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Ryabchun, Alexander; Babu, Dhanya; Movilli, Jacopo; Plamont, Rémi; Stuart, Marc C A; Katsonis, Nathalie

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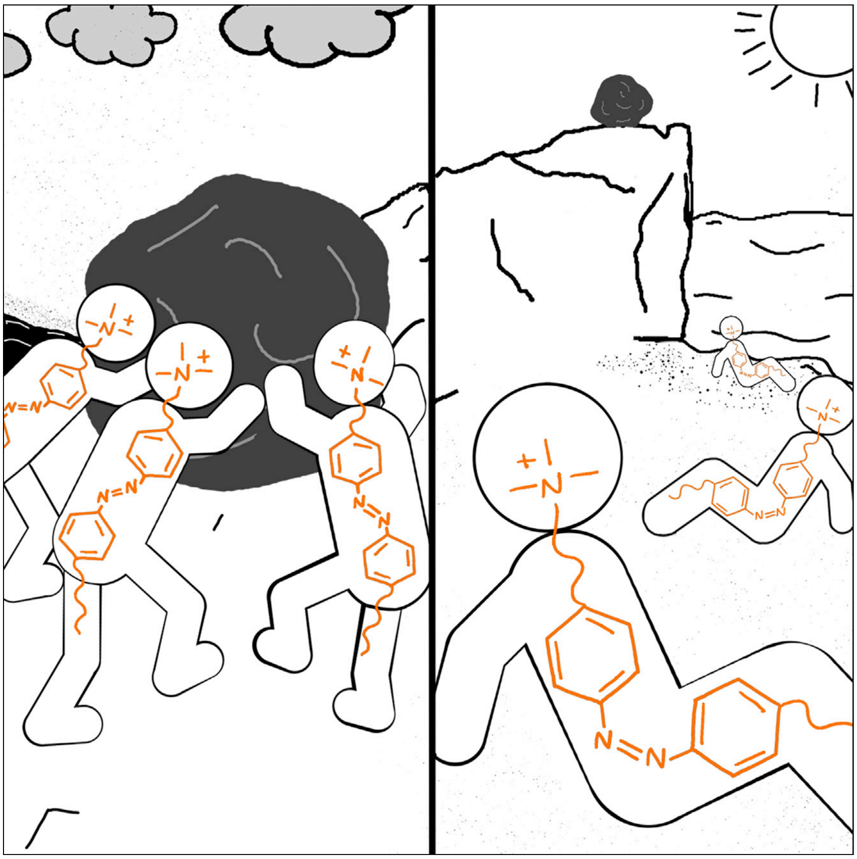

We show that the motion of autonomously moving oil droplets can be gated by coupling molecular photochemistry to interfacial processes. The molecular switches used here form micelles that fuel the motion of the oil droplet. A change in geometry of the micelles in response to light impacts the movement pattern of droplets, resulting in a run-and-halt behavior. As light controls the movement of the droplets, under irregular illumination conditions, motile droplets evolve positive photokinetic movement.

Alexander Ryabchun, Dhanya Babu, Jacopo Movilli, Rémi Plamont, Marc C.A. Stuart, Nathalie Katsonis

n.h.katsonis@rug.nl

Highlights

Molecular photoswitches mediate the motility of droplets

Photoactive micelles formed by molecular switches fuel droplet motion

Photoactive micelles gate motility in response to light

Droplets evolve motile patterns such as run-and-halt and photokinetic motion

7 AFFORDABLE AND CLEAN ENERGY

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Run-and-halt motility of droplets in response to light

Alexander Ryabchun,[1] Dhanya Babu,[1] Jacopo Movilli,[1] Rémi Plamont,[1] Marc C.A. Stuart,[1] and Nathalie Katsonis[1,2,*]

SUMMARY

Microscopic motility is a property that emerges from systems of interacting molecules. Unraveling the mechanisms underlying such motion requires coupling the chemistry of molecules with physical processes that operate at larger length scales. Here, we show that photoactive micelles composed of molecular switches gate the autonomous motion of oil droplets in water. These micelles switch from large *trans*-micelles to smaller *cis*-micelles in response to light, and only the *trans*-micelles are effective fuel for the motion. Ultimately, it is this light that controls the movement of the droplets via the photochemistry of the molecules composing the micelles used as fuel. Notably, the droplets evolve positive photokinetic movement, and in patchy light environments, they preferentially move toward peripheral areas as a result of the difference in illumination conditions at the periphery. Our findings demonstrate that engineering the interplay between molecular photo-chemistry and microscopic motility allows designing motile systems rationally.

