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Rapid synthesis of self-propelled tubular micromotors for "ON-OFF" fluorescent detection of explosives

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SI Video-1 The motion of a Pt micromotor in 1 wt% H_2O_2.

SI Video-2 The fluorescence changes of the self-propelled COF-functionalized micromotor before and after exposure to 5 ppm TNP aqueous solution for 10 min.

SI Video-3 Magnetically guided motion of a Fe_3O_4-Pt micromotor.

Experimental Section

Materials

1,3,6,8-Tetrakis(4-formylphenyl)pyrene (TFPPy, 97 %) was purchased from Alfa Chemistry. Hydrazine hydrate (AR, 80 %), hydrogen peroxide (H_2O_2, AR, 30 wt%) and chloroform ($CHCl_3$, AR, ≥ 99.0 %) were purchased from Xi Long SCIENTIFIC (CXL). Polyvinylpyrrolidone (PVP), iron oxide nanoparticles (Fe_3O_4 NPs, 20 nm) and sodium dodecyl sulfate (SDS, ACS, ≥ 99.0 %) were purchased from Aladdin. Ethanol (75 %), *o*-dichlorobenzene (*o*-DCB, AR, ≥ 99.0 %), acetic acid (AcOH, AR, ≥ 99.5 %), tetrahydrofuran (THF, AR, ≥ 99.0 %) were all purchased from Sinopharm Chemical Reagent. 2,4,6-Trinitrophenol (TNP, 10 ng/μL) was purchased from DR EHRENSTORFERTM (LGC). The glass slides used are all commercial glass slides without any treatment. Chemicals were used as received and the solutions were prepared with ultra-pure water (18.2 MΩ.cm@25°) from a Millipore Simplicity water purification system.

Apparatus

The ultrasonication process was carried out with the KQ5200E ultrasonic cleaner (KUNSHAN ULTRASONIC INSTRUMENT CO., LTD). Sputtering was carried out with the SBC-12 ion sputter coater (KYKY TECHNOLOGY CO., LTD). The Scanning Electron Microscope (SEM) images were taken by the Field Emission Scanning Electron Microscope (MAIA3 LMH). All the optical images and videos in this paper were taken with an OLYMPUS BX43 microscope equipped with a camera. The analysis of the motion trajectory, velocity and fluorescence intensity of the micromotors are all obtained by the analysis of the OLYMPUS cellSens Dimension system.

Preparation of azine-linked covalent organic framework (Py-Azine COF)

Typically, the Pyrex tube (10 mL) filled with a mixture of 15.0 mg TFPPy (0.024 mmol), 2 mL *o*-DCB, 1.94 μL hydrazine hydrate (0.06 mmol) and 0.2 mL AcOH (6 M) was degassed by freezing-pumping-thawing cycles for several times. After vacuum sealing, Pyrex tube was heated at 120° ± 5° for 7 days. After cooling to room temperature, the resulting mixture was centrifuged and collected. The obtained yellow precipitates were washed six times with a mixed solution of $CHCl_3$ and THF (1:1 by vol.), and dried overnight under vacuum at 120° ± 5°.

Preparation of self-propelled COF-functionalized micromotors

The functional particles (40 mg Fe_3O_4 NPs or 40 mg Py-Azine COF) were dispersed in a 5 wt% PVP solution (10 mL) by ultrasonication. The above solution was evenly coated on the commercial square glass slide without any treatment, followed by drying in the oven (60 °C). After that, the glass slide was placed in a vacuum sputtering apparatus to sputter a layer of Pt with 60 s (8 mA, 6 Pa/mmHg). The glass slide was ultrasonicated subsequently in water about 30 s (40 kHz), and the aqueous suspension of microtubes with a swiss-roll shape can be obtained. The product was centrifuged and washed three times with deionized water.

