Supporting information

Nanopatterning of Mobile Lipid Monolayers on Electron-Beam-Sculpted Teflon AF Surfaces

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SI 1. Contact angle measurements

We have characterized electron beam irradiated Teflon AF by means of contact angle measurements. A decrease from 118 ° to 94° for as-spun and irradiated Teflon AF surfaces, respectively, was measured. **Figure S1** shows photographs of water droplets on the two surfaces, which were used to determine the contact angles.

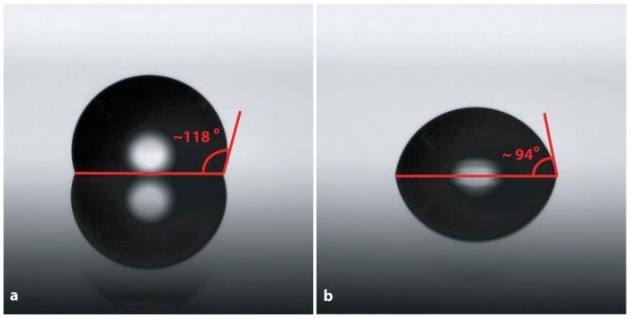

Figure S1: Water contact angles on **a)** Teflon AF, **b)** on e-beam exposed Teflon AF

SI 2. XPS spectra

XPS spectra were recorded with a focus on the carbon and oxygen binding energies. The occurrence of new binding energy peaks suggests structural modifications in the polymer following e-beam irradiation. In comparison with unexposed Teflon AF (Figure S2a and b), the oxygen spectrum of exposed Teflon AF (Figure S2c and d) shows the appearance of a peak around 533 eV on the low energy side of the C-O peak, suggesting the formation of a small amount C=O double bonds between C and O species. This implies the existence of electronegative functional groups in irradiated fluoropolymer.

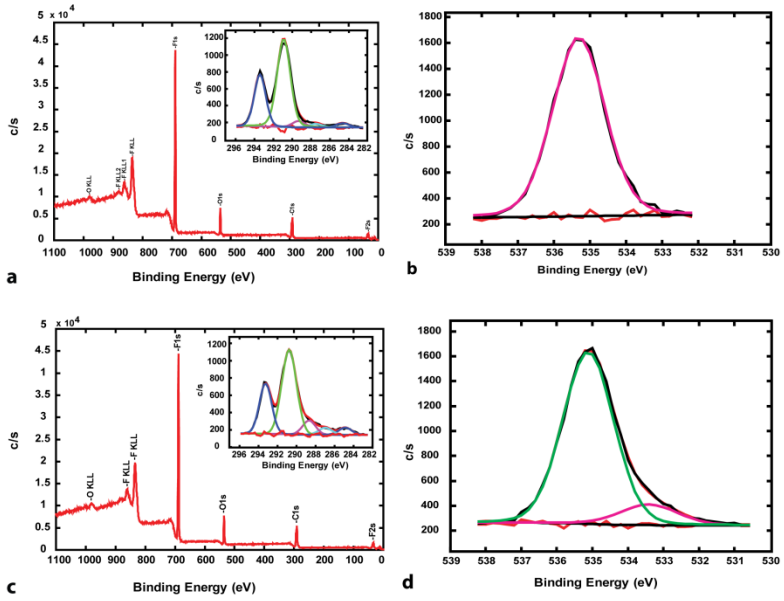

Figure S2: a) Carbon XPS spectra of unmodified Teflon AF. b) Oxygen XPS analysis of unmodified Teflon AF. c) Carbon XPS spectra of e-beam irradiated Teflon AF. d) Oxygen XPS analysis of e-beam irradiated Teflon AF.

SI 3. E-beam exposure dose and frame integrity

Additional experimental data, illustrating the dependency of frame integrity on the exposure dose and the width of the frame.

