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A light-powered shape-configurable micromachine†

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Electronic Supplementary Information

Video S1. The sheet-like micromachine is motionless under an optical microscope when placed in the aqueous solution containing the tracer particles.

Video S2. The moving with outward surface water flow behavior of the sheet-like micromachine under tilted light irradiation (0.5 W/cm^2, 60˚).

Video S3. The outward surface water flow behavior of the sheet-like micromachine under vertical light irradiation (0.2 W/cm^2).

Video S4. The control over the motion behavior of the micromachine (switching between outward surface water flow and moving with outward water flow) by changing the irradiation angle.

Video S5. The moving behavior of the sheet-like micromachine under parallel light irradiation (0.1 W/cm^2).

Video S6. The moving/one-side water flow behavior of the sheet-like micromachine under parallel light irradiation with increased intensity (0.2 W/cm^2).

Video S7. The sheet to tube shape transition of the micromachine under vertical light irradiation with increased intensity (1.2 W/cm^2).

Video S8. The roll-up tube sinks into the solution due to the increased hydrophilicity.

Video S9. The tube to sheet shape transition of the micromachine under vertical light irradiation (1.2 W/cm^2).

Video S10. The reversible sheet to curled-sheet shape transition of the micromachine under vertical light irradiation (1.2 W/cm^2).

Video S11. The roll-up tube is motionless under tilted light irradiation (0.5 W/cm^2, 60˚).

Experimental Section

Materials: poly (3-hexylthiophene-2,5-diyl) (P3HT), 1,2-dichlorobenzene, sodium n-dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), Tween 20, potassium chloride (KCl), potassium hydroxide (KOH), Rhodamine 6G (R6G), positively charged (2.2 μm) and neutral (2-3 μm) polystyrene (PS) microspheres were purchased from Sigma-Aldrich Company. 2 μm negatively charged SiO_2 microsphere was purchased from Sinopharm Chemical Reagent Co. Ltd. Photoresist (AZ1815) were obtained from GermanTech Co. Ltd. The SCAA-104 filter with a pore diameter of 0.22 μm was purchased from ANPEL Scientific Instrument Co. Ltd. Polypyrrole nanoparticles were synthesized according to the literature method.[1] Proton indicator (pyranine) was obtained from J&K Scientific.

Fabrication Methods: Glass slides were cut into small pieces (20×20 mm^2), which were cleaned with a Piranha solution (H_2SO_4/H_2O_2, 7:3 (v/v)) at 70 ˚C for 30 min, rinsed thoroughly with the de-ionized water and dried with nitrogen. The P3HT solution was prepared by dissolving 20 mg/mL P3HT in 1,2-dichlorobenzene at 40 ˚C for 30 min. The solution was filtered by utilizing a SCAA-104 filter. Prior to the photolithography, 50 μL of the photoresist (AZ1815) was first spin-coated onto the glass surface at a speed of 4000 rpm for 45 s. After baking for 2 min on a hot plate at 100 ˚C, the photoresist film was formed on the substrate. The photoresist film was then patterned by the standard photolithographic method, which was carried out on a SUSS MicroTec photolithography system. A photomask was utilized to obtain the desired patterns. The patterns were then developed by using 0.4 % KOH aqueous solution for 30 s, washed with deionized water and dried with nitrogen. 35 μL of 1,2-dichlorobenzene solution containing P3HT was then applied on the patterned photoresist film and spin-coated at 700 rpm for 30 s followed by 2000 rpm for 2 s in a glove box filled with nitrogen. The P3HT film was slowly dried in the nitrogen atmosphere, which was then annealed at 120 ˚C for 10 min. The P3HT patterns were formed by dissolving away the photoresist in alcohol. Finally, the P3HT patterns

were peeled off from the glass substrate by immersing the patterns in water for 3 min. The fabrication of polypyrrole patterns followed the same procedure as shown above except that the polypyrrole nanoparticle solution was applied instead of P3HT solution.

