Novel functionalization of unsized carbon fiber using *in situ* generated diazonium from substituted anilines

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SUPPLEMENTARY INFORMATION

General chemical experimental

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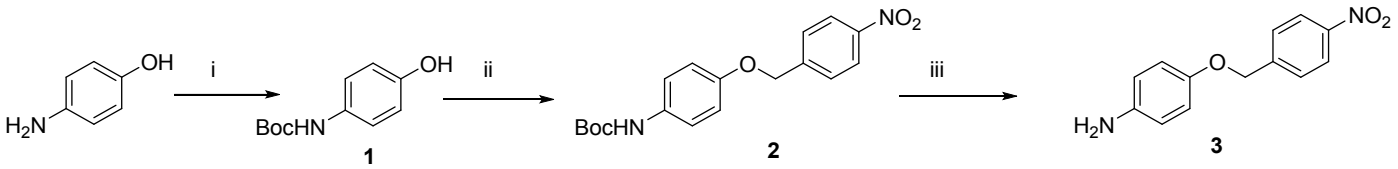
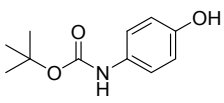
All ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Jeol JNM-EX 270 MHz as indicated. Samples were dissolved in deuterated chloroform ($CDCl_3$) with the residual solvent peak used as an internal reference ($CDCl_3$ – δH 7.26 ppm). Flourine spectra are reported with trifluorotoluene (0.05%) in $CDCl_3$ being used as an external reference (-63.72 ppm). Proton spectra are reported as follows: chemical shift δ (ppm), (integral, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant J (Hz), assignment).

Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) measurements were conducted using an Alpha FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector and a single-reflection diamond ATR sampling module (Platinum ATR QuickSnap™). The samples were analysed in a thin film (from a chloroform solution) from 400 to 3900 wavenumbers and all absorption bands are reported in wavenumbers (cm^{-1}). Background spectra of a clean ATR surface were acquired prior to each sample measurement using the same acquisition parameters

Part 1 -Full characterisation/analysis of unoxidized fiber/treatment preliminary study

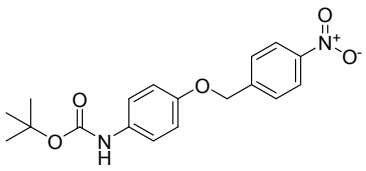


Synthesis of *tert*-butyl (4-hydroxyphenyl)carbamate (1)



To a stirred biphasic mixture of CH_2Cl_2/H_2O (4:3, 35 mL), *p*-aminophenol **4** (2.0 g, 18.33 mmol), $NaHCO_3$ (1.54 g, 18.33 mmol) and NaCl (1.08 g, 18.33 mmol); Boc_2O (4.0 g, 18.33 mmol) was added in one portion. The mixture was then left to stir vigorously under reflux for 2 h, at 50 °C. The mixture was cooled to room temperature and transferred to a separating funnel and washed with saturated NaCl (3 × 60 mL). The organic phase was separated, dried ($MgSO_4$), filtered and solvent removed *in vacuo* to afford the title compound as a white solid (3.12 g, 81%). Consistent with literature[48]: ^{1}H NMR (270 MHz, CD_3OD): δ = 7.15 (d, 2H, $^{3}J_{HH}$ = 8.64 Hz, Ar*H*), 6.69 (d, 2H, $^{3}J_{HH}$ = 6.67 Hz, Ar*H*), 4.87 (s, 1H, O*H*), 1.50 (s, 9H, *t*-Bu).

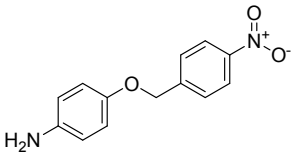
Synthesis of *tert*-butyl (4-((4-nitrobenzyl)oxy)phenyl)carbamate (2)



To a stirring mixture of *tert*-butyl (4-hydroxyphenyl)carbamate **3** (350 mg, 1.67 mmol), sodium iodide (250 mg, 1.67 mmol) and acetone (5 mL); KOH (141 mg, 2.51 mmol) was added in one portion. The mixture was heated to reflux for 1 h at 55 °C, then nitrobenzylbromide **5** (543 mg, 2.51 mmol) was added in one portion. It was left to reflux overnight and was transferred to a separating funnel, adding

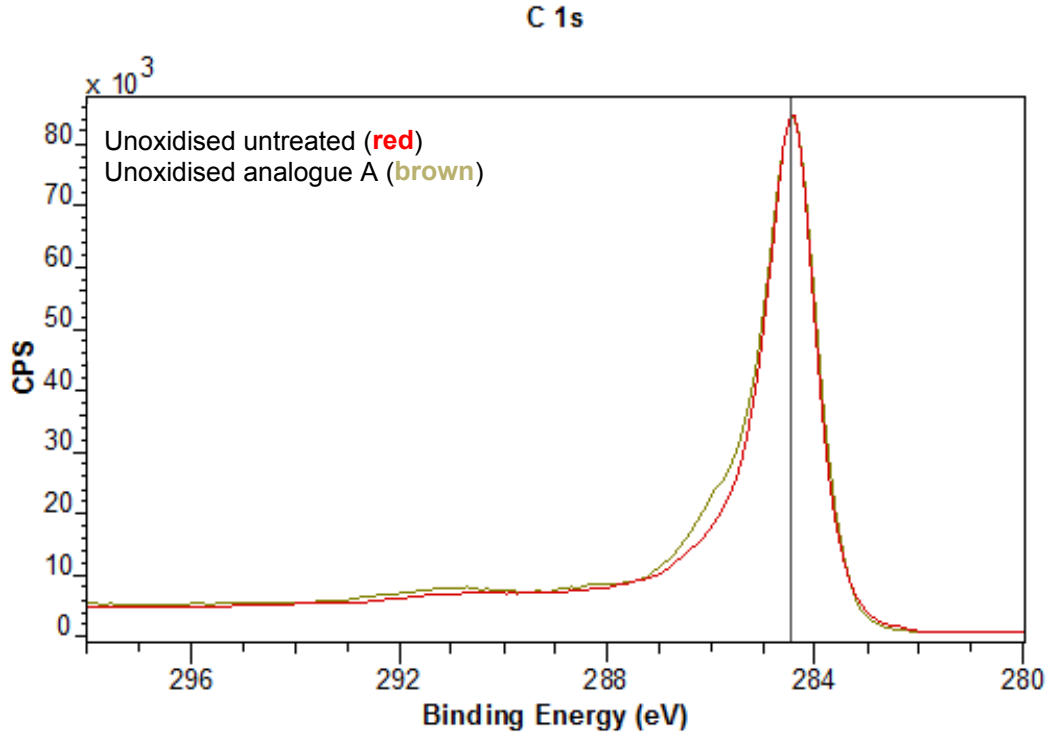
CH_2Cl_2 (25 mL) and washing with saturated NaCl (3 × 65 mL). The organic phase was separated, dried ($MgSO_4$), filtered, solvent removed *in vacuo* and recrystallised in ethanol to afford the title compound as a bright yellow solid (366 mg, 64%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.23 (d, 2H, $^3J_{HH}$ = 6.94 Hz, Ar*H*), 7.58 (d, 2H, $^3J_{HH}$ = 9.15 Hz, Ar*H*), 7.27 (d, 2H, $^3J_{HH}$ = 10.88 Hz, Ar*H*), 6.88 (d, 2H, $^3J_{HH}$ = 8.91 Hz, Ar*H*), 5.12 (s, 2H, CH_2), 1.49 (s, 9H, *t*-Bu). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 28.4, 69.1, 80.5, 115.4, 120.6, 123.9, 127.7, 132.4, 144.7, 147.6, 153.1, 154.2. HRMS (ESI, *m/z*) calculated for $[C_{14}H_{17}NO_3 + Na]^+$ 367.12644 found *m/z* 367.13205.

