ChemistryOPEN

Supporting Information

Interphase Engineering of a Cellulose-Based Carbon Fiber Reinforced Composite by Applying Click Chemistry

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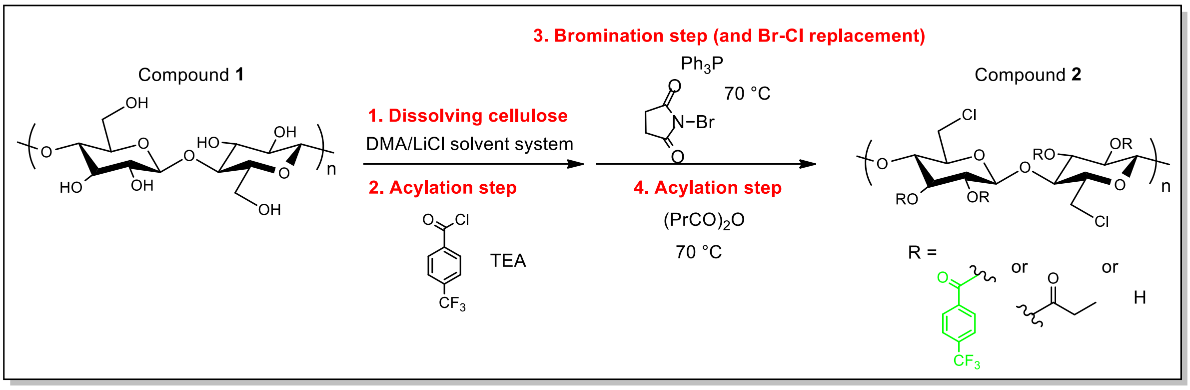
1. Synthetic procedures

1.1. One-pot synthesis of *O*-acylated 6-chloro-6-deoxycellulose



1) Dissolution of microcrystalline cellulose (Avicel® PH 101, Compound **1**) was performed in DMA/LiCl solvent system according to Heinze et al.[1] Briefly, 3 g cellulose (18.5 mmol anhydroglucose units) was stirred in 120 mL DMA at 130 °C for 2 h. Thereafter, the system was cooled to 100 °C at which point, 9 g anhydrous LiCl was added. The cellulose completely dissolved as the system cooled down to room temperature.

2) 0.5 mL triethylamine (3.7 mmol) was added to the system, followed by dropwise addition of 0.55 mL 4-(trifluoromethyl)benzoyl chloride (3.7 mmol), and the reaction mixture was stirred overnight at room temperature.

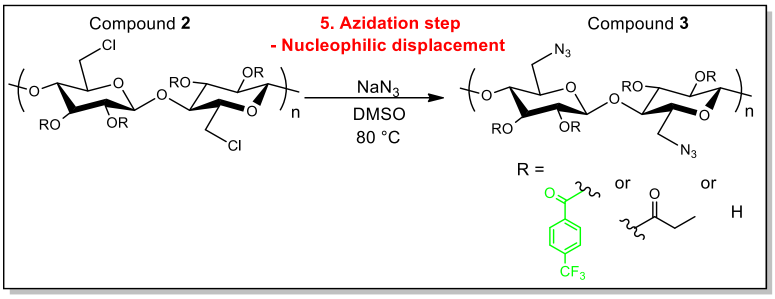
3) 19.43 g triphenylphosphine (74 mmol) was dissolved in 30 mL DMA and another solution was prepared with 13.18 g *N*-bromosuccinimide (74 mmol) inside. The triphenylphosphine solution was measured to the solution containing the cellulose derivative dropwise, following dropwise addition of the *N*-bromosuccinimide solution. The system was kept at 70 °C under Ar atmosphere for 2 h.

4) 23.7 mL propionic anhydride was added to the reaction mixture (185 mmol) and it was stirred overnight at 70 °C. The product was precipitated in 50/50% water-methanol mixture and re-precipitated using acetone as a solvent. The resulting product was dried in a vacuum oven at 50 °C for 24 h.

The resulting product was identified as XPS-tagged propionated 6-chloro-6-deoxycellulose (Compound **2**) according to the ^{1}H-, ^{13}C-NMR (Figure S1 and S2, respectively) and FTIR spectra (Figure S3). The DS value was determined to be 2.16 for the propionate units and 0.03

for the XPS-tag from the integrals in Figure S1. After benzoylation reaction, the ^{1}H-NMR spectrum indicated that all the hydroxyl groups were substituted, and therefore, the DS value was 0.81 in respect to the chlorine substituent.

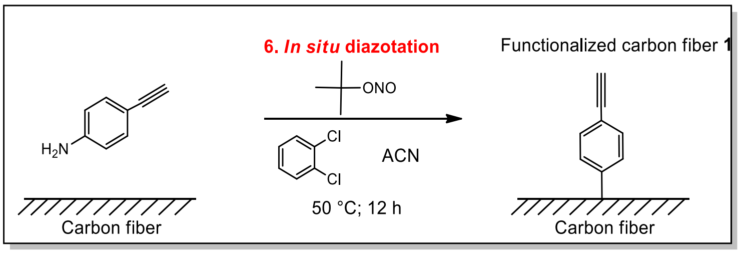
1.2. Synthesis of *O*-acylated 6-azido-6-deoxycellulose



3 g XPS-tagged propionated 6-chloro-6-deoxycellulose (18.52 mmol anhydroglucose units, Compound **2**) was dissolved in 100 mL anhydrous DMSO. 6.02 g NaN_3 (92.6 mmol) was measured into the flask and dissolved under vigorous stirring. The reaction system was kept at 80 °C for 24 h under Ar atmosphere. The product was precipitated in deionized water and the collected filtrate was reprecipitated after drying using acetone as a solvent. The resulting product was dried in a vacuum oven at 50 °C for 24 h.

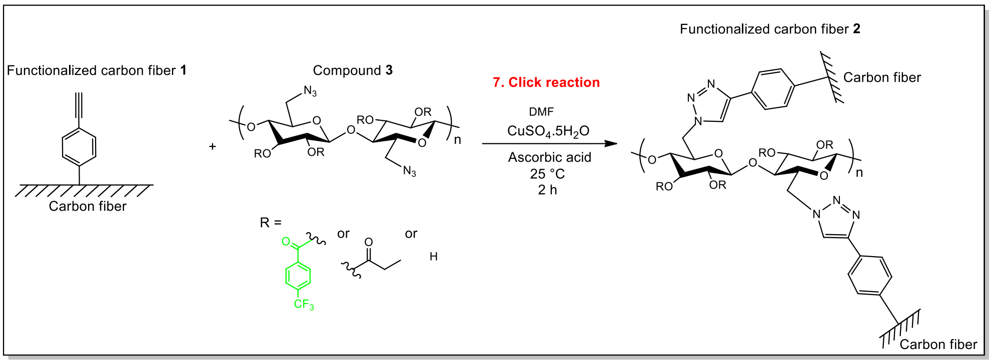
The resulting product was identified as XPS-tagged propionated 6-azido-6-deoxycellulose (Compound **3**) according to the ^{1}H-, ^{13}C-NMR (Figure S4 and S5) and FTIR spectra (Figure S3). The DS value in respect to the $–N_3$ substituent was determined to be 0.77 from elemental analysis.

1.3. Functionalization of the carbon fiber surface with phenylacetylene moiety



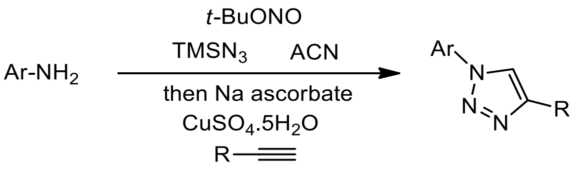
The diazotization and *in situ* grafting process was derived from Bahr and Tour.[2] The same procedure was applied in recent studies on carbon fibers.[3,4] 30 mL *ortho*-dichlorobenzene, 15 mL acetonitrile and 85.5 mg 4-ethynylaniline (0.73 mmol) was bubbled with nitrogen for 10 min (degassing process). 25 mg carbon fiber was then immersed in the solution under nitrogen atmosphere. To this solution, 170 µL isoamyl nitrite (1.5 mmol) was added and the reaction flask was heated to 50 °C. After 24 h reaction time the solvents were decanted and the fibers were washed with dichloromethane until yielding a clear solution. Thereafter, the fibers were rinsed with 200 mL dichloromethane, water and acetone using a Buchner funnel, and then placed in a vacuum oven for 24 h at 50 °C.

1.4. Click reaction of *O*-acylated 6-azido-6-deoxycellulose on the carbon fiber surface



25 mg carbon fiber (Functionalized carbon fiber **1**) was immersed in 50 mL DMF containing 1 g cellulose derivative (Compound **3**). To this solution, 0.2497 g $CuSO_4.5H_2O$ (1 mmol) and 0.344 g ascorbic acid (2 mmol) dissolved in 20 mL DMF was added. The reaction was stirred at room temperature for 2 h. After that, the fibers were washed with 200 mL 1 M aqueous EDTA, dichloromethane, water and acetone. The functionalized carbon fibers were placed in the vacuum oven for 24 h at 50 °C.

