

Phototransformative Supramolecular Assembly of Amphiphilic Diarylethenes Realized by the Combination of Photochromism and Lower Critical Solution Temperature Behavior

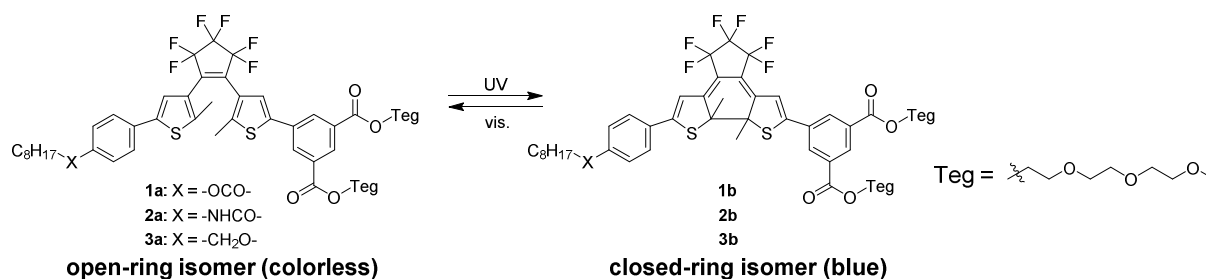
Kenji Higashiguchi,¹ Hajime Yotsuji,¹ Ryuma Sato,² Yasuteru Shigeta,² and Kenji Matsuda²

¹*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

²*Center for Computational Sciences, University of Tsukuba, 305-8577 Ibaraki, Japan*

E-mail: higashi@sbchem.kyoto-u.ac.jp

An amphiphilic diarylethene with one alkyl chain and two tri(ethylene glycol) chains **3**^[1] undergoes photoinduced reversible morphological transformation by alternate irradiation with UV and visible light. It is understood as photoinduced phase transition between the high- and low-temperature phases of LCST transition. In this study, in order to reveal the mechanism of the photoinduced morphological transformation concomitant with LCST transition and to investigate the effect of local intermolecular interaction, hydrogen-bonding units are introduced into the amphiphilic diarylethene and the behavior upon photoirradiation was investigated.^[2]



Amphiphilic diarylethenes with octyloxycarbonyl and *N*-octylcarbamoyl groups were designed and synthesized. These ester- (**1**) and amide-linked (**2**) compounds formed micrometer-sized supramolecular assemblies in water and these assemblies exhibited photoinduced macroscopic morphological transformation upon alternate irradiation with UV and visible lights. Ester-linked diarylethene **1** showed a transformation between colorless spheres and red-purple hazy fringe, while microspheres of amide-linked diarylethene **2** showed the change in color, size, and shape, but the spheres did not show division as shown in Fig. 1.

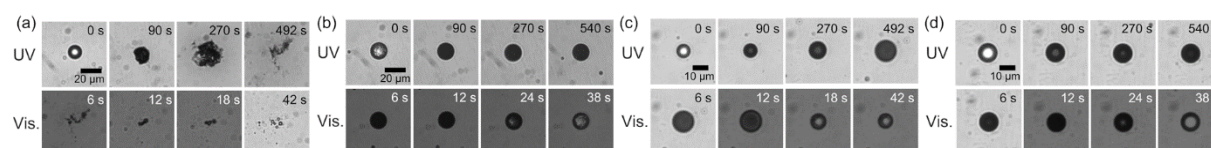


Figure 1. Temperature-dependent photoinduced macroscopic morphological transformation of the supramolecular assemblies composed of amphiphilic diarylethenes: (a) **1** at 20 °C, (b) **1** at 40 °C, (c) **2** at 20 °C, (d) **2** at 40 °C. For each Figure, upper and bottom rows represent the change during irradiation with UV (365 nm) and subsequent visible (546) lights, respectively.

TEM images showed that the sphere of the open-ring isomers have coacervate structures with bicontinuous aqueous and organic phases. The closed-ring isomers were found to form nanofibers and thin layers for ester- and amide-linked compounds, respectively (Fig. 2).

