Electronic Supporting Information

Fatty Acids as Biomimetic Replication Agents for Luminescent MOF Patterns

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Materials and Instruments

All chemicals, except for L-serine and urea, where purchased from Sigma Aldrich. L-serine was purchased from Alfa Aesar and Urea was purchased from Mallinckrodt Pharmaceuticals. Silicon wafers were purchased from M.M.R.C. Pty Ltd. Glasses for optical and fluorescence microscopy were purchased from Roth (ISO 8037/1). Polydimethylsiloxane (PDMS) stamps were prepared in the laboratory of Gianluca Grenci (Mechanobiology Institute, National University of Singapore).

Photographs were taken with a Huawei P9 smartphone with ISO 200 settings. Optical microscopy was done with a Zeiss Axio Scope.A1. Fluorescence microscopy was done with an OLYMPUX IX73 inverted microscope (OLYMPUS, Austria) using 10x magnification, UMPlanFL N, 10x/0.30 W, ∞/ - / FN26.5 objective (OLYMPUS). Illumination was performed using an Omicron LedHUB High-Power LED Light Engine, equipped with a 340 nm LED light source (Omicron, Germany), images were captured using a Retiga R1 CCD camera (QImaging, Canada). Device control and image acquisition was performed using VisiView image acquisition and control software (Visitron Systems, Germany). The intensity of the luminescent material on each biomolecule spot was calculated with the imageJ software. SEM images were collected with a TESCAN Vega (20 kV acceleration voltage, sputter gold coating of samples). FT-IR measurements were done with an alpha Bruker using transmission mode (resolution 2 cm^{-1}). XRD measurements were done using a Rigaku SmartLab X-Ray Diffractometer (9 kW, Cu source). The luminescent properties were investigated using a Horiba Fluorolog3 fluorometer.

Experimental

Fingerprint experiment: Following a previously published procedure[1], a fingerprint on a Si (100) wafer was immersed in a freshly prepared 1:1 mixture of MOF-precursors (20 mM $TbCl_3$ * 6 H_2O, 20 mM Na_2BDC) for the following reaction times: 30 s, 1 min, 5 min and 15 min. Subsequently, the wafer was washed three times with distilled water and dried under air flow. Pictures were taken in a dark room under UV light (254 nm, 15W). Figure S1a

In order to investigate, which of the chemical fingerprint components triggers the MOF growth most effectively, we reduced the kinetic of the biomimetic replication process by reducing the MOF precursor concentrations. Figure S1d shows a fingerprint on a polished Si (100) wafer prepared, as described in the procedure above, using a lower concentration of MOF precursors (5 mM $TbCl_3$ * 6 H_2O and 5 mM Na_2BDC).

These new conditions were applied to maximise the difference between the biomimetic replication on the individual fingerprint components in all the following experiments.

Screening experiment: From each biomolecule 2 µl of a 2 mg/ml solution was drop-cast on the glass slide. For BSA also 2 µl of a 30 mg/ml solution was drop-cast.[1] The defined spots (0.3x0.6 mm) were generated by using a template mask. Once the solvent was evaporated, the glass slide was inserted into an aqueous solution of the MOF precursors freshly prepared (50 ml, 5 mM $TbCl_3$, 5 mM Na_2BDC) and let react for

certain times (30 seconds, 1 minute, 5 minutes and 15 minutes; samples denoted as a. r., after reaction) at room temperature and static conditions.[2,3] For each reaction time triplicates were made. After the desired reaction time, the glass slide was rinsed 3 times with distilled water and then soaked in distilled water for 1 minute to remove the MOF crystals that can be formed in the bulk of the solution from the dissolved biomolecules and that could sediment and adsorb on the surface.

SEM samples preparation: The samples were prepared by dropcasting 20 µl of a 2 mg/ml solution of the biomolecule on a piece of Si (100). After solvent evaporation, the samples were exoposed for a certain amount of time (1 minute, 5 minutes and 15 minutes) to an aqueous solution of the MOF precursors freshly prepared (5 ml, 5 mM $TbCl_3$, 5 mM Na_2BDC) at room temperature and static conditions. After the desired reaction time, the reaction was quenched by rinsing 3 times with water and the sample was dried with a nitrogen flow. The samples were sputter-coated with a thin Au film prior the analysis. To calculate the MOF particle surface coverage (Figure 2e), we analyzed the SEM micrographs (100x magnification) acquired after different reaction times with the software imageJ (Figure S23-S25).

FT-IR and XRD samples preparation: 10 µl of a 40 mg/ml solution of the biomolecules were dropcasted each on a 1.5 cm x 1.5 cm piece of Si (100). This treated silicon piece was then exposed to an aqueous solution of MOF precursors freshly prepared (10 ml, 5 mM $TbCl_3$, 5 mM Na_2BDC) for 15 minutes. After the desired reaction time, the reaction was quenched by rinsing 3 times with water and the sample was dried with nitrogen. For the preparation of the pure $Tb_2(BDC)_3*(H_2O)_4$-MOF, the aqueous solution of MOF precursors was mixed (10 ml, 5 mM $TbCl_3$, 5 mM Na_2BDC, room temperature, static conditions) and the white product was isolated after 24 hours via centrifugation. The white powder was washed 3 times with ethanol, dried at room temperature and pressure. Finally, the Tb-MOF powder were suspended in ethanol (40 mg/ml) and 10 µl of this suspension was drop-cast on a 1.5 cm x 1.5cm piece of silicon.

Patterning: 300 µl of a 40 mg/ml solution of palmitic acid in ethanol was spin-coated on the PDMS stamp (this procedure was repeated 3 times to ensure the homogeneity of the coating). Then, the coated PDMS stamp was applied on the desired substrate for 10 minutes under a pressure of 10 kPa. The fatty acid patterned sample was then placed in an aqueous solution of the MOF precursors (50 ml, 5 mM $TbCl_3$, 5 mM Na_2BDC) for 5 min at room temperature and static conditions. After 5 minutes, the sample was removed from the MOF precursors solution, rinsed 3 times with distilled water, soaked in distilled water for 1 minute and finally dried with a nitrogen flow.

Time evolution of the luminescent signal: From each biomolecule, 10 µL of a 2 mg/ml solution was drop-cast on the bottom of a Supelco Screw Top vial. After evaporation of the solvent, a freshly prepared aqueous 1:1 mixture of MOF precursors (5 mM $TbCl_3 * 6 H_2O$, 5 mM Na_2BDC) was added and the samples illuminated with a UV lamp (Herolab GmbH Laborgeräte, Type NU-8, 8W, emission: 325 - 375 nm). Pictures were taken in a dark room every 30 s for 15 min (Video V1, Fig. S21).

MOF excitation spectrum: The excitation spectrum of the MOF grown on a COOH-functionalized Si surface was recorded between 245 nm and 400 nm using an OG455 filter in front of the emission channel (Horiba Fluorolog3, λ_{em} = 543 nm).

MOF emission spectrum: The emission spectrum of the MOF grown on a COOH-functionalized surface was recorded between 450 nm and 650 nm using an OG455 filter in front of the emission channel (Horiba Fluorolog3, λ_{ex} = 250 nm).

Tb-MOF biomimetic replication on fingerprints

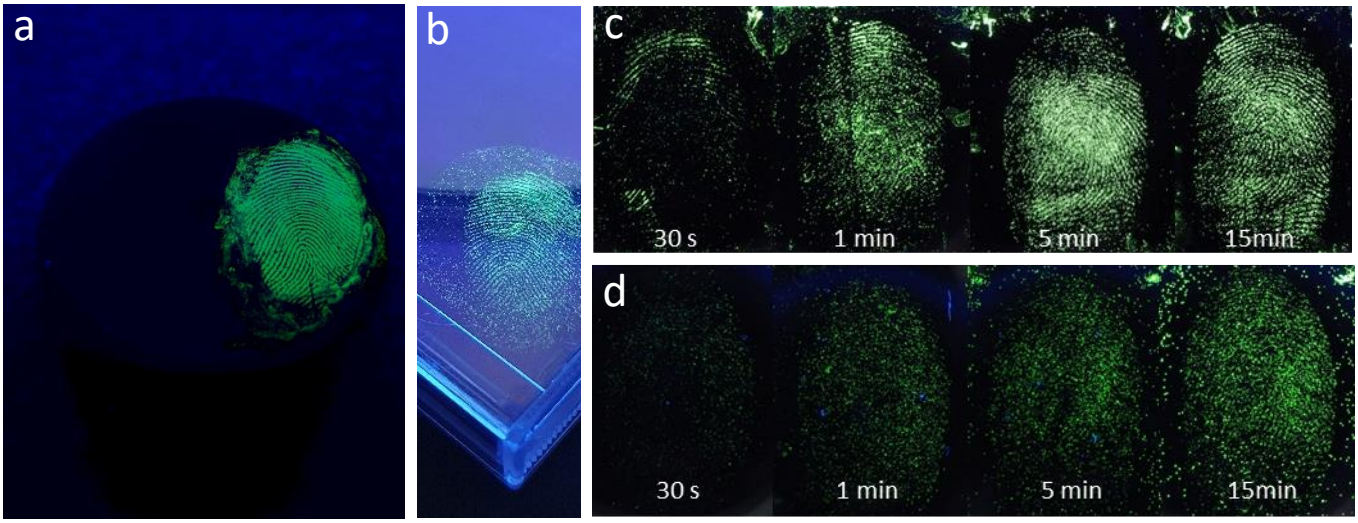


Figure S1. a) camera picture of Tb2(BDC)3*(H2O)4 MOF grown on a fingerprint on high density polyethylene (HDPE) cap of a 50 ml centrifuge tube (the same picture was used in Fig. 1 of main text); b) camera picture of Tb2(BDC)3*(H2O)4 MOF grown on a fingerprint on a polystyrene (PS) compact disk case. c) camera picture of Tb2(BDC)3*(H2O)4 MOF grown on a fingerprint on a Si wafer. For a), b) and c) the surface with fingerprint was exposed to 20 mM precursor solutions of TbCl3. The reaction time is 5 mins unless differently specified. d) Luminescence of the Tb2(BDC)3*(H2O)4 MOF grown on a fingerprint on a Si wafer using 5 mM precursor solutions of TbCl3 and Na2BDC for 30 s, 1 min, 5 min and 15 min. For all the pictures, a 254 nm UV lamp was used.

Tb-MOF emission and excitation spectra

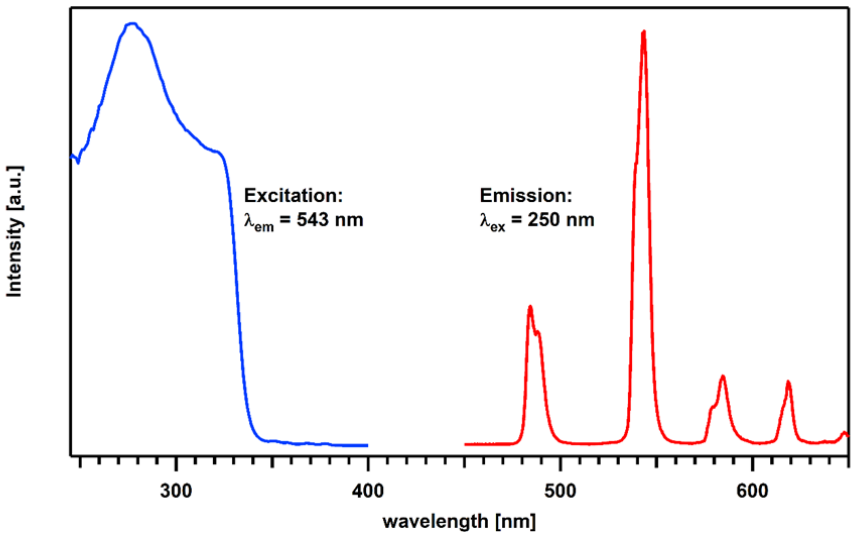


Figure S2. Excitation (blue) and emission (red) spectra of MOF grown on COOH-functionalized Si surface. (Fluorolog, OG455 filter in front of the emission channel). The emission spectrum was found to be independent on the excitation wavelength (250 nm and 300 nm were used) that is explained by the fact that efficient excitation is only possible via the coordinated terephthalic acid antenna. The emission of lanthanides generally occurs from defined spectroscopic levels. So, despite that excitation to a higher level might happen, a relaxation down to one of these luminescent levels is observed.[4] This suggests that, as summarized by Kasha's rule, photon emission is expected in appreciable yield only from the lowest excited state and so that the emission wavelength is independent from the excitation wavelength. The emission spectra of Tb-MOF reported in the literature show no significant differences when 254 or 312 nm is used as excitation source, and the data that we collected using 250 nm as excitation wavelength is consistent with literature reports.[5,6] For our purpose (imaging), the excitation wavelength should be sufficient to yield a detectable fluorescence and different excitations where used according to the need (e.g. portable UV lamp for time course experiment).