Motion study of the micromotors

The experiments investigating the motion of the tubular micromotors were conducted in solution containing 1, 2, 3, 4, 5 wt% H_2O_2 and constant concentration of SDS (1 wt%). A mixture of tubular micromotors, H_2O_2 and SDS was dropped on a bare glass slide. The velocities of micromotors were analyzed using the OLYMPUS cellSens Dimension system. All optical images and videos were taken by the microscope equipped with a camera. All images and videos are original, and have not been modified or beautified by photoshop.

Fluorescence detection of TNP using COF-functionalized micromotors

The propelled COF-functionalized micromotors were using for the fluorescence detection experiment. An aqueous mixture (100 μL) of COF-functionalized micromotors, TNP (10 ppm), H_2O_2 (30 wt%) and SDS (10 wt%) was prepared. The resulting final mixed solution includes 5 ppm TNP, 1 wt% H_2O_2 and 1 wt% SDS. The total number of COF-functionalized micromotors in above solution (100 μL) were around 150. At every two minutes, 5 μL of the mixture was taken out to measure the fluorescence intensities of micromotors. The static COF-functionalized micromotors were used for the controlled experiment. An aqueous mixture (100 μL) of COF-functionalized micromotors, TNP (10 ppm) and SDS (10 wt%) was prepared. The number of micromotors were kept the same with that in the experiment of propelled micromotors. The fluorescence intensities of the static COF-functionalized micromotors were measured every ten minutes. In the experiments, 470 nm was chosen as the excitation wavelength. All optical images and videos were taken by the microscope equipped with a camera. The fluorescence intensities of COF-functionalized micromotors were analyzed by using the OLYMPUS cellSens Dimension system. All the data points were the average values obtained from 10 independent experiments.

Magnetic guidance study of the micromotors

For the magnetic guidance studies, a commercial magnet was used to provide external magnetic field. All optical images and videos were taken by the microscope equipped with a camera. All images and videos are original, and have not been modified or beautified by photoshop.

Magnetic separation of the micromotors

A certain amount of Fe_3O_4-Pt micromotors were dispersed in deionized water. Pictures were taken after ultrasonic dispersion and magnetic separation with ordinary commercial magnets, respectively.

Study on the influence of H_2O_2 on fluorescence intensity of Py-Azine COF

An aqueous mixture (100 μL) of Py-Azine COF, H_2O_2 (1 wt%) and SDS (1 wt%) was prepared. At every ten minutes, 5 μL of the mixture was taken out to measure the fluorescence intensities of Py-Azine COF. In the experiments, 470 nm was chosen as the excitation wavelength.

Study on the influence of PVP on fluorescence detection of COF-functionalized micromotors when detecting explosives

The static COF-functionalized micromotors were used to study the effect of PVP on the fluorescence intensity of micromotors without explosives. An aqueous mixture (100 μL) of COF-functionalized micromotors, PVP (5 wt%) and SDS (1 wt%) was prepared. The propelled COF-functionalized micromotors were using for the fluorescence detection experiment. An aqueous mixture (100 μL) of COF-functionalized micromotors, TNP (5 ppm), PVP (5 wt%), H_2O_2 (1 wt%) and SDS (1 wt%) was prepared. The static COF-functionalized micromotors were used for the controlled experiment. An aqueous mixture (100 μL) of COF-functionalized micromotors, TNP (5 ppm), PVP (5 wt%) and SDS (1 wt%) was prepared. The total number of COF-functionalized micromotors in above solution (100 μL) were around 150. At every ten minutes, 5 μL of the mixture was taken out to measure the fluorescence intensities of micromotors.