1.5. Click reaction for grafting small molecules on the carbon fiber surface



The one-pot click reaction on solid phase was performed according to the highly efficient procedure elaborated by Barral et al.[5] 66.5 µL aniline (0.73 mmol) was dissolved in 20 mL acetonitrile and cooled to 0 °C using an ice bath. 130 µL isoamyl nitrite (*t*-BuONO; 1.095 mmol) was measured into the flask followed by dropwise addition of 116 µL $TMSN_3$ (0.87 mmol). The reaction medium was allowed to warm to room temperature within 2 h. After that, 25 mg phenylacetylene-functionalized carbon fiber was added to the system along with 25.7 mg sodium ascorbate (0.145 mmol) and 8.99 mg $CuSO_4.5H_2O$ (0.036 mmol) dissolved in 2 mL water. The reaction mixture was stirred overnight at room temperature. The fibers were washed with 200 mL 1 M aqueous EDTA, dichloromethane, water and acetone. The functionalized carbon fibers were placed in the vacuum oven for 24 h at 50 °C.

1.6. Deprotection step of 4-[(*N*-Boc)aminomethyl]aniline-functionalized carbon fiber

The deprotection step was carried out according to Servinis et al.[3] Briefly, functionalized fibers were added to 20 mL 2 M anhydrous HCl - 1,4-dioxane solution, and left to react for 24 h at room temperature. After that, the fibers were washed with 3 × 150 mL water and then treated with 2 M 20 mL NaOH solution for 10 min, three times. Thereafter, the fibers were washed with 100 mL water five times and with 150 mL acetone using a Buchner funnel. The functionalized samples were dried in a vacuum oven at 50 °C for 24 h.

1.7. Electrochemical grafting – synthesis of the diazonium salt

Synthesis of the diazonium salt for electrochemical grafting experiment was performed according to Kosynkin et al.[6] 0.2336 g $NOBF_4$ (2 mmol) was measured in a flask under argon atmosphere and dry acetonitrile (10 mL) was injected through a rubber septum. The flask was then cooled down in an acetonitrile/liquid nitrogen bath (-41 °C). Thereafter, 0.2343 g 4-ethynylaniline (2 mmol) dissolved in 10 mL acetonitrile was added over 30 min using a syringe. The solution was stirred for 2 hours at -30 °C and then directly used for the electrochemical experiments due to the instability of the diazonium species.

1.8. Electrochemical grafting – cyclic voltammetry experiments

Cyclic voltammetry experiments were carried out with a 3-electrode system using an ALS/CHInstruments Elechtrochemical Analyzer Model 1200A potentiostat and a SVC3 voltammetry cell (ALS Co., Ltd, Tokyo, Japan). Ag/Ag^+ non-aqueous reference electrode (RE-7, ALS Co., Ltd, Tokyo, Japan) and a platinum counter electrode were applied (ALS Co., Ltd, Tokyo, Japan). The working electrode was ~20 cm long carbon fiber (25 mg) fixed to the terminal using a copper tape. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The working electrode was cycled between 1 and -1 V vs. $Ag/AgNO_3$. 0.2 V s^{-1} scan rate and 10 mM diazonium salt concentration was applied. After the electrochemical experiments, the fibers were cleaned thoroughly with 200 mL acetone, dichloromethane and deionized water and dried in a vacuum oven at 50 °C for 24 h.

2. Characterization of cellulose derivatives

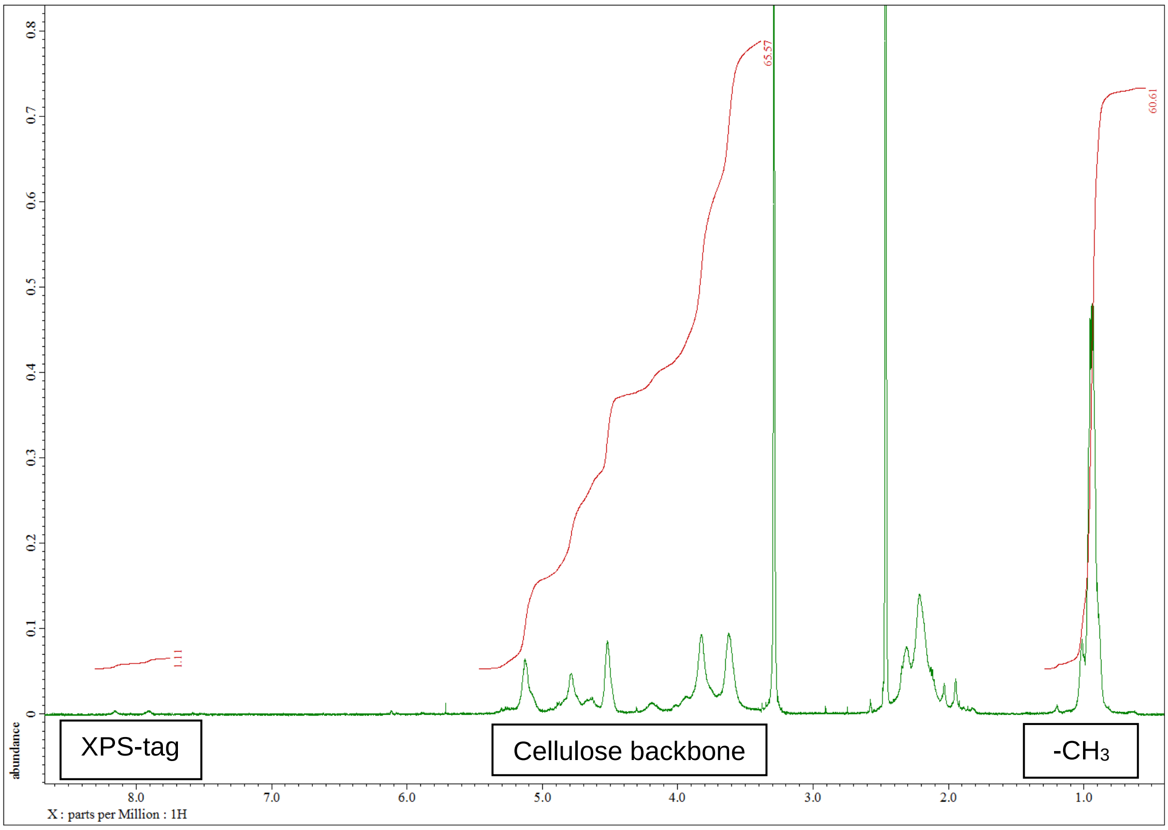


Figure S1. ^{1}H-NMR spectrum of XPS-tagged propionated 6-chloro-6-deoxycellulose (Compound **2**).

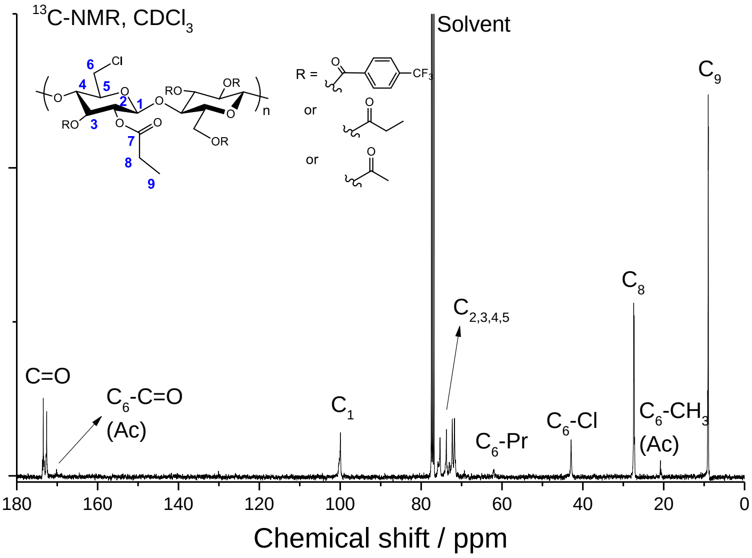


Figure S2. ^{13}C-NMR spectrum of XPS-tagged propionated 6-chloro-6-deoxycellulose (Compound **2**). The appearance of acetyl groups is due to a well-known side reaction, when the DMA solvent takes part in the S_N2 reaction with the alkoxyphosphonium salt intermediate during the bromination process.[7,8]

