Supporting Information

Simultaneous size and color tuning of polymer microparticles in a single-step microfluidic synthesis: Particles for fluorescence labeling

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Chemicals

Tripropylene glycol diacrylate (TPGDA) (ABCR GmbH & co., Germany), Novec 7500 (Product of 3MTM), Picosurf (5 % in Novec 7500, sphere fluidic), 2-hydroxy-2-methylpropiophenone (Aldrich), Nile red (Sigma, Sigma-Aldrich), 12-(7-Nitrobenzofuran-4-ylamino)dodecanoic acid (NBFD) (Fluka, Sigma-Aldrich), Sudan black B (Merck), Reichardt's dye (Sigma-Aldrich), Cetyltrimethyl ammonium bromide (CTAB) (Sigma-Aldrich), Sodium dodecyl sulfate (SDS) (Sigma-Aldrich). All chemicals were used as received without further purification. The deionized water (Aqua purified G 7795, Miele, Germany) has been throughout all experiments.

Texts

The microgel particles having various applications in diverse area such as, carriers for drug delivery and the delivery for therapeutic agents, template for the SERS measurements, the base for nanoparticle dispersion for catalysis, and label or marker for the segment and cell diagnostics. The polytripropylene glycol diacrylate (Poly-TPGDA) microparticles have been prepared via photo-polymerization step in microfluidic set-up. Microreaction technology has several precious advantages over conventional batch process for the particle synthesis. In microreactor, the better mixing of various reactants can easily achieved, and therefore, the control of the size of particles obtained subsequently. Along with better mixing of solvent, better homogeneity of the particles can be precisely achieved. In the microfluidic, in general, the

dispersed phase forms the controlled segment in the continuously flowing carrier phase. The droplet size can be controlled by the flow rate ratio of carrier and dispersed liquid, or by using different concentration of surface active agents in carrier phase. Silicon, glass and polymer based micromixtures are frequently used as a microreactors. Here, in our experiment, we have used silicon hole plate with predefined size of holes in micro-nozzle array for droplet generation. The holes in the silicon plate have created via lithographic techniques.

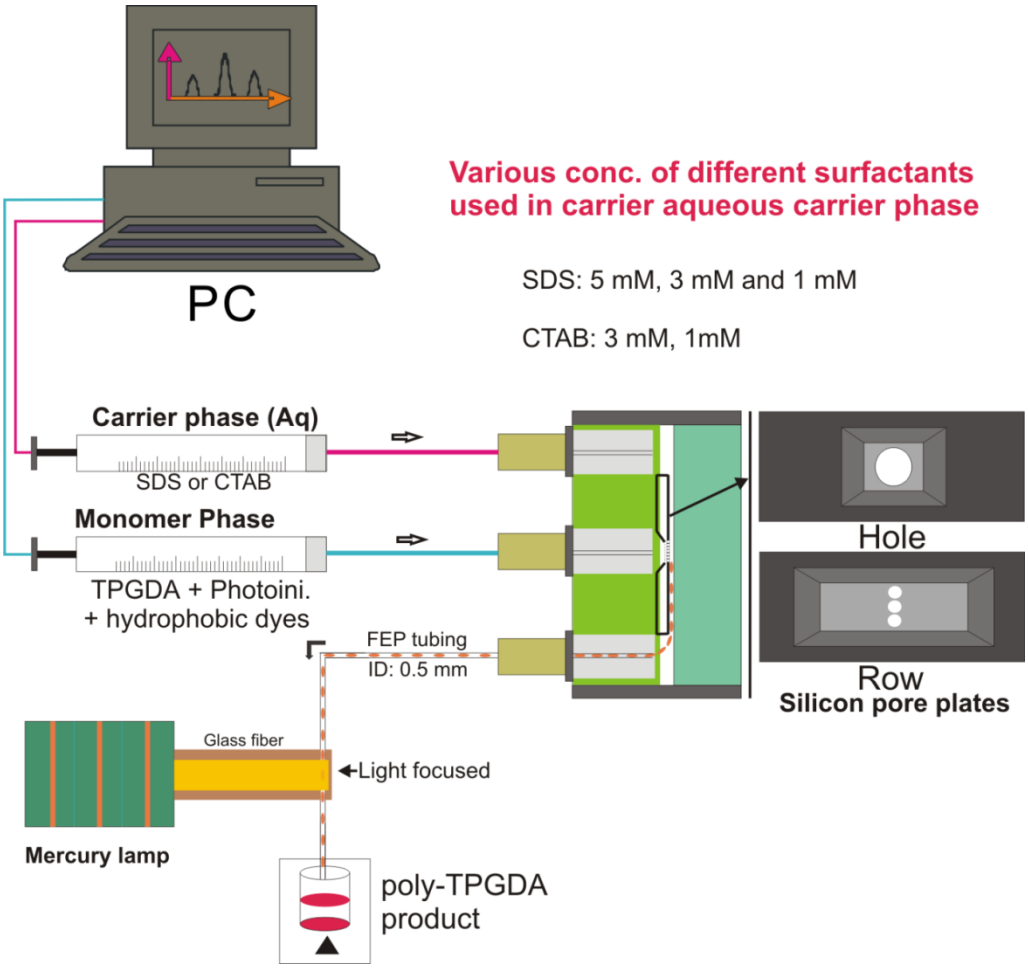


Figure S1. Microfluidic arrangements for the poly-TPGDA particles synthesis.

