Metal-Organic Frameworks as Micromotors with Tunable Engines and Brakes

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Supporting Information

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General Methods

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Centrifugation was performed using a Beckman Coulter Allegra X-22R Centrifuge, with a fixed-angle rotor at 6800 rpm for 10 min. Microscopy videos were captured by an inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a Hamamatsu digital camera C11440.

Synthesis of UiO-67-bpy$_{0.25}$. $ZrCl_4$ (120 mg, 0.51 mmol), benzoic acid (2.0 g, 16.4 mmol), H_2bpdc (biphenyldicarboxylic acid, 94 mg, 0.39 mmol), and H_2bpydc (2,2'-bipyridine-5,5'-dicarboxylic acid, 32 mg, 0.13 mmol) were placed in a bottle with 20 mL DMF. The solids were dispersed via sonication for ~10 min, followed by incubation at 120 °C for 24 h. After cooling, solids were collected by centrifugation and the solvent was decanted. The solids were washed with DMF (2×20 mL), followed by soaking in ethanol (EtOH) for 3 d, with the solution exchanged with fresh EtOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

Metalation of UiO-67-bpy$_{0.25}$ with Co(II) or Mn(II). Metal salt (0.1 mmol, $Co(OAc)_2$ or $Mn(OAc)_2$) was dissolved in 2 mL MeOH and 0.5 mL DMF. UiO-67-bpy$_{0.25}$ (36 mg, 0.1mmol) was added into the solution and dispersed via sonication for ~5 min, then incubated at 55 °C for 24 h. After 24 h at 55 °C, the supernatant was decanted by centrifugation and the solids were washed profusely with DMF (3×10 mL) and MeOH (4×10 mL). The solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum to afford UiO-67-

$Co(bpy)_{0.25}$ and UiO-67-$Mn(bpy)_{0.25}$. SEM-EDX was used to quantitate the degree of metalation by Co^{2+} and Mn^{2+}.

MOF Micromotor Propulsion Characterization. The autonomous propulsion of the MOF micromotors in aqueous solution was achieved by using hydrogen peroxide fuel at different concentrations (5%, 10%, 15% (v/v) in water). A 2 μL drop of micromotor suspension in water was placed on a glass slide followed by a 2 μL drop of hydrogen peroxide fuel. Microscopy videos were captured by an inverted optical microscope with a digital camera. The videos were tracked and analyzed using the NIS Elements AR 3.2 software. In the chemical braking tests, the hydrogen peroxide fuel was added containing NDI or EDTA at a concentration of 0.3 M. A 2 μL drop of this combined chelator/fuel solution was added to the micromotor suspension, resulting a final chelator concentration of 0.15 M. Videos were captured and tracked in the same manner as experiments without chelator.

Powder X-ray Diffraction (PXRD) Analysis. ~20-30 mg of UiO-67 derivative samples were dried under vacuum prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ=1.5418 Å), with a scan speed of 0.2 sec/step, a step size of 0.03° in 2θ, and a 2θ range of ~5 to 40° (sample dependent). The experimental backgrounds were corrected using Jade 5.0 software package.

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy. ~2-5 mg of activated UiO-67 derivative materials was transferred to conductive carbon tape on a sample holder disk, and coated using a Ir-sputter coating for 8 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum. Oxford EDX and Inca software are attached to determine elemental mapping of particle surfaces at a working distance at 10 mm.

Electron microscopy images with ~19000× magnification were finely focused, and collected at 10 mm working distance.

Supporting Videos

Supporting Video 1. Propulsion of UiO-67-bpy$_{0.25}$ micromotor engines metalated with Co^{2+} and Mn^{2+} in a peroxide fuel concentration of 15%.

Supporting Video 2. Behavior of UiO-67-bpy$_{0.25}$ crystal without metalation compared with the same micromotor metalated with Co^{2+} in a peroxide fuel concentration of 5%.

Supporting Video 3. Propulsion of UiO-67-Co(bpy)$_{0.25}$ micromotor engine (metallated with Co^{2+}) at the 0 min and 15 min after adding IDA (0.15 M) braking.

Table S1. Metal ratio before and after treatment with chemical brakes (IDA or EDTA), as measured by SEM-EDX.