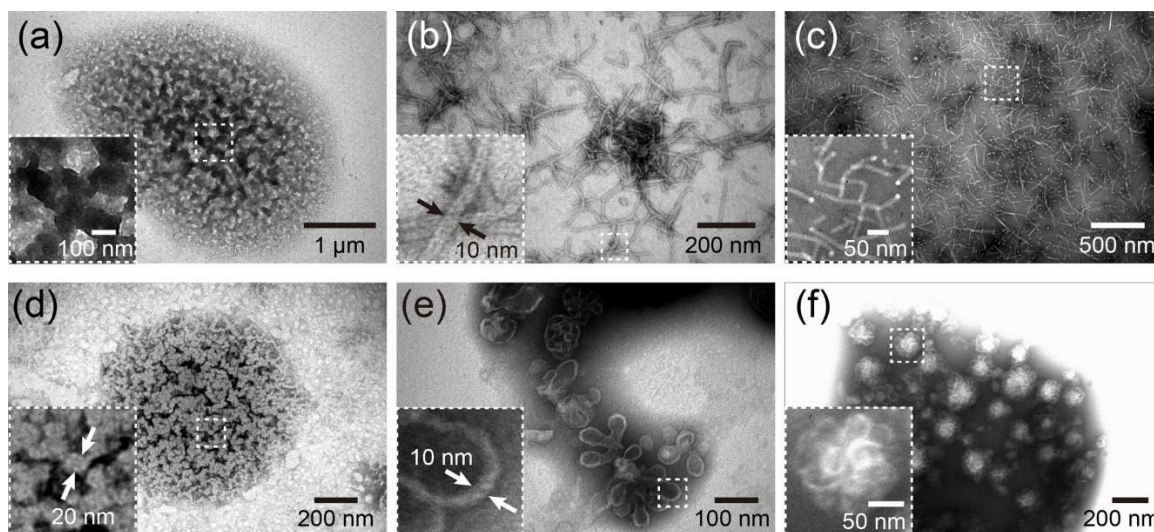


Figure 2. TEM images of the supramolecular architecture of diarylethene (a-c) **1** and (d-f) **2**. (a, d) The sphere state having coacervate structure of open-ring isomer. (b, e) After UV irradiation to sphere state on the TEM grid and the expanded image (insets). (c, f) The hydrated state of >95% closed-ring isomer. The temperature was controlled at 5 °C for preparation of hydrated sample as shown in (b), (c), (e), and (f).

These compounds showed absorption spectral shift by the temperature change originating from LCST transition (Figs. 3a and b). For both compounds, when the content of the closed-ring isomer increased by irradiation with UV light, the supramolecular architectures changed from dehydrated to hydrated phase (Figs. 3c and d). These results open up the way of rational design of phototransformative supramolecular assembly by the combination of photochromism and lower critical solution temperature behavior.

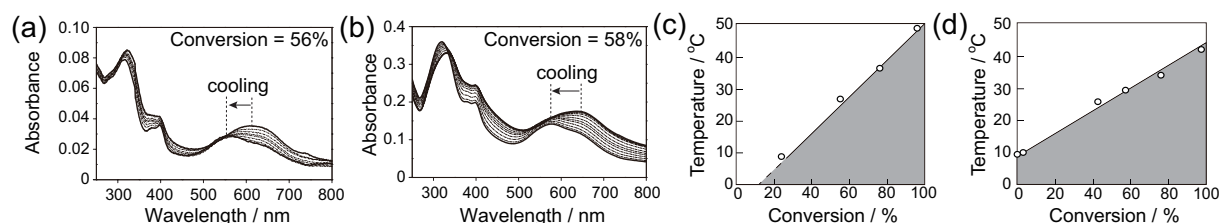


Figure 3. UV-vis absorption spectra at different temperatures for diarylethenes (a) **1** and (b) **2**. Phase diagram of the LCST temperature obtained by the plots of absorption maxima in the UV-vis absorption spectra for the samples with different content of the closed-ring isomer of (c) **1** and (d) **2**. The white and gray regions correspond to the dehydrated and hydrated phases in LCST transition, respectively

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References:

- [1] K. Higashiguchi, G. Taira, J.-i. Kitai, T. Hirose, K. Matsuda *J. Am. Chem. Soc.* **2015**, 137, 2722-2729.
- [2] H. Yotsuji, K. Higashiguchi, R. Sato, Y. Shigeta, and K. Matsuda, *to be submitted*.