INTRODUCTION

The ability to move toward light, nutrients, and thermal sources plays a vital role in the survival of microorganisms. Besides adapting the direction of their swim by chemotaxis[1] and phototaxis,[2] several bacteria and algae can also adapt the speed of their swim to the magnitude of a stimulus, a phenomenon known as photokinesis.[3] The net effect of photokinesis is that swimming cells stay longer in regions where the illumination conditions are the most favorable.[4,5] Molecular photo-switches are at the origin of this complex behavior: light triggers the all-*trans* isomerization of retinal, and this signal is transduced via relay systems.[6,7]

Unraveling the mechanisms by which adaptive movement can emerge in ensembles of molecules requires developing minimalistic molecular systems that move autonomously,[8] such as droplets,[9–11] liposomes,[12] stomatocytes,[13,14] and protocells.[15] We focus on the movement of oil droplets in aqueous lipid solutions. The mechanism by which such droplets evolve chemotactic movement in aqueous solutions of lipids has been reviewed recently.[16] Essentially, micelles formed by lipids in water take up droplet molecules into their hydrophobic core. The solubilization breaks the homogeneous lipid coverage of the droplet by depletion, and a local gradient in interfacial tension is thus created at the interface.[17–19] The heterogeneity in interfacial tension induces so-called "Marangoni flows" both inside and outside the droplet, which combine to propel the droplet forward. Motile droplets driven by interfacial Marangoni flows have demonstrated biomimetic motion along helical trajectories[20–22] and predator-prey behavior.[23]

THE BIGGER PICTURE

From the swim of bacteria to the beat of a heart, macroscopic movement is a hallmark of life and is ultimately driven by molecular machines. Artificial molecular machines display sophisticated motion with the potential to be harnessed into the purposeful movement of compartments. However, our perception of macroscopic movement differs from the rules that govern movement at the molecular scale. Large-scale functional movement can only emerge when molecular chemistry is coupled to physical processes that operate at larger length scales. We show that the geometry of the amphiphilic switches (molecular level) determines the geometry of micelles (supramolecular level), which in turn determines whether droplet movement can emerge (ensemble level). Eventually, the droplets display motile patterns reminiscent of those of swimming cells. We conclude that molecular behavior can be related to droplet motility rationally, which is a prerequisite for the design of functional motile systems.

Here, we show that the photochemistry of molecular switches is at the origin of complex motility patterns, including run-and-halt motion and photokinetic behavior in systems of interfacially propelled droplets. In our work, the molecular switches are directly involved in the photoactive micelles that fuel the motion—as opposed to mediating a change in the interfacial tension of the overall system.[24,25] We also found that the geometry of the micelles impacts the effectiveness of micellar solubilization and therefore controls whether propelling flows can emerge or not. Overall, the work shows that photochemical reactions, operating from the molecular scale upwards, can communicate with the motion of ensembles in synthetic systems and thus contributes to our understanding of how the movement of ensembles can emerge from the rules of molecular chemistry.

RESULTS AND DISCUSSION

Droplet motion in the presence of one of the switch isomers

In aqueous solutions of amphiphiles, droplets move autonomously because micelles solubilize them gradually into the water. In our work, these micelles are formed by amphiphilic switches. The solubilization of the droplet by the micelles modifies the interfacial distribution of the amphiphilic switches present at the droplet-water interface, and the resulting gradients of interfacial density of amphiphiles are associated with gradients of interfacial tension. These gradients initiate internal and external Marangoni flows that propel the droplet forward.[26–28] The system parameters defining the speed,[29] direction,[30] and trajectory[31] of the droplets are the concentration and chemical structure of the amphiphiles, as well as the size of the motile droplets and the viscosity of the aqueous solution in which they move.

