## Vapour processed self-rolled poly(dimethyl siloxane) microcapillaries form microfluidic devices with engineered inner surface (Supplementary Information)

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## The fabrication scheme

*Remark :* The role of the P4VP layer consists in reducing the adhesion of the PDMS films to the substrate during tube rolling in chloroform vapour. Simultaneous swelling of the two layers disrupts the mechanical contact between them and facilitates the detachment of PDMS from the substrate. Without the P4VP film, no rolling was observed, since the adhesion of PDMS to a virgin glass surface was too strong. Without the auxiliary layer, adhesion of PDMS to a glass substrate was too strong and rolling was inhibited.

P4VP was chosen as the intermediate layer also because it is not dissolved in toluene, which can therefore be used as a thinning agent for PDMS, reducing it's viscosity and enabling formation of thinner films and hence smaller diameter tubes.



**Figure S1**. Slits in the PDMS film produced by UV laser with a 30  $\mu$ m spot size. Right image: a part of the H-like slit.







**Figure S4.** Dependence of a tube's inner diameter on the thickness of the PDMS film. Conditions of the oxygen plasma were identical for all experiments (experimental setup: Plassys MDS 1, power: 100 W, duration: 30 min, pressure: 2x10<sup>-1</sup> mBar)



Figure S5. Cross-section of two micro-tubes embedded in a PDMS matrix. The diameter of both tubes is approximately 500  $\mu$ m.



**Figure S6.** Optical microscope image of the cross-section of a PDMS rolled-up microtube (RUM) embedded in a PDMS matrix. Due to high adhesion of the PDMS matrix to the tubes formed from the same material, and due to the elasticity of the tubes, it was possible to perform the PDMS punching towards the tubes at normal temperature without collapse of the tubes at the position of the cut (Figure S3). In order to prevent filling of the tube interiour by liquid PDMS in course of the tube embedding in the PDMS matrix, the extremities of the tubes were sealed with a commercial gel glue. Tight compliance of the consecutive layers of the tubes to each other made the tube walls impermeable to liquid PDMS. Since the diameter of the connector tubes was slightly larger than the diameter of the punched holes, the connection was tight and no additional hermetization was required. Hollow-core tubes are clearly seen inside in the matrix due to the refraction index difference between the air inside the tubes was damaged and the tubes were filled by PDMS, they became practically invisible inside the block of PDMS in which they were encapsulated."



**Figure S7**. Chemiluminescent reaction in a pair of PDMS microcapillaries. Left: general view of the experiment. Right: electrical current in the electrode is switched off (A) and switched on (B).



**Video V1** A real time video of the setup with encased electrode and PDMS microtube filled by a chemiluminescent mixture. The electrical current in the electrode varied between I = 0 A and I = 0.66 A, as the tension varies between U = 0 and U = 2.2 V. Joule heating lead to a more intense rate of the chemiluminescent reaction, as detected by more intense light emission at the electrode. The tube interior was partially masked by the electrode. At the maximal tension, the mixture may be overheated and gas bubbles formed inside the tubes.