Stretchable and Reactive Membranes of Metal–Organic Framework Nanosurfactants on Liquid Droplets Enable Dynamic Control of Self-Propulsion, Cargo Pick-Up, and Drop-Off

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Sub-micrometer metal–organic framework (MOF) particles form sturdy yet dynamic—that is, structurally reconfigurable and chemically active—coatings at the interface between an aqueous droplet and the surrounding organic phase. Upon an external stimulus, the MOF particles change their interfacial orientation/packing, allowing the membranes to stretch, open, and close. At the same time, these MOF particles catalytically decompose hydrogen peroxide fuel to provide the gas-bubble recoil needed to propel the droplets; when the droplets are covered with only patches of the ZIF-67 MOFs, the recoil and self-propulsion are directional. A combination of all these effects underlies the construction of a chemical system in which the external objects are engulfed by the droplet opening up and closing its MOF membrane, are subject to chemical processing inside of the droplet, are transported to another location, and are ultimately expelled into the surrounding solvent, in effect realizing a primitive chemical mimic of phagocytosis.

As the research on dynamic self-assembly matures,[1–4] its focus is gradually shifting from materials that exhibit specific forms of non-equilibrium self-organization[5–8] to those that can integrate multiple dynamic functions and act as primitive “systems” adapting to the state of environmental controls.[4,9–12] Such functions may derive from surface tension effects setting up gradients and flows[13–15] to which the components of a system may respond—accordingly, various types of stimulus-responsive surfactants have been developed on scales from molecular[16–19] to nano,[20,21] while simultaneously responding to magnetic and optical fields, in effect giving rise to dynamic systems of droplets and microreactors.[21] Herein, we demonstrate another form of functional integration, this time using crystals (few hundred nm in size) of porous, metal–organic frameworks (MOF)[32,33] that form dynamic monolayer “membranes” at interfaces between water droplets and the surrounding organic phase. When, upon environmental stimuli, the droplets change their volumes, the MOF surfactants adjust their interfacial orientations to help stabilize the membranes during stretching, opening-up, or closing-down. Simultaneously, by virtue of harboring reactive metal sites, the MOF surfactants catalyze chemical reactions that power droplets’ self-propulsion, which is directional in “patchy” droplets having only parts of their surface covered with the reactive MOF particles. Combining these effects, the droplets that can engulf external objects are constructed, processed chemically, transported to different locations, and then the debris is expelled from the droplet’s interior, in effect realizing a rudimentary “colloidal phagocytosis”.[27,28,34] It is envisioned that if these proof-of-the-concept demonstrations are furthermore developed, they can find uses in active droplet-based chemical systems[28,35] and emulsions capable of various pick-up/drop-off tasks, possibly with applications in waste remediation.

As surface-active species, cubic particles of Zeolitic Imidazolate Framework-67 (ZIF-67) with an edge length of $L = 430 \pm 50$ nm and synthesized in aqueous solution according to a literature
procedure[36] (Figure 1a) were used. The structure of the ZIF-67 particles was characterized by powder X-ray diffraction (Figure S3, Supporting Information). These particles were chosen for two reasons: 1) Although their surface presented neutral imidazoles and was hydrophobic, the imidazoles in the interior were all deprotonated rendering the particle’s bulk partially hydrophobic and partially hydrophilic (for details, see ref. [37])—this combination is crucial to the particles’ surfactant-like behavior[33]; 2) The cobalt atoms at the MOF’s nodes are highly reactive in the activation[38] and decomposition[39] of certain peroxides, which are used to propel MOF crystallites.[40,41] This property is important for the MOF monolayers propelling the droplets.

