Supporting Information

(Sub-) Microscale Structuring of Cellulose Thin Films using a Polymer Brush-Assisted Microcontact Printing (PolyBrushMiC) Routine

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Table of Contents:

1. Experimental Details

1.1 Instrumentation

NMR Spectroscopy. ^{1}H (400 MHz), ^{19}F (377 MHz), and ^{13}C (101 MHz) NMR spectra were recorded on a Bruker spectrometer using DMSO-d_6, $CDCl_3$, and CD_3CN as solvents. Chemical shifts were referenced to residual solvent signals (δ = 2.50 ppm for DMSO-d_6, 7.26 ppm for $CDCl_3$, and 1.94 ppm for CD_3CN in ^{1}H NMR). Spectra were processed with MestReNova 12.0.

Size exclusion Chromatography (SEC). SEC measurements were performed with devices obtained from Agilent Technologies (PSS, 1260 Infinity II, Mainz, Germany). Measurements were performed in THF solution with a flow rate of 0.5 mL min^{-1}, calibrated with polystyrene (PS) standards at 35°C, using a PSS SDV Linear M (3µm 8x300mm) column.

Mass spectra analysis. ESI mass spectra were recorded using an ESI-Q-TOFmicro (Quadrupol-Time of Flight), Micromass Waters Inc., UK, equipped with an ESI source in positive ion modus. Mass spectra were measured in acetonitrile. The spectra were analyzed on MestreNova 12.0.

Microcontact Printing (µCP). Printing experiments were carried out using a ZumoLab microcontact printer (Zumo-MCP, KS series; 0.2 kN, 2 mV V^{-1}, SN: #68180, #68181) from ZUMOLab GmbH (Wesseling, Germany). The printer incorporates a precision module (PSK-090-NN-1, length 340 mm, stroke 150 mm) from Bosch Rexroth. Two GTM force sensors are integrated for precise force monitoring. The drive configuration (99 (01) KGT 16x5/T5/C2) employs a 5 mm pitch ball screw with preloaded backlash compensation, meeting precision class T5 with an accuracy of 23 µm per 300 mm. Motion is powered by a Rexroth MS2N04-B0BTN-CMSH1-NNNNE-NN servo motor equipped with a holding brake and single-cable connection. System control and power delivery are provided by Rexroth IndraDrive controllers with HCS01 compact inverter units (HCS01.1E-W0013-A-02-B-ET-EC-EP-NN-NN-FW). A CAD representation of the instrument has been previously reported.[1]

Fluorescence Microscopy. Microscopy analysis was performed on the instrument from Leica Microsystems (DMi8). Dry objectives of HCX PL FLUOTAR 20x/0.50 and 40x/0.80 were used. Images were analyzed on ImageJ (https://imagej.org) v1.54.

Image analysis. Images of printed substrates were first background-subtracted (rolling ball radius = 50 pixels), and the brightness was corrected. A cropped part of the images was then selected (285 × 285 pixels for **Figure 3)**. The obtained intensity profile of the images shown in **Figure 3** were plotted from the printed patterns at different durations (**Figure S29**). The intensity was normalized and plotted against the distance. Image sizes of 315 × 308 pixels were used in **Figure S29**. Printing multiple times with a single stamp was also performed as shown in **Figure S31**. Images were captured as before. Image sizes of ~ 245 × 242 pixels were depicted in **Figure S31**. Figure S28, S30, S31, S32a, S32b, S34 are of 2048 × 2048 pixels, 654 × 645 pixels, 14467 × 1449 pixels, 285 × 235 pixels, 361 × 372 pixels, and 436 × 512 pixels, respectively. These images were background-subtracted (rolling ball radius = 20 pixels) and brightness corrected. Using imageJ the diameters of the patterned spots (10x) were measured, and average length was used for **Figure S34b**. Additionally, fluorescence intensity was plotted by selecting a section on **Figure S34b** using "Plot Profile" option of imageJ.

Atomic Force microscopy (AFM). AFM measurements were performed on a scanning probe microscope (AIST-NT Technology) using BudgetSensors Top150AI-G probes. Cellulose coated wafers were analyzed in AC (tapping) mode at a scan rate of 0.2 Hz. The characterization of rough Si wafer and cellulose coated rough Si wafer surface were performed using a Bruker FastScan AFM equipped with ScanAsyst. Surface topography was recorded in tapping mode at 0.2 Hz scan rate. Image processing was conducted with Gwyddion software (v2.7), applying mean-plane levelling and polynomial background subtraction (polynomial degree 2). Only mean plane levelling was done for the rough sides.

FTIR spectroscopy. Infrared spectroscopy was carried out on a Nicolet iS5 (Thermo Scientific), fitted with an iD7 ATR unit containing a germanium crystal, a resolution of 2 cm^{-1} and 64 scans per measurement from 400 to 4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS). XPS measurements were conducted on an AXIS Supra+ spectrometer (Kratos Analytical, U.K.) using monochromatic Al Kα radiation (300 W) at a take-off angle of 90°, corresponding to an analysis depth of ~10 nm. Spectra were processed with CASA-XPS software.

Surface-enhanced Raman spectroscopy (SERS). Raman spectra were collected using a LabRAM HR-Evolution instrument (Horiba Jobin-Yvon, France). The excitation laser was 561 nm, and the laser power was kept at 1% (~1 mW at the focal point). The light was focused on the printed surface using a 100X objective (Olympus, N.A. 0.9). The irradiation time was 3 s, and each point was accumulated 4 times. An area of 25×15 μm^2 with one-point measurements at 0.7 µm spacing was mapped. The step was kept at 0.7 in both x and y directions.

1.2 Materials and Methods

Materials. The commercially available standard kit of SYLGARD 184 from Dow Corning was used for the PDMS preparation. 4-Cyano-4-[[(dodecylthio)carbonothioyl]thio]pentanoic acid (>97%), 3-aminopropyl(triethoxy)silane (APTES, > 99.8%), Trichloro(1H,1H,2H,2H)-tridecafluoro-n-octyl)silane (>97%), α-lipoic acid (99%), 4-chloro-7-nitrobenzo-2,1,3-benzoxadiazole (>98%, NBD-Cl), trifluoroacetic anhydride (≥ 99%) were purchased from TCI Europe. 4,4-Azobis(4-cyanovaleric acid) (ACVA, ≥ 98%) was purchased from Sigma Aldrich. Sarcosine (98%), triethylamine (TEA), oxalyl chloride (98%), *N*,*N*′-dimethylacetamide (DMAc, 99%), di(ethyleneglycol)methylethermethacrylate (DEGMA, 95%), succinic anhydride, were purchased from Sigma Aldrich. Histamine dihiydrochloride (≥ 98%), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%), sodium hydroxide (NaOH, 99%), lithium chloride (98.5%), thionyl chloride (≥ 98%), imidazole (> 99%), 6-aminohexanoic acid (> 99%) were purchased from Roth (Germany). The inhibitor from DEGMA was removed by passing through activated alumina from Merck (neutral, Brockmann I). The cellulose used is a pulp from Sappi with a DP_{Cuen} of 892**.** This is a dissolving pulp, which has been produced using a prehydrolysis Kraft process. *N*, *N*-dimethyl formamide (DMF) was obtained from VWR**.** Dimethyl sulfoxide (DMSO) and dichloromethane (DCM) were purchased from Th. Geyer (Chemsolute). 1,3-dihydroxynapthalene (99+%) was obtained from Acros. SiO_2 monodisperse microsphere particles (4.08 µm) were purchased from Cospheric.

Acetonitrile and methacryloyl chloride (97% stab., 15% cyclic dimer) were obtained from Acros organic and Alfa Aesar, respectively. Au nanospheres (40 nm, 0.05 mg mL^{-1}) dispersed in water were obtained from nanoComposix. Plasma treatment was carried out using PlasmaFlecto10.

2. Experimental Protocols

2.1 Monomer preparation for grafting from the stamp surface

Synthesis of histamine methacrylamide (HMAm). The synthesis was performed following an established literature procedure.[2] Histamine dihydrochloride (2.00 g, 10.9 mmol) was dissolved together with NaOH (1.30 g, 32.6 mmol) in Milli-Q water (25mL) in a 100 mL round-bottom flask equipped with a mechanical stirrer and a dropping funnel. The mixture was cooled in an ice bath, and a solution of

methacryloyl chloride (1.14 g, 10.9 mmol) in DCM (10 mL) was introduced dropwise over 1 h under vigorous stirring. Subsequently, the reaction was allowed to reach room temperature and stirred for another 4 days. After extracting DCM out, the aqueous phase was collected and freeze-dried. The obtained residue was dissolved in isopropanol (35 mL) thoroughly and filtered. The precipitate (solid) was further redissolved in isopropanol (2x) and filtered. The filtrate was concentrated. The concentrated solution (2 mL) was slowly added to a large volume of pre-cooled hexane (400 mL) and left at 0 - 4 °C overnight. The product was precipitated and collected by filtration. The precipitate was again dissolved in isopropanol to precipitate in cold hexane. The precipitation was rinsed with cold isopropanol/hexane solution and then the obtained solid was recrystallized in isopropanol and dried afterwards to yield HMAm as a white solid (50 %).

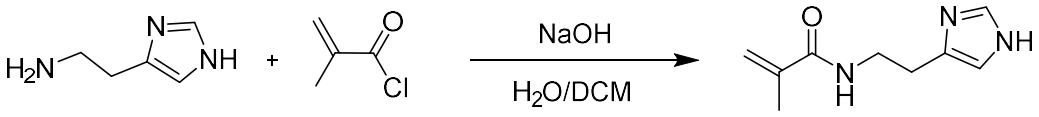

Figure S1. Synthesis of histamine methacrylamide (HMAm).

^{1}H NMR (400 MHz, D_2O) ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.65 – 7.51 (m, 1H), 6.94 – 6.79 (m, 1H), 5.59 – 5.48 (m, 1H), 5.38 – 5.15 (m, 1H), 3.45 – 3.30 (m, 1H), 3.06 (t, J = 6.9 Hz, 1H), 2.86 – 2.68 (m, 2H), 1.78 (t, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, D_2O) δ 177.49, 142.35, 136.03 (d, J = 45.4 Hz), 120.24, 40.27 – 37.00 (m), 25.77, 18.89. MS (ESI-positive): calculated for $C_9H_{13}N_3O$ [M], 179.1058; found 179.1206, calculated for $C_9H_{13}N_3ONa$ $[M + Na]^+$, 202.0956; found 202.0499, calculated for $C_{11}H_{16}N_4ONa$ $[M + CH_3CN + Na]^+$, 243.1221; found 243.0674.

2.2 Fabrication of stamp for grafting

PDMS stamp fabrication and CTA attachment from the stamp surface. SYLGARD 184 PDMS prepolymer and curing agent (10:1, w/w) were cast on a Si master with 4 μm stripe patterns positioned between two glass plates and subsequently cured to yield a patterned PDMS sheet. The glass plates were first plasma treated (100 W, 60 s, 60 air) and hydrophobized with trichloro(*1H*,*1H*,*2H*,*2H*)-tridecafluoro-n-octyl)silane for 40 min in a closed chamber. After curing, the PDMS sheets were washed by Soxhlet extraction with DCM for ca. 8 h, dried under vacuum (40 °C, 1 h), and cut into ~1 cm² stamps. The surfaces were activated by air plasma (100 W, 60 s) and subsequently functionalized with APTES in a PFA chamber containing APTES (300 μL) and NH_4OH (300 μL, 30% aq.), heated at 70 °C for 2 h. For CTA coupling, the APTES-modified stamps were treated overnight with a DMF solution of CTA (10 mg, 0.0248 mmol), DCC (10 mg, 0.048 mmol), and TEA (10 μL, 0.072 mmol). The stamps were washed successively with Milli-Q water and ethanol, followed by drying under a gentle air stream.

Grafting poly(90%di(ethyleneglycol)methylethermethacrylate-*co*-10%histamine methacrylamide) from stamp surface. The polymerization technique was followed by previous literature procedure.[3] The inhibitor was removed from DEGMA by passing it through an alumina column. DEGMA (169 mg, 0.9 mmol) and HMAm (18 mg, 0.1 mmol) were added to DMSO (1.5 mL). An initiator-to-CTA ratio [I]:[CTA] of 1 was taken for polymerization. 4-Cyano-4-[[(dodecylthio)carbonothioyl]thio]pentanoic acid (CTA, 1 mg, 0.0025 mmol) and ACVA (0.721 mg, 0.0025 mmol) were taken from their respective stock solution in DMSO and added to the monomer solution. A final 2 mL solution was prepared. The CTA-functionalized stamp was immersed in the solution and degassed with N_2 for 30 min. Polymerization reaction was carried out at 70 °C for 30 h. After the reaction the stamp was washed with DMSO and Milli-Q water and dried with compressed air and N_2 flow. The polymers formed in the solution due to excess CTA in the solution were dialyzed using a 3.5 kDa dialysis tube (Spectra/Por, Spectrum Laboratories, Inc) and freeze-dried. ^{1}H NMR and SEC data were

measured afterwards. A similar CTA attachment and polymer grafting procedure was shown in our previous work.[3]

Preparation of silica particles-filled grafted stamp. Initially, a PDMS stamp underwent plasma treatment and subsequent APTES functionalization. The treated stamp was then soaked overnight in a solution of succinic anhydride (SA, 5 mg, 50 µmol) with TEA (5%, 50 µL) in 1 mL of THF, followed by washing with THF and ethanol. Separately, 4 µm SiO_2 particles were plasma-treated (100 W, 300 s, air) and functionalized with APTES using the same protocol.

The carboxylic acid groups on the SA-modified stamp were then employed to attach the APTES-functionalized particles. To achieve this, the particles were dispersed in a DCC solution (2 mg, 0.0097 mmol in 500 µL DMF). A 50 µL portion of this dispersion was spread on a hydrophobized glass slide (prepared via CVD with trichloro(1H,1H,2H,2H)-tridecafluoro-n-octyl)silane) using a syringe pump. The pump was equipped with a glass rod for shearing at 0.4 mL min^{-1} as the solution was applied on the glass slide. As the particles were spread on the glass surface, the stamp was pressed onto the glass slide, aligning the particles within its grooves. The stamp was then pressed with a flat PDMS stamp a couple of times on top, to remove any excess particles on the stamp surface.

Next, 200 µL of DCC solution in DMF was added to the particle-filled stamp and left for 6 hours. Afterward, the stamp was gently rinsed with DMF and immersed overnight in the CTA solution for CTA functionalization, following the previously described procedure. Finally, this particle-decorated stamp was used to graft poly(90% di(ethyleneglycol)methylether methacrylate-co-10% histamine methacrylamide) following the same polymerization method as before.

