Supporting Information

Triggered "On/Off" Micro-Pumps and Colloidal Photo-Diode

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Experimental:

Materials. Aniline (Alfa Aesar), 4-hydroxyl benzaldehyde (TCI), N-hydroxyphthalimide triflate (PAG-1), N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate (PAG-2), acryloyl chloride, azobisisobutyronitrile (AIBN, re-crystallized in hexanes), molecular sieve (4Å, dried at 200°C overnight right before use), (Aldrich), hexane, dichloromethane (dried with $CaCl_2$ and distilled before use) are from EMD chemicals. Tracers are purchased from either PolyScience® or Invitrogen®.

Video capture: All videos were captured using a CCD camera attached to an optical microscope (Zeiss Axiovert 200 reflectance/ transmission). The HBO 100 UV lamp attached to the microscope was used for the pumping experiments. The light wavelength was predominantly 365 nm with a maximum power of 2.5 Wcm^{-2} at the center. In a typical experiment a 9 mm diameter, 0.12 mm thick CoverWell imaging spacer was placed on a microscope slide and the appropriate solutions were added. The deionized (DI) water that was used for all experiments (Millipore Corp.Milli-Q system) had a specific resistance of 18 MΩ cm (i.e., "equilibrium water"). The glass slides and other glassware were obtained from VWR International.

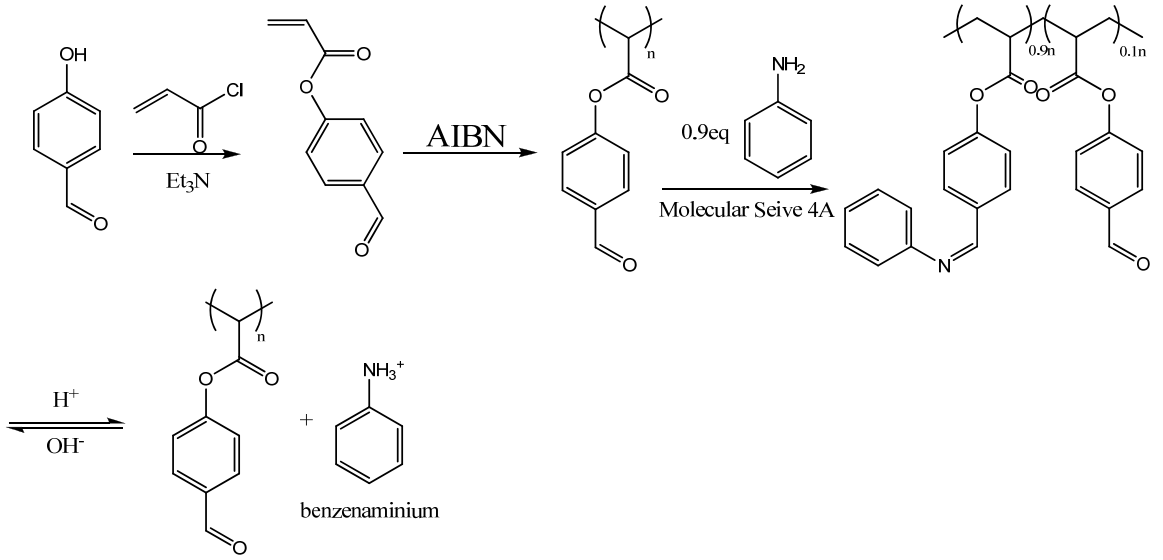
Synthesis of 4-formyphenyl acrylate (FA). 2 g of 4-hydroxyl benzaldehyde, 2.5 mL of triethylamine and 50 mL of dichloromethane were mixed. The solution was cooled with ice bath and 1.45 mL of acryloyl chloride was added over 30 mins. The reaction was stirred overnight. Organic phase was washed with $NaHCO_3$ solution and then water 3 times and dried with $MgSO_4$. The organic phase was concentrated and purified using column chromatography (eluent: dichloromethane, $R_f = 0.8$). The product is white needle-like crystal. ^{1}H-NMR (300 MHz, CD_2Cl_2, ppm), 9.98 (s, 1H); 7.92 (d, 2H); 7.30 (d, 2H); 6.50(s, 1H); 6.37(s, 1H); 5.80 (s, 1H).

