

ADVANCED MATERIALS

Supporting Information

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Spatioselective Growth of Metal-Organic Framework
Nanocrystals on Compositionally Anisotropic Polymer
Particles

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1. Materials

CuCl, ethyl α -bromoisobutyrate as a initiator, and 4,4'-bipyridyl (bpy) were purchased from Sigma-Aldrich and used without further purification. *n*-Butyl methacrylate and *t*-butyl methacrylate were purchased from Sigma-Aldrich and used after passing a short alumina column. The fluorescence dyes poly[(*m*-phenylenevinylene)-*alt*-(2,5-dibutoxy-*p*phenylenevinylene)] (MEHPV) and poly[tris(2,5-bis(hexyloxy)-1,4-henylenevinylene)-*alt*-(1,3-phenylenevinylene)] (PTDPV), which were used as CLSM markers with blue and green emission. Iron oxide nanocrystals (30 nm diameter) suspended in chloroform and stabilized with oleic acid were purchased from Ocean Nanotech, USA.

2. Instrumentation

The confocal laser scanning microscopy (CLSM) images of particles were visualized using an Olympus FluoView 500. Two different lasers, 405 nm laser and 488 nm Argon laser were used to excite the MEHPV and PTDPV dyes, respectively. The barrier filters were set to 430-460 nm for MEHPV, 505-525 nm for PTDPV. The glass transition temperatures (T_g) of copolymers evaluated using 3 based on their DSC thermograms. The measurements were carried out using a TA Instruments Q2000 Modulated DSC at a scanning rate of 10 °C/min. In order to obtain SEM images, the samples were coated with gold before analysis and the particle morphology was examined using an AMRAY 1910 Field Emission Scanning Electron Microscope (FEG-SEM). Fourier transformed Infrared (FTIR) spectra of KBr pellets were obtained using a Nicolet 6700 spectrometer.

3. Synthesis of copolymers

Cinnamoyl ethyl methacrylate is synthesized using literature procedure.⁽¹⁾

Poly(n-butyl methacrylate)-co-(cinnamoyl ethyl methacrylate), P(nBMA-co-CEMA). n-Butyl methacrylate (8.85 g, 62.2 mmol), cinnamoyl ethyl methacrylate (1.62 g, 6.22 mmol), ethyl α -bromoisobutyrate (0.0334 g, 0.171 mmol), and DMF (10.47 g) were placed in a 50 mL flask and purged with N₂ for 30 min. CuCl (0.123 g, 1.24 mmol) and bpy (0.388 g, 0.248 mmol) were added and purged with N₂ for another 30 min. The reaction mixture was heated at 50 °C for 24 h. After cooled down to room temperature, the mixture was poured into MeOH (100 mL) to precipitate. The solid was dissolved in CH₂Cl₂ and purified by reprecipitation using MeOH. Yield 8.8 g ($M_n = 67600$, $M_w = 78300$; $T_g = 27$ °C); ¹H NMR (CDCl₃) 7.72 (d, $J = 16$ Hz, 1H) 7.60 (br, 2H) 7.38 (br, 3H), 6.56 (m, 1H), 4.39 (br, 2H), 4.30 (br, 2H), 3.92 (br, 20H), 1.80 (br, 2H), 1.80 (br, 20H), 1.69 (br, 20H), 1.37 (br, 20H), and 0.93 (m, 63H) ppm; IR (KBr) 2690, 2935, 2873, 1728, 1639, 1485, 1466, 1383, 1311, 1271, 1244, 1173, 1155, 1066, 966, and 946 cm⁻¹.

Poly(t-butyl methacrylate)-co-(cinnamoyl ethyl methacrylate), PtBMA-co-CEMA. t-Butyl methacrylate (9.00 g, 63.3 mmol), cinnamoyl ethyl methacrylate (1.65 g, 6.33 mmol), ethyl α -bromoisobutyrate (0.034 mg, 0.174 mmol), and DMF (10.65 g) were placed in a 50 mL flask and purged with N₂ for 30 min. CuCl (0.138 g, 1.39 mmol) and bpy (0.435 mg, 2.78 mmol) were added and purged with N₂ for another 30 min. The reaction mixture was heated at 50 °C for 24 h. After cooled down to room temperature, the mixture was poured into MeOH (100 mL) to precipitate. The solid was dissolved in CH₂Cl₂ and purified by reprecipitation using MeOH. Yield 3.9 g ($M_n = 36300$, $M_w = 38900$; $T_g = 114$ °C); ¹H NMR

(CDCl₃) 7.72 (d, $J = 16$ Hz, 1H), 7.59 (br, 2H), 7.37 (br, 3H), 6.58 (m, 1H), 4.38 (br, 2H), 4.19 (br, 2H), 2.04 (br, 2H), 1.80 (br, 20H), 1.39 (br, 90H), and 1.01 (br, 33H) ppm; IR; 2980, 2935, 1274, 1639, 1479, 1460, 1392, 1367, 1254, 1140, 972, and 849 cm⁻¹.