Because of the unsaturated coordination of the Co2+ surfaces sites, the ZIF-67 particles have the ζ-potential of +50 mV and disperse well in water, various water/salt solutions, or water/ethylene glycol mixtures. However, when water-based droplets are surrounded by an organic phase (here, 1,2-dichlorobenzene, (DCB), also dichloromethane, chloroform, toluene, hexane, dodecane, hexadecane, octadecene, etc.), it can take few days for the particles to localize to the water–oil interface. This is because the dielectric constant of the organic phase is lower than that of water, and the charged particle’s electrostatic reflection in the water–oil interface has the same polarity as the particle[42]—in effect, for the particle to reach the interface, it needs to overcome an energy barrier (due to charge-image charge repulsion).[43,44] The barrier crossing can be accelerated to within few minutes by vigorous shaking[43] (emulsification) and the particles become strongly bound to the droplet surfaces by interfacial tension forces.[45,46] Importantly, once at the interface, the particles form stable monolayers (Figure 1b–d). Indeed, if a volume of liquid \( V_w \) is divided into \( N \) equal droplets by emulsification, the diameter of each droplet satisfies the equation \( \frac{4}{3} \pi r^3 = \frac{V_w}{N} \). On the other hand, if the total volume of cubic particles with edge \( L \) added to the mixture is \( V_p \), and these particles cover fraction \( S \) of the droplets’ area, then \( \frac{V_p}{L^3} = \frac{N \cdot 4 \pi r^2 S}{L^2} \). Combining these two equations gives droplet diameter \( d = 2r = 6SL \cdot \left( \frac{V_w}{V_p} \right)^{1/3} \) inversely proportional to volume ratio \( \frac{V_p}{V_w} \). Linear fitting of experimental diameters \( d \) versus \( \left( \frac{V_p}{V_w} \right)^{1/3} \) (Figure 1c) yields \( S = 0.585 ± 0.01 \), which is close to the value of \( S = 0.51 ± 0.02 \) (obtained by direct counting of particles deposited on a NaCl crystal grown in an evaporating droplet; see SEM images in Figure 1d.e). Assuming (cf. below) that particles form a square lattice, this surface coverage corresponds to average interparticle gaps of \( (L / \sqrt{S_0} - L) = 172nm \)—still, even with such relatively large gaps, the droplets are remarkably rugged and do not fuse when put in contact and even pressed against each other. In the experiments, such stable droplets were prepared with sizes from 0.2 to 1.7 mm and with size dispersity in the order of 20% (Figure 1c and Figure S4, Supporting Information).

Figure 1. MOF particles as surfactants. a) Scheme of a water droplet covered with cubic Zeolitic Imidazolate Framework-67 (ZIF-67) particles and suspended near the 1,2-dichlorobenzene/air interface. Dashed horizontal line traces the air/DCB interface. Right column shows a transmission electron microscopy (TEM) image of the ZIF-67 particles and, below, a cartoon illustrating ZIF-67’s sodalite-type crystal structure (tetrahedral Cobalt (II) ions are colored blue and are connected by 2-methylimidazolate linkers). b) Optical micrograph of 350 ± 40 μm droplets coated with cubic ZIF-67 particles. c) Linear relationship between the inverse of the mass of the ZIF-67 particles used (at constant 1 mL volume of the aqueous phase) and the diameter of the particle-coated droplets. Error bars correspond to the standard deviation of the droplet diameter (\( N = 100 \)). The dashed line is the theoretically predicted linear fit (as the total volume \( V_p \) of particles is proportional to the total mass \( m \) of particles, theoretical diameter of the droplet is \( d \propto \frac{1}{V_p} \propto \frac{1}{m} \), see derivation in the text). d,e) Scanning electron microscopy (SEM) images of particle monolayer deposited on a NaCl crystal. The aqueous solution initially contained 2M of NaCl solution. As the droplet was allowed to evaporate at ambient conditions, a single NaCl crystal was formed onto which the MOF particles were deposited.