Synthesis of 4-((4-nitrobenzyl)oxy)aniline (3)

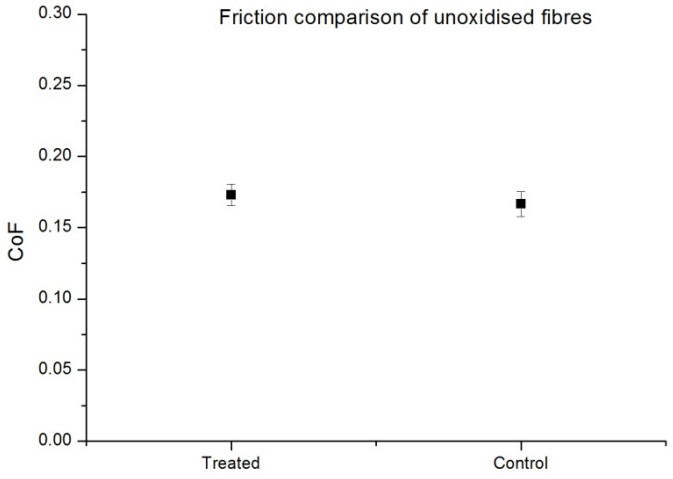


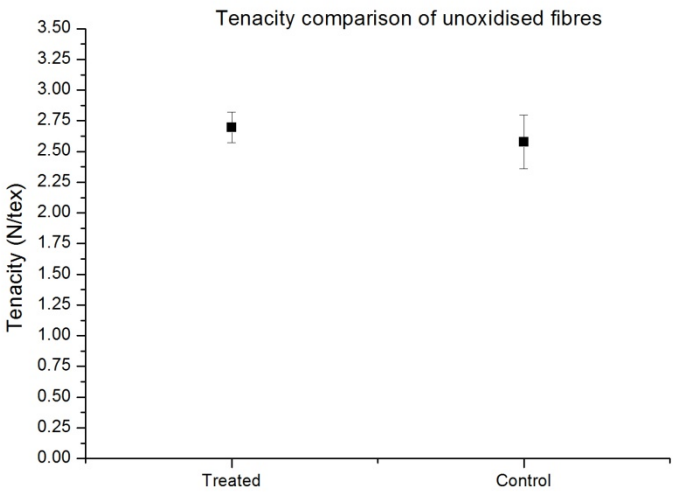
In a stirring solution of *tert*-butyl (4-((4-nitrobenzyl)oxy)phenyl)carbamate **2** (500 mg, 1.45 mmol) and CH_2Cl_2 (16 mL), TFA (4 mL) was added and left to stir for 2.5 h. The solvent was removed *in vacuo* to obtain a clear oil. The clear oil was dissolved with CH_2Cl_2 (3 × 60 mL) and had solvent removed *in vacuo* to help remove any left over TFA. The dried product was transferred to a separating funnel and had H_20 (30 mL) and Ethyl Acetate (60 mL) added, which was washed with sodium bicarbonate (3 × 50 mL). The organic phase was separated and had the solvent removed *in vacuo* to afford an orange solid (275 mg, 77%). ^{1}H NMR (400 MHz, DMSO): δ = 8.25 (d, 2H, $^3J_{HH}$ = 8.04 Hz, Ar*H*), 7.68 (d, 2H, $^3J_{HH}$ = 8.04 Hz, Ar*H*), 6.74 (d, 2H, $^3J_{HH}$ = 8.80 Hz, Ar*H*), 6.51 (d, 2H, $^3J_{HH}$ = 8.80 Hz, Ar*H*), 5.12 (s, 2H, CH_2), 4.66 (s, 2H, NH_2). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 69.6, 116.1, 116.5, 123.8, 127.7, 140.9, 145.2, 147.6, 151.3. HRMS (ESI, *m/z*) calculated for $[C_{14}H_{17}NO_3 + H]^+$ 245.09207 found *m/z* 245.09148.

