

Supplementary Information for Highly Monodisperse Conjugated Polymer Particles Synthesized with Drop-based Microfluidics

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All materials were purchased from Sigma-Aldrich and used without further purification.

Fabrication of microfluidic devices: Microfluidic devices were produced via soft lithography. Poly(dimethylsiloxane) (Sylgard 184, Dow Corning) (PDMS) was poured onto a silicon wafer patterned with SU-8 photoresist features of a positive channel geometry (Microchem, SU-8 2025). The PDMS was then cured in an oven at 65°C for at least 6 hours. After the PDMS had cooled to room temperature, slabs of PDMS, containing the channel geometry were cut from the silicon template. Holes at the ends of the channels were punched using a Harris Uni-Core biopsy punch (0.25 mm). The slabs of PDMS were then washed with isopropyl alcohol to remove debris from punching and dried in a stream of air. The PDMS and a pre-cleaned glass substrate were exposed to an oxygen plasma for 10 s at 25 W intensity. After the plasma treatment, the PDMS was immediately pressed (channels towards substrate) onto the glass substrate and heated to 65°C for ten minutes. This treatment bonds the PDMS irreversibly to the substrate.

The bonded devices were parylene-C coated at Kisco Conformal Coating (Milford, CT, USA) with a parylene-C thickness of 25 μm, resulting in ca. 250 nm of parylene-C at the channel intersection inside the device.

Rendering the devices hydrophilic was achieved by exposing the parylene-C coated PDMS device to an oxygen plasma of 100 W for 3 min. The channels were immediately flushed with water and quickly connected to the fluid reservoirs to produce droplets.

Procedure for monodisperse conjugated polymer particles: A 10% solution of poly(vinyl alcohol) and a solution of poly(9,9-dioctylfluorene) (0.005-0.5 g/L) in toluene were placed into separate pressure vessels. PEEK tubing was placed into the liquid reservoirs inside the pressure vessels and connected with the parylene-C coated microfluidic chip. The PVA solution container was pressurized first, which drove the PVA solution to the chip for flooding of the channels. Then the pressure on the polyfluorene solution was increased until the stable dripping-regime was entered and droplets of 20 μm were produced. This was monitored via an inverted microscope fitted with a CCD camera. The droplets were collected in a glass vial, which was filled with PVA solution, to prevent the emulsion from drying out. The collected emulsion was slowly stirred with a magnetic stirrer to avoid immediate creaming of the emulsion. The different emulsions were collected over several days and stirred for two additional days after collection, to remove toluene and obtain the monodisperse particle dispersions.

Purification of monodisperse conjugated polymer particles: The particles were separated from the reaction mixture by centrifugation and resuspended in a 0.5 wt% solution of 5 wt% of SDBS in water; this is repeated at least 5 times. The particles are then washed two more times with pure DI water, before SEM analysis or further experiments.

Scanning Electron Microscopy: The particles were deposited from their dispersions by drying in air. After drying the colloidal assemblies were sputter coated with a 5-10 nm film of gold prior to SEM analysis. The images were recorded on a Zeiss Supra SEM at 5 kV using Everhart-Thornly- and Inlens detectors.

Particle sizes: The particle sizes were determined from SEM images of crystalline colloidal samples taken with the inlens detector. ImageJ analysis software was used to determine the particle size distribution. Typically the size was averaged over at least 300 particles. The mean sizes and standard deviations are presented in Fig. 2a.

Fluorescence Microscopy and Spectroscopy of conjugated polymer particles: For fluorescence microscopy, the particle dispersions were diluted and placed between a substrate and cover glass. An inverted fluorescence microscope Leica DMIRB microscope equipped with a digital camera (QImaging, QICAM 12-bit) was used to observe blue fluorescence from the conjugated polymer particles. The fluorescence spectra were recorded using a frequency tripled 355 nm Nd:YAG laser with a pulse length of ca. 10 ns and a repetition rate of 10 Hz. Dry samples of particles were placed in a vacuum chamber and excited using 355 nm laser light. The emission was collected in reflection and guided to a monochromator/spectrometer for spectral analysis.