Molecular switches can contribute to the engineering of complex movement at increasing length scales.[32–34] For example, spiropyran switches produce protons *in situ*, which accounts for an environmental change that induces droplet movement.[35,36] In contrast, azobenzene switches respond to light with substantial changes in their shape and dipolar moment. We use an azobenzene switch that forms micelles in water (Figure 1). The synthetic procedure and characterization of this molecule are provided in the supplemental information (Figures S1 and S2). This switch undergoes a *trans*-to-*cis* isomerization upon irradiation with UV light (λ = 365 nm). The back *cis*-to-*trans* conversion occurs at room temperature spontaneously and can be accelerated by irradiation with visible light (Figure S3).[37]

The critical micellar concentration (CMC) of the *trans*-isomer and *cis*-isomer are CMC_{trans} = 0.5 mM and CMC_{cis} = 1.2 mM, respectively (Table S1; Figure S4). These values are in good agreement with literature reports.[25] Above a minimal concentration, the switches form micelles that promote the solubilization of the oil from the droplets into the water, resulting in a decrease in droplet size. The diameter of a droplet is reduced by ~5% after ~30 min of motility (Figure S5A). Micellar solubilization leads to symmetry-breaking events because it modifies the interfacial tension of the droplet at random positions, and ultimately the droplet propels forward.[17,38] Here, the droplets are liquid crystal droplets of 4′-pentyl-4-biphenylcarbonitrile. Liquid crystals typically show Marangoni motility in soapy water.[39] The monodisperse droplets were produced in a microfluidic set-up, with sizes ranging from 35 to 185 μm (Figure S5B). The droplets were then transferred to a closed chamber containing an aqueous solution of azobenzene. The density of the aqueous solution was adjusted to that of the droplets by the addition of D_2O.

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[1] Stratingh Institute of Chemistry, University of Groningen, 9747 AG Groningen, the Netherlands

[2] Lead contact

*Correspondence: n.h.katsonis@rug.nl

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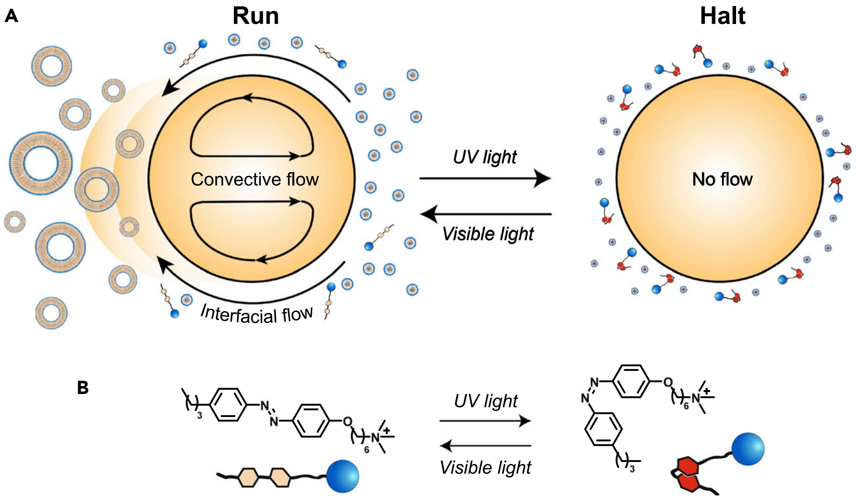

Figure 1. Run-and-halt behavior of motile droplets in response to light
(A) An oil droplet immersed in an aqueous solution of amphiphilic switches displays run-and-halt behavior in response to light. The illumination conditions are homogeneous, and therefore heterogeneity at the droplet interface is not a result of the illumination conditions.
(B) Reversible isomerization of the azobenzene switch in response to light. Supramolecular aggregates of the *trans*-switch solubilize the droplet into water, thus creating flows that set the droplet in motion. A moving droplet leaves a trail of vesicles that incorporate oil molecules in their membranes. Upon irradiation with UV light (λ = 365 nm), the switch photoconverts into the *cis*-form, and movement stops. The droplet picks up its run once visible light is switched on again.