Synthesis of poly (4-formyphenyl acrylate) (PFA). 1.76 g FA monomer and AIBN (0.02 eq.) were dissolved in 5 mL dichloromethane. Oxygen was removed three times via freeze-thaw pumping process and the solution was finally purged with nitrogen. The polymerization was carried out in 75°C oil bath for 12 hrs and PFA polymer was recovered by precipitating in cold hexane (M_n = 22.4 KDa, PDI = 3.7 by dynamic light scattering).

Synthesis of PFA aniline Schiff base (polyimine) (PFA-S).[S1] PFA polymer, aniline (0.9 equiv. to aldehyde groups) and molecular sieve (4Å, 400mg/1mmol aldehyde group) were mixed with dry dichloromethane at room temperature. The imine formation was monitored by ^{1}H NMR spectroscopy. After reaction, the integration of the peak corresponding to C*H*O (9.98 ppm) was compared with the peak corresponding to C*H*=N (8.3 ppm). The integration ratio was 1:0 (before reaction) and approx. 1:8 (after reaction). The average molecular weight also increased from 22.4 KDa to 28.8 KDa which matches with theoretical calculation based on 90% conversion of aldehyde groups to imine groups ($M_{n,\ theoretical}$ = 28.4 KDa). The mixture was filtered with celite and the filtrate was concentrated and then precipitated in excess amount of hexane. The yellow polymeric imine was vacuum dried overnight (M_n = 28.8 KDa, PDI = 2.9 by dynamic light scattering).

Pattern printing. The mask was printed on a polyacrylate surface using epilog mini laser printer and a PDMS layer was cast on it. The PDMS layer was subsequently peeled off after curing and was used as our pattern. The reservoirs on each end of the pattern were 10 x 10 mm. PAG-2 crystallites were packed in two 1 x 1 mm compartments on either side of a 4 x 1 mm channel connecting the two reservoirs (Figure 5).

Photoacid pump experiment. Crystallites of PAG-1 were placed on a glass slide and covered with hybridization chambers (Grace Bio-Labs Cat No. 631051). Water suspension of sulfate, carboxylate, and amine functionalized polystyrene tracers (2 μm diameter) (Invitrogen Cat. Nos.: S37500, C37278, A37366, respectively) were added to the chamber and the videos were captured at 50x magnification.



Scheme S1. Synthetic route to PFA-S Schiff base polymer (polyimine).

PFA-S pump experiment. PFA-S polymers were dissolved in dichloromethane (20 mg/mL). One drop of this solution was put onto a glass slide and the polymer film was vacuum dried overnight. Then the polymer film was carefully cut into approx. 0.3 x 0.3 mm and excess polymer was scraped off. The PFA-S film was covered with hybridization chamber (Invitrogen Cat. No: S24731). Tracers (6 μm diameter) (Polyscience Cat. No:17141) in HCl (1M, 0.1M and 0.01M) or phosphate buffer solution (pH = 7, control) were added in the chamber. The ionic strength of all solutions was adjusted to 1M by adding extra NaCl if necessary. The videos were captured at 5X magnification.

PFA-S/PAG (source-drain) experiment. PFA-S polymers and PAG were dissolved in dichloromethane (20 mg/mL for PFA-S, 100 mg/mL for PAG-2). One drop of PFA-S solution was put onto a glass slide and one drop of PAG solution was put next to PFA-S droplet. The glass slide was vacuum dried overnight. Then the PFA-S film (drain) and PAG (source) were carefully cut into approx. 0.3 × 0.3 mm with the distance of approx. 300 μm apart. The PFA-S/PAG was covered with hybridization chamber (Grace-Bio Cat. No: 631051). Water suspension of sulfate tracers (2 μm diameter) (Invitrogen Cat. No: S37500) was added in the chamber. The videos were captured at 20X magnification.

Particle Tracking

PAG Pump. In each experiment, 30 randomly selected particles were tracked using PhysVis software for 6 s. The velocity distribution histograms were plotted using Microsoft Excel.

PFA-S Pump. Velocity vs pH data: In each experiment 20 randomly selected particles were tracked using Tracker software for 6 consecutive time-steps of 5 s (pH, 0 & pH, 1), and 12.5 s (pH, 2), respectively (120 data points for each distribution plot). The velocity distribution histograms were plotted using Microsoft Excel.

Velocity vs distance data at pH 0 : In each experiment 20 randomly selected particles were tracked using Tracker software for 6 consecutive time-steps of 5 s (120 data points for each distribution plot). The velocity distribution histograms were plotted using Microsoft Excel

Source-Drain Photo-diode Pump. 30 randomly selected particles were tracked for two consecutive 0.5 s time-steps at 10 s intervals for 40 s total using PhysVis software (60 data points every 10 s). The velocity distribution histograms were plotted using Microsoft Excel.

