Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Graphene-aramid nanocomposite fibres via superacid co-processing

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Experimental details

PPTA synthesis

The following section details the optimised procedure for the synthesis of poly(p-phenylene terephthalamide) – B7-PPTA. Glassware was thoroughly dried before use and all steps (prior to the final quench) were performed under N_2 gas.

Dry LiCl [anhydrous, >98%, Alfa Aesar] 5.29 g, 123 mmol, was added to 360 ml of 1-methyl-2-pyrrolidone (NMP) [anhydrous, >99%, Sigma] and stirred magnetically at 60 °C until complete dissolution of the LiCl (ca. 60 minutes). 180 ml of this NMP/LiCl solution was then transferred to a 2 L 3-neck round bottomed flask and allowed to cool to room temperature (ca. 20 °C). Pyridine [99.9%, Sigma] 15.52 ml, 193 mmol was then added with light overhead stirring before addition of benzene-1,4-diamine (also known as p-phenylene diamine, PPD) [>99%, Sigma] 11.12 g, 103 mmol, which was stirred via light overhead stirring until complete dissolution. The contents of the flask were then cooled to -21 °C. Meanwhile, benzene-1,4-dicarbonyl dichloride (also known as terephthaloyl chloride, TPC) [>99%, flakes, Sigma] 21.53 g, 106 mmol, was added to the remaining NMP/LiCl solution and subject to light magnetic stirring at room temperature until complete dissolution (c.a. 2 minutes). This was then added dropwise to the cooled PPD solution at a rate of ca. 8 ml min^{-1} with constant overhead stirring (250 rpm) at -21 °C. The viscosity of the mixture increased substantially as the addition proceeded.

After addition of the TPC, the reaction mixture was allowed to increase to room temperature and left to stir for a further 2 h. At this point the viscosity was very high and impeded the stirring rate of the overhead stirrer. The mixture was then heated to 60 °C and left to stir overnight (ca. 16 h). The following morning, the reaction mixture had formed a solid yellow mass. An excess of water was added to quench the reaction, before the yellow mass was broken up with a spatula. This was followed by vacuum filtration and several rounds of washing (1x 0.1 M Na_2CO_3, 5x H_2O, 2x ethanol and 1x acetone) to remove impurities, before drying on a hotplate for ca. 20 h at 80 °C and subsequent drying under vacuum at 100 °C for 16 h. After drying, the calculated yield was 108.9 % indicating the presence of residual solvents, salts or impurities which could not be removed. The use of a slight molar excess of TPC to PPD (1.02:1) may also have become incorporated into the polymer. Yields in excess of 100% have also been reported by others.[1]

Spinning dope preparation

To prepare the spinning dope solutions, approximately 0.1195 g, 0.02988 g, 0.00597 g, 0.00149 g and 0.00299 g of both C750 and M25 GNPs [XG Sciences] were weighed out into vials before addition of 5 ml (8.765 g) of anhydrous CSA [99%, Sigma]. These (along with a control sample with no GNPs) were then heated and stirred magnetically at 80 °C for 1 h, before bath sonication at 30 °C for 1 h. 1.195 g of B7-PPTA was then added to each vial, before magnetic stirring at 65 °C overnight (*c.a.* 16 h) – giving 12% w/w B7-PPTA in CSA solutions, with 0.1, 0.25, 1, 2.5 and 10 % graphene loading (by mass) relative to the PPTA (Fig. S1). Graphene loadings in excess of 10% were also attempted, however the viscosity of the solutions in this case were too high to be extruded through the needle and therefore no fibres could be obtained.