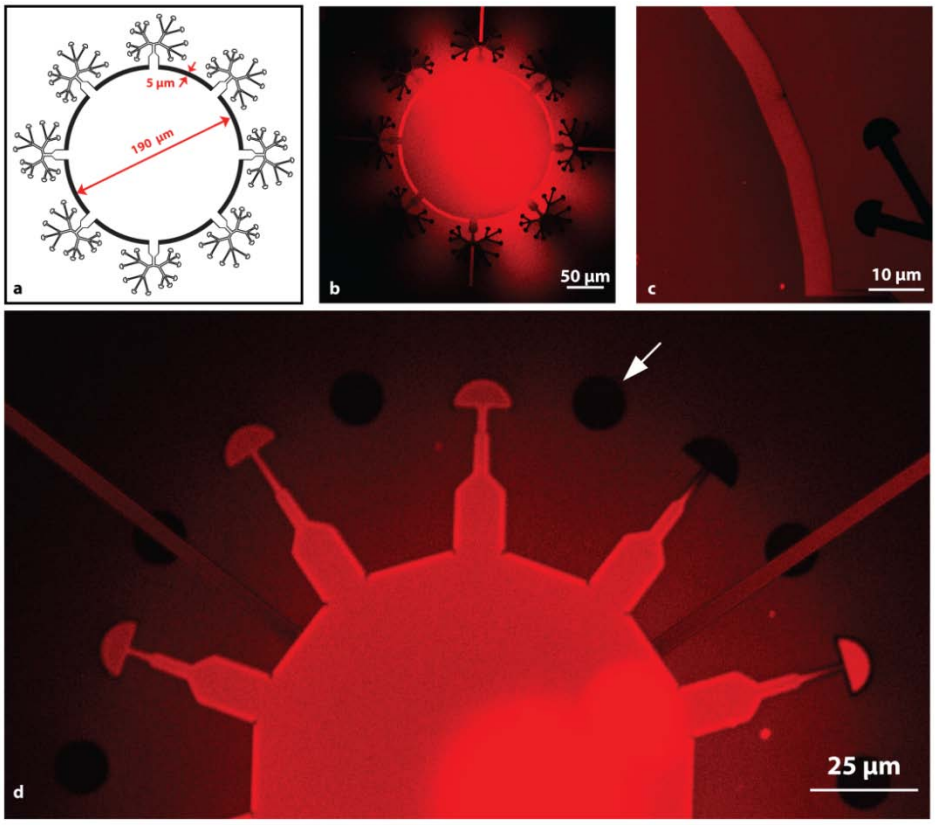

Figure S3: **a-c)** Lipid leakage on a pattern with 4 nm deep trenches (obtained by exposure of a 5 µm wide frame with a dose of 375 µC cm^{-2}), **a)** Pattern layout. The circular deposition area is 200 µm (190 µm + 2x5 µm frame width) in diameter. **b)** Spreading progress after 10 min. Under these conditions the lipid film crosses over the exposed areas faster than it reaches the terminating collection pools at the end of the lanes **c)** Detail of the barrier. The fluorescence intensity of the barrier is 1.5 times higher than the intensity in the spreading film, **d)** The white arrow points to one of several circular control areas, which consist of unexposed patches surrounded by a 1 µm exposed border. The control confirms by the absence of fluorescence signal inside the circular region that the lipid material outside the deposition area covers the surface through the spreading process (across the barrier), and not via through-solution transport.

SI 4. Roughness studies of Teflon AF and e-beam exposed Teflon AF

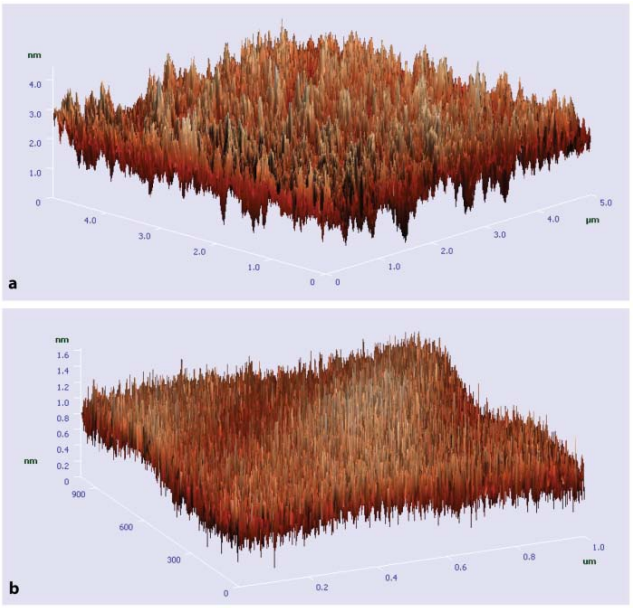

Figure S4: AFM images of Teflon AF surfaces roughness before and after exposure to e-beam radiation, **a)** Unexposed Teflon AF, **b)** Exposed Teflon AF. The exposed area has a 3x reduced surface roughness.

