

## Supporting Information to

# Fuel Concentration Dependent Movement of Supramolecular Catalytic Nanomotors

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## 1. Materials

All reagents and chemicals were used as received unless otherwise indicated. Styrene was distilled prior to use to remove the inhibitor.

Ultra pure MilliQ water was obtained with a Labconco Water Pro PS purification system (18.2 M $\Omega$ ) and was used for the self-assembly of polymersomes and for the dialysis experiments. Spectra/Por® Dialysis Membrane MWCO: 12-14,000 was used for dialysis of polymersomes and their shape transformation into stomatocytes. Ultrafree-MC centrifugal filters 0.22  $\mu\text{m}$  were purchased from Millipore. Polyvinylpyrrolidone (Mn  $\sim$  10000) and potassium tetrachloroplatinate (II) 99.9% were purchased from Sigma-Aldrich. L (+) ascorbic acid was purchased from Acros Organics and used as received.

Synthesis of the amphiphilic block-copolymers containing polyethylene glycol as hydrophilic and polystyrene as hydrophobic units of different lengths was carried out using atom-transfer living radical polymerization (ATRP) via a previously published procedure.<sup>1</sup>

## 2. Instrumentation

NMR spectra were recorded on a Varian Inova 400 spectrometer with CDCl<sub>3</sub> as a solvent and TMS as internal standard. Molecular weights of the block copolymers were measured on a Shimadzu Prominence GPC system equipped with a PL gel 5  $\mu\text{m}$  mixed D column (Polymer Laboratories) and differential refractive index and UV (254 nm) detectors. THF was used as an eluent with a flow rate of 1 mL/min. Polystyrene standards in the range of 580 to 377,400 Da were used for calibration. **Dynamic light scattering (DLS)** experiments were performed on a Malvern Zetasizer Nano S equipped with a He-Ne (633 nm, 4 mW) laser and an Avalanche photodiode detector at an angle of 173 °. All DLS data were processed using a Dispersion Technology Software (Malvern Instruments). Ultrasonication for the synthesis of the nanoparticles was performed on a VWR Ultrasonic Cleaner Model 75D.

**Transmission electron microscopy (TEM)** was performed on a JEOL 1010 microscope equipped with a CCD camera operating at an acceleration voltage of 60 kV. Sample specimens were prepared by placing a drop of the solution on a carbon-coated Cu grid (200 mesh, EM science) and subsequent air-

drying. Each size distribution histogram was constructed using more than 70 particles. Processing and analysis of the TEM images was performed with ImageJ,<sup>2,3</sup> a program developed by the NIH and available as public domain software at <http://rsbweb.nih.gov/ij/>.

### **3D Electron tomography**

Electron tomography was performed on a Tecnai 20 electron microscope with a LaB6 electron source (FEI Company, Eindhoven). Images of the tilt-series were aligned with respect to a common origin and rotation axis using Au NP fiducial markers of 5 nm size. The series of tilt images were analyzed with the open source software, IMOD, developed by Boulder laboratory.<sup>4</sup>

### **3. Synthesis of preformed platinum nanoparticles**

**PVP capped Pt-NP** (sizes from 20-100 nm) were synthesized a modified sonication technique reported previously.<sup>5</sup>

Polyvinylpyrrolidone capping agent ( $M_n \sim 10000$ ) (10 mg) was dissolved in 1 ml of a 20 mM solution of  $K_2PtCl_4$  aged for at least 24 hrs. An amount of 17.5 mg of ascorbic acid dissolved in 0.5 ml of MilliQ water was added at once to the platinum salt solution and the vial was sonicated for 30, 40, and 60 min at room temperature to generate PVP capped platinum nanoparticles of sizes between  $\sim 20$ , 40, to 80 nm. When the temperature of the sonication bath was increased to 45 °C larger nanoparticles of  $\sim 100$  nm were obtained. Two centrifugation/washing cycles were performed to remove the excess of the capping agent before further use of the particles for the entrapment experiments. After the final wash, freshly prepared platinum nanoparticles were redispersed in MilliQ water and sonicate for 1 min prior to use.

### **4. Shape transformations of polymersomes into stomatocytes**

In a typical experiment poly(ethylene glycol)<sub>44</sub>-*b*-polystyrene<sub>177</sub> (20 mg) was dissolved in a 2 ml mixture of THF/dioxane of different ratios, with THF 80% with respect to dioxane in a 15 ml capped vial equipped with a magnetic stirrer and closed with a rubber septum. The solution was stirred for 30 min at room temperature to allow complete dissolution of the polymer. A fixed 50% volume of water (2 ml) of MilliQ