Characterizations: Scanning electron microscopy (SEM) measurement was performed on a Quanta 200 FEG (FEI Company) SEM. The light source utilized in the current study was Model X-Cite 120Q mercury lamp (Excelitas Technologies) with a power of 120 W. The light consisted of five different emission wavelengths, peaked around 371, 409, 442, 554 and 582 nm, respectively. The lamp had a tunable intensity, which ranged from 0 %, 12 %, 25 %, 50 % to 100 %, corresponding to 0, 0.1, 0.2, 0.5 and 1.2 W/cm^2 light intensity, respectively. Atomic force microscopy (AFM) measurement was carried out on a Bruker Dimension scanning probe microscope at room temperature. The PeakForce Tapping mode was utilized for all AFM measurement. A silicon tip was utilized to measure the surface morphology of the P3HT microstructure in the air. For the measurement of the thickness changes in the liquid phase, the P3HT sample, which was fixed on the silicon surface by double sided tape, was placed in the deionized water and then irradiated with white light (60˚, 1.2 W/cm^2, 60 s). The changes in the surface morphology, height were then measured with a silicon tip (force constant of 36.7 N/m). For the micromachine study, the P3HT microstructure was first placed on the surface of the aqueous solution, which contained surfactants (SDS, 0.1 mM) and tracer particles (positively charged PS microsphere unless otherwise mentioned). The white light was then applied to illuminate the P3HT microstructure at a distance of 1 cm with different incident angles and intensities. The motion and shape changes of the micromachine were then recorded by using an OLYMPUS U-TV0.5XC-3 microscopy. The moving and water flow velocity were obtained by using PhysVis software. The contact angle measurements were performed using a Dataphysics OCA 20 contact angle system. Fluorescent images were captured using a Leica DM4000M fluorescence microscope, which were then analyzed by ImageJ software. The temperature of the micromachine under high intensity irradiation was measured by using an I5771-01 non-contact infrared thermometer (Aladdin Company). The zeta potential of all charged PS spheres

was measured using Zetaseizer Nano-ZS (Malvern Instruments). To study the generation of the protons during the light irradiation process, a pH indicator, i.e. pyranine, was added to the solution. In order to study the sensitivity of the proton indicator, we prepared 2 mg/mL pyranine solutions with different pH. 100 μL of this mixture solution was then dropped on a cover glass. The fluorescence intensity was obtained by analyzing the integrated optical density (IOD) per fluorescence area (IOD/area) based on the captured fluorescence image according to the literature method.[2] We measured the surface tension by pendant drop method using DataPhysics OCA contact angle equipment.
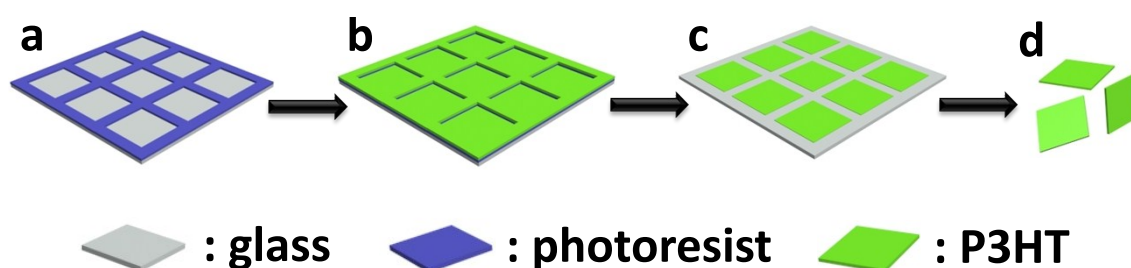
Figure S1. (a-d) Schematic illustration showing the fabrication process of the P3HT-based micromachine.
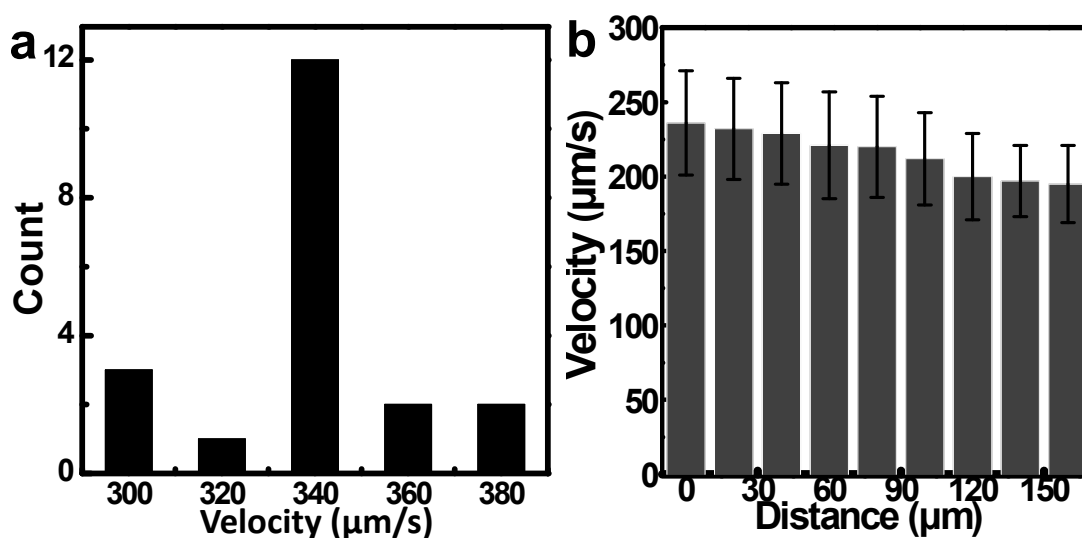
Figure S2. (a) The moving velocity distribution of the micromachine (0.5 W/cm² light intensity, 60° irradiation angle). (b) The average velocities of the tracer particles as a function of the distance to the border of the micromachine (A side).
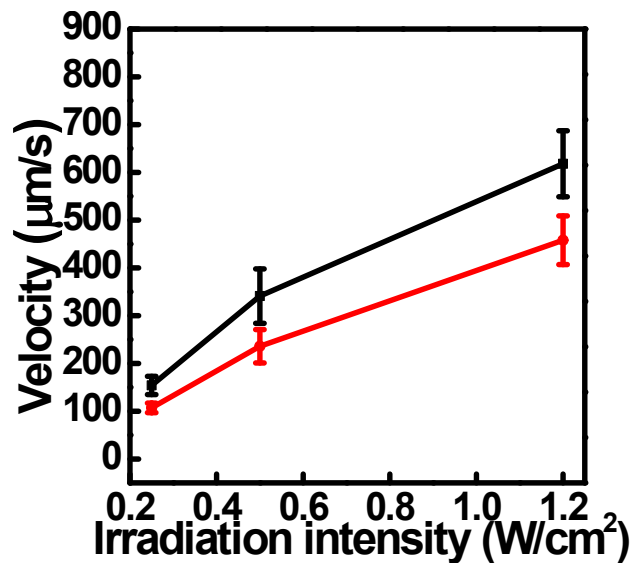
Figure S3. Dependence of the average moving and water flow velocity of the sheet-like micromachine on the irradiation intensity (black curve: moving velocity; red curve: water flow velocity along A side).
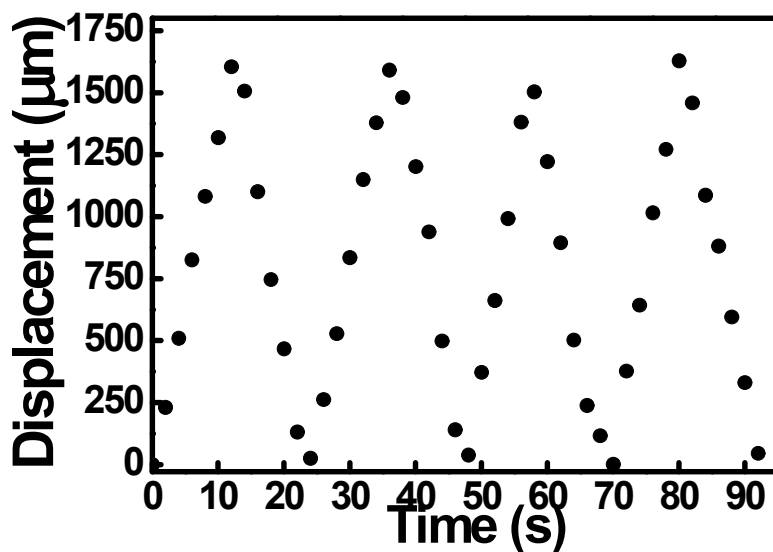