2.3 Substrate preparation (Cellulose thin film):

Cellulose solution preparation: Cellulose dissolution was performed according to an existing literature procedure.[4] Accordingly, cellulose (0.5 g) was dispersed in DMAc (18 g) and heated to 120 °C. Upon reaching this temperature, the mixture was subjected to vacuum (~100 mbar) until the solvent began to boil, and this process was repeated twice. After 1 h, the boiling–vacuum cycle was performed once more. Following a total heating time of 2 h, the solution was cooled to 80 °C and LiCl (1.5 g, pre-dried at 105 °C for 2 h) was added. The mixture was then cooled to room temperature and stirred overnight. Subsequently, the solution was diluted with DMAc (80 mL) and aliquoted into 2 to 3 mL fractions. The cellulose solutions can be stored at room temperature for several weeks.

Preparation of cellulose thin film on Si wafer. Si wafers were cut into approximately 1 cm^2 pieces, and immersed in ethanol to sonicate for 10 min. The wafers were then cleaned using the RCA procedure by immersion in a 6:1:1 mixture of Milli-Q water, H_2O_2, and NH_3 (30%) at 80 °C for 20 min, followed by thorough rinsing with Milli-Q water and ethanol. Plasma activation was performed at 100 W for 60 s under air. A solution of branched polyethyleneimine (PEI, 1 g L^{-1}, 60 µL) was spin-coated, followed by spin coating of the cellulose solution (60 µL, heated to 110 °C) at 4000 rpm for 60 s. Note that excessive thermal treatment led to the degradation of cellulose. Accordingly, the heating period should be kept short.

The wafers were then rinsed with Milli-Q water and ethanol. The wafers were dried at 90 °C for 4 h under vacuum and stored under N_2. The rough side of a Si wafer was also spin-coated with PEI and cellulose and treated using the same procedure.

The substrate was characterized *via* AFM and ATR-FTIR. For ATR-FTIR measurements, the samples were pressed onto the ATR crystal. Background spectra and a clean Si wafer for control were measured, as well as the cellulose pulp and the cellulose coated Si wafer.

2.4 Ink preparation:

Synthesis of *N*-4-(7-nitrobenzo-2-oxa-1,3-diazolyl)-sarcosine (NBD-sarcosine acid): The synthesis was performed according to the literature.[5] NBD-Cl (500 mg, 2.51 mmol, 1 eq.), sarcosine (224 mg, 2.51 mmol, 1 eq), and NaOH (301 mg, 7.53 mmol, 3 eq) were added together and stirred in MeOH in the dark overnight. To the solution, 40 mL water was added. The solution was then acidified with 1 M HCl to extract with EtOAc (4x). The organic phase is dried over Na_2SO_4 and filtered. The product was obtained as a solid after solvent evaporation without any further purification (79% yield).

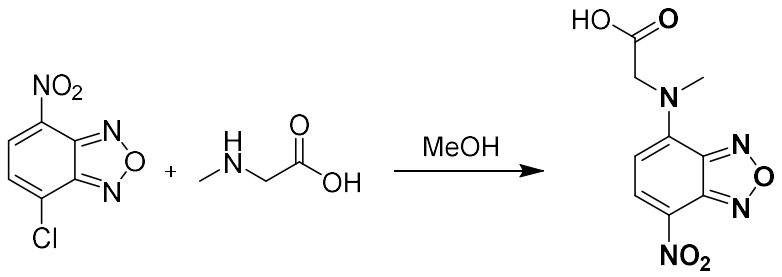

Figure S2. Synthesis of NBD-sarcosine acid.

^{1}H NMR (400 MHz, CD_3CN): δ 8.47 (d, J = 9.0 Hz, 1H), 6.32 (d, J = 9.0 Hz, 1H), 4.85 (s, 2H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN): δ 169.97, 146.03, 145.42 (d), 136.81, 132.84, 130.32, 103.39, 57.40, 42.74. MS (ESI-positive): calculated for $C_9H_8N_4O_5H$ $[M + H]^+$, 253.0572; found 253.8863, 252.9907, calculated for $C_9H_8N_4O_5Na$ $[M + Na]^+$, 275.0392; found 276.8428, calculated for $C_{11}H_{11}N_5O_5H$ $[M + CH_3CN + H]^+$, 294.0838; found 294.8508.

Synthesis of *N*-4-(7-nitrobenzo-2-oxa-1,3-diazolyl)-sarcosine acid chloride (NBD-sarcosine acid chloride) (*i1*): NBD-sarcosine acid (30 mg, 0.12 mmol, 1 eq.) were dissolved in mixture of dry DCM and THF. Oxalyl chloride (17 mg, 0.132 mmol, 1.1 eq) were added dropwise at 0°C. A drop of catalytic DMF was also added. The reaction was stirred in for 3 h in the dark. The solvent was evaporated extensively to obtain the fluorescent dye used as ink for μCP. The ink was used without further purification.

^{1}H NMR (400 MHz, CD_3CN): δ 8.46 (d, *J* = 9.0 Hz, 1H), 6.32 (d, *J* = 9.0 Hz, 1H), 4.85 (s, 2H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN): 170.06, 147.02, 145.87 (d, *J* = 20.3 Hz), 136.79, 132.82, 123.80, 103.34, 57.45, 42.74.

Synthesis of *N*-4-(7-nitrobenzo-2-oxa-1,3-diazolyl)-sarcosine acid anhydride (NBD-sarcosine acid anhydride) (*i1*$_a$). NBD-sarcosine acid (5 mg, 0.02 mmol, 1 eq.) were dissolved in mixture of dry toluene and a small amount of acetonitrile (1.3 mL of toluene and 0.2 mL of ACN). DCC (2 mg, 0.01 mmol, 0.5 eq) was added to the solution and stirred overnight at room temperature. This mixture was used as an ink solution without any further purification.

Synthesis of 6-(2,2,2-trifluoroacetamido)hexanoic acid. The synthesis was done according to literature.[6] 6-Aminohexanoic acid (1 g, 7.62 mmol) was reacted with trifluoroacetic anhydride (2.1 mL, 15.24 mmol) by heating the mixture at 80 °C for 3 h. After completion, the reaction was diluted with EtOAc (20 mL) and the organic phase was washed with water (200 mL). The organic layer was separated, dried over Na_2SO_4, filtered. The solvent was evaporated under reduced pressure to afford the product as a white solid (90%). The solid was dried extensively to obtain the pure product.

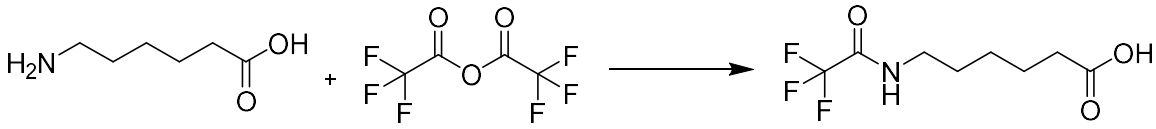

Figure S3. Synthesis of 6-(2,2,2-trifluoroacetamido)hexanoic acid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (s, 1H), 3.38 (q, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.64 (dp, *J* = 21.9, 7.3 Hz, 4H), 1.40 (qd, *J* = 9.9, 9.1, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.15, 157.32 (d, *J* = 36.8 Hz), 117.29, 39.63, 33.57, 28. 52, 25.92, 23.92. ^{19}F NMR (377 MHz, $CDCl_3$): δ -75.96. MS (ESI-positive): calculated for $C_8H_{12}F_3NO_3H$ $[M + H]^+$, 228.0847; found 228.0070, calculated for $C_8H_{12}F_3NO_3Na$ $[M + Na]^+$, 250.0666; found 249.9941, calculated for $C_{10}H_{20}F_3NO_5H$ $[M + 2CH_3OH + H]^+$, 292.1371; found 294.8521, calculated for $C_{13}H_{22}F_3N_3O_4H$ $[M + 2CH_3CN + CH_3OH + H]^+$, 342.1640; found 341.0650 and 342.0703.

Synthesis of 6-(2,2,2-trifluoroacetamido)hexanoyl chloride (*i2*). 6-(2,2,2-trifluoroacetamido)hexanoic acid (200 mg, 0.88 mmol) was dissolved in 2 mL dry DCM. Thionyl chloride (0.5 mL, 6.9 mmol) was added and stirred overnight. The solution was distilled to remove solvent and excess thionyl chloride. 10 mL dry DCM was added to the residue. The solvent was removed from the product and dried under high vacuum. The obtained acid chloride was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (s, 1H), 3.39 (q, *J* = 6.8 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.65 (dp, *J* = 22.1, 7.3 Hz, 4H), 1.41 (qd, *J* = 9.9, 9.1, 5.9 Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$): -75.95.

Synthesis of lipoyl chloride (i3). This synthesis was according to the literature.[7] α-Lipoic acid (1 g, 4.9 mmol) was dissolved in MeOH (4 mL), and 0.1 N NaOH solution (40 mL) was added. The mixture was stirred at 50 °C for 1 h, and any precipitate formed was removed by filtration. The resulting solution was freeze-dried to obtain sodium lipoate. Sodium lipoate (500 mg, 2.19 mmol) was dissolved and added in four portions at 10 min intervals to a stirred solution of oxalyl chloride (2.30 g, 18 mmol) in toluene (8 mL). The reaction was stirred for 4 h, and the solvent was evaporated to yield a yellowish solid. To remove residual oxalyl chloride, the solid was dissolved and evaporated once more, affording lipoyl chloride (**i3**) for subsequent use.

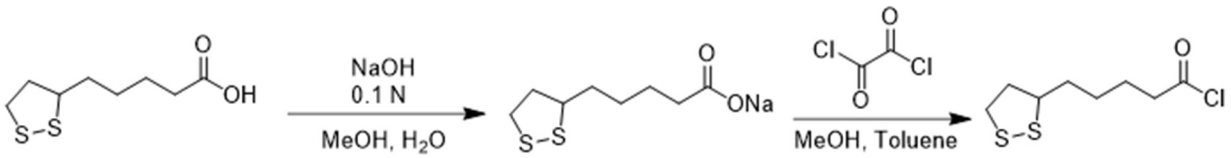

Figure S4. Synthesis of lipoyl chloride (**i3**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58 (dq, J = 8.2, 6.4 Hz, 1H), 3.26 – 3.05 (m, 2H), 2.48 (tt, J = 12.5, 6.0 Hz, 1H), 2.34 (t, J = 7.4 Hz, 2H), 1.92 (dq, J = 13.8, 6.9 Hz, 1H), 1.79 – 1.61 (m, 4H), 1.56 – 1.44 (m, 2H).

2.5 Inking of the stamp:

For inking, 2 mg of the respective ink molecules (i1, i2, and i3) were dissolved in dry DCM, and triethylamine (TEA, 4 µL) was added. The PDMS stamps were immersed in this solution and kept in the dark overnight. Post-inking, the stamps were thoroughly washed with dry DCM, using a Soxhlet extractor under N_2 flow (distilling under $CaCl_2$), except for i2, where washing was performed in a vial by replacing the solvent 4 times at 1 h intervals. Finally, the stamps were dried under vacuum for 1 h. Inking was also

done with NBD-sarcosine anhydride formed in the reaction mixture with DCC overnight at room temperature and the stamp was washed thoroughly using Soxhlet for 5 h and dried under vacuum for 1 h.

Negative control experiments with fluorescent i1, fluorinated i2 dyes were done with bare stamps. In the first case, two bare stamps were inked with i1 (2 mg mL^{-1}) in presence and absence of free imidazole (3 eq) in solution. Washing and drying of the stamp in the first case (in presence of imidazole in the solution) was done similarly as the positive control, however in the second case (in absence of imidazole) the washing was done in a vial by immersing the stamp in dry DCM a few times followed by drying in the oven before printing. In the second case, a bare stamp was inked with i2 and then washed in dry DCM in a vial by replacing solvents (4x) as mentioned above. The sample was then dried under vacuum.

2.6 Imidazole-mediated esterification:

Synthesis of *N*-acetyl imidazole. The preparation of the compound was according to literature.[8] Imidazole (1g, 14.68 mmol) was dissolved in THF (30 mL). Acetyl chloride (7.34 mmol, 576 mg) was added dropwise at 0 °C. The reaction was stirred overnight, and the precipitation was filtered off. The solvent was evaporated to obtain the product (90% yield).

^{1}H NMR (400 MHz, DMSO, d_6): δ 8.39 (t, J = 1.1 Hz, 1H), 7.68 (t, J = 1.5 Hz, 1H), 7.06 (dd, J = 1.7, 0.8 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, DMSO, d_6) δ 167.89 (d, *J* = 2.4 Hz), 137.45, 130.32, 22.83.

***N*-acetyl imidazole reaction with phenyl-β-*D*-glucopyranoside.** *N*-acetyl imidazole (20 eq, 34.3 mg, 0.312 mmol) was added to phenyl-β-*D*-glucopyranoside (1 eq, 4 mg, 0.0156 mmol) in 1.5 mL dry DMSO. The reaction was run for 24 h at room temperature. Subsequently, methanol was added to the reaction solution to quench excess *N*-acetyl imidazole. The solvent was removed completely by freeze drying. Afterwards, the resulting solid was re-dissolved in DMSO-d_6. The solution is measured *via* NMR without any further purification (Figure S5 and S6).

2.7 Printing on cellulose films:

Fabrication of the custom-made printing chamber. A custom-made printing chamber was prepared using Fused Deposition Modelling (FDM) 3D printing. For this purpose, a 3D model of the printing chamber and the piston was designed using Blender (**Figure S28**) and subsequently processed with a slicing software (Ultimaker Cura). The geometry was sliced with an infill density of 100% employing a rectilinear fill pattern to ensure a fully solid, mechanically robust structure. The custom-made printing chamber was fabricated using a fused deposition modeling (FDM) 3D printer (Anycubic Kobra 2 Pro,Anycubic). A non-coloured PC-PBT polymer blend filament (Polymaker™) was chosen as it provided excellent chemical inertia for our conditions. The chamber was printed at an extrusion temperature of 260 °C, without extrusion cooling fans, and a build-plate temperature of 110 °C using a constant printing speed of 80 mm s^{-1}. After completion, the printed chamber and piston were detached from the building plate and left to cool. Additionally, in order to ensure smooth surface characteristics of the piston, the contact side of the piston was further modified by gluing a silicon wafer onto the surface.

Printing of fluorescent dye (i1) on cellulose thin film substrate. A Si wafer coated with cellulose thin film was immersed in dry DMSO for 15 min prior to printing. This wafer was transferred to a custom-made square shaped chamber and immersed under dry DMSO. The stamp was placed on top in presence of the solvent and pressed with a fitting lid to restrict any movement. A printing force of 4 N was applied for 40 min. The substrate was rinsed properly with water and EtOH and dried with N_2 flow to visualize the patterns under fluorescence microscope. The cellulose-coated rough Si wafer was also patterned with similar printing parameters.

In the positive control, a patterned grafted stamp was inked with **i1**, while in the negative control experiments, first, a patterned bare stamp was inked in presence of imidazole (3 eq). Second, a bare stamp was inked in absence of any imidazole. Subsequent printing under the same conditions were performed.

An analogous positive printing process was also carried out, substituting DMSO with dry acetonitrile (ACN). Both the particle-decorated stamps and replicated DVD patterns were inked with NBD-sarcosine anhydride and printed using the same procedure, maintaining identical parameters.