SI 5. Fluorescence Recovery After Photobleaching (FRAP)

To compare the spreading behavior of monolayer lipid on Teflon AF and e-beam exposed Teflon AF, a FRAP experiment has been performed in the exposed frame region. As it is seen in **figure S5 a and b,** fluorescence recovery occurs much more rapidly on unexposed Teflon (time window 3min). The diffusion constant $D_{\text{Teflon AF}}$ is in accordance with the earlier determined value of 0.8 $\mu m^2/s$ (FRAP).

Another independent FRAP experiment exclusively on the exposed area shows region-dependent differences in recovery rate. The source of recovery is mainly the interface to the lipid reservoir (right edge) **(Figure S5 c and d).**

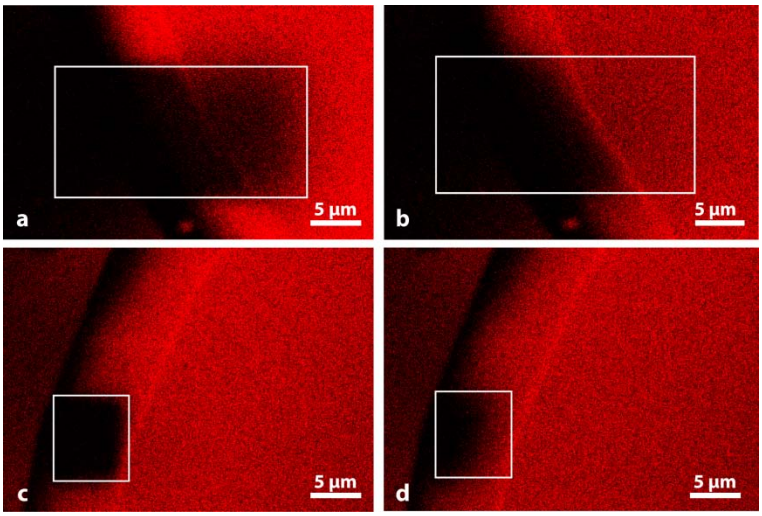

Figure S5: Confocal images of two exemplary FRAP experiments. **a-b)** demonstrating faster recovery on unbleached Teflon vs exposed edge, where time between (a) and (b) is 3 minutes. **c-d)** showing different recovery rate in radil *vs.* axial direction, where time between (c) and (d) is 6 minutes.

The spreading of the lipid film and its average self-diffusion coefficient on the e-beam exposed frame have been investigated by selecting a “FRAP area, as well as a “spreading reference”, and an “intensity reference” of identical dimensions **(Figure S6a)**. Before bleaching, an intensity profile in the “FRAP area” has been measured, which is used as a reference for the initial lipid distribution. The intensity profile has been monitored in the radial and tangential directions (within respect to the spreading front and the circular geometry of the framed spreading area).