XPS C1s spectra

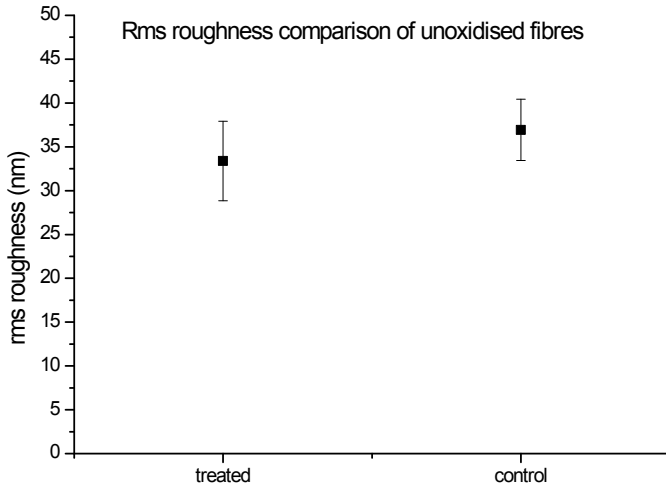


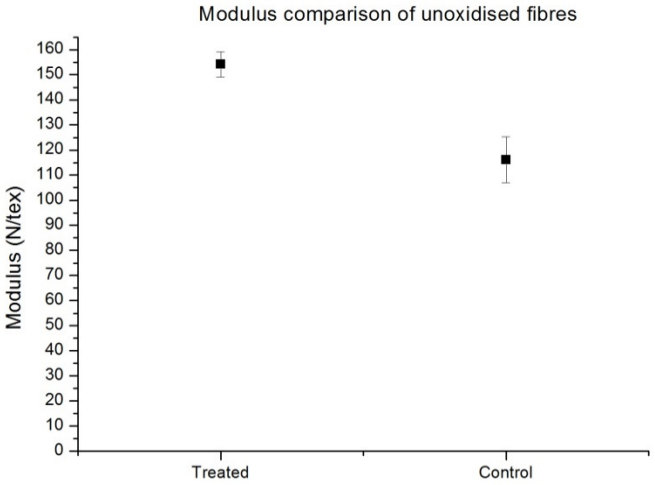
Single fiber analysis



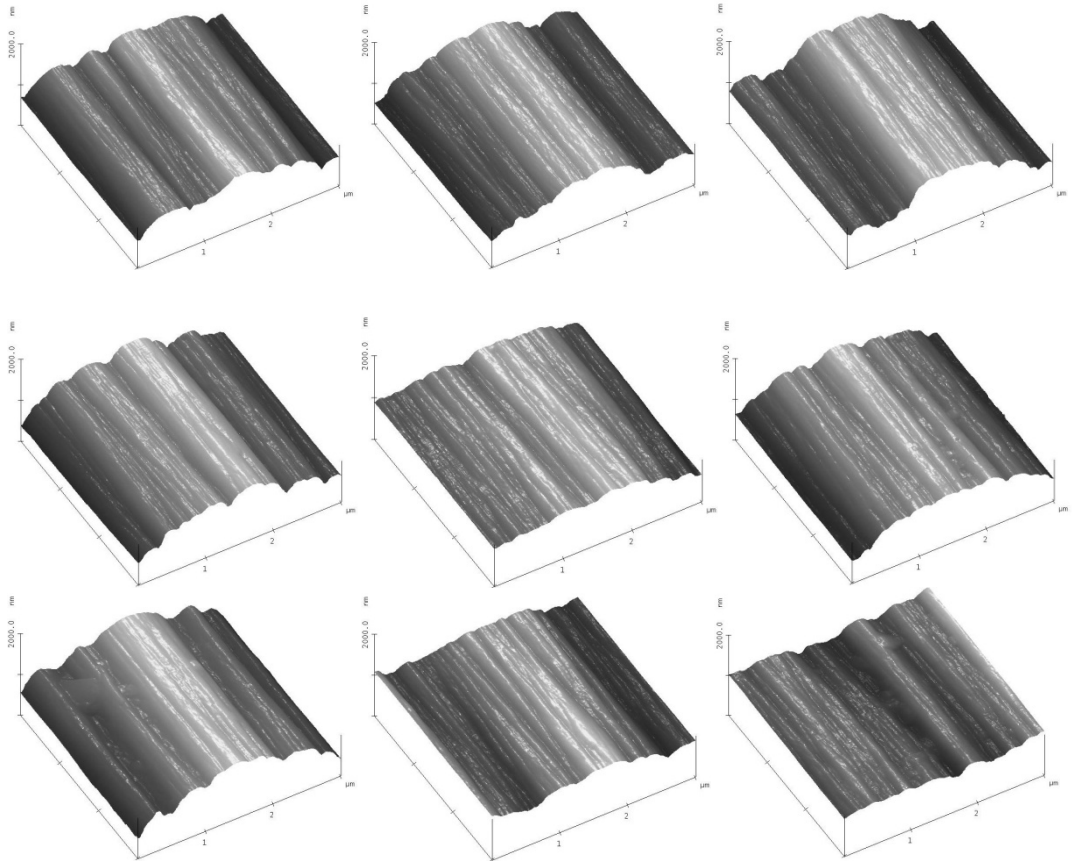


3 x 3 nm SPM images for unoxidized carbon

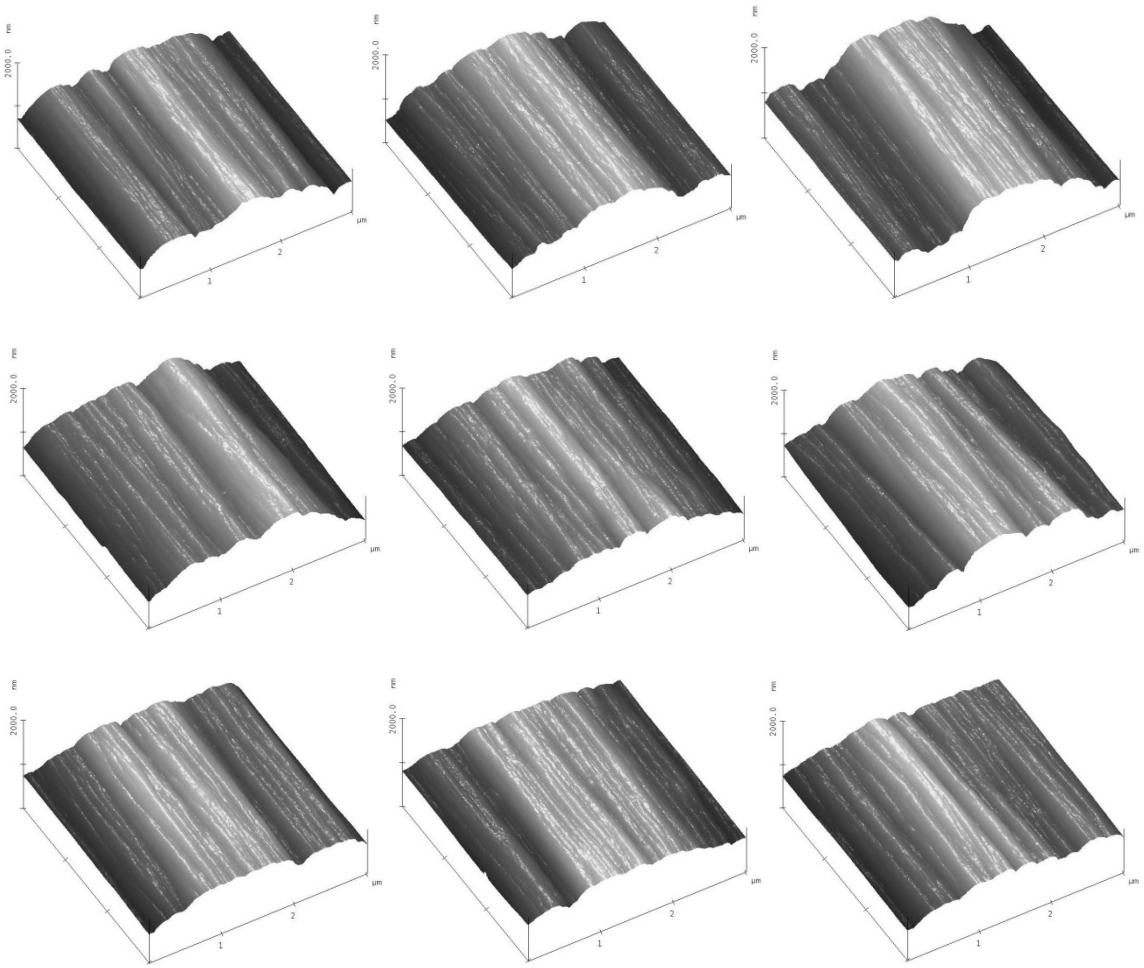




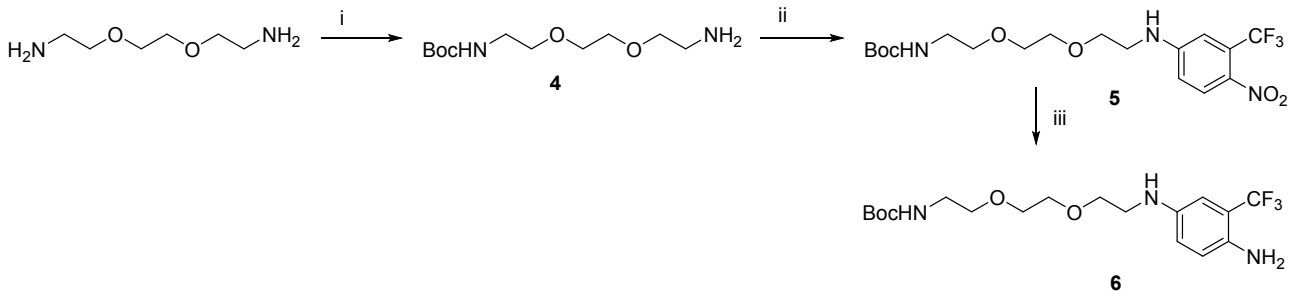
fiber



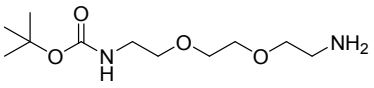
3 x 3 nm SPM images for treated unoxidized carbon fiber



Part 2 - Full characterisation/analysis of oxidized fiber/"ortho" analogue treatment study



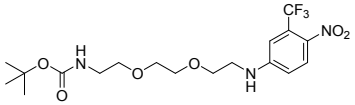
Synthesis of *tert*-butyl [2-[2-(2-aminoethoxy)ethoxyethyl]carbamate (4)



A solution of di-*tert*-butyl dicarbonate (3.0 g, 13.75 mmol) in CH_2Cl_2 (100 mL) was added dropwise over 2 hours to a stirring solution of 2,2-(Ethylenedioxy)bis(ethylamine) (6.021 mL, 41.24 mmol) and CH_2Cl_2 (150 mL) at 0°C for 2 hours. The reaction was then stirred a further 18 hours at room temperature, and the resulting mixture transferred to a separating funnel where it was washed with saturated aqueous NaCl (5 × 50mL). The organic phase was

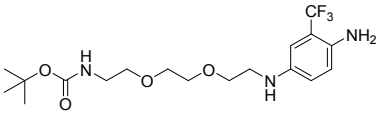
dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a viscous colourless off-white oil in >95% purity (3.312 g, 97%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.59 (s, 4H, ($CH_2O)_2$), 3.51 (m, 4H, ($CH_2O)_2$), 3.29 (q, $^3J_{HH}$ = 5.4, 5.13, 2H, CH_2NH), 2.85 (t, $^3J_{HH}$ = 5.4, 4.86, 2H, CH_2NH_2), 1.42 (s, 9H, C($CH_3)_3$).[1]

***tert*-buyl 2-[2-[2-[4-nitro-3-(trifluoromethyl)phenylamino]ethoxy]ethoxy]ethylcarbamate (5)**



A solution of **4** (1.091g, 7.61 mmol), 5-Fluoro-2-nitrobenzotrifluoride (0.709 mL, 5.07 mmol), and DMF (8 mL) was added to a quartz microwave vessel with a stirrer bar, and fitted with a pressure cap. The solution was stirred under 200W microwave irradiation at 100°C for 80 minutes. The crude mixture was then diluted with ethyl acetate and washed with three portions of saturated sodium chloride solution (15 mL x 3) to remove any traces of residual DMF, followed by drying over $MgSO_4$, and removal of ethyl acetate *in vacuo*. The crude product was purified by column chromatography (2:3 PET spirits: Ethyl acetate), to afford a bright yellow oil (1.627g, 74%) R_f 0.17. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.01(d, $^3J_{HH}$ = 8.91, 1H, Ar*H*), 6.93 (br.s, 1H, Ar*H*), 6.66 (m, 1H, Ar*H*), 4.92 (br.s, 1H, N*H*COO), 3.72 (m, 2H, CH_2CO), 3.63 (s, 4H, $(CH_2)_2$CO), 3.57 (m, 2H, CH_2CO), 3.53 (br.s, 1H, N*H*Ar), 3.41 (t, $^3J_{HH}$ = 4.86, 2H, CH_2NH), 3.30 (m, 2H, CH_2NH), 1.43 (s, 9H, ($CH_3)_3$). $\nu_{(max)}$ cm $^{-1}$: 3364 (N-H), 2975-2873 (-CH_2-, -CH_3), 1693 (ester C=O), 1611 (N=O), 1515 (aromatic C=C-C), 1327 (N=O), 1270 (C-NH), 1150 (C-F, C-O-C). HRMS (ESI, *m/z*) calculated for $[C_{18}H_{26}F_3N_3O_6 + H]^+$ 438.18465 found: *m/z* 438.18423. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.01, 151.98, 136.44, 129.14, 126.98 (q), 122.32 (q), 112.65, 111.33, 79.48, 70.51, 70.18, 68.86, 42.98, 40.33, 28.41. ^{19}F NMR (470 MHz, $CDCl_3$): - 60.27.