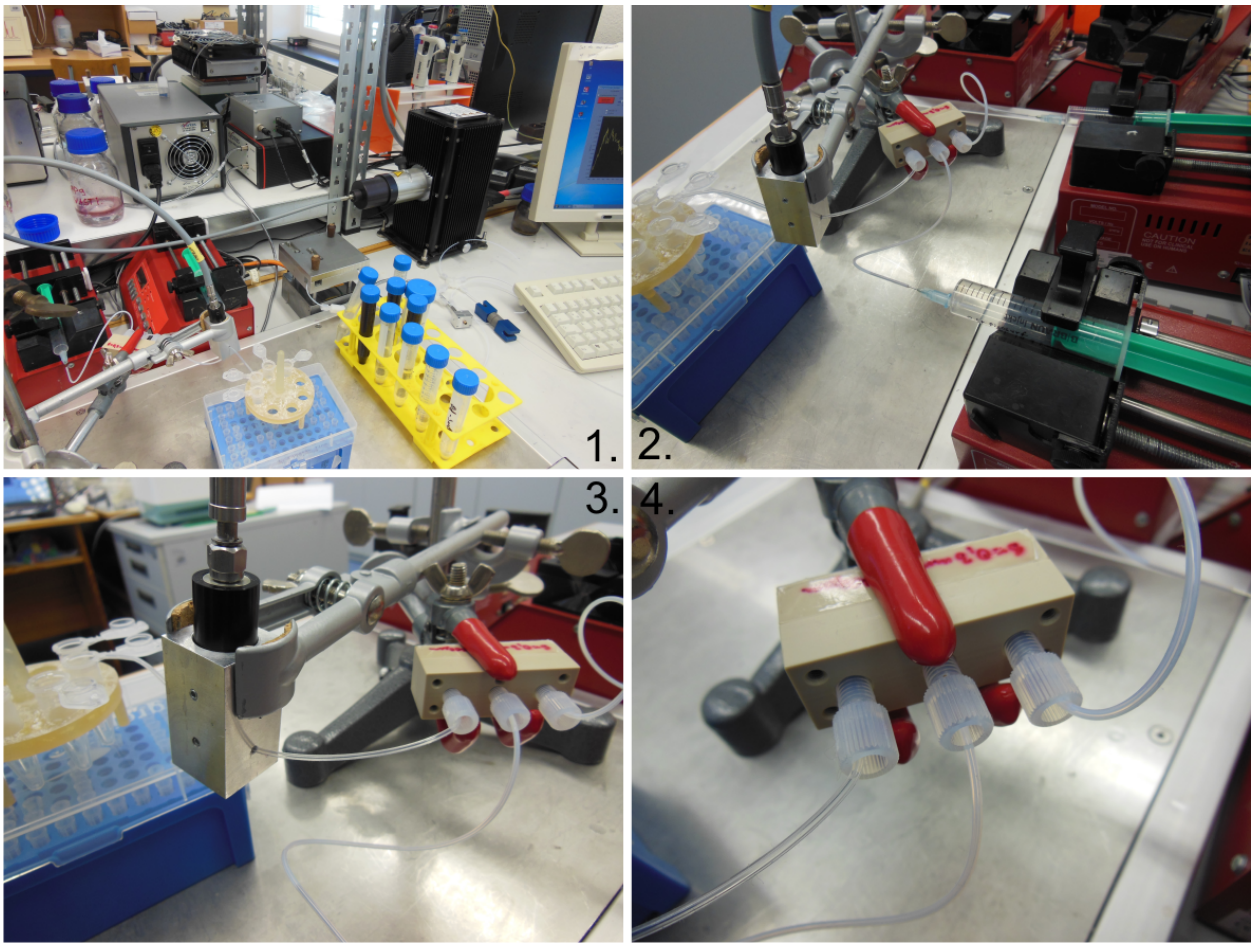


Figure S2. Camera photos of microfluidic set-up at different magnification.

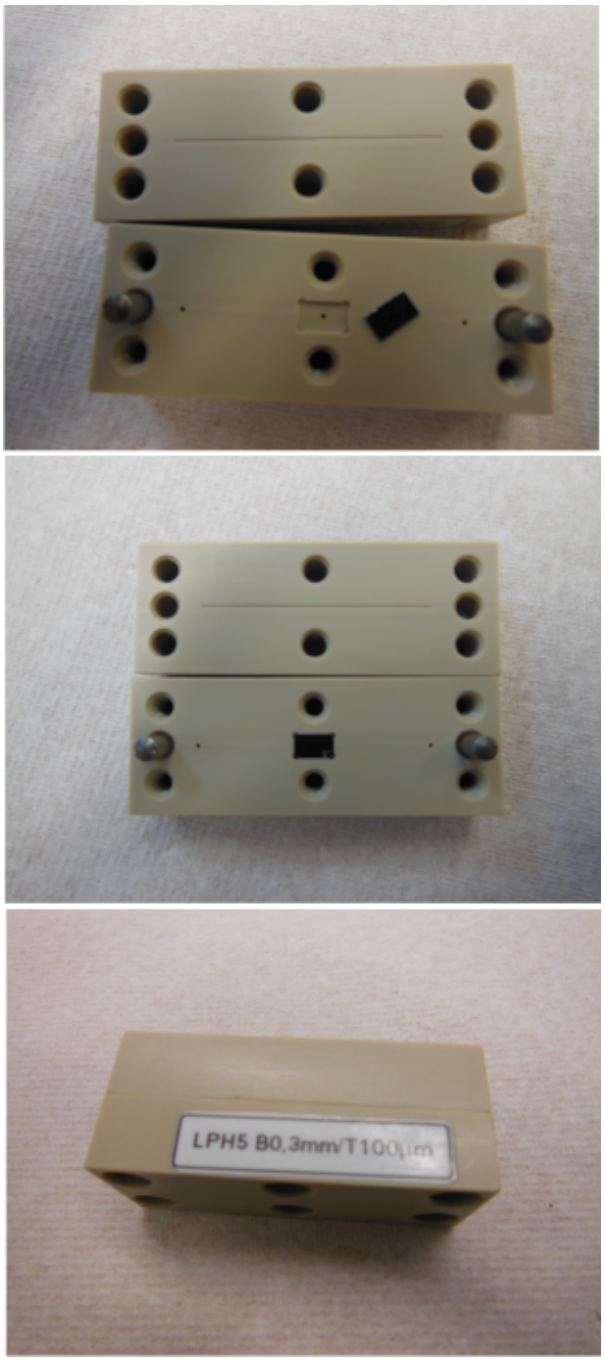


Figure S3. Camera pictures of microreactor for the position of Si chip inside the two surfaces of the chamber.