Printing of fluorinated dye (i2) on cellulose thin film substrate for XPS. A similar printing method was followed as mentioned above. A flat inked stamp (grafted as described before, but without any pattern) was pressed from the top with a printing force of 4 N for 40 min. The substrate was washed with DCM to remove any residual ink and dried under N_2 flow. The wafer was then rinsed again with water and EtOH and dried with N_2 flow to probe *via* XPS. Alongside this, negative control with a bare stamp was performed. The stamp was inked overnight followed by washing according to the same protocol. Several spots (between 4-8) were randomly selected for the measurement. Error bars for the atomic concentrations (%) are provided as standard deviations.

Printing lipoyl chloride (i3) on cellulose thin film substrate for SERS. The stamp inked with **i3** was used in this case. Similar washing and drying steps were maintained. Printing was also done in a similar fashion at 4 N force for 2 h. The substrate was rinsed with water and EtOH, followed by drying under N_2 flow. The substrate was immersed in a 0.05 mg mL^{-1} aqueous dispersion of Au nanoparticles (AuNPs, 40 nm diameter) for 10 min. The cellulose substrate was then washed thoroughly with water and dried under N_2 flow. The sample was then measured via SERS. Control experiments were performed using three substrates: a bare cellulose wafer, a cellulose wafer with deposited Au nanoparticles (AuNPs), and a cellulose wafer functionalized with lipoic acid. The bare cellulose wafer was immersed in an aqueous dispersion of AuNPs (40 nm diameter, 0.05 mg mL^{-1}) for 10 minutes, following the previously described protocol. For the lipoic acid functionalized wafer, a solution of i3 in acetonitrile (2 mg mL^{-1}) was prepared, and the wafer was soaked overnight, then rinsed with dry acetonitrile. After drying under a nitrogen stream, AuNP deposition was performed on this substrate under the same conditions. All substrates were subsequently analyzed by SERS for comparison.

µCP on cellulose coated surface for different durations. Above mentioned printing protocol (used for **i1**) was employed to print on Si wafer surfaces coated with cellulose films. The substrate was printed with the inked stamp at 4 N force for 10, 20, 40, 60, and 120 min in the presence of dry DMSO in the printing chamber.

Multiple µCP on cellulose coated surface with a single stamp. A single inked stamp was used for printing 4 times. After each printing the stamp was re-inked and washed to perform the next printing. The substrate was printed with the inked stamp at 4 N force 40 min in the presence of dry DMSO in the printing chamber.

3. Figures and Tables

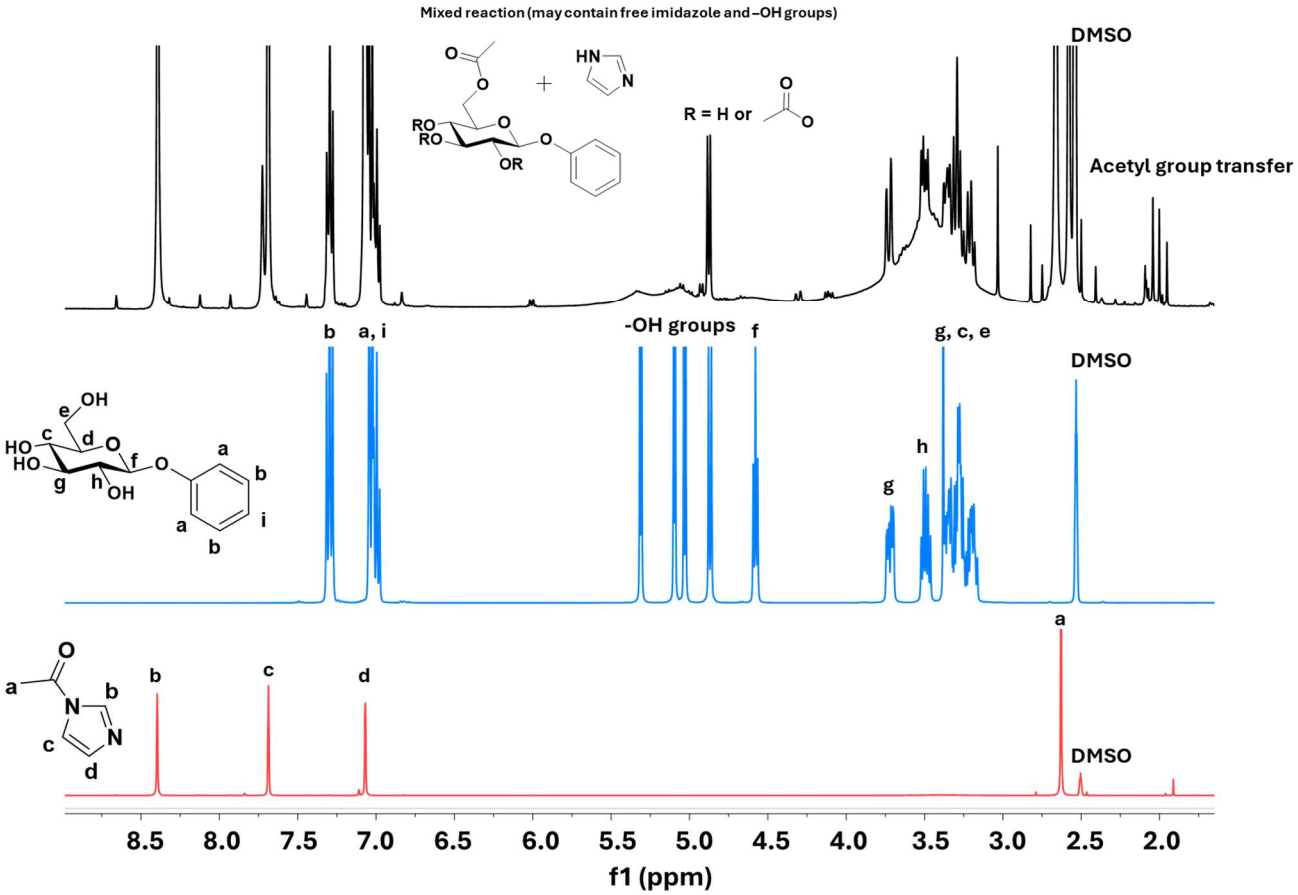

Figure S5. ^{1}H NMR (400 MHz, in DMSO-d_6, 2.50 ppm) of imidazole mediated esterification reaction. *N*-acetyl imidazole, phenyl-β-*D*-glucopyranoside, and the mixed-compounds are shown in stack. The acetyl peak transfers from *N*-acetyl imidazole to sugar, as different signal around 2.0 ppm represent the acetylated hydroxy groups, however a complete acetylation of -OH is not observed.

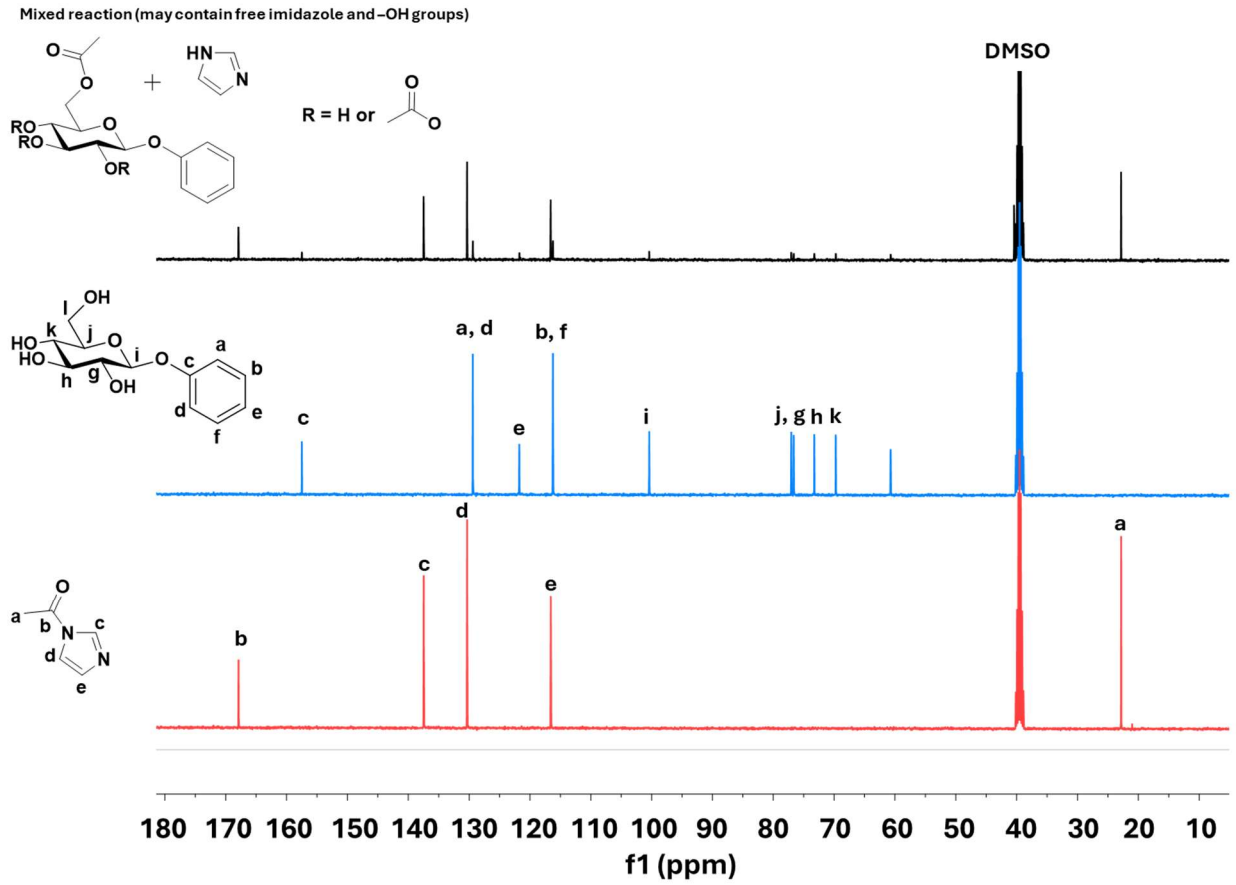

Figure S6. ^{13}C NMR (100 MHz, in DMSO-d_6) of imidazole mediated esterification reaction in solution. *N*-acetyl imidazole, phenyl-β-*D*-glucopyranoside, and the mixed-compounds are shown in stack.

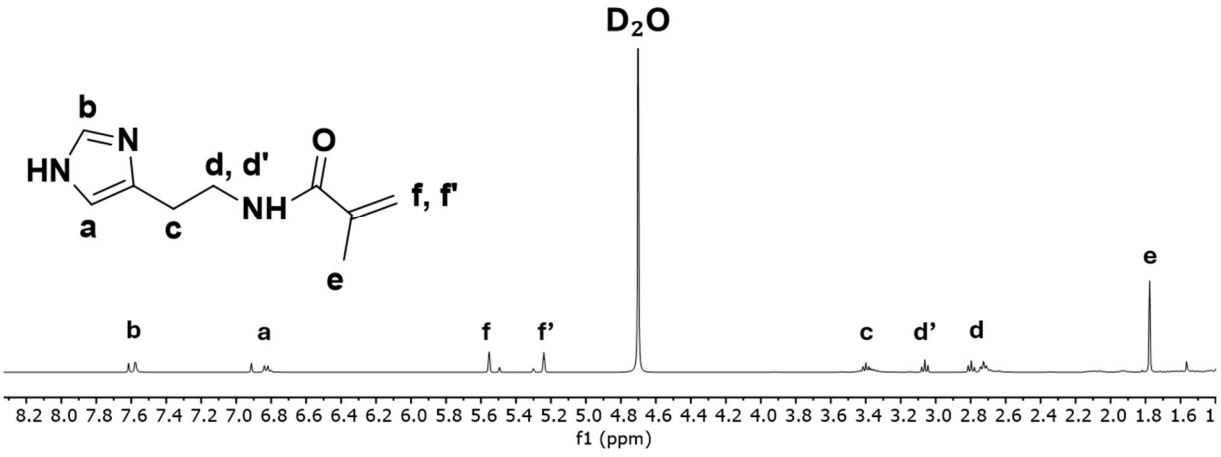

Figure S7. ^{1}H NMR of histamine methacrylamide (HMAm), performed in D_2O (4.7 ppm).

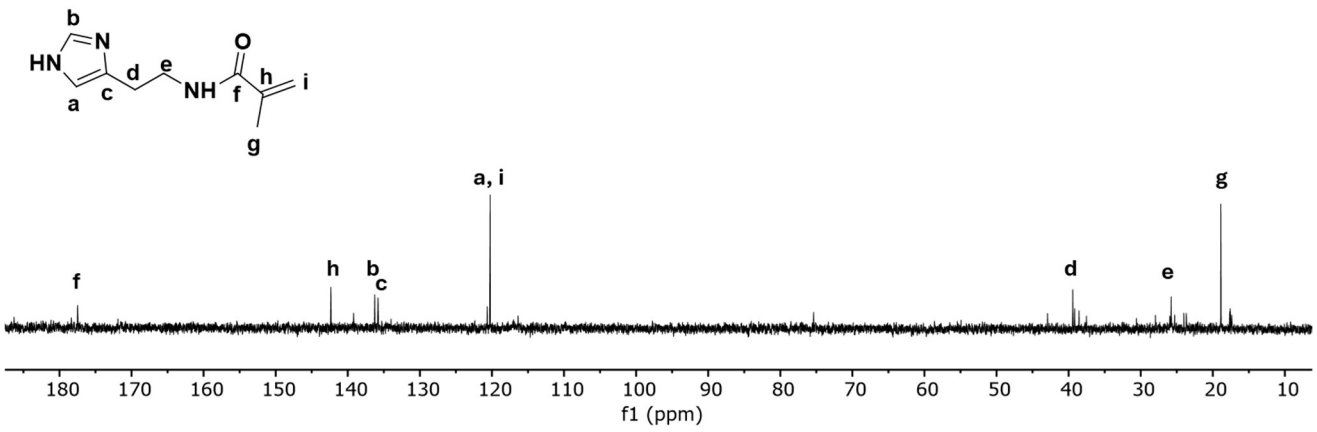

Figure S8. ^{13}C NMR of histamine methacrylamide (HMAm, measured in D_2O).