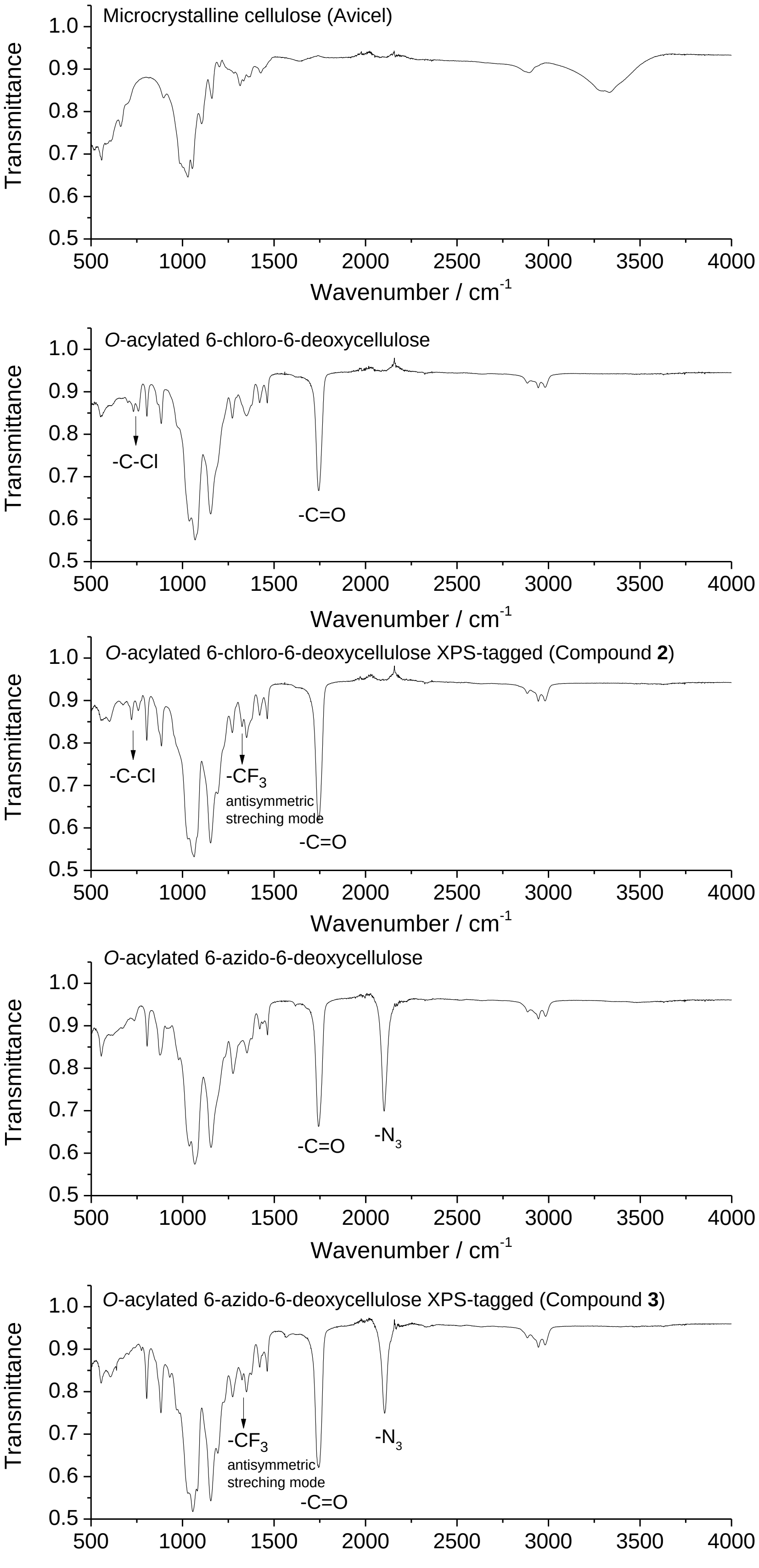


Figure S3. FTIR spectra of synthesized cellulose derivatives.

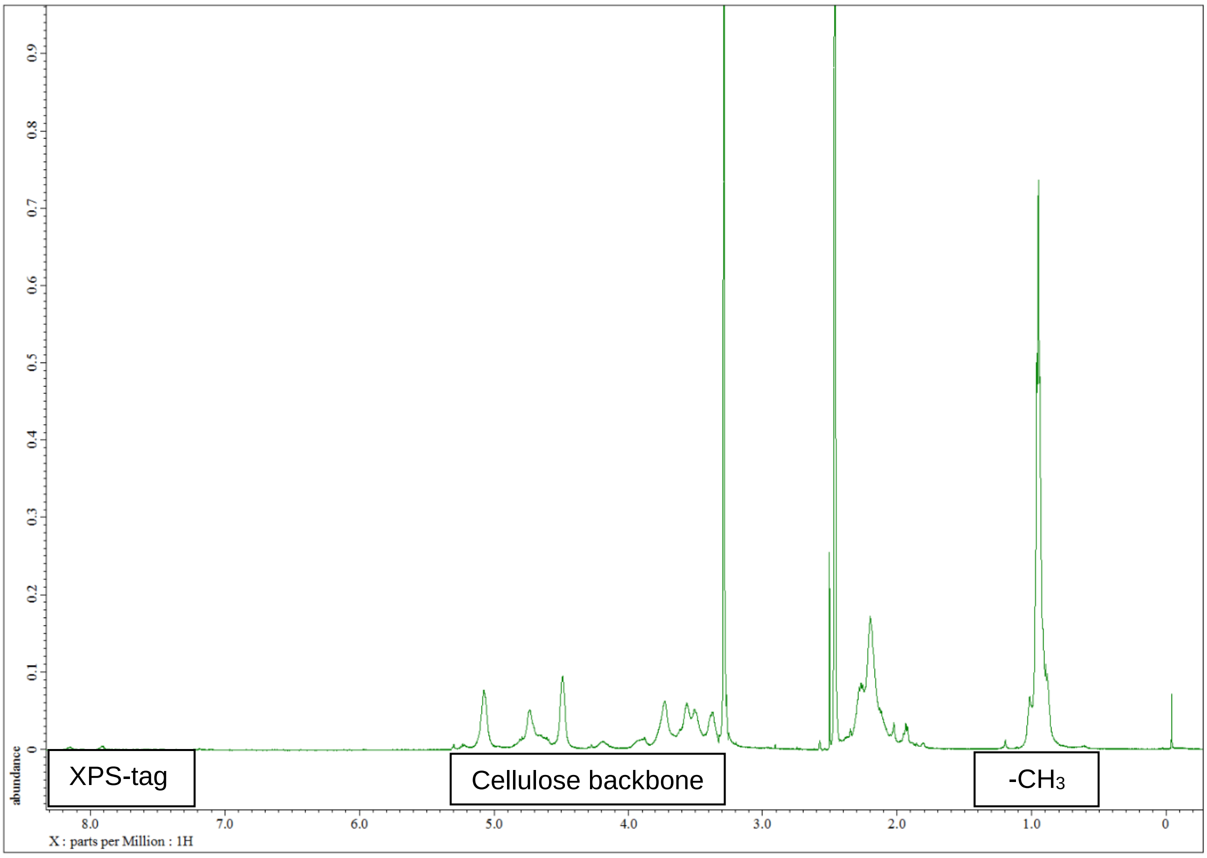


Figure S4. ^{1}H-NMR spectrum of XPS-tagged propionated 6-azido-6-deoxycellulose (Compound **3**).

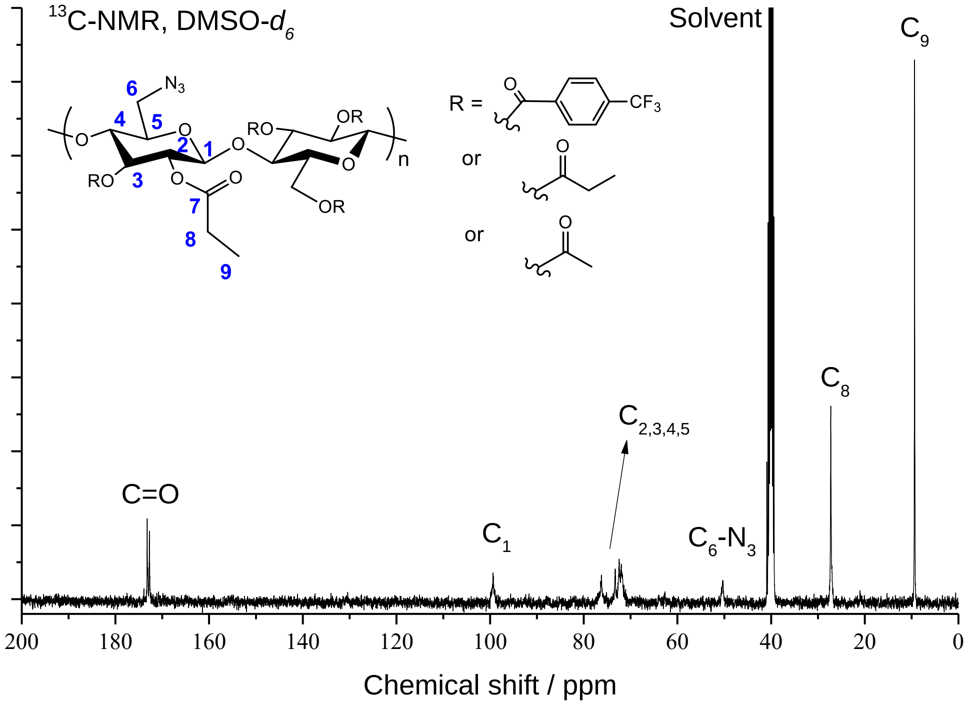


Figure S5. ^{13}C-NMR spectrum of XPS-tagged propionated 6-azido-6-deoxycellulose (Compound **3**).