Figure S4. Displacement of the sheet-like micromachine indicating the back and forth movement which is controlled by the light irradiation. The irradiation (0.5 W/cm^2, $60°$) is applied at 0 s to start the micromachine and withdrawn after 12 s to stop the motion. The light is then applied from the opposite direction so that the micromachine returns to the original position. This back and forth motion is cycled for 4 times.
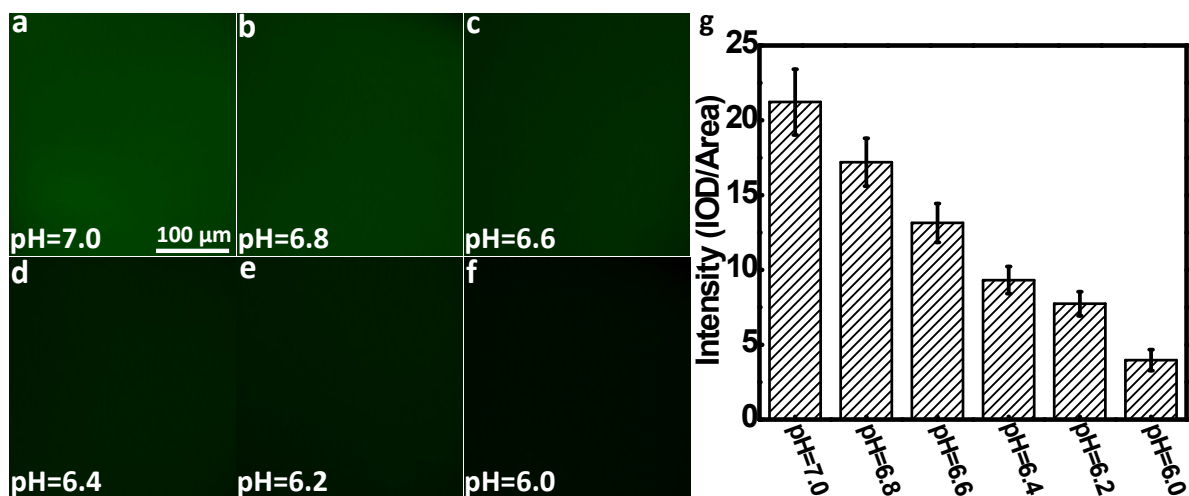
Figure S5. (a-f) pH dependent fluorescence of the pyranine pH indicator. The corresponding fluorescence intensity of pyranine in different pH solution is shown in (g).
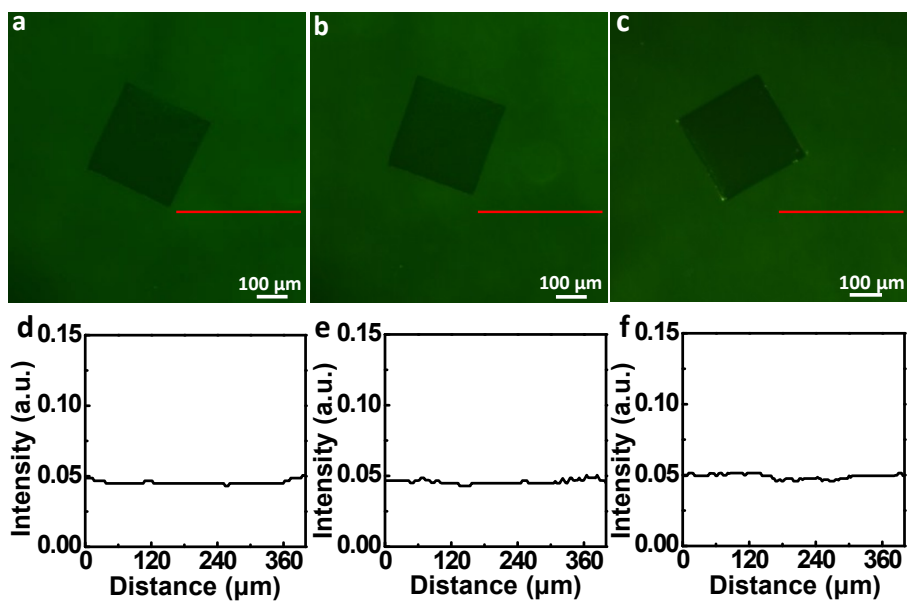
Figure S6. Fluorescence images showing the fluorescence of the pyranine pH indicator near the P3HT structure (a) before and after irradiation (2 min) with (b) 0.2 W/cm², (c) 1 W/cm² light. The corresponding intensities are around 0.05, which are analyzed by the ImageJ software and shown in (d-f), respectively.
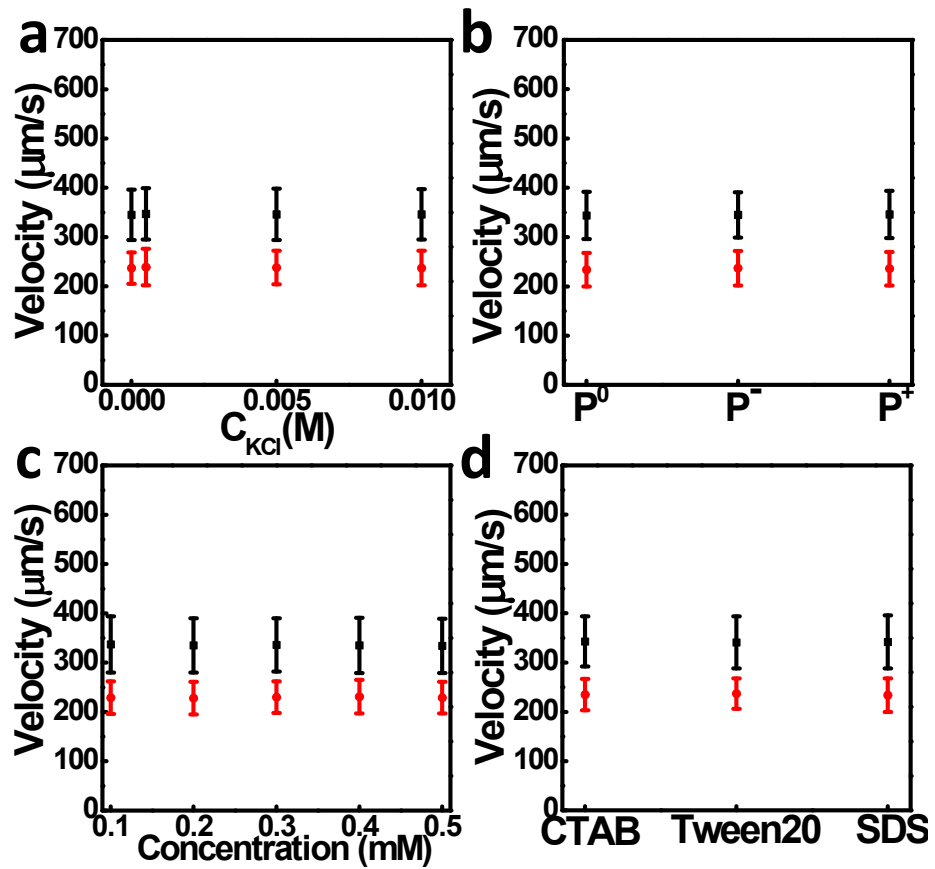