In a solution of *trans*-azobenzene, the droplets move in all directions (Figure 2A), provided that the concentration of the switch is above a given concentration that we define as the critical propulsion concentration[29] (CPC_{trans} = 0.8 mM). The CPC is typically larger than the CMC_{trans} = 0.5 mM. Visually, the shape of the droplet fluctuates as it moves. These shape fluctuations are likely a consequence of combined effects: in a system where strong Marangoni flows dominate, a strong coupling[40] is established between the liquid crystal droplet and the *trans*-azobenzene that also has a liquid crystalline character. Because of this coupling, the interfacial flows resulting from the interfacial tension gradient that keeps the droplet in motion overcome the interfacial forces keeping the spherical shape of the droplet and thus the droplet shape is modified. Recent literature shows that the coupling between a liquid crystal droplet and its liquid crystalline environment is substantial and can lead to droplet shape changes.[41] One recent research reports that droplets can change shape in response to a temperature-induced decrease in interfacial tension.[42]

We found that increasing the concentration of *trans*-azobenzene leads to an increase in the average speed of the droplets, likely because the concentration of micelles that fuel motility increases with the concentration of switch in water (Figure 2B). In contrast, the presence of the *cis*-form in solution does not initiate droplet movement at any concentration across the entire range. This motile behavior has a molecular origin: the bent shape and high dipole moment of the *cis*-isomer make it more hydrophilic.[43,44] The *cis*-isomer is thus not as effective a surfactant as the *trans*-isomer, as confirmed by interfacial tension measurements at the oil-azobenzene solution interface ($\Delta\gamma$ = 15 mN/m; Figure 2C) and air-azobenzene solution interface (Figure S6). The interfacial tension of amphiphiles varies with their concentration in solution. As the amphiphile concentration increases, the interfacial tension drops

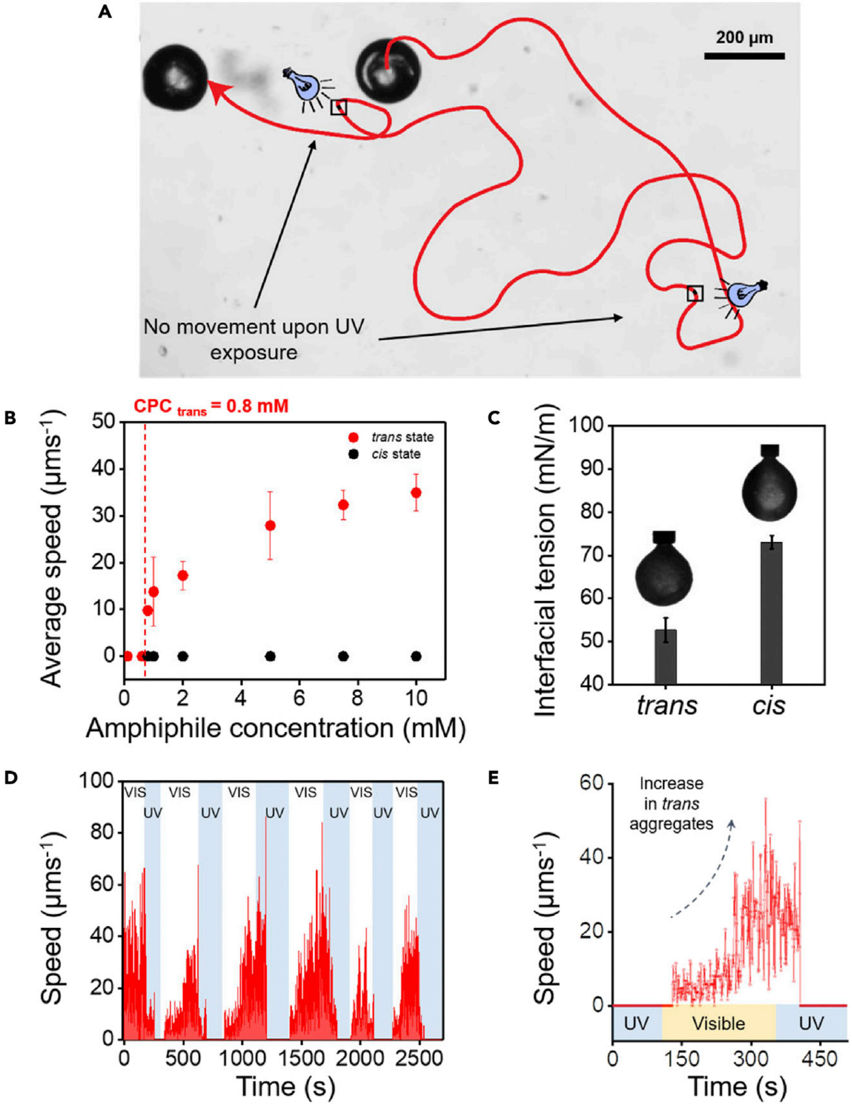

Figure 2. Insights into the run-and-halt behavior of droplets

(A) Trajectory of an oil droplet in a 2 mM *trans*-azobenzene aqueous solution. The trajectory corresponds to 17 min of movement. The black squares pinpoint positions where the droplet halts as a response to illumination with UV light. Droplet run is resumed by irradiation with visible light.