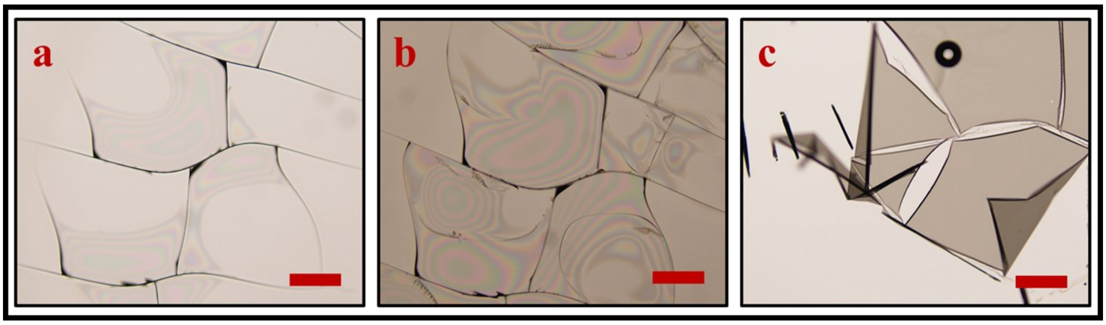

Fig. S1 Optical photos of (a) before and (b) after sputtering the Pt layer on the PVP coating. Scale bar = 200 µm. (c) The rolling-up behaviour of tubular Pt micromotors in ultrasonic progress. Scale bar = 200 µm.

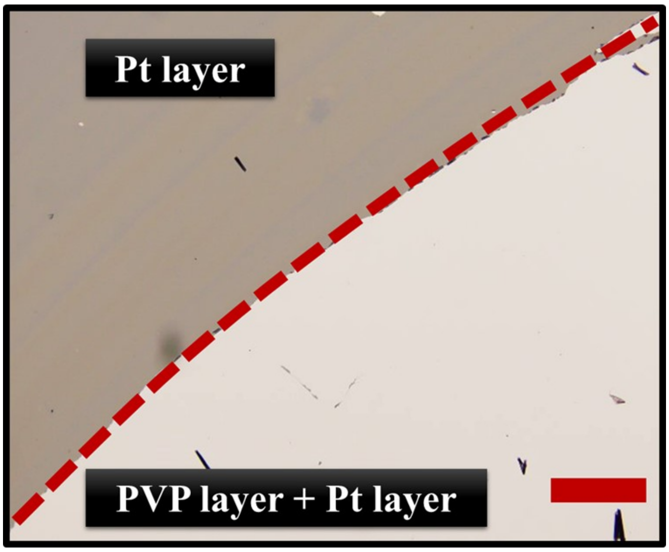

Fig. S2 An optical photo of the glass slide without (dark-coloured area) and with (bright-coloured area) the PVP layer after ultrasonication in water. Scale bar = 200 µm.

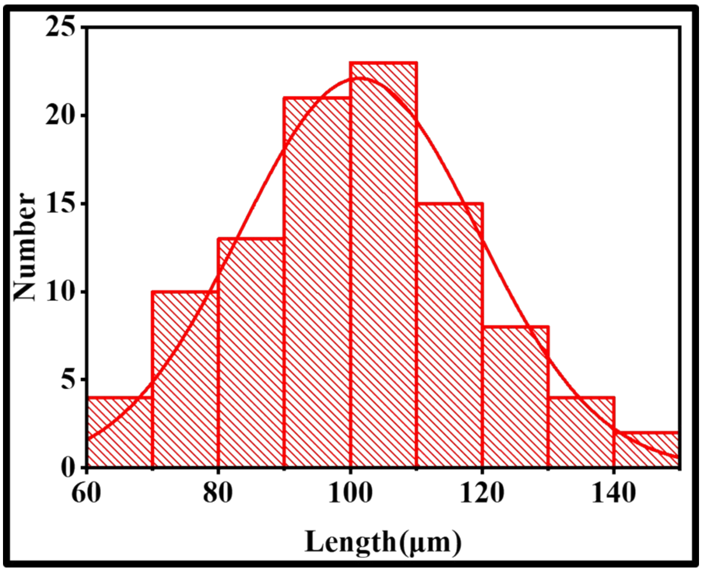

Fig. S3 The length distribution of the tubular micromotors obtained after ultrasonic treatment for 30 s. Total number = 100.

