Supporting Information for Luminescence Thermometry for In Situ Temperature Measurements in Microfluidic Devices

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Experimental Section

Chemicals All chemicals were used without further purification. The following chemicals were purchased from Sigma-Aldrich: Cyclohexane (99.5%, CH), oleic acid (90%, OA), ethanol (>99.8%, EtOH), methanol (>99.85%, MeOH), sodium hydroxide (>97%, NaOH), ammonium fluoride (>98%, NH_4F), ammonium hydroxide (28 wt% in H_2O, ammonia), rare-earth acetate hydrates (99.9%, $RE(Ac)_3{\bullet}xH_2O$), tetraethyl orthosilicate (99.999%, TEOS), and IGEPAL CO-520 ($(C_2H_4O)_n{\bullet}C_{15}H_{24}O$ with n ~ 5, average Mn = 441 g mol^{-1}, NP-5). 1-octadecene (90%, ODE) was purchased from Acros Organics.

Setup Luminescence measurements using the fiber probe were performed using a MDL-III-980nm-500mW laser. Upon excitation light was collected via a fiber patch chord and a shortpass filter to the OceanOptics QEPro CCD detector. Higher spatial resolution was obtained by recording spectra at various positions on the heated chip using a Leica SP8 confocal microscope equipped with a calibrated stage and an infrared laser (Coherent Chameleon II, Ti:Sapphire) tuned to 980 nm. At each position a spectrum was recorded of the emission from a 9 µm x 9 µm field of view obtained via a 40x/0.55 air objective lens. At the spectral resolution limit of the instrument, intensity was measured within a 5nm spectral window at intervals of 3nm with an integration time of 2.6s at each wavelength. With this microscope, spectra were obtained by scanning a 16x16 pixel raster across the field of view and recording the intensity within the spectral window at each pixel. To obtain a single value for each wavelength point, and improve SNR, these pixel intensities were integrated.

NP synthesis. $NaYF_4@SiO_2$ nanoparticles (NPs) doped with 18% Yb^{3+} and 2% Er^{3+} of ca. 50 nm were prepared via an initial synthesis of $NaYF_4$ core particles (ca. 25 nm) and subsequent SiO_2 overgrowth as reported earlier.[1,2]

Silicon/glass chip. The microreactor is fabricated in the cleanroom of the MESA+ Nanolab at the University of Twente. The reactor consists of a silicon and Mempax (borosilicate glass) substrate anodically bonded together. Fluidic channels are etched into the silicon substrate by Deep Reactive Ion Etching (DRIE). A 200 nm SiO_2 layer is thermally grown onto walls of the channels by dry oxidation of the silicon substrate. Channels are 150 µm deep and vary from 150–300 µm in depth. Buffered HF is used to wet etch small trenches (200 nm) into the Mempax substrate into which a 10 nm tantalum adhesion layer and 190 nm platinum is sputtered. Subsequently, the Ta/Pt electrodes are covered with 1 µm of SiO_2 via plasma-enhanced chemical vapor deposition to insulate them from the channels.

PDMS/glass chip. For fabrication of the PDMS/glass chips a mold out of SU-8, a commonly used epoxy-based photoresist, is made in the MESA+ Nanolab at the University of Twente. Using photolithograpy, SU-8 structures of 100 µm high and 200 µm wide are fabricated on a silicon substrate. After development these structures are used as a softlithography mold for casting PDMS. A PDMS vs. curing agent mass ratio of 10:1 is used. The PDMS is then poured on the silicon/SU-8 mold after which it is cured in an oven for two hours at 60 °C. After curing, in- and outlets of 1 mm are punched in the PDMS chip, subsequently the PDMS is treated in an O_2 plasma oven for 2 minutes after which it is bonded to a glass substrate. Finally the PDMS/glass chip is heated to 60 °C for 30 minutes to ensure proper bonding.

The mixing of the liquids in the PMDS/glass chip can be enhanced using different on-chip configurations. One example is shown in Figure S1. Here, a staggered herring bone mixer is shown which can enhance mixing. This is illustrated by mixing water and a red dye solution as shown in Figure S1c. The fluids do not mix due to the laminar flow until the encounter with the staggered herringbone mixer and quickly after a homogeneous red solution is obtained, indicating successful mixing.

Glass/glass chip. The chip consists of two wafers of borosilicate glass on top of each other. Semicircular channels are etched with HF in the top wafer: a protective layer of resin (1.7 µm of olin photoresist) is spin-coated and patterned on the wafer to expose only specific regions to the acid which can subsequently be used to draw the channels. On the top wafer, 100 nm of platinum is specifically deposited over a small recess and an adhesive layer of tantalum using lithography to design electrodes, connecting pads, and a heat sink which consists of large area of platinum in both sides of the channels to dissipate heat laterally. Finally 1 µm of silicon dioxide is grown on top of it via plasma-enhanced chemical vapor deposition (except on the connecting pads) to avoid chemical reaction in our solutions at the contact of platinum. Holes are made in the top wafer by powder blasting to access the connecting pads and the two wafers and bonded together at high temperature and high pressure, and finally diced into several microfluidic chips. The channels cross the dicing lines to provide opening inlets and outlets.