Screening experiment

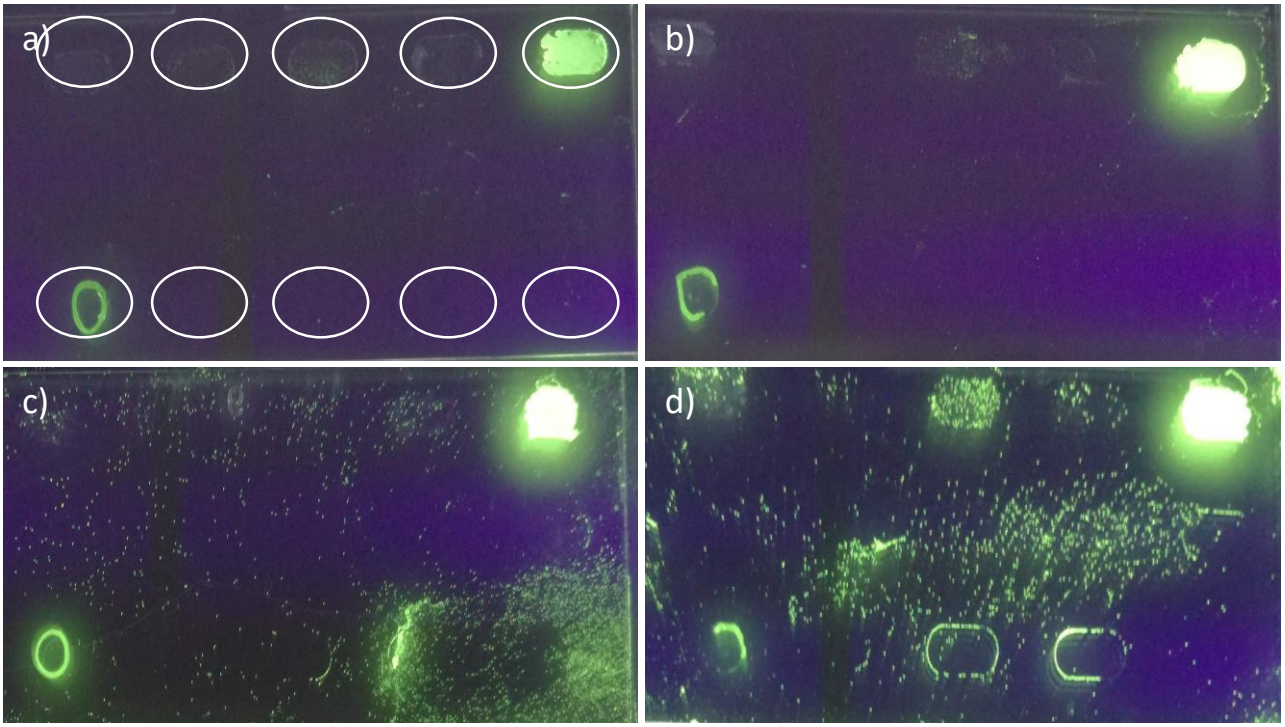


Figure S3. a) Glass slide with spots of the biomolecules (*upper row*, f.l.t.r.: cholesterol, squalene, triglyceride, wax, fatty acid; *lower row*: f.l.t.r.: BSA (30 mg/ml), BSA, lactate, urea, amino acid) a. r. for 30 seconds. b) Glass slide with biomolecules a. r. for 1 minute. c) Glass slide with biomolecules a. r. for 5 minutes. d) Glass slide with biomolecules a. r. for 15 minutes. Each spot is 0.3x0.6 mm.

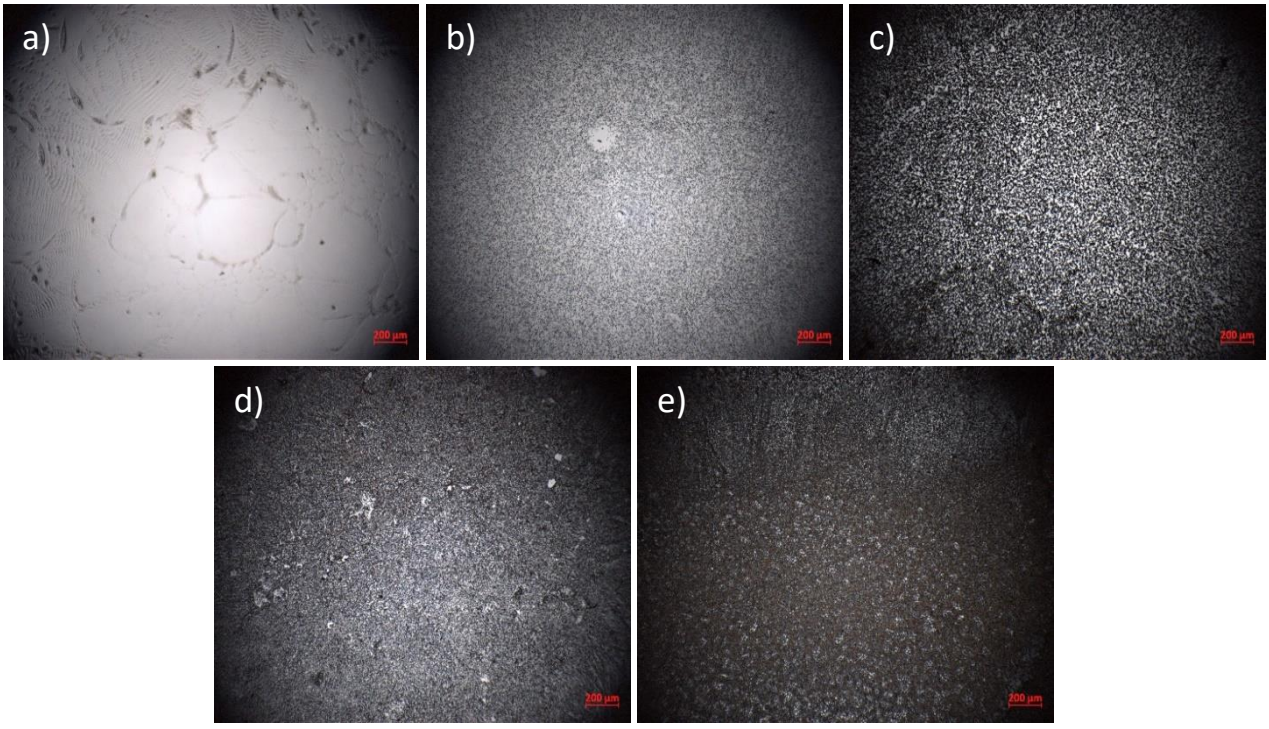


Figure S4. a) Fatty acid spot on glass slide. b) Fatty acid spot a. r. for 30 seconds. c) Fatty acid spot a. r. for 1 minute. d) Fatty acid spot a. r. for 5 minutes. e) Fatty acid spot a. r. for 15 minutes

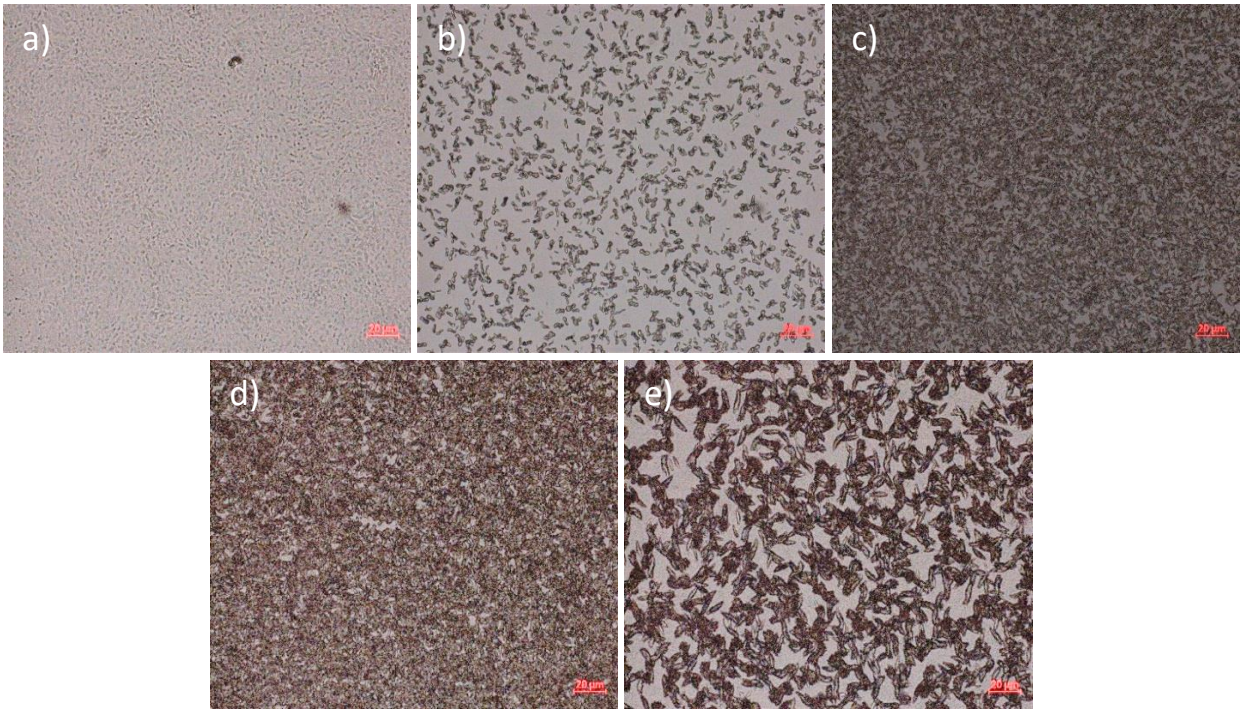


Figure S5. a) Fatty acid spot on glass slide. b) Fatty acid spot a. r. for 30 seconds. c) Fatty acid spot a. r. for 1 minute. d) Fatty acid spot a. r. for 5 minutes. e) Fatty acid spot a. r. for 15 minutes

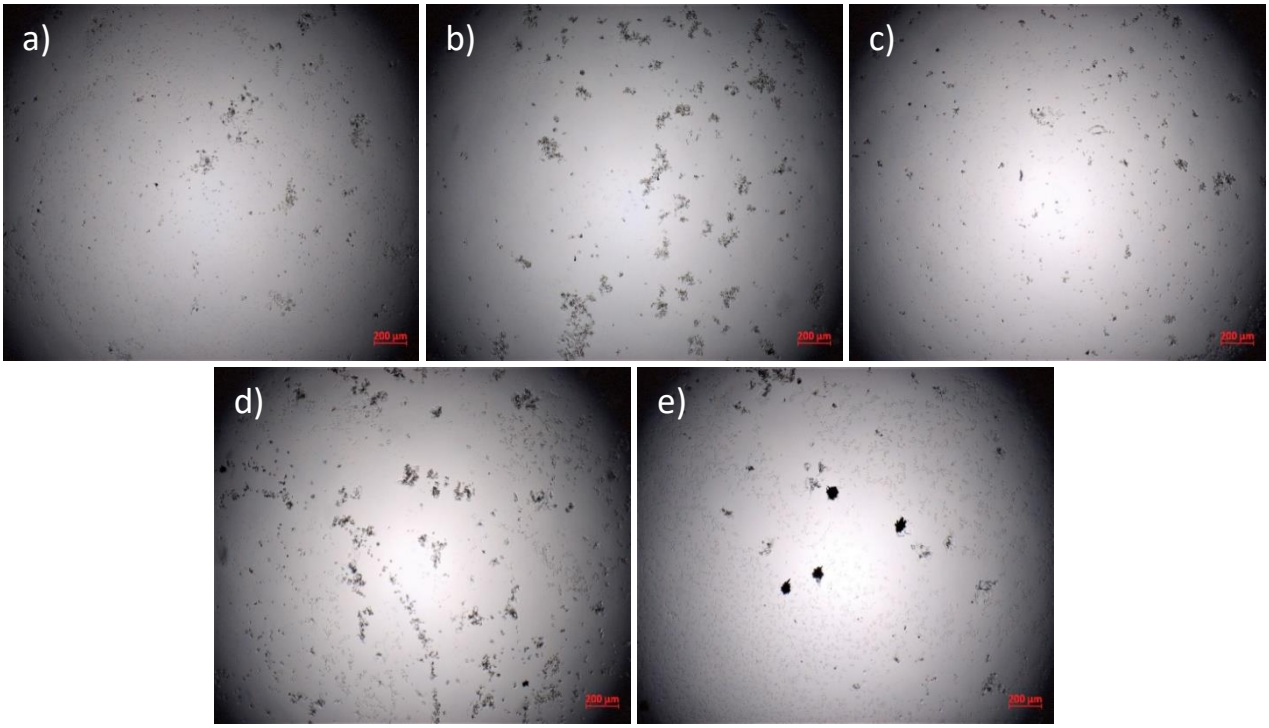


Figure S6. a) Wax spot on glass slide. b) Wax spot a. r. for 30 seconds. c) Wax spot a. r. for 1 minute. d) Wax spot a. r. for 5 minutes. e) Wax spot a. r. for 15 minutes