Figure S7. The influence of (a) electrolyte, (b) tracer particles with different surface charges, (c) SDS concentration and surfactant species on the motion behavior of the sheet-like micromachine. The irradiation intensity and angle are 0.5 W/cm^2 and 60°, respectively. Black: moving velocity, red: water flow velocity.
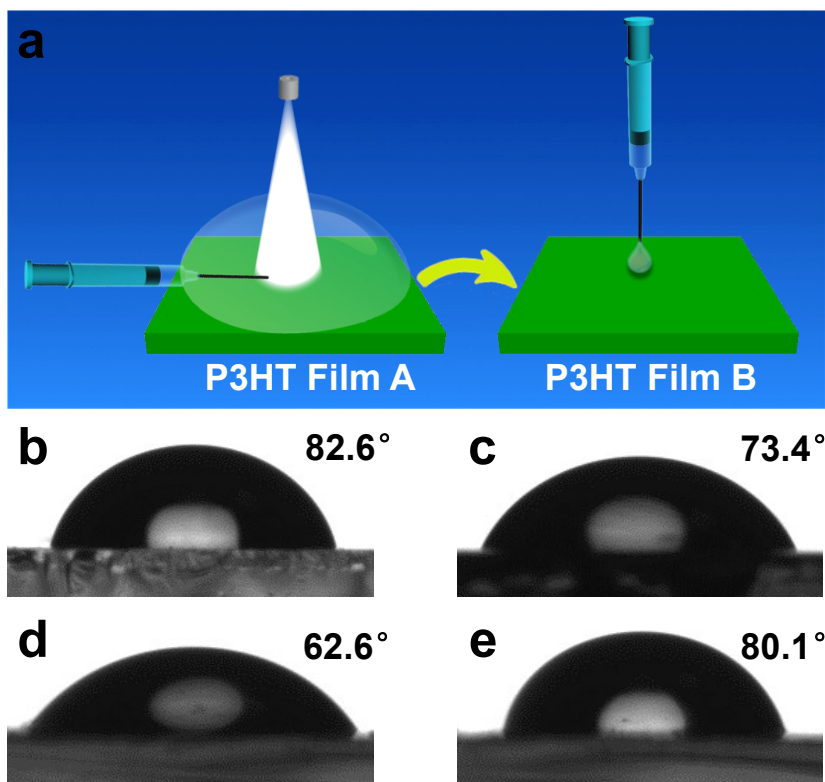
Figure S8. (a) Schematic illustrating the contact angle measurement. SDS solution is sucked out by a micro syringe near the surface of P3HT film A under different conditions and dropped on P3HT film B for contact angle measurement. (b-e) Photographs showing the contact angle of SDS droplet on the surface of P3HT film B. The SDS solution is taken near the surface of P3HT film A (b) prior to light irradiation, or from the irradiated area after 2 min exposure to (c) 0.2 and (d) 0.5 W/cm^2 light, or (e) from the non-irradiated area.
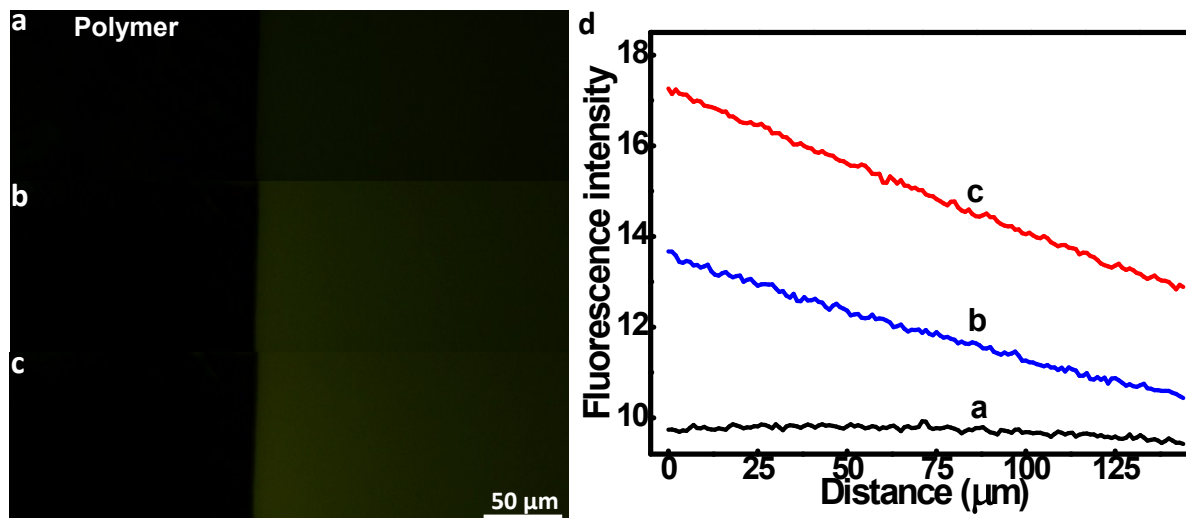
Figure S9. (a) Fluorescence image showing the fluorescence near the border of P3HT and a solution containing SDS (60 mM) and R6G (4.7×10^{-4} M). Fluorescence image of the same position after 2 min irradiation with (b) 0.2 and (c) 0.5 W/cm^2 light. (d) The intensity profiles as a function of the distance to the border of the P3HT structure for images (a-c).
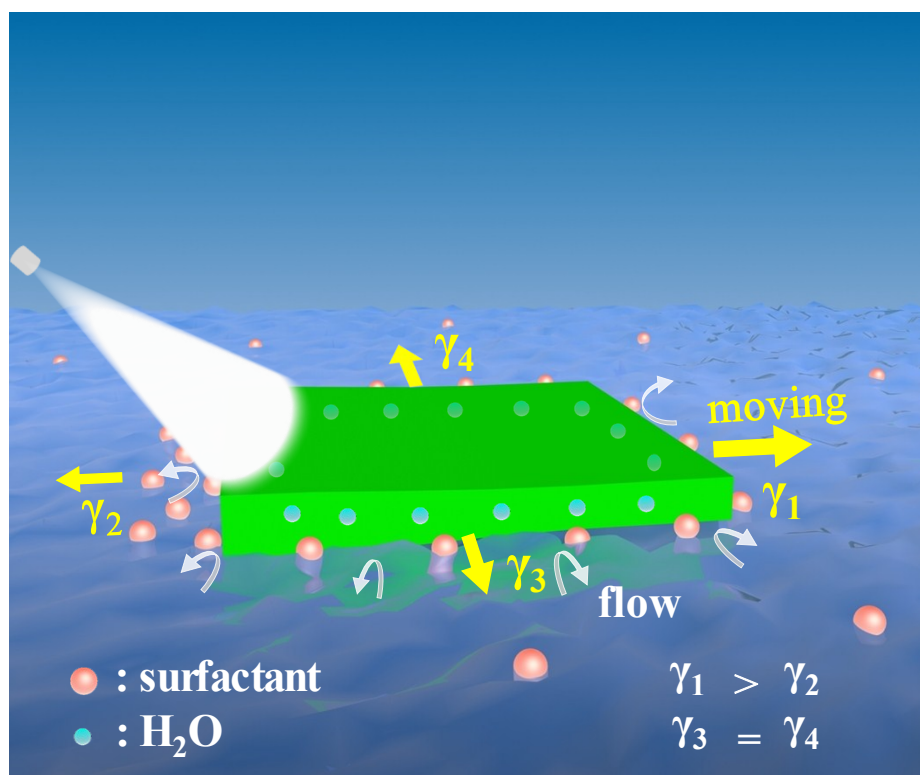