***tert*-buyl 2-[2-[2-[4-amino-3-(trifluoromethyl)phenylamino]ethoxy]ethoxy]ethylcarbamate (6)**



A solution of **5** (3.062g, 7.00 mmol) and palladium on activated carbon (0.305 g, 10% w/w) in methanol (200 mL) was stirred at room temperature under a hydrogen atmosphere for 16 hours. The palladium was then removed by vacuum filtration through a celite plug, followed by purification through column chromatography (1:1 PET spirits: Ethyl acetate) to yield a dark brown oil (2.067 g, 68 %) R_f 0.26. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.67 (m, 3H, Ar*H*), 5.00 (br.s, 1H, N*H*COO), 3.67 (m, 2H, CH_2CO), 3.61 (s, 4H, ($CH_2O)_2$), 3.52 (m, 2H, CH_2CO), 3.30 (m, 2H, CH_2NH), 3.23 (m, 2H, CH_2NH), 1.42 (s, 9H, ($CH_3)_3$). $\nu_{(max)}$ cm $^{-1}$: 3364 (N-H), 2975-2873 (-CH_2-, -CH_3), 1693 (ester C=O), 1515 (aromatic C=C-C), 1270 (C-NH), 1150 (C-F, C-O-C). HRMS (ESI, *m/z*) calculated for $[C_{18}H_{28}F_3N_3O_4 + H]^+$ 408.21047 found: *m/z* 408.21092. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.98, 140.45, 136.10, 126.03, 123.86, 119.28. ^{19}F NMR (470 MHz, $CDCl_3$): - 62.54.

C1s XPS spectra

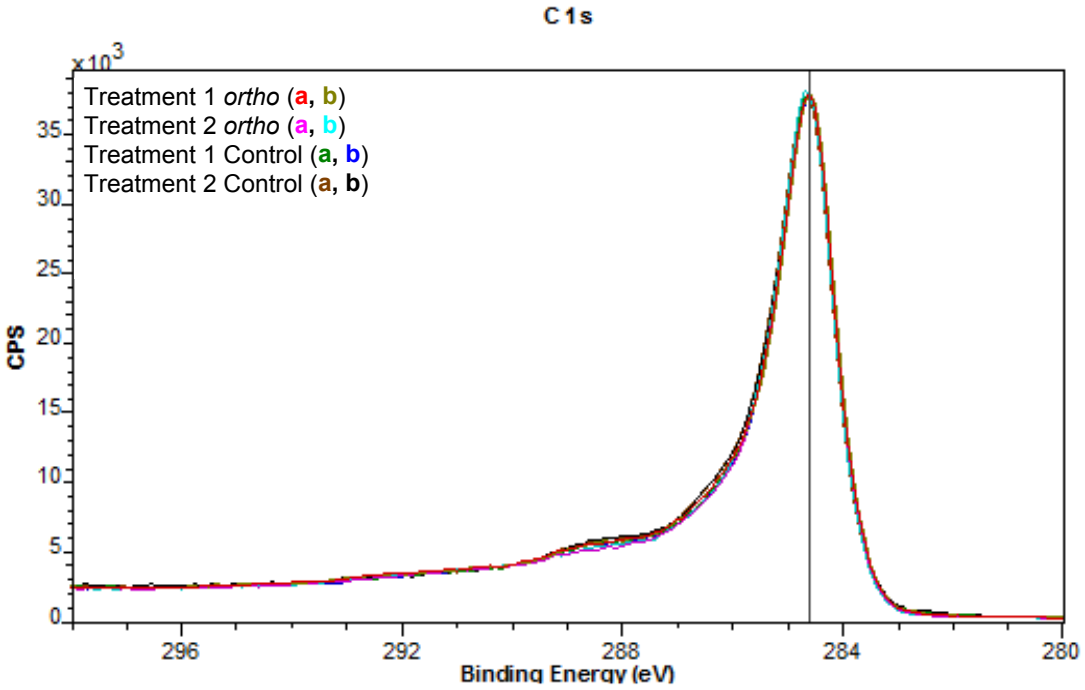


Figure. C1s spectra presented for *ortho*-substituted treatment 1 and 2 along with respective controls. Two spectra recorded (a and b) for each sample.

O1s XPS spectra

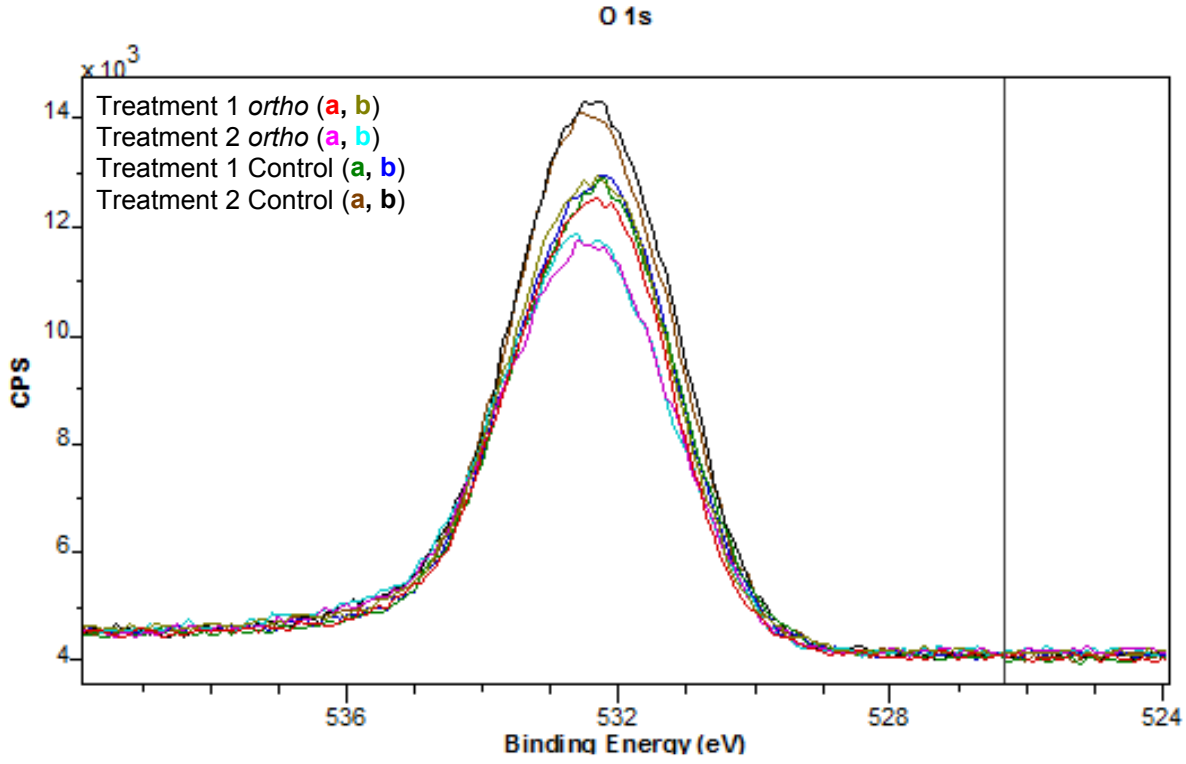
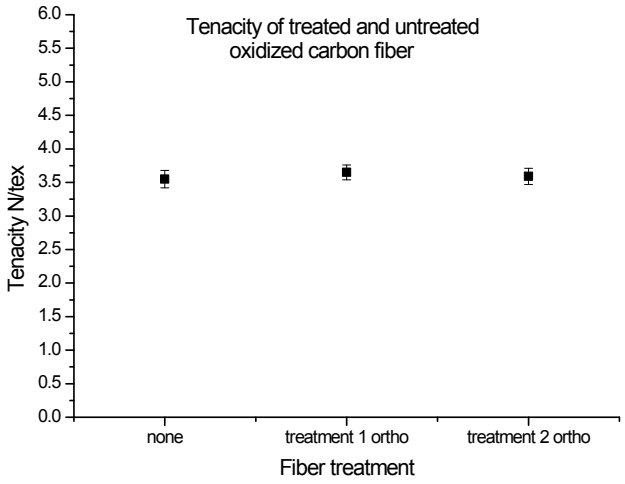
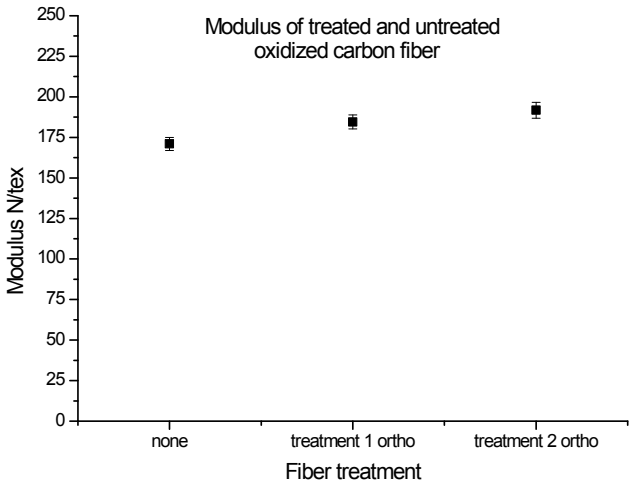
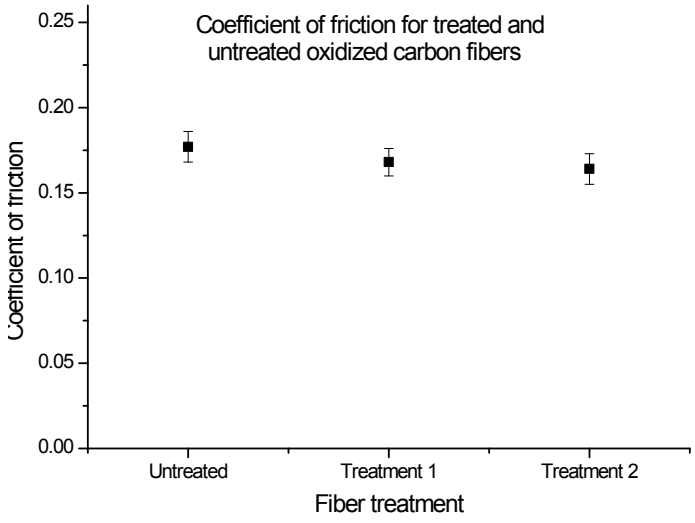