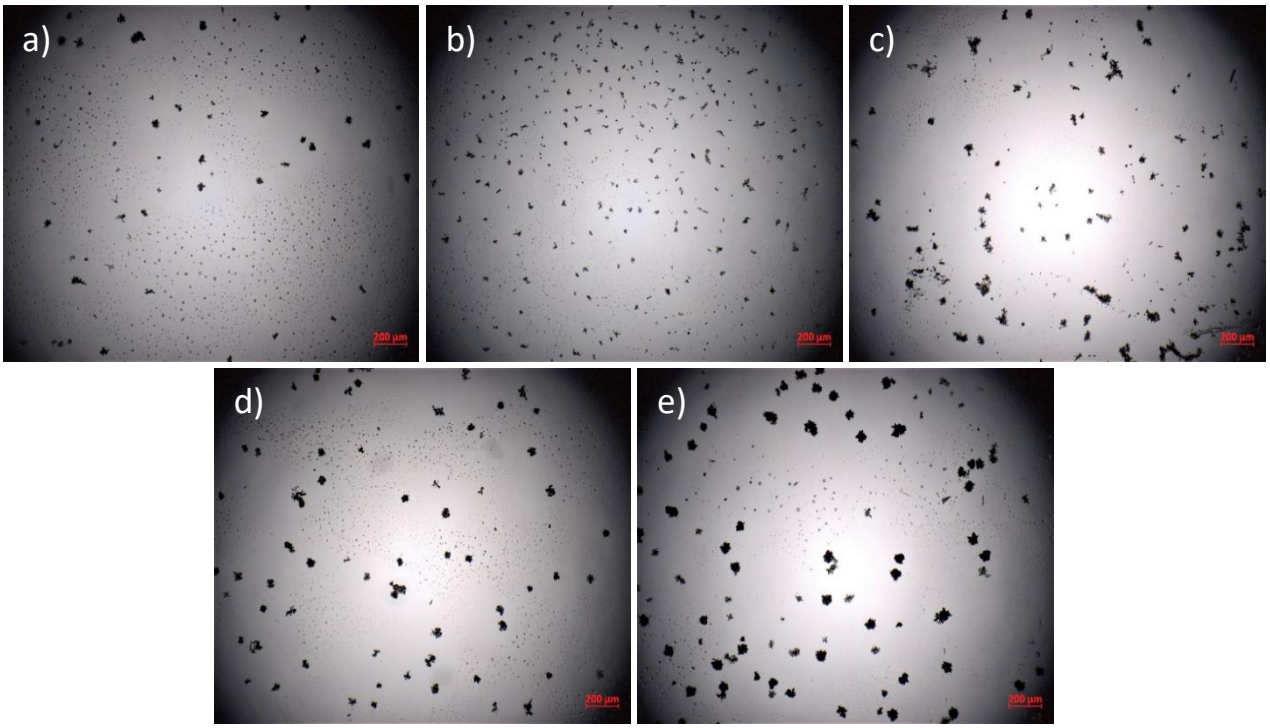


Figure S7. a) Triglyceride spot on glass slide. b) Triglyceride spot a. r. for 30 seconds. c) Triglyceride spot a. r. for 1 minute. d) Triglyceride spot a. r. for 5 minutes. e) Triglyceride spot a. r. for 15 minutes

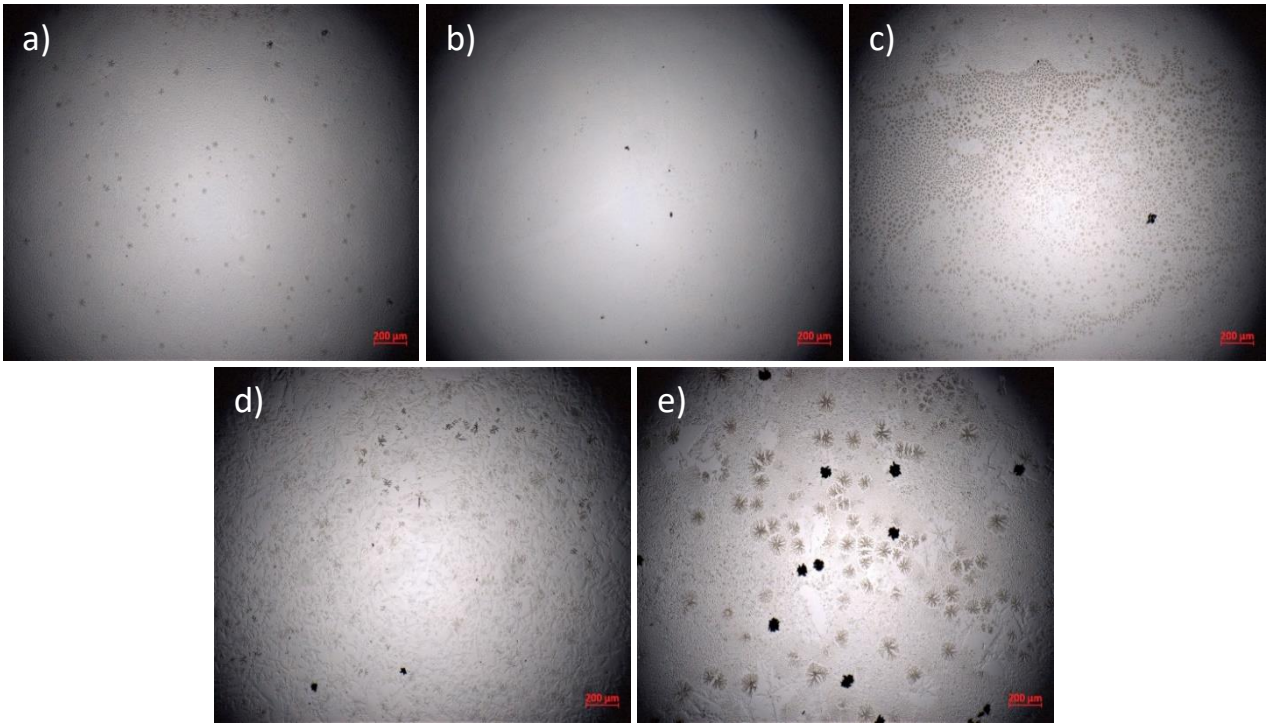


Figure S8. a) Cholesterol spot on glass slide. b) Cholesterol spot a. r. for 30 seconds. c) Cholesterol spot a. r. for 1 minute. d) Cholesterol spot a. r. for 5 minutes. e) Cholesterol spot a. r. for 15 minutes

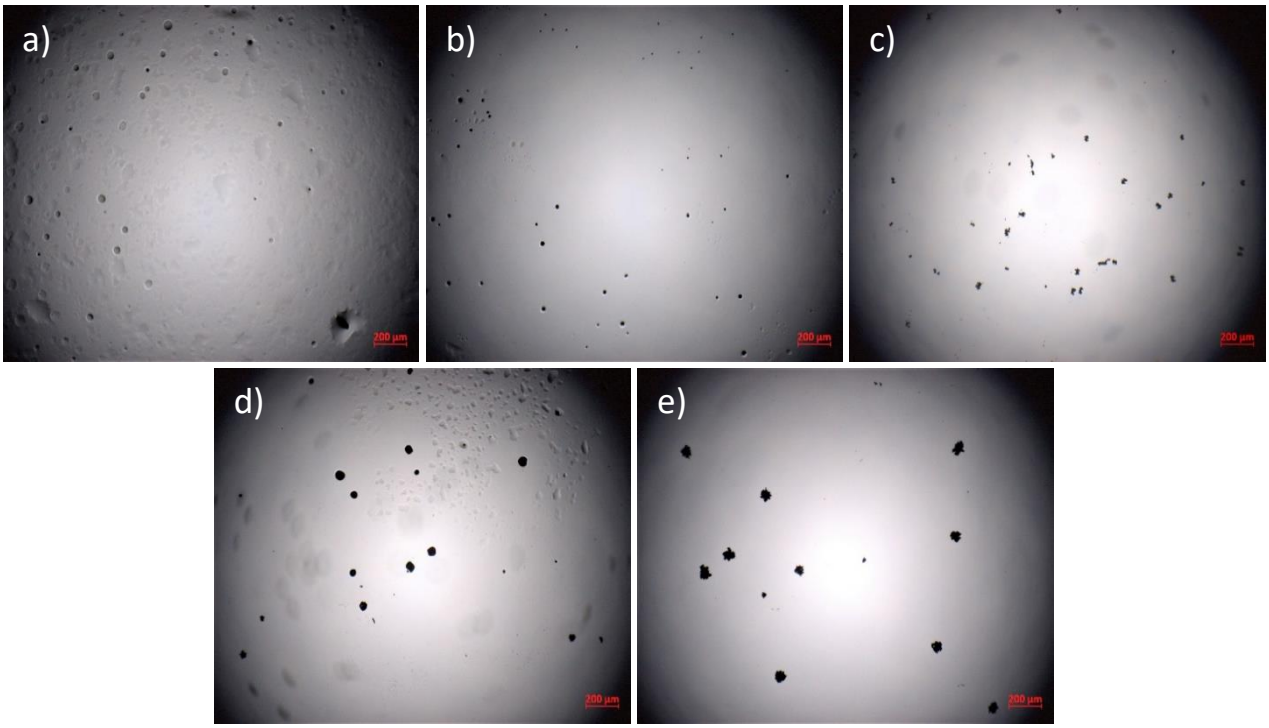


Figure S9. a) Squalane spot on glass slide. b) Squalane spot a. r. for 30 seconds. c) Squalane spot a. r. for 1 minute. d) Squalane spot a. r. for 5 minutes. e) Squalane spot a. r. for 15 minutes

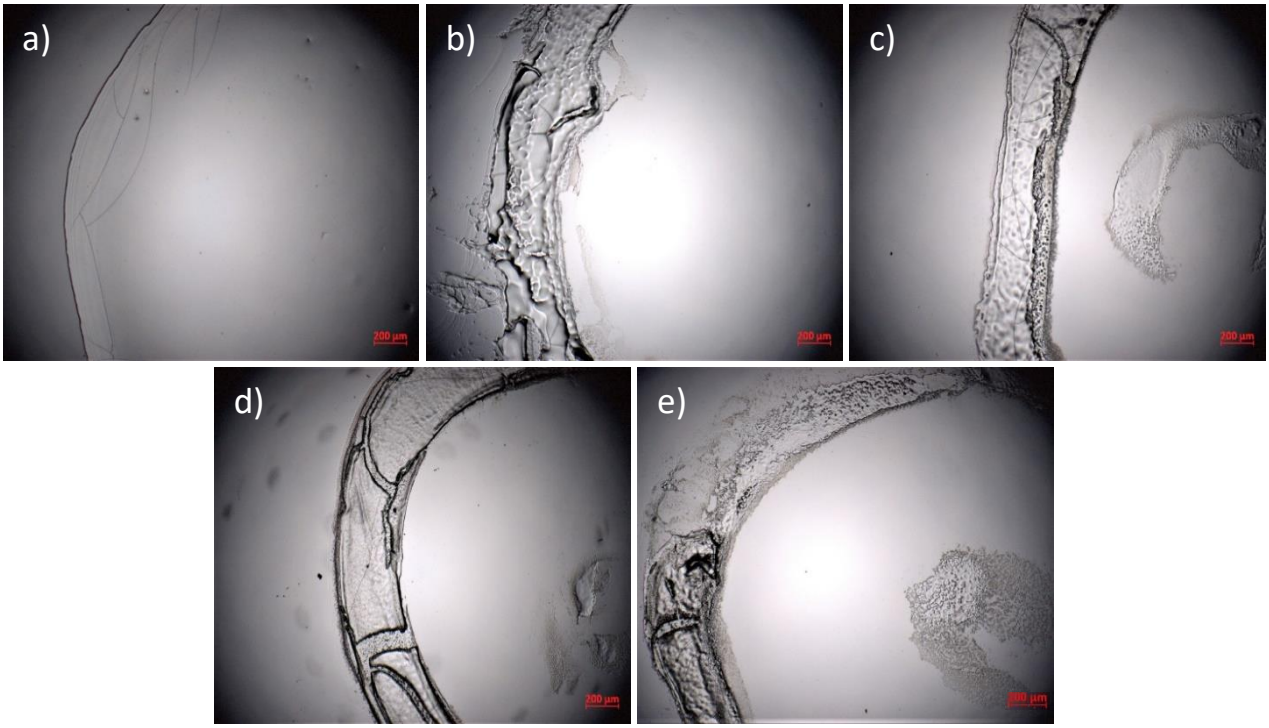


Figure S10. a) BSA spot on glass slide. b) BSA spot a. r. for 30 seconds. c) BSA spot a. r. for 1 minute. d) BSA spot a. r. for 5 minutes. e) BSA spot a. r. for 15 minutes

Fourier-Transform Spectroscopy

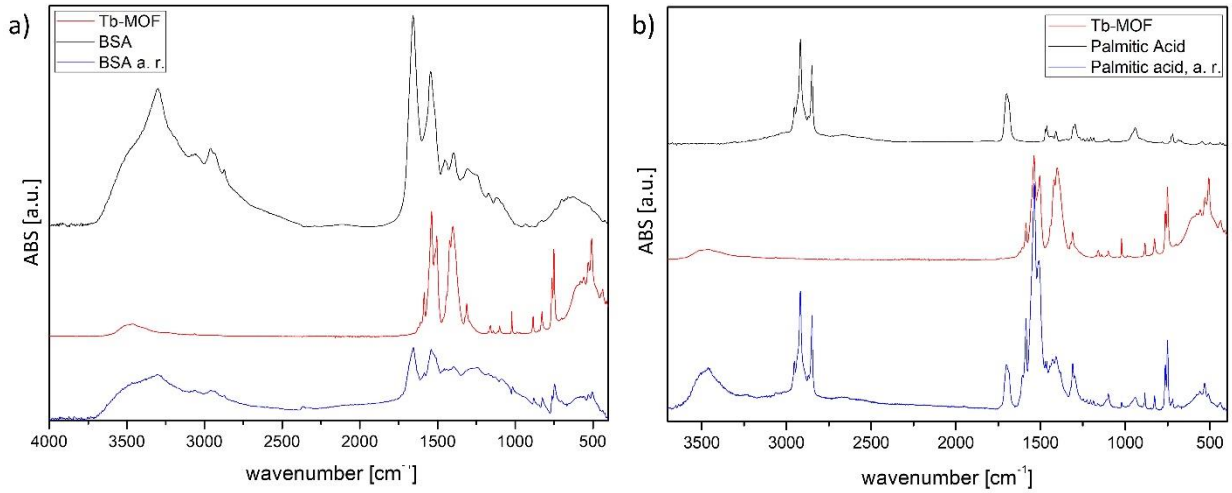


Figure S11: a) FT-IR spectra of BSA, Tb-MOF and BSA a. r. . b) FT-IR spectra of fatty acid, Tb-MOF and fatty acid a. r. .

