

## Photochromism and Chirality Propagation of Chromene Amphiphile Aggregates in Aqueous Ethanol Solutions

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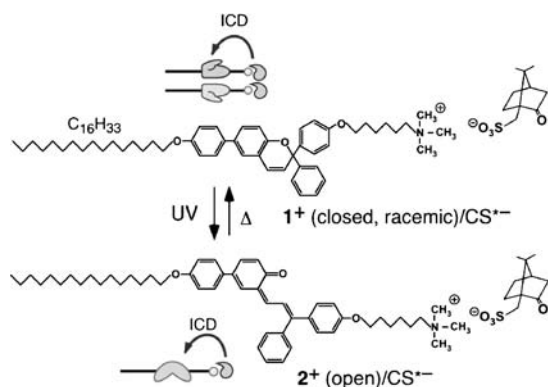
Spectroscopic and morphologic characteristics of a racemic chromene cationic amphiphile  $1^+$  having a chiral camphor sulfonate counter anion ((+) or (-)  $CS^{*-}$ ) were studied in aggregates in aqueous ethanol solutions. The media-dependent photochromism of  $1^+/CS^{*-}$  and the enantio-preferential selective ring-closing process after UV irradiation were observed owing to the propagation of the chirality from the counter anion  $CS^{*-}$ .

A number of polymer systems that convert chiral information to their higher-order architecture have been widely studied.<sup>1</sup> In most systems, conformational alternation of molecular moiety is controlled by small chiral molecules or chiral sub-structures. Furthermore, chiral assemblies of the supramolecular aggregate consisting of achiral molecules are also commanded by chiral counter parts, as known as the sergeant-soldier effect.<sup>2</sup>

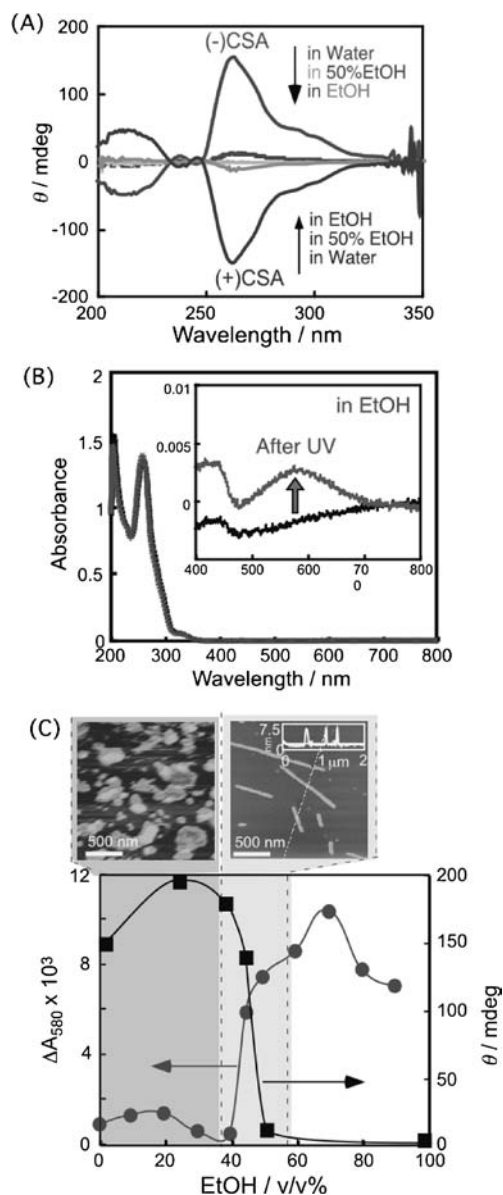
Herein, we studied the supramolecular characteristics and photochromism of a chromene cationic amphiphile  $1^+$  having a chiral camphor sulfonate ((+) or (-)  $CS^{*-}$ ) as a counter anion in aggregates in aqueous ethanol solutions. The racemic  $1^+$  became partially the enantio-excess  $1^+$  during the ring-closing process from the  $2^+$  form due to the chiral propagation of the counter camphor anion  $CS^{*-}$  (see Scheme 1).

The chromene cationic amphiphile, 6-(4-hexadecyloxyphenyl)-2-[4-(6-trimethylammonio)hexyloxyphenyl]-2-phenyl-2*H*-chromene ( $1^+$ ) was synthesized as a photochromic amphiphile.<sup>3</sup> This amphiphile has a 2,2-diphenyl-2*H*-chromene moiety at the center of this molecule. It is well known that certain chromenes have photochromic properties.<sup>4</sup> It means that the closed form  $1^+$  would be photoisomerized to a colored open form  $2^+$ . The open form  $2^+$  would revert to the closed form  $1^+$  thermally at room temperature.

We studied CD spectra and photochromic properties of  $1^+/$



Scheme 1.