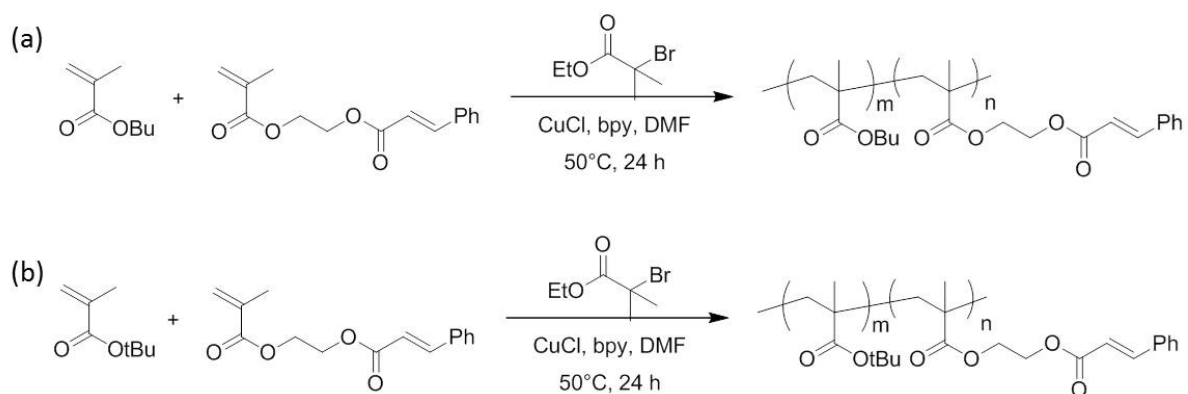


Fig S1. Synthesis of (a) P(*n*BMA-*co*-CEMA) and (b) P(*t*BMA-*co*-CEMA).

