

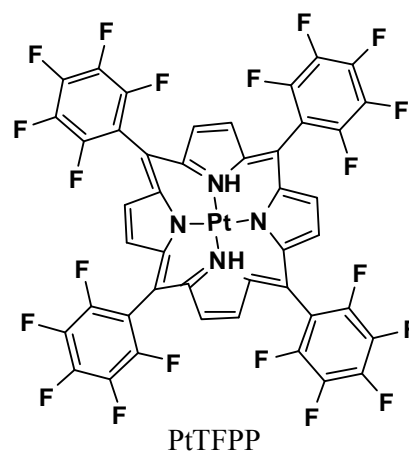
Supporting Information for

Microfluidic Synthesis of Monodisperse PDMS Microbeads and their Application as Discrete Oxygen Sensors

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Experimental Section

Materials and Chemicals. The Sylgard 184 silicone elastomer kit was obtained from Dow Corning Crop. The kit is composed of two fluids, Part A (base, consisting of vinyl-terminated siloxane oligomers) and Part B (curing agent, consisting of siloxane oligomers and catalyst). Sheets of polymethylmethacrylate (PMMA) (FF grade; 4" x 4" x 1/16") were purchased from Piedmont Plastics. The surfactant sodium dodecyl sulfate (SDS) was purchased from TCI America. The porphyrin dye Pt(II) meso-tetrakis(pentafluorophenyl) porphine (PtTFPP) was purchased from Frontier Scientific. The structure of PtTFPP is shown on the right. All chemicals were used as received without any further treatment.



Solution Preparation. The continuous phase was prepared by dissolving 5 wt% of SDS in distilled-deionized (DI) water. The dispersed phase was a mixture of Sylgard Parts A and B at a weight ratio of 6:4. Mixing of these liquid parts was done by a vortex mixer, followed by bath sonication. For experiments with the dye, PtTFPP was first dissolved in toluene and this solution was mixed with Sylgard Part A. The mixture was placed under vacuum overnight at 90°C to evaporate the toluene (final concentration of PtTFPP in the mixture was 0.5 wt%). The above material was then mixed with the curing agent (Part B) at a 6:4 weight ratio.

Microfluidic Device Fabrication and Operation. The microfluidic chip comprised a PMMA substrate (4" x 2" x 1/16") containing microchannels bonded to a PMMA lid containing access ports. The smaller microchannels were fabricated by mechanical milling using a 50 μm diameter end mill on a CNC milling machine with a depth of 50 μm, and the bigger microchannel was milled using a 150 μm diameter end mill with a depth of 100 μm. Holes for the needle interface were drilled into the substrate plate using a 650 μm drill bit. The machined PMMA plate was sequentially cleaned by DI water and isopropyl alcohol to remove the milling debris, followed by a 24 h degassing step in a 40°C vacuum oven to remove the residual solvents. After vacuum drying, both the processed PMMA and a raw PMMA chip were oxidized by an 8 min exposure to ultraviolet (UV) light in the presence of ozone. The oxidized PMMA wafers were immediately mated together and thermally bonded at 85°C in a hot press under a pressure of 3.45 MPa for 15 min. The world-to-chip interfaces were established by inserting hypodermic stainless steel

needles into the 650 μm diameter mating holes, with an additional 30 min of annealing at 85°C to release the residual stresses from the fitting process. Commercial plastic PVC tubing were used to connect the needle ports on the PMMA chip with syringes. Precision syringe pumps (PHD 2000, Harvard Apparatus) were used to control the infusion of fluids into the chip. Typical infusion rates were 50 $\mu\text{L}/\text{min}$ for the continuous phase and 1 $\mu\text{L}/\text{min}$ for dispersed phase.

Microbead Characterization. Optical characterization of the beads was performed using either a Nikon Eclipse LV-100 Profilometer microscope or a Nikon Eclipse TE2000s inverted fluorescence microscope. Scanning Electron Microscopy (SEM) was done using a Hitachi SU-70 instrument. Beads were sputter-coated with a layer of gold for 90 s before SEM imaging.

Sensing Experiments with the Beads. Dye-incorporated microbeads were placed in a modified multiwell plate equipped to allow continuous gas flow. Beads were exposed to gas with different partial pressures of oxygen ($P_{\text{O}_2} = 0 \text{ atm}, 0.01 \text{ atm}, 0.05 \text{ atm}, 0.1 \text{ atm}$ and 0.2 atm), which were obtained by mixing nitrogen and air. The emission intensity from the beads was captured on an inverted microscope (Zeiss Axiovert Z1, Thornwood NJ). A green LED (Thorlabs, Newton NJ) was used to illuminate the microbeads and images were captured using a CCD camera (CoolSnap HQ, Tucson AZ) with an integration time of 100 ms. All images were background corrected and analyzed using NIH Image J software.

Viscosity Calculations. The viscosity of a mixture of two liquids can be calculated by the Refutas equations.¹ Here, this was used to estimate the viscosity of a mixture of Sylgard 184 Parts A (base) and B (curing agent).

(1) First the Viscosity Blending Number (VBN) is calculated for base and curing agent by:

$$VBN = 14.534 \times \ln[\ln(\nu + 0.8)] + 10.975 \quad (\text{eq S1})$$

where ν is the kinematic viscosity in centistokes (cSt).

(2) Then the VBN of the blend mixture was obtained by:

$$VBN_{Blend} = [x_{Base} \times VBN_{Base}] + [x_{Curing Agent} \times VBN_{Curing Agent}] \quad (\text{eq S2})$$

where x_{Base} and $x_{Curing Agent}$ are mass fractions of the corresponding components.

(3) Finally, the blend kinematic viscosity was calculated by:

$$\nu_{Blend} = \exp\left(\exp\left(\frac{VBN_{Blend} - 10.975}{14.534}\right)\right) - 0.8 \quad (\text{eq S3})$$

Sample calculations are shown in the table below for a 10:1 and 6:4 mixtures of base and curing agent. The respective kinematic viscosities of Part A and B were obtained from the Dow Corning Product Data Sheet:

Table S1: Viscosity Calculations of Mixtures using the above equations.

Item	Viscosity (cSt)	VBN	VBN _{Blend}	Blend Viscosity (cSt)
Base	5000	33.49	/	/
Curing Agent	110	42.11	/	/
10:1 Mixture	/	/	41.32	3196.3
6:4 Mixture	/	/	38.66	827.3

- (1) Maples, R. E. *Petroleum refinery process economics*; 2nd ed.; PennWell Corp.: Tulsa, Okla., 2000.