Supporting Information for

A Thermoresponsive Fluorogenic Conjugated Polymer for a Temperature Sensor in Microfluidic Devices

Sungmin Ryu,† Imsung Yoo,† Simon Song,*,† Bora Yoon,‡ and Jong-Man Kim,*,‡

† *Department of Mechanical Engineering, Hanyang University, Seoul 133-791, Korea*

‡ *Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea*

e-mail: siminsong@hanyang.ac.kr; jmk@hanyang.ac.kr

Preparation of PDA vesicles: PDA vesicles employed in this study were prepared as follows. The amine terminated diacetylene monomer, PCDA-EDEA (15 mg), prepared according to the known procedures,[1] was dissolved in 2 mL of chloroform in a 40 mL vial. The organic solvent was removed by purging with N_2 gas to make a thin film inside the vial. Deionized water (30 mL) was added to the vial to yield a total monomer concentration of 1 mM. The sample was then heated at 80 ^{o}C for 15 min and probe-sonicated for 15 min. The resulting solution was filtered through a 0.8 μm filter, and the filtrate was allowed to stand at 4 ^{o}C for 12 h before being mixed with ethylene glycol (EG) (PCDA: EG = 98: 2, v/v) to increase the viscosity. Polymerization was carried out at room temperature by irradiating the solution with 254 nm UV light (1 mW/cm^2) until the absorption at 640 nm reaches a maximum (ca. 5 min).

Preparation of microfluidic chips: A microfluidic chip consists of a polydimethylsiloxane (PDMS) substrate with a microchannel network and a glass wafer with an ITO film microheater and thin film thermocouples. The PDMS substrate is fabricated by using standard soft lithography and molding techniques described in our previous report.[2] The microheater and thermocouples are integrated on the chip as follows. First, a glass wafer is thoroughly rinsed with acetone, IPA, and DI water and is dried with nitrogen gas. A photoresist (PR) (AZ 4620) is spin-coated for 10 s at 500 rpm and 40 s at 2500 rpm to a uniform thickness of 3 μ m on the wafer, and is baked at 100 ^{o}C for 4.5 min. Next, the wafer is exposed to UV light (Jaesung Corp.) for 8.5 min through a film mask with a microheater pattern, developed for 2.5 min, and thoroughly cleaned with DI water. Then, the ITO is deposited by sputtering (Sputter System, Sorona) on to the wafer to a thickness of 200 nm. Finally, an ITO film microheater with a width of 50 μm is completed by the lift-off process that strips off PR with acetone.

Thin-film thermocouples made of copper and constantan were integrated on the glass wafer. Copper lines of a 200 nm thickness were first patterned with E-beam evaporator (EBX1000, Ulvac) after spin-coating and developing PR on the wafer by the same method as described beforehand and depositing a 20 nm Ti film by E-beam evaporating (EBX1000, Ulvac) for a better adhesion of copper to the glass. Using the lift-off process, PR was stripped off to complete the copper patterning. Next, constantan lines were patterned with the same procedure as the copper lines with careful alignment (MA6-II, Suss MicroTec). Only exception is that constantan was deposited by thermal evaporating (Daeki Hi-Tech). For redundancy, four thermocouples were incorporated at each of the entrance and exit of the main channel. As the final process, the microheater and thermocouples were electrically insulated by sputtering SiO_2 of 800 nm in thickness on the wafer (Daeki Hi-Tech).

Sensor test and temperature measurements: Fluorescent signals emitted from thermally stressed PDA droplets were imaged using an inverted fluorescence microscope (IX71W, Olympus) with a 4x objective and a color CCD camera (DP70, Olympus). The two syringe pumps (KDS120, KD Scientific) were used to supply solutions of PDAs and corn oil to the chip: one for the PDA flow and the other for the sheath flows of oil, maintaining the flow rates at 0.02 mL/h and 0.12 mL/h, respectively. Syringes were connected to the inlets of the microchannels through capillaries and microfluidic fittings (LabSmith). A thermocouple amplifier (SCXI-1102, National Instruments), operated by LabView Software (National Instruments), was used to acquire voltages out of thin film thermocouples.

