## **Supporting Information**

## Online Monodisperse Droplets Based Liquid-Liquid Extraction on a Continuously Flowing System by Using Microfluidic Devices

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**Figure S1.** Procedures of hydrophilic modification using PAH and PSS. (a) The microchip was treated by oxygen plasma, and surface of PDMS and glass became negative charged. (b) Positive charged PAH was injected into the microchannel and then attracted on the surface of the channel by negative charge. (c) Free PAH molecules were washed away by NaCl solution. (d) Negative charged PSS solution was injected into the microchannel and then attracted on the surface of the surface of the channel by positive charge. (e) Free PSS molecules were washed away by NaCl solution. (f) Structures of PAH and PSS. The procedures (b) $\sim$ (e) were repeated two more times.



**Figure S2.** Theoretical analysis for droplets capture and limitation. (a) Small droplets were totally trapped by guiding tracks and buoyancy made these droplets stay in the guiding tracks. (b) If the small droplets came out from the guiding tracks, they had to overcome the buoyancy to enter the main channel. (c) Big droplets in guiding tracks were under the control of gravity and surface tension. (d) These bigger droplets could come out from the guiding tracks just by simply changing their shape, in which cases the impact of gravity was not as important as the surface tension did.



**Figure S3.** Droplets collection procedure on the microfluidic device. (a) Real sample solution flowed into the collecting channel when the flow rate in the collecting channel was too low (0.5  $\mu$ L/min). (b) Droplets collection when the flow rate in the collecting channel was 1  $\mu$ L/min. (c) Droplets collection when the flow rate in the collecting channel was 2  $\mu$ L/min. (d) Absorbing reagent flowed into the connecting channel when the flow rate in the collecting channel was too high (4  $\mu$ L/min). (e) Fluorescence intensity changed with the flow rate in the collecting channel.