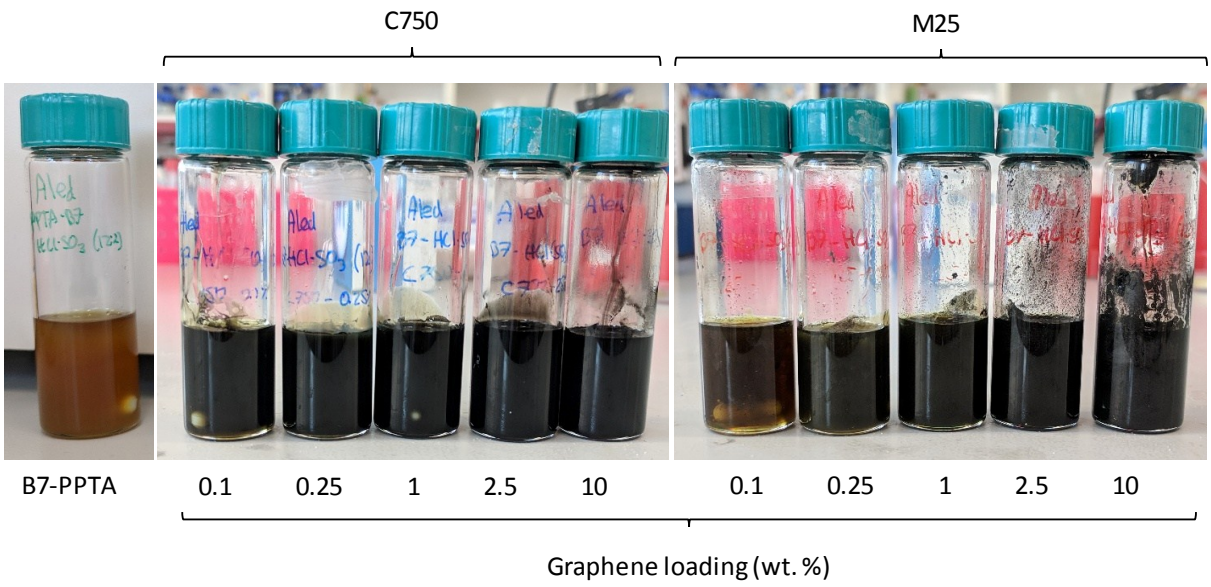

Figure S1. Visible light images of B7-PPTA solutions in CSA with varying amounts of C750 and M25 GNPs.

Fibre spinning

A custom-made wet-spinning rig was set up to produce the B7-PPTA-graphene fibres (Fig S2). The prepared dopes were transferred to 2 ml glass syringes and extruded through a 25-gauge hypodermic needle (inner diameter: 260 µm) into a water coagulation bath at a rate of 50 μL^{-1} using a syringe pump (Just Infusion™ NE-300). Note that the needle tips were filed to a blunt edge using abrasive paper before use for safety reasons. The spinning dopes were maintained at approximately 50 °C during the spinning process as they solidified if allowed to cool to room temperature. The fibre collection speed was set to match the extrusion velocity.

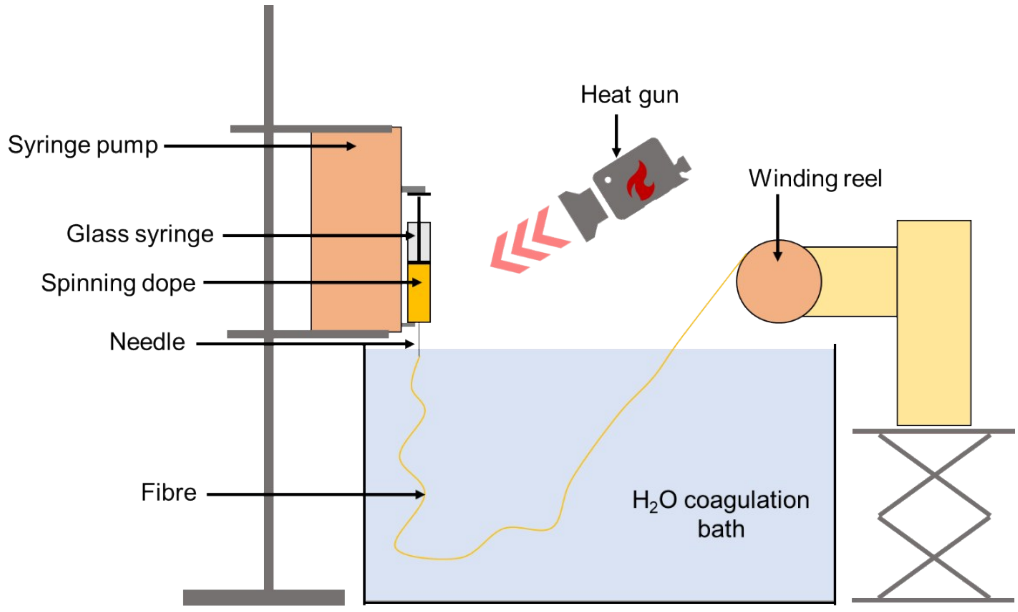

Figure S2. Schematic representation of the custom made wet-spinning rig employed to produce B7-PPTA-graphene fibres.