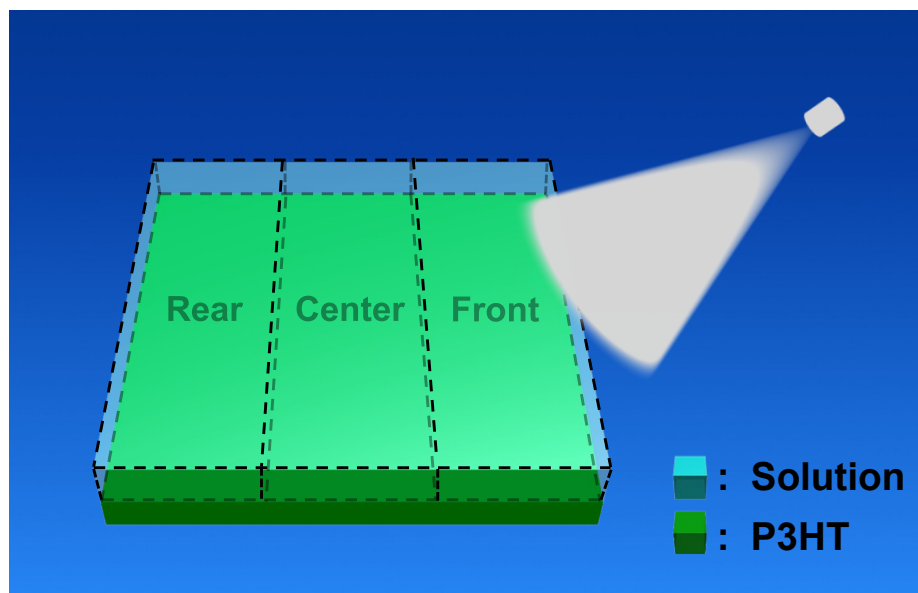**Figure S10.** Schematic showing the tentative motion mechanism of the P3HT-based micromachine.