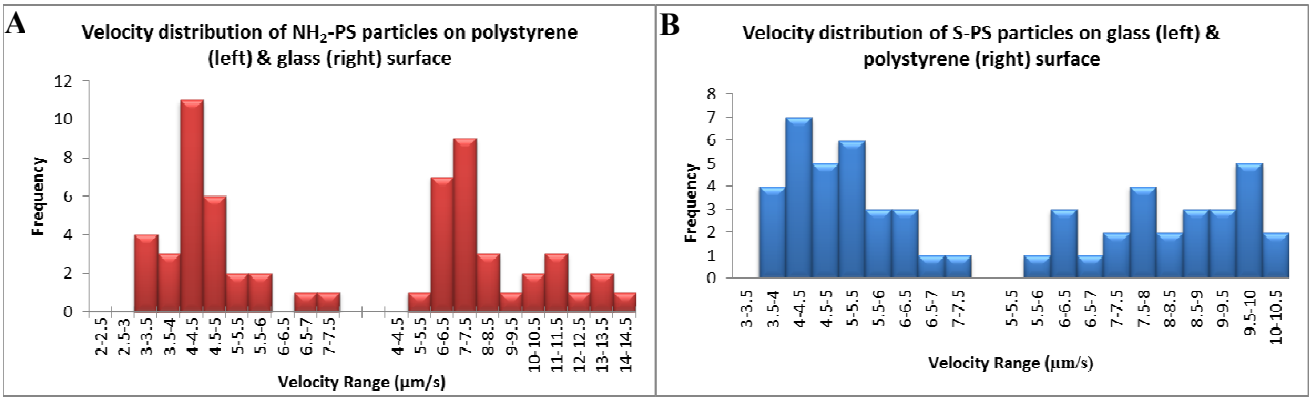


Figure S1: Velocity distribution histograms obtained for (A) NH_2-PS particles and (B) S-PS particles using the PAG pump.

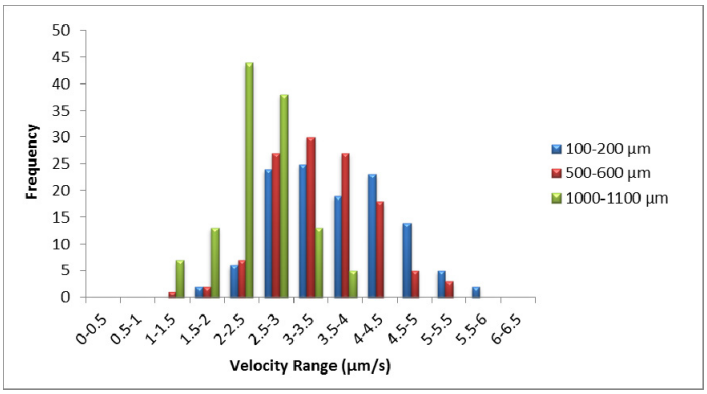


Figure S2. Velocity distribution histograms of HOOC-PS tracers at 100 to 1100 µm away from the PFA-S pump upon addition of 1 M HCl to the PFA-S film at 25 °C, demonstrating long range pumping.

Supporting Videos

Video S1: PAG pumping using amine functionalized tracer particles with UV on and off at 50X magnification.

Video S2: PAG pumping using COOH functionalized tracer particles with UV on and off at 50X magnification.

Video S3: PAG pumping resulting in self-assembled patterns using amine functionalized tracer particles with UV on and off at 50X magnification.

Video S4: PAG pumping causing colloidal transport through micro-channels using amine functionalized tracer particles. Video captured at 5X magnification with the UV turned on-off-on. Video speeded 5 times using Virtualdub software.

Video S5: PFA-S pumping using COOH functionalized tracer particles at pH 1 at 5X magnification. Video speeded 25 times using Virtualdub software.

Video S6: PFA-S control using COOH functionalized tracer particles at pH 7 at 5X magnification. Video speeded 25 times using Virtualdub software.

Video S7: PAG and PFA-S photo-diode's colloidal transport using sulfate functionalized tracer particles with UV on at 5X magnification; Video captured in between the PAG and PFA-S films, showing both films along with transport direction. Video speeded 5 times using Virtualdub software.

References

(S1) Youn, S. W. *J. Org. Chem.* **2006**, *71*, 2521.