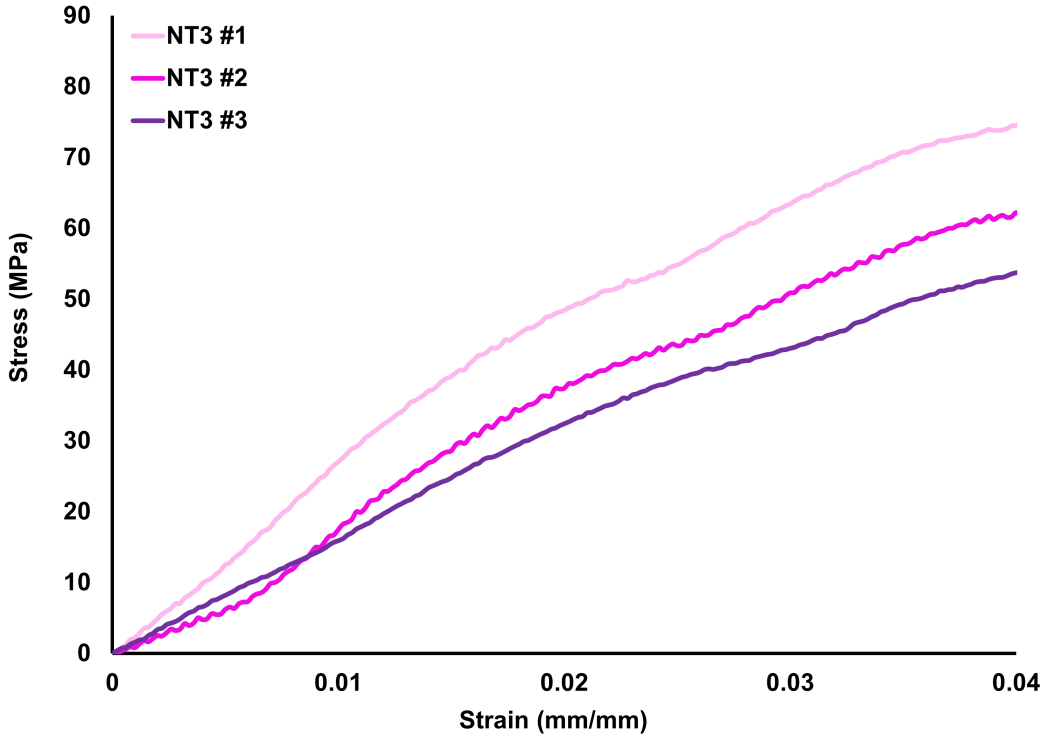


Figure S44. Tensile tests of touch spun **NT3** nanofibers.

K. References

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