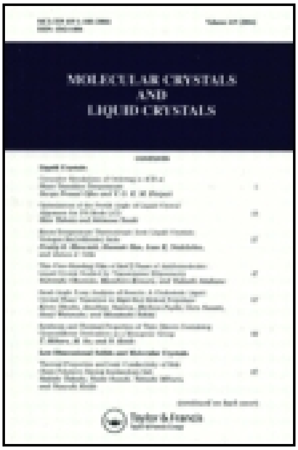

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Light-Guided Movement of a Liquid Droplet

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Light-Guided Movement of a Liquid Droplet

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This report demonstrates a novel strategy for the light-guided motion of a liquid droplet on photoresponsive surfaces based on reversible changes in surface free energy induced by light. When a liquid droplet in a mm-scale was placed on a substrate surface modified with a calix[4]resorcinarene derivative having photochromic azobenzene units, photoirradiation caused a gradient in surface free energy due to the photoisomerization of surface azobenzenes, leading to directional motion of the liquid droplet. This motion is ascribed to a force imbalance between two opposite edges of the liquid droplet induced by light.

Keywords: liquid motion; surface free energy; photoisomerization; monolayer; calix[4]resorcinarene; azobenzene

INTRODUCTION

A gradient in surface free energy of a solid substrate creates a directional force and can induce the motion of a liquid droplet placed on it. A classical example of the liquid motion is the Marangoni flow,[1] in which a temperature gradient induces a gradient of surface tension resulting in the liquid motion. Another type of the liquid motion reported by Whitesides *et al.* is due to a gradient of hydrophobicity prepared by the asymmetric modification of a silica surface by silylation.[2] The movement of a water droplet to an uphill direction was demonstrated on an oblique surface. Consequently, if a gradient of surface free energy of a substrate can be generated by light, the movement of a liquid droplet on it should be controllable. A solid surface modified with photochromic azobenzenes is a promising material to control its surface free energy by light, because *trans/cis* photoisomerization of the azobenzene molecules causes reversible changes in physicochemical properties of the surface such as a dipole moment and an orientational direction of the molecules. Typical examples of controlling surface energy based on the photoisomerization include wettability,[3,4] dispersibility[5] and solubility[6] changes. To our knowledge, there has been no method to position a liquid droplet stimulated by the photoisomerization although light has some distinctive advantages of its non-contacting and spatially selective energy transfer.

Here we report a new concept to move a liquid droplet based on reversible and asymmetrical changes in surface free energy induced by photoirradiation of substrate surfaces modified with an *O*-octacarboxymethylated calix[4]resorcinarene (Figure 1: CRA-CM) having octylazobenzene residues.

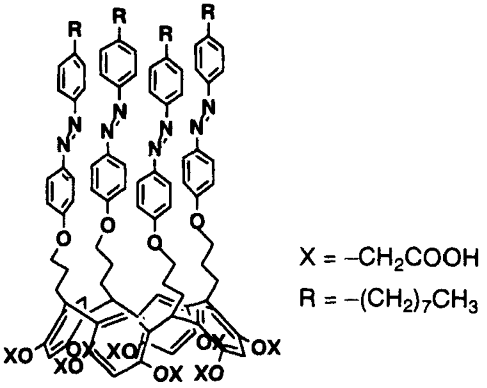

FIGURE 1 Chemical structure of CRA-CM.

EXPERIMENTAL

CRA-CM was synthesized according to our previous report.[7] An aminosilylated silica plate was obtained by the treatment of a fused silica plate with a toluene solution of (3-aminopropyl)diethoxymethylsilane. The aminated substrate was immersed in a THF solution (1×10^{-4} mol dm^{-3}) of the CRA-CM at 40 °C for 30 min. A chemisorbed CRA-CM monolayer was prepared after rinsing with THF and drying at 80 °C for 30 min. Light sources of UV light (365 nm) and visible light (436 nm) were obtained from a 200-W Hg-Xe lamp (San-ei Electric MFG. Co., Supercure-203S) by passing through suitable combinations of glass filters. Contact angles were measured with a contact angle meter (Kyowa Interface Science, SA-11) in air at room temperature (23 °C). Contact angles for *cis*-state correspond to those in a photostationary state after UV light irradiation.

RESULTS AND DISCUSSION

As a photoresponsive substrate, we used the chemisorbed monolayer formed by a crown conformer of *O*-octacarboxymethylated calix[4]resorcinarene (CRA-CM) possessing four octylazobenzene residues[7] on an aminosilylated silica plate as following reasons. First, the molecular structure of CRA-CM is designed to guarantee a sufficient free volume required for the photoisomerization, even if the cyclic framework of CRA-CMs are densely packed in the monolayer.[8] Accordingly, highly photoisomerizable azobenzene units of the CRA-CM directed to air is anticipated to be suitable for inducing large changes in surface free energy by light, leading to the light-guided motion of a liquid droplet. Second, the chemisorbed monolayer on the animosilylated surface exhibits excellent desorption-resistance toward various kinds of polar solvents including water.[8b] This situation led us to carry out reliable experiments to evaluate a contact angle change and liquid motion.