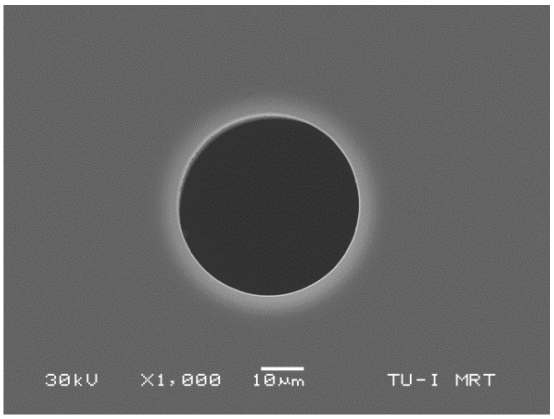


Figure S4. SEM image of the Si chip with single hole (front side picture).

Hole plates with single hole (diameter: 40 μm), and with five holes (row arrangement, diameter: 20 μm) were used in the particles synthesis experiments. The silicon chip with the micro hole was placed inside the micro-channel assembly. The width of the capillary slit of about 0.2 mm was adjusted between the both surfaces of the channel walls. Monomer droplets were generated at T-junction by a flowing continuous phase. The Si-membrane (0.7 x 0.7 mm^2) with single hole was placed on a rectangular-shaped chamber with sloped side walls inside the Si-chip with an outer size of 0.9 x 0.9 mm^2. Moreover, the chamber length 4.8 cm, width 1.8 cm, and the thickness of the combined both walls of the chamber was 2.05 cm. The total length and width of the chip is 5 mm and 2 mm, respectively.

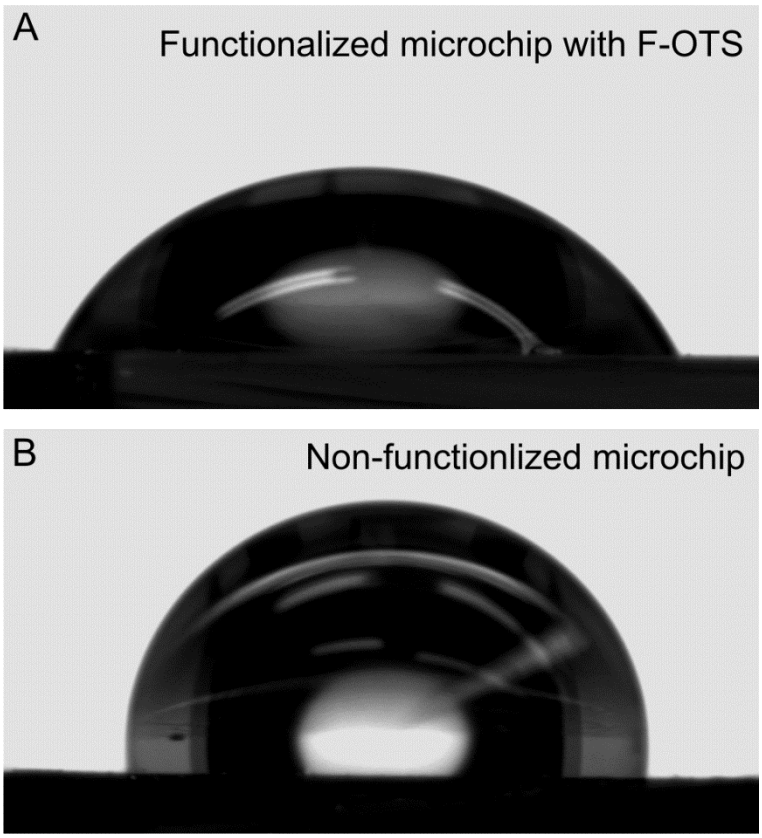


Figure S5. Images of the Novec 7500 (fluorinated carrier liquid) drop placed on the (A) functionalized (with trichloro (1H,1H,2H,2H-perfluorooctyl)silane) and (B) non-functionalized Si-microchip for the generation of precise size droplet during the microfluidic synthesis of the microparticles (images taken from the contact angel instrument). The droplet volume on the chip is same for both images (8 μL).