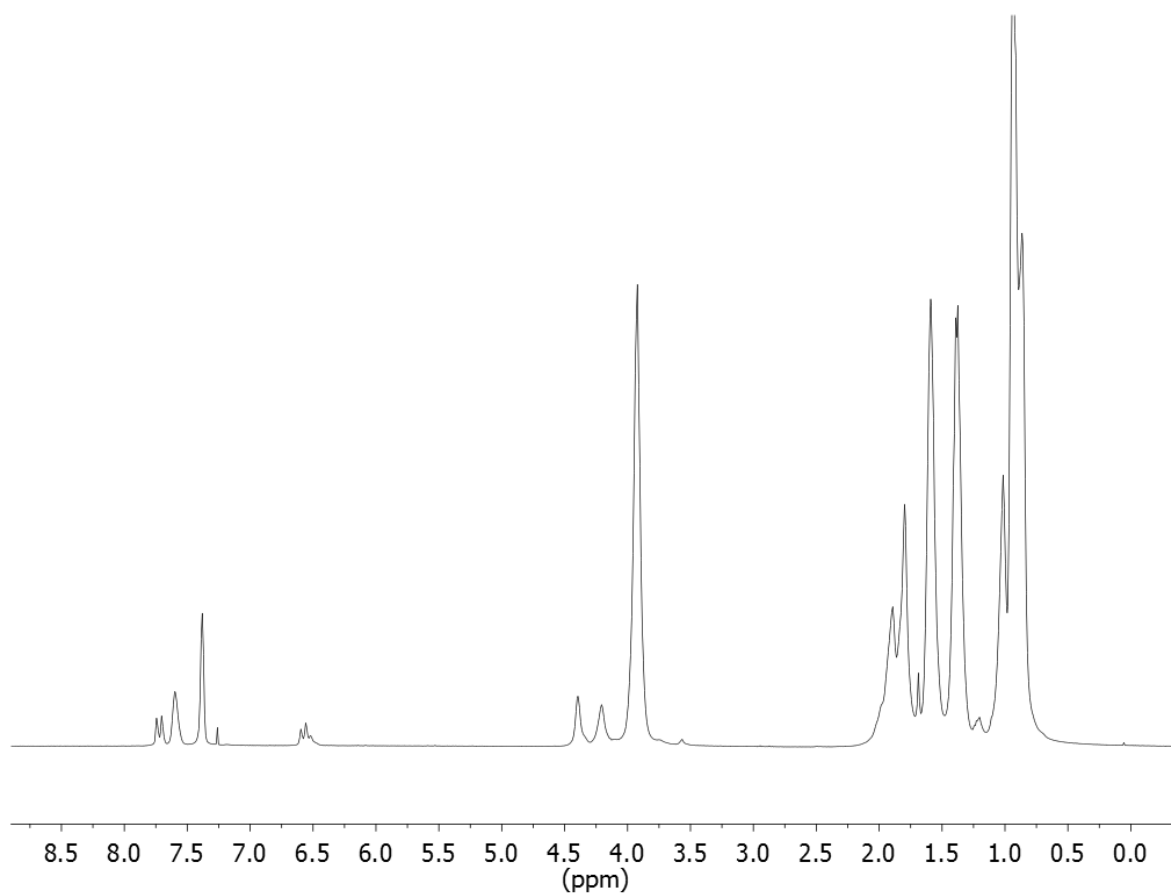


Fig S2. ^1H NMR spectrum of poly(*n*BMA-*co*-CEMA)