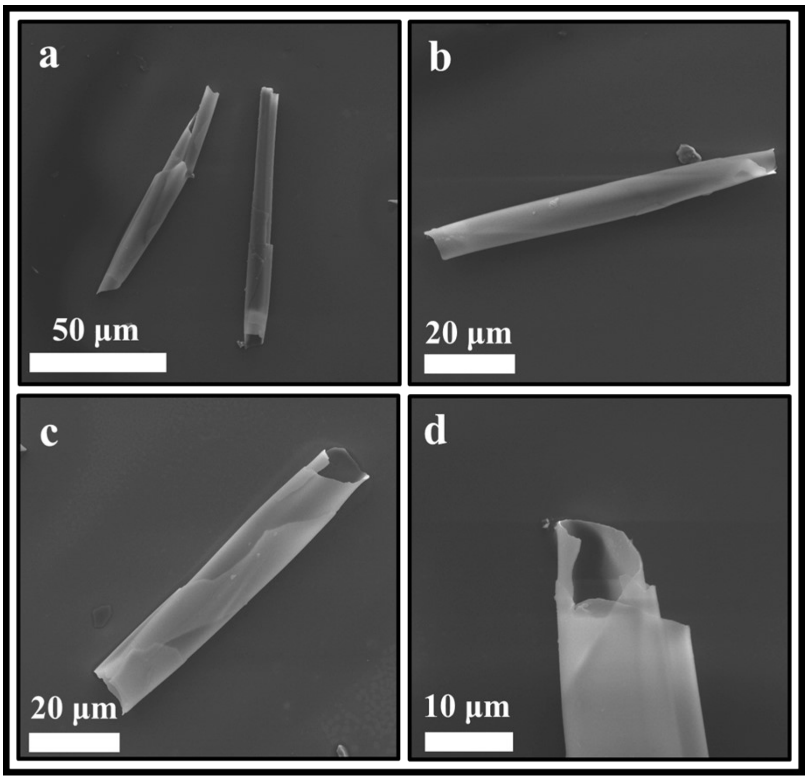

Fig. S4 SEM images of tubular Pt micromotors at different magnifications.

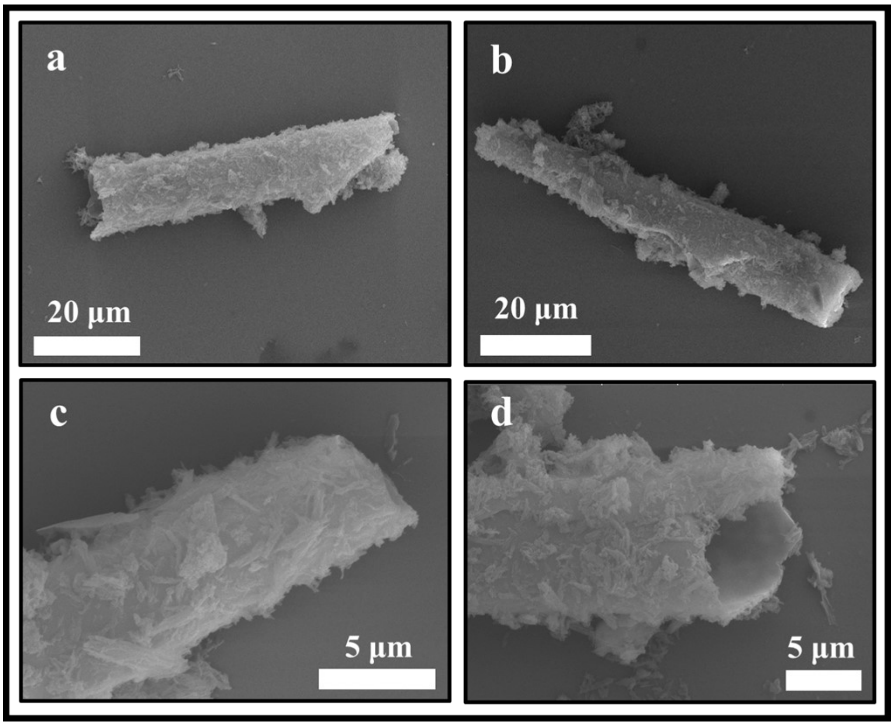

Fig. S5 SEM images of the COF-functionalized Pt micromotors at different magnifications.