The photoresponsive behavior of the CRA-CM monolayer was monitored by contact angle measurements. A change in advancing contact angles of water ($\Delta\theta$ = 8°) was observed upon irradiation with 365 nm light, because *cis*-isomers (θ = 86°) providing a higher surface free energy than *trans*-isomers (θ = 94°) are formed photochemically at the outermost surface. However, photo-induced *in-situ* spreading behavior of a water droplet on the *trans*-surface could not be observed even after irradiation with 365 nm light. In our system, it seems that a liquid motion on a substrate is primarily governed by dynamic factors rather than thermodynamic properties of the outermost surface. During studies on contact angle changes of liquids of various kinds by light, we found that polar liquids exhibiting low contact angle hystereses can bring about *in-situ* spreading and dewetting behavior by photoirradiation. Consequently, it was anticipated that a liquid droplet can move to higher surface free energy of a *cis*-surface if we prepare a photochemical gradient on the CRA-CM monolayer.

To obtain a surface with the photochemical gradient, we used the gradient in light intensity generated at an edge of a focused light beam. The asymmetrical photoirradiation is likely to bring about spatially controlled levels of photoisomerization on a surface to generate asymmetrical surface energies. When a light gradient between two contact lines of a droplet is sufficiently steep (above 5 times), the movement of the droplet in the direction of higher surface free energy could be achieved. Figure 2 shows a directional motion of an NPC-02 (a nematic liquid crystal, a binary mixture of 4-propyl-4'-ethoxy- and 4-propyl-4'-butoxy-phenylcyclohexanes) droplet on a *cis*-surface by asymmetrical irradiation with 436 nm light. A speed of 50 μm/sec was achieved for the motion of about a 2 μl droplet. The speed of the droplet intrinsically relied on the intensity and gradient of the light.

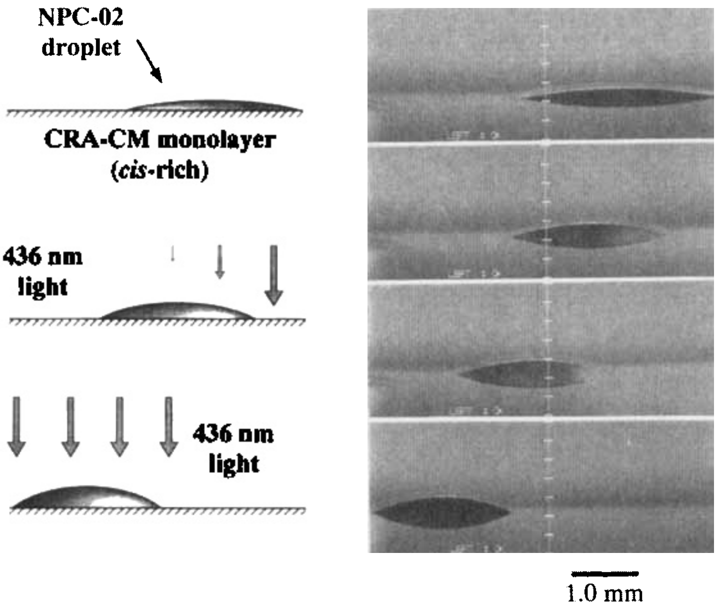

FIGURE 2 Lateral photographs of the directional motion of an NPC-02 droplet on a CRA-CM monolayer in its *cis*-rich state when the substrate was irradiated with an asymmetrical 436 nm light perpendicular to the surface.

Whitesides[2] and Brochard[9] propose that a force imbalance experienced by a droplet is the driving force for liquid motion. For the motion induced by the asymmetrical photoirradiation, a free surface near a wetting front of the droplet is still remained in *cis*-rich state even though the contact angle at the point should have increased already. This situation causes a force imbalance between advancing and receding edges of the droplet, leading to the light-guided motion of a liquid droplet.

CONCLUSION

Using a substrate modified with an *O*-octacarboxymethylated calix[4]resorcinarene having azobenzene residues, we have demonstrated the first example of the light-guided movement of a liquid droplet on it. An asymmetrical photoirradiation leading to a spatial gradient in surface free energy of the photoresponsive substrate made it possible to move a liquid droplet in the direction of higher surface energy. Our method should be useful in the study on spreading of liquids and on the liquid motion assisted by a surface tension gradient.

References

[1] A. W. Adamson, A. P. Gast, *Physical Chemistry of Surfaces* John Wiley & Sons, New York (1997).

[2] M. K. Chaudhury, G. M. Whitesides, *Science* **256,** 1539 (1992).

[3] G. Möller, M. Harke, H. Motschmann, D. Prescher, *Langmuir* **14,** 4955 (1998).

[4] L. M. Siewierski, W. J. Brittain, S. Petrash, M. D. Foster, *Langmuir* **12,** 5838 (1996).

[5] M. Ueda, H.-B. Kim, K. Ichimura, *J. Mater. Chem.* **4,** 883 (1994).

[6] M. Irie, *Pure & Appl. Chem.* **62,** 1495 (1990).

[7] K. Ichimura, S.-K. Oh, M. Fujimaki, Y. Matsuzawa, M. Nakagawa, *J. Inclusion Phenomena Macrocycl. Chem.* in press.

[8] a) M. Fujimaki, S. Kawahara, Y. Matsuzawa, E. Kurita, Y. Hayashi, K. Ichimura, *Langmuir* **14,** 4495 (1998); b) S. -K. Oh, M. Nakagawa, K. Ichimura, *Chem. Lett.* 349 (1999).

[9] F. Brochard, *Langmuir* **5,** 432 (1989).