(B) Average speed of the droplets with increasing concentration of *trans*-azobenzene (red) and *cis*-azobenzene switch (black). Each data point is an average of five measurements (error bars represent standard deviation). The droplets were ~140 μm in diameter.

(C) Interfacial tension measured at the interface of oil and an aqueous solution of either *trans*-azobenzene or *cis*-azobenzene. Measurements were performed at 20°C.

(D) Run-and-halt behavior can be repeated six times by alternating illumination. The data are shown for a 135 μm-diameter droplet moving in a 5 mM azobenzene solution.

(E) The droplets accelerate during illumination with visible light. The data are shown for a 135 μm-diameter droplet in a 5 mM azobenzene solution.

until it reaches a plateau and becomes constant.[45] The difference in surfactant properties between the *trans*-form and the *cis*-form is further evidenced by the fact that the CMC of the *trans*-form is lower than that of the *cis*-form. Moreover, and for the same reasons, the *cis*-isomer is less compatible with liquid crystalline organizations.[46,47]

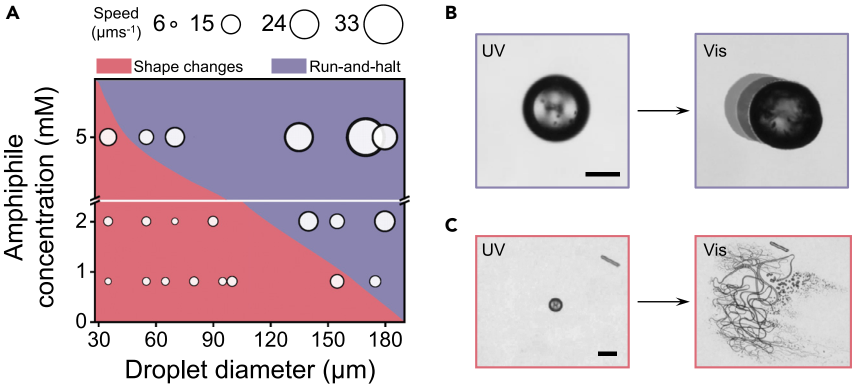

Figure 3. Systems parameters governing the movement of the droplets

(A) The possibility of run-and-halt behavior depends on the size of the droplets and on the concentration of azobenzene in water. The purple area corresponds to conditions in which run-and-halt behavior is observed. The pink area corresponds to conditions where run-and-halt behavior is not observed because the shape of the droplets is not preserved upon *cis*-to-*trans* conversion of the switch. The size of the circles scales with the speed of the droplets as measured experimentally.

(B) Optical microscopy images showing motile oil droplets under visible light illumination. Scale bar represents 50 μm.

(C) Small droplets undergo shape transformation and further decomposition under visible light illumination. Scale bar represents 50 μm.

Run-and-halt behavior of the motile droplets in response to light

In a *trans*-solution, the droplets run in any direction. They stop moving shortly after homogeneous illumination with UV light (~27 mW/cm^2), as the switch converts from *trans* to *cis* (Video S1; Figure S7). Motility picks up again with reversible *cis*-to-*trans* photoisomerization that is achieved in the whole sample by homogeneous illumination with visible light. The re-establishment of movement takes longer that stopping the movement because *cis*-to-*trans* photoconversion is performed by the polychromatic visible light of the microscope (~3.2 mW/cm^2). Run-and-halt cycles could be repeated up to six times by alternating illumination with UV and visible light (Figure 2D). We note that in our system, the possibility of run-and-halt behavior is dependent on both the diameter of the droplets and the concentration of the switches in water. Specifically, run-and-halt can be observed for droplets ranging between 30 and 180 μm in diameter, on the condition that the *trans*-azobenzene is sufficiently concentrated (Figure 3A).