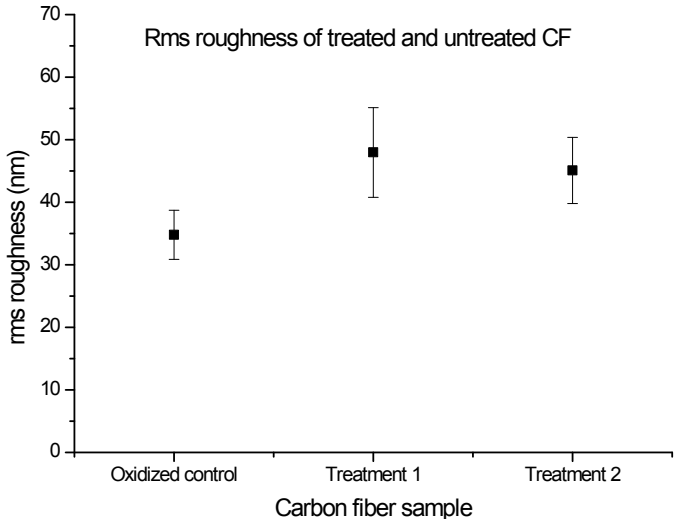
Figure. O1s spectra presented for *ortho*-substituted treatment 1 and 2 along with respective controls. Two spectra recorded (a and b) for each sample.