Characterisation equipment

Scanning electron microscopy (SEM) images were taken on a Hitachi S300 N (USA) instrument with a 5 kV accelerating voltage and a working distance of 10 mm. Prior to measurements, samples were mounted onto 1 cm diameter aluminium sample stubs using double-sided conductive carbon tape before being sputter-coated (Gatan Model 682 Precision Etching Coating System, USA) with an ~8 nm layer of an Au/Pd alloy to enhance conductivity. Fourier transform infrared spectroscopy measurements were taken using a Thermo Scientific Nicolet iS5 (UK) equipped with an n iD5 attenuated total reflectance (ATR) attachment. Each measurement was an average of 32 scans over a wavenumber range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1}. Uniaxial tensile testing of the fibres was performed using an Instron 3344 (Instron Ltd., USA) instrument. Samples of 2 cm in length were initially set in laser-cut cardboard testing frames using a commercial 2-component epoxy resin adhesive. 8 replicates of each measurement were attempted, however fibre brittleness meant most broke before reliable data could be obtained (*e.g.*, during clamping into the instrument). Computational analysis was performed using Avogadro software (version 1.2.0): briefly, two PPTA oligomers (degree of polymerization: 6) were constructed according to the reported PPTA crystal structure [M. G. Northolt and J. J. Van Aartsen, J. Polym. Sci. Polym. Lett. Ed. 11(5), 333 (1973).] along with a planer sheet of sp2 hybridized carbon atoms (16 x 22) set 3.6 nm apart. A molecular dynamics geometry optimization using an MMFF94 force field (500 steps, steepest decent algorithm) was then performed. 5-point Brunauer−Emmett−Teller (BET) surface area measurements were performed using an Anton Paar Quantatech Autosorb IQ-XR-AG-AG after degassing for 2 hours at 200 °C. Wide angle X-ray diffraction (WAXD) measurements were taken using a PANalytical X'Pert Pro (UK) instrument using a copper Kα radiation source, diffraction angle of 5 – 60° and scanning rate of 2° min^{-1}. Optical and polarized light microscope images were taken using a Leica TSC SP5 Confocal Microscope. Raman spectroscopy was performed using a Renishaw InVia Raman Microscope fitted with a 633 nm laser and calibrated with a Si wafer reference.