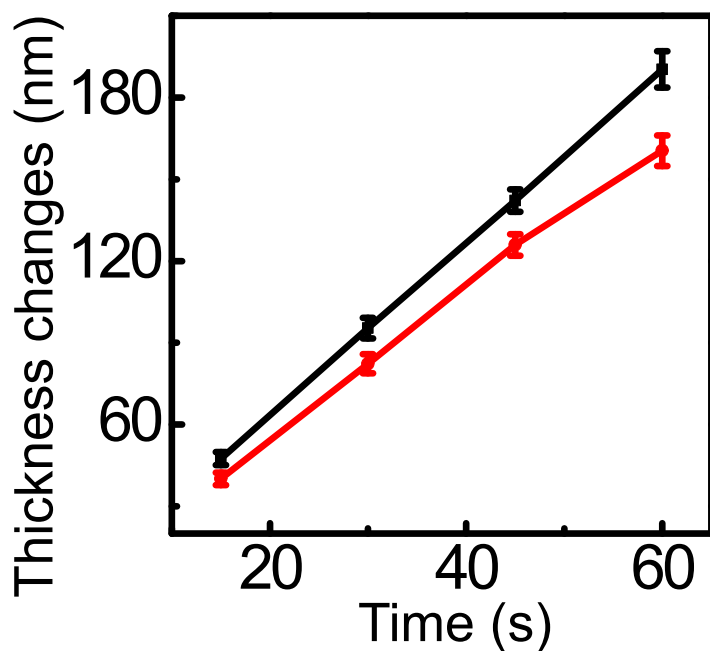**Figure S11.** The calculation model to estimate the surface tension difference.