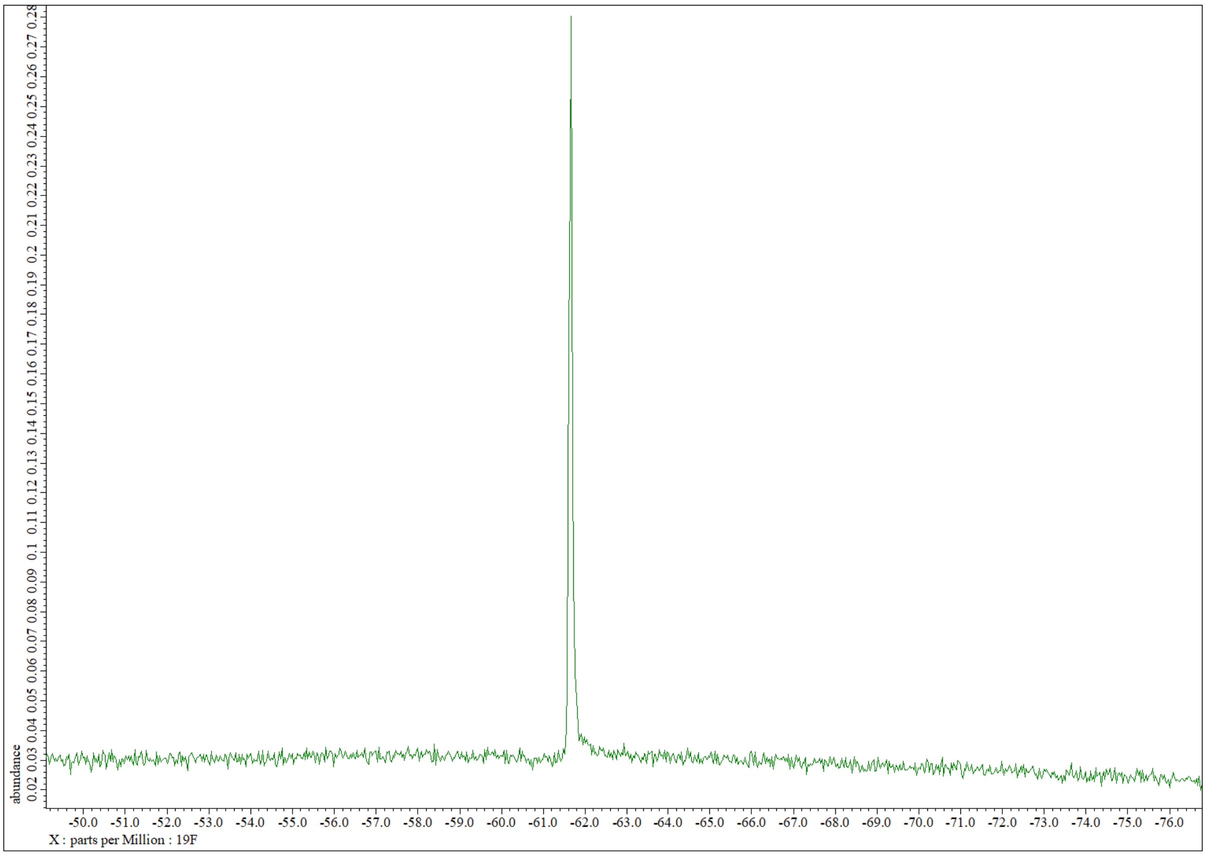
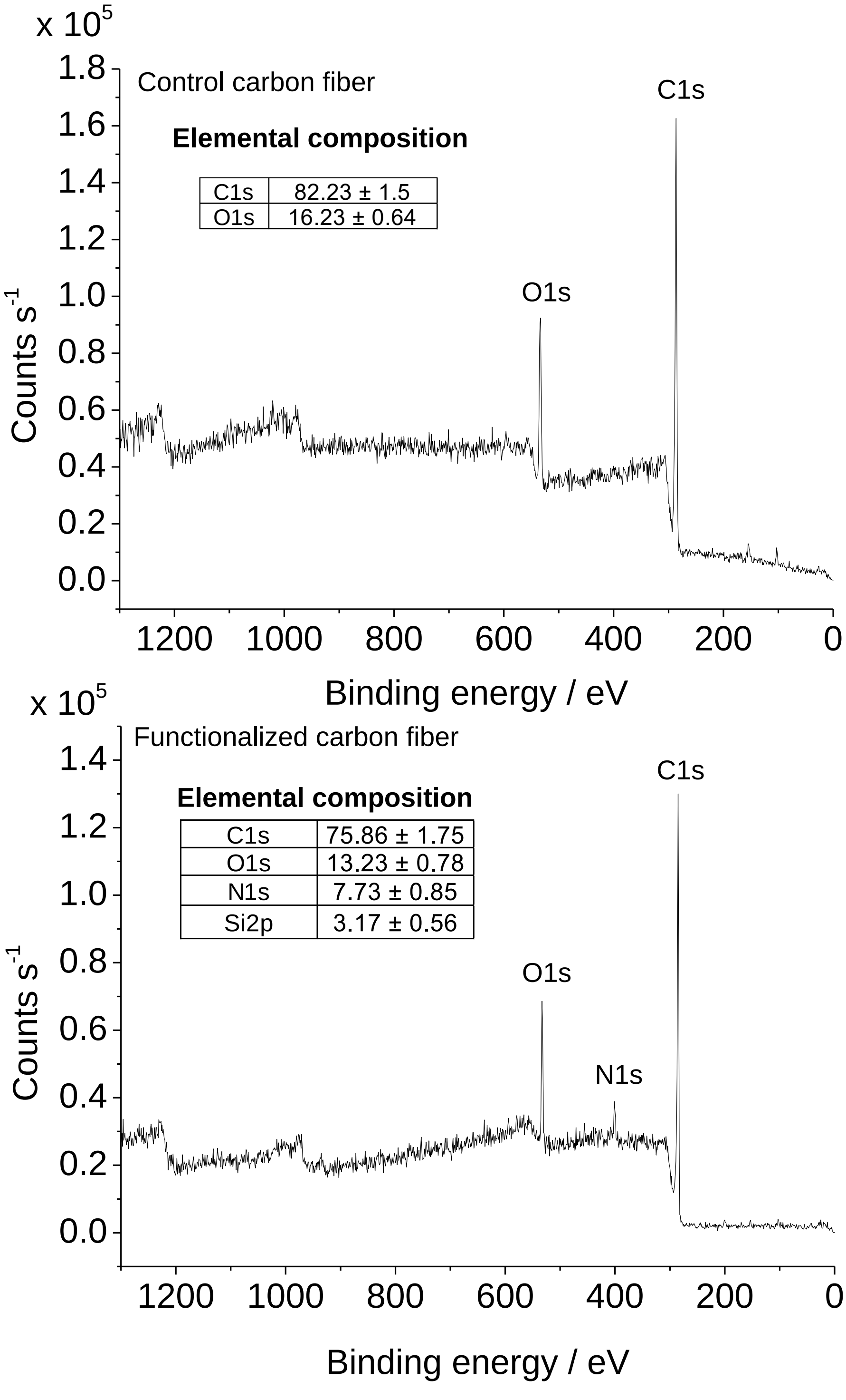


Figure S6. ^{19}F-NMR spectrum of XPS-tagged propionated 6-azido-6-deoxycellulose (Compound **3**).

3. XPS spectra



Elemental composition

C1s	82.23 ± 1.5
O1s	16.23 ± 0.64

Elemental composition

C1s	75.86 ± 1.75
O1s	13.23 ± 0.78
N1s	7.73 ± 0.85
Si2p	3.17 ± 0.56

Figure S7. Survey spectra of control fiber and samples functionalized with cellulose derivative (Functionalized carbon fiber **2**).

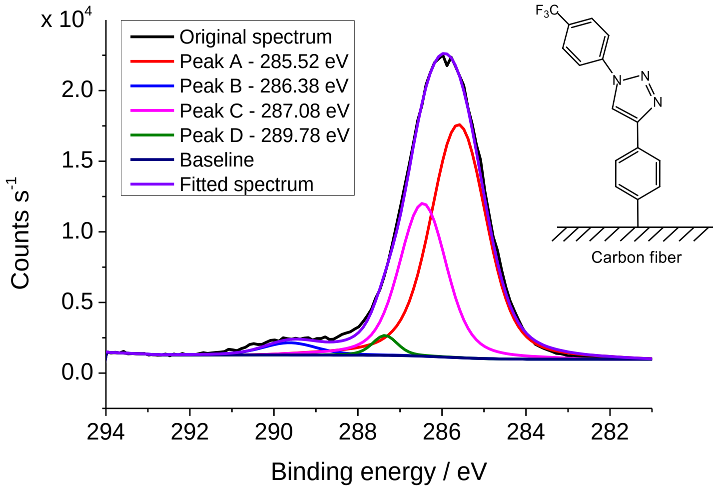


Figure S8. High-resolution C1s spectrum of functionalized carbon fiber sample – validation of click reaction with aniline derivatives using the model compound shown on the figure.