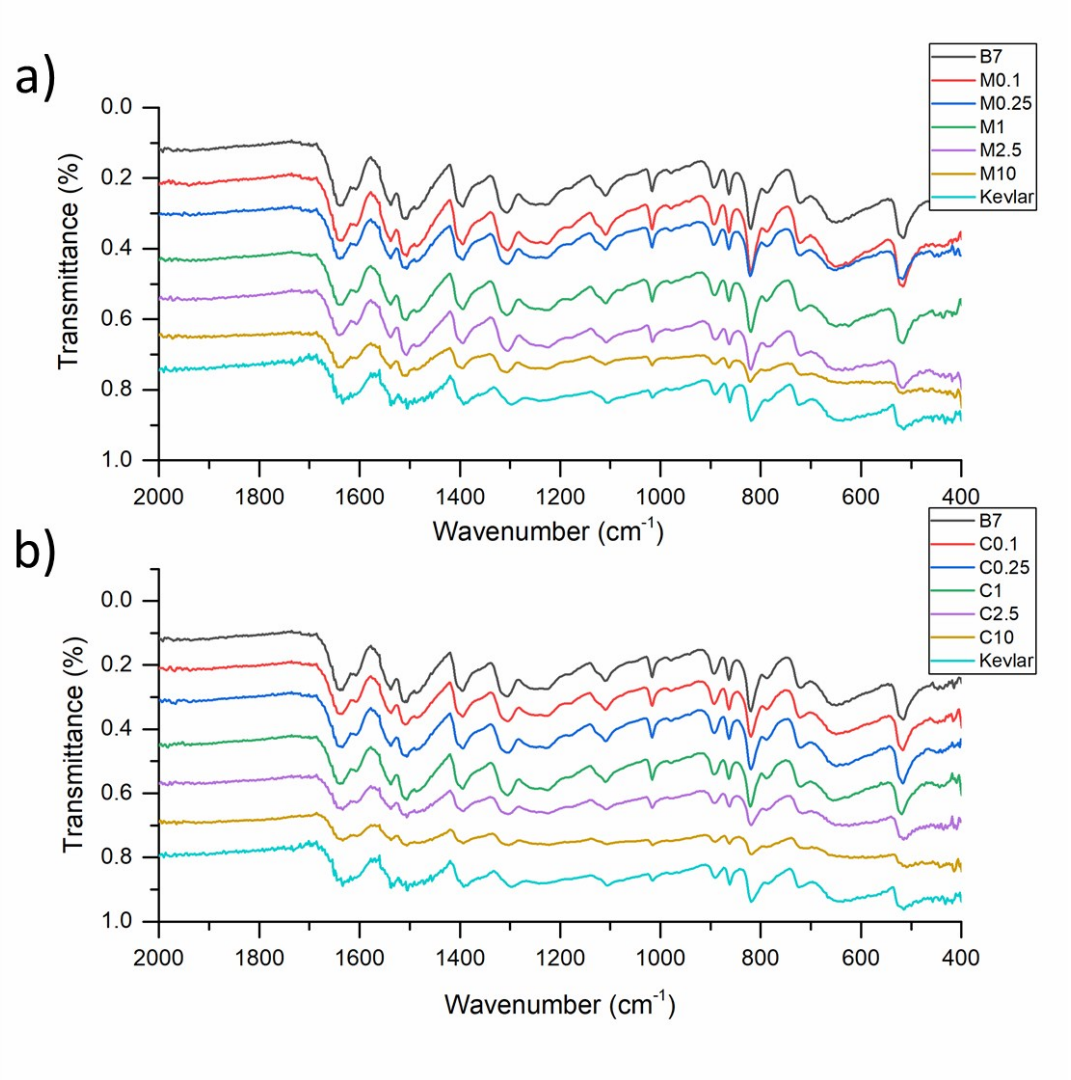

Figure S3. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) data for B7-PPTA fibres with a) M25 GNPs and b) C750 GNPs. Traces offset for clarity.