Temperature Calibration: In order to measure the temperature in the main channel accurately, thin-film thermocouples were calibrated to determine their Seeback coefficient which is known to be different from those of the bulk thermocouple.[3] The Seeback coefficient is a proportionality constant that correlates the voltage of a thermocouple with the temperature difference between the sensing position and end of the thermocouple. As shown in Figure S1A, by varying the temperature difference from -18 to 55°C, we determined that the Seeback coefficient is 11.7 μ V/K. By using this coefficient, we were able to measure temperatures at the entrance and exit of the main channel as a function of the microheater power. The results, shown in Figure S1B, indicate that the channel temperature is readily controlled in the range of room temperature to over 100°C.

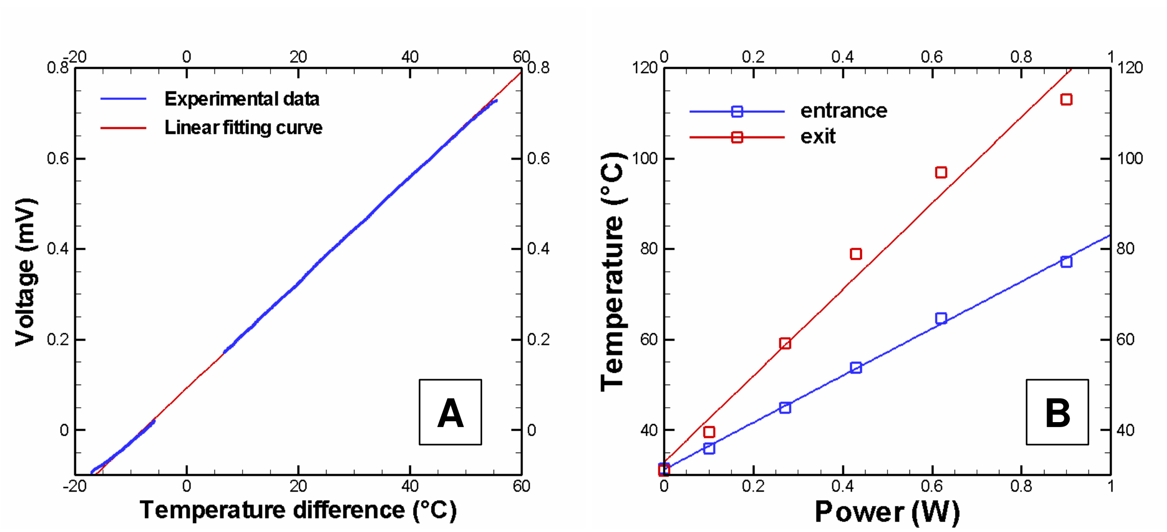

Figure S1. (A) Calibration of the results of thin film thermocouples. The slope is the Seeback coefficient. (B) Temperature differences between the entrance and exit of the main channel with respect to microheater power.

Fluorescence Intensity vs microheater Powers: Before we integrated thin-film thermocouples on the microfluidic chips, we examined the linearity of fluorescence intensity of PDA sensors against power supplied to the microheater. As shown in Fig. S2, the intensity varies linearly with increasing the power for a certain range.

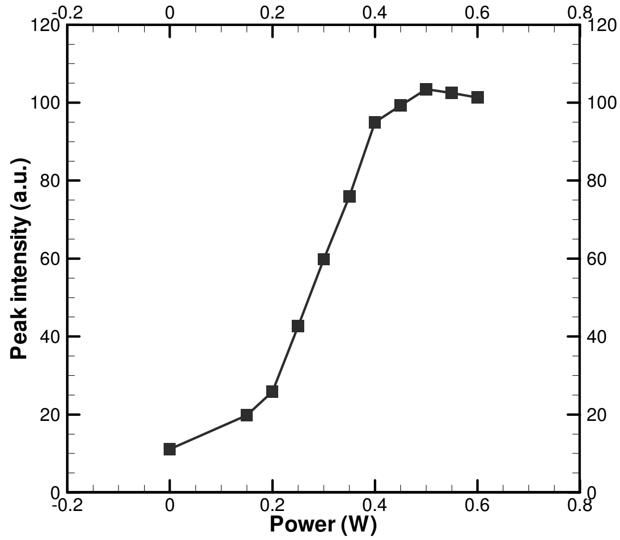

Figure S2. Variation of PDA sensor fluorescence with power supplied to the microheater.

References

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