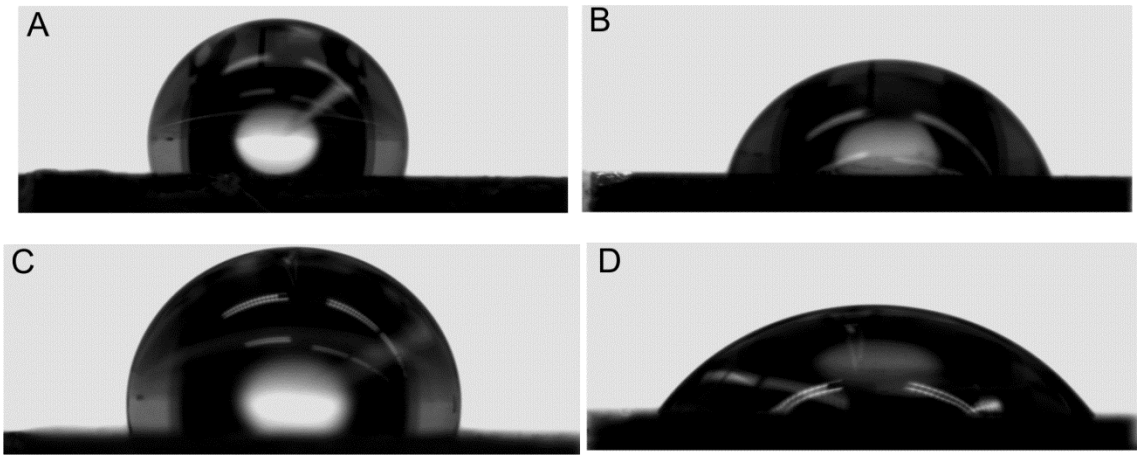
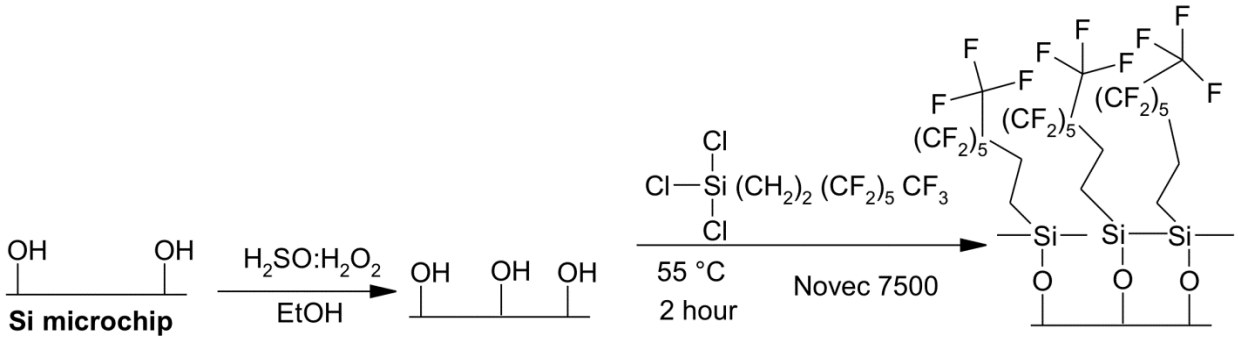
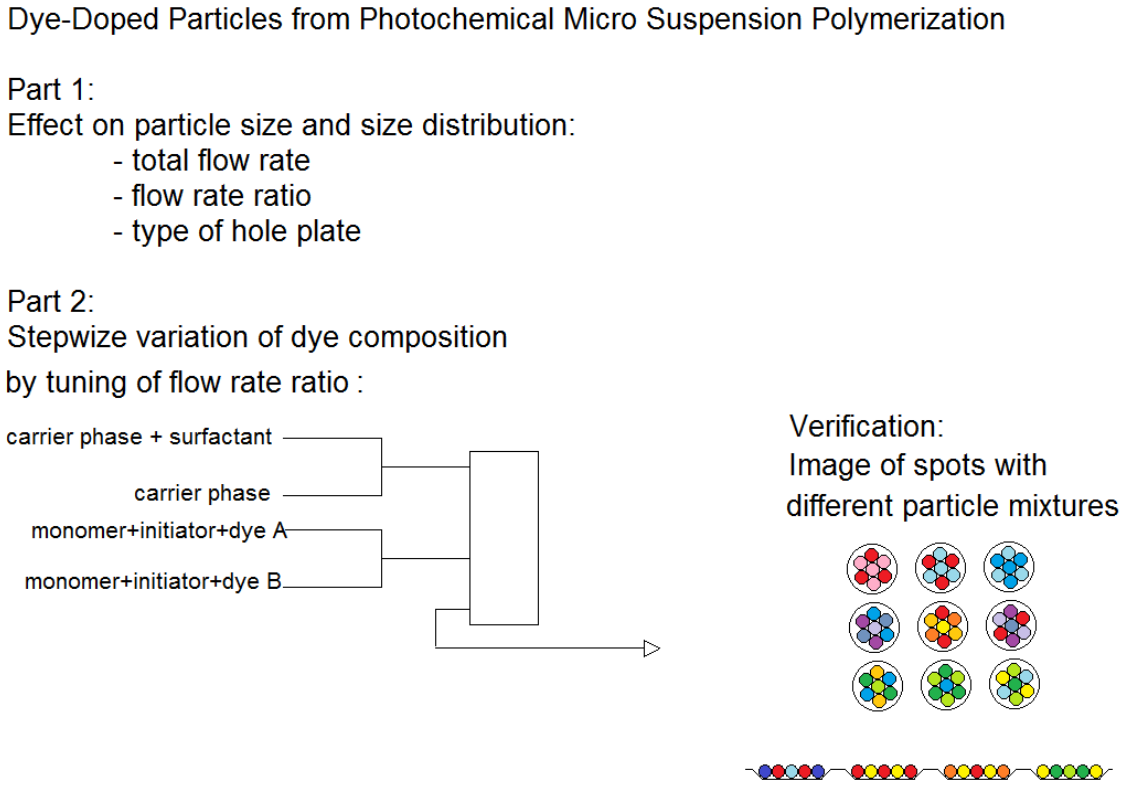


Figure S6. (A) and (B) are the images of the monomer (TPGDA) drop and water drop on the normal (non-functionalized) Si microchip respectively. (C) and (D) are the images of monomer (TPGDA) and

Novec 7500 (fluorinated carrier liquid) on the fluoro-functionalized Si microchip with Trichloro(1H,1H,2H,2H-perfluorooctyl)silane, respectively. The droplet volume on the chip is same for image A and B (5 µL) and for C and D (8 µL).



Scheme S1. Chemical reaction for silanizing the Si microchip.



Scheme S2. Scheme for particles synthesis.