Larger droplets propel faster, which agrees with what is known for chemically fueled motile droplets, as bigger droplets can maintain a larger gradient of interfacial tension.[48] Upon visible light irradiation, *cis*-to-*trans* conversion allows the active *trans*-isomer to reach CPC, and a gradient in interfacial tension can be formed and sustained, making the droplets move (Figure 3B). Droplets move in the solution of *trans*-azobenzene switch as *trans* micelles solubilize oil molecules from the droplet creating a heterogeneity in the interfacial tension at the droplet interface, inducing Marangoni flows that propel the droplet. Analysis of the droplet speed during run-and-halt behavior shows that the droplets accelerate in the course of illumination with visible light (Figures 2D and 2E). This acceleration loosely follows the increase in concentration of *trans*-azobenzene and is analogous to positive photokinetic behavior in which the speed of microorganisms adapts to changes in the illumination conditions.

If the oil droplets are too small, they do not display run-and-halt behavior: in that case, they do propel in a concentrated *trans*-solution and halt upon *trans*-to-*cis*

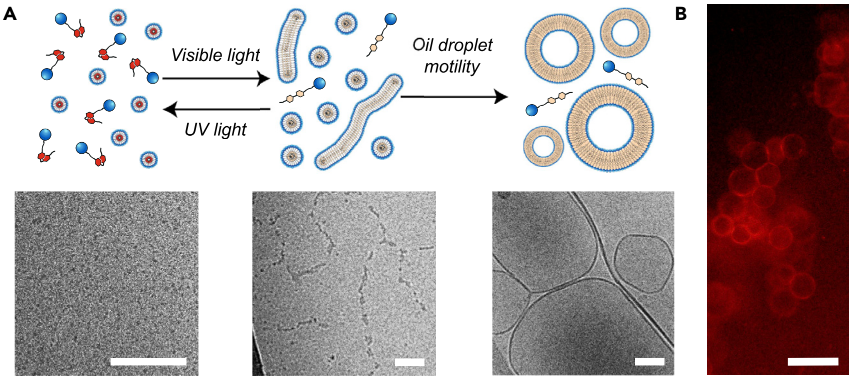

Figure 4. Photoactive micelles are the fuel that drives droplet motion

(A) The micelles that are formed by the *trans*-azobenzene switch are the fuel that drives the motion of the droplets. Giant vesicles are produced as waste of this motion and never observed before propulsion. Cryo-TEM images of *cis*-micelles (left) and *trans*-micelles (center) formed in a 7.5 mM solution in the absence of oil droplets. After droplet movement has occurred, vesicles are found (right). The scale bars correspond to 100 nm.

(B) Fluorescence microscopy shows that the aggregates formed as waste in the trail of moving droplets are vesicles. These vesicles are photoresponsive (not shown here). Here, the droplets were doped with Nile red and propelled in a 5 mM *trans*-solution. The scale bar corresponds to 20 μm.

photoconversion. However, when irradiated with visible light, they do not pick up movement again, and instead they lose their spherical integrity (Figure 3C). This shape transformation indicates that the progressive *cis*-to-*trans* photoconversion is too slow to induce a substantial gradient of interfacial tension in small droplets. In recent work, a small decrease in interfacial tension was proven sufficient to modify the shape of liquid crystal droplets substantially.[42,49]

The *trans*-micelles are those fueling the droplet movement. At low concentrations, this isomer forms spherical micelles with a diameter of ~4.7 nm, and at higher concentrations, it forms larger micellar aggregates (Figure 4). In contrast, the *cis*-azobenzene forms only spherical micelles with a diameter of ~3.6 nm (Figure S8).[50] The diameter of the *cis*-micelles is smaller than that of the *trans*-micelles, likely because the *cis*-switch is shorter than the *trans*-switch (~0.9 versus ~0.5 nm).[51] The fact that both forms of the switch form micelles with different size and geometry is a signature of their difference in shape and polarity and constitutes evidence for their differential effectiveness in solubilizing the oil from the droplets.