Figures

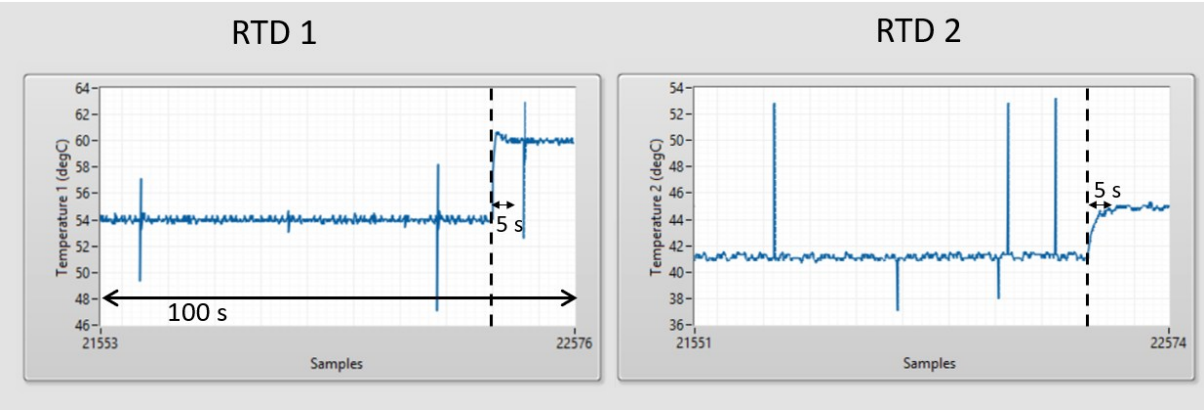

Fig S1 – illustration of the stability of the temperature controle over time. The temperature is very stable over time as illustrated here over the first 80 seconds of the figure, and the response when the target temperature is modified is very quick at both RTD positions(typically 5 seconds, as illustrated). The noise peaks/spikes are probably caused by interference with the RTD by the pulse-width modulated (PWM) square wave signal that is used to switch the heaters on/off.

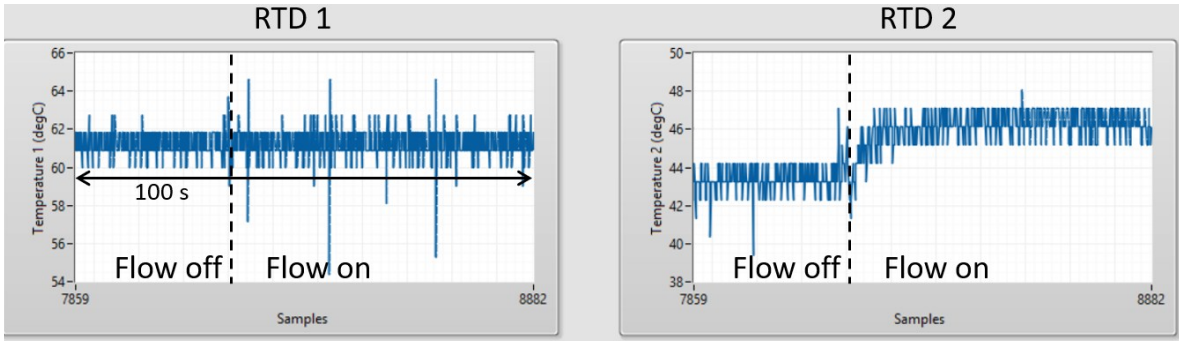

Fig S2 – illustration of the stability of the temperature controle over time with respect to flow off and flow on conditions. The temperature at the downstream measurement position (RTD 2), raises with 2 to 3 °C, when the flow is switched on. The regulated temperature at RTD 1, does not vary with flowrate. The noise peaks/spikes are probably caused by interference with the RTD by the pulse-width modulated (PWM) square wave signal that is used to switch the heaters on/off.

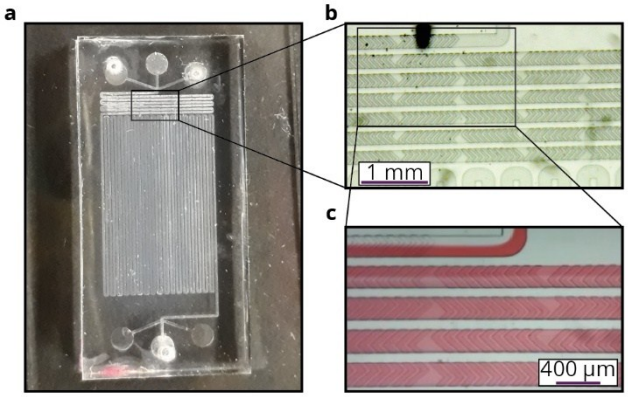

Figure S3 – PDMS microfluidic device with staggered herringbone mixer. Photograph of PDMS microfluidic device (a), a zoom in on the staggered herringbone mixer at the start of the device (b) and the mixing using water and a red dye (c).