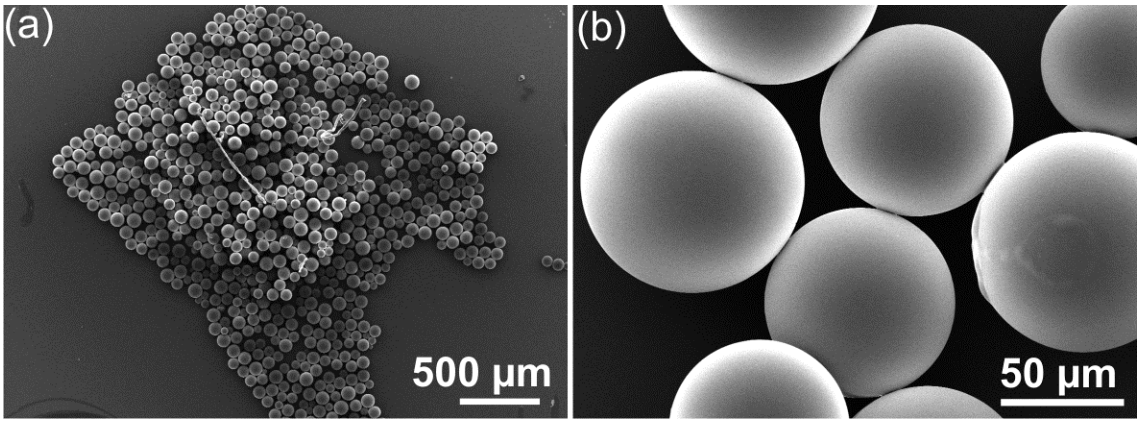


Figure S7. Lower and higher magnified SEM images of the particles obtained in microfluidic set up.

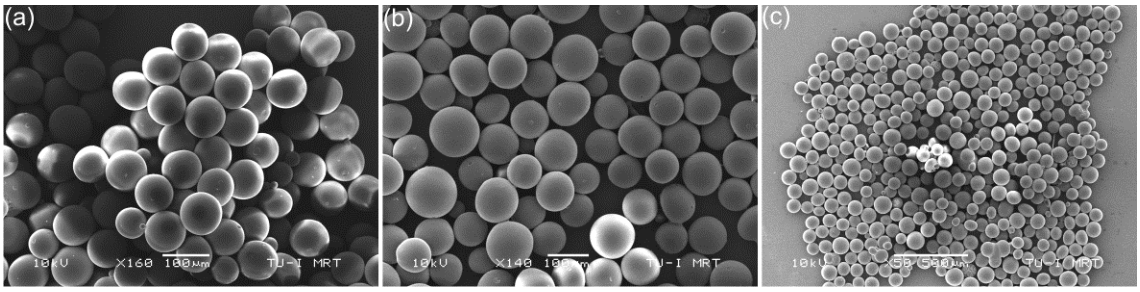


Figure S8. Different magnification of SEM images of particles obtained in the microfluidic set-up.

Figure S9. Light microscope image of bigger size polyTPGDA particles (size around 500 µm, similar to tube diameter) obtained when only PP9 used as a carrier phase (without picosurf surfactant).

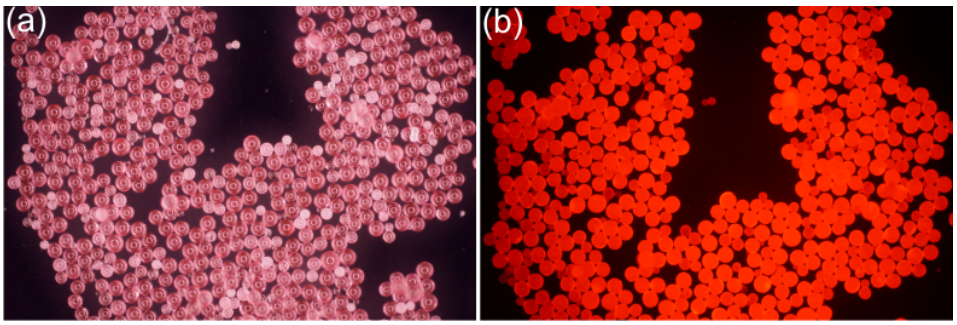


Figure S10. Fluorescence microscope images of the Nile red-doped poly-TPGDA microparticles under different light: (a) dark field image, and (b) fluorescence light (excitation) at wavelength ~ 550 nm.

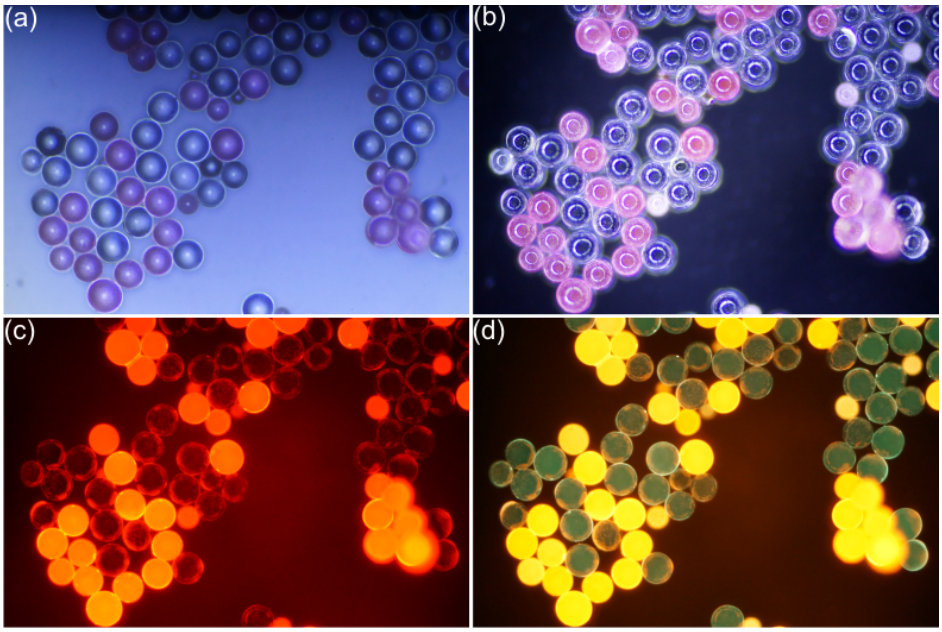


Figure S11. Higher magnified fluorescence microscope images of the mixture of two different dyes, Nile red and NBFD-doped poly-TPGDA microparticles, and imaging at the illumination of different wavelength of light; (a) transmission light image, (b) dark field image, (c) excitation at ~ 550 nm wavelength , and (d) excitation at ~ 460 nm wavelength.