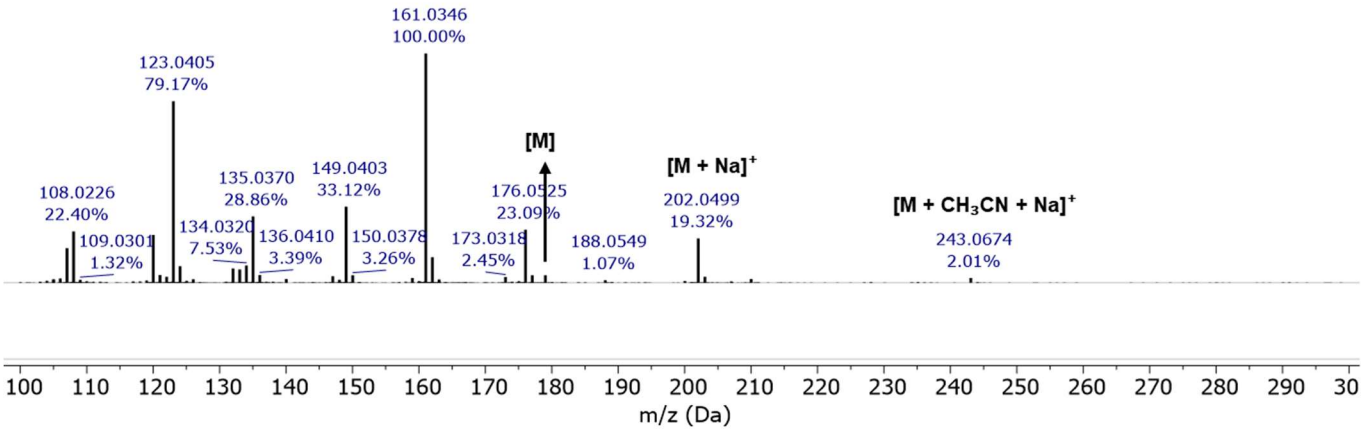

Figure S9. Mass spectra of HMAm analyzed in CH_3CN.

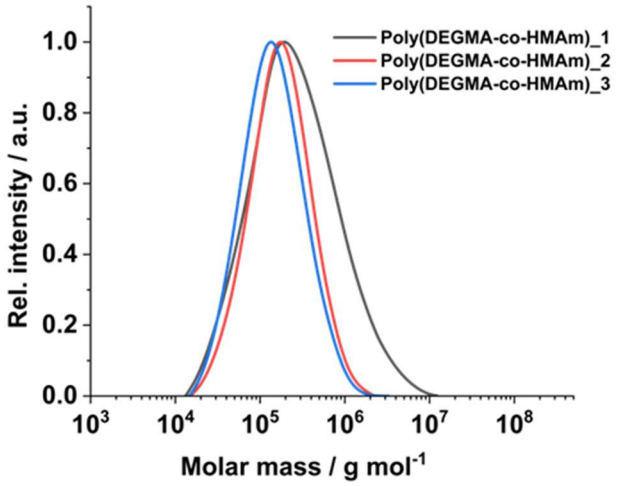

Figure S10. Representative SEC chromatograms of poly(90%DEGMA-*co*-10%HMAm) polymers formed in the grafting solution (THF, PS standard).

Table S1. Number average molecular weight (M_n) and dispersity (Đ) obtained from SEC (THF, PS standard) for the poly(90%DEGMA-*co*-10%HMAm) formed in the grafting solution. The polymers correspond to three separate grafting solutions, each producing grafted stamps used in this study.

Sample	Targeted DP	M_n (kg mol^{-1})	Đ
Poly(DEGMA-co-HMAm)_1	500	139	3.66
Poly(DEGMA-co-HMAm)_2	500	123	1.95
Poly(DEGMA-co-HMAm_3	500	101	1.94

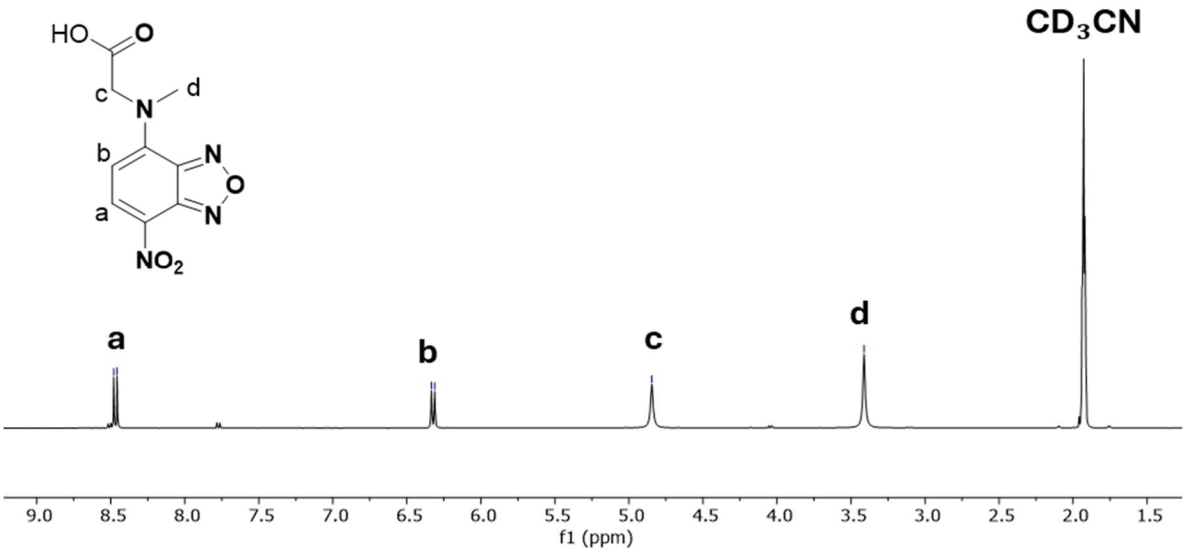

Figure S11. ^{1}H NMR (in CD_3CN) of NBD-sarcosine acid.

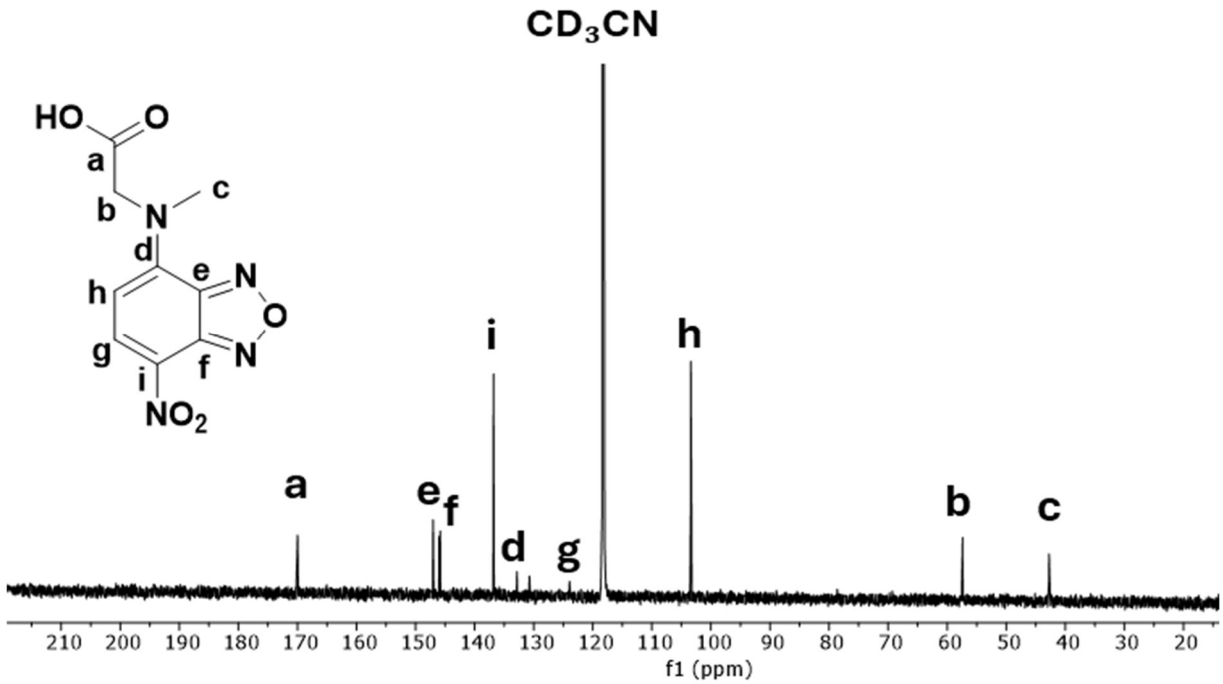

Figure S12. ^{13}C NMR (in CD_3CN) of NBD-sarcosine acid.

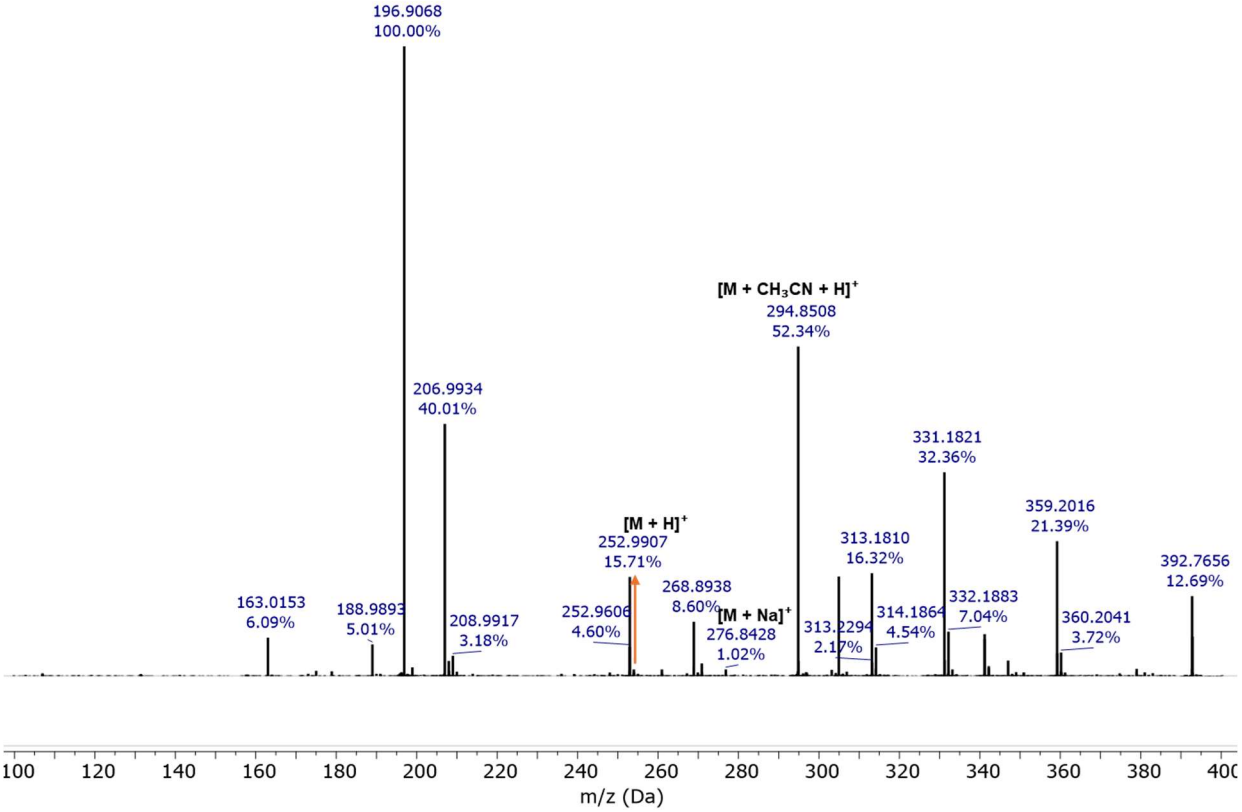

Figure S13. Mass spectra of NBD-sarcosine acid analyzed in CH_3CN.

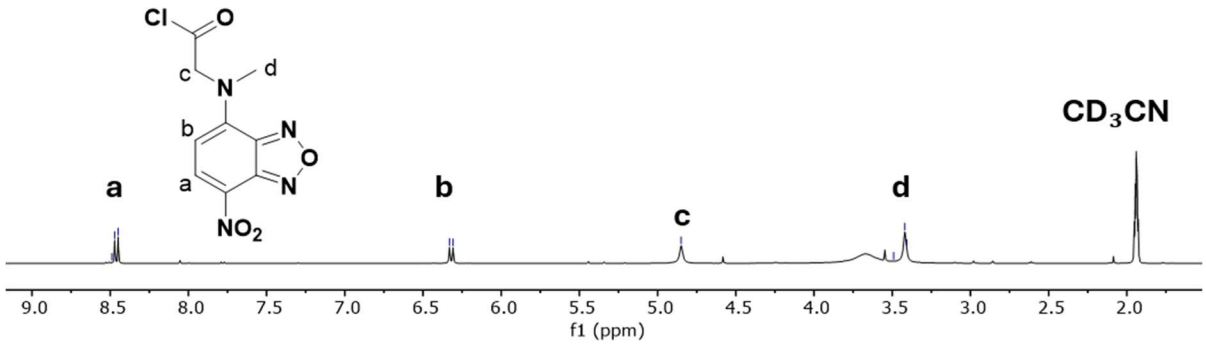

Figure S14. ^1H NMR (in CD_3CN) of NBD-sarcosine acid chloride (**i1**).

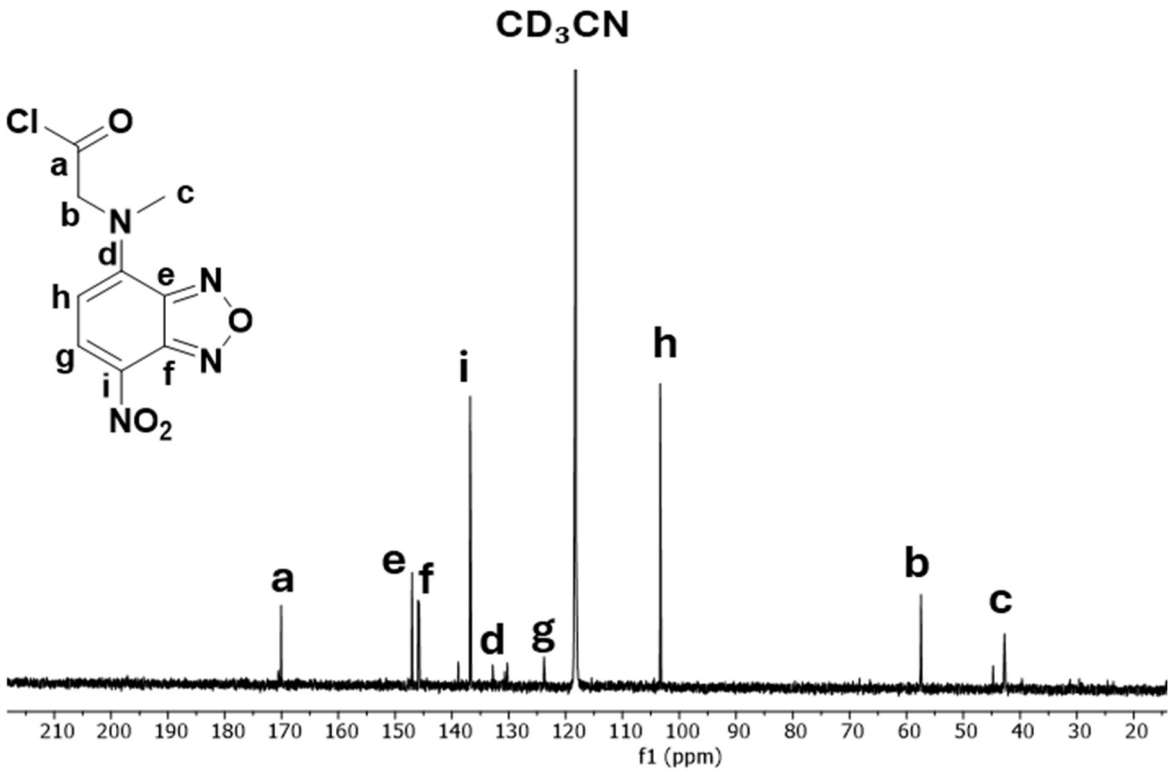

Figure S15. ^{13}C NMR (in CD_3CN) of NBD-sarcosine acid chloride (**i1**).

