Spectral Bistability of Two-dimensional Molecular Assemblies due to a Peculiar Crystal–to–Crystal Phase Transition

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An ordered cast film of azobenzene-containing molecular membranes had two stable crystalline states at room temperature; spectral bistability of guest cyanine dye reflecting two crystalline states was observed as well as the azobenzene chromophore.

The design and control of the molecular orientation in molecular assemblies are required for molecular crystals in the field of 'crystal engineering'[1] and for Langmuir–Blodgett films in 'molecular devices'.[2] A bilayer membrane is a suitable candidate for the designed molecular assembly owing to its two-dimensional ordering. Kunitake and co-workers succeeded in immobilizing the aqueous bilayer membranes as highly oriented solid films by various methods.[3—5] The bilayer membrane of azobenzene-containing amphiphile C_8Azo-$C_{10}N^+$ was also immobilized as a self-supporting film by the casting method, and the regular molecular orientation was determined by the X-ray analysis.[6]

We report here the spectral bistability of the azobenzene-containing molecular membrane (1) due to a peculiar crystal–to–crystal phase transition.[7] Two types of absorption spectrum attributed to the respective two crystalline states are stable at room temperature. The absorption spectrum of cyanine dye (2) bound to the molecular membrane is changed by the crystal–to–crystal transition and the spectral bistability of the cyanine dye is also observed as well as the azobenzene chromophore.

A crystal–to–liquid crystal phase transition is typical behaviour of the aqueous bilayer membrane on heating. A thermally induced phase transition is also found in the immobilized bilayer membrane. The film of $C_{12}AZoC_5N^+$, cast from an
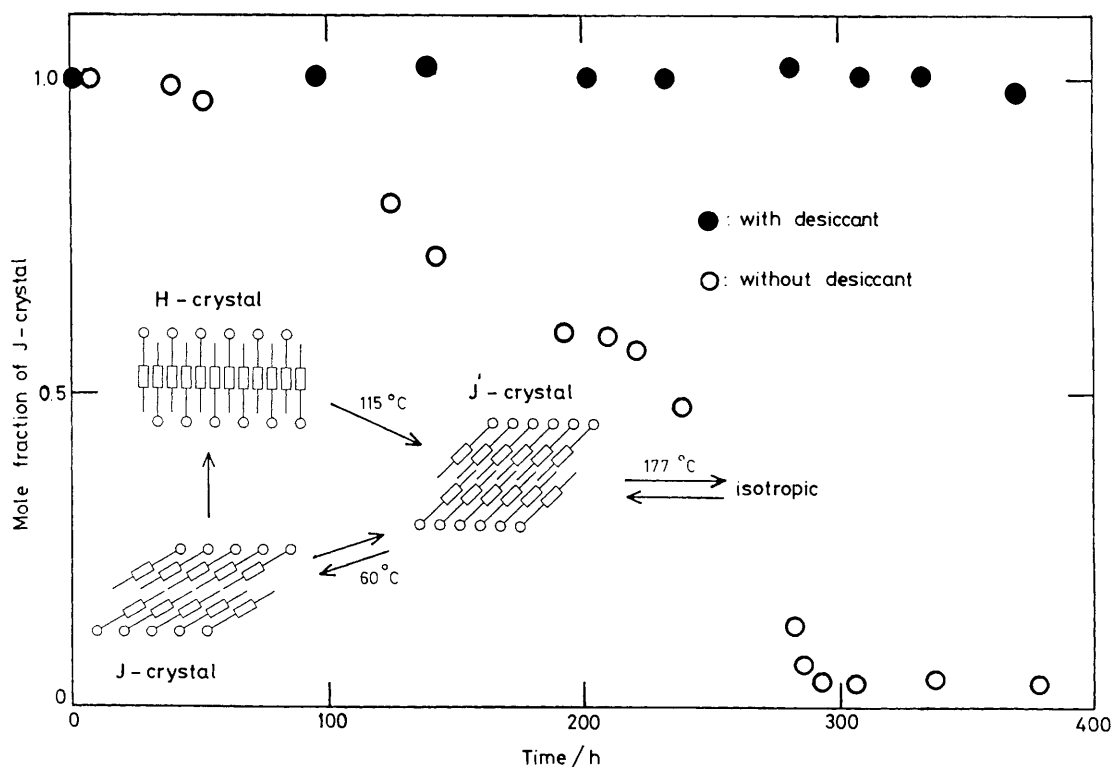