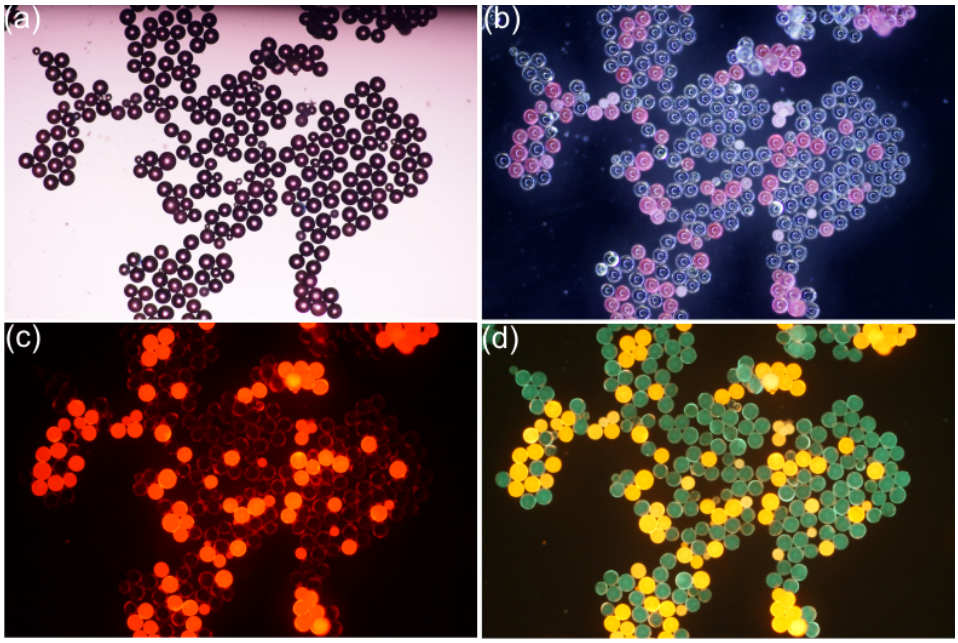


Figure S12. Fluorescence microscope images of the mixture of poly-TPGDA particles doped with two different dyes separately, Nile red and NBFD, and imaging at the illumination of different wavelength of

light; (a) transmission light image, (b) dark field image, (c) excitation at 510-560 nm wavelength , and (d) excitation at 450-490 nm wavelength.

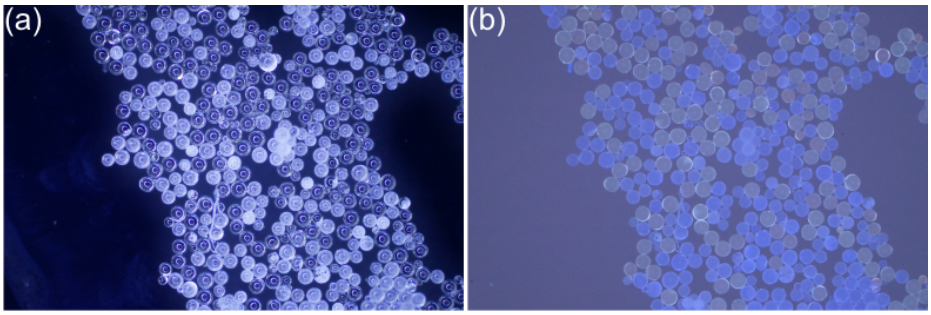


Figure S13. Fluorescence microscope images of the mixture of two different hydrophobic dyes, Sudan Black B and Reichardt's dye-doped polyTPGDA microparticles, and imaging at the illumination of different wavelength of light; (a) dark field image, and (b) excitation at ~ 400 nm wavelength.

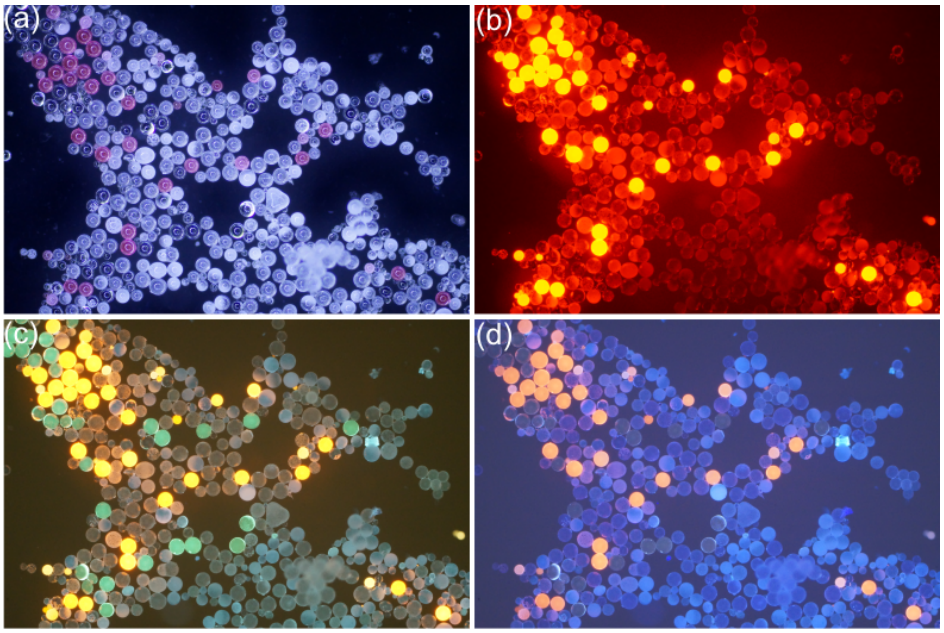


Figure S14. Fluorescence microscope images of the mixture of polyTPGDA particles embedded with three different dyes, Nile red, NBFD and Sudan Black B, and imaging at the illumination of different wavelength of light; (a) dark field image, (b) excitation at ~ 550 nm wavelength , (c) excitation at ~ 460 nm wavelength , and (d) excitation at ~ 410 nm wavelength .