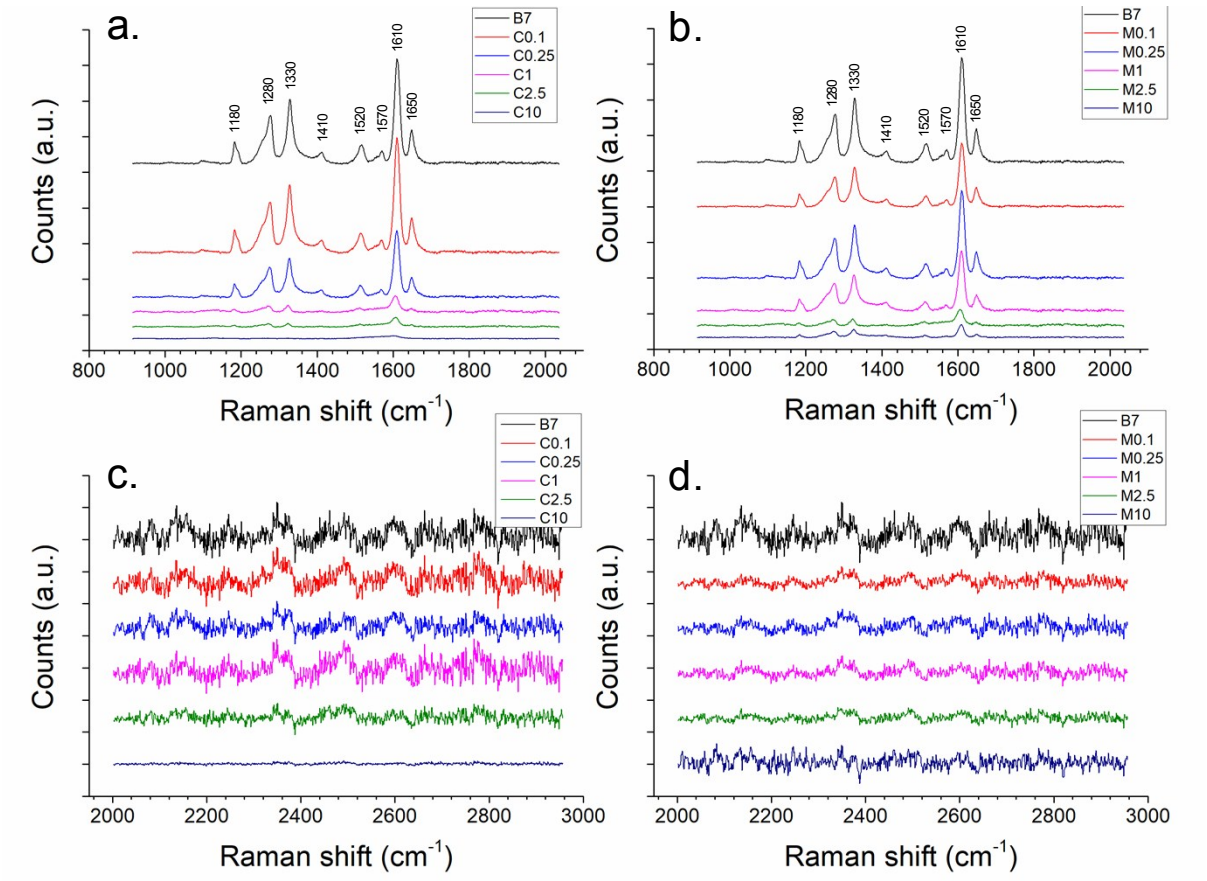

Figure S4. Raman data for B7-PPTA with C750 GNPs (a, c) and M25 GNPs (b, d). Note that higher graphene loadings result in a lower signal-to-noise ratio likely due to increased scattering/adsorption of the laser.