MOF	**Treatment**	**M/Zr ratio (M = Co or Mn)**
UiO-67-Co(bpy)$_{0.25}$	As-synthesized	20%
	With IDA	2%
	With EDTA	1%
UiO-67-Mn(bpy)$_{0.25}$	As-synthesized	25%
	With IDA	1%
	With EDTA	1%

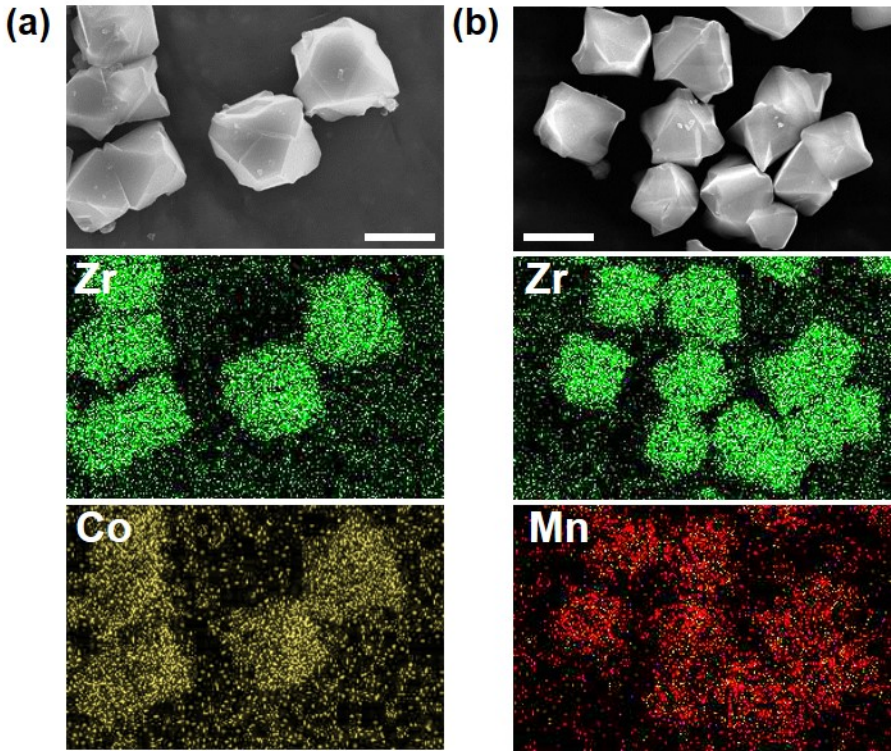

Figure S1. SEM and EDX characterization of UiO-67-bpy$_{0.25}$ metallated with: (a) Co(OAc)$_2$ and (b) Mn(OAc)$_2$. Scale bar: 5 μm.