Despite their robustness, the droplets are able to respond dynamically and reversibly—and with unique structural transitions within the MOF-particle monolayers—to environmental changes. When a droplet of pure water, without any ZIF-67 surfactant layer, is suspended near the interface between DCB (density 1.3 g cm\(^{-3}\)) and air by buoyancy, and is exposed to the vapors of methanol (or ethanol, see Figure S5, Supporting Information), it grows in size but, up to ≈90% v/v MeOH content, its shape remains spherical (Figure S6, Supporting Information). In sharp contrast, when the water droplet is covered with the ZIF-67 monolayer, the same methanol exposure takes the droplet through an interesting sequence of transformations illustrated in Figure 2 and 3 as well as Movie S1, Supporting Information. Within the initially spherical droplet of surface area \( S_0 \), the ZIF particles are arranged “face-to-face,” approximately on a square lattice (cf. left portion of Figure 2a). As methanol is
absorbed and the surface area $S$ of the droplet increases, the cubes tilt and their two opposite vertices point “into,” respectively, the water and the organic phases (cf. right portion of Figure 2a). Such “edge-to-edge” interfacial packing of the cubes has been theoretically shown to be caused by capillary interactions alone and to be energetically favorable at contact angles near $90^\circ$ ($\approx 75^\circ - 115^\circ$).\(^{[47]}\) and was observed experimentally for Ag nanocubes at a liquid–liquid interface.\(^{[48]}\) However, as this packing requires $\sqrt{3} \approx 1.73$ times more area per particle than the “face-to-face” arrangement of the same cubes, it begins to appear only when there is spare surface area on the droplet—in other words, a gradual transition to “edge-to-edge” packing was observed not only because methanol uptake changes aqueous/DCB and aqueous/MOF surface energies, but also because it increases $S$. As this transition takes place (Figure 3a,b), the stretching interface is still effectively covered with MOF particles—in their tilted orientations, covering larger per-particle areas—which prevents the coalescence of nearby droplets. It is noted that although the tilted cubes can, in principle, protect an area up to $S = \sqrt{3} \cdot S_0 \approx 1.73 \cdot S_0$, the droplet

Figure 2. Opening and closing of the MOF membranes on the droplets coated with ZIF-67 surfactants. a) Scheme illustrating droplet’s opening upon exposure to the vapors of methanol. Portions of the surface covered with the ZIF-67 particles are colored in pale purple. SEM images below (at two different magnifications) show the organization of the ZIF-67 particles in the monolayers covering the droplet: face-to-face close-packed for the initial, “compact” droplet and edge-to-edge packed for the “opened” one. SEM images were taken by deposition of droplets onto a silicon wafer substrate and drying. b) Experimental optical micrographs of the opening process. Crack appearing at $\approx 10$ s is indicated by an arrow. c) Experimental optical micrographs illustrating how the ZIF-67 monolayer gradually wraps around an evaporating droplet and ultimately folds into a closed structure with three sharp corners. Partial reversibility of droplet folding and opening upon, respectively, exposure to/evaporation of methanol is further illustrated in Figure S8, Supporting Information.
never reaches this extreme and, instead, at $S \approx 1.2 \cdot S_0$ (i.e., when fraction of “edge-to-edge” packing reaches about 30%), a crack opens in the particle layer near the top of the droplet (Figure 2b, 10 s and Figure 3c). Location of the crack is prescribed by the surface tension being lower near the upper part of the droplet—such “vertical” gradient of surface tension was reported previously\(^{[49]}\) and is due to a higher concentration of methanol in the upper part of the droplet (methanol diffuses from above and is lighter than water). Eventually, the region devoid of particles forms a capillary bridge with the DCB/air interface (Figure 3d). As more methanol is infused and devoid of particles forms a capillary bridge with the DCB/air interface and the interface between aqueous phase and air is formed. e) Droplet assumes bowl-like shape and gradually spreads as more and more methanol enters the droplet. Specifically, the shape of the droplet is determined by Neumann’s triangle of surface tension forces ($\gamma_{0}, \gamma_{1}, \gamma_{2}$) between aqueous phase, DCB, and air. As long as $\gamma_1 > \gamma_2$, capillary force constrains particles to the droplet–DCB interface, and prevents them from crossing to the DCB–air interface. f) When this condition no longer holds, capillary force drives particles away from the droplet into the DCB–air interface.

Figure 3. Evolution of ZIF-67-coated water droplet in DCB after the methanol vapors are introduced into the air above DCB phase. a) Initial state. Initial surface area of the spherical droplet is denoted as $S_0$. b) As surface area $S$ increases by about 10% with respect to $S_0$, orientation and packing of cubic particles on the droplet surface changes from “face-to-face” type (see left part of main-text Figure 2a) to “edge-to-edge” type (right part of Figure 2a). c) Further increase in droplet area $S$ is accompanied by opening of a “crack” in particle layer at the top of the droplet. d) Crack in the particle layer touches the DCB–air interface and the interface between aqueous phase and air is formed. e) Crack opens in the particle layer near the top of the droplet. f) Crack in the particle layer touches the DCB–air interface and the interface between aqueous phase and air is formed. e) Droplet assumes bowl-like shape and gradually spreads as more and more methanol enters the droplet. Specifically, the shape of the droplet is determined by Neumann’s triangle of surface tension forces ($\gamma_{0}, \gamma_{1}, \gamma_{2}$) between aqueous phase, DCB, and air. As long as $\gamma_1 > \gamma_2$, capillary force constrains particles to the droplet–DCB interface, and prevents them from crossing to the DCB–air interface. f) When this condition no longer holds, capillary force drives particles away from the droplet into the DCB–air interface.