Giant vesicles are formed in the trail of the moving droplets and can thus be considered the waste of the motile process. It is likely that both the *trans*-form and the oil removed from the droplet co-exist in the bilayer of these vesicles (Figures 4A and 4B). We conclude that micelle-to-vesicle transition occurs upon solubilization of the oil from the droplets. We anticipate that this transition occurs because once solubilized from the drops into the micelles, the oil molecules are likely to be localized in the interior of *trans*-micelles (close to the azobenzene fragment), thus increasing the volume of the hydrophobic tail, which favors the formation of larger aggregates with lower curvature, i.e., vesicles. Micelle-to-vesicle transition upon addition of organic molecules to charged micelles has been reported before.[52]

During illumination with UV light, *trans*-to-*cis* photoconversion of the azobenzene takes place. The *cis*-form is more soluble than the *trans*-form, which explains why UV irradiation of *trans*-micelles leads to vesicular collapse. Figure S9 shows

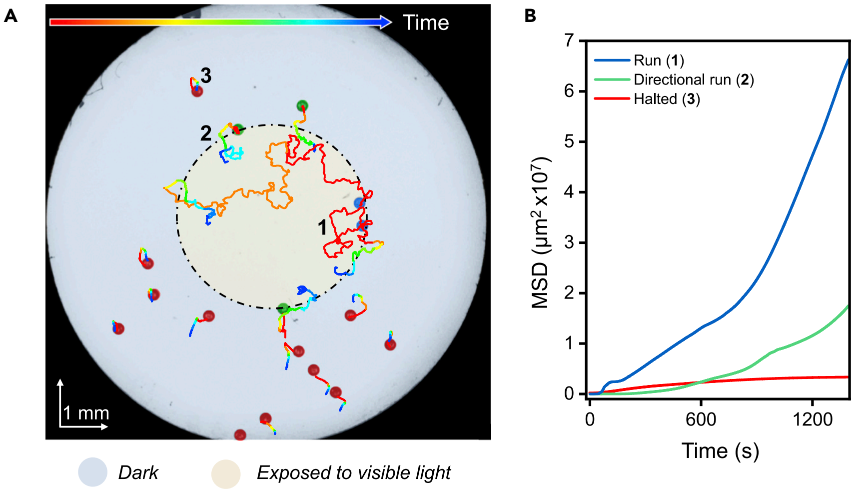

Figure 5. Motility patterns in a patchy light environment

(A) Optical microscopy image of a chamber showing the initial position of the droplet and its trajectory during movement. The time-scale of the experiment is 114 min. Initially, oil droplets are injected into the chamber filled with *cis*-solution, and the chamber is sealed. A circular spot in the chamber, indicated by black dashed line, is then briefly irradiated with visible light ($\lambda = 455$ nm) directly through the microscope, and the video subsequently starts.

(B) Evolution of the mean square displacement in time shows that droplets in the area that has been illuminated start moving shortly after irradiation with visible light has occurred. Outside that zone, droplets move directionally toward the area that has been illuminated, except if they are too far away in the dark zone. Overall, the motile droplets tend to end their motile behavior at the periphery of the illuminated areas.

sequential optical microscope images of the *trans*-vesicles illuminated with UV light. Overall, UV irradiation removes the surfactant from the vesicles because the *cis*-form is more soluble. The collapse of these vesicles carrying oil in their bilayer, under illumination, indicates that they can act as carriers that release oil molecules in response to illumination with UV light. We anticipate that this mechanism may be exploited for drug delivery purposes.[53] In previous reports, vesicles were involved in motile systems where a chemical reaction at a droplet interface yields a new vesicular amphiphile;[54] however, here the vesicles constitute waste material.

Photokinetic motion of droplets in a patchy light environment

In patchy light environments, positive photokinetic behavior concentrates the swimming cells in mid-low light areas.[5] We consequently set off to research the effect of localized irradiation with visible light on the behavior of a population of droplets. In a circular chamber filled with a *cis*-solution, the droplets do not move (Figure 5A; Video S2). Upon localized illumination with visible light ($\lambda = 455$ nm for 10 s), a circular area is created in which there is a high concentration of *trans*-azobenzene. Illumination with visible light was kept short to avoid light-driven diffusio-osmosis[55,56] or chromo-capillary effects.[25] Droplets located within this area started moving actively, while the droplets located far from this area keep stationary (Figure 5A). This supports the observation that only *trans*-aggregates can act as fuel for droplet motion. We note that thermal effects are negligible, as the irradiation is short and heat transfer is much faster than the diffusion of molecules. Moreover, the half-life time of the *cis*-isomer exceeds 20 h at room temperature;[37] therefore, *cis*-to-*trans* relaxation is negligible in the UV pre-exposed area. Analysis of droplet movement in the area that has been illuminated shows that the droplets are trapped, with a tendency to remain at the interface with the dark zone (Figure 5A). Stationary droplets that are in the vicinity of the central area that was exposed to visible light start moving toward it (Figure 5B) after a short lag. (Figure S10). Overall, we show that patchy illumination with visible light results in the droplets accumulating preferentially at the interface between the two areas with a different history of illumination.