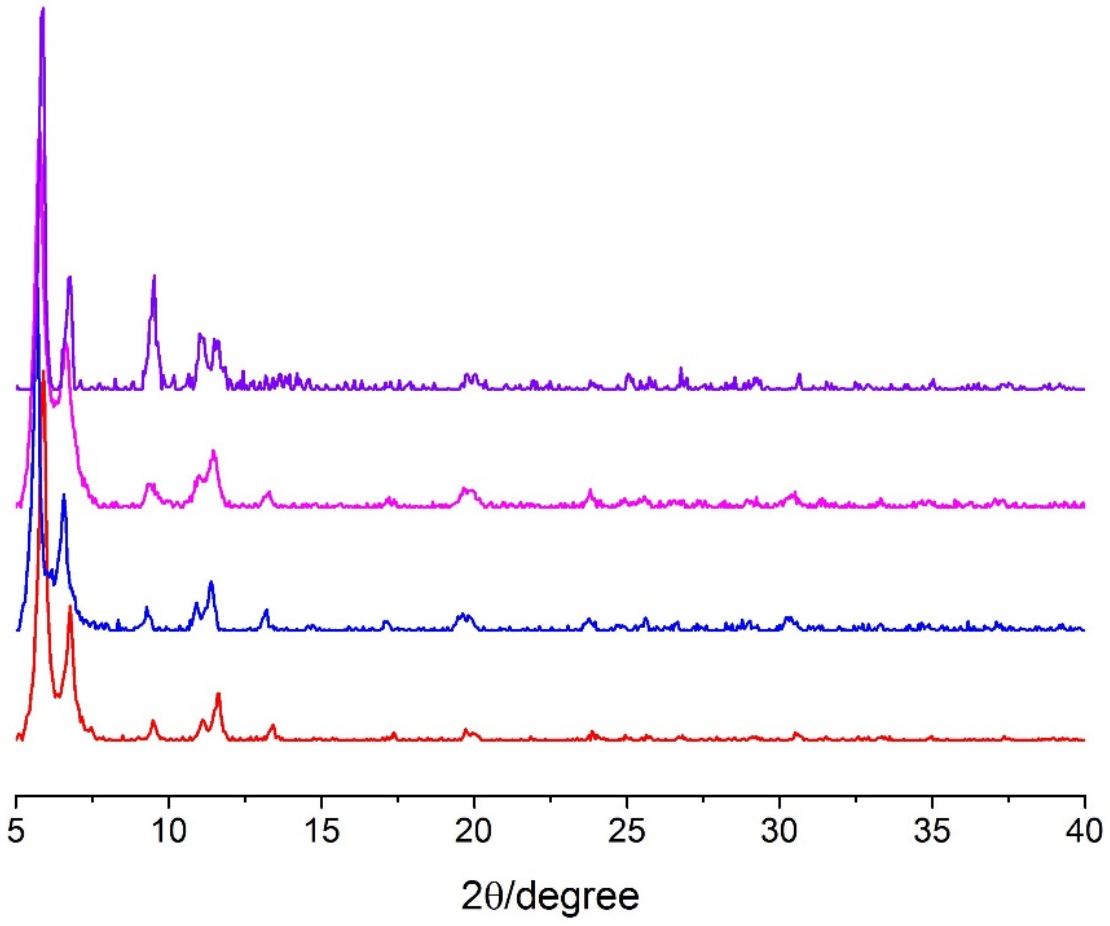

Figure S2. PXRD of MOF micromotors after treatment with braking chelators for 1 h: UiO-67-Co(bpy)$_{0.25}$ with EDTA (red), UiO-67-Mn(bpy)$_{0.25}$ with EDTA (blue), UiO-67-Co(bpy)$_{0.25}$ with IDA (magenta), andUiO-67-Mn(bpy)$_{0.25}$ with IDA (violet).

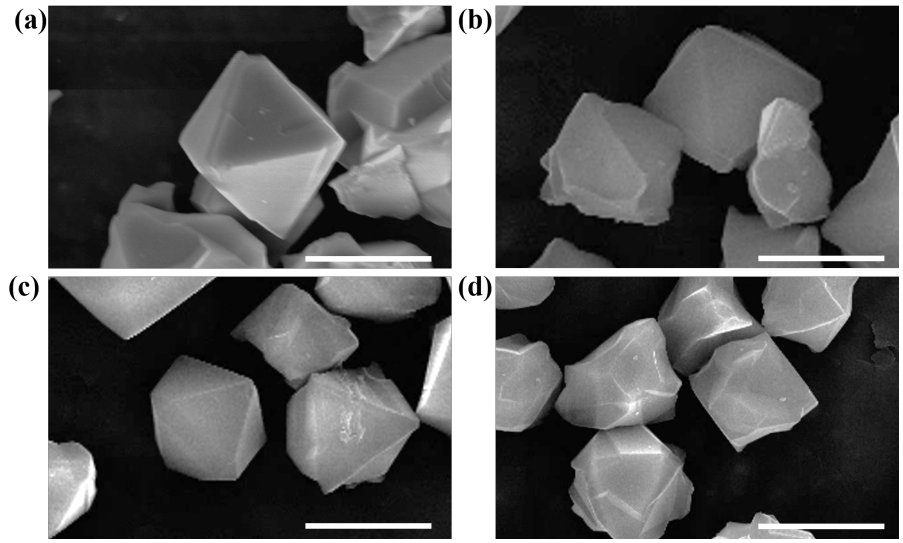

Figure S3. SEM of MOF micromotors after treatment with braking chelators for 1 h: (a) UiO-67-Co(bpy)$_{0.25}$ with EDTA, (b) UiO-67-Co(bpy)$_{0.25}$ with IDA, (c) UiO-67-Mn(bpy)$_{0.25}$ with EDTA, and (d) UiO-67-Mn(bpy)$_{0.25}$ with IDA. Scale bars: 5 μm.