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When the source of MeOH is removed and this solvent evaporates from the droplet, the reverse process commences and particle monolayer begins to close. As with other liquid droplets covered with solid shells,\(^{[40]}\) reduction in the interfacial area covered by the ZIF-67 particles is accompanied by buckling, wrinkling, and crumpling. The convective flows accompanying MeOH evaporation cause the initial bending of the particle membrane (Figure 4a,b), formation of sharp corners and folds around the perimeter (Figure 4c,d), their “inward” growth, (Figure 4e) and, ultimately, closing of a polygonal structure (Figure 4f). It is noted that the gradual decrease in the number of sharp corners, $N_C$, is a general feature of the process—in fact, a systematic study of tens of folding droplets reveals that as time passes, $N_C$ decreases from $\approx 9$ to 2 or 3 (see time–frequency plot in Figure 4g; also Figure S7, Supporting Information illustrating how these values of $N_C$ can be controlled by imposing geometric constraints). It is also noted that the process of opening and folding is at least partly reversible upon, respectively, cyclical exposure to and evaporation of MeOH (Figure S8, Supporting Information). This implies that the total amount of ZIF-67 particles in the membrane is conserved, which is expected because there are no particles left in the droplet’s bulk after emulsification, and because the energy required to remove one particle from the interface (approximated as a product of the interfacial tension and the area occupied by one particle) is, in this system, about 10$^5$ times the thermal energy.

The second pillar of the dynamic systems we envisioned is the catalytic activity of the ZIF-67 membranes. Figure 5a illustrates that when a water droplet covered with ZIF-67 particles contains a solution of 15 wt% H$_2$O$_2$, this “fuel” is decomposed\(^{[40,41]}\) on the catalytic Co$^{2+}$ sites, producing O$_2$ bubbles detaching from the particle membrane and providing recoil to propel the droplets. With spherical droplets, however, the bubbles are emitted at random locations and the resulting motions of the droplet are also
random. Therefore, to impart directional motions, the technique reported recently by Yang et al.\textsuperscript{(21)} was used to electrostatically "weld" individual droplets covered with different surfactants (Figure 5b) – in particular, one droplet was covered with catalytically active ZIF-67 particles and the other with catalytically inactive species such as Au-Fe\textsubscript{3}O\textsubscript{4} nanoparticle dimers, zeolitic imidazolate framework-8 (ZIF-8), or UIO-66(Zr) MOF microparticles (Figure 5c). When such composite droplets encountered and incorporated droplets of H\textsubscript{2}O\textsubscript{2} fuel, O\textsubscript{2} bubbles were emitted only from the ZIF-67 domain resulting in a directional motion (Figure 5d; also Figure S9 and Movie S2, Supporting Information), whose velocity scales with fuel concentration (Figure 5f). It is noted that no bubbles of O\textsubscript{2} formed inside the droplet, as the surface tension of the aqueous phase is higher than the surface tension of DCB, and this difference promotes bubble growth into the DCB phase, with interfacial ZIF-67 particles serving as seeds for bubble growth. Also, the velocity of directional motion is maximized when droplets of similar sizes are fused (Figure 5e,g): smaller areas of catalytically active surfactant result in lower rate of oxygen generation, whereas for larger areas, bubbles are emitted in random directions, causing fluctuations of the propulsion vector. It is noted that the mechanism of droplet propulsion is not just kinetic recoil but involves convective and viscous drag effects as well. Figure 5h summarizes the results of a computational fluid dynamics model (cf. Section 2, Supporting Information for details) which solves for the volume fraction occupied by the liquid and gas phases without defining each gas bubble in detail. This model demonstrates that the origin of the droplet propulsion here is similar to other cases where a convective flow is being induced on one side of the droplet (e.g., photothermally\textsuperscript{(21)}). Namely, the droplet moves not only because the surrounding liquid flows away (to the left in Figure 5h) and generates additional pressure at the gas-generating side (this contribution can be viewed as jet thrust at the Reynolds number of order unity), but also because the liquid flowing through the "gap" between the top of the droplet and the liquid–air interface drags the droplet along with it (this drag force is directed to the right in Figure 5h). The model accounting for these two effects gives good agreement (at least at short times, before H\textsubscript{2}O\textsubscript{2} runs out) between experimentally observed and simulated droplet velocity profiles (Figure 5i). This propulsion mode does not require the specific properties of any other interface but the surface of the droplet itself, in contrast to the reported self-propulsion of "liquid marble" droplets driven by Marangoni flow\textsuperscript{(51)} that relies on locally modifying surface tension of a second, flat air/liquid interface supporting the droplet. Marangoni flows, in our case, are prevented by the presence of a jammed interfacial layer of particles imposing the no-slip condition on the droplet boundary.