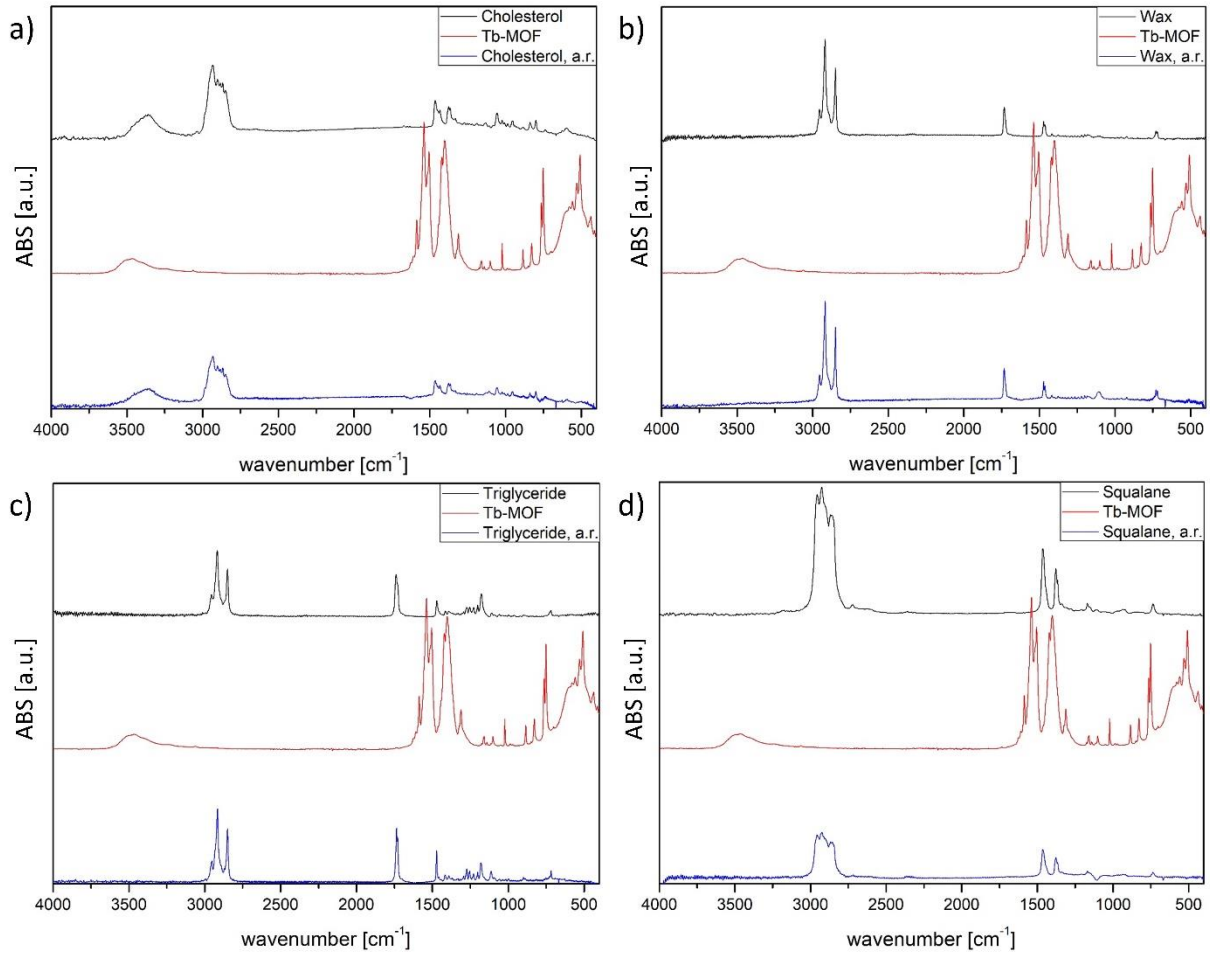


Figure S12. a) FT-IR spectra of cholesterol and cholesterol a. r. . b) FT-IR spectra of wax, Tb-MOF and wax a. r. . c) FT-IR spectra of triglyceride, Tb-MOF and triglyceride a. r. . d) FT-IR spectra of squalene, Tb-MOF and squalene a. r. .

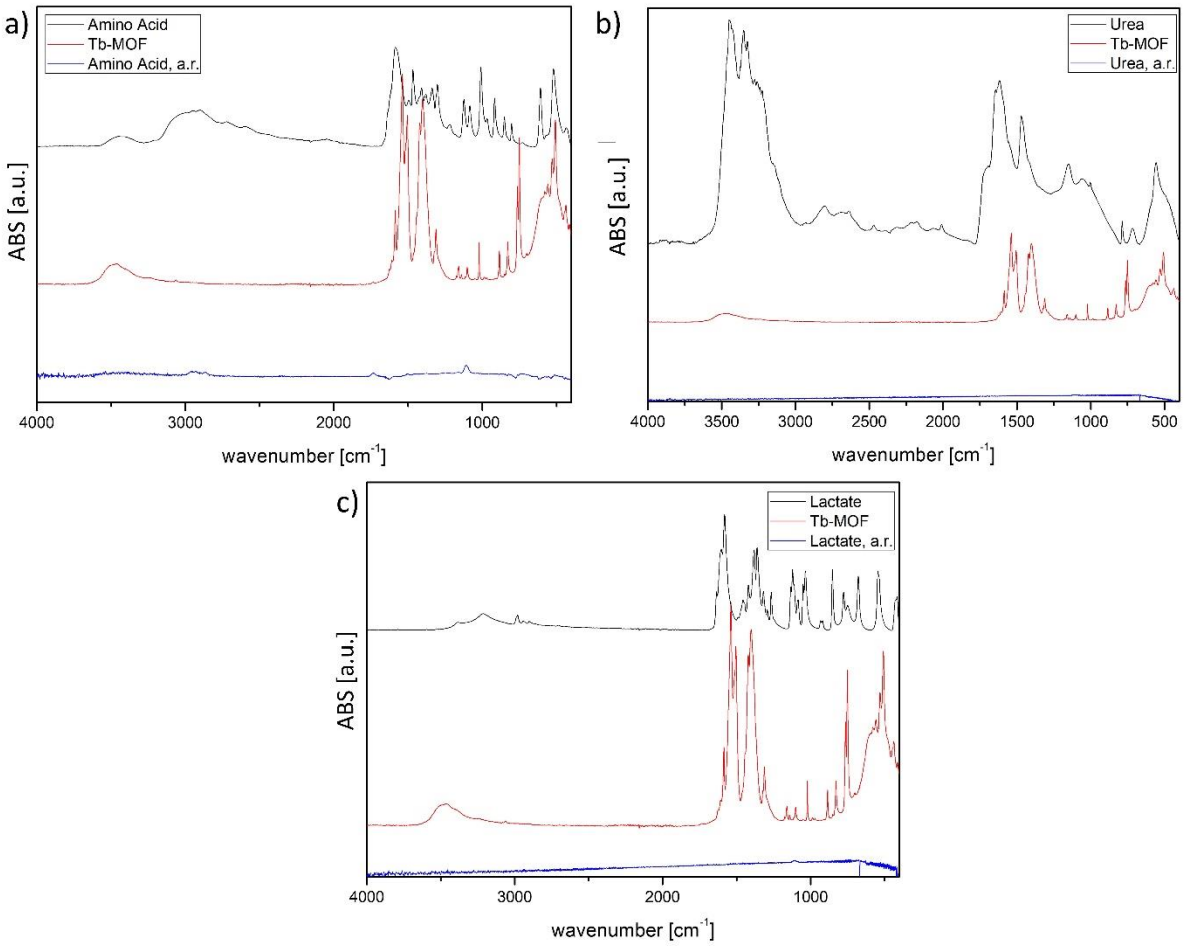
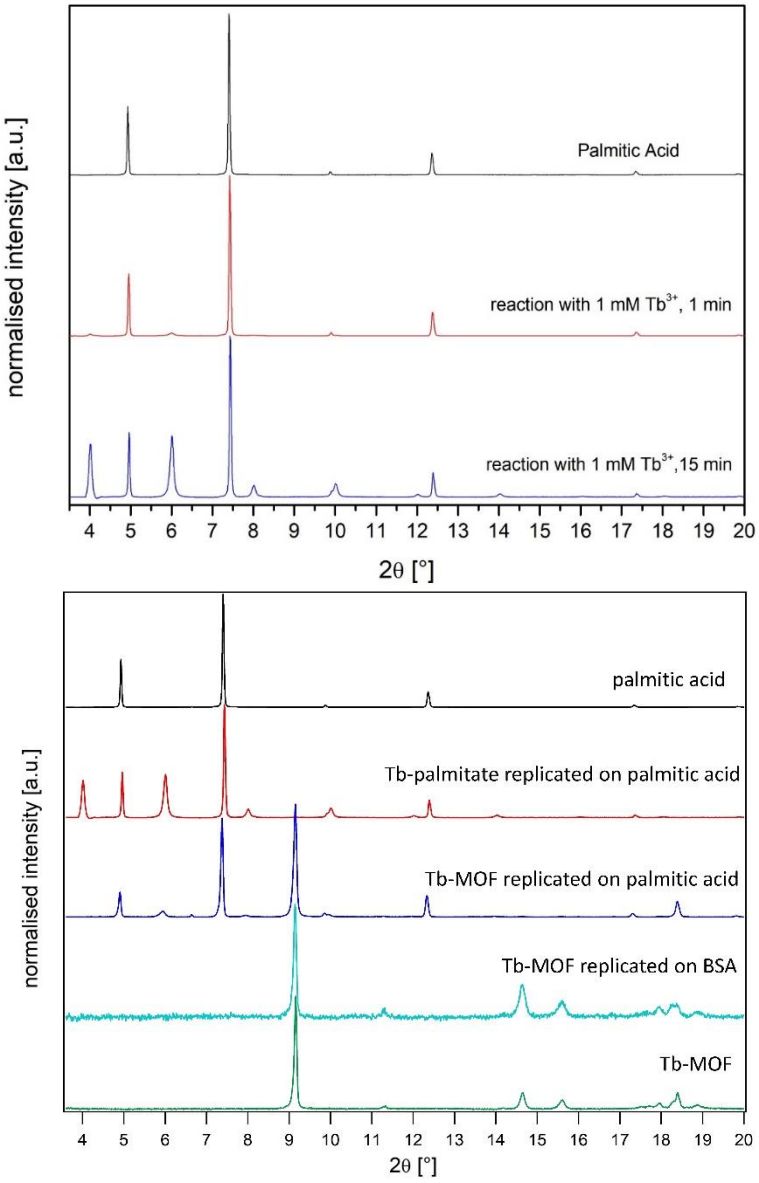


Figure S13. a) FT-IR spectra of amino acid, Tb-MOF and amino acid a. r. . b) FT-IR spectra of urea, Tb-MOF and urea a. r. . c) FT-IR spectra of lactate, Tb-MOF and lactate a. r. .



FigureS14. XRD patterns of the Tb-palmitate transition layer (upper figure) and of palmitic acid, Tb-Palmitate, Tb-MOF, Tb-MOF grown on BSA and on palmitic acid (lower figure).

Fluorescence Microscopy

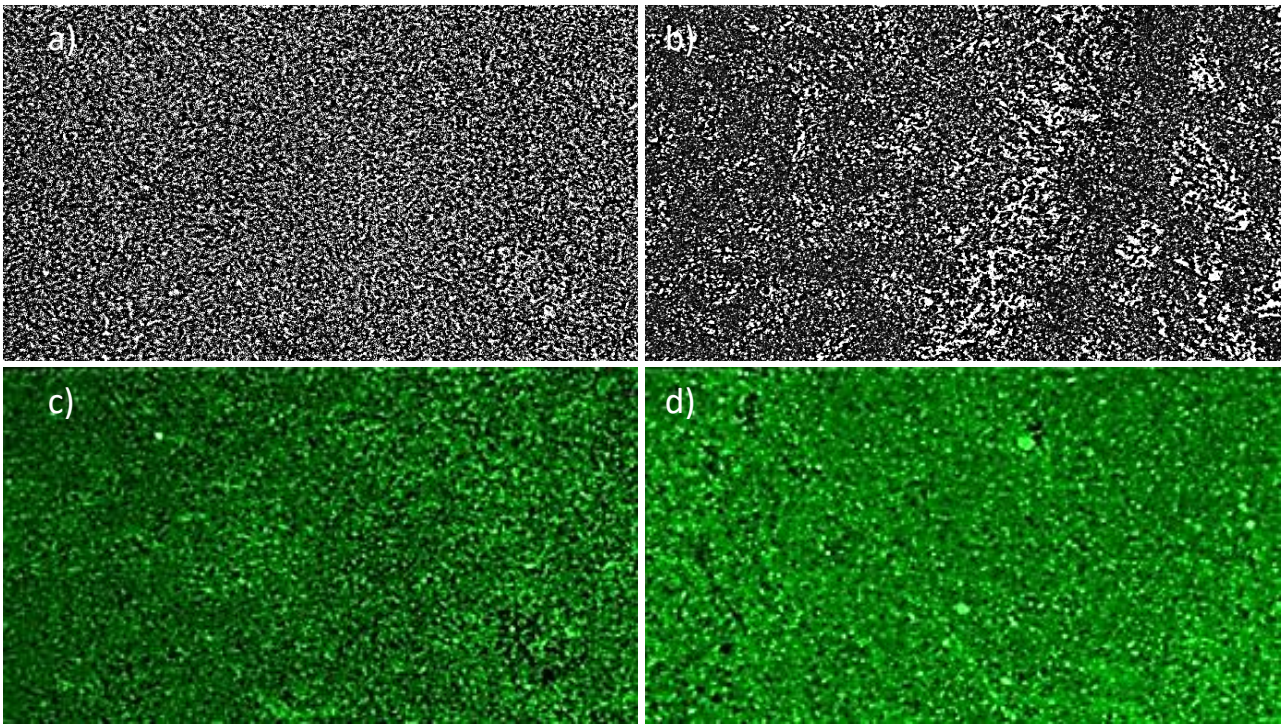


Figure S15. a) Brightfield image of fatty acid a. r. for 1 minute. b) Brightfield image of fatty acid a. r. for 5 minutes. c) Fluorescence image of fatty acid a. r. for 1 minute. d) Fluorescence image of fatty acid a. r. for 5 minutes. Investigated area: 250x150 µm.