Conclusion

Our work shows that photoactive micelles can be used as switchable fuel to impart complex motility to microscopic droplets in water. The molecular switches are thus directly involved as fuel for motion—in contrast to state-of-the-art research, where the role of the switches is limited to the *in situ* production of protons that account for an environmental change. In our system, run-and-halt behavior emerges because only the *trans*-micelles can solubilize the oil droplets and thus create propelling flows. This behavior also provides insight into the mechanism supporting the movement of the droplets, namely that droplet movement can be gated at the supramolecular level by photoactive micelles. The geometry and size of the micellar assemblies is thus key to mediating the transmission of movement across length scales.

Furthermore, when their environment involves patches of visible light, the droplets accumulate in regions at the interface between the dark areas and those that have been exposed to visible light. The photochemistry of molecular switches can thus promote the emergence of complex motile patterns in droplets, including not only run-and-halt motion but also photokinetic movement, both of which are reminiscent of the behavior of swimming cells. Ultimately, it is light that controls the movement of these liquid compartments via the micelles, which are used as fuel. This interplay between light and the motion of molecular ensembles may become relevant in future studies related to the emergence of movement in life-like systems and molecular materials.

We conclude that artificial molecular switches are effective in bridging photochemistry with the swimming of active microscopic particles. Further investigation of the interplay between molecular chemistry and the behavior of active systems may lead to an improved understanding of how molecular-scale events can translate across length and timescales into the coordinated motion of molecular ensembles.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Nathalie Katsonis (n.h.katsonis@rug.nl).

Materials availability

This study did not generate new materials.

Data and code availability

The script for motile droplets tracking is available on request.

Production of oil droplets

Oil droplets with a low size dispersity were produced by using a home-made microfluidic set-up (details can be found in the supplemental information). The nematic liquid crystal 4′-pentyl-4-biphenylcarbonitrile (5CB) was purchased from Synthon Chemicals. The oil droplets of 5CB were produced in a 2 w/v% aqueous solution of polyvinyl alcohol (Sigma). The droplets were produced by using microfluidic chips of different channel sizes (30–200 μm) and by adjusting the relative flow rates of the oil and aqueous phases.

Motility experiments

A 60 μL aqueous solution of the azobenzene switch was introduced into a chamber prepared by attaching a 1-mm-thick silicone film (Electron Microscopy Sciences) with a circular well of 9 mm of diameter on a microscopy glass slide. A volume of 6 μL of dispersion containing ≈3–5 droplets was then introduced into the chamber. The glass cover was then sealed using a glass cover slip to prevent evaporation and any external flows affecting the experiment. An Eclipse LV100N POL (Nikon) optical microscope equipped with a DS-Fi3 (Nikon) camera was used to record the videos. All captured videos were analyzed as described in the supplemental information.

The sealed chamber was irradiated with UV light (Thorlabs LED, λ = 365 nm, 27.7 mW/cm^2) until the droplets stopped propelling. Visible light illumination was provided by the white light of the microscope (3.2 mW/cm^2 measured at λ = 455 nm). The light intensity was measured using a PM-100D power meter (Thorlabs) equipped with a thermal power sensor.

For the patchy light environment, a chamber filled with the aqueous solution of azobenzene was first irradiated with UV light until the photostationary state was reached. The LED was then switched off, the oil droplets were introduced by injection, and the chamber was sealed. Irradiation of the chamber with visible light was performed by shining an LED lamp through the microscope for ~10 s (LED Thorlabs, λ = 455 nm, 10.4 mW/cm^2), so that there was no need to move the sample. The irradiation area was controlled by the microscope's iris field diaphragm that was ~3.5 mm in diameter. During observations under the microscope, a longpassfilter (λ < 550 nm) was used to prevent unwanted *cis*-to-*trans* photoisomerization.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.chempr.2022.06.017.

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AUTHOR CONTRIBUTIONS

A.R., D.B., and J.M. planned the work and carried out the experiments. R.P. contributed materials. M.C.A.S. performed the TEM experiments. N.K. directed the research. All authors contributed to the design of the project and the writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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