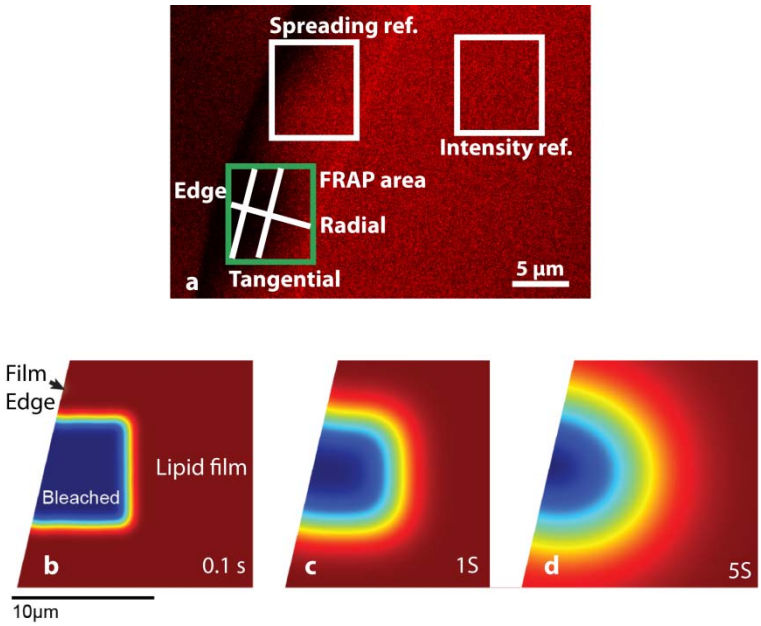

Figure S6: Processing of experimental data. **a)** The intensity has been normalized against bulk lipid film (“Intensity ref.”) and intensity profiles along the radial and tangential direction of the border line in “Spreading ref” area have been monitored at the same time during fluorescence recovery. “Spreading ref” represents an area similarly located as “FRAP area” on the exposed frame, but is not bleached. **b-d)** Recovery simulation (COMSOL 4.1 and “Transport of Dilute Species (chds)” in 2D). The three sides of the FRAP area are connected with a larger lipid film and one is an isolated boundary. The diffusion constant is calculated using the ratio of the initial temporal slopes of normalized integral (spatial) intensities from experiments and simulations, where the diffusion constant of the simulation is $\mathbf{D = 1\ \mu m^2/s}$.

By monitoring the integral intensity change during recovery in the "FRAP area", using the ratio of initial slope of the normalized curve as 0.000471, the average diffusion constant can be calculated as D= 0.0017 $\mu m^2/s$ **(Figure 7C)**. This result is compared with the simulated model of recovery at the same area using COMSOL. **(Figure 6d)** where the relative intensity is calculated as 0.28, giving the average diffusion constant $as\ D = 0.0017\ \ \mu m^2 s^{-1}$ **(Figure 7D)**. Note that this diffusion constant is significantly lower than the value for a monolayer on unexposed Teflon AF.

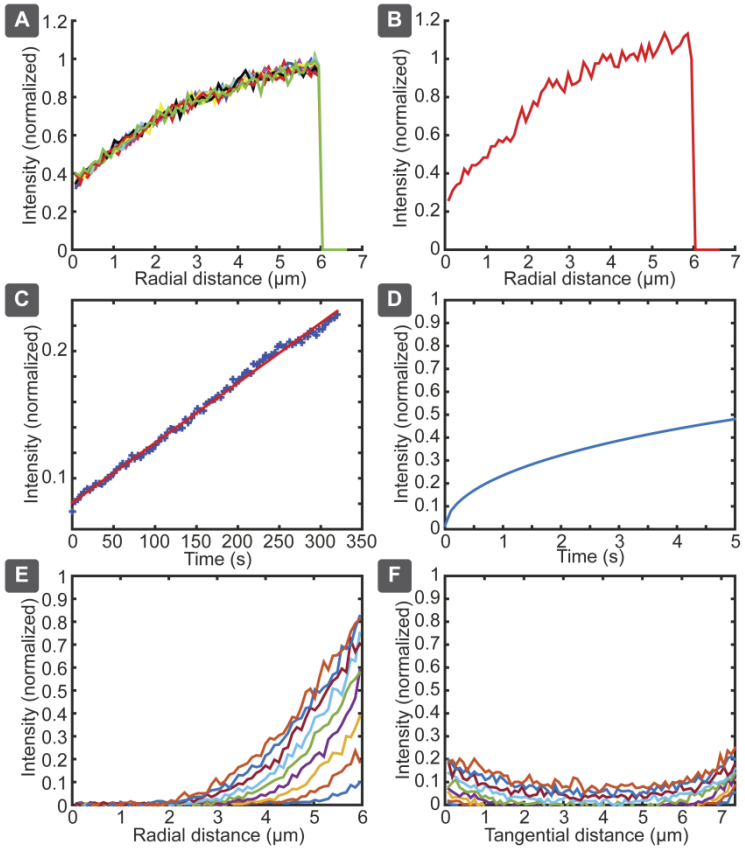

Figure S7: A) Radial fluorescence intensity profile in "Spreading ref" area. The 9 curves represent different time points (time-step 36s) **B)** Initial radial fluorescence profile in the "FRAP area", **C)** Experimental integral fluorescence intensity change during recovery in "FRAP area". The intensity has been normalized. Slope: 0.000471 s^{-1}, **D)** Simulated FRAP integral recovery, **E)** Normalized fluorescence profiles at different times (time-step 36s) in radial direction, **F)** Normalized fluorescence profiles at different times (time-step 36s) in tangential direction.

To check if there is any difference in diffusion from different directions the FRAP area is split into two different directions: along the radial axis and tangential axis in respect to the overall circular geometry. In both cases the axis lines have been put through the centre of the "FRAP area" and the intensities have been evaluated along these lines. **Figure 7E and F** show the intensity curves versus the radial and tangential distances, respectively. The recovery is significantly slower from the tangential sides (initial fluorescence intensity on tangential line is about 0.9 (so only about 10% less than in bulk lipid film).