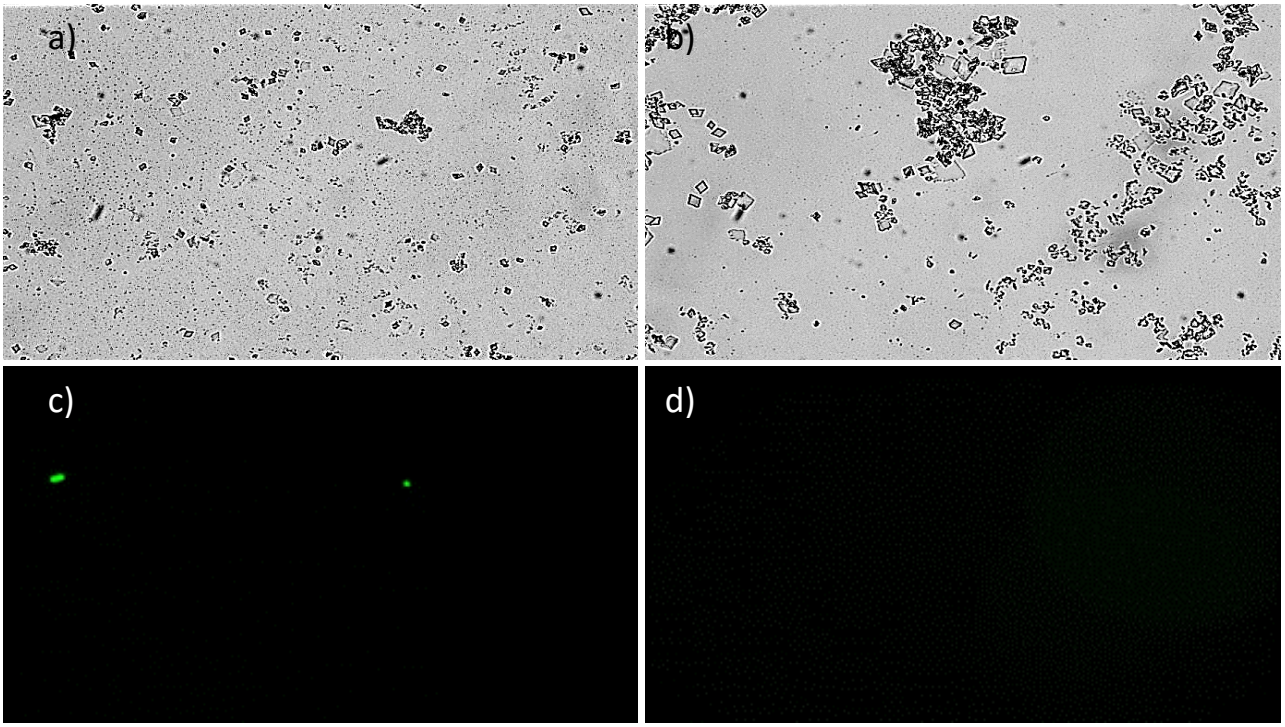


Figure S16. a) Brightfield image of wax a. r. for 1 minute. b) Brightfield image of wax a. r. for 5 minutes. c) Fluorescence image of wax a. r. for 1 minute. d) Fluorescence image of wax a. r. for 5 minutes. Investigated area: 250x150 µm.

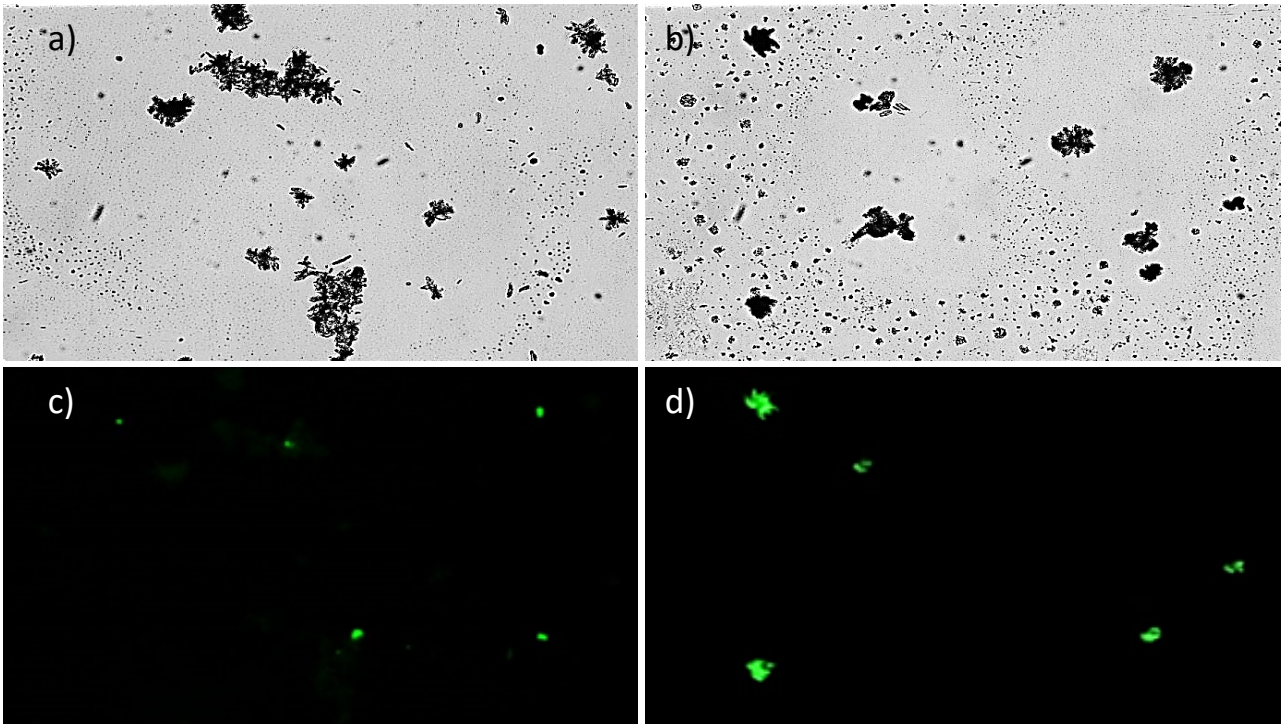


Figure S17. a) Brightfield image of triglyceride a. r. for 1 minute. b) Brightfield image of triglyceride a. r. for 5 minutes. c) Fluorescence image of triglyceride a. r. for 1 minute. d) Fluorescence image of triglyceride a. r. for 5 minutes. Investigated area: 250x150 µm.

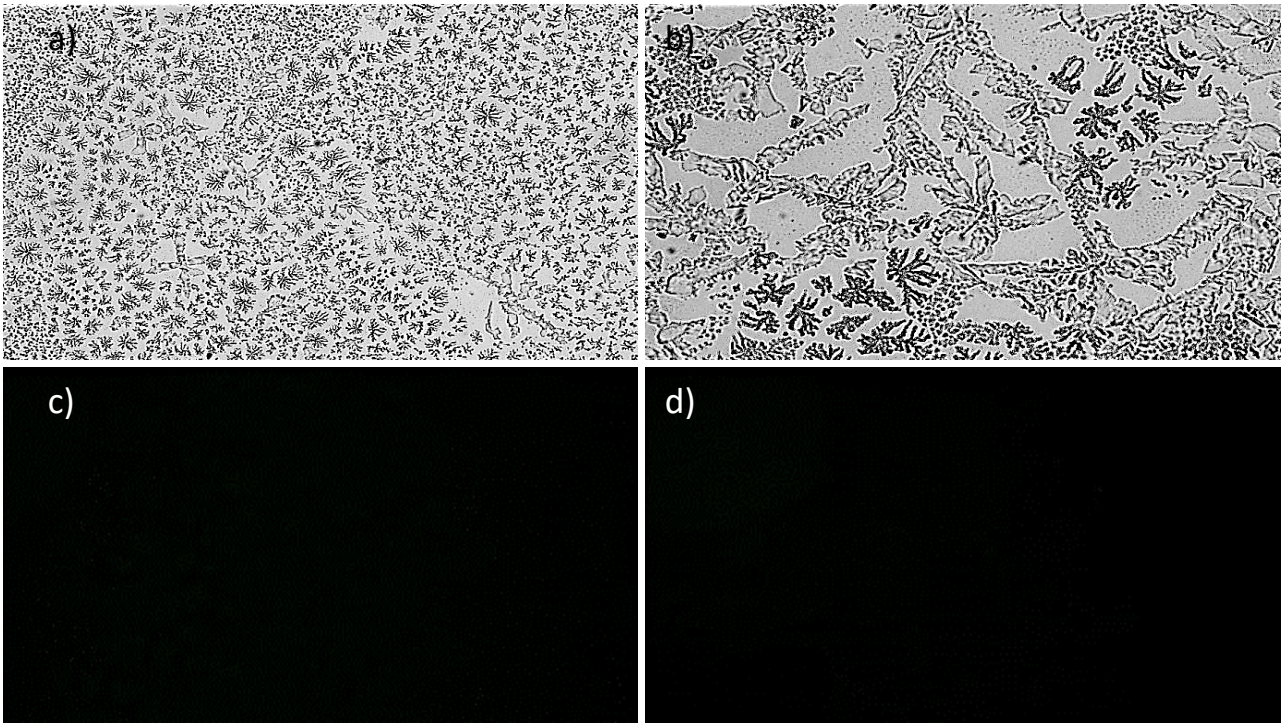


Figure S18. a) Brightfield image of cholesterol a. r. for 1 minute. b) Brightfield image of cholesterol a. r. for 5 minutes. c) Fluorescence image of cholesterol a. r. for 1 minute. d) Fluorescence image of cholesterol a. r. for 5 minutes. Investigated area: 250x150 µm.

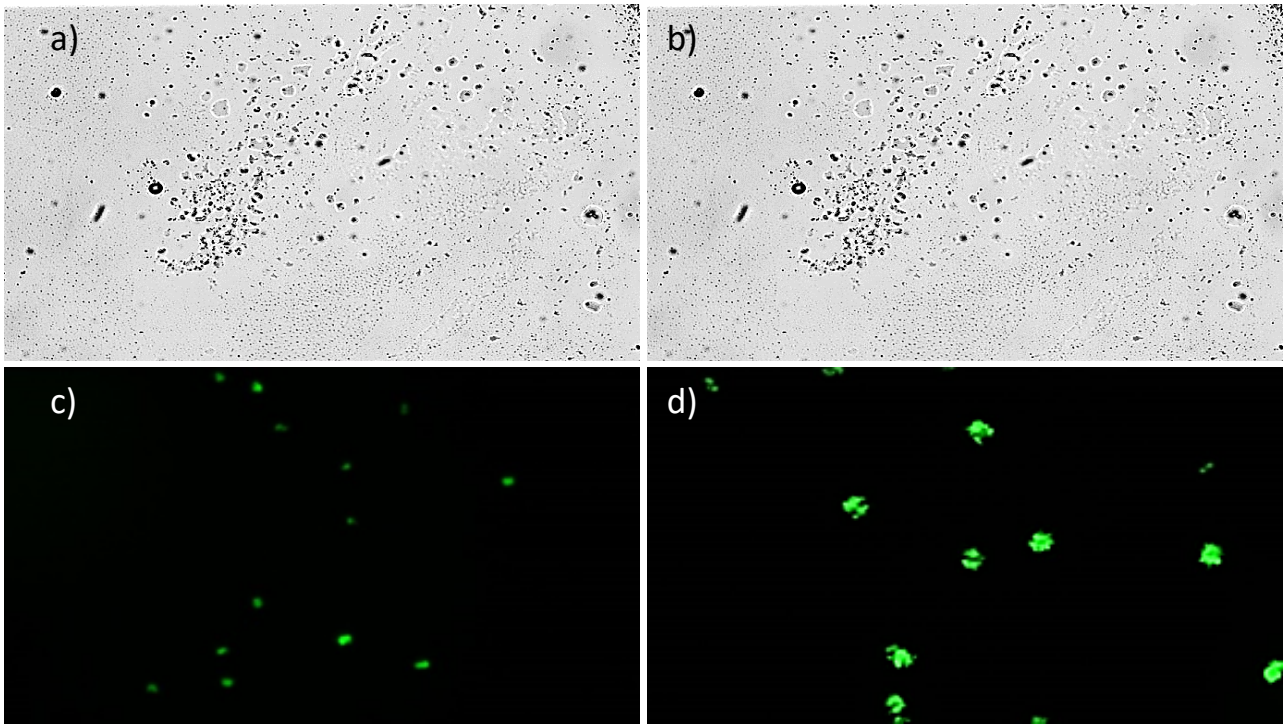


Figure S19. a) Brightfield image of squalane a. r. for 1 minute. b) Brightfield image of squalane a. r. for 5 minutes. c) Fluorescence image of squalane a. r. for 1 minute. d) Fluorescence image of squalane a. r. for 5 minutes. Investigated area: 250x150 µm.