(1) $C_nAzoC_mN^+$

(2)
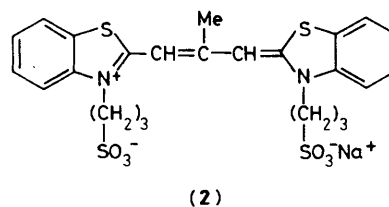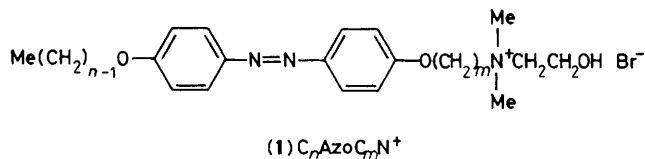
Figure 1. Stability of the J-crystal at room temperature. The J-crystal was formed from the H-crystal *via* the J'-crystal by thermal annealing. The insert shows the schematic model of the crystal–to–crystal phase transition of the azobenzene molecular film of $C_8AzoC_{10}N^+$. Retention of the J-crystal was calculated from the absorption spectrum.

aqueous solution, showed two phase transitions at 133 and 182 °C in differential scanning calorimetry (DSC). The X-ray diffraction of the film at room temperature showed Debye–Scherrer rings similar to the crystalline powder.[8] The transition at 133 °C was, however, attributed not to the crystal–to–liquid crystal phase transition but to a crystal–to–crystal phase transition, because unexpected sharp reflections were found at 150 °C. The latter transition was found to be the melting point by polarized light microscopy.

The peculiar crystal–to–crystal transition was also found in the film of $C_8AzoC_{10}N^+$.[7] Curious thermal behaviour was found in the DSC measurements. In the first heating, the crystal–to–crystal transition and the crystal–to–isotropic liquid transition were found at 115 and 177 °C, respectively. In the second heating, the 115 °C peak shifted to 60 °C. No chemical reaction occurred during the heating processes, because the melting point was identical in the second heating. The structure of the low-temperature crystal was changed by thermal annealing. The intensity distribution and the long spacing (3.75 nm) of the X-ray diffraction of the annealed film was completely different from that of the original low-temperature crystal (long spacing; 3.90 nm). The X-ray diffraction at 120 °C in the second heating of the annealed film was the same as that of the high-temperature crystal (long spacing; 4.20 nm). The results of the X-ray and DSC experiments show that the $C_8AzoC_{10}N^+$ film has three crystalline states; the two low temperature states transform into the high-temperature crystal at 115 °C and 60 °C, respectively (see Figure 1). In contrast the $C_{12}AzoC_5N^+$ film has two crystalline states, because the transition temperature was identical during the second heating.

Shimomura *et al.*[9] have found that the absorption spectra of the aqueous bilayer membranes of $C_nAzoC_mN^+$ were strongly

dependent both on the molecular orientation and on temperature. Although the absorption spectra of the liquid crystalline state were identical (λ_{max} 340 nm) in all the aqueous bilayer membranes, hypsochromism (λ_{max} 300 nm) and bathochromism (λ_{max} 370 nm) were found in the crystalline bilayer of $C_8AzoC_{10}N^+$ and $C_{12}AzoC_5N^+$, respectively. The X-ray structural analysis of single crystal of $C_{12}AzoC_5N^+$ showed that the bathochromism was attributed to the head-to-tail orientation of transition dipoles (J-aggregate),[8] while the parallel stacking (H-aggregate)[6] of the azobenzene chromophores led to the hypsochromism.