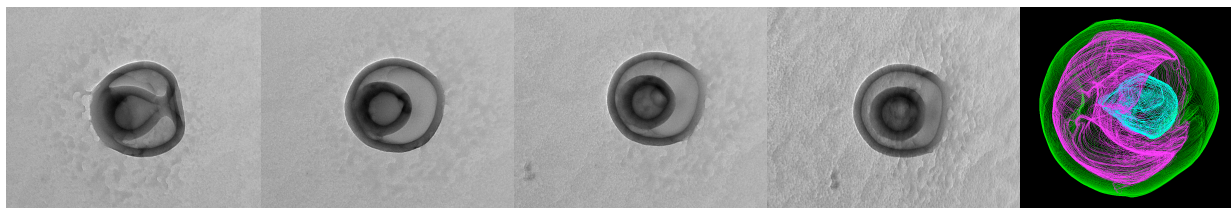
water was after added to the organic phase with vigorous stirring (900 rpm) via a syringe pump using a 5 ml syringe equipped with a steel needle. The syringe pump was set up for an addition rate of 1ml/h. The solution turned cloudy after the addition of 0.5 ml of water. After complete addition of water the colloidal mixture was transferred in a dialysis bag and dialyzed against water. The dialysis water was replaced after 1 h followed by frequent changes for 48 h to generate bowl-shape stomatocytes with a small opening (5 nm).

#### **4. Supramolecular assembly of the stomatocyte nanomotors**

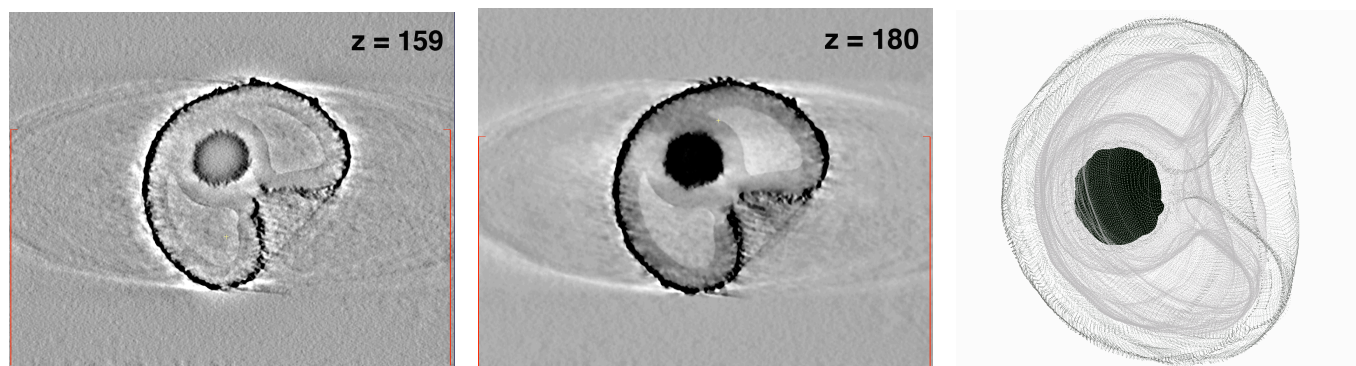
Poly(ethylene glycol)44-*b*-polystyrene177 (20 mg) was dissolved in a mixture of THF and 1,4-dioxane (2 mL, 1.6/0.4 ratio) in a 15 ml capped vial equipped with a magnetic stirrer and closed with a rubber septum. The solution was stirred (rate: 400 rpm) for 30 min at room temperature to allow complete dissolution of the polymer. 0.7 mL of MilliQ water followed by 1.3 ml of different size PVP capped PtNP (30-100 nm) solution was then added to the organic phase with vigorous stirring (900 rpm) via a syringe pump using a 5 ml syringe equipped with a steel needle. The syringe pump was set up for an addition rate of 1ml/h. The solution turned cloudy after the addition of the water (0.7 ml) indicating that polymersomes were already formed. The syringe was changed and the rest of the aqueous platinum nanoparticles solution (1,3 ml) of 80 nm size was added. After complete addition of the aqueous solution of platinum nanoparticles, the colloidal mixture was transferred in a dialysis bag and dialyzed against water. The dialysis water was replaced after 1 h followed by frequent changes for 48 hrs. The organic mixture 80% THF / 20% dioxane used for polymer dissolution generated stomatocytes with a narrow opening less than 5 nm as determined by TEM.

#### **5. Characterization of the assembled nanomotor via 3D electron tomography**

Electron tomography technique provides a comprehensive reconstruction of the 3D structure of the stomatocyte motor by collecting images of the specimen at different tilting angles ( $\pm 70^\circ$ ) along one axis with  $1^\circ$  increments. The series of tilt images were analyzed with the open source software, IMOD, developed by Boulder laboratory to generate the reconstructed.



**Supplementary Fig. S1.** Detailed 3D tomography analysis of the stomatocyte; electron tomography image at different rotation angles along x-axis and the 3D electron reconstruction of the stomatocyte.



**Supplementary Fig. S2.** Detailed 3D tomography analysis of the nanomotor; electron tomography image at different heights on z-axis through the sample and the 3D electron reconstruction of the nanoparticle filled stomatocyte.