4. Chemical mapping of carbon fiber samples

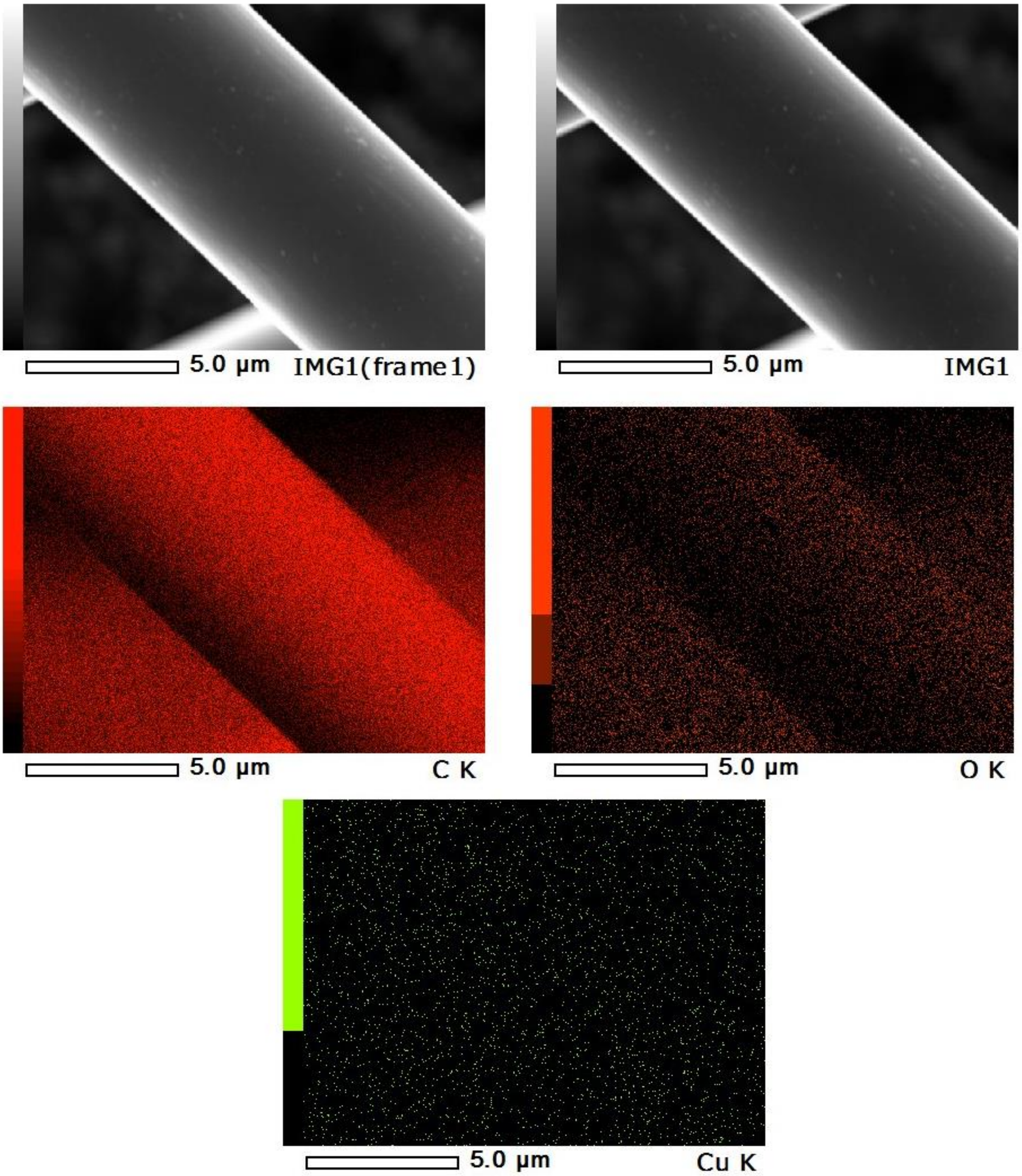


Figure S9. Chemical mapping carried out on an unfunctionalized control carbon fiber sample. Please note that Cu signal is from the sample holder.