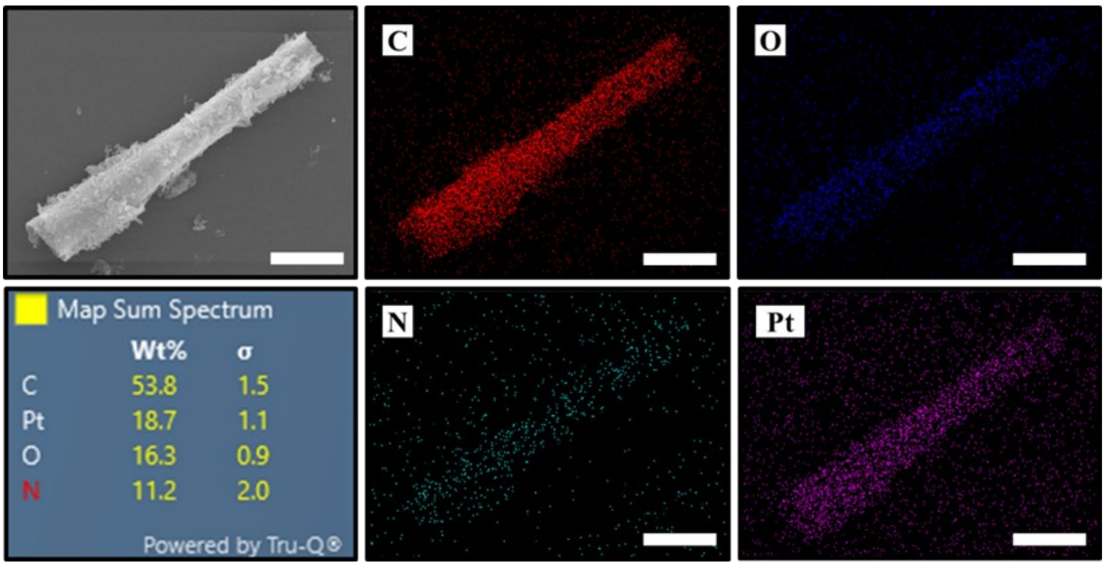

Fig. S6 The SEM image of one COF-functionalized Pt micromotor and corresponding EDX elemental mapping. Scale bar = 20 μm.

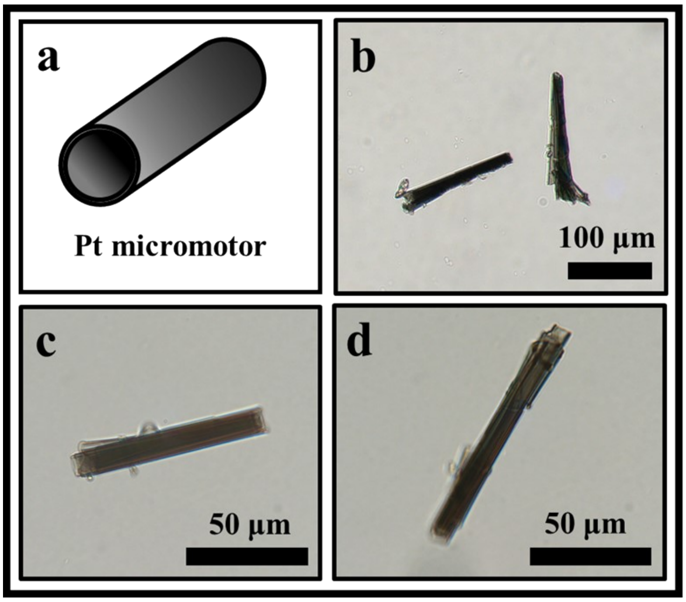

Fig. S7 (a) Schematic diagram of the tubular Pt micromotor. (b)-(d) Optical images of the tubular Pt micromotor.