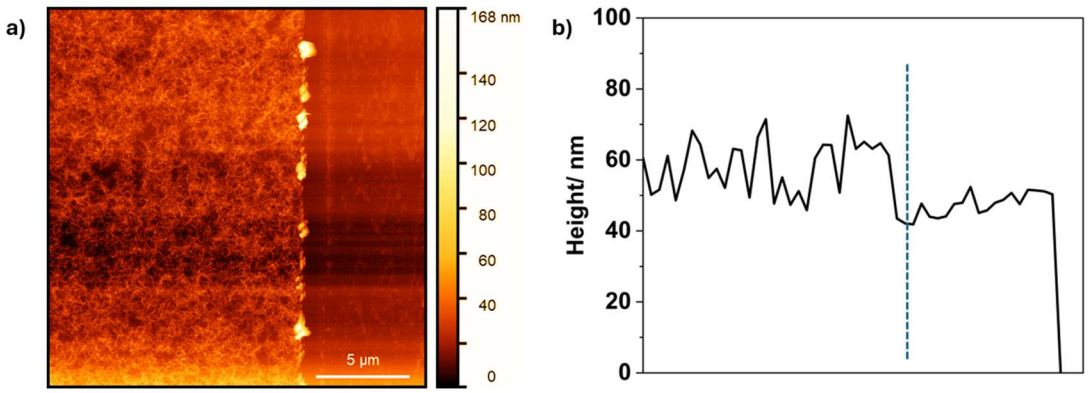

Figure S16. a) AFM height image of the scratched cellulose thin film on Si wafer, and b) the height profile of the thin film extracted by Gwiddyon.

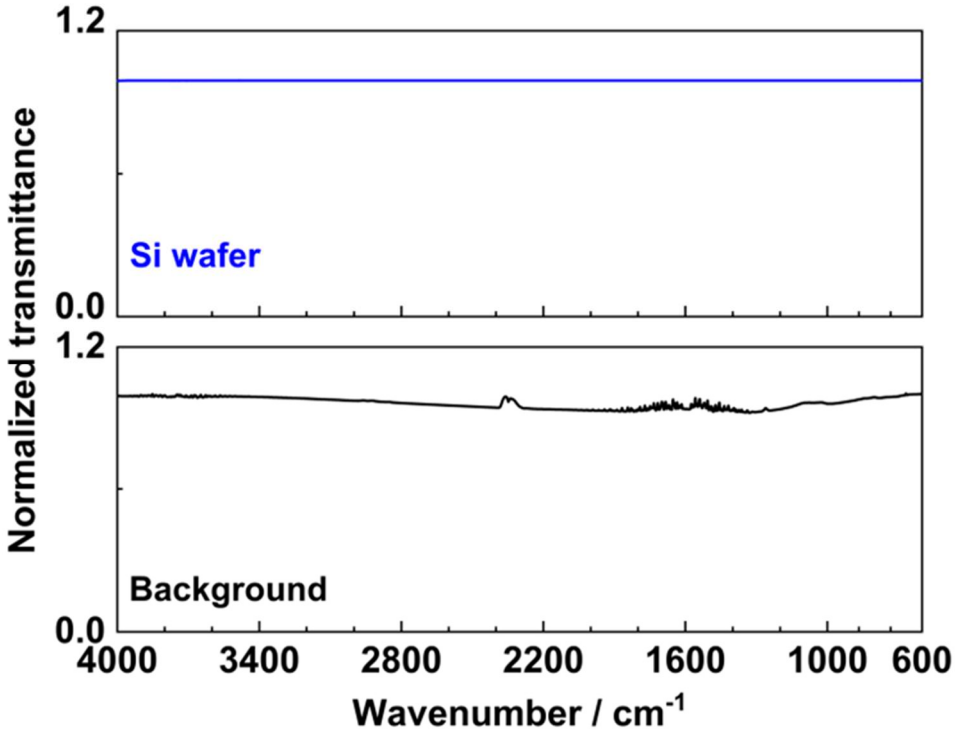

Figure S17. FTIR spectra of clean Si wafer and the background.

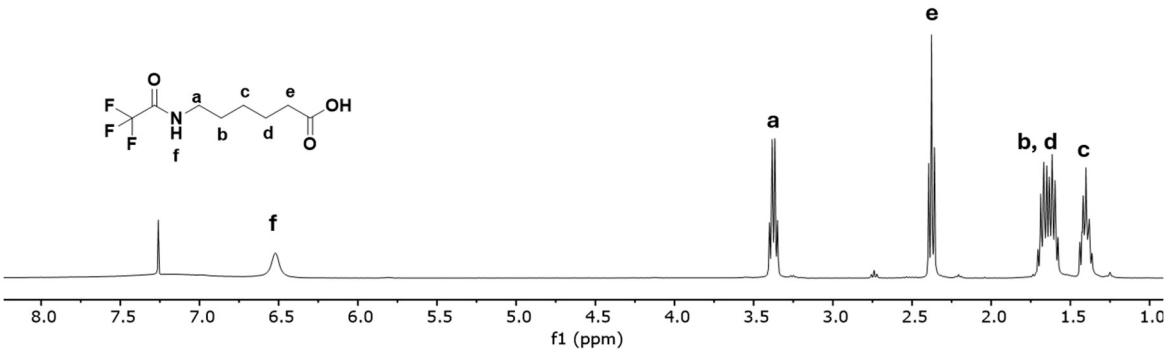

Figure S18. ^{1}H NMR (in $CDCl_3$, 7.26 ppm) of 6-(2,2,2-trifluoroacetamido)hexanoic acid.

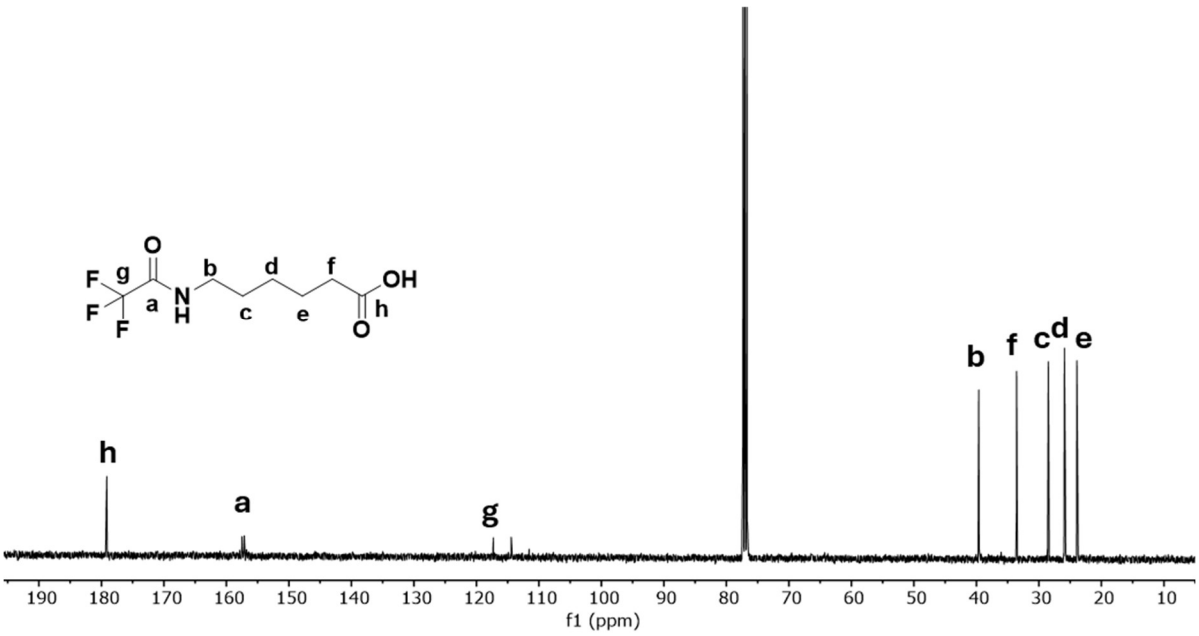

Figure S19. ^{13}C NMR (in $CDCl_3$) of 6-(2,2,2-trifluoroacetamido)hexanoic acid.

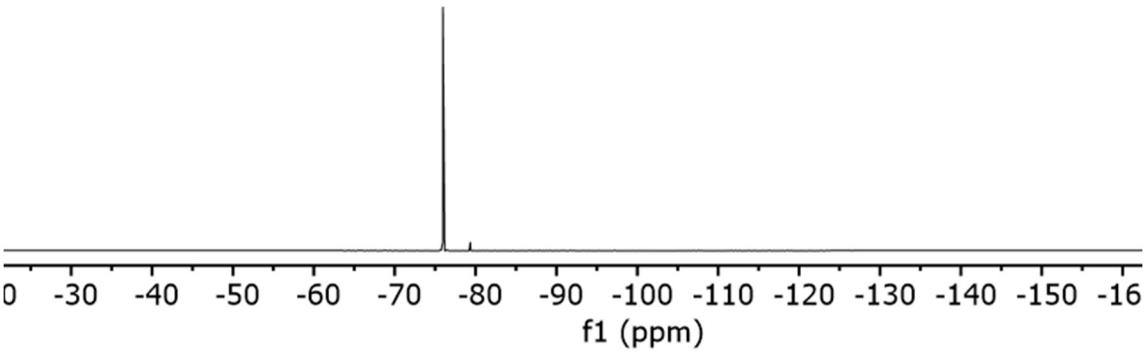

Figure S20. ^{19}F NMR (in $CDCl_3$) of 6-(2,2,2-trifluoroacetamido)hexanoic acid.

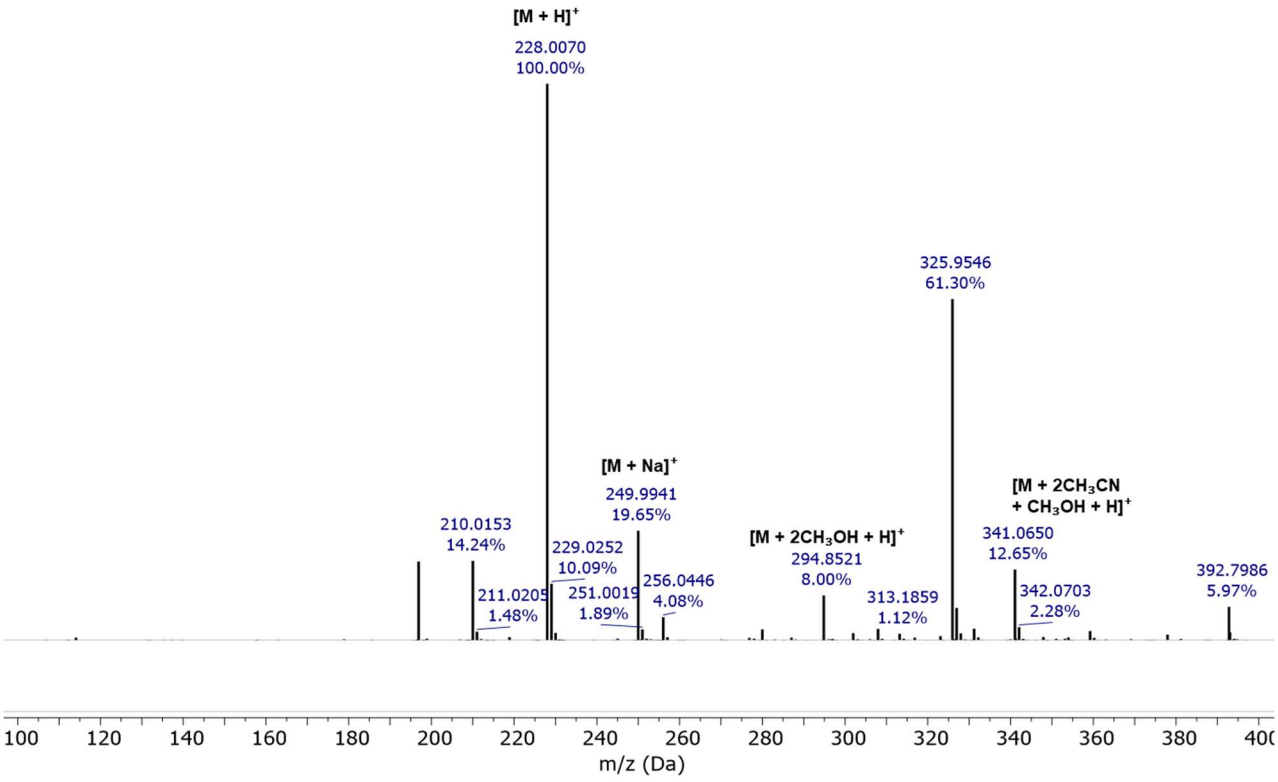

Figure S21. Mass spectra of 6-(2,2,2-trifluoroacetamido)hexanoic acid analyzed in CH_3CN.

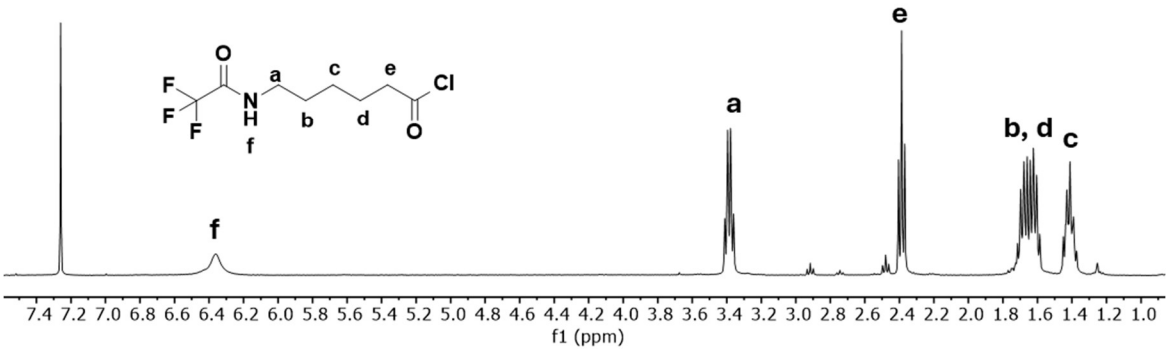

Figure S22. ^{1}H NMR (in $CDCl_3$, 7.26 ppm) of **i2** (6-(2,2,2-trifluoroacetamido)hexanoyl chloride).