With the above considerations at hand, description of the proof-of-concept "phagocytosis" experiments in which self-propelled droplets pick up, process, and dispose of outside particles is amenable. In Figure 6 (also Movies S3, S4, Supporting Information), a small (600 × 600 × 300 μm\textsuperscript{3}) piece of 2 wt% agarose gel dyed with gold nanoparticles is floating at the air/DCB interface near a peanut-shaped droplet covered with ZIF-67 particles. Upon exposure to methanol vapors, the droplet opens (Figure 6b,g, t = 2 min). If methanol content is low enough such that the interfacial tensions of droplet–air and droplet–DCB interfaces remain higher than the surface tension DCB–air interface, capillarity drives the gel inside the droplet (Figure 6b,g, t = 5 min). When the supply of methanol is terminated and methanol evaporates, the droplet folds up, in the process enveloping the gel (Figure 6c,g, t = 6–15 min). Next, when
Figure 5. Directional droplet propulsion powered by the decomposition of H$_2$O$_2$ on ZIF-67 surfactant particles. a) Generation of O$_2$ gas bubbles off a droplet filled with 15 wt% H$_2$O$_2$. b,c) Formation of an asymmetric, “dumbbell” droplet by electrostatically welding two spherical droplets, one covered with ZIF-67 particles and one with Fe$_3$O$_4$-Au nanoparticle dimers. Short pulses of the electric field produced by a Zerostat gun (≈ 10 kV near the gun’s tip) induce dielectrophoretic force under which the particles migrate toward the “top” and “bottom” poles of each droplet. The surfactant-free region near the equator allows the droplets to merge while the jamming of surfactant particles results in only slow relaxation of particle’s shape (for details, see ref. [21]). d) A typical trajectory of a two-component ZIF-67 / Fe$_3$O$_4$-Au droplet merged with a droplet of 30% wt H$_2$O$_2$ fuel. e) Different composite droplets prepared by merging individual droplets of different sizes. Shown are the droplets right before merging. Parameter $\sigma$ quantifies the ratios of surface areas covered by the catalytically active ZIF-67 and inactive Fe$_3$O$_4$-Au surfactants. The velocity of the droplet (f) scales with H$_2$O$_2$ concentration and (g) is maximal for equal-sized droplets, $\sigma = 1$. h) Liquid flow (black triangular arrows show velocity, grey lines are streamlines), and volume fraction of the O$_2$ gas phase (indicated by color, see color scale on the right) in a vertical cross-section of 3D computational fluid dynamics model of “bubbly flow” near the self-propelling droplet at $t = 10$ s after the start of O$_2$ generation. Droplet remains at a fixed shallow depth under the flat horizontal liquid–air interface (top edge of the figure). Only one hemisphere of the droplet generates gas (in this cross-section, the left half of the droplet). Cross-section passes through the center of the droplet. Gravity vector is pointing down, as indicated by the purple arrow. i) Experimental velocity versus time for the droplet trajectory in (d) (red line) compared with the velocity simulated with “bubbly flow” model (green line) for realistic gas flow rate.
Figure 6. “Colloidal phagocytosis” mediated by dynamic, ZIF-67 membranes. a–f) Schemes illustrating the overall strategy for the droplet opening, cargo pick-up, transport, closing up, and release. $\gamma_1$ is the interfacial tension of interface between DCB and aqueous phase; $\gamma_2$ is the surface tension of DCB.