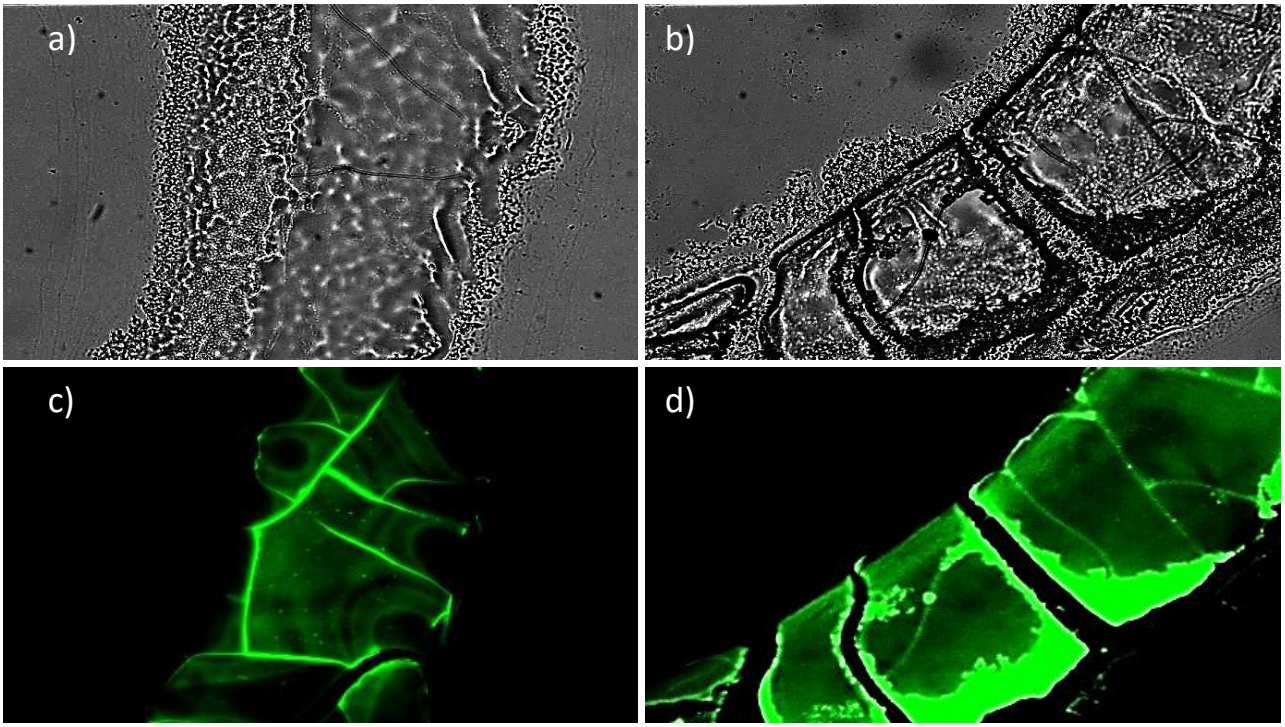


Figure S20. a) Brightfield image of BSA a. r. for 1 minute. b) Brightfield image of BSA a. r. for 5 minutes. c) Fluorescence image of BSA a. r. for 1 minute. d) Fluorescence image of BSA a. r. for 5 minutes. Investigated area: 250x150 µm.

Time evolution of the luminescent signal

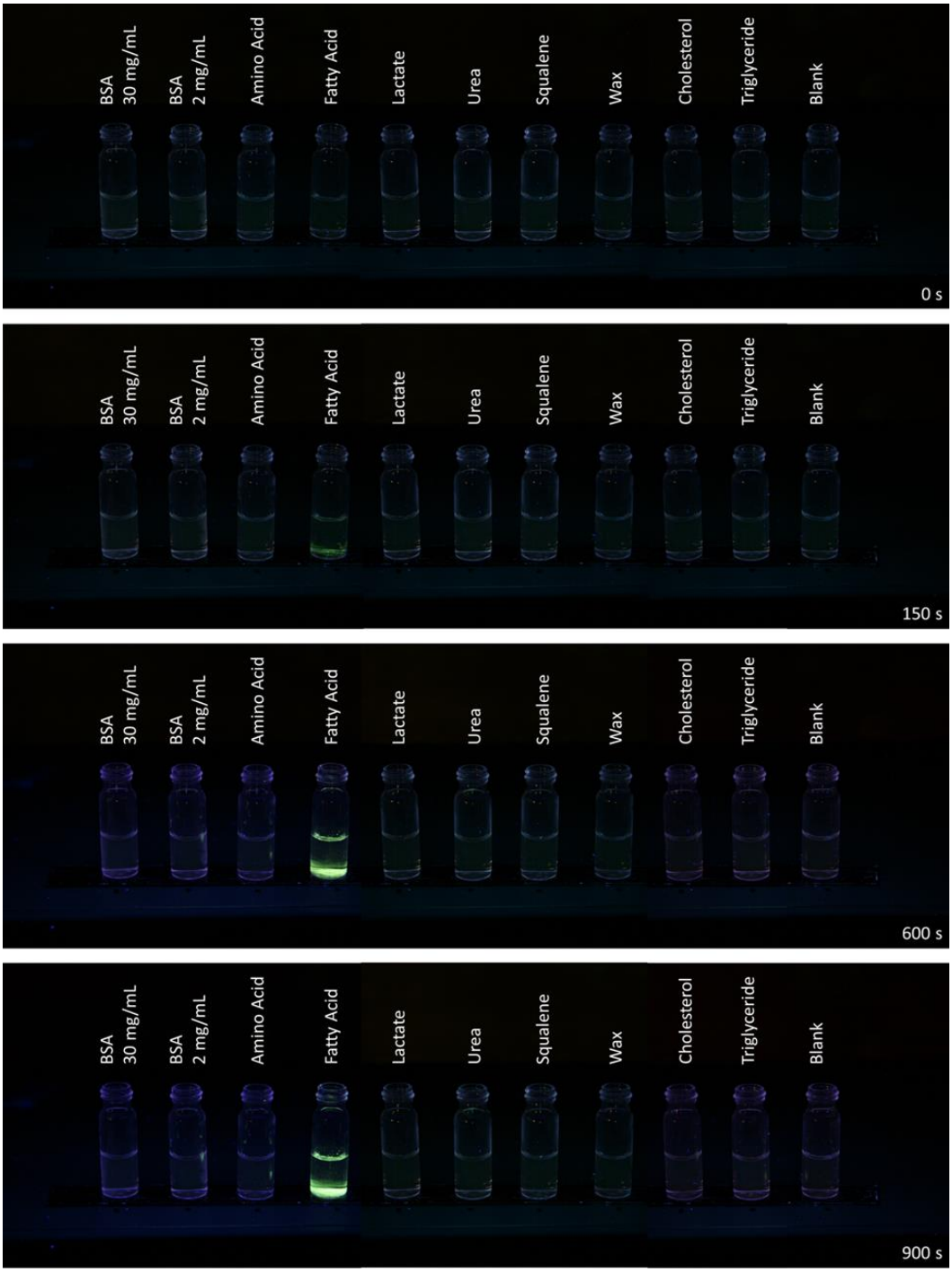


Figure S21. Camera pictures of vials containing a film of the different biomacromolecules on the bottom. To capture the pictures under UV excitation, all the investigated components of the fingerprint residue were drop-cast on the bottom of glass vials, following the same protocol used to perform the screening experiments of Fig. 2. Once the films were dried, the vials were placed under a UV light and a freshly prepared aqueous 1:1 mixture of MOF precursors (5 mM $TbCl_3$ * 6 H_2O, 5 mM Na_2BDC) was added and we started recording a video (video V1). With this time course investigation we clearly prove that only the fatty acid film triggers a detectable crystallization of fluorescent MOF. The pictures were acquired after the addition of the MOF precursors. Laboratory UV lamp (emission range: 325-375 nm; pictures extracted from video V1) was used for the excitation.

Box-plots

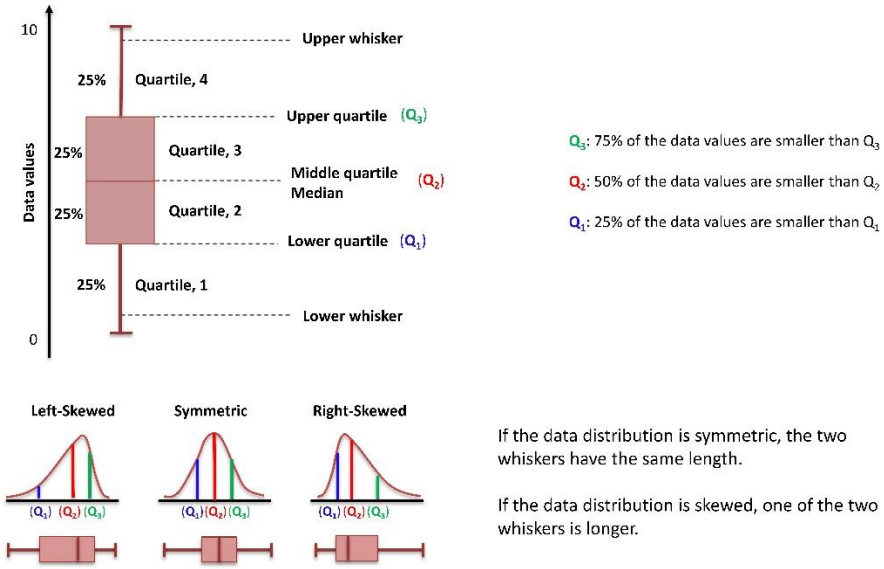


Figure S22. Guideline for the interpretation of a box-plot (e.g. Figure 2b). A boxplot is a graphical tool that visualizes the distribution of the data. The box represents the middle 50% of the data. It extends from the lower quartile (Q_1) to the upper quartile (Q_3) and its width visualizes the Interquartile Range, namely a measure of data variability. The line in the box indicates the median value (Q_2) and it splits the data in two halves. The lines stretching from the box (whiskers) represent the lower and upper 25% of the data.

Scanning Electron Microscopy

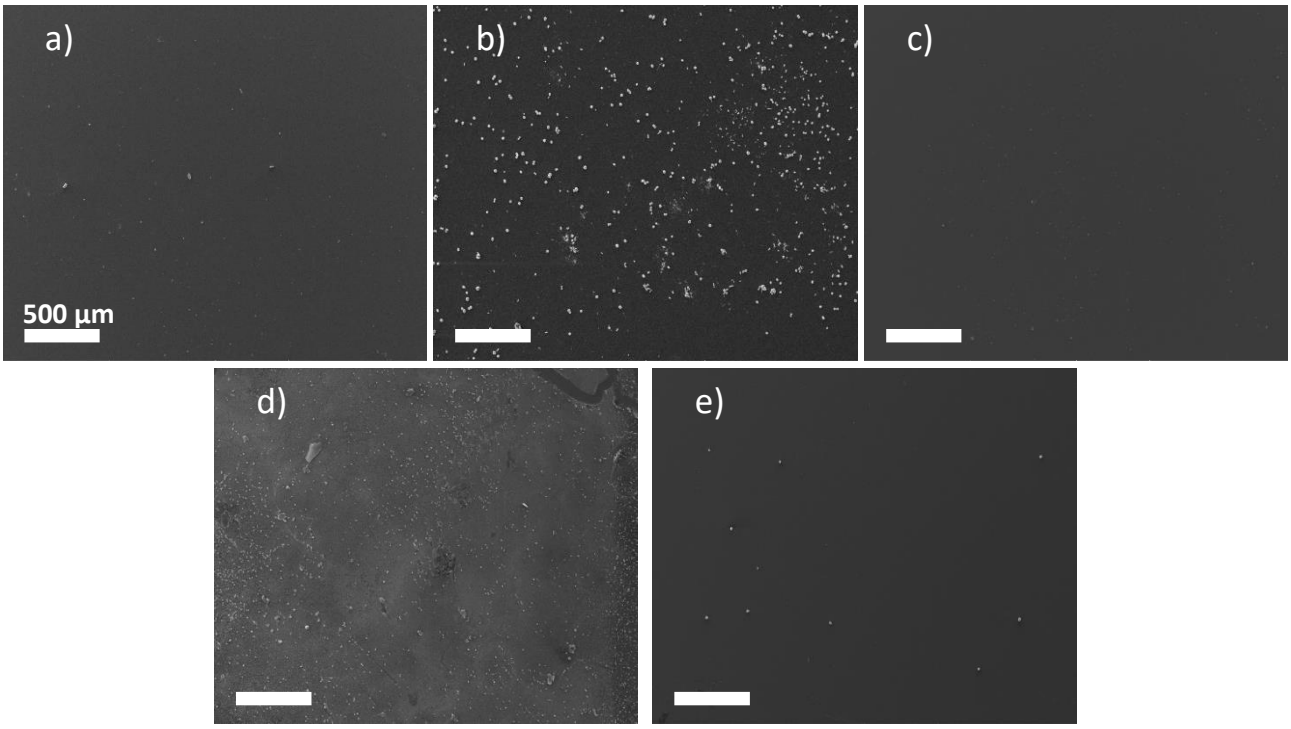


Figure S23. a) SEM image of blank silicon a. r. for 1 min. b) SEM image of amino acid on silicon a. r. for 1 min. c) SEM image of squalane on silicon a. r. for 1 min. d) SEM image of fatty acid on silicon a. r. for 1 min. e) SEM image of BSA on silicon a. r. for 1 min.