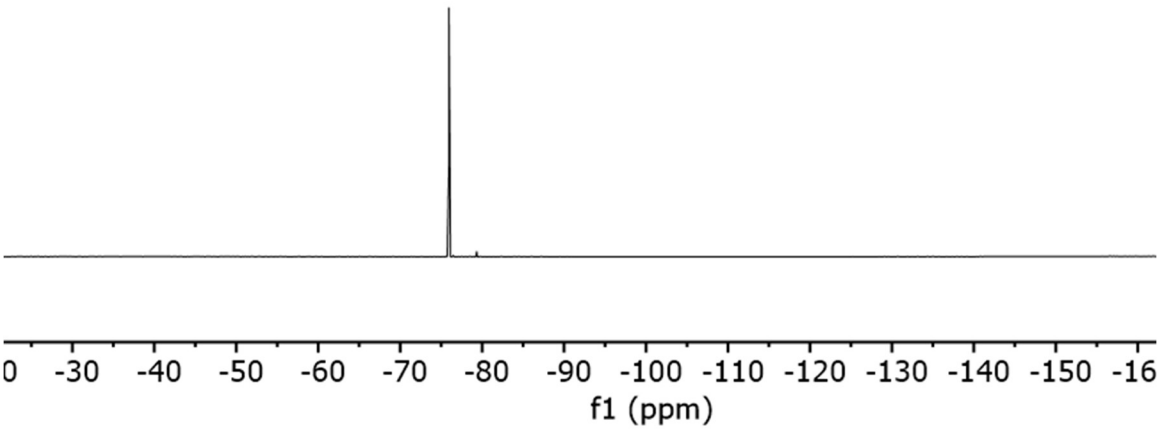

Figure S23. ^{19}F NMR ($CDCl_3$) of **i2** acyl chloride.

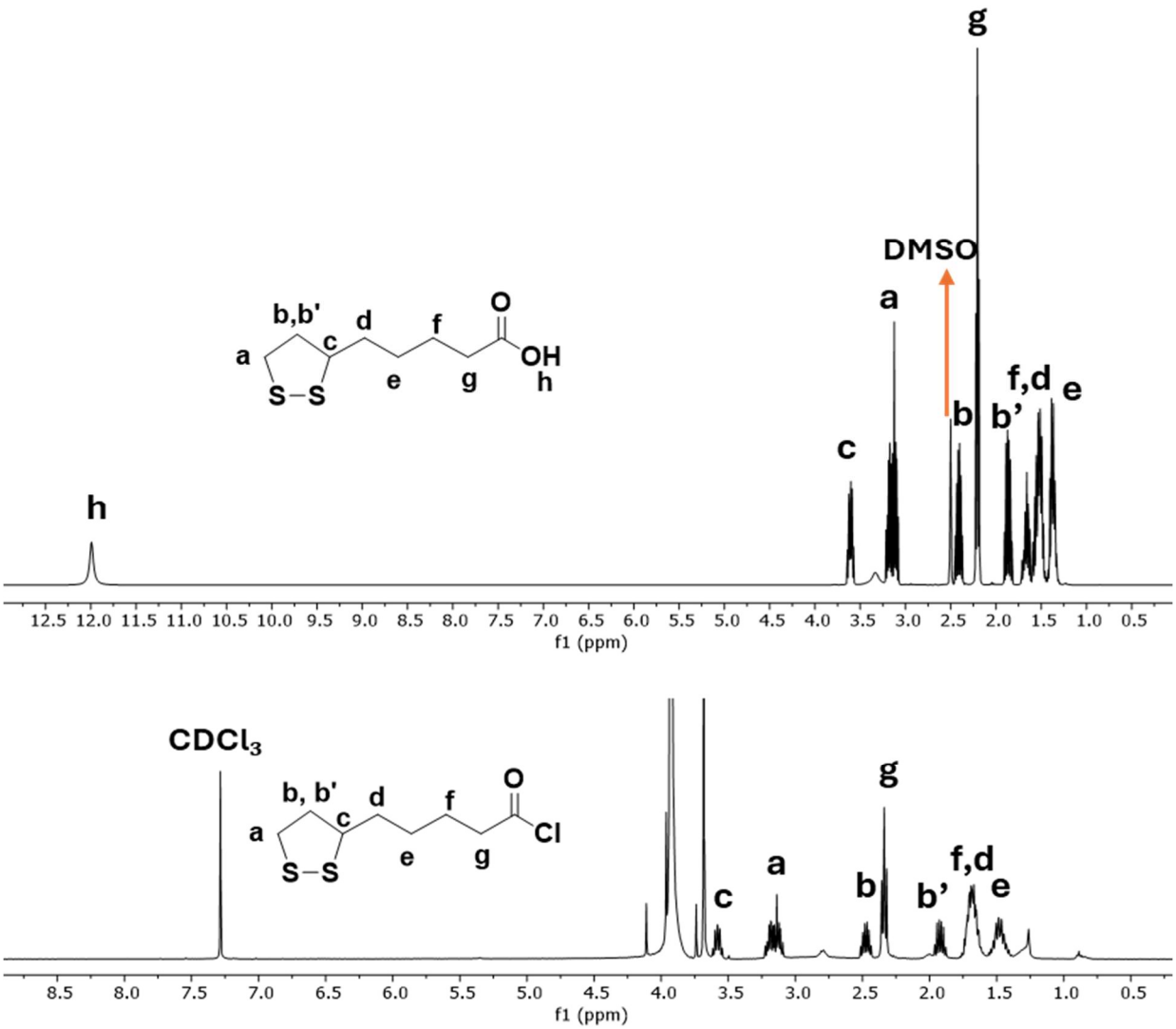

Figure S24. ^{1}H NMR of i3 (lipoyl chloride, in $CDCl_3$). The top figure shows lipoic acid control obtained commercially (in DMSO-d_6).

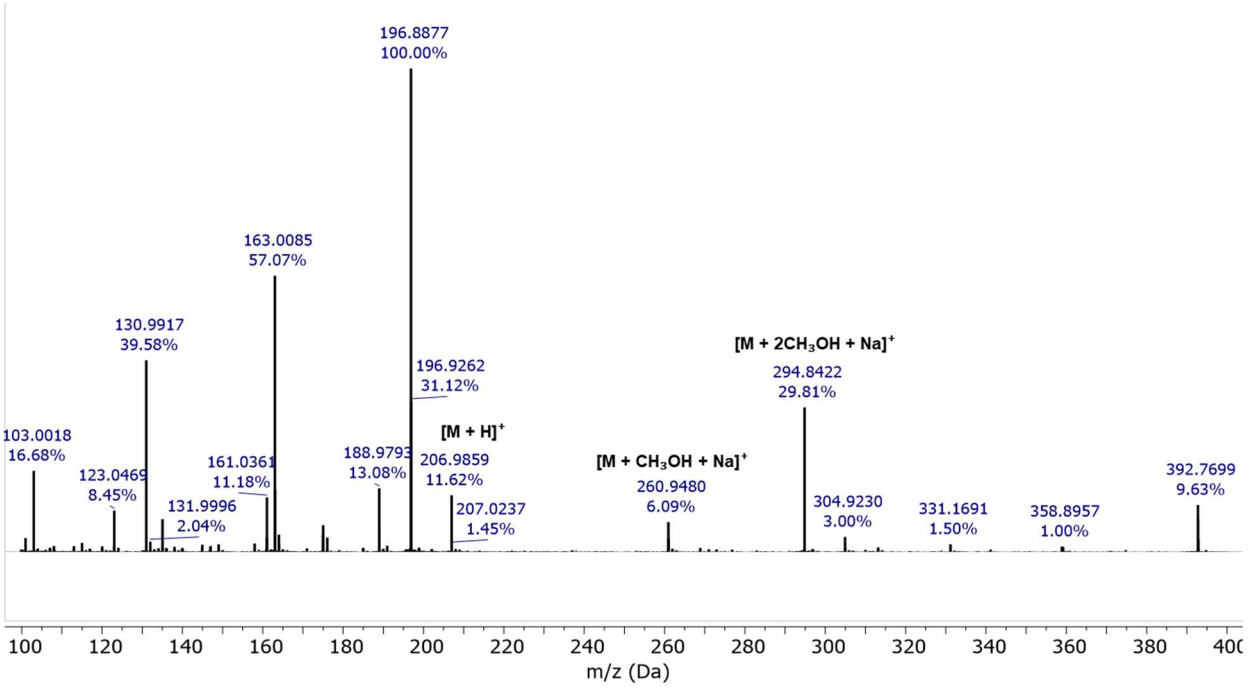

Figure S25. Mass spectra of lipoic acid measured in CH_3CN. MS (ESI-positive): calculated for $C_8H_{14}O_2S_2H$ $[M + H]^+$, 207.0513; found 207.0237, calculated for $C_9H_{18}O_3S_2Na$ $[M + CH_3OH + Na]^+$, 261.0595; found 260.9480, calculated for $C_{10}H_{22}O_4S_2Na$ $[M + 2CH_3OH + Na]^+$, 293.0857, found 294.8422.

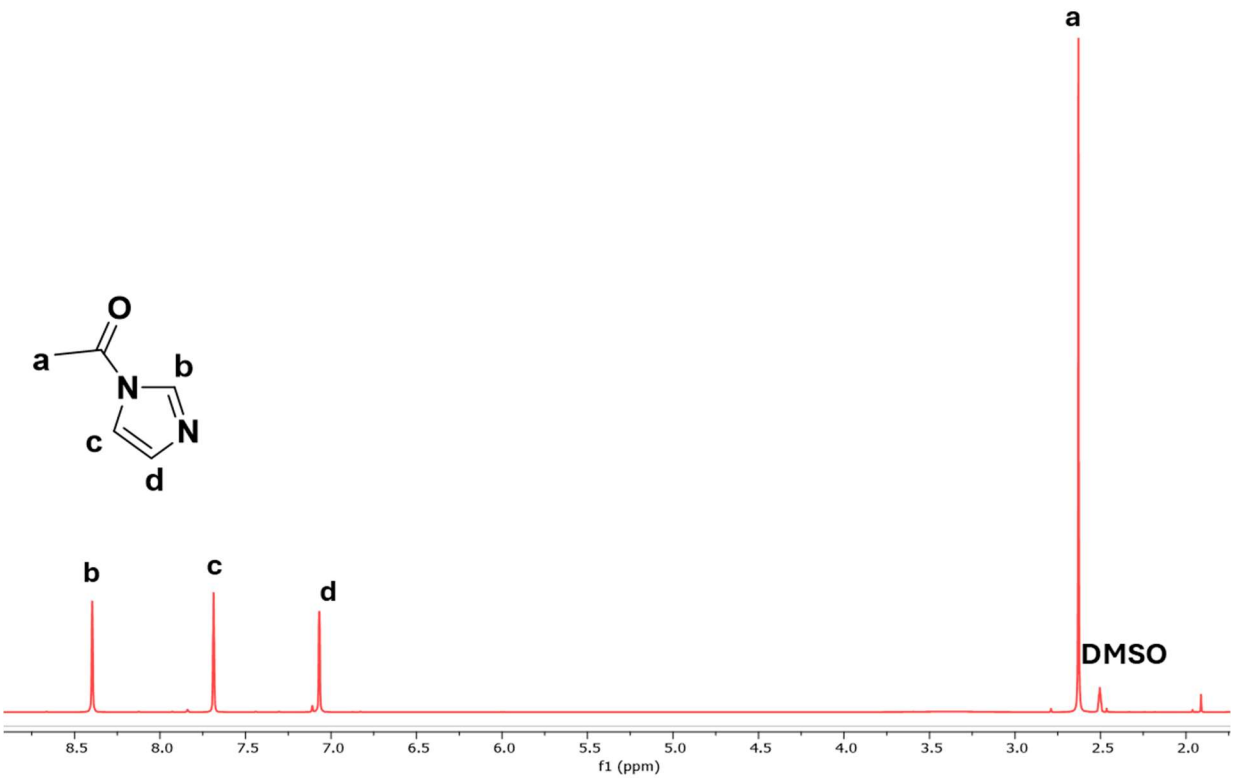

Figure S26. ^1H NMR in DMSO-d_6 of *N*-acetyl imidazole.

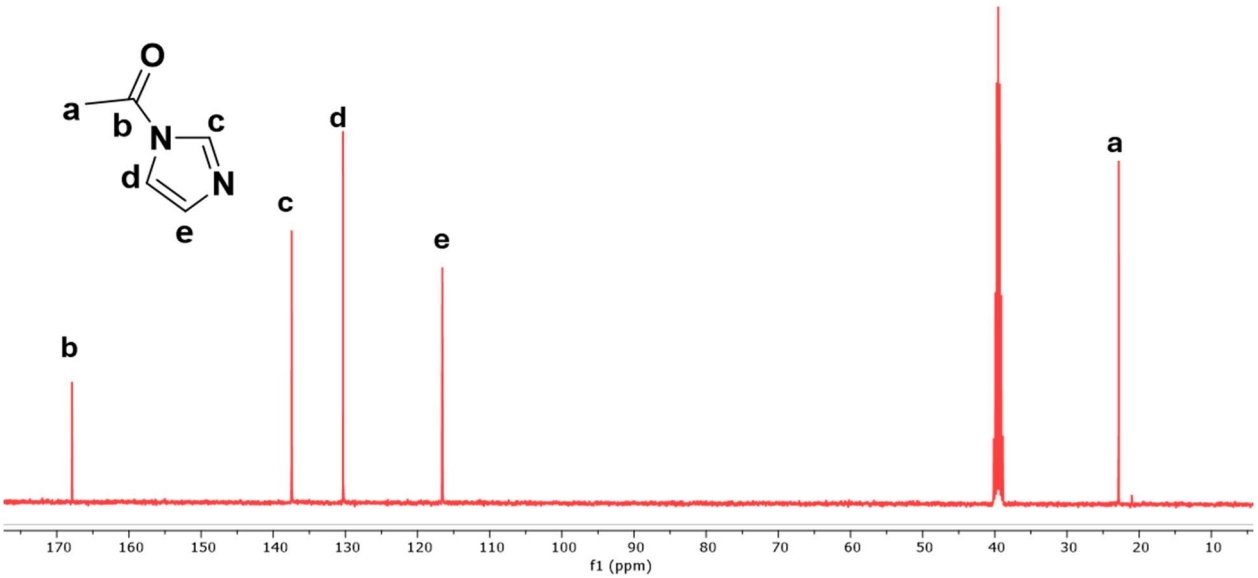

Figure S27. ^{13}C NMR in DMSO-d_6 (39.52 ppm) of *N*-acetyl imidazole.