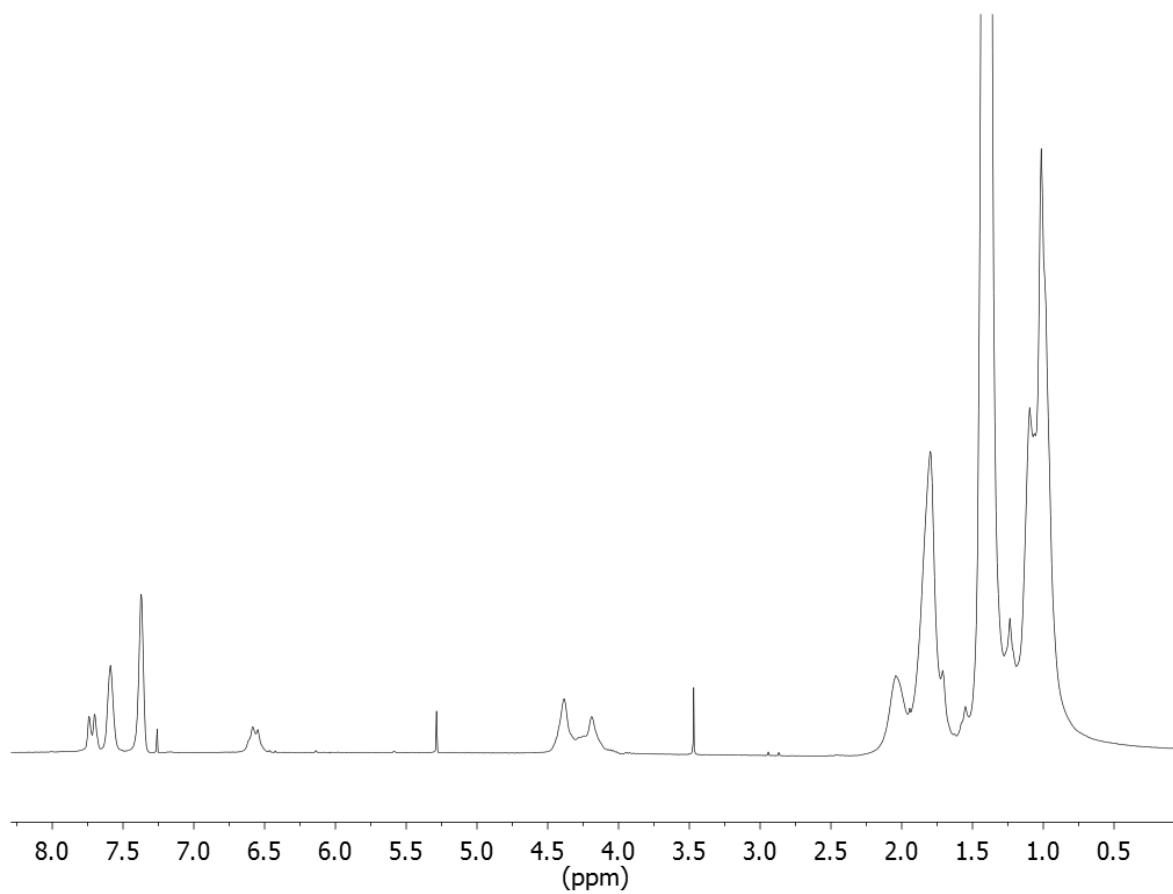


Fig S3. ^1H NMR spectrum of poly(*t*BMA-*co*-CEMA)

