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Photoactuation of Droplet Motion

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Moving small objects by light is not only appealing to the imagination but also has practical applications when localized remote actuation is highly desirable, such as in microfluidics. Visible light is ideally suited to act upon microsystems, because it is easily bent and shaped in microbeams, can be coupled to standard electronics by optoelectronic components, and is most often nondestructive. As photons possess both momentum and energy, light can be converted into work by exchange of either momentum or energy. Photon momentum transfer is usually weak, although it can be used to devise optical tweezers or solar sails based on radiation pressure. Much more efficient, however, is the use of photon energy.[1] Invariably, the energy is first used to excite matter. Then, a cascade of reactions takes place, typically leading to the storage of energy as electrochemical potential in a battery or as enthalpy in a chemical fuel. The stored energy can subsequently be used to generate work and move objects, corresponding to the indirect transformation of light energy into kinetic energy.

However, direct conversion of light into mechanical work is also possible, as shown recently by Baigl and co-workers.[2] In their study, the energy of light serves to change locally the chemical potential of a surfactant at the surface of an oil droplet floating on water, which translates into a local change of surface tension by virtue of the Gibbs adsorption equation (Figure 1).[3] The resulting surface-tension gradient is the surface equivalent of osmotic pressure; it results in convection currents appearing at the surface of the droplet, thus driving the fluid from regions of lower surface tension to regions of higher surface tension. Part of the surface of the droplet thus pulls on the fluid it contains, as would an elastic membrane, leading to a net displacement of the droplet.

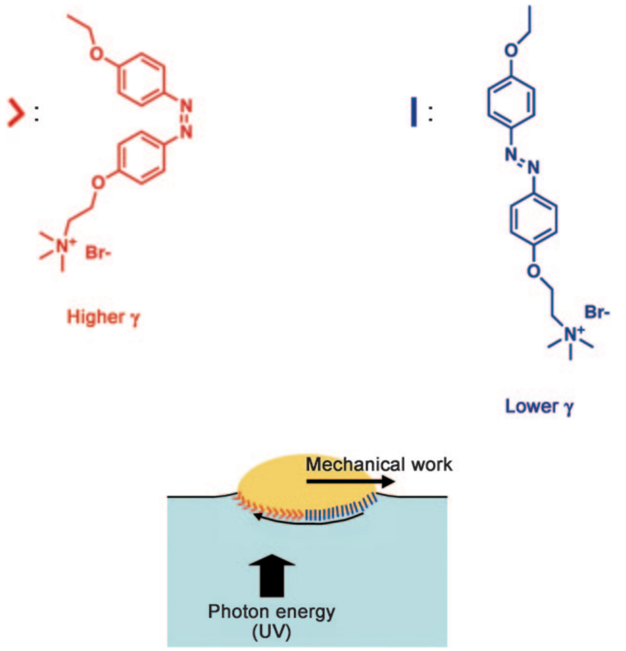

Figure 1. Photoactivated droplet motion as demonstrated by Baigl and co-workers.[2] The modulation of surface tension γ by the photoinduced configurational change of an azobenzene-based surfactant results in convection currents and a net displacement of the droplet.

The surfactant used by Baigl and co-workers is an azobenzene-based photochromic amphiphilic molecule (see Figure 1) that reversibly changes configuration upon irradiation, thus allowing cyclic execution of the process. Background illumination in the visible range serves to set molecules to their *trans* configuration, whereas a local UV beam excites them to their *cis* configuration. Because the resulting force moves the droplet away from the UV beam, and since the convection currents tend to suppress the gradient of surface tension, continuous droplet motion requires displacement of the UV beam in concordance with the droplet. This approach effectively replenishes the UV-lit spot in excited molecules, thereby maintaining the driving force for the displacement. Significantly, displacement rates close to a third of a millimeter per second can be obtained in this way.

In another experimental configuration, a cylindrical shell of UV light is shined on the sample while the central spot is illuminated by visible light. Droplets in the central spot are thus repelled by the UV shell and stay trapped. Hence, droplets can be either moved or pinned at specific locations using proper illumination schemes. Other types of displacements would be of interest for practical applications; continuous rotation of the droplet is such a case, which was not yet demonstrated. This rotation should be possible by irradiating the droplets with a proper sequence of spatially

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localized pulses. In this last case, only light energy would be used to stir the droplet, in contrast to the case of linear motion, where some energy must be spent to displace the guiding beam.

There have been studies in which surface-tension gradients have been used to generate droplet motion on solid surfaces. The surface-tension gradients were usually generated by temperature[4] or chemical[4,5] gradients; however, such spatially fixed gradients do not allow continuous droplet motion. Such motion was achieved using light-induced gradients on solid surfaces grafted with photoresponsive molecules;[6] in this case, the motion of the light beam allows for continuous motion, as is also the case in the work of Baigl and co-workers. However, there is an important difference between these studies and the recent study, in which the droplet moves together with its “surface-tension transmission belt”. Indeed, in the Baigl team’s work, the gradient is attached to the droplet itself and is under constant dynamic control; the only condition to meet for motion to occur (except for asymmetric illumination) is the existence of an interface of the droplet with an immiscible liquid—a quite general condition that makes the system much more amenable to real applications than earlier systems in which the droplet moves only over a properly designed solid surface. In this respect, the system of Baigl and co-workers has some similarity with recent examples of self-propelled microsystems, such as soap boats,[7] hydrogen peroxide powered asymmetric catalytic rods,[8] and light-powered solid rafts for which the interfacial tension gradient is generated by the heat dissipated when light is absorbed at a specific location of the raft.[9]

An important aspect of the system is its relatively rapid response, which permits displacement rates as high as hundreds of micrometers per second. These rates partly result from the low barriers to segmental motion experienced by the photochromic moieties, which are incorporated in a monolayer-thick fluid interface. However, there are many dynamical aspects of the system that would warrant a more thorough investigation, such as the rate of diffusion of surfactant molecules from the interface into the bulk liquid phases and vice versa, their lateral diffusion rate in the interfacial layer, or their lifetime in a given configuration. Such factors will have to be studied further to fully understand the speed limit of the droplets.

The results allow us to envision systems in which a large number of microreactor droplets would roam over the surface of a fluid, spinning, translating, and combining together according to a specific temporal sequence, each droplet being externally controlled by a beam of light. To manage the many beams required to track and manipulate thousands of droplets will certainly require advanced tracking and optical technology; however, if we consider that pulses of light rather than continuous illumination might also be used to move the droplets, the situation is not that bad. Such a technology would pave the way to completely new synthetic methodologies, in which small volumes coupled to precise sequences of events would lead to important advances in synthetic and analytical chemistry, as the field of microfluidics is striving to achieve. Obviously, the generality of the method is still to be demonstrated for other solvents and general environmental conditions. But if this general applicability is established, a bright future lies ahead for the manipulation of droplets by light.

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