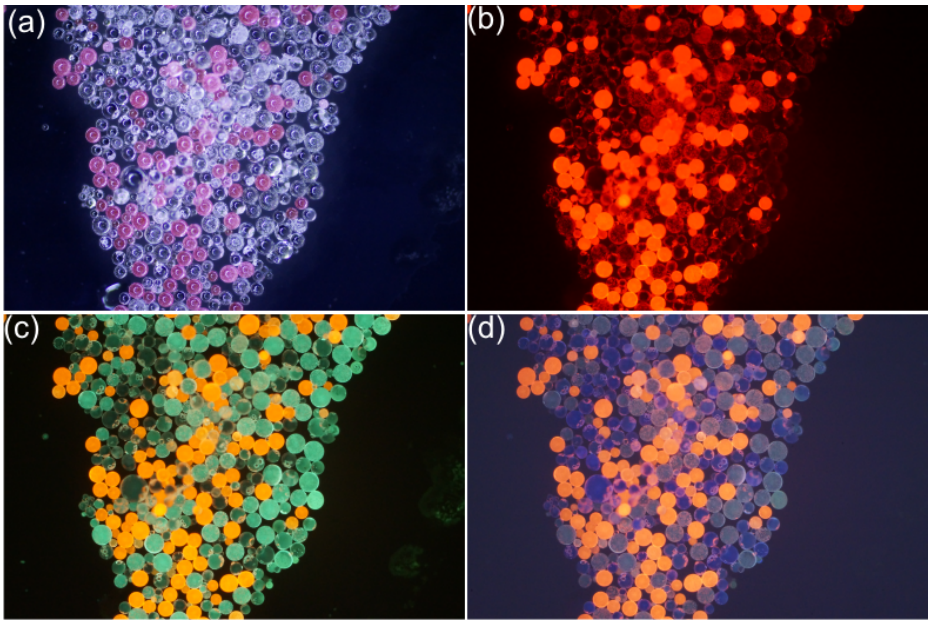


Figure S15. Fluorescence microscope images of the mixture of polyTPGDA particles embedded with three different dyes, Nile red, NBFD and Reichardt's dye, and imaging at the illumination of different wavelength of light; (a) dark field image, (b) excitation at ~ 550 nm wavelength , (c) excitation at ~ 460 nm wavelength , and (d) excitation at ~ 400 nm wavelength.

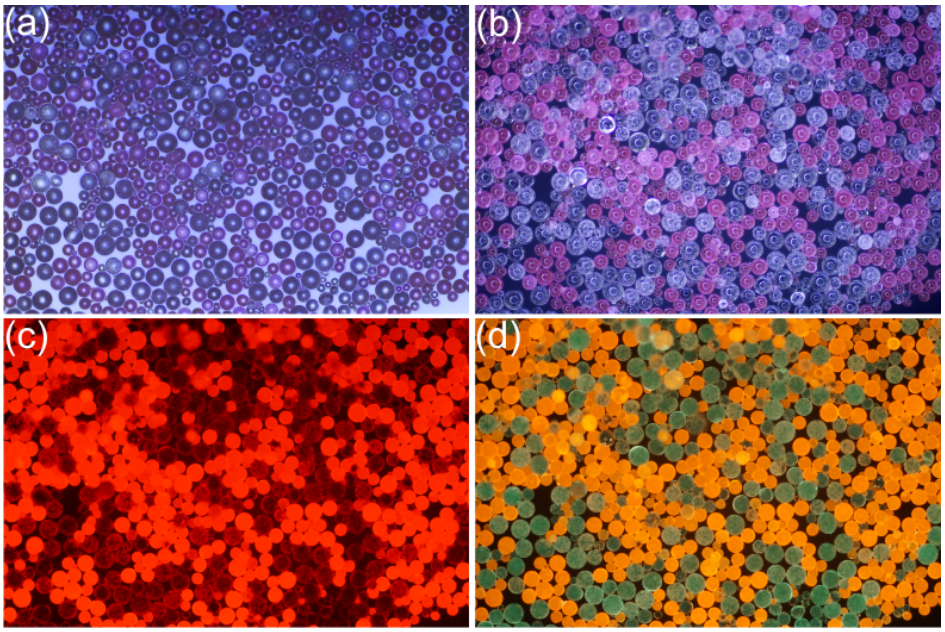


Figure S16. Fluorescence microscope images of the mixture of polyTPGDA particles embedded with two different dyes, Nile red and NBFD at different concentration ratio of particles (**70:30**, Red:Yellow) , and imaging at the illumination of different wavelength of light; (a) transmission light image, (b) dark field image, (c) excitation at ~ 550 nm wavelength, and (d) excitation at ~ 460 nm wavelength.

