**Electronic Supplementary Information For**

# On-demand microfluidic control by micropatterned light irradiation of a photoresponsive hydrogel sheet

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## Materials

*N*-isopropylacrylamide (NIPAAm, Aldrich) was purified by recrystallization from toluene/hexane (4:1), dried under a vacuum and stored at -20 °C. Tetrahydrofuran (THF, Wako) was dried over anhydrous magnesium sulfate. 1',3',3'-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2'-indoline) (Acros Organics), acryloyl chloride (Wako), triethylamine (Wako), 3-(trimethoxysilyl)propylmethacrylate (Aldrich), *N*,*N*'-methylenebisacrylamide (BAAm, Wako), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TEMED, Aldrich) and ammonium peroxodisulfate (APS, Aldrich) were used without further purification. Milli-Q water (Millipore) was used for preparation of solutions and hydrogel.

## Synthesis of the acrylated spirobenzopyran monomer

A solution of 1.47 g (5.0 mmol) of 1',3',3'-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2'-indoline) and 2.0 mL (14.3 mmol) of triethylamine in dry THF (50 mL) was stirred at 0 °C. A total of 0.57 mL (7.0 mmol) of acryloyl chloride was added to the mixture, and then the mixture was stirred at 25 °C for 15 hr. After the solvent was removed in a vacuum, ethyl acetate and a saturated sodium hydrogen carbonate aqueous solution were added and the aqueous phase was extracted with ethyl acetate. The recovered organic phase was washed with brine, dried over anhydrous magnesium sulfate and filtered. After evaporation of the solvent, the residue was purified by silica gel column chromatography (1/6 ethyl acetate/*n*-hexane as an eluent) to obtain the acrylated spirobenzopyran monomer (1.14 g, 3.29 mmol, 65w/w%) [1].

## Surface modification of the glass plate

A 25 mm diameter and 1 mm thick precleaned circular microscope cover glass plate was cleaned in an ultrasonic bath with a strong soap solution and acetone successively, each for 30 min, then rinsed with water and dried. The cleaned cover glass was immersed in a 1 w/w% 3-(trimethoxysilyl)propyl

methacrylate solution in a 1/100 acetic acid/water solution for 1 hr at ambient temperature. After that, the cover glass was allowed to dry at ambient temperature, rinsed with ethanol, rinsed with water and dried.

**Preparation of the photoresponsive hydrogel sheet covalently linked to the glass plate**

The spirobenzopyran-functionalized poly(*N*-isopropylacrylamide) (pSPNIPAAm) hydrogel was synthesized in a THF/water mixture solution by free-radical polymerization with APS as an initiator and TEMED as a catalyst [2]. Prior to the preparation, nitrogen gas was bubbled through the solvents for 1 hr. The NIPAAm monomer (83.1 mg, 0.735 mmol), acrylated spirobenzopyran co-monomer (5.2 mg, 0.015 mmol) and the BAAm (5.8 mg, 0.0375 mmol) cross-linker were dissolved in the THF/water mixture (1.0 mL, 70/30 volume ratio). Next, TEMED (1 μl) and an APS (1 mg) aqueous solution (20 μL) were added. The molar ratio of monomer/co-monomer/cross-linker was 98:2:5. The mixture was poured between two circular cover glasses, one of which was surface modified, separated by a 200 μm teflon spacer. Polymerization was carried out at 10 °C for 24 hr. The samples were washed several times to remove unreacted monomers and stored in a 10 mM HCl aqueous solution to swell the hydrogel sheet. Before the microfluidic system construction, the swelling medium was changed to a 1.0 mM HCl aqueous solution, in which most of the spirobenzopyran chromophores are in protonated open-ring form being ready for photoisomerization [3].

**Fabrication of PDMS microchannel**

A polydimethylsiloxane (PDMS) microchip was fabricated using the standard soft lithographic techniques [4-6]. Firstly, a silicon wafer was spin-coated with negative photoresist SU-8 50 (MicroChem). A microchannel pattern on a photomask was transferred to the photoresist using a K-310P100S mask aligner (Kyowariken). After post-exposure bake, the photoresist was developed in ethyl lactate, and the silicon wafer with the microchannel pattern was used as a master wafer. The master wafer was placed in a desiccator under a vacuum for 2 hr with a vial containing a few drops of tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (Gelest), which facilitated easy detachment of a PDMS plate from the master wafer. PDMS prepolymer and curing agent (Sylgard 184, Dow Corning) were mixed thoroughly and poured onto the master wafer. After curing in an oven at 90 °C for 1 hr, a PDMS plate was peeled off from the master wafer.