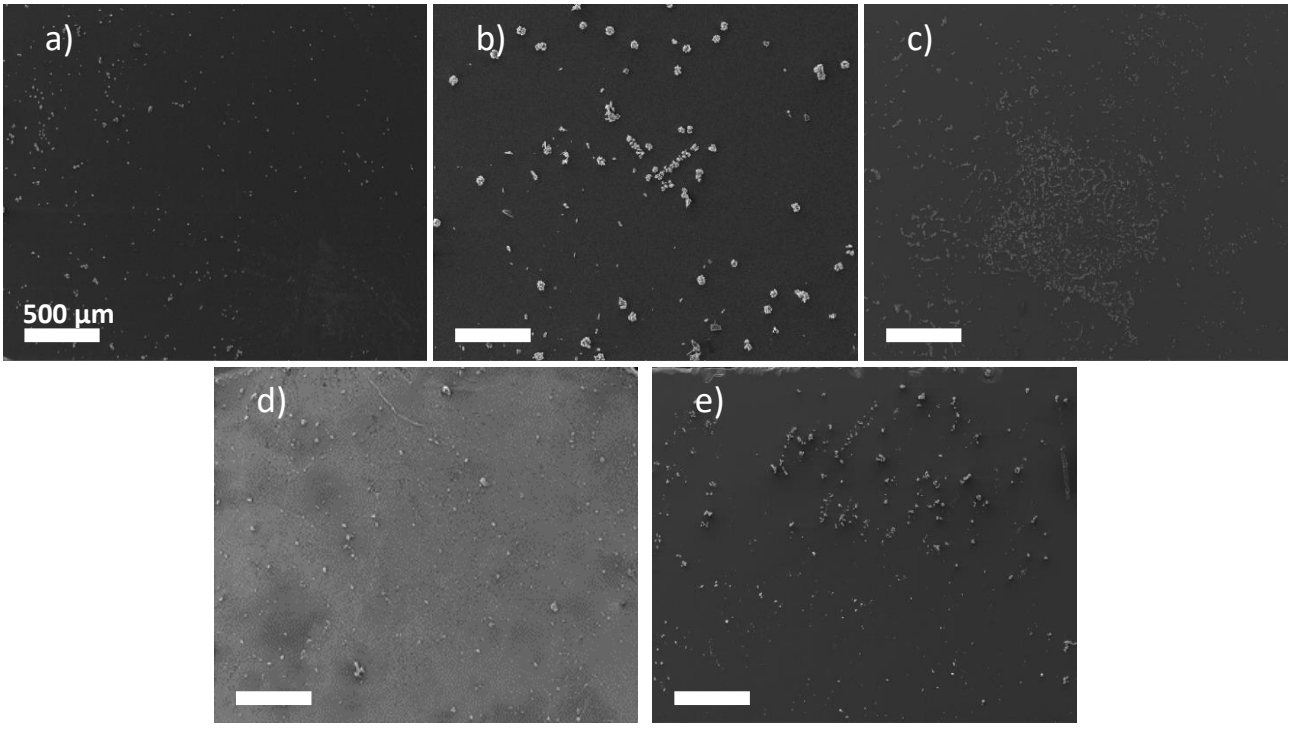


Figure S24. a) SEM image of blank silicon a. r. for 5 min. b) SEM image of amino acid on silicon a. r. for 5 min. c) SEM image of squalane on silicon a. r. for 5 min. d) SEM image of fatty acid on silicon a. r. for 5 min. e) SEM image of BSA on silicon a. r. for 5min.

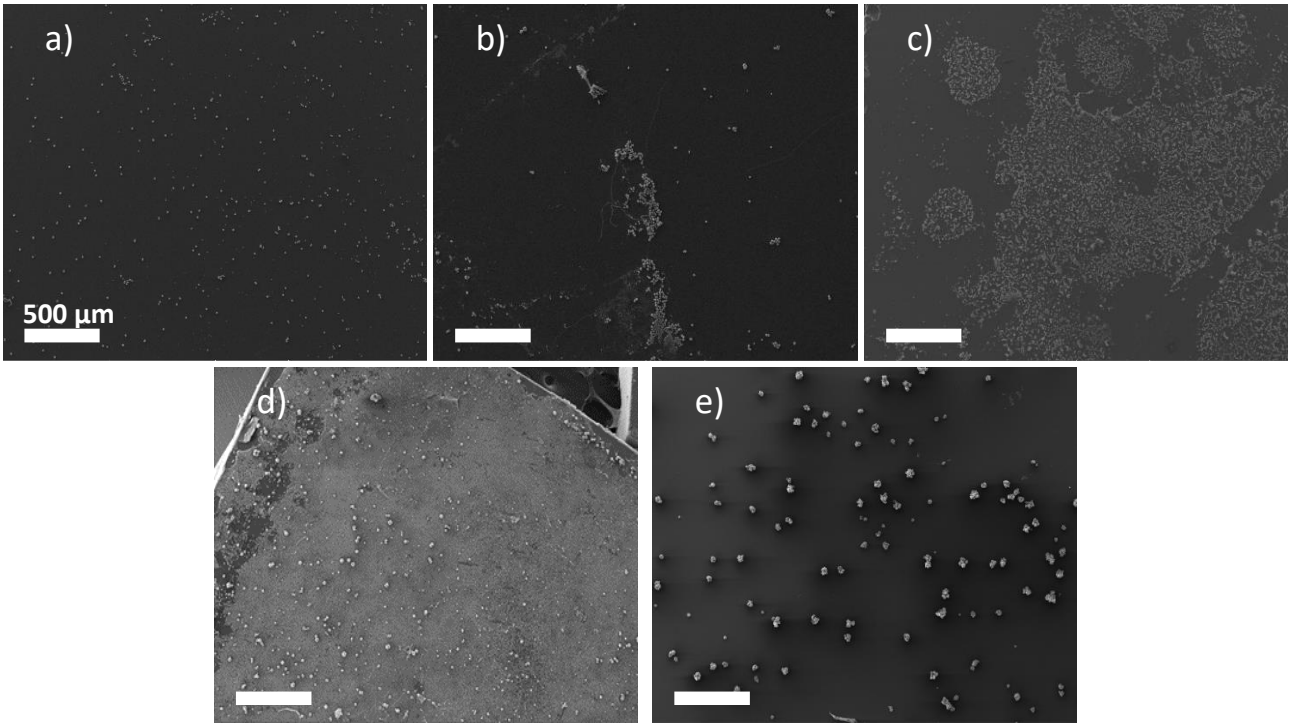


Figure S25. a) SEM image of blank silicon a. r. for 15 min. b) SEM image of amino acid on silicon a. r. for 15 min. c) SEM image of squalane on silicon a. r. for 15 min. d) SEM image of fatty acid on silicon a. r. for 15 min. e) SEM image of BSA on silicon a. r. for 15 min.

Patterning

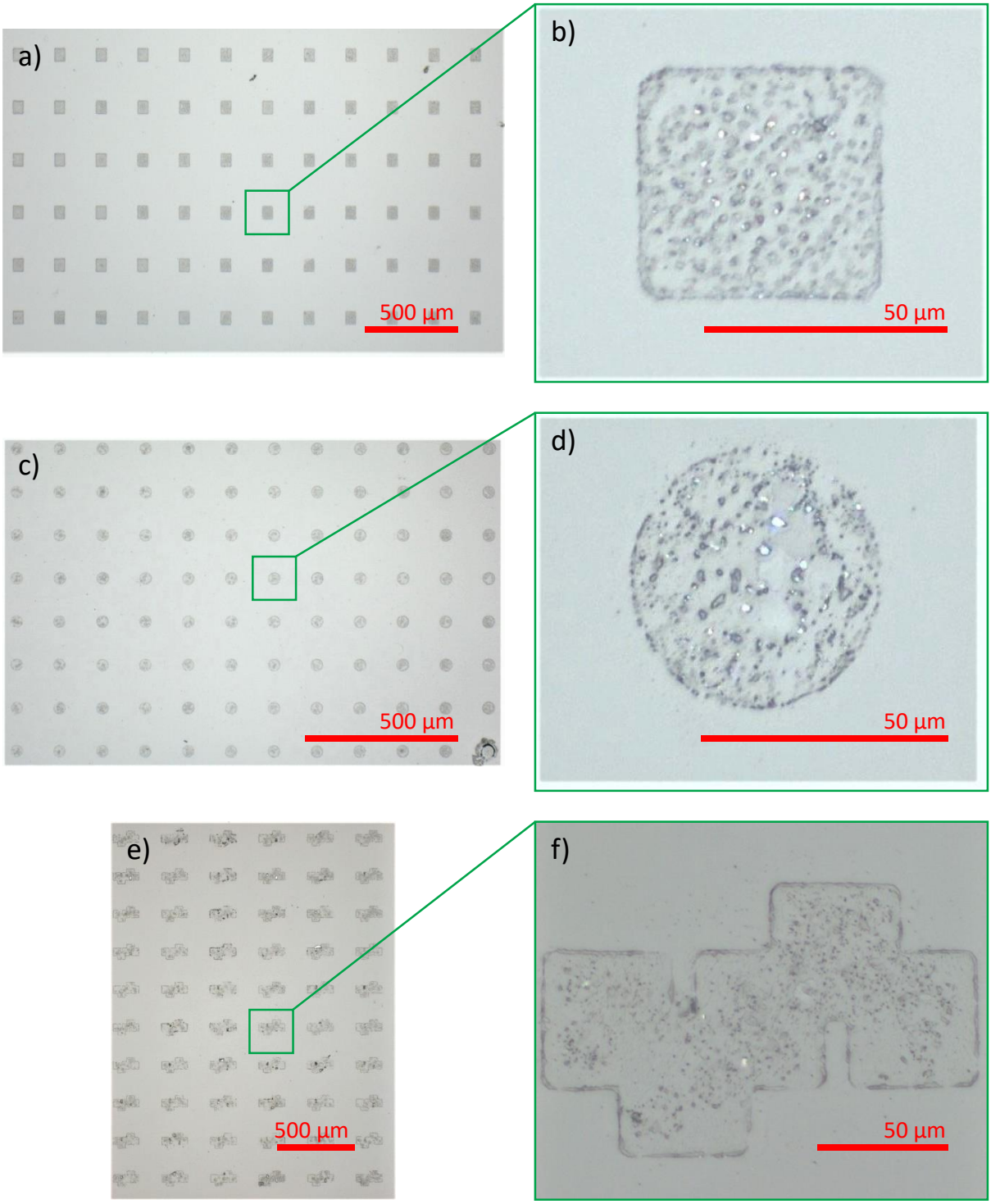


Figure S26. a), b) Optical microscopy image of the fatty acid square patterns printed on glass and their magnification; c), d) Optical microscopy image of the fatty acid in a circle pattern printed on glass and its magnification; e), f) Optical microscopy image of the fatty acid in a *TU Graz* Logo pattern printed on glass and its magnification.

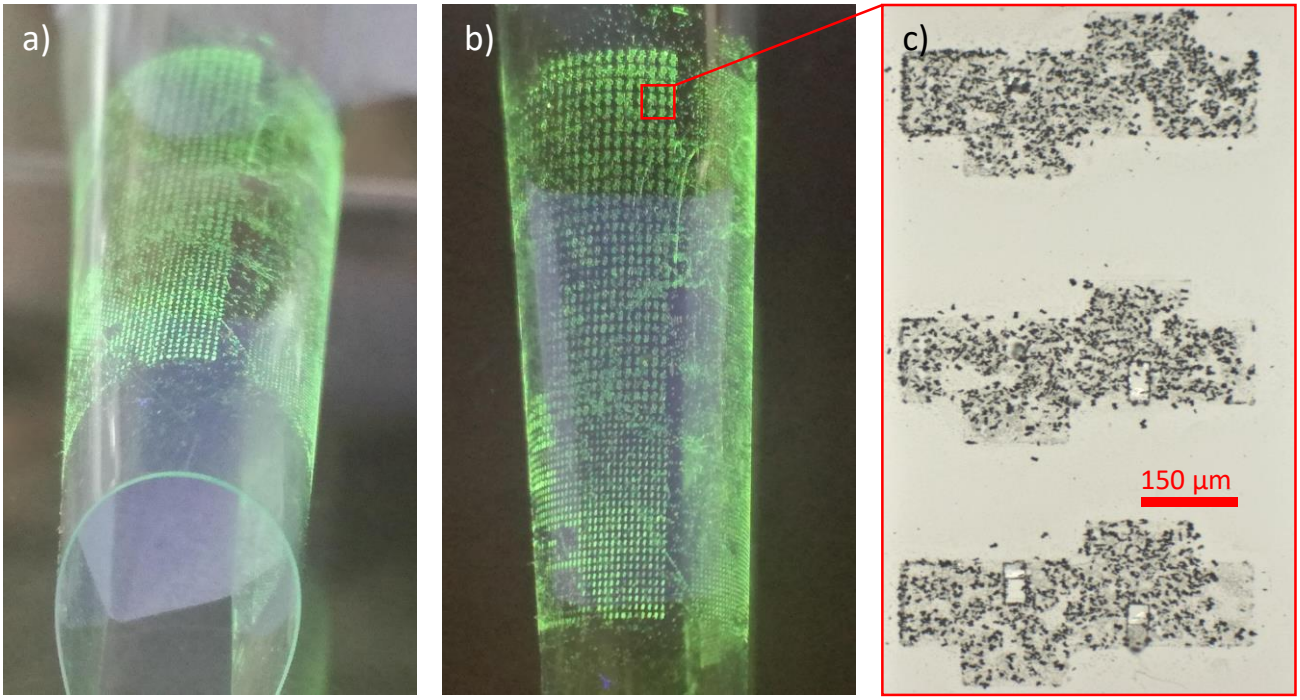


Figure S27. Photographs (a,b) and optical microscopy images (c)of the replicated luminescent Tb-MOF on printed fatty acid in a *TU Graz* pattern under UV light (254 nm) on a flexible PP foil and its magnification.