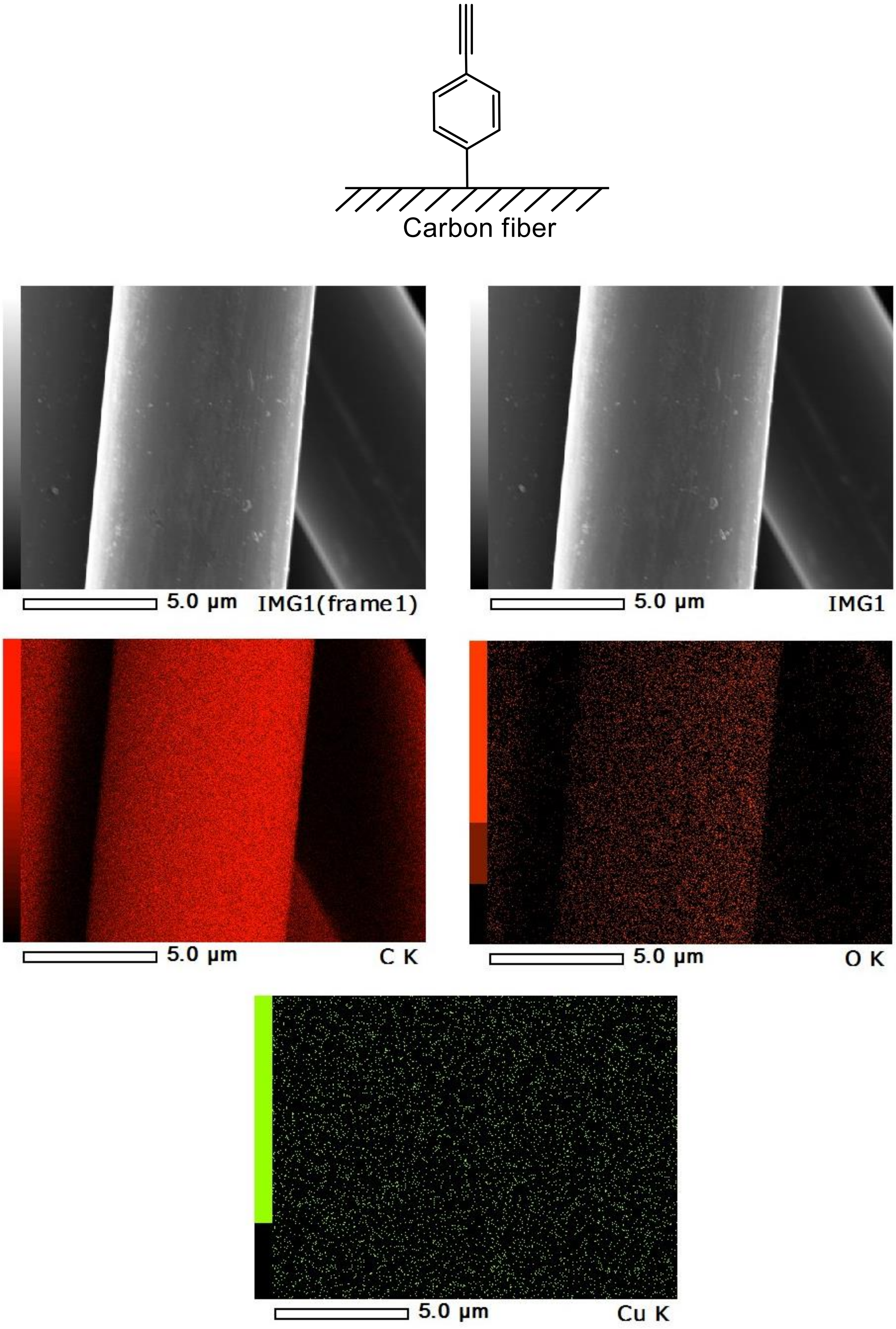


Figure S10. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

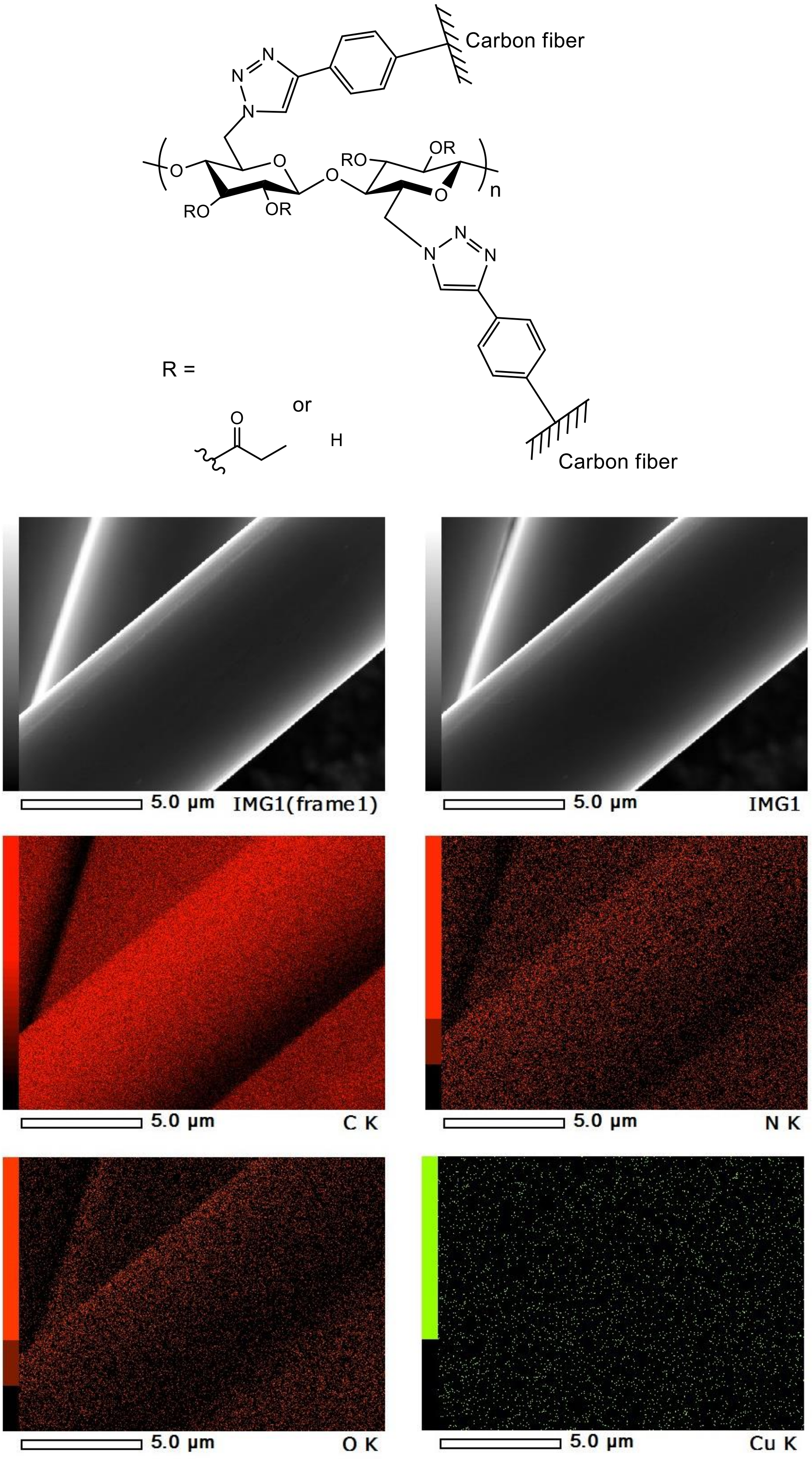


Figure S11. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

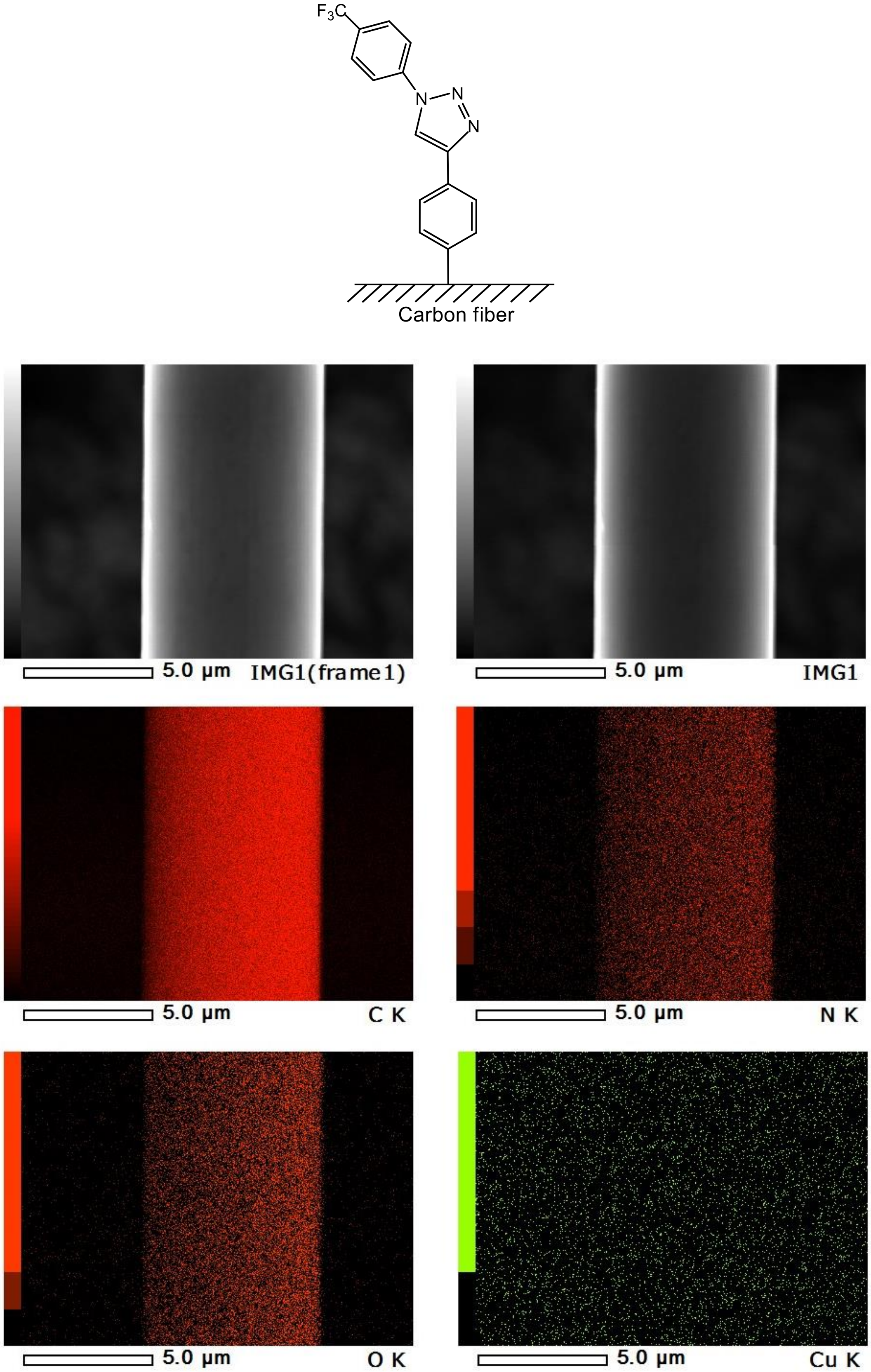


Figure S12. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

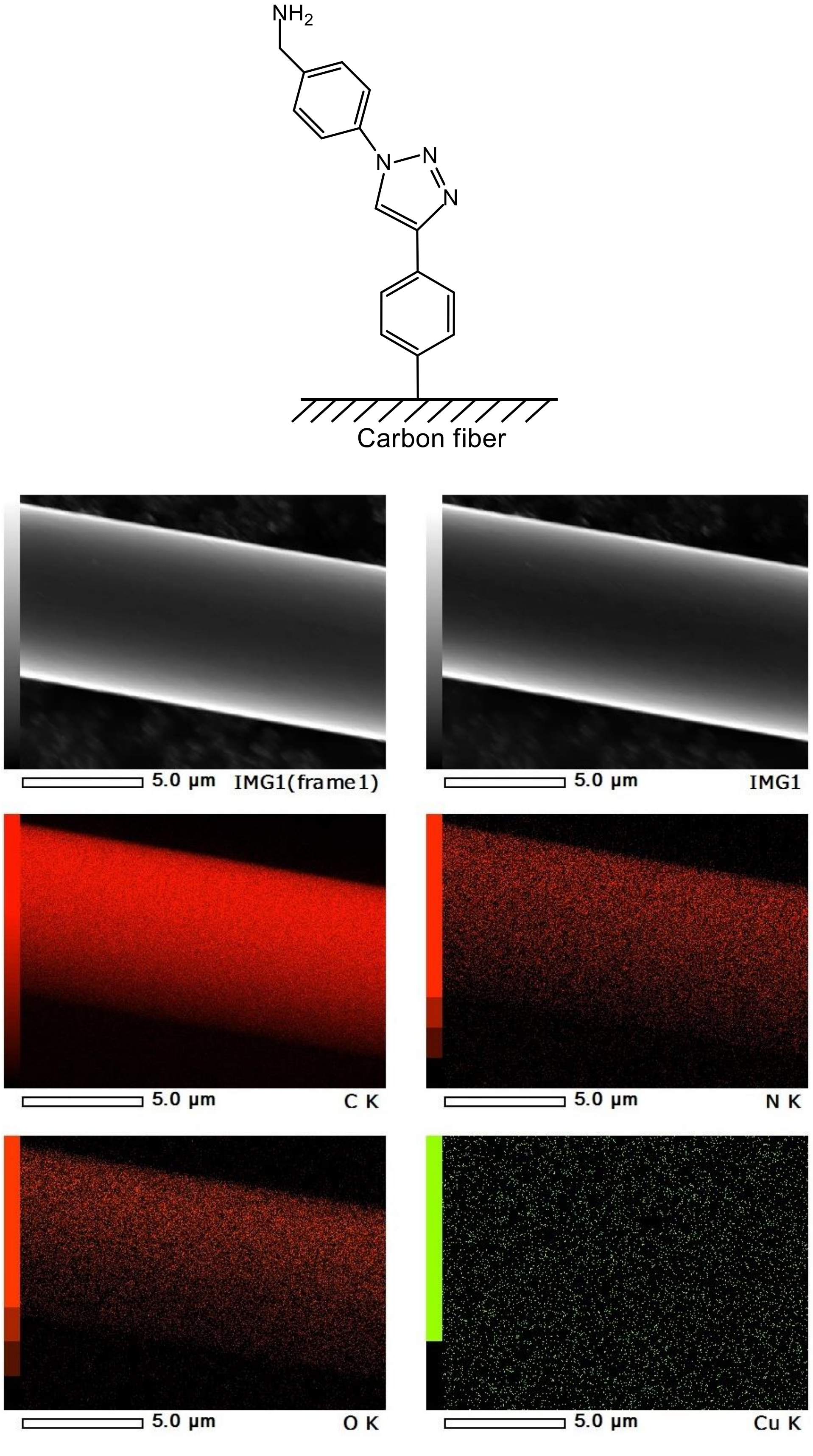


Figure S13. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

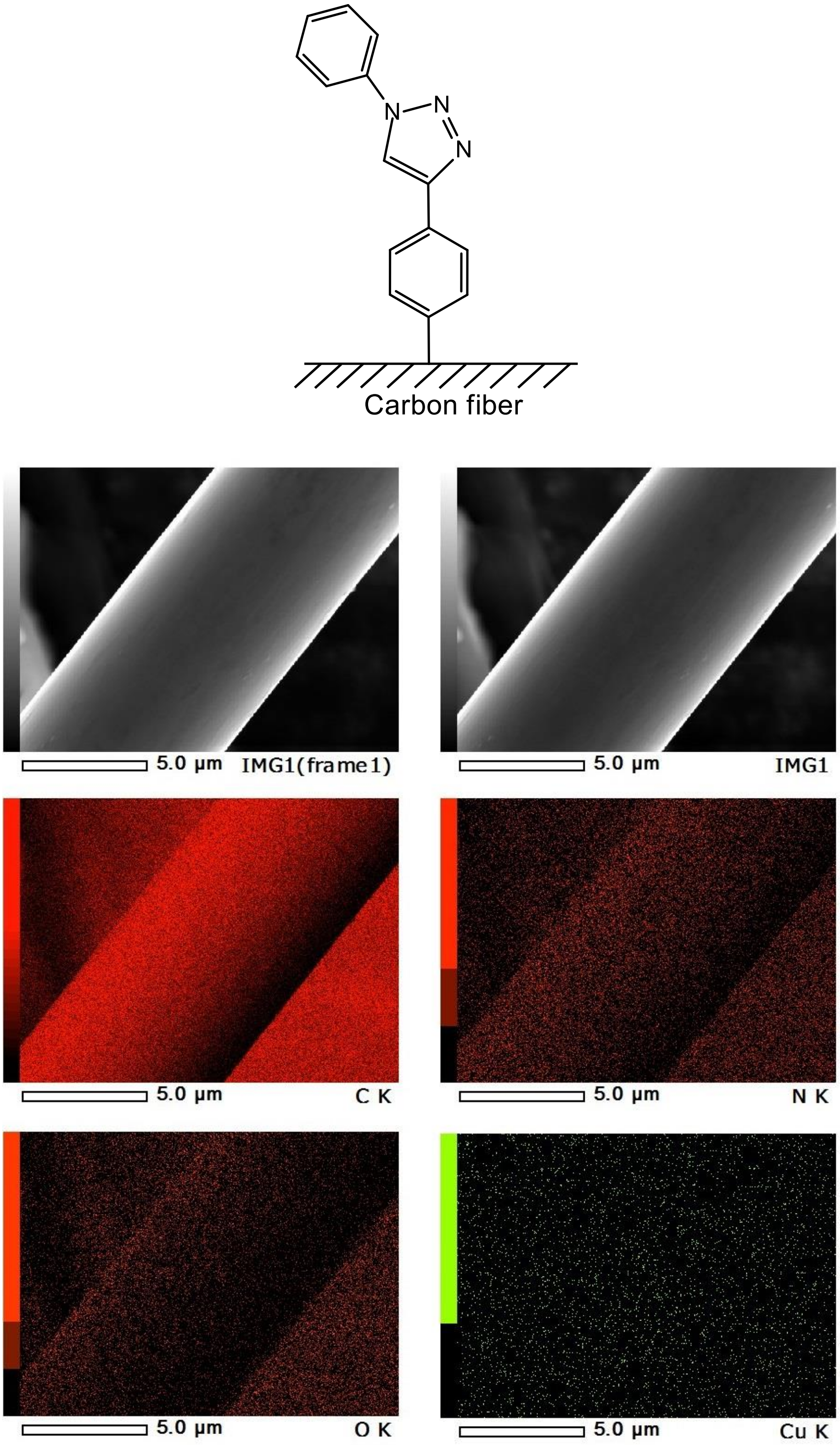


Figure S14. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

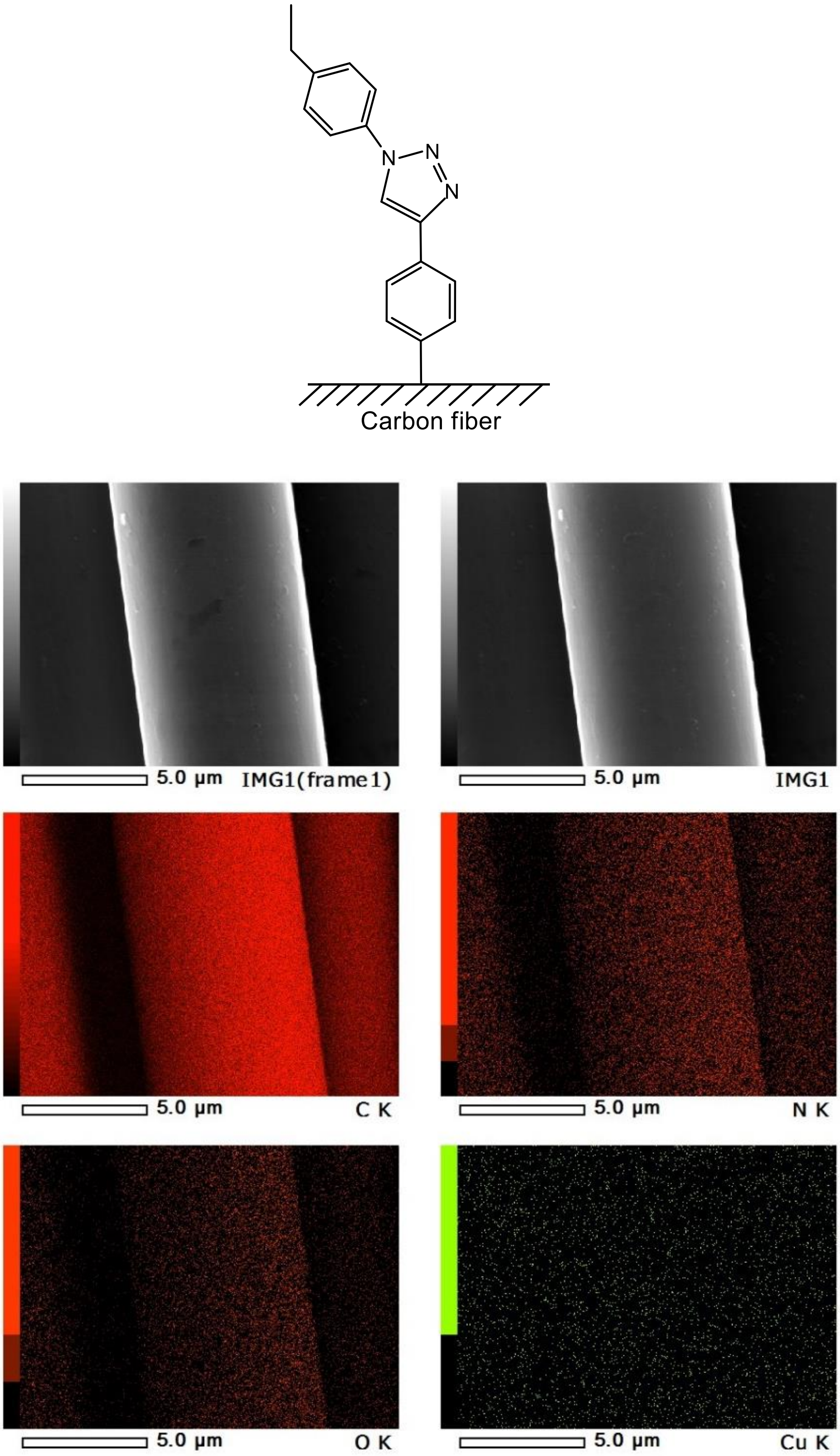


Figure S15. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

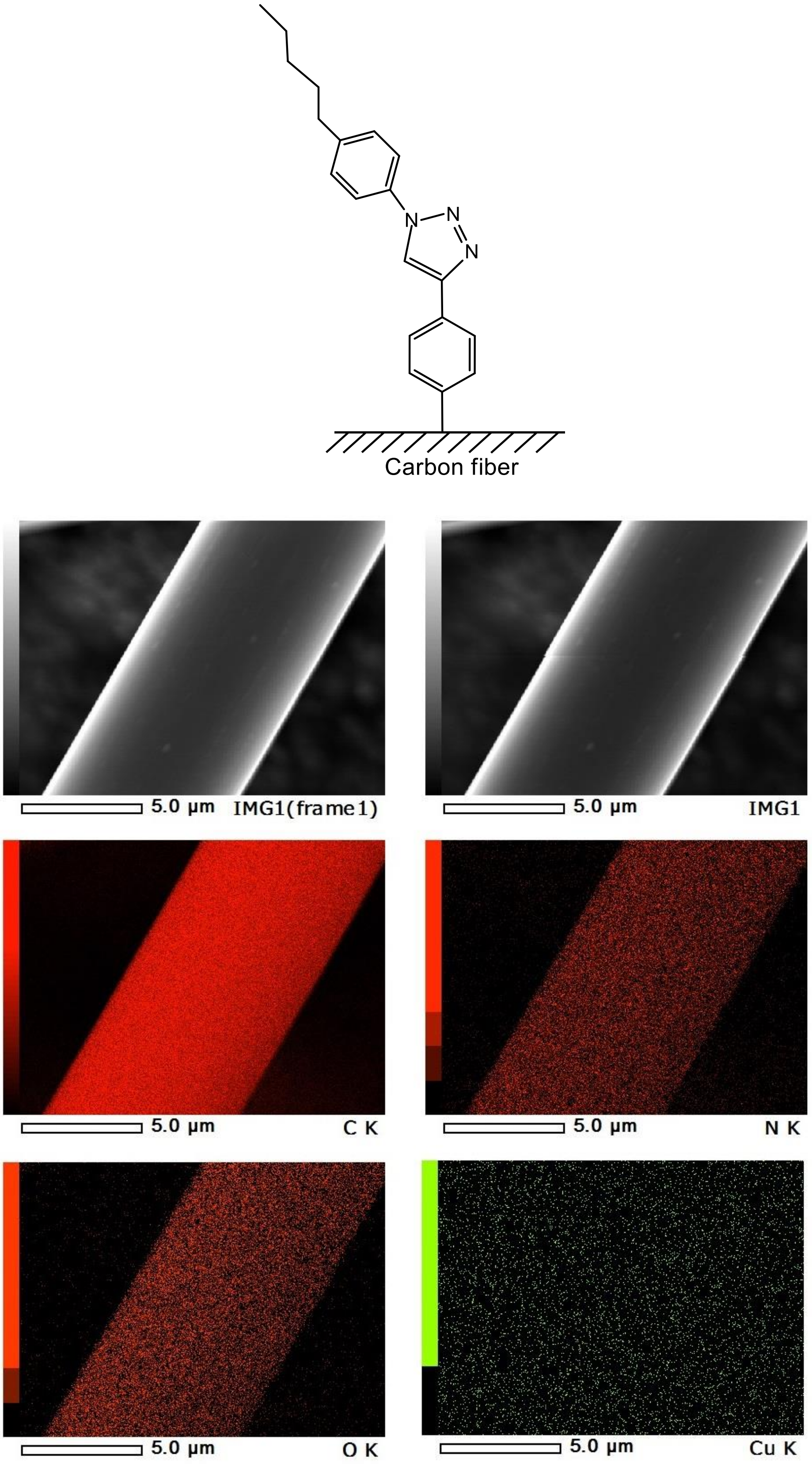