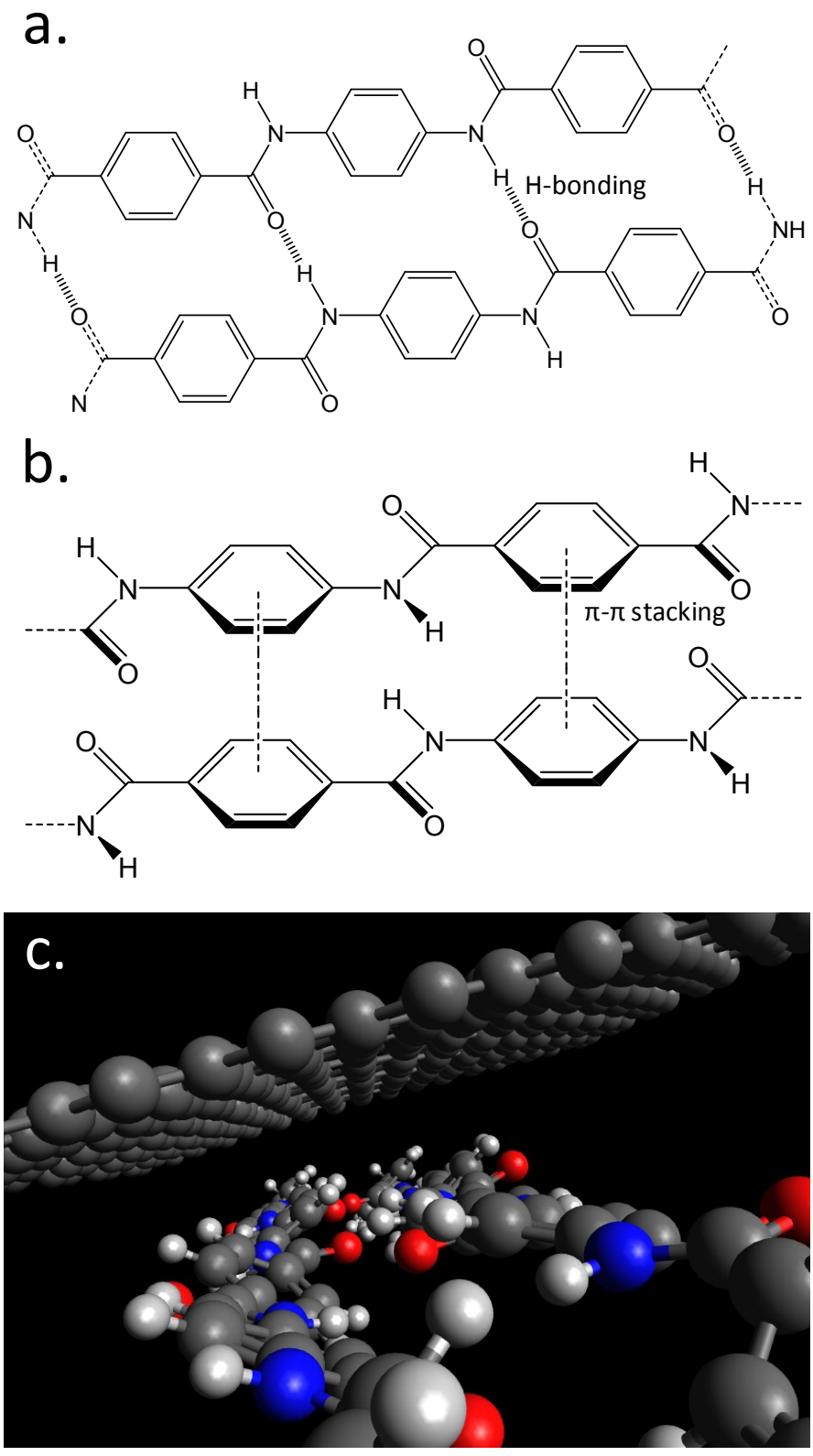

Figure S5. Depictions of a) intramolecular H-bonding and b) π-π stacking interactions of PPTA. c) computational model based on PPTA and a graphene sheet: angle between ring planes is <30° indicating the possibility of stabilising π-π interrelations

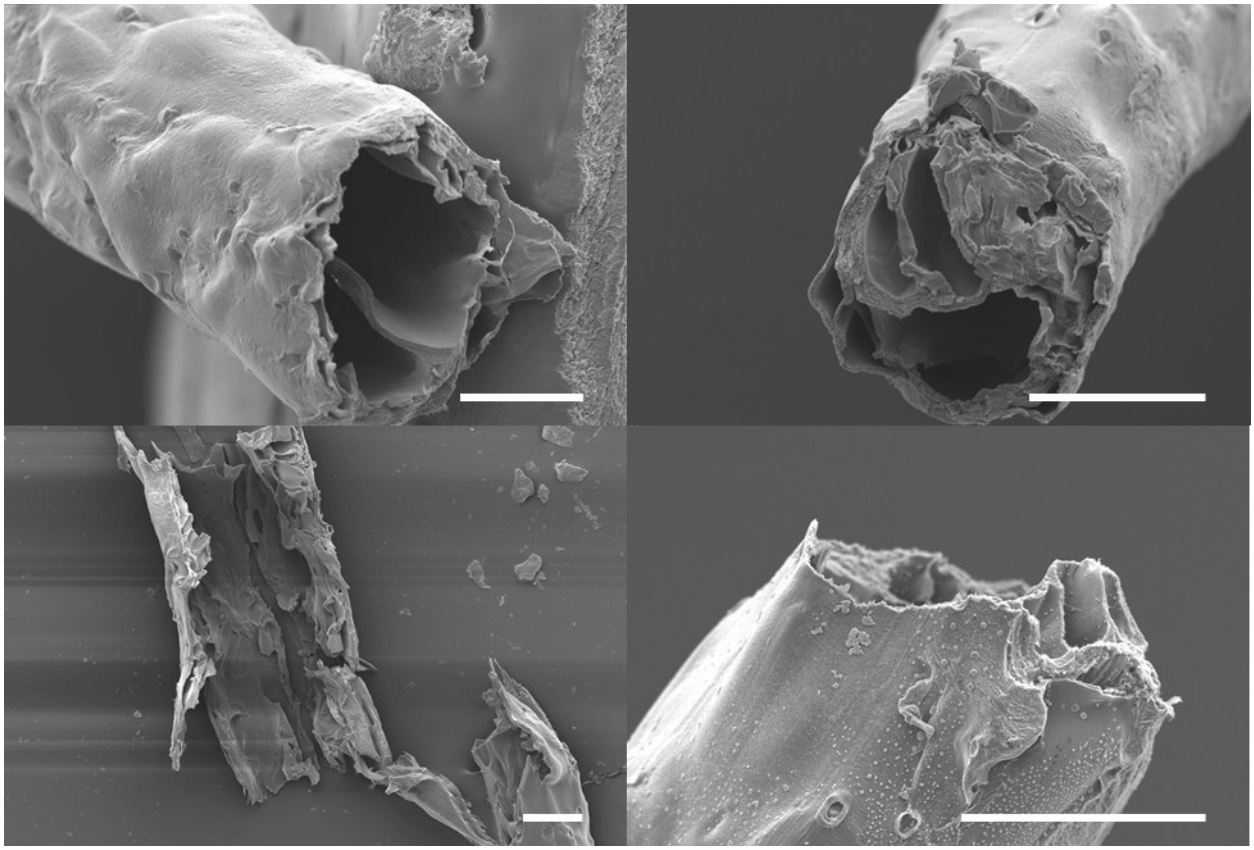

Figure S6. SEM images of B7-PPTA fibres showing porous cavities. Scale bar = 50 µm