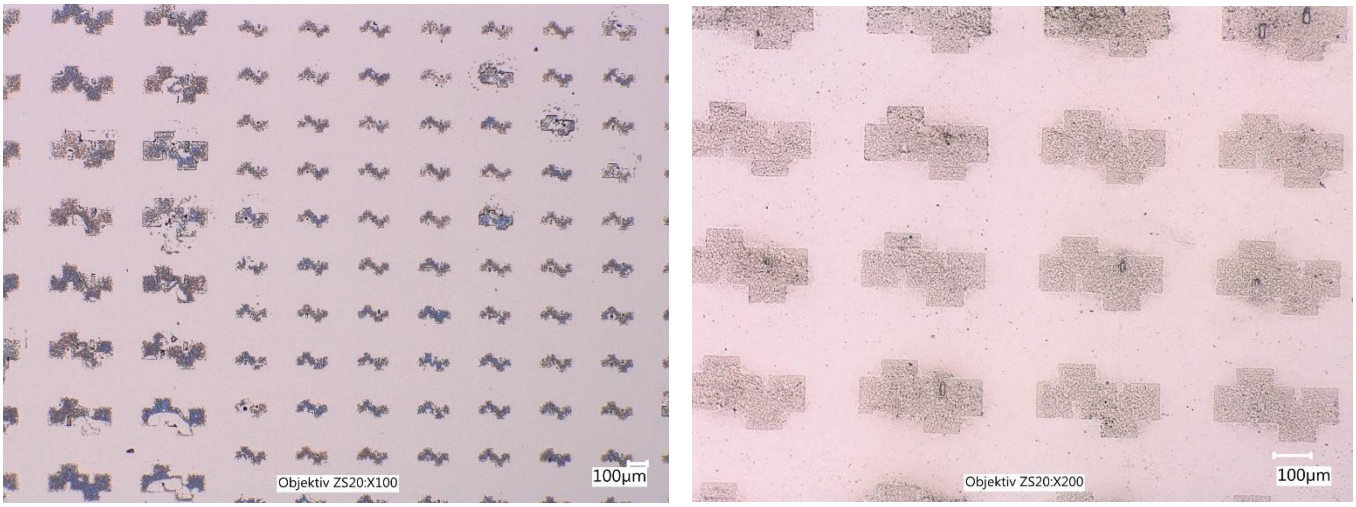


Figure S28. Optical microscopy images of the fatty acid in a *TU Graz* pattern printed on a Si wafer (left) and a polystyrene sheet (right).

Summary of the insoluble substrates tested in this work

In our study, fatty acids - either as pure films or as insoluble component of fingerprints - were benchmarked against several non-soluble bulks materials (Table S1):

Table S1

	Non-soluble bulk materials:	solubility	Luminescence signal from a MOF film (**fatty acid=strong**)
1)	Silica (SiO_2)	Insoluble in water	Weak (See figure S3d)
2)	Silicon (Si)	Insoluble in water	Very weak - absent
3)	Polypropylene (PP)	Insoluble in water	Very weak - absent
4)	High density Polyethylene (HDPE)	Insoluble in water	Very weak – absent
5)	Polystyrene (PS)	Insoluble in water	Very weak – absent
	Non-soluble film materials:		
6)	trimyristin	Insoluble in water	Very weak - absent
7)	palmityl palmitate	Insoluble in water	Very weak - absent
8)	squalane	Insoluble in water	Very weak - absent
	Chemically functionalized non-soluble film materials:	solubility	Luminescence signal from a MOF film (**fatty acid=strong**)
9)	COOH-functionalised Si	Insoluble in water	Strong
10)	OH-functionalised Si	Insoluble in water	Weak
11)	Vinyl-functionalised Si	Insoluble in water	Very weak – absent
12)	CH_3-functionalised Si	Insoluble in water	Very weak – absent

From this examination we conclude that a film that can promote the MOF crystal growth must possess: 1) affinity for cations and 2) low solubility in water.

Examples of the influence of MOF precursors and biomacromolecules solubility on the biomimetic replication process

The choice of the solvent influences the solubility of the MOF precursors and of the biomacromolecules according to the tables below (Tables S2-S3).

Table S2

	Solvent: **Water**		
	Biomolecule	MOF precursors	Biomimetic replication
Fatty acid	insoluble	soluble	**successful**
Triglyceride	insoluble	soluble	unsuccessful
Protein	soluble	soluble	unsuccessful

Table S3

	Apolar solvents (ethyl acetate, Chloroform)		
	Biomolecule	MOF precursors	Biomimetic replication
Fatty acid	soluble	insoluble	unsuccessful
Triglyceride	soluble	insoluble	unsuccessful
Protein	insoluble	insoluble	unsuccessful

Here we illustrate the biomimetic replication experiments performed in water and solvents that have medium and high solubility for both palmitic acid and trimyristin such as ethyl acetate and chloroform (solubility data are summarized in Tables S4 and S5). Palmitic acid and trimyristin were chosen as biomolecules since they form insoluble films in water.

Table S4

Biomolecule	**Solvent**		
	Water	Ethyl acetate	Chloroform
Palmitic acid (FA)[a]	insoluble	6.1 g/100g solvent	15.1 g/100g solvent
Trimyristin (TRI)[b]	insoluble	7.51 g/100g solvent	34.32 g/100g solvent

[a] C. W. HOERR, A. W. Ralston, J. Org. Chem. 1944, 09, 329–337.
[b] K. Loskit, Z. Phys. Chem 1928, 134U, 135–155.

Table S5

MOF-precursors	**Solvent**		
	Water	Ethyl acetate	Chloroform
$TbCl_3$ * 6 H_2O [a]	Soluble	insoluble	insoluble
Disodium terephthalate	14 g/100g solvent [b]	insoluble	insoluble

[a] David R. Lide: CRC Handbook of Chemistry and Physics, 87th Edition. 2006, ISBN 978-0-8493-0487-3, S. 4–88.
[b] Wallace, Franklin D., and John C. Carr. "Removal of dissolved disodium terephthalate from aqueous solution also containing sodium hydroxide." U.S. Patent No. 4,215,224. 29 Jul. 1980.

The films of palmitic acid and trimyristin on Si (1 cm^2) were prepared starting from the same amount of precursors used for Fig. S3. Following the same experimental procedure, the films were exposed to a freshly prepared 1:1 mixture of MOF precursors (5 mM $TbCl_3$ * 6 H_2O, 5 mM Na_2BDC) in the different solvents for the following reaction times: 30 s, 1 min, and 5 min. Subsequently, the wafers were washed with water and dried under an air flow. Pictures were taken in a dark room under UV light (254 nm) and are reported in Fig. S29. As control, the same experiment was performed using a clean Si piece (sample NO). After conversion, the luminescence of the MOF was observed only from the samples converted in water. Indeed, the use of ethyl acetate and chloroform:

1) rapidly decompose the films based on palmitic acid and trimyristin;
2) inhibits the dissolution of the MOF precursors.[1]

To further verify that apolar solvents would prevent the formation of the Tb-MOF, we performed the reaction in an optical glass cuvette while monitoring the luminescence signal with a Fluorolog 3 spectrofluorometer (HORIBA Scientific, excitation: 290 nm; emission: 545 nm). From this experiment, we confirmed that only when water is used as a solvent, it is possible to detect an intense luminescent signal (Fig. S30).

In summary, the modification of the current process to make other fingerprint components (biomolecules) useful for biomimetic replication does not seem a trivial task. Based on the solubility and the experimental data, apolar solvents do not lead to the solubilization of the Tb-MOF precursors. The condition that leads to the solubilization of the MOF precursors, while keeping the biomolecule-based film intact is satisfied by using water as a solvent.

[1] Visually, it is possible to observe that the MOF precursors do not quantitatively dissolve in chloroform and ethyl acetate. For example, while the solubility of both FA and TRI are high in chloroform, the BDC ligand is insoluble. The same is true for the Tb salt.

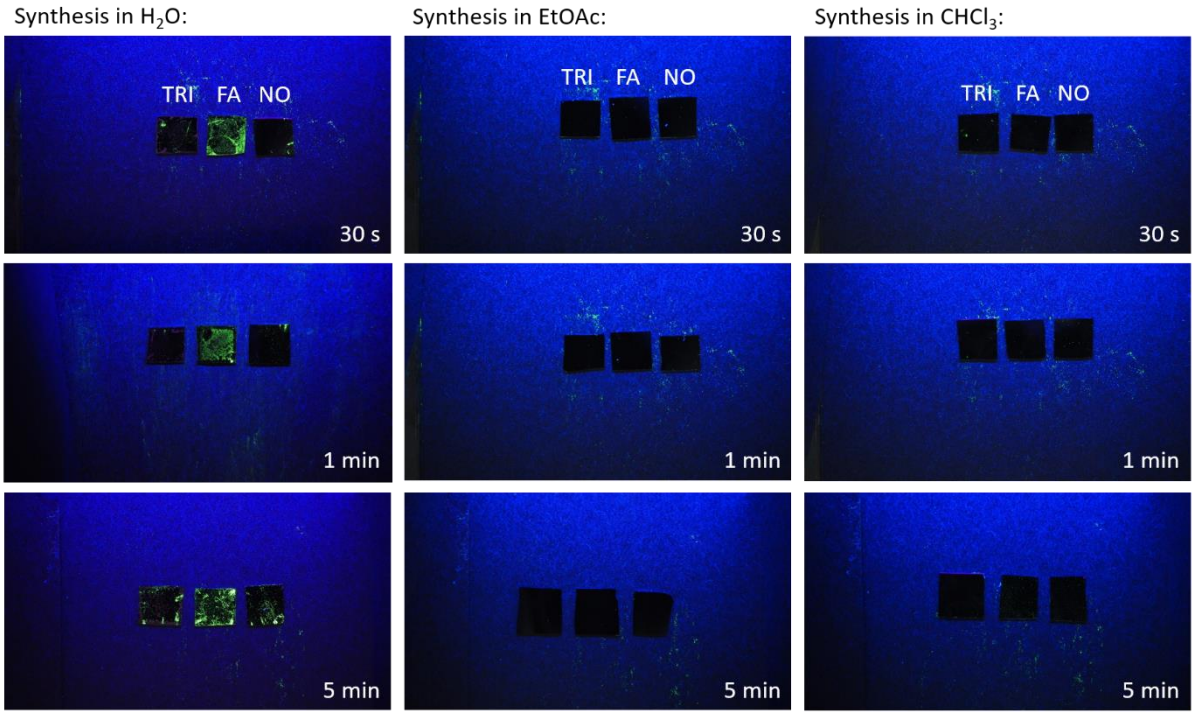


Figure S29: Pictures of the triglyceride (TRI) and fatty acid (FA) films on Si and of a blank (NO, clean Si) after the exposure to Tb-MOF precursors in different solvents (water, ethyl acetate and chloroform) for different time (30s, 1 min and 5 min). The pictures were acquired under UV light (254 nm).

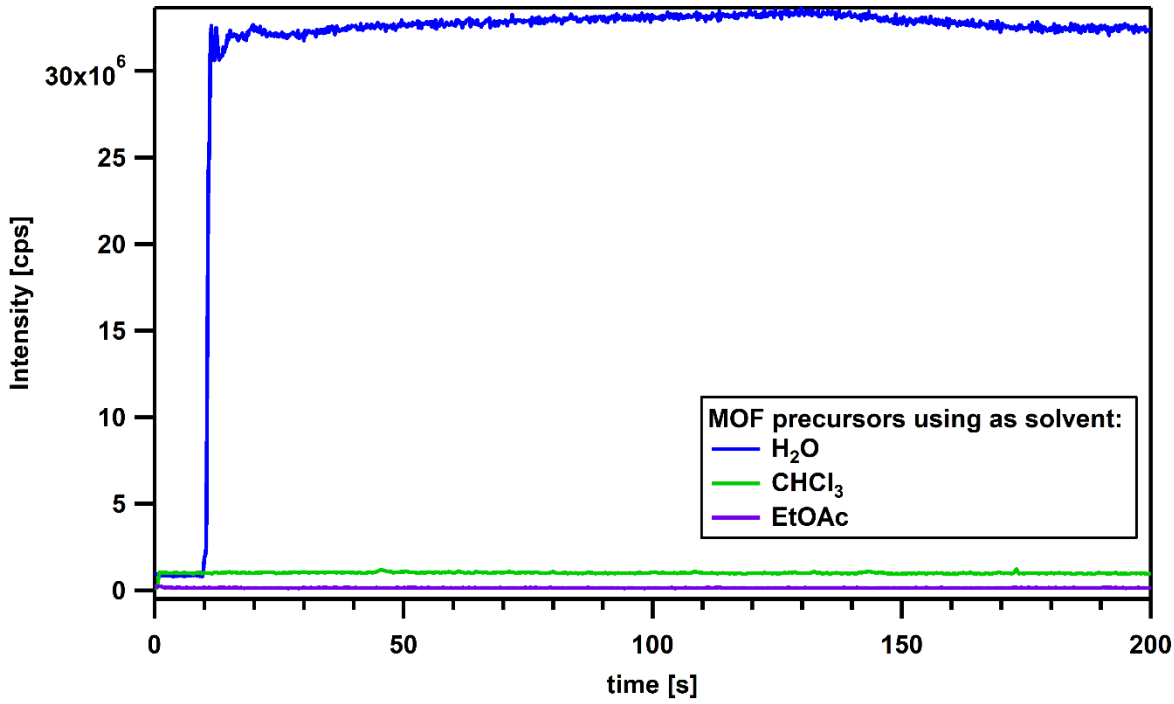


Figure S30: Time dependency of luminescence intensity originating from Tb3+ (λex 290 nm, λem 545 nm) upon mixing of precursors in an optical glass cuvette.

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