Single fiber analysis

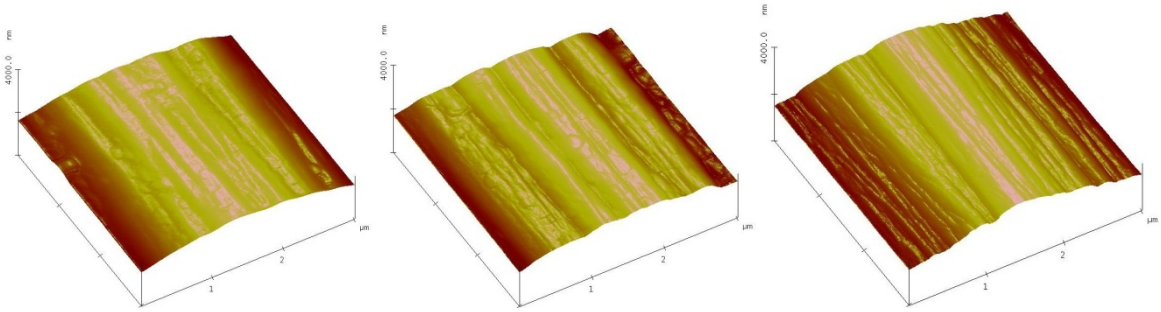


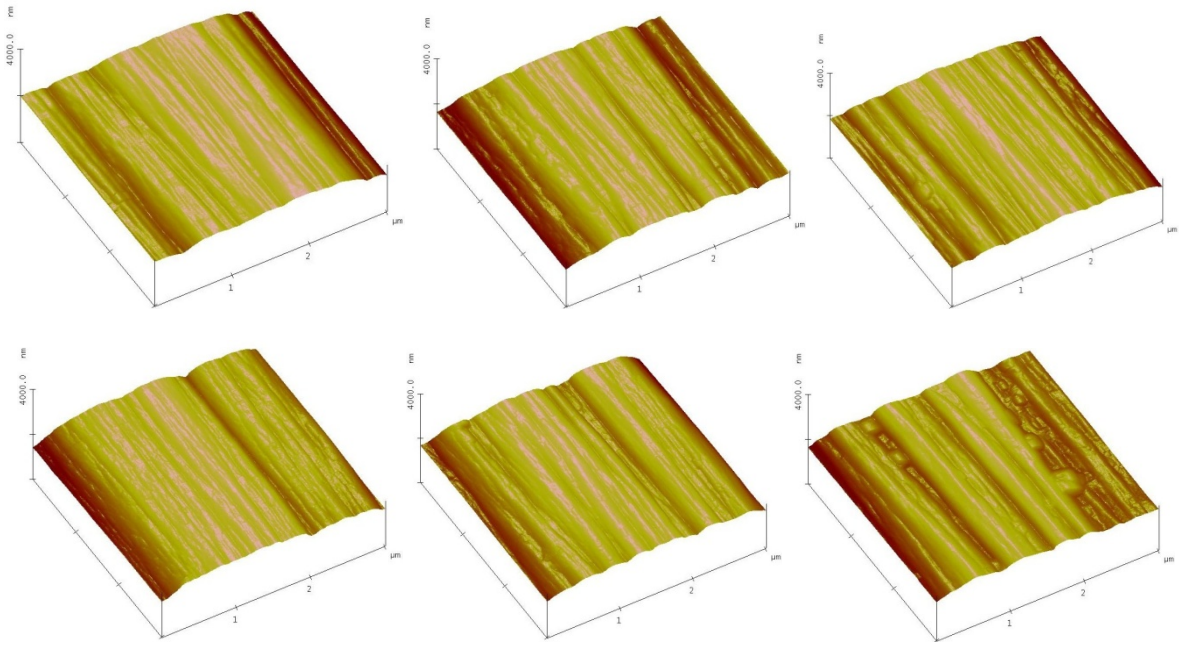




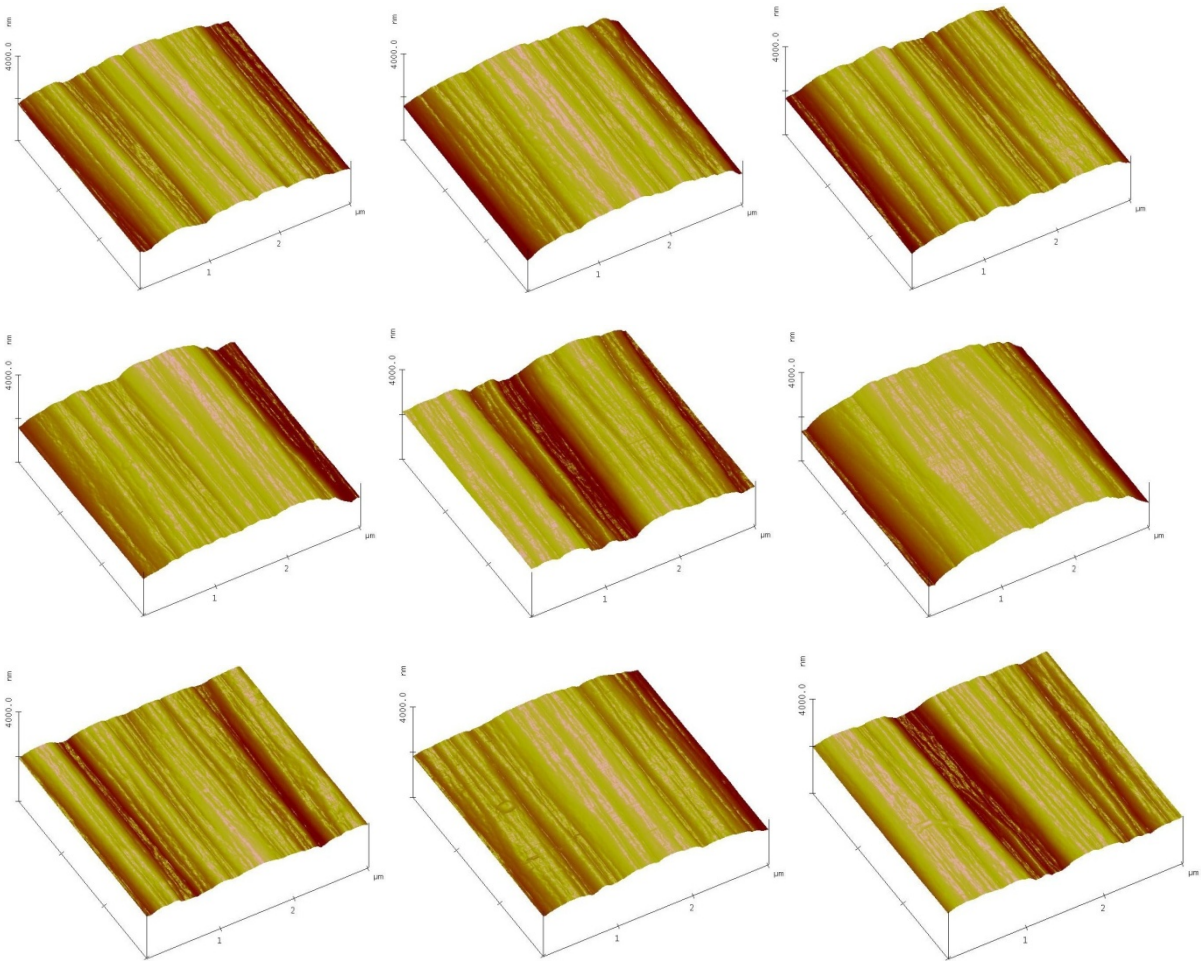


3 x 3 um images for oxidized carbon fiber

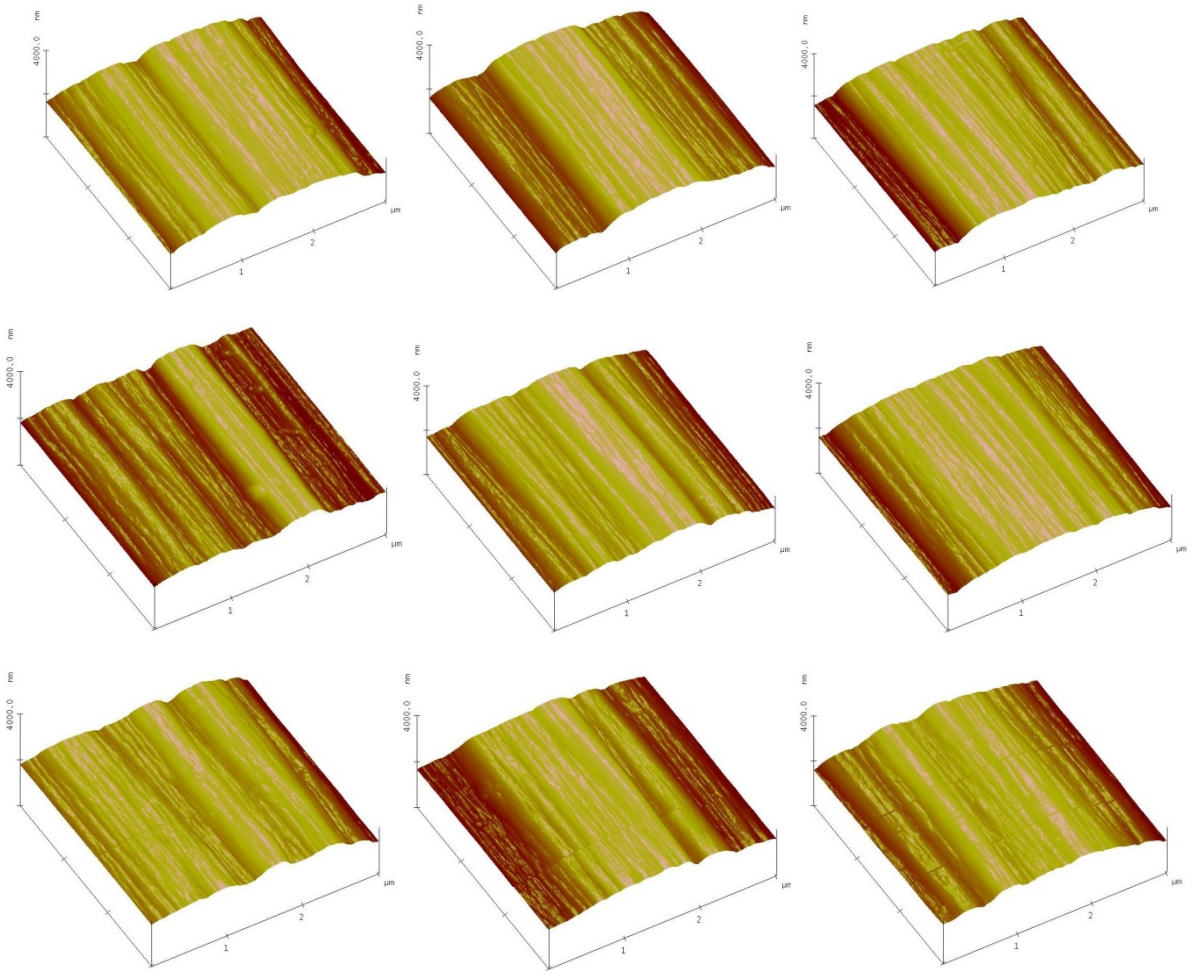




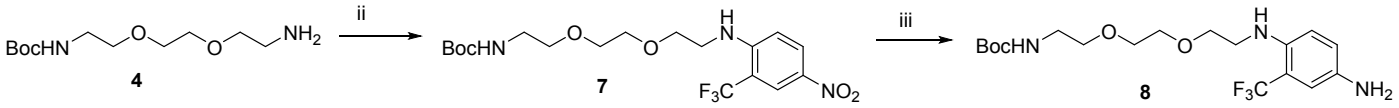
3 x 3 um images of oxidised fiber after diazonium “ortho” treatment 1



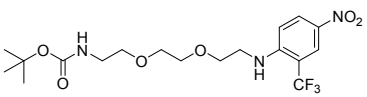
3 x 3 um images of oxidised fiber after diazonium "ortho" treatment 2



Chemical synthesis and characterisation of oxidized fiber "meta" analogue



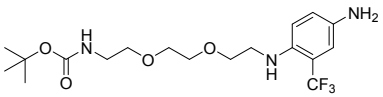
tert-butyl (2-(2-(2-((4-nitro-2-(trifluoromethyl)phenyl)amino)ethoxy)ethoxy)ethyl)carbamate (7)



A solution of **4** (2.007g, 8.08mmol), 2-Fluoro-5-nitrobenzotrifluoride (0.555 mL, 4.04 mmol), and DMF (3 mL) was added to a quartz microwave vessel with a stirrer bar, and fitted with a pressure cap. The solution was stirred under 200W microwave irradiation at 100°C for 80 minutes. The crude mixture was then diluted with ethyl acetate and washed with three portions of saturated sodium chloride solution (15 mL x 3) to remove any traces of residual DMF, followed by drying over $MgSO_4$, and removal of ethyl acetate *in vacuo*. The crude product was purified by column

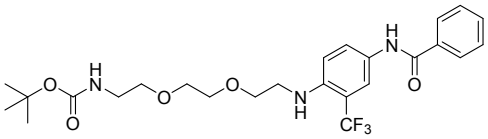
chromatography (1:1 PET spirits: Ethyl acetate), to afford a yellow oil (1.629 g, 92 %) R_f 0.31. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.37 (d, $^3J_{HH}$ = 2.7, 1H, Ar*H*), 8.23 (m, 1H, Ar*H*), 6.71 (d, $^3J_{HH}$ = 9.18, 1H, Ar*H*), 5.54 (br.s, 1H, N*H*COO), 4.88 (br.s, 1H, N*H*Ar), 3.73 (t, 4H, (CH_2)$_2$CO), 3.57 (m, 2H, CH_2CO), 3.53 (br.s, 1H, N*H*Ar), 3.41 (t, $^3J_{HH}$ = 4.86, 2H, CH_2NH), 3.30 (m, 2H, CH_2NH), 1.43 (s, 9H, (CH_3)$_3$). $\nu_{(max)}$ cm $^{-1}$: 3440 (N-H), 2977-2873 (-CH_2-, -CH_3), 1706 (ester C=O), 1619 (N=O), 1538 (aromatic C=C-C), 1320 (N=O), 1280 (C-NH), 1157 (C-F, C-O-C). HRMS (ESI, *m/z*) calculated for [$C_{18}H_{26}F_3N_3O_6$ + Na]$^+$ 460.16659 found: *m/z* 460.16731: ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.93, 150.06, 136.53, 129.05, 123.89 (q, $J^3_{C\text{-}F}$= 5.00), 123.68 (q, $J^1_{C\text{-}F}$=271.25), 112.37 (q, $J^2_{C\text{-}F}$=31.25), 111.05, 79.09, 70.36, 70.21, 70.10, 68.31, 43.00, 40.19, 28.27: ^{19}F NMR (470 MHz, CDCl3): δ = -64.39