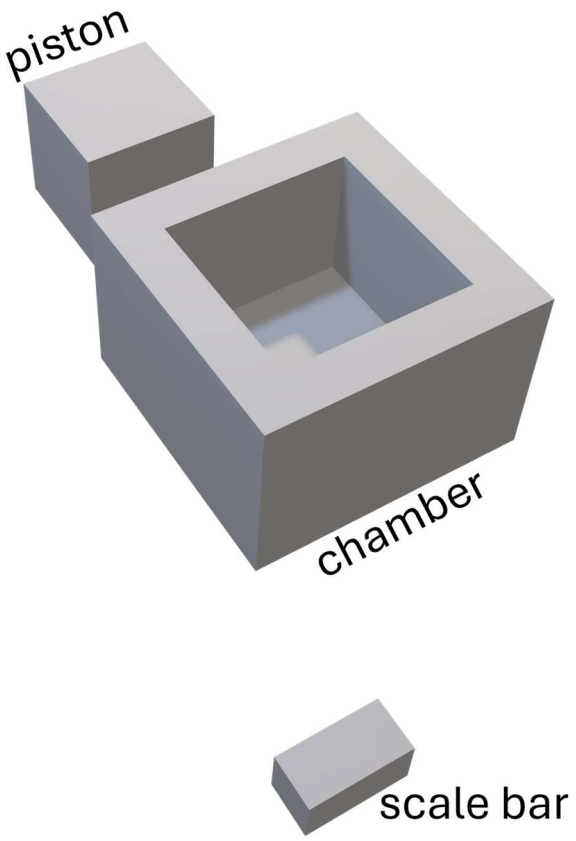

Figure S28. 3D model of the 3D printed printing chamber. The scale bar is 1 cm × 0.5 cm × 0.5 cm.

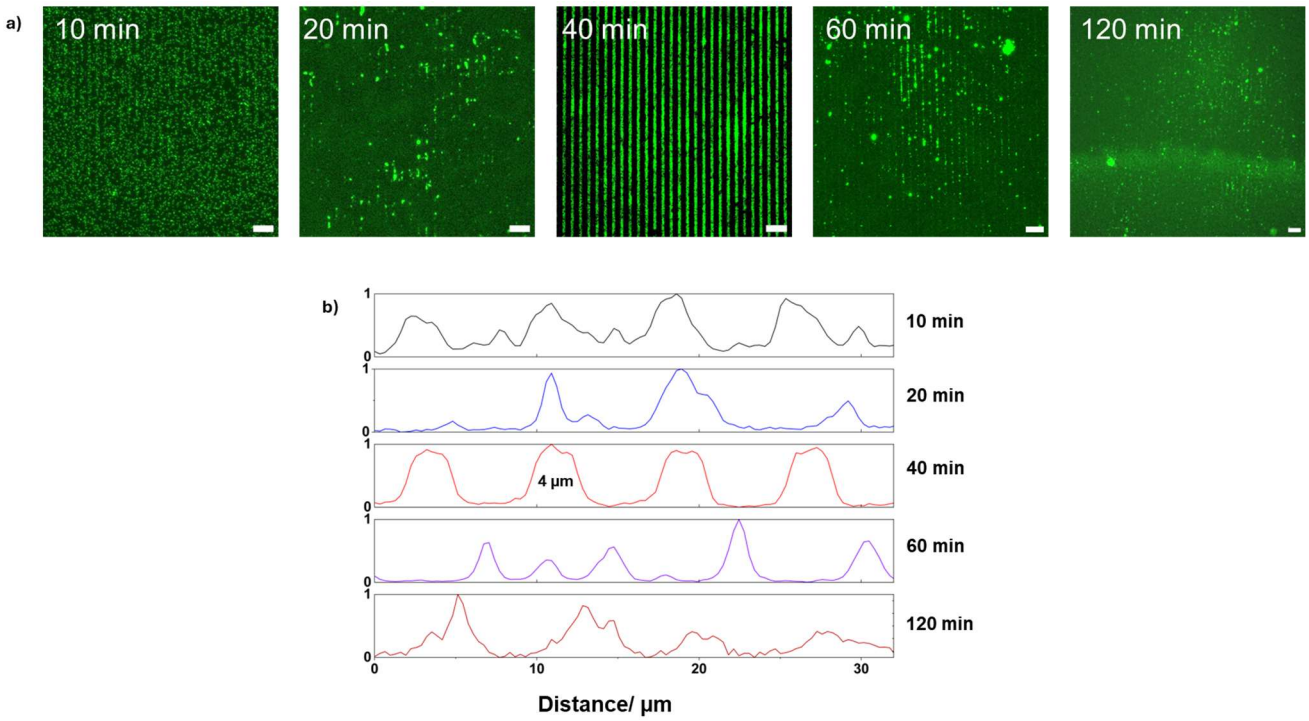

Figure S29. Printing experiment on cellulose thin film for different printing durations. NBD-sarcosine based fluorescent dye printed on cellulose film.

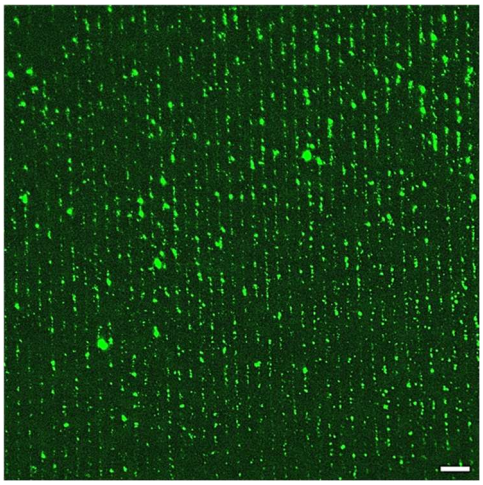

Figure S30. Printing on cellulose thin films in presence of acetonitrile (ACN) instead of DMSO. Scale bars are 20 µm.

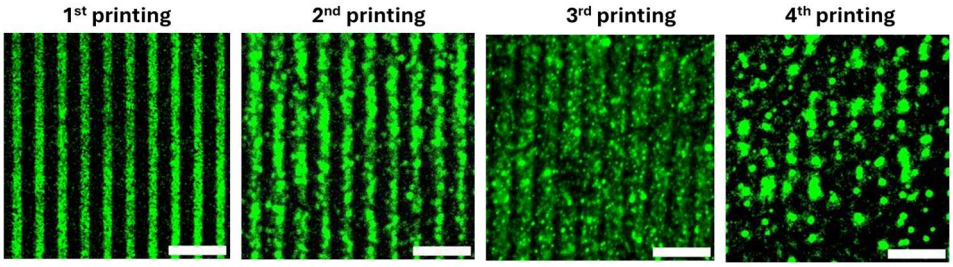

Figure S31. Repeated printing experiment on cellulose thin films with a single stamp. NBD-sarcosine based fluorescent dye printed on cellulose film, using the dye acid chloride for inking. Scale bars are 20 µm.

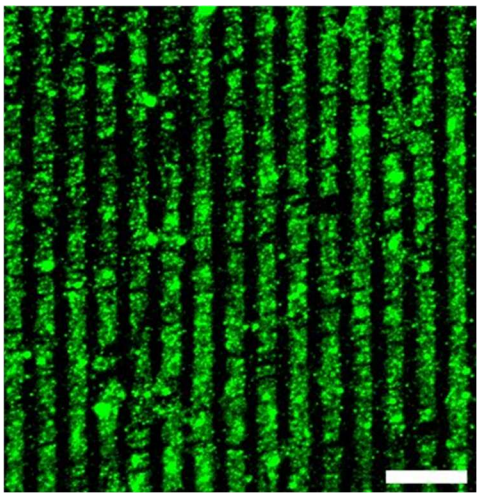

Figure S32. Printing on cellulose thin film. NBD-sarcosine anhydride was used to ink the stamp before printing. Scale bars are 20 µm.

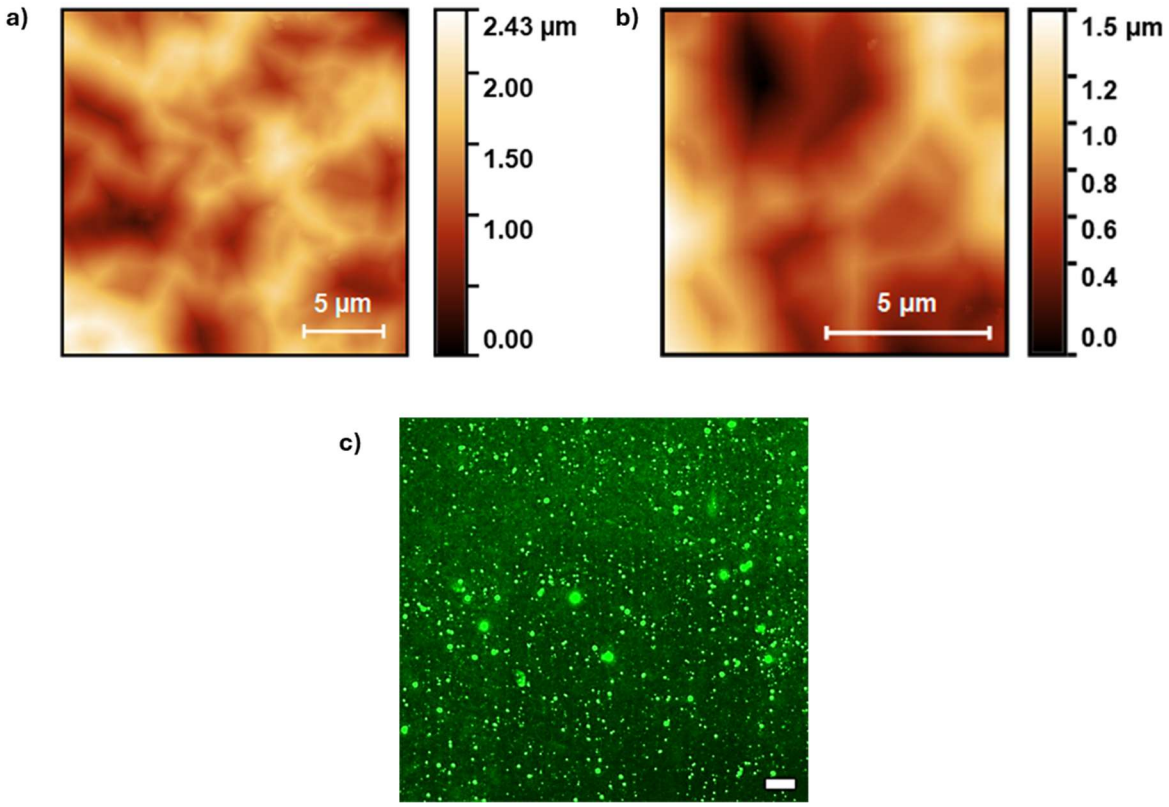

Figure S33. a) and b) AFM height images of back (rough) side (S_a = 285 nm) of a Si wafer and cellulose coated rough Si wafer (S_a = 220 nm), respectively. c) Printing on cellulose thin films coated on the rough side of a Si wafer. NBD-sarcosine anhydride was used to ink the stamp. Scale bars are 20 µm.

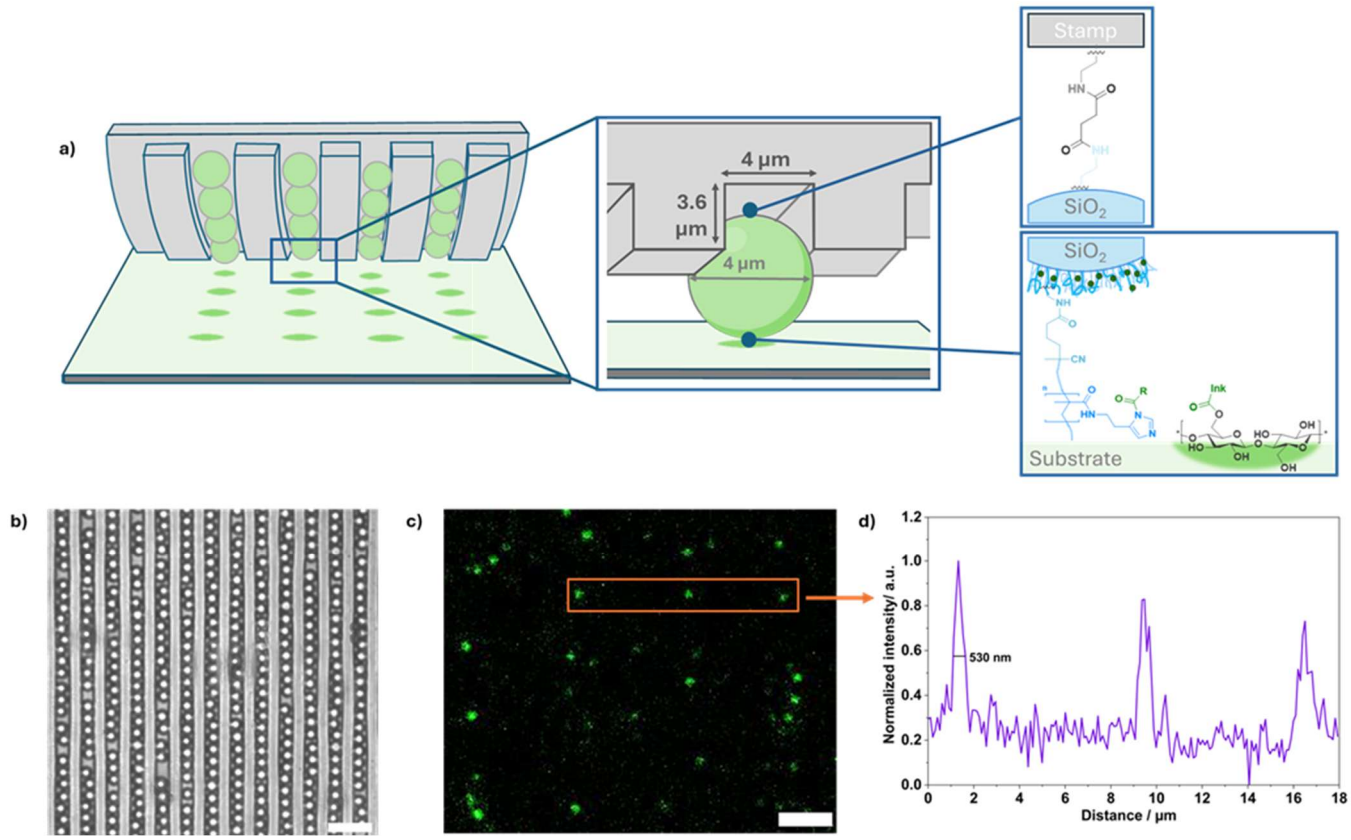

Figure S34. a) Schematic illustration of a printing process, using microparticles with 4 µm diameters as a stamp. Accordingly, the particles were aligned in a flexible PDMS support possessing micro-sized grooves. The particles were subjected to polymer grafting, allowing the PolyBrushMiC process on a cellulose support. For this purpose, the PDMS support was first amino-functionalized using APTES. Next, carboxylic acid groups were introduced onto the stamp by functionalization with succinic anhydride to allow covalent immobilization of the amino-functionalized SiO_2 particles within the grooves via amide coupling. Subsequently, the chain transfer agent (CTA) was attached via DCC coupling using the remaining unbound amino groups of the particles, allowing for surface-initiated RAFT polymerization to graft polymers from the free particle surface. The detailed procedure is described in the experimental section. b) Light microscope image of particles-filled PDMS support. The particles are attached to the stamp surface before grafting. c) Printing on cellulose thin films using the 4 µm microstamps. NBD-sarcosine anhydride was used to ink the stamp. d) Intensity profile of the printed patterns from the particle-attached stamp. Scale bars are 20 µm.