Spectral changes due to the crystal–to–crystal phase transition were also observed in the cast films. The film of $C_{12}AzoC_5N^+$ showed a spectral change. Absorption maximum shifted to 350 nm in the above mentioned phase transition from 370 nm, which was the maximum of the typical J-aggregate of crystalline $C_{12}AzoC_5N^+$. When the high-temperature crystal was kept at room temperature. The absorption spectrum immediately returned back to the J-spectrum, the spectral change was reversible with change in temperature. The spectral change of the $C_8AzoC_{10}N^+$ film was, however, quite different from that of $C_{12}AzoC_5N^+$. An extreme colour change of the $C_8AzoC_{10}N^+$ film from pale yellow to deep orange happened at 115 °C. Below the transition at 115 °C, the low-temperature crystal showed the typical absorption of the H-aggregate. The absorption maximum shifted to 360 nm in the high-temperature crystal. At room temperature, the absorption maximum moved to 370 nm, not to 300 nm, within several seconds and the spectral shape was typical of the J-aggregate. The deep orange colour of the J-aggregate remained at room temperature. Two spectral states of the H-aggregate and the J-aggregate observed at low temperature coincide with the two types of
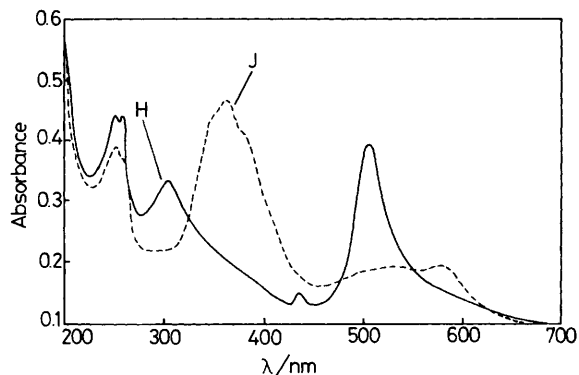
Figure 2. Spectral bistability of the cyanine dye (2) adsorbed on the azobenzene film at room temperature. $[C_8AzoC_{10}N^+]/[(2)] = 7.5$.

crystalline states, H-crystal and J-crystal, observed in the X-ray experiments.

As shown in Figure 1, the J-crystal was surprisingly stable under dry conditions, and has now been kept over 3000 hours in a desiccator. When kept without any desiccant, the J-crystal was gradually transformed to the H-crystal under the isothermal conditions. Isothermal crystal–to–crystal transformation from the J-crystal to the H-crystal was presumably triggered by water, because the rate of the transition was accelerated in moisture. The transition cycle between the H-crystal, the J-crystal, and the high-temperature crystal (named J′-crystal)[7] is completely reversible. A schematic model of the phase transition and structure of the $C_8AzoC_{10}N^+$ film is summarized in Figure 1.

Nakashima et al.[3] have found that the crystal–to–liquid crystal phase transition could be used for the spectral control of guest cyanine dyes[10] electrostatically bound to the immobilized bilayers. Absorption spectrum of the guest cyannine dye (2) was also expected to be affected by the crystal–to–crystal transition of the matrix membrane. As shown in Figure 2, spectral change of the cyanine dye from 507 to 572 nm was synchronized with the crystal–to–crystal transition of the matrix membrane by thermal annealing. The 572 nm species was stable in the dry, as well as the J-aggregate of the matrix. The sharp absorption at 507 nm, suggesting the formation of the H-aggregate of the dye molecules,[11] has not

hitherto been reported in the bilayer matrices. The H-aggregate of the dye was also regenerated in moisture as well as the H-aggregate of the azobenzene chromophores.

It is worth mentioning that the two stable crystalline states of the $C_8AzoC_{10}N^+$ film at low temperature lead to spectral bistability not only of the azobenzene chromophore but also of the guest, cyanine dye. In the normal films of $C_{12}AzoC_5N^+$, however, the spectral bistability of the azobenzene chromophore could not be observed, because $C_{12}AzoC_5N^+$ showed only one crystalline state at a certain temperature. Guest cyanine dye adsorbed on the immobilized membrane of double-chain amphiphiles[3] also could not show spectral bistability, because the crystal–to–liquid crystal transition is intrinsically reversible with temperature change.

We believe that the unique properties of the crystal–to–crystal transition of the azobenzene molecular membrane could be useful for 'crystal engineering' as a tool for making tailor-made crystals because of the well defined crystal structures. A memory effect of the spectral bistability could also be available for 'molecular memory', devices.

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