**Experimental setup for micropatterned light irradiation:**

A computer-controllable maskless micropattern projection unit (DESM-01, Engineering System Co.) [7] mounted on an IX-71 inverted fluorescent microscope (Olympus) was used for micropatterned light irradiation (Figure S1). A micropattern designed with a personal computer was irradiated to the sample with 10 μm resolution through x1.25 magnification objective lens. The wave length and the intensity of the irradiating light were 436 nm and 14 mW/cm$^2$, respectively. Fluid flow in the pSPNIPAAm hydrogel sheet was observed with a VB-7000 cooled CCD camera

(Keyence) mounted on the microscope. The resolution of the present irradiation system using x1.25 objective lens was around 10 μm per pixel. The irradiation system could irradiate micropattern with resolution of as high as 1.5 μm per pixel by using high magnification x10 objective lens.

**Introduction of a latex bead suspension into microchannels**

Microchannel formation and microvalve opening were visualized by flow of a suspension of latex beads (0.39 μm diameter, Duke Scientific) labeled with red fluorescent dye, rhodamine. A latex bead suspension, initially 2 w/w%, was diluted to 0.3 w/w% in a 1.0 mM HCl solution. The latex bead suspension was introduced into the microfluidic systems from the inlet ports with 5 kPa applied pressure. The applied pressure was controlled by changing the height of the reservoir containing the latex bead suspension. Micropatterned light was irradiated by means of the micropattern projection unit with keeping the applied pressure and temperature at 5 kPa and 29 °C, respectively. The latex bead suspension flow was observed with the fluorescent microscope.

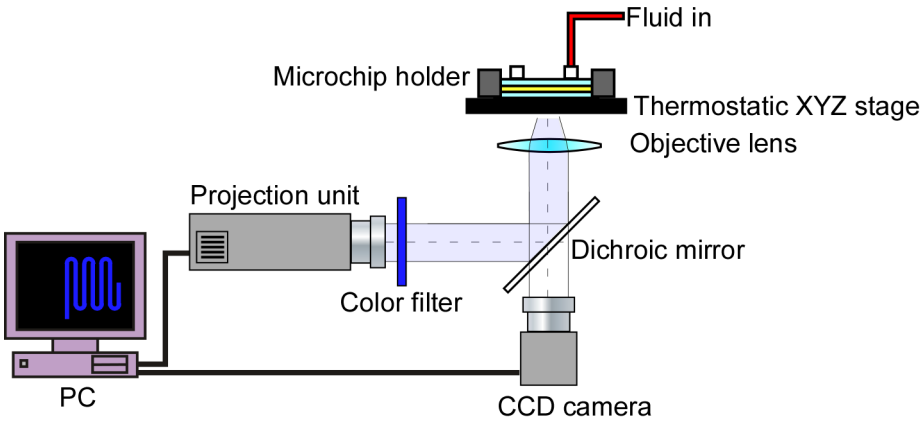


**Figure S1.** Computer-controllable maskless micropattern projection unit mounted on a microscope.

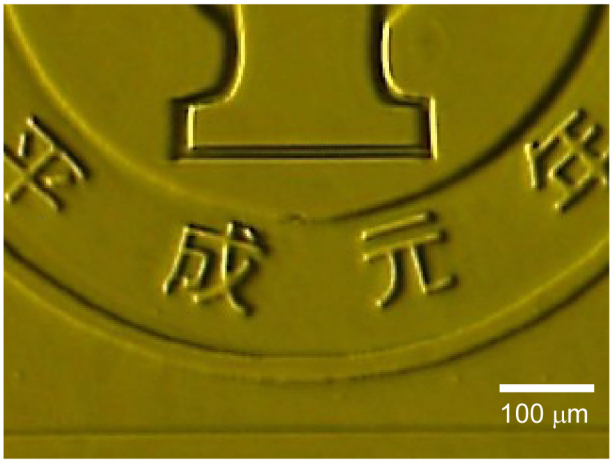


**Figure S2.** Microstructure on the pSPNIPAAm hydrogel sheet formed by micropatterned light irradiation through x10 objective lens.

**References**

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