***tert*-buyl 2-[2-[2-[4-amino-2-(trifluoromethyl)phenylamino]ethoxy]ethoxy]ethylcarbamate (8)**



A solution of **7** (0.277 g, 0.63 mmol) and palladium on activated carbon (g, 10% w/w) in ethyl acetate (200 mL) was stirred at room temperature under a hydrogen atmosphere for 16 hours. The palladium was then removed by vacuum filtration through a celite plug, followed by purification by column chromatography (1:1 PET spirits: Ethyl acetate) to yield a dark orange/brown oil (0.254 g, 98 %) R_f 0.26. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.82 (d, $^3J_{HH}$ = 2.7, 1H, Ar*H*), 6.76 (m, 1H, Ar*H*), 6.58 (d, $^3J_{HH}$ = 8.64, 1H, Ar*H*), 5.00 (br.s, 1H, N*H*COO), 3.66 (m, 2H, CH_2CO), 3.57 (s, 4H, (CH_2O)$_2$), 3.48 (m, 2H, CH_2CO), 3.25 (m, 4H, CH_2NH), 1.38 (s, 9H, (CH_3)$_3$). $\nu_{(max)}$ cm $^{-1}$: 3432-3355 (N-H), 2975-2871 (-CH_2-, -CH_3), 1700 (ester C=O), 1519 (aromatic C=C-C), 1244 (C-NH), 1145-1102 (C-F, C-O-C). HRMS (ESI, *m/z*) calculated for [$C_{18}H_{28}F_3N_3O_4$ + H]$^+$ 408.21047 found: *m/z* 408.21189: ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.04, 138.81, 136.81, 125.98, 123.81, 120.61, 115.06 (q, $J^1_{C\text{-}F}$=29.00), 114.25, 113.81 (q, $J^2_{C\text{-}F}$=5.63), 79.135, 70.18, 69.33, 43.97, 40.29, 28.35: ^{19}F NMR (470 MHz, CDCl3): δ = -63.11

***tert*-buyl 2-(2-(2-(4-benzamido-2-(trifluoromethyl)phenylamino)ethoxy)ethoxy)ethylcarbamate (9)**



A solution of **8** (0.177 g, 0.43 mmol), triethyl amine (0.091 mL, 0.65 mmol) and benzoyl chloride (0.050 mL, 0.43 mmol) in chloroform (3 mL) was stirred at 0°C for 5 hours. The crude reaction mixture was then washed with 3 equal portions of saturated sodium chloride solution (3 x 50 mL), dried over $MgSO_4$, and solvent removed *in vacuo*. Purification was undertaken using column chromatography (1:1 PET spirits: Ethyl acetate, 0.25% Net_3) and the desired (colour, description) product was obtained in high yield (0.187 g, 85%) R_f 0.27. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.51 (br. s, 1H, ArN*H*COO), 7.82 (m, 2H, Ar*H*), 7.63 (m, 2H, Ar*H*), 7.41 (m, 4H, Ar*H*, ArN*H*), 6.63 (d, $^3J_{HH}$ = 9.18, 2H, Ar*H*), 5.03 (br. s, 1H, N*H*COO), 3.67 (t, $^3J_{HH}$ = 5.13, 2H, CH_2CO), 3.57 (m, 4H, (CH_2O)$_2$), 3.45 (t, $^3J_{HH}$ = 5.13, 2H, CH_2CO), 3.25 (m, 4H, (CH_2NH), 1.38 (s, 9H, (CH_3)$_3$). $\nu_{(max)}$ cm $^{-1}$: 3445-3312 (N-H), 2975-2873 (-CH_2-, -CH_3), 1693 (ester C=O), 1515 (aromatic C=C-C), 1270 (C-NH), 1150 (C-F, C-O-C). HRMS (ESI, *m/z*) calculated for [$C_{25}H_{33}F_3N_3O_5$

+ H]$^+$ 512.23668 found: *m/z* 512.23677: ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.09, 156.09, 142.84, 134.66, 131.61, 128.53, 127.45, 126.62, 125.81, 123.64, 120.10 (q, $J^2_{C\text{-}F}$=5.42), 113.64 (q, $J^1_{C\text{-}F}$=29.62), 112.52, 79.25, 70.31, 70.21, 43.29, 40.29, 28.35: ^{19}F NMR (470 MHz, CDCl3): δ =-63.40

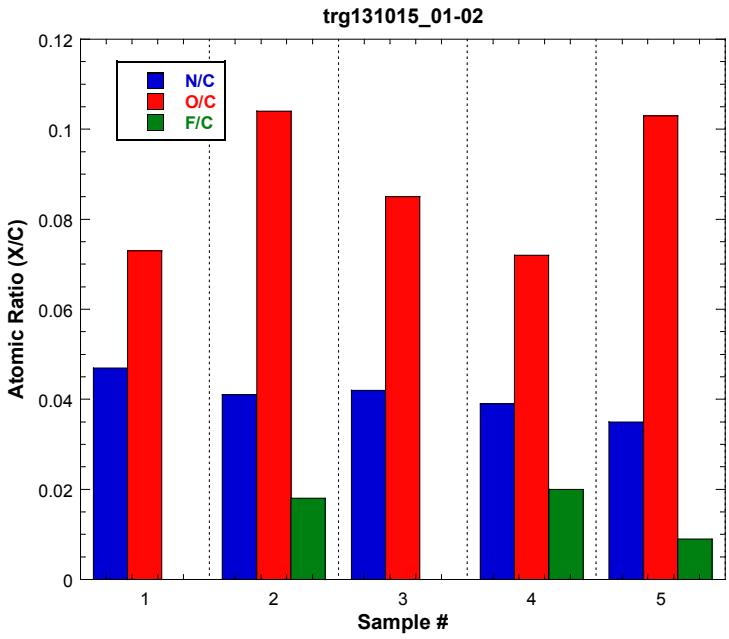
First pass XPS results for "meta" analogues

	Treatment 1 control	**Treatment 1**	**Treatment 2 control**	**Treatment 2**
Previous treatment	None	None	None	Treatment 1
Reagents	None	Compound **2,** *tert*-butyl nitrite	HCl, NaOH	HCl, NaOH
Solvent	*O*-DCB, Acetonitrile	*O*-DCB, acetonitrile	1,4-dioxane H_2O	1,4-dioxane H_2O
Conditions	50°C 24 hours	50 °C 24 hours	R.T. 16 hours	R.T. 16 hours
Cleaning	DCM, Acetone, Ethanol	DCM, Acetone, Ethanol	H_2O, Acetone	H_2O, Acetone

XPS atomic ratios for untreated/control/and treated samples

	#1 Oxidised, untreated CF		**#2 Treatment 1**		**#3 Treatment 1 control**		**#4 Treatment 2**		**#5 Treatment 2 control**	
	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*
C	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*
N	0.047	*0.001*	0.041	*0.002*	0.042	*0.001*	0.039	*0.001*	0.035	*0.001*
O	0.073	*0.001*	0.104	*0.001*	0.085	*0.001*	0.072	*0.000*	0.103	*0.002*
F	0.000	*0.000*	0.018	*0.000*	0.000	*0.001*	0.020	*0.001*	0.009	*0.001*
Na	0.000	*0.000*	0.002	*0.000*	0.002	*0.000*	0.005	*0.000*	0.012	*0.001*
Zn	0.000	*0.000*	0.001	*0.000*	0.000	*0.000*	0.000	*0.000*	0.001	*0.000*
Ca	0.000	*0.000*	0.010	*0.001*	0.003	*0.001*	0.002	*0.000*	0.003	*0.000*
Si	0.002	*0.000*	0.004	*0.000*	0.002	*0.000*	0.003	*0.000*	0.002	*0.000*
S	0.000	*0.000*	0.006	*0.000*	0.001	*0.000*	0.001	*0.000*	0.001	*0.000*
Cl	0.000	*0.000*	0.002	*0.000*	0.001	*0.000*	0.003	*0.000*	0.002	*0.000*