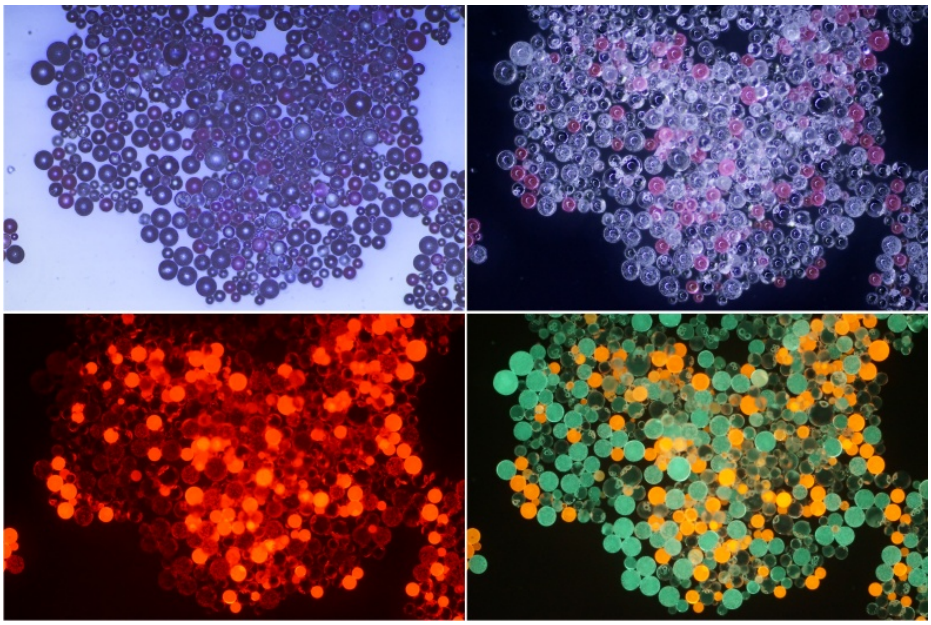


Figure S17. Fluorescence microscope images of the mixture of polyTPGDA microparticles embedded with two different dyes, Nile red and NBFD at different concentration ratio of particles (**30:70**, Red:Yellow) , and imaging at the illumination of different wavelength of light; (a) transmission light image, (b) dark field image, (c) excitation at ~ 550 nm wavelength, and (d) excitation at ~ 460 nm wavelength.

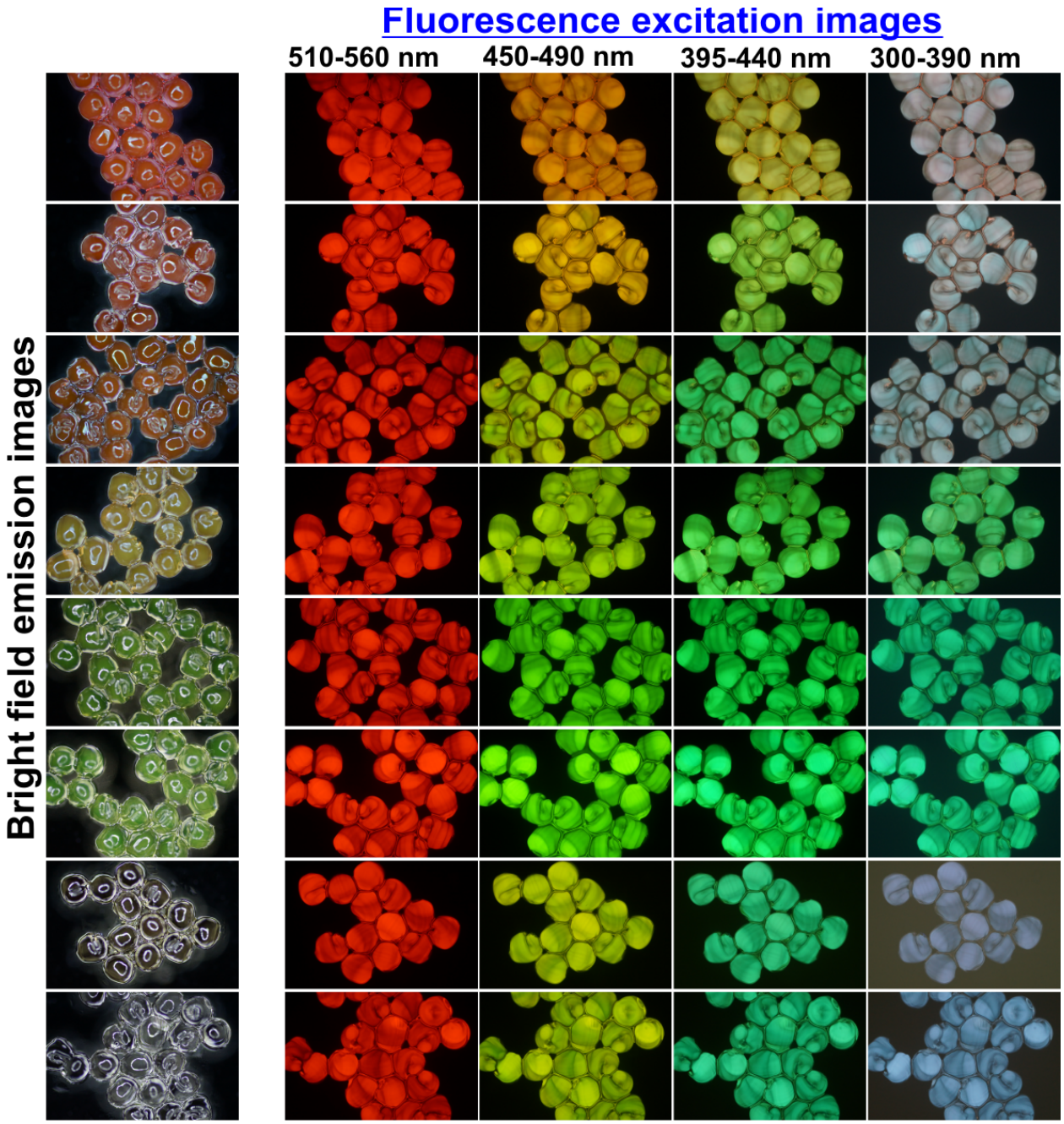


Figure S18. Fluorescence microscope images of the different kinds of particles generated by in-situ combination of variable concentration of four different dyes, 1. Nile red, 2. NBFD, 3. Sudan black B and 4. Reichardt's dye with 1:2:3:4 percentage ratio, 30:10:5:5 (µL/min), 25:10:10:5, 15:10:15:10, 10:30:5:5, 5:30:8:7, 5:25:10:10, 5:10:15:20 and 5:10:10:25 (Total monomer flow rate is 50 µL/min). Left side images are dark field images, and the same particles are excited at different fluorescence wavelengths.