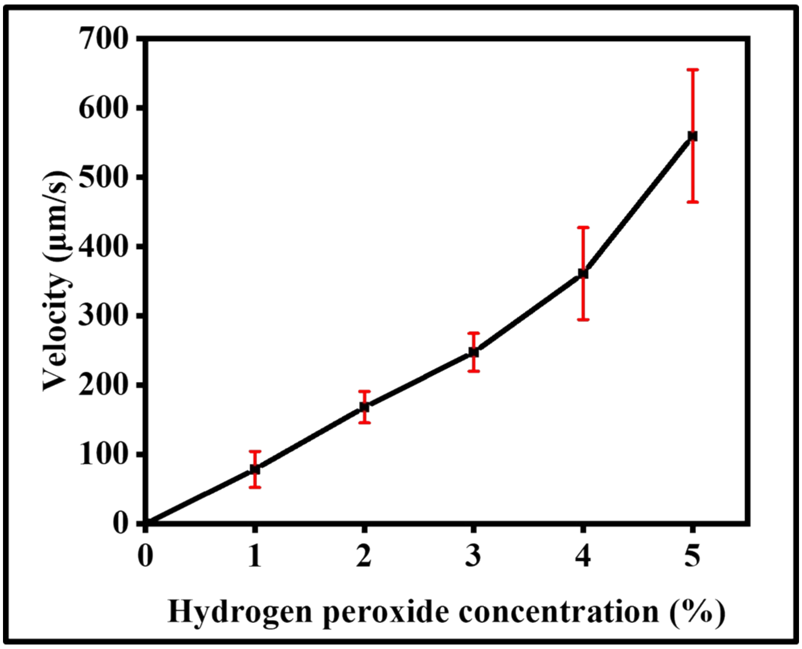

Fig. S8 Line chart of dependence of the velocity of Pt micromotors on the concentration of H_2O_2. Tracking data were obtained from 10 independent experiments to obtain the average speed. The error bars indicate standard deviation.

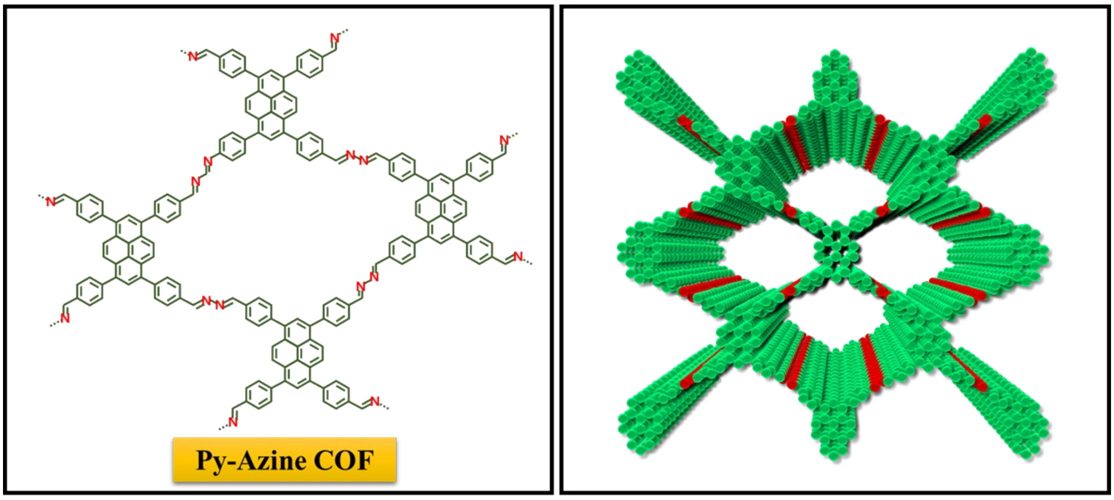

Fig. S9 Structural diagrams of Py-Azine COF.