Figure S12. The thickness changes for the front (black curve) and rear (red curve) side of P3HT film under light irradiation (60º, 1.2 W/cm²).
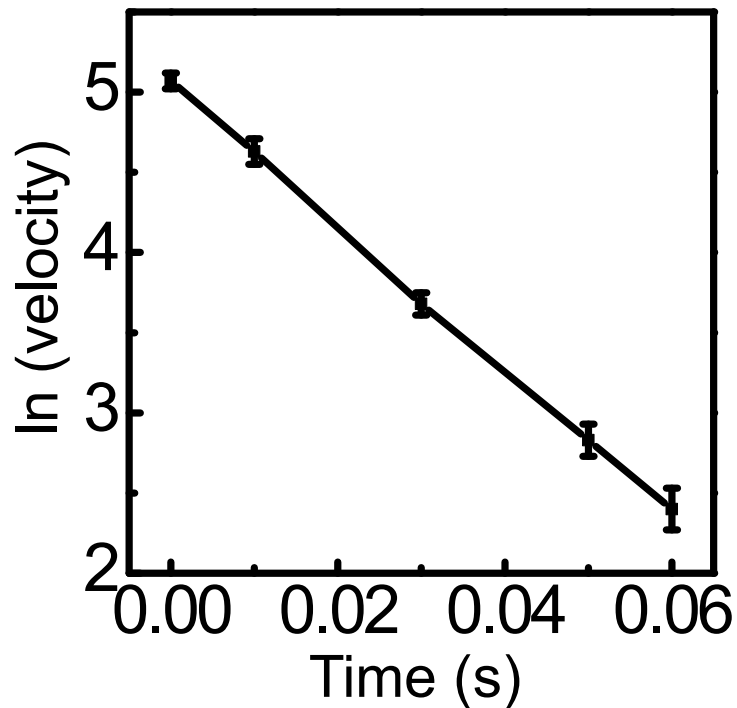
Figure S13. The logarithmic plot of velocity (v(t)) vs time in the relaxation process.
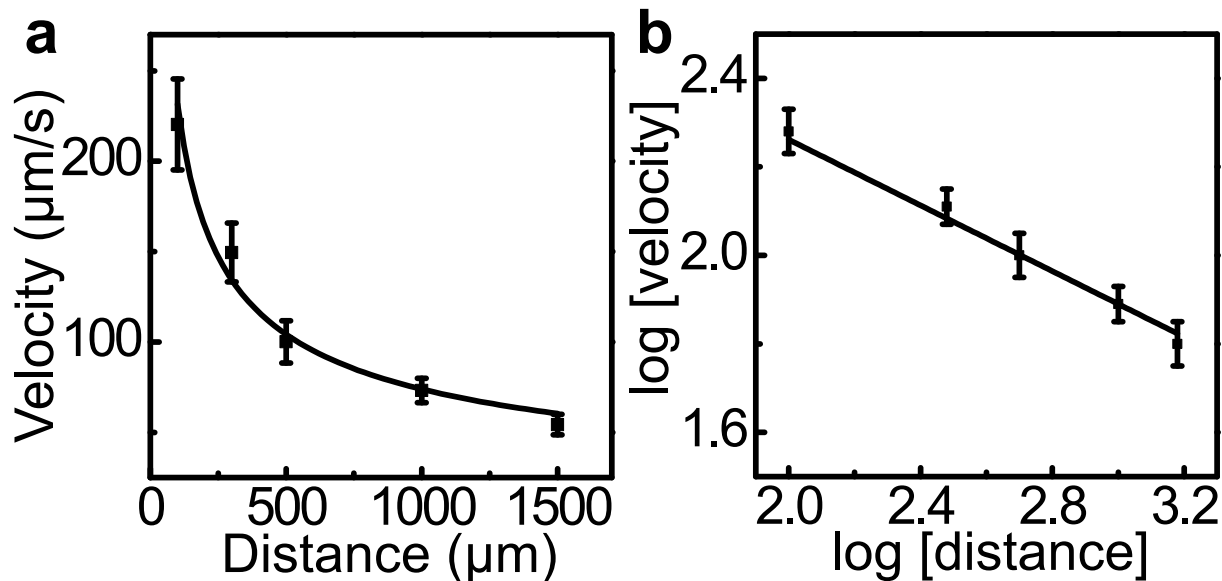