Ratios displayed in graph form



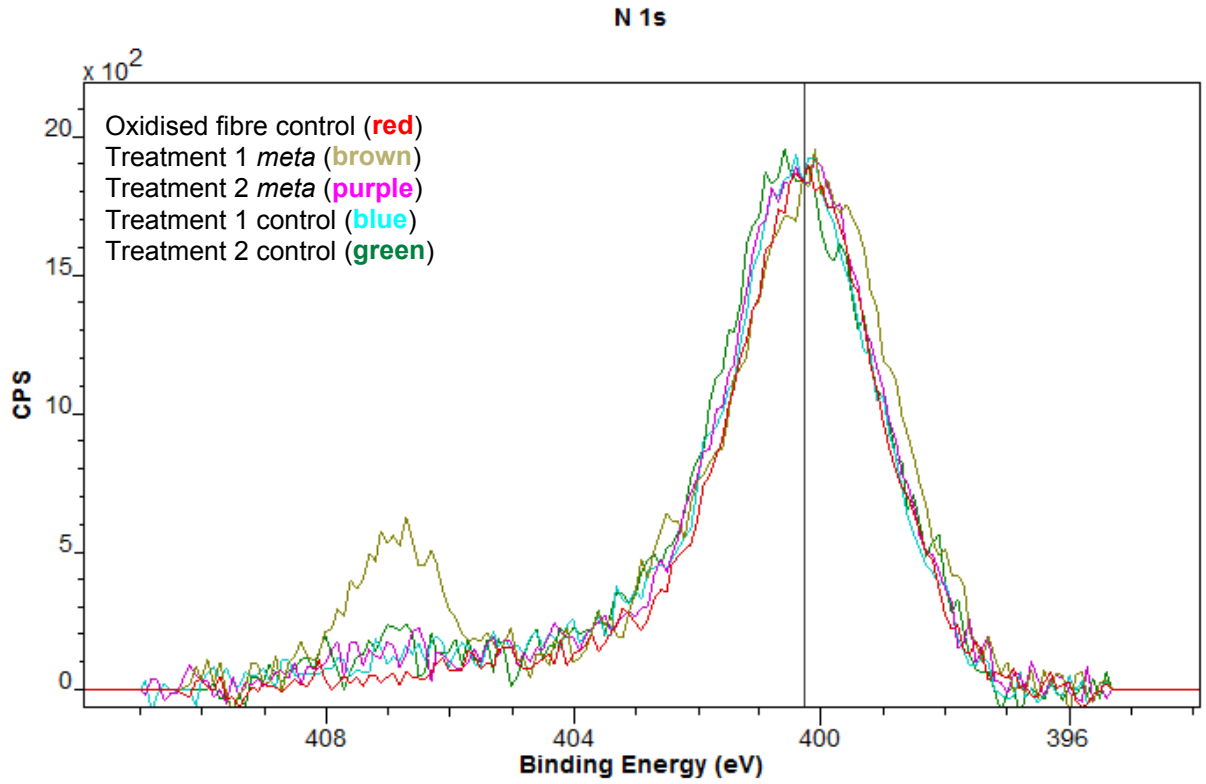


Figure.

The initial results obtained from the analysis of fibers which had been treated with the *meta* diazonium compound (treatment 1, 2, and their respective controls) showed a highly promising increase in fluorine signal, due to the presence of the CF_3 tagged compound. Unfortunately there were two unexpected and distinct changes which were noted: 1) a marked increase in fluorine signal after the deprotection step in "treatment 2 control" and, 2) a large shift in binding energy appearing at approximately 407 eV in the N1s spectrum.

The exact source of the fluorine contamination in the treatment 2 control sample was unknown, but it was speculated that it may have been due to general silicone glassware contamination which occurs in the lab, which often holds fluorine contaminants. The appearance of a distinct new nitrogen species at 407 eV was attributed to the presence of unreacted *tert*-butyl nitrite. The nitrite functional group, much like a nitro group, resonates at a distinct frequency (in a range of 406 to 408 eV) due to the oxidation state of the nitrogen when bond to two oxygens.

Because of these unexpected contaminations, conclusions could not be drawn about the success of the new treatment. Attempts were then made to rule out the effects of adsorption in the detection of fluorine signal for the treatment 1 and 2 samples, by subjecting the samples to a second pass washing procedure (following the original washing and drying protocol for a second time) as well as preparing a new set of controls with a wider set of parameters:

0 = oxidised carbon fiber (untreated)

1 = treatment 1 (rewashed)

1a = treatment 1 control = just solvent and heating

1b = treatment 1 control = solvent/heating/nitrite present (only a quick rinse to see nitrite signal)

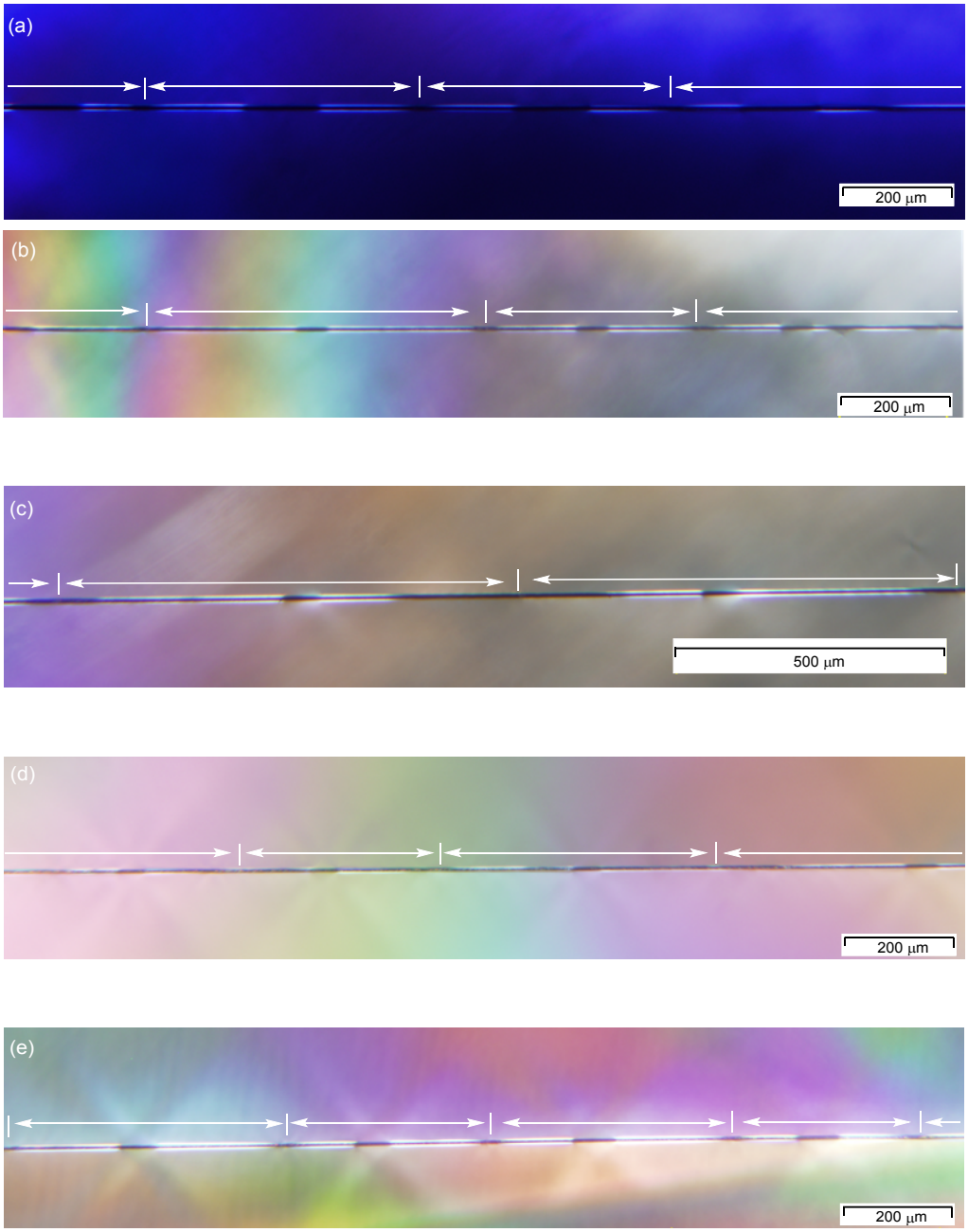
1c = treatment 1 control = solvent/heating/nitrite present (normal washing/drying protocol)

2 = treatment 2 (rewashed)

2a = treatment 2 control (1c then subjected to treatment 2)

IFSS images showing fibre fragmentation

The images shown in Fig.20 further highlight the effect of surface treatment on fragmentation behaviour. Images ‘a’ (untreated), ‘b’ (*ortho* treatment 1) and ‘c’ (*ortho* treatment 2) show very little matrix stress, with a steady increase in fragment length from (a) through to (c). Image ‘d’ (*meta* treatment 1), much like (b) has no obvious matrix effects coupled with an increase in fragment size, whereas image ‘e’ (*meta* treatment 2) demonstrates the visual decrease in fragment size, coupled with the frequent presence of transverse matrix splitting at points of fiber breakage (ESI).



5x magnification optical microscope images of single fiber fragmentation samples for (a) oxidized untreated fiber, (b) *ortho* treatment 1, (c) *ortho* treatment 2, (d) *meta* treatment 1, (e) *meta* treatment 2