The time derivative of the spatial integral of these curves around 0 is linearly proportional to D; the radial diffusion gives a slope of 4.8e-3 $\mu m^2 s^{-1}$, while the tangential is about 1.2 e-5 $\mu m^2 s^{-1}$. The simulation data (assuming the diffusion constant $1 \mu m^2 s^{-1}$), however, results in the slope of 0.25 $\mu m^2 s^{-1}$ which gives the radial diffusion about 0.02 $\mu m^2 s^{-1}$ and tangential 0.0004-0.0008 $\mu m^2 s^{-1}$. **(Table S1)**

Table S1 Different diffusion coefficients calculated by comparing experimental data and simulation

Description	**Value**
Average diffusion constant in FRAP *	$D_{average} = 0.0017\,\mu m^2/s$
Radial diffusion from the right edge**	$D_{radial} = 0.02\,\mu m^2/s$
Tangential diffusion from the top and bottom edge **	$D_{tan} = 0.0004 - 0.0008\,\mu m^2/s$

***** This value is based on the rather crude assumption that there is one diffusion constant throughout the bleached area. It is not a molecular diffusion constant, but rather an effective average over the entire FRAP area, which itself is inhomogeneous as it is located on the edge.

****** These values are only estimates, that indicate the difference, rather than real quantitative values. It is impossible to extract them precisely due to complex interplay between spatial diffusion variation D(r) and geometries of FRAP area, and the edges. *A better defined geometry of the spreading area has to be provided for more precise results.*

SI6: Interaction of the e-beam patterned Teflon AF surface with unilamellar nanovesicles

Additional experimental data showing deposition of a lipid monolayer on the e-beam patterned Teflon AF surface by means of bulk-exposure to small unilamellar vesicles (diameter ~100 nm) in aqueous suspension. The surface coverage is due to deposition (adhesion, rupture, fusion and spreading) of the vesicles on the surface. The e-beam exposed areas remain dark (no wetting/lipid film formation). This is in accordance with the finding that manually deposited multilamellar vesicles do not wet the exposed Teflon AF areas.

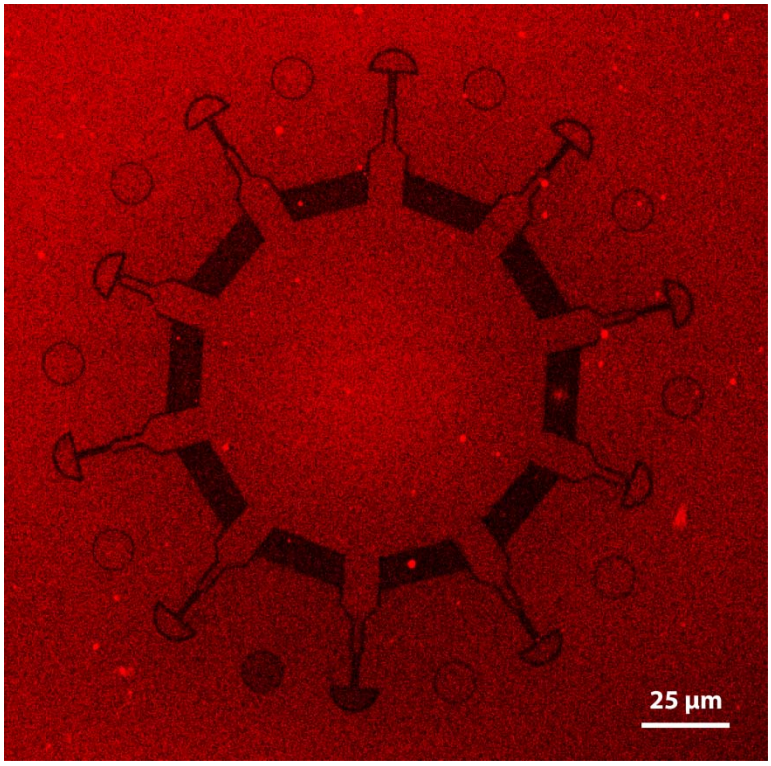

Figure S8: Fluorescence micrograph showing the surface coverage of an e-beam patterned Teflon AF surface by bulk exposure to a suspension of single unilamellar nanovesicles. The red colored areas are unexposed Teflon AF, covered with a lipid monolayer resulting from adhesion, rupture and fusion of SUVs, the dark areas are the lipophobic e-beam exposed structures.