Figure S14. (a) The velocity of tracer particles correspond to the distance from the micromachine under 0.5 W/cm^2 light intensity irradiation. (b) The corresponding logarithmic plot.
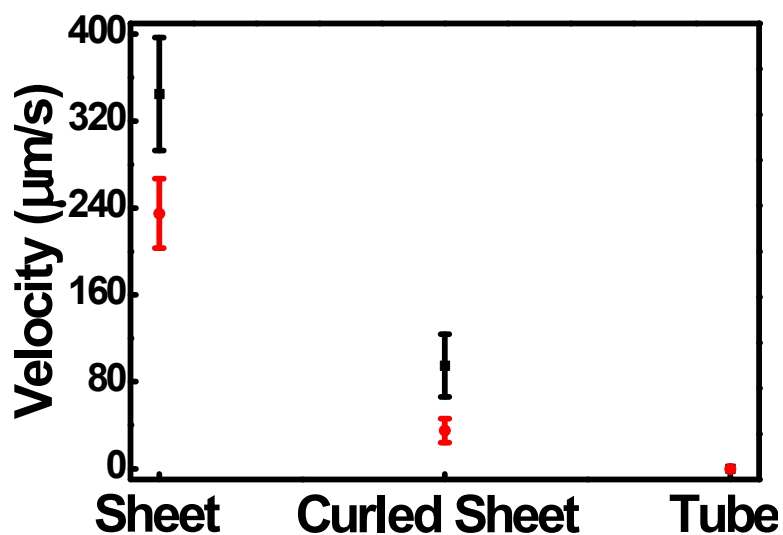
Figure S15. Dependence of the moving and the water flow velocity of the micromachine on its shape. Black and red points are the moving and water flow (along A side) velocities, respectively.
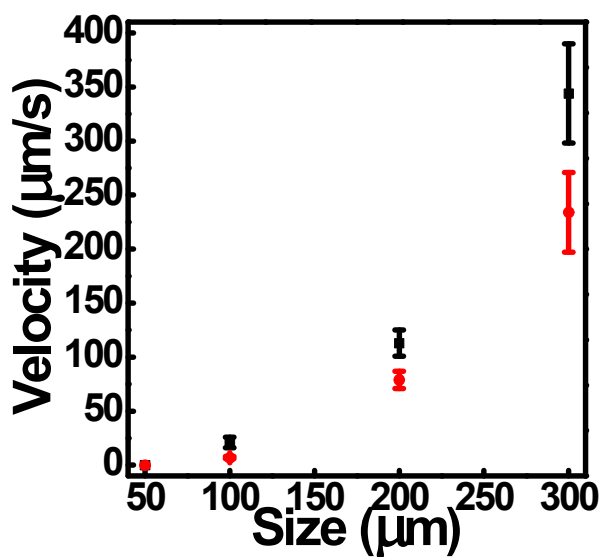

Figure S16. The size-dependent motion velocity of the sheet-like micromachine. The irradiation intensity and angle are fixed at 0.5 W/cm^2 and 60˚, respectively. Black and red points are the moving and water flow (along A side) velocities, respectively.

Reference

1   J. Y. Hong, H. Yoon and J. Jang, *Small*, 2010, **6**, 679-686.
2   M. Liu, Y. Y. Sun, T. P. Wang, Z. R. Ye, H. Zhang, B. Dong and C. Y. Li, *J. Mater. Chem. C*, 2016, **4**, 5945-5952.