4. Hydrodynamic co-jetting

45 mg of P(*n*BMA-*co*-CEMA) and a trace amount of PTDPV were dissolved in 0.3 mL of CHCl₃. Separately, a mixture of 35 mg of P(*n*BMA-*co*-CEMA) and 10 mg of P(*t*BMA-*co*-CEMA) with a trace amount of MEHPV was dissolved in 0.3 mL of CHCl₃. Two polymer solutions were loaded in two syringes (Becton-Dickinson, 1 ml) that were held together using a syringe holder. The polymer solutions were delivered at a constant flow rate of 0.25 mL/h via a vertically positioned syringe equipped with 23 G needles (Nordson EFD, USA) that were assembled in side-by-side configuration and connected to the cathode of a DC voltage source (Gamma High Voltage Research, USA). A driving potential of 5 kV resulted in a stable jet and particles were collected on a sheet of aluminum foil and a tip-to-ground distance was 20 cm.

5. Shape-evolution of polymethacrylate bicompartmental particles

A typical shape-evolution procedure of microparticles were performed with a concentration of approximately 10,000 particles in 1 mL of 2% (v/v) Tween 20/DI water in Eppendorf tube and ultrasound (Ultrasonic Processor, Cole-Parmer, USA) at room temperature.

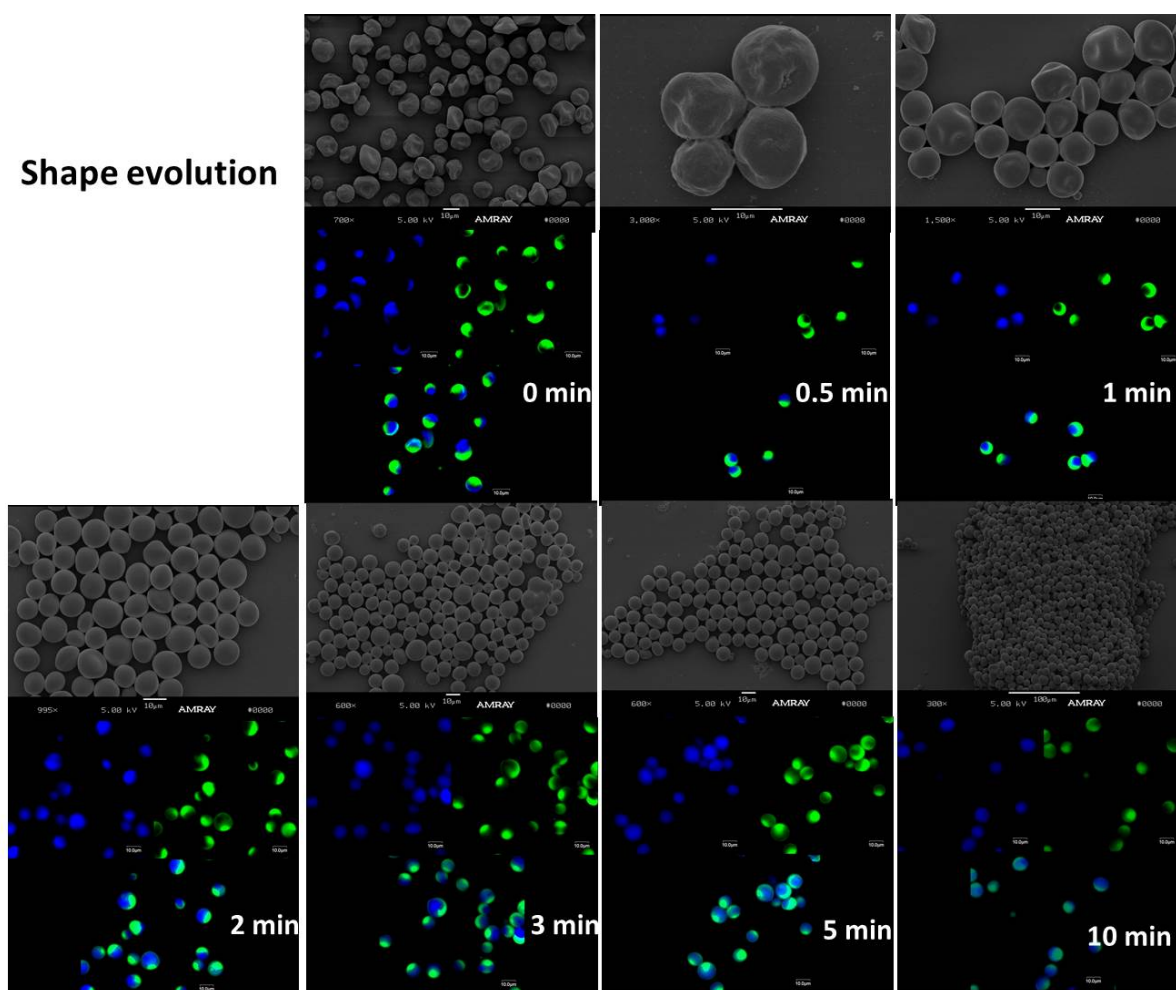


Fig S4. Screening of shape-evolution of bicompartmental particles with ultrasonication time. The upper figure represents an SEM image and the bottom displays CLSM images of particles after ultrasonication for designated time.

6. Photocrosslinking and deprotection

The photocrosslinking of bicompartmental particles were performed using a Rayonet RMR-600 that was equipped with eight 4W lamps ($\lambda = 300$ nm). After shape evolution, the particle suspension was spread and dried on a glass slide that was exposed to UV light for 2 hr. The particles were dispersed in water and collected in a 1 mL Eppendorf tube after centrifugation. The particles were dispersed in EtOH and centrifuged. After removing the supernatant, CH_2Cl_2 (0.4 mL) and trifluoroacetic acid (0.2 mL) were added to the tube, and the tube was rotated for 2 hr. THF was added to fill the tube and the particles collected by centrifugation. After removing the supernatant, the particles were washed with THF three time, EtOH, and finally H_2O .

7. Spatioselective MOF crystallation

The anisotropically carboxylic acid-functionalized bicompartamental particles immersed in a 0.01 M of $\text{Cu}(\text{OAc})_2$ solution for 1 min and then centrifuged (2000 rpm, 5 min). After decanting the supernatant, the particles were washed with EtOH and DMF, and dried shortly. The particles were, then, suspended in a 0.01 M of trimesic acid (H_3BTC) solution for 1 min and collected by centrifugation and washing. The MOF growth of $\text{Cu}_3(\text{BTC})_2$ crystals on the bicompartamental particles in this report were achieved by seven layer-by-layer growth cycles.