g) Time sequence of optical microscopy images showing how a hydrogel dyed with gold nanoparticles enters into the aqueous interior of a water/ZIF-67 droplet unfolding when exposed to MeOH vapors (0–5 min) and how it is engulfed when MeOH evaporates and the droplet closes up (6–15 min). h) To propel this droplet, it is merged with another droplet covered with inactive ZIF-8 surfactant and a droplet of H$_2$O$_2$ fuel. i) The resulting motion is captured in the time-lapse images. j) By increasing the methanol content in the droplet, interfacial tensions of droplet–DCB and droplet–air interfaces are decreased below the value of DCB–air surface tension. The capillary forces are thus directed away from the droplet, dispersing particles onto the DCB–air interface and forcing the gel cargo out of the droplet. k–m) Schemes and (n–p) experimental images of a similar pick-up/release sequence but with the inside of the droplet loaded with (Na$_2$CO$_3$, 1 mM) reacting with FeCl$_3$ (1 mM) contained in the incoming hydrogel piece. The degraded gel turns brown due to the reaction of Fe$^{3+}$ and OH$^-$ producing brownish Fe(OH)$_3$ precipitate.
such a droplet merges (Figure 6d,h) with another droplet covered with non-catalytic ZIF-8 surfactants and a droplet of H$_2$O$_2$ fuel, the asymmetric structure—still housing the gel—begins to move, as illustrated in Figure 6e,i. When methanol is again delivered and this delivery is allowed to continue until the interfacial tensions of the droplet–air and droplet–DCB interfaces become lower than the surface tension $\gamma$ of DCB–air interface (this happens at approximately 90% w/w MeOH content in the drop), capillary forces now drive the gel cargo out of the droplet and onto the DCB–air interface (Figure 6f,j; also see Figure 3f and S10, Supporting Information). At this stage, the carrier droplet is no longer reusable, as part of the MOF surfactants are also dispersed onto the interface (cf. bottom right panel of Figure S10, Supporting Information). A slightly more advanced version of this process is illustrated in Figure 6k. Here, the droplet contains 1 mM Na$_2$CO$_3$ gel soaked with 1 mM FeCl$_3$. When such a gel is engulfed by the droplet, a chemical reaction between Fe$^{3+}$ and OH$^-$ ensues—when the gel piece is moved around and ultimately released (as above), its contents are reacted “processed” and the brownish color is due to the Fe(OH)$_3$ precipitate.

These are, of course, only toy chemical examples—at the same time, they signal some interesting possibilities for constructing active droplets harboring more advanced types of chemistry that could “metabolize” incoming pollutants or, say, droplets of oil spills. As shown in this article, the key to such applications is the ability to open and close the colloidal membrane mediated by the unusual properties and ordering transitions within the MOF surfactant layer. It is believed similar principles could be useful in constructing the so-called artificial cells$^{[27,34,52]}$ capable of primitive “phagocytosis” controlled by external stimuli.

**Experimental Section**

**Synthesis of MOF (ZIF-67) Cubic Particles:** 10 mL of aqueous solution containing 290 mg of Co(NO$_3$)$_2$·6H$_2$O (98%, Sigma-Aldrich) and 5 mg of hexadecyltrimethylammonium bromide (CTAB, 95%, Sigma-Aldrich) was added into 70 mL of aqueous solution with 4.54 g of 2-methylimidazole (99%, Aldrich) under magnetic stirring (500 r.p.m.). With the addition of cobalt salt, the color of the solution was instantly changed from colorless to blue. The solution was continuously stirred for 30 min, followed by precipitation and centrifugation (5000 r.p.m. for 5 min). The blue solid was washed once with deionized water (D.I. water, 18.2 MΩ, MilliQ), and redispersed in 8 mL deionized water with a concentration of 20 g L$^{-1}$.