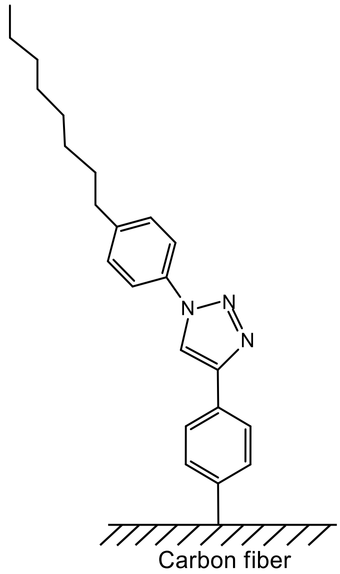


Figure S16. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.



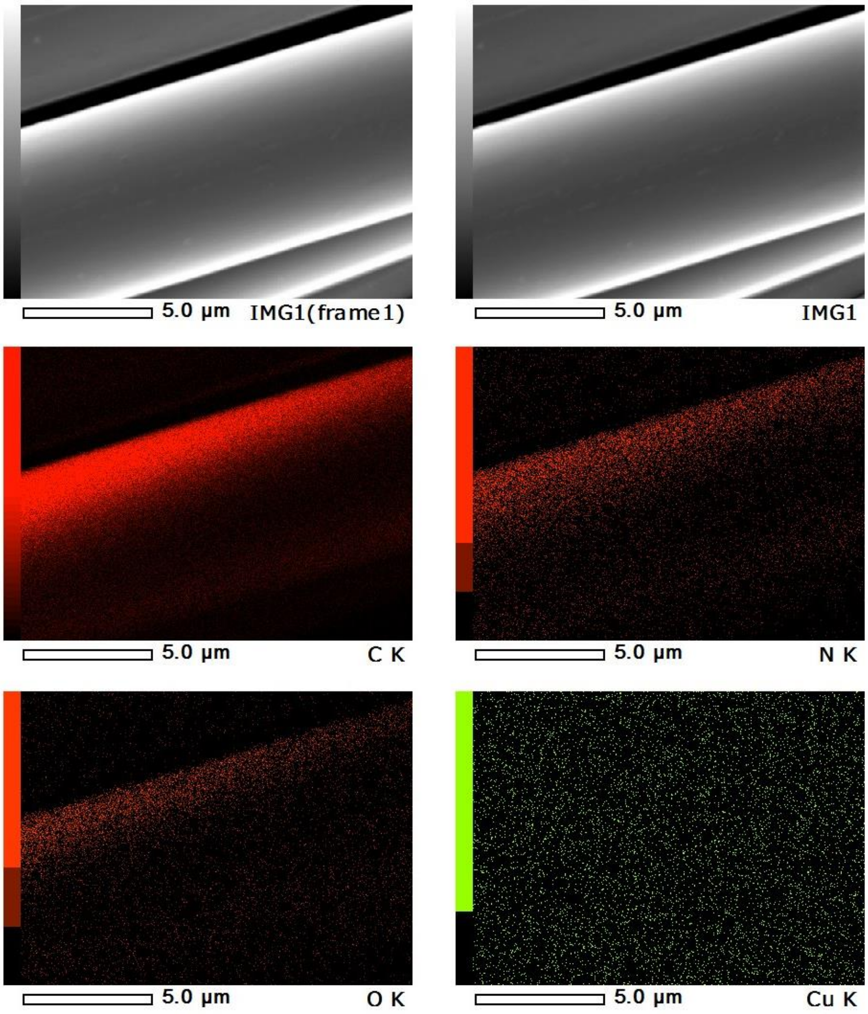


Figure S17. Chemical mapping carried out on a functionalized (structure is shown above) carbon fiber sample.

5. Cyclic voltammetry experiments

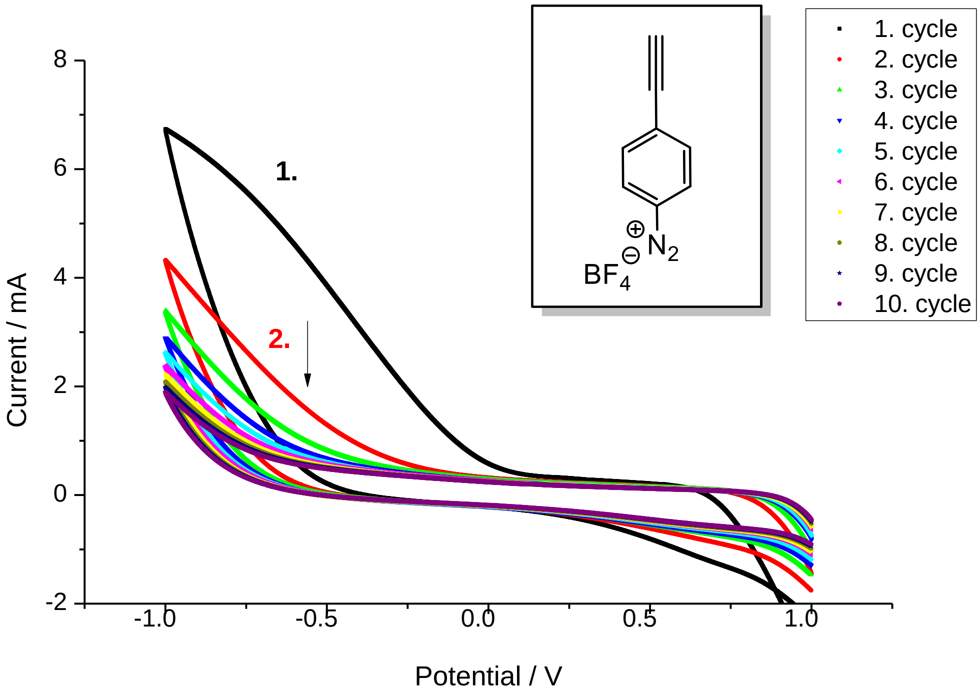


Figure S18. Cyclic voltammogram recorded for 4-(ethynyl)benzenediazonium tetrafluoroborate at 10 mM concentration using a scan rate of 0.2 V s^{-1}.

6. References

[1] T. Heinze, T. F. Liebert, K. S. Pfeiffer, M. A. Hussain, *Cellulose* **2003**, *10*, 283.

[2] J. Bahr, J. M. Tour, *Chem. Mater.* **2001**, *13*, 3823.

[3] L. Servinis, L. C. Henderson, L. M. Andrighetto, M. G. Huson, T. R. Gengenbach, B. L. Fox, *J. Mater. Chem. A* **2015**, *3*, 3360.

[4] L. Servinis, K. M. Beggs, T. R. Gengenbach, E. H. Doeven, P. S. Francis, B. L. Fox, J. M. Pringle, C. Pozo-Gonzalo, T. R. Walsh, L. C. Henderson, *J. Mater. Chem. A* **2017**, *5*, 11204.

[5] K. Barral, A. D. Moorhouse, J. E. Moses, *Org. Lett.* **2007**, *9*, 1809.

[6] D. Kosynkin, T. M. Bockman, J. K. Kochi, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2003.

[7] S. C. Fox, K. J. Edgar, *Cellulose* **2011**, *18*, 1305.

[8] K. Furuhata, K. Koganei, H. S. Chang, N. Aoki, M. Sakamoto, *Carbohyd. Res.* **1992**, *230*, 165.