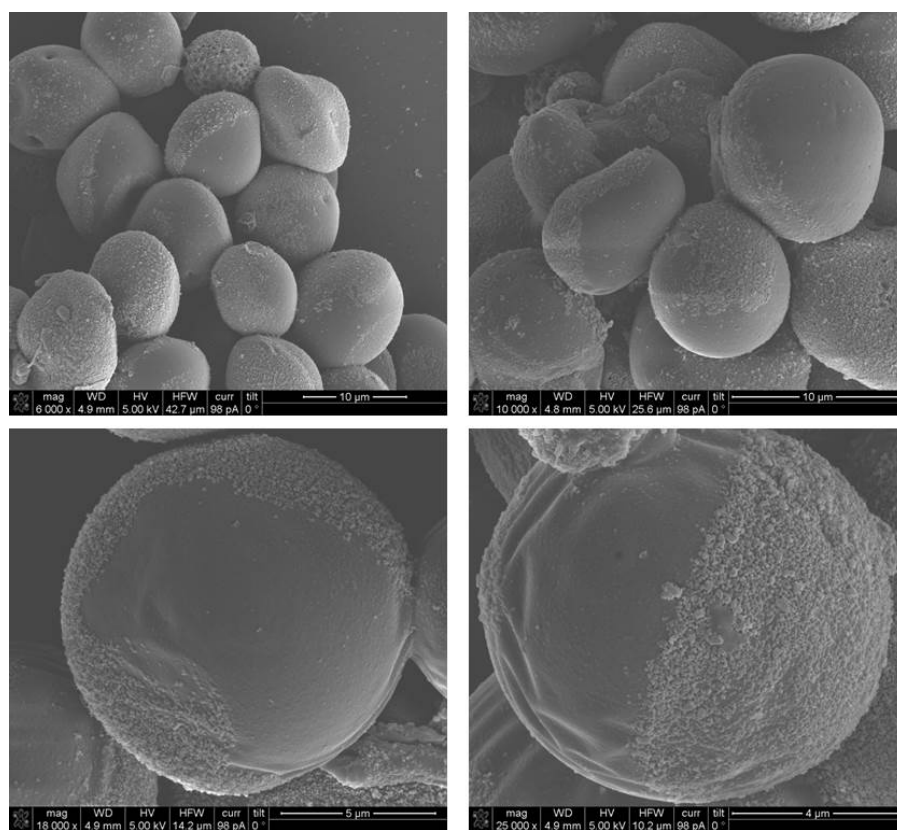


Fig S5. SEM images of spatioselectively MOF-functionalized bicompartamental particles.

8. Magnetite/MOF-functionalized anisotropic particles

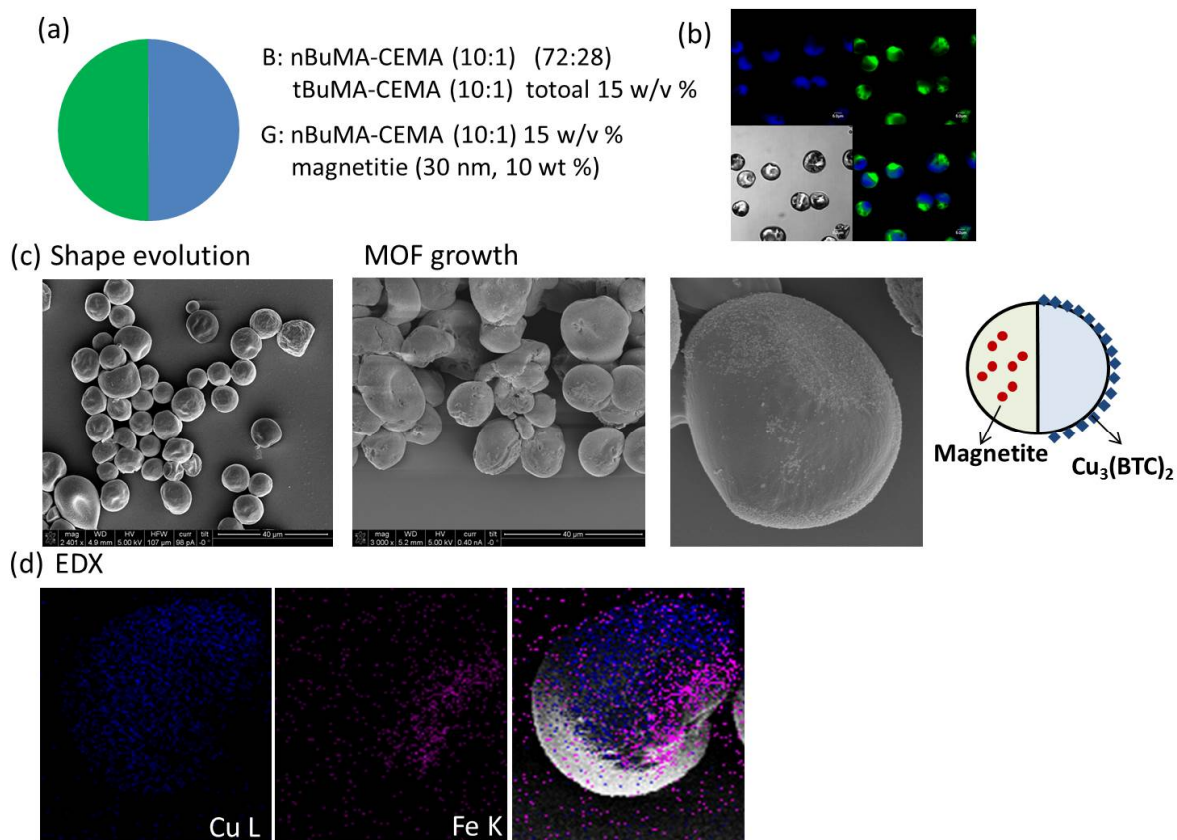


Fig S6. Anisotropically magnetite and MOF-functionalized hybrid microparticles. (a) composition of jetting solutions; (b) CRISM images after jetting; (c) SEM images after shape evolution and MOF growth; (d) Energy-dispersive X-ray spectroscopy images.

9. Reference

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