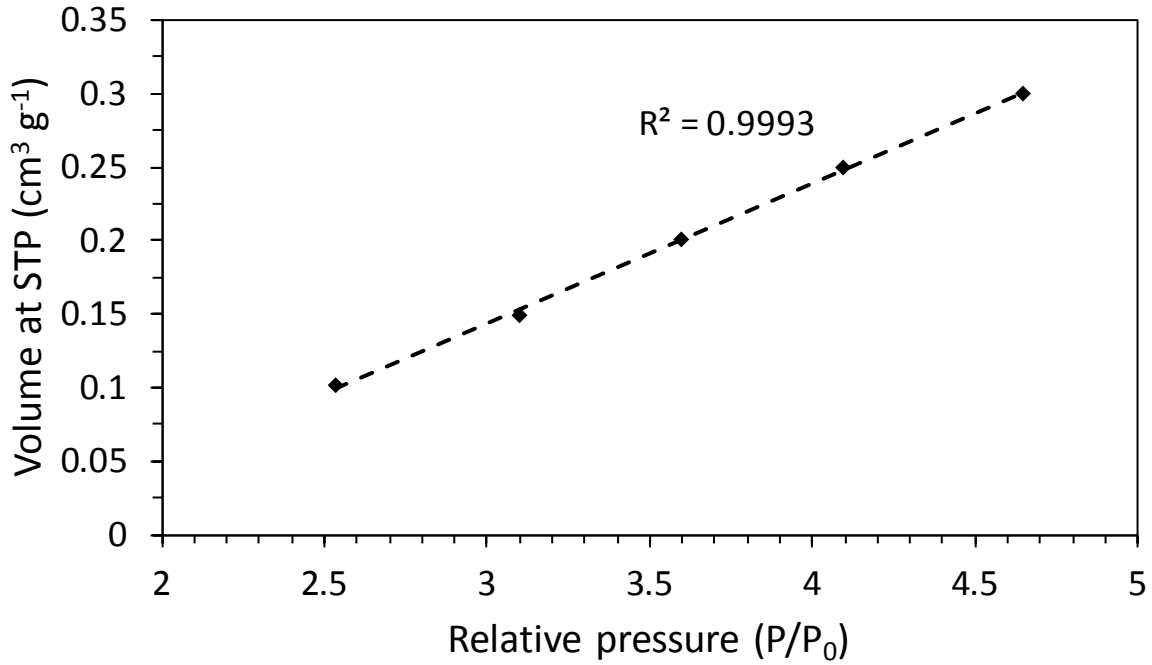

Figure S7. 5-point N_2 gas-sorption BET isotherm for B7-PPTA with 0.1% loading of C750 as a representative example. Specific surface area calculated as 16.6 m^2g^{-1}

Table S1. Summary of the viscosity and M_w of the PPTA batches as well as commercial Kevlar®. Samples were dissolved in fuming sulfuric (20% SO_3, Sigma) acid and tested at 20±1 °C

Substance	**Concentration**	**μ (mPa·s)**	**$[\mu]_{red}/[\mu]_{Inh}$ (dL g^{-1})**	**M_w $[\mu]_{red}/[\mu]_{Inh}$ (kDa)**
B0-PPTA	6%	382	-	-
B1-PPTA	6%	32	-	-
B2-PPTA	6%	666	-	-
B3-PPTA	6%	487	-	-
B4-PPTA	6%	1017	-	-
B5-PPTA	6%	623	-	-
B6-PPTA	6%	209	-	-
B7-PPTA	6%	1286	-	-
Kevlar-49®	6%	4375	-	-
B7-PPTA	0.5 - 5 mg ml^{-1}	59 - 89	1.11 / 1.13	4.5 / 4.7
Kevlar-49®	0.75 - 1.5 mg ml^{-1}	70 - 80	6.92 / 5.90	61.7 / 79.2