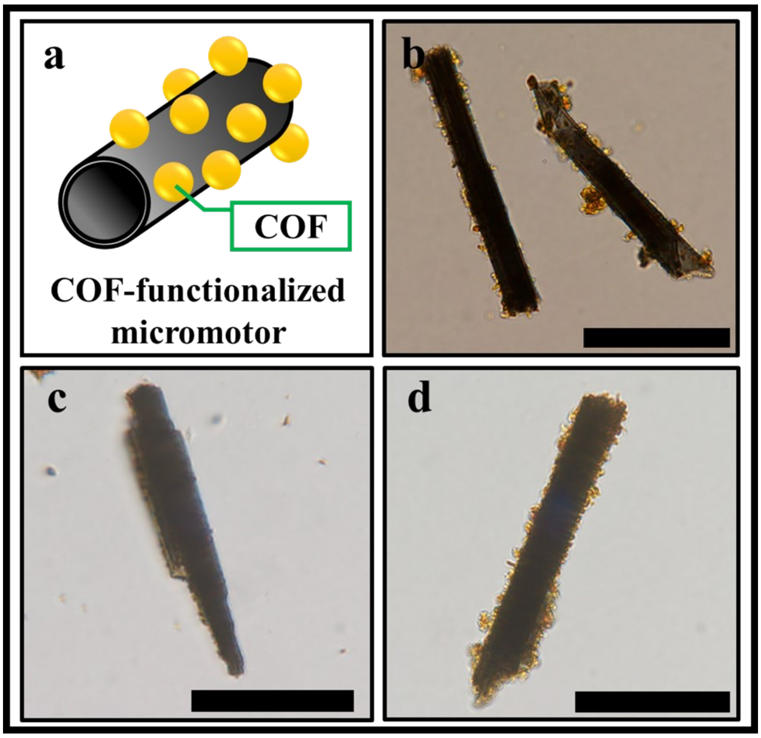

Fig. S10 (a) Schematic diagram of the COF-functionalized micromotor. (b)-(d) Optical images of the COF-functionalized micromotors. The scale bar is 50 μm.

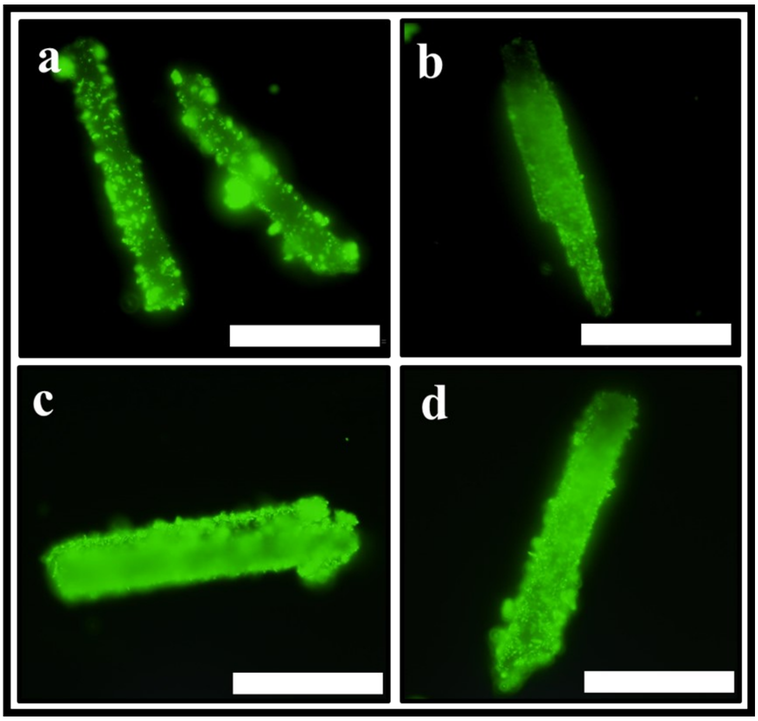

Fig. S11 Fluorescence images of COF-functionalized micromotors. The scale bar is 50 μm.