**Synthesis of ZIF-8 Microplates:** An amount of 735 mg of Zn(NO$_3$)$_2$·6H$_2$O was dissolved in 50 mL of methanol by sonication. Another solution was prepared by dissolving 811 mg of 2-methylimidazole and 811 mg of 1-methylimidazole in 50 mL of methanol. The second solution was poured into the first solution under magnetic stirring (500 r.p.m.) for 1 min. After 24 h, a white precipitate was collected by centrifugation (5000 r.p.m., 5 min), washing with methanol, and drying under reduced pressure.

**Synthesis of Nanoparticle Dimers:** Au nanoparticles were prepared according to the method used by Peng et al.$^{[11]}$ with slight modifications. 2 mmol of tert-butylamine-borane complex (97%, Strem) was dissolved in toluene (2 mL) and oleylamine (70%, Sigma-Aldrich, 2 mL) by sonication. This reducing solution was rapidly injected into a precursor solution containing toluene (10 mL), oleylamine (10 mL), and HAuCl$_4$·3H$_2$O (98.9%, Sigma-Aldrich, 200 mg) in nitrogen atmosphere at room temperature ($\approx$ 23 °C). The reduction occurred instantaneously, as evidenced by a change in color from orange to purple red. The reaction was left stirring in nitrogen atmosphere for 30 min and ethanol (50 mL) was then added to precipitate the Au nanoparticles. The Au nanoparticles ($\approx$ 6 nm in diameter) were collected by centrifugation (6000 r.p.m., 5 min), purified by three rounds of precipitation in ethanol (20 mL), and redispersed in hexane, giving a concentration about 10 g L$^{-1}$ of Au.

Seeded growth was used to synthesize Au-Fe$_3$O$_4$ dimers according to a previous study by Wu et al.$^{[14]}$ with some modifications. An iron precursor solution containing iron(III) acetylacetonate (97%, Sigma-Aldrich, 280 mg), oleic acid (90%, Sigma-Aldrich, 10.8 mL), and oleylamine (70%, Sigma-Aldrich, 16 mL) in a 100-mL three-neck flask was heated to 180 °C within 30 min and left stirred at 180 °C for 10 min under argon flow. A seed solution of 20 mg Au nanoparticles in hexane (0.5 mL) and oleylamine (1.5 mL) was injected into the flask, followed by the addition of oleic acid (4 mL). And, 180 min after injection, the solution was further-more heated to 300 °C. The reaction was kept at 300 °C for 30 min. Subsequently, the flask was cooled down to room temperature, and the nanoparticles were purified by three rounds of precipitation in acetone (30 mL), and centrifugation (7000 r.p.m., 10 min) with dissolution in toluene after each step. Finally, the nanoparticles comprised $\approx$ 6 nm Au domains and $\approx$ 12 nm Fe$_3$O$_4$ domains were dissolved in 1,2-dichlorobenzene (DCB, 99%, Sigma-Aldrich) at concentration of $\approx$ 4 g L$^{-1}$.

**Preparation of Microscopic Water Droplets Suspended in Oil:** Herein, 0.2 mL of MOF particle aqueous solution was diluted to 1 mL by adding 0.8 mL of DI water. The solution was then placed in a 15-mL conical, polypropylene vial containing 3 mL of 1,2-dichlorobenzene. The as-formed oil–water emulsion was agitated by a vortex mixer for 2 min (3000 r.p.m.) to yield aqueous droplets. This water-in-oil emulsion was kept in a fridge at $\approx$ 5 °C for 60 min, followed by agitation by vortex mixer for another 2 min (3000 r.p.m.). Water droplets coated with MOF particles were produced and stored in the fridge ($\approx$ 5 °C). The size of the droplets could be tuned by adjusting the concentration of the MOF particles.

**Characterization Techniques:** Transmission electron microscopy characterization of MOF particles was performed on a JEOL JEM 2100 microscope operating at 200 kV. Samples were prepared using 400-mesh, carbon-coated copper grids (Ted Pella Inc.), SEM characterization of MOF particles was performed on a Hitachi S4800 microscope.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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B.A.G. conceived the project and supervised the research. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

cargo transports, colloidal phagocytosis, dynamic systems, interfacial self-assembly, metal–organic frameworks, self-propulsion.