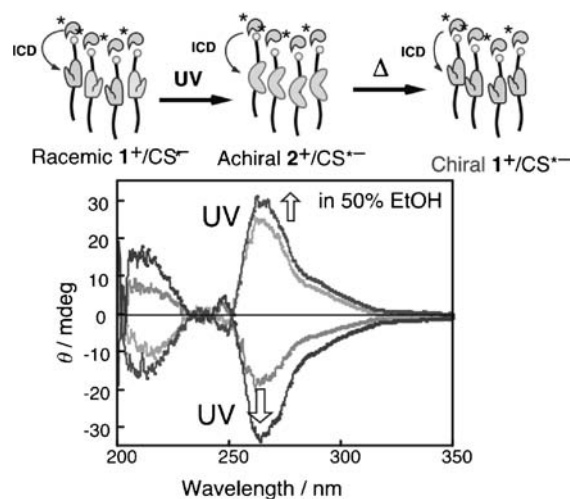
**Figure 1.** (A) CD spectra of  $1^+/CS^{*-}$  (25 mM) in pure water, in 50 vol % EtOH, and pure EtOH. (B) UV-vis absorption spectra of  $1^+/CS^{*-}$  (25 mM) in pure EtOH before and after the UV irradiation. (C) Dependence of absorbance changes at 580 nm of  $1^+/CS^{*-}$  (25 mM) with the UV irradiation and  $\theta$  values of ICD at 260 nm on ethanol contents in aqueous solutions. Photographs are AFM tapping mode images of  $1^+/CS^{*-}$  aggregates in pure water and 50 vol % EtOH solution.

$CS^{*-}$  in aqueous ethanol solutions. When the  $1^+/CS^{*-}$  was dispersed in pure water, the large induced CD (ICD) spectra at the aromatic absorption band near 260 nm was observed depending on chiralities of the chiral commanding counter (+) or ( $-$ )  $CS^{*-}$  anion (Figure 1A). When it was irradiated with the UV light (Mineralight lamp UVGL-25, 254 nm, 16 W), very few spectral changes were observed (data not shown). On the contrary, when  $1^+/CS^{*-}$  was dissolved in pure ethanol, no ICD was observed. However, the weak absorption of band at 580 nm was appeared under UV irradiation due to the photoisomerization to the colored open form  $2^+$  (Figure 1B, inserted).

Figure 1C shows dependence of the ICD at 260 nm, the photochromic property of absorption at 580 nm, and atomic force microscopy (AFM) observations of the aggregates on ethanol contents in aqueous solutions. For AFM experiments, aggregate solutions were put onto freshly peeled mica substrates for 10 s. Then, solutions were spin out. Absorbed aggregates on the mica substrates were investigated. In the low ethanol content region including pure water, the  $1^+/CS^{*-}$  was confirmed to form large disk-like aggregates from the AFM photograph in Figure 1C, where the large ICD was observed, but the little photoisomerization was observed. Thus, in the tightly packed aggregates, the effective propagation of the chiral information from (+) or ( $-$ )  $CS^{*-}$  to the aromatic moiety of  $1^+$  was observed. On the contrary, the photoisomerization hardly occurred in the tightly packed aggregates as a trade-off relationship. When increasing the ethanol content to 50 vol %, the  $1^+/CS^{*-}$  formed highly uniform rod-like structures (diameter: ca. 7 nm, Figure 1C), which supposed to be a loose or relaxed aggregates.<sup>2b,5</sup> In these aggregates, the ICD was decreased, but the photoisomerization became to be observed. In the high ethanol content region including pure ethanol, any large aggregates were not observed by AFM, where the ICD was diminished but the large photoisomerization was observed. Thus, in the proper ethanol content such as 50 vol % EtOH, both the propagation of the chiral information from the counter anion  $CS^{*-}$  to the amphiphile  $1^+$  and the photoisomerization from the closed  $1^+$  to the open  $2^+$  form was observed owing to the loose packed rod-like aggregate structures.

Although the open-ring hexadienone form has no chirality, closed-ring forms of chromene derivatives have a chiral sp<sup>3</sup> carbon. Therefore, chromene enantiomers undergo photochemical and thermal racemization via open–close rearrangement cycles. In other words, the open form  $2$  could be regarded as a pro-chiral molecule. Under the chiral commanding condition, the total chiral symmetry of amphiphile  $1^+$  would be violated. In the presence of the chiral commander (+) or ( $-$ )  $CS^{*-}$ , it is expected that the ring-closing reaction following the photoinduced ring-opening process would produce one enantiomer preferentially.

UV irradiation was performed onto the loose aggregation of  $1^+/CS^{*-}$  in 50 vol % EtOH solution. After the confirmation of the complete ring closing reaction of  $1^+$  by the UV–vis spectroscopy, the CD spectroscopy was investigated. The ICD was increased after the UV irradiation (Figure 2). No CD spectral changes were observed in pure water after the UV irradiation. Moreover, after the UV irradiation of  $1^+$  in pure EtOH or 50 vol % EtOH, the ICD enhancement did not observed. Thus, when the open form  $2^+$  prepared by the photoisomerization



**Figure 2.** CD spectral changes with the UV irradiation of  $1^+/CS^{*-}$  (25  $\mu$ M) in 50 vol % EtOH solutions.

reverts to the closed form  $1^+$ , the chiral propagation from the counter  $CS^{*-}$  anion causes the deviation the chirality of  $1^+$  in the loose aggregates. It is known that the racemization rates of chromene enantiomers are small.<sup>6</sup> So that the enantioselective ring-closing process after the UV irradiation, the reverse process of racemization, would also have the low reaction rate. Unfortunately, we could not quantify the enantio excess of an enantiomer of  $1^+$  after the UV irradiation with a chiral chromatography.

In conclusion, the photochromic and chirality propagation abilities of the chromene amphiphile  $1^+$  could be controlled by the ethanol content of solution. In the proper relaxed aggregates, we could visualize the slight excess of one enantiomer of  $1^+$  during the ring-closing process after the UV irradiation.

## References and Notes

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