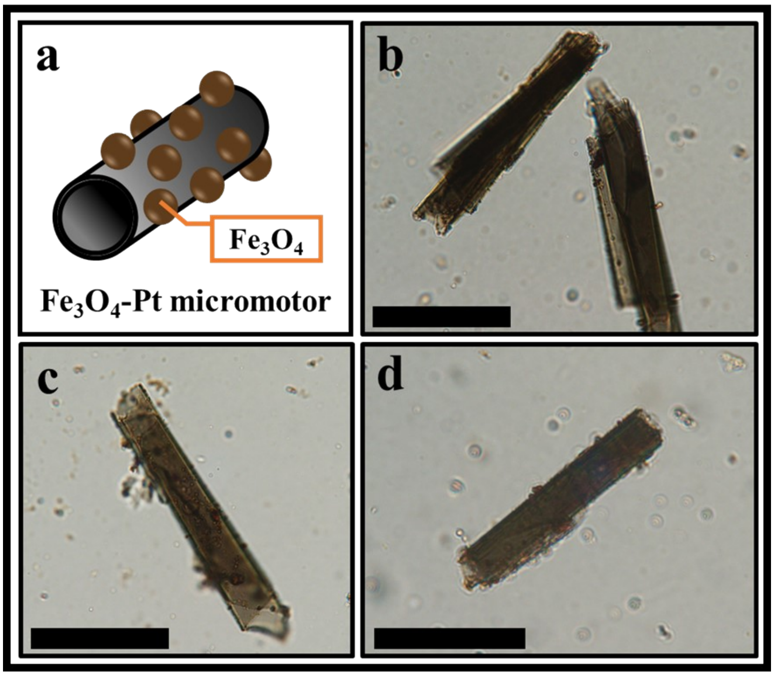

Fig. S12 (a) Schematic diagram of the Fe_3O_4-Pt micromotor. (b)-(d) Optical images of the Fe_3O_4-Pt micromotors. The scale bar is 50 μm.

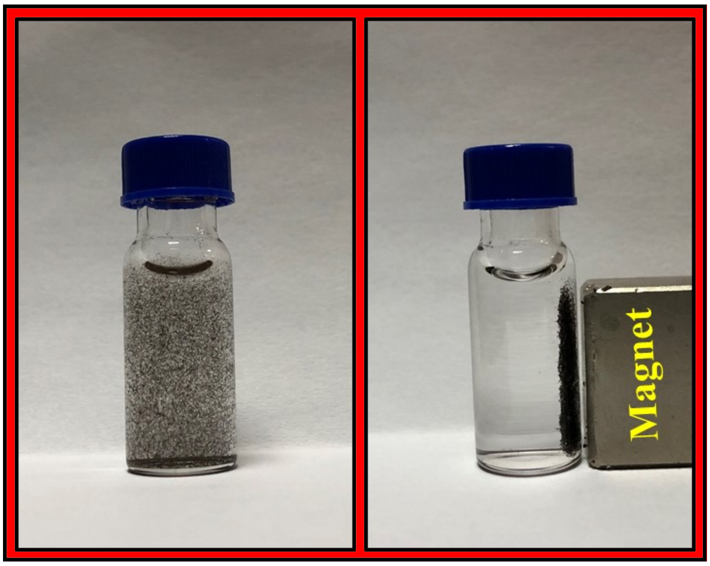

Fig. S13 A digital photograph of the magnetic separation.