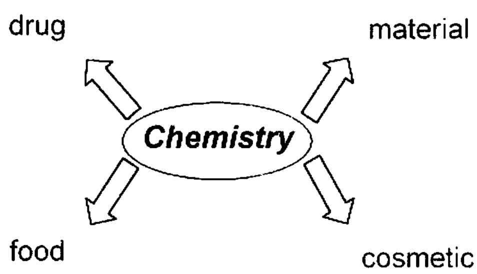
2006. 11. 4. Sae Makino(M2)

Reversible control of viscoelasticity and color

- the contribution of chemistry to life in society -

1. Introduction



2. Reversible control of viscoelasticity of fluids

Surfactant

-Definition-

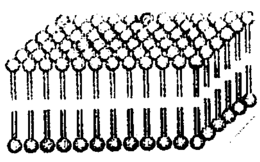
It is an amphiphilic substance that has both hydrophilic and hydrophobic groups in one molecule.

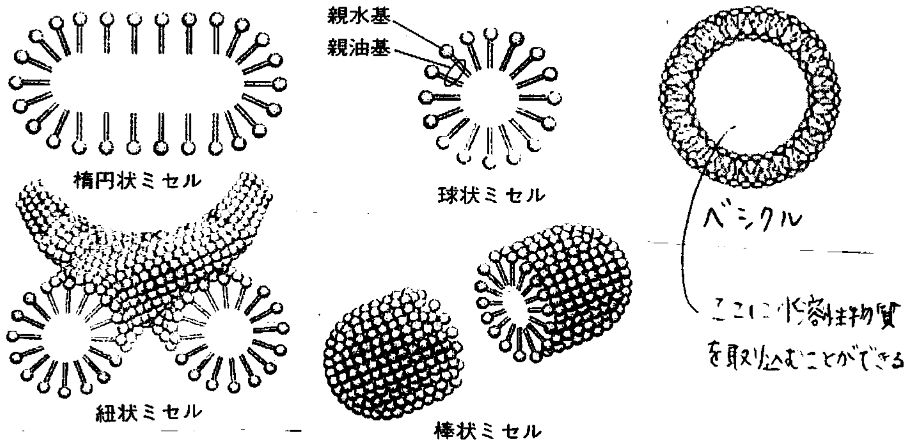
-Properties-

+ Forming molecular assembles +
  such as micelles, vesicles and lamellar structures
+ Penetration function +
  the surface tension of water declines by connecting with water and hydrophilic groups of surfactant.
+ Emulsion +
  It solubilizes water-insoluble or oil-insoluble substances in its interior.
+ Dispersion +
  It entraps powder and particle which can't mix with water in its interior.

-Variety-

1. Anionic surfactant
2. Cationic surfactant
3. Catanionic surfactant
4. Nonionic surfactant





<u>cmc (critical micelle concentration)</u>

In low concentration, single surfactants adsorb to the surface of water and oil.
Increasing concentration, they aggregate each other to be stable.
The concentration of forming micelles is called "**cmc**".

Apply external stimuli to especial surfactant

⇩

Formation and disruption of micelles

⇩

Reversible control of the viscoelasticity of solution

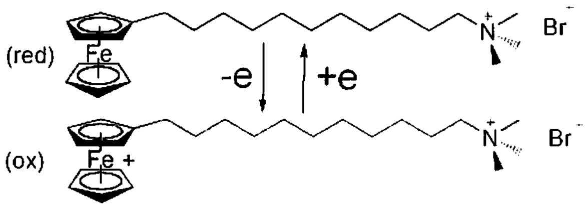
⇩

Application to drugs, cosmetics, materials etc..

2-1. By electric stimuli

1. FTMA/NaSal

M. Abe et al. *J. Am. Chem. Soc.* **2004**, *126*, 12282-12283



FTMA ((11-ferrocenylundecyl)trimethylammonium bromide) is a cationic ferrocenyl surfactant.

It self-assembles into wormlike micelles.

Reversible control the viscoelasticty of solution by turning the degree of entangment of wormlike micelles through redox reaction of FTMA.

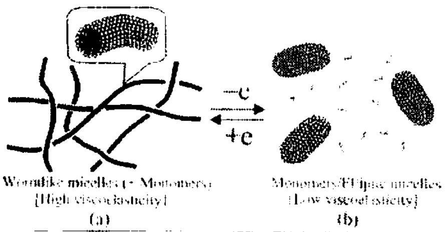
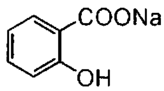


fig4 red ox

Reduced ferrocenyl group -- hydrophobic
Oxidized ferrocenyl group (ferricinium cation) -- hydrophilic



NaSal (Sodium salicylate)
-the supporting electrolyte
to prevent the change in aggregation state-

Fig 1. (accompanying sheet)

a: $C_{NaSal}/C_{FTMA(red)} = 0$
b: $C_{NaSal}/C_{FTMA(red)} = 0.2$ ---Flow immediately
c: $C_{NaSal}/C_{FTMA(red)} = 0.4$ ---No flow
d: $C_{NaSal}/C_{FTMA(ox)} = 0.4$ ---Easily flow

The dissolution into monomers of a portion of the molecules forming warmlike micelle after oxidation.
And the number of aggregates formed in the mixture decreases.
elliptic aggragates whose length is much shorter than wormlike micelles are likely to be formed. (Fig 4.)

2. FTMA/SDBS

M. Abe et al. *Langmuir*. **2003**, *19*, 9343-9350.

SDBS (Sodium dodecylbenzene sulfonate)
-an anionic surfactant-

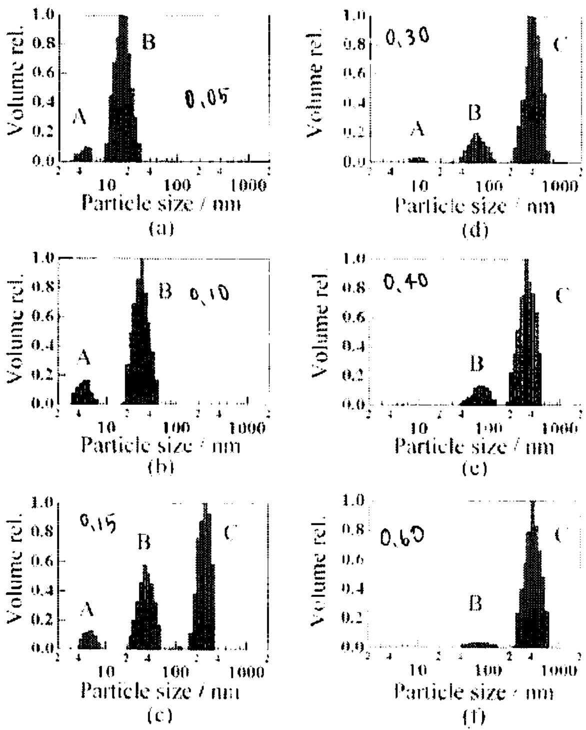


Figure 1. Particle size distribution for aqueous mixtures of FTMA and SDBS measured with quasi-elastic light scattering (7 mM FTMA, 0.02 M NaBr, [SDBS]/[FTMA] = (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.30, (e) 0.40, and (f) 0.60).

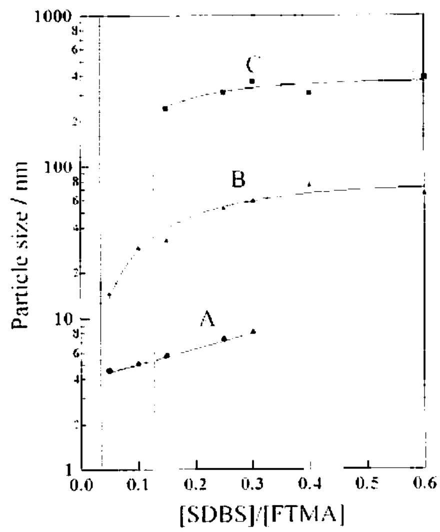


Figure 2. Particle size distribution for aqueous mixtures of FTMA and SDBS as a function of the molar ratio (7 mM FTMA, 0.02 M NaBr).

$0 \leq$ [SDBS] / [FTMA] ≤ 0.02
+ yellowish solution
+ mixed micelles, no vesicle

$0.05 \leq$ [SDBS] / [FTMA] ≤ 0.30
+ 4-8 nm size
+ the size increased with increasing mixing ratio.
+ mixed micelles

$0.05 \leq$ [SDBS] / [FTMA] ≤ 0.60
+ 15-80 nm size
+ vesicle

$0.15 \leq$ [SDBS] / [FTMA] ≤ 0.60
+ 200-600 nm size
+ large vesicle having a multilamellar membrane
+ increasing of the turbidity
+ precipitation of a small amount of turbid cloud wisp

$0.90 \leq$ [SDBS] / [FTMA] ≤ 1.00
+ yellowish crystalline precipitates
because of the neutralization of electric charges between FTMA and SDBS.

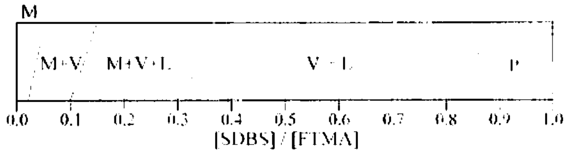


Figure 5. Phase behavior of aqueous solutions of FTMA and SDBS (with 0.02 M NaBr). The FTMA concentration is fixed at 7 mM (M, micelle; V, vesicle; L, lamellar phase; P, precipitate).

At low ratio, mixed micelles were formed.
At high ratio, vesicles and lamellar liquid crystals were formed

In the cationic and anionic surfactant mixtures, the electrostatic interaction between their hydrophilic groups causes the mixtures to form a pretended double-tailed complexes. So, they form vesicles.

[Electrochemical reaction]

[SDBS] / [FTMA] $\leq$ 0.30
--- mixed micelles

FTMA monomers are oxidized
(near electrode)

FTMA micelles diffuse to the electrode

FTMA molecules leave micelles as a monomers

Dissociated FTMA monomers react on the electrode

The reaction proceed further

0.4 $\leq$ [SDBS] / [FTMA] $\leq$ 0.30
--- vesicles, lamellar liquid crystals

The average size of the aggregates increases

The bilayers have a higher hydrophobicity

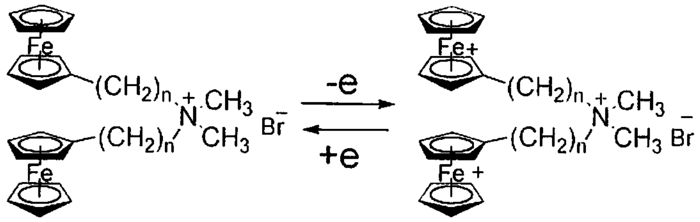
Vesicles deposited onto the hydrophobic carbon electrode

At low mixing ratio, the oxidation process was dominated by diffusion-controlledprocess.
At high mixing ratio, the oxidation process was dominated by adsorption species on the electrode.

By examinations of the electrochemical behavior of other mixed surfactants systems with FTMA,
the aggregation states with various compositions and concentrations with ease

3. n-BFDMA (n = 5,11)

M. Abe et al. *Langmuir* **1996**. *12*, 921-924.
M. Abe et al. *Langmuir*. **2001** *17*, 8044-8048.



11-BFDMA (bis(11-ferrocenylundecyl)dimethylammonium bromide) is a double-chain-type cationic ferrocenyl surfactant.

First surfactant which having two alkyl chains and two ferrocenyl groups in one molecure.

[Solution properties]

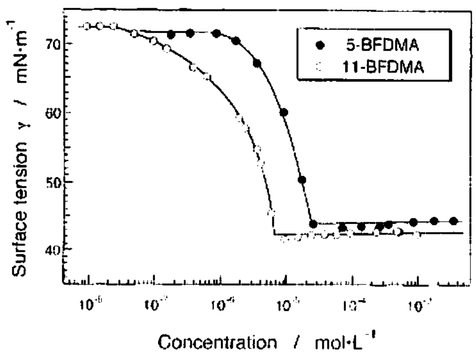
+ The aggregation form of n-BFDMA is dependent on its concentration+

5-BFDMA changes to form monomer - micelle - liquid crystal with increasing concentration.
11-BFDMA changes to form monomer - liquid crystal - a lamellar phase liquid crystal.
In the liquid crystalof 11-BFDMA solution, vesicles spontaneously are formed above the special concentration range. (not"cmc")

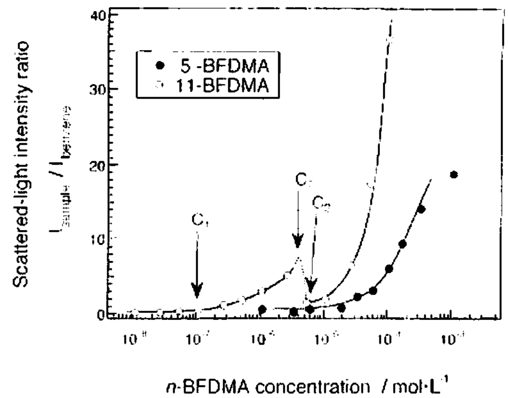
<Krafft point> The temperature of beginning to form micelles is called "Krafft point".
The solubility of a surfactant is found by it.

The Krafft point of 5-BFDMA --- below 0°C
The Krafft point of 11-BFDMA --- 21 °C
} The solubility of n-BFDMA decreases with increasing chain length of the hydrophobic moiety.

<Surface tension>



<Scattered-light intensity> The intensity of the scattered light reflects the number and the size of the molecular aggregates.

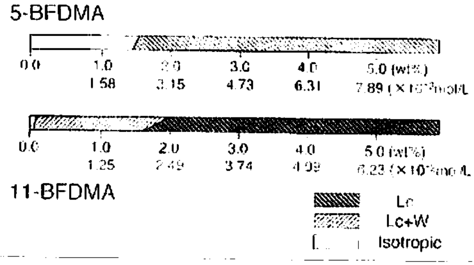


cmc of 5-BFDMA is 3×10^{-5} mol/l
cmc of 11-BFDMA is 6×10^{-6} mol/l

These values are smaller than that the value of a single hydrophobic tailed ferrocenyl surfactant.

In the case of 5-BFDMA, the scattered light intensity increases above 3×10^{-5} mol/. (=same as the minimum value of surface tension)
In the case of 11-BFDMA, it decreases temporarily.
→ the aggregates may change at C_2

<Phase behavior>



in detal

<Size>
Below C_2 --- 80 nm
At C_3 --- 300 nm
Above C_3 --- 1 μ m

<Observation by TEM >
At C_3, Beginning of forming spontaneous vesicle
After sonication, vesicles with smaller size were obtained.

--11-BFDMA --

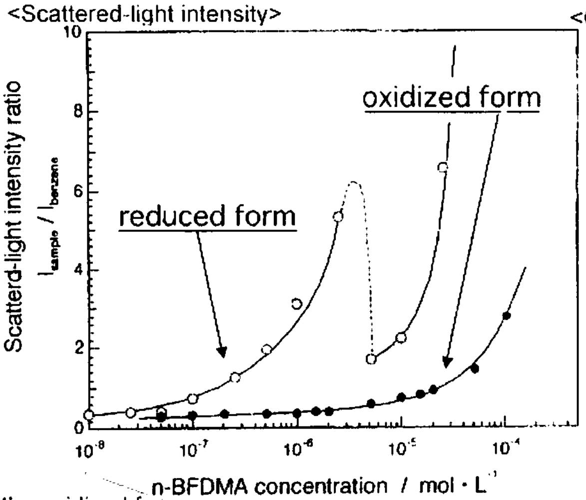
0 - 2.0×10^{-2} mol/l --- forming spontaneous vesicles
2.0×10^{-2} - 6.23×10^{-2}mol/l --- lose fluidity, high viscosity
Above 6.23×10^{-2} mol/l --- forming of lamellar phase

Liquid crystal formation due to...
+ the increase of the hydrophobicity by introduction of the ferrocenyl moiety
+ the enhanced molecular interaction between ferrocenyl groups

Spontaneous vesicle formation caused by...
+ the area occupied by the hydrophilic moiety decreases with each other
+ the molecular geometry of 11-BFDMA becomes similar to a rodlike type which is appropriate for vesicle formation

Vesicles made of the redused form of 11-BFDMA disintegrate and change into smaller molecular aggregates including micelles through oxidation of ferrocenyl groups

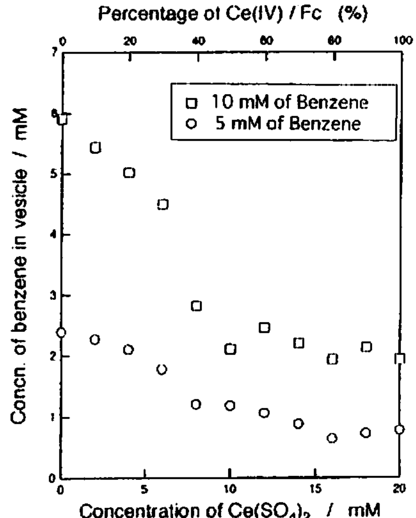
<Scattered-light intensity>



the oxidized form
--- rise monotonically with concentration

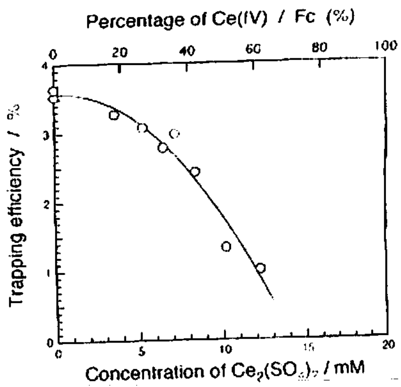
<Observation by TEM>
+ small aggregate 50 nm
+ vesicles were not observed

<Concentration of benzene in vesicle>



With increasing percentage of oxidized ferrocenyl groups, the concentration of benzene solubilized decreased.

<Trapping efficiency>



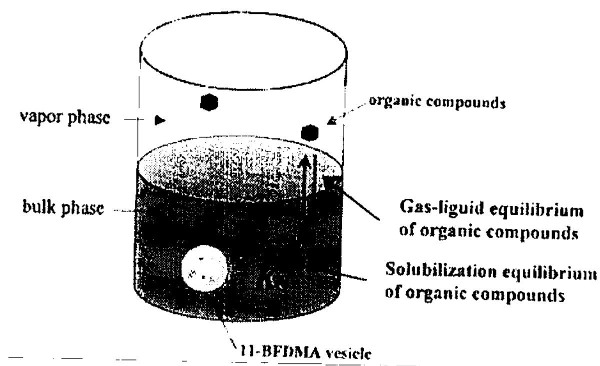
The trapping efficiency decreased with increasing oxidation of ferrocenyl groups.
Above ca.70%, its value was 0.
---Because the release of glucose entrapped in the vesicles into the bulk solution caused by oxi-ferrocenyl groups.

Summary

When the two ferrocenyl groups were oxidized, spontaneously formed vesicles of 11-BFDMA.....
underwent disruption
change to smaller molecular aggregates.

An oil-soluble subatance solubilized in bimolecular layers
and
a water-soluble substance trapped in the inner aqueous phase of 11- BFDMA vesicles
were released into the bulk solution.

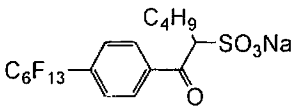
The release extent was found to depend on
the oxidation percentage of the surfactant



2-2. By thermal stimuli

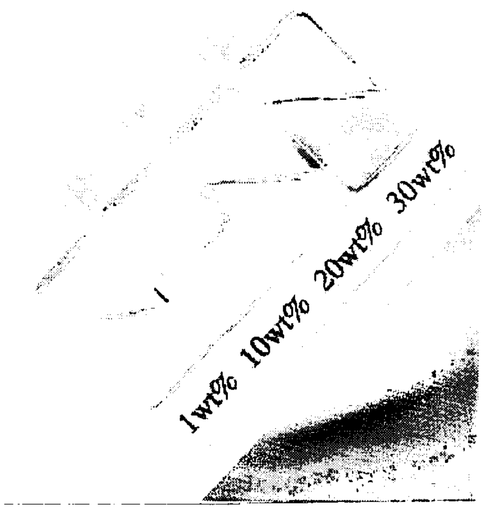
M. Abe et al. *Langmuir*. **1997**, *13*, 2932-2934.
M. Abe et al. *Langmuir*. **1997**, *13*, 5054-5055.
M. Abe et al. *Langmuir*. **1998**, *14*, 4753-4757.

FC6-HC4



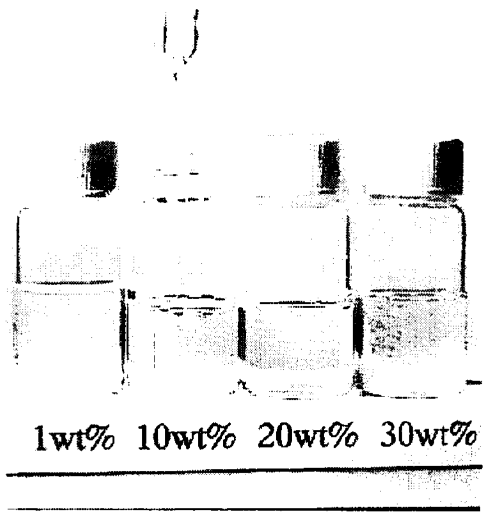
It is a fluorinated hybrid surfactant.
----a fluorocarbon chain } within one molecule
a hydrocarbon chain }

[Concentration]



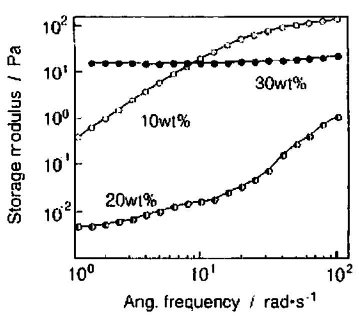
Only 10 wt%solution has high viscosity

Why does this surfactant exhibit a unique behavior?



10 wt% solution has a characteristic solution.

In general, viscosity of **a single-linked hydrocarbon** or **a single-linked fluorocarbon surfactant** tends to monotonically increase with an increase in the surfactant concentration.
However, the viscosity of this hybrid surfactant reaches the maximum value at a certain concentration.



In general, it is the characteristic of concentrated suspension that the storage modulus (貯蔵弾性率) does not depend on angular frequency(角振動数).

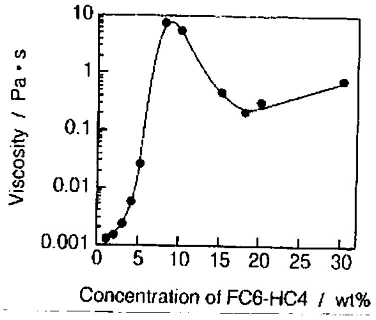
1) 30 wt% --- this characterisity
   lamellar liquid crystalline phase
2) 20 wt% --- hardly any formation of aggregates
   beginning of formation of liquid crystallines
3) 10 wt% --- high strorage modulus
   it depends on angular ferquency
   defferent form of aggregate from 30 wt%
4) 1 wt% --- not observed because of no elastcity

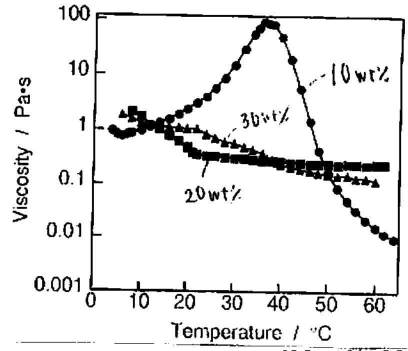
The structural change of the water molecule ? ⟹ By ^{1}H-NMR,
the motion of water molecules **is not restricted** around 10 wt% solution.

The structural change of the micelle ? ⟹ **Varies** depending on the increase of the concentration

⟹ The surface orientation change due to the structural change of the micelle is the main reason of unique viscoelasticity.

[Temperature]





[10 wt%]
6°C- 36°C --- increases 100 times
rise up to 64°C --- decreases 10^{-4} times

[20 wt%, 30 wt%]
decrease with rising temperature

[¹H-NMR]
no unusual behavior either at 10 wt% or at 36°C
----- the structure of water molecules does **not concerned** in unique viscoelasticity.

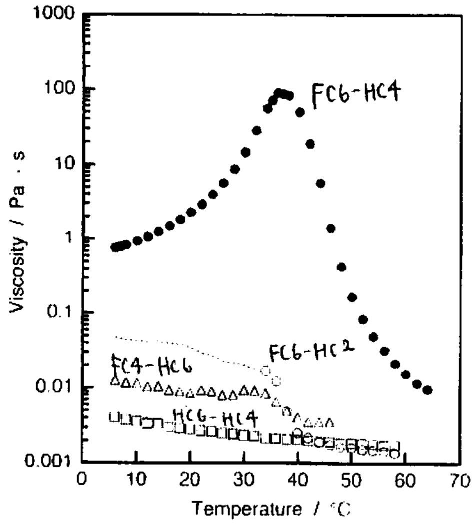


Figure 1. Temperature dependence of viscosity for 10 wt % aqueous FC6-HC2 solution (○), 10 wt % aqueous FC4-HC6 solution (△), 10 wt % aqueous HC6-HC4 solution (□), and 10 wt % aqueous FC6-HC4 solution (●).

[Chemical structure]

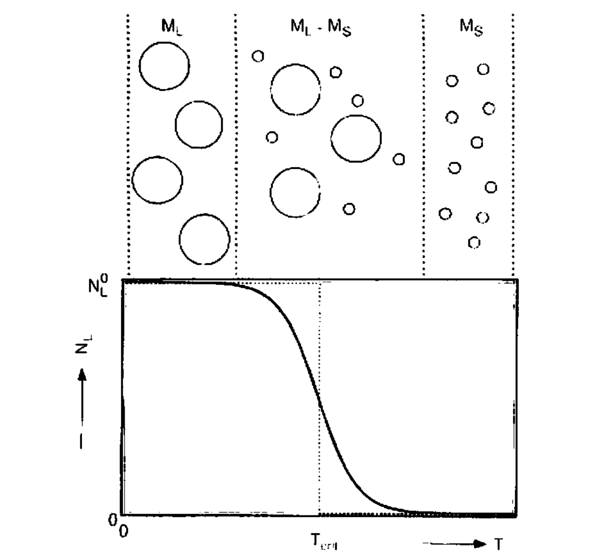
FC6-HC2, FC4-HC6, HC6-HC4 } no unique viscositic behavior
FC6-FC4 could not be synthesized

⟹ **FC6-HC4 is an important structure.**

[observation by electron micrograph]

the micelle condition in **10** wt% solution at 20°C
small molecular assemblies **80** nm
large molecular assemblies **500** nm
----- All spherical micelles.
not one large micelle, the aggregation of small micelles

The concentration increases
↓
The number of small micelles increases
↓
It is easy to form large aggregates through the hydrophobic interaction between hydrocarbon chains
↓
Large molecular assemblies of the surfactant formed at low temperatures are degraded to small molecular assemblies as temperature is raised.



The viscosity is dependent on **the friction emerging from collisions between molecular assemblies**.
collisions between....
large and large
small and small
large and small

The viscosity of the system shows a maximum when the friction between large and small is higher than that between same sizes.

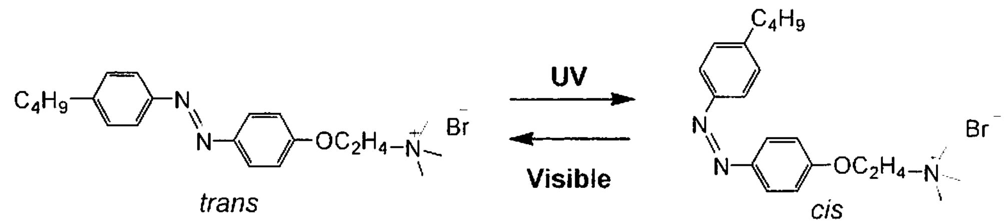
⟹ At 36°C, the frequency of collision is a maximum.

FC6-HC2 : the hydrophobic interaction is not strong enough to form large molecular assmblies.
FC4-HC6 : cannot form micelles instead of lamellar liquid crystals
HC6-HC4 : fluorocarbon chain is essential.
FC6-FC4 : cannot be synthesized because of the too low reactivity

<u>fluorocarbon chain</u> --- being incorporated into the micelle core
<u>hydrocarbon chain</u> --- located near the micelle surface and then make large molecular assemblies through hydrophobic interaction

2-3. By light stimuli -photoisomerization-

AZTMA (4-butylazobenzene-4'-(oxyethyl)-trimethylammonium bromide) is an azobenzene-modified cationic surfactant.

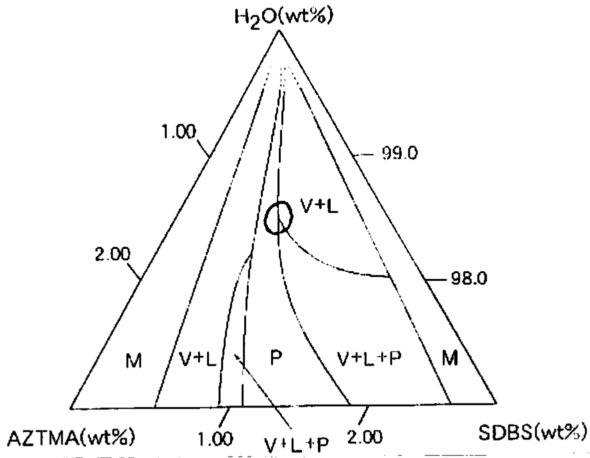


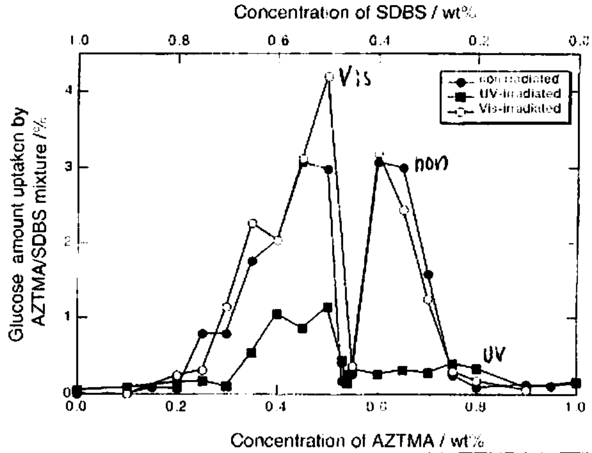
1. AZTMA-SDBS

M. Abe et al. *J. Phys. Chem.*, **1999** *103*, 10737-10740

+ Vesicle formation-disruption +

SDBS (Sodium dodecylbenzene sulfonate) -an anionic surfactant-





1. one surfactant + water ---- mixed micelles phase
2. along the equimolar line (AZTMA : SDBS = 54.7 : 45.3) ---- precipitates
3. Both cation-rich and anion-rich side ---- vesicles (mixing composition)

[*trans*] [*cis*]

AZTMA 0.3-0.5 / 0.6-0.75 --- high low (hardly encapsured glucose)

AZTMA 0.547 ---zero

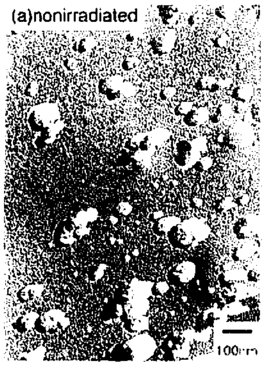
[AZTMA : SDBS = 0.6 :0.4]

3.1 % (non) → 0.3 (after UV) → 3.2 (following vis)