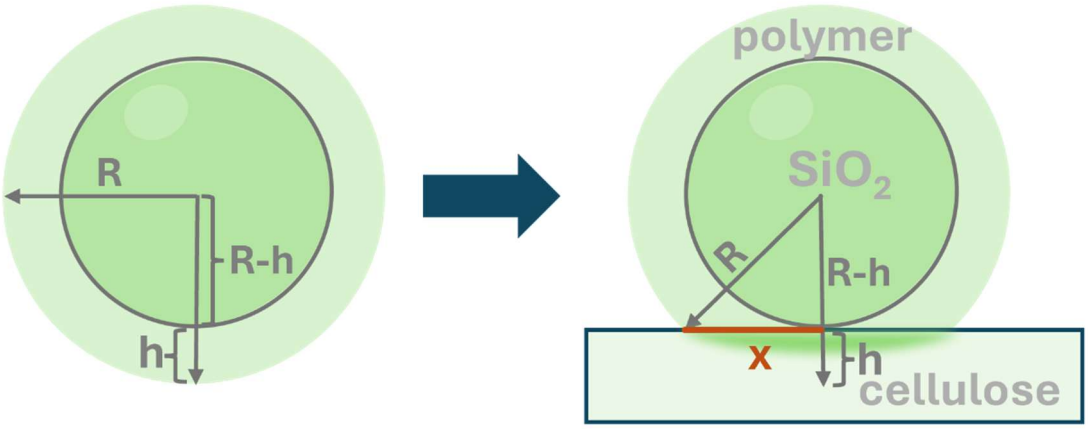

Figure S35. Estimation of the patch diameter produced by microcontact printing on a cellulose film using a polymer brush-functionalized microsphere as the patterning stamp.

To estimate the printing precision of the PolyBrushMiC method, we performed a straightforward printing experiment, using rigid SiO_2 microsphere that was attached to a flexible PDMS support as a "microstamp" to print onto a cellulose substrate. During the µCP process, the particle caps physically contact the substrate. Applying the PolyBrushMiC approach, the microsphere stamp is coated with a polymer brush with a thickness **h**, resulting in a total radius **R** of the microstamp. During printing, the microstamp is pressed against the cellulose film, fully compressing the soft polymer shell. To estimate the contact radius **x** of the resulting circular contact area (the patch), we apply the following relation:

$$R^2 = x^2 + (R - h)^2$$

The patch radius x can be expressed as:

$$x = \sqrt{2\,h\,R - h^2}.$$

With a patch diameter d = 2 x, we find:

$$d = 2\sqrt{2\,h\,R - h^2}.$$

Assuming an overall particle radius of 2 µm, we find patch diameters of:

$d \approx 400\,nm$ for a brush thickness of 10 nm, and

$d \approx 564\,nm$ for a brush thickness of 20 nm.

The measured patch diameter of ~ 530 nm lies within the anticipated size range. Taking into account the physical limitations of the experimental setup, it can be assumed that ink transfer occurs predominantly within the true contact area between the microstamp and the cellulose film, rather than being governed by diffusive spreading. It should also be emphasized that this simplified model neglects any compressibility of the cellulose film, an effect that would be expected to further increase the resulting patch diameter.

A more precise assessment of the printing resolution could be achieved by employing microspheres with smaller diameters, which may generate correspondingly smaller patches. Accurate characterization of such reduced feature sizes would likely require the use of superresolution fluorescence microscopy techniques.

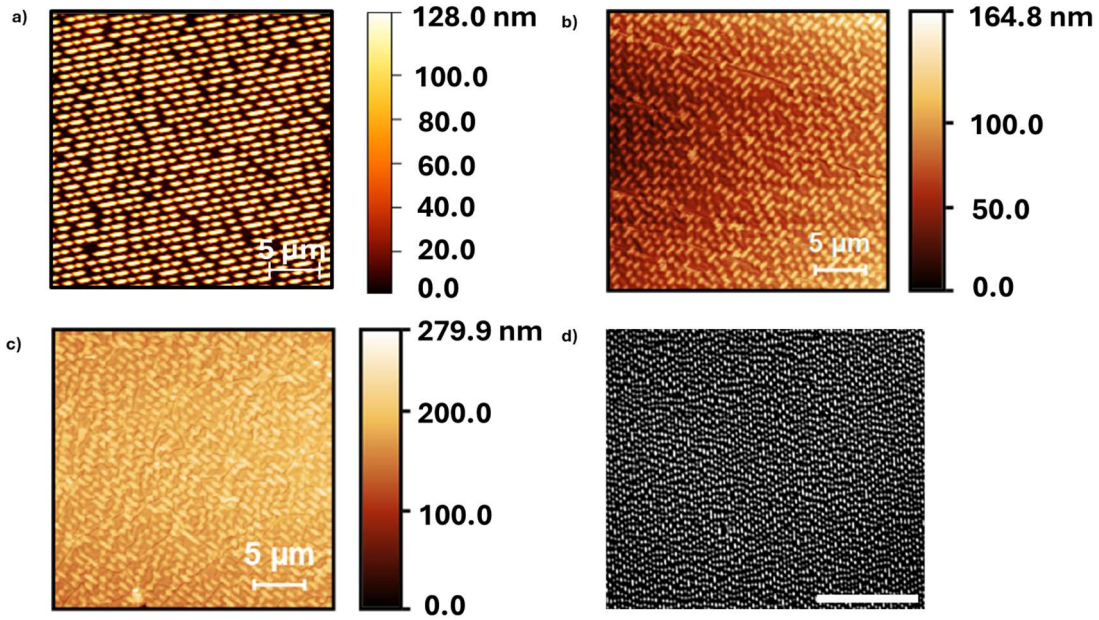

Figure S36. AFM height image of a) patterns on pristine polycarbonate disc of a DVD, b) replicated DVD-patterned stamp, c) DVD-patterned grafted stamp, d) light microscope image of the patterned stamp.

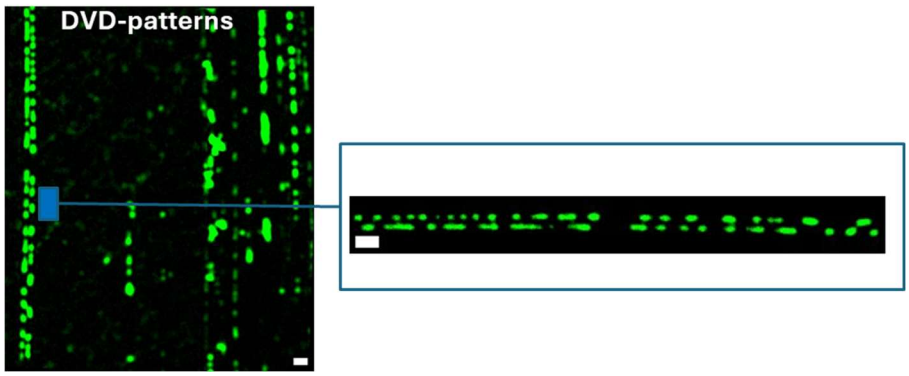

Figure S37. Nanometer size patterns (DVD-patterned, ca. 250 – 750 nm) were transferred from the stamp. The inset shows distinct patterns in a higher resolution, however, the complete transfer of the patterns was challenging and needs optimization of the process. Scale bars are 2 µm.

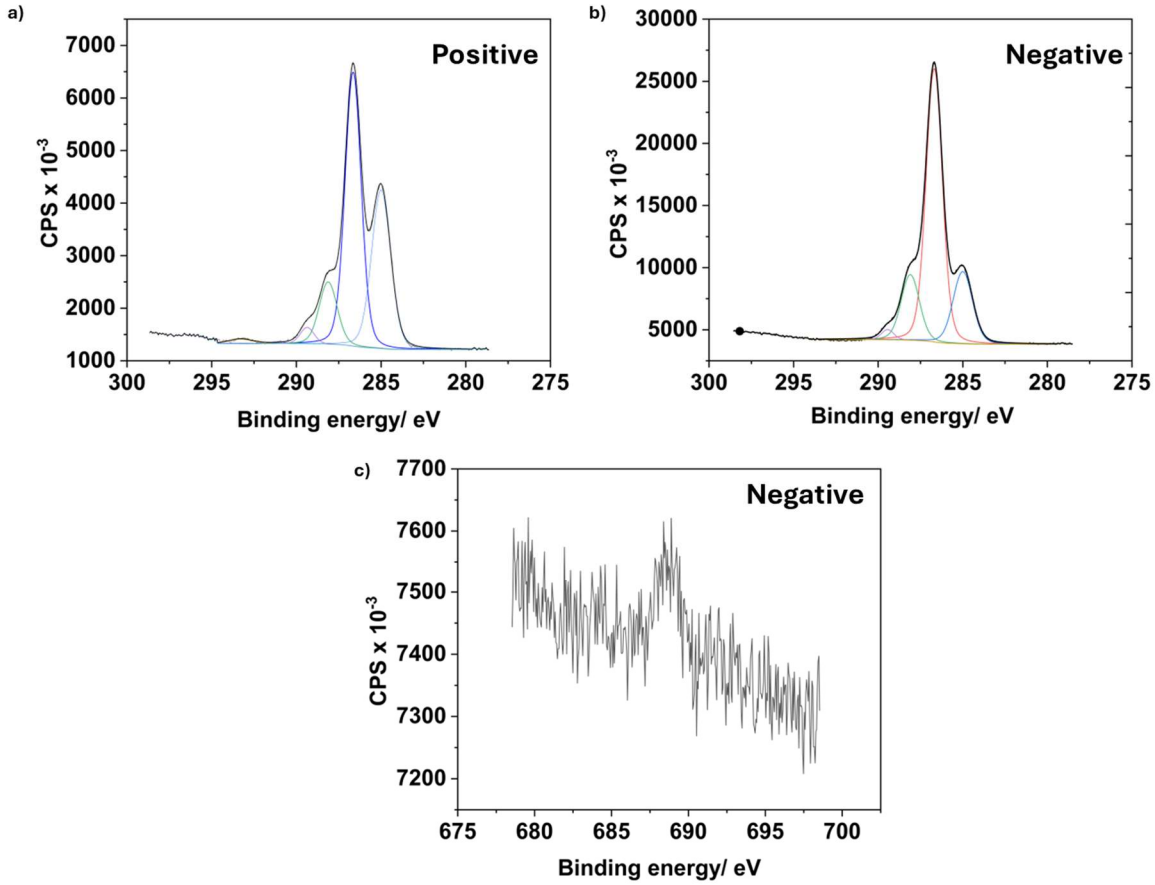

Figure S38. XPS curves of printed substrates. a) positive control (C 1s, with grafted stamp); negative controls printed with bare stamp: b) C 1s and c) F 1s.

Degree of functionalization (DF):

The ratio of fluorine and carbon = $\frac{F}{C} = \frac{0.8}{40} = 0.02$

We know, the ink trifluoramidohexanoic acid contains 8 carbon and 3 fluorine atoms. On the other hand, the anhydro-glucose unit (AGU) of cellulose contains 6 carbon atoms.

The ratio of $\frac{F}{C}$ can also be written as, $\mathrm{R} = \frac{F_{acid} \times DF}{C_{cellulose} + (C_{acid} \times \mathrm{DF})}$

$$\mathrm{R} = \frac{3 \times DF}{6 + (8 \times \mathrm{DF})}$$

$$\mathrm{R}\{(6) + (8 \times \mathrm{DF})\} = (3 \times \mathrm{DF})$$

$$(6 \times \mathrm{R}) = (3 \times \mathrm{DF}) - R(8 \times \mathrm{DF})$$

$$(6 \times 0.02) = (3 \times \mathrm{DF}) - 0.02(8 \times \mathrm{DF})$$

$$(0.12) = 2.84 \times \mathrm{DF} = 0.042$$

Since we have 3 -OH groups in an AGU, we get the DF (%) = $100 \times (\frac{0.042}{3}) = 1.4\%$

The calculation method was followed from the literature.[9]

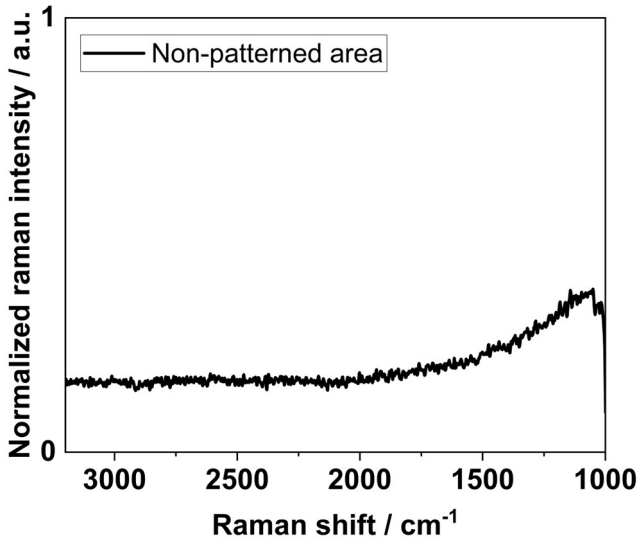

Figure S39. SERS spectra of non-patterned area of a patterned substrate with **i3** (lipoic acid).

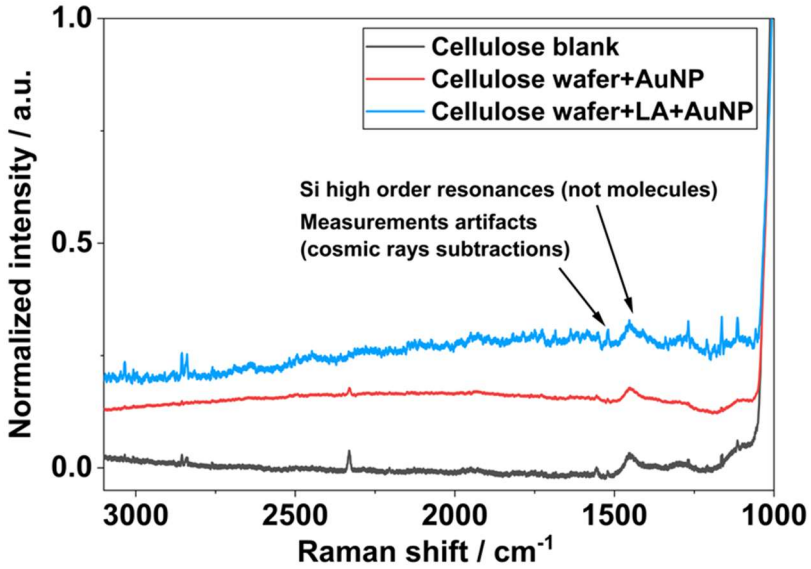

Figure S40. SERS spectra comparison of AuNPs deposited **i3**(lipoic acid)-functionalized substrate with a pristine cellulose coated Si wafer and AuNPs deposited cellulose wafer. Lipoic acid functionalized substrate shows signals resembling the AuNPs deposited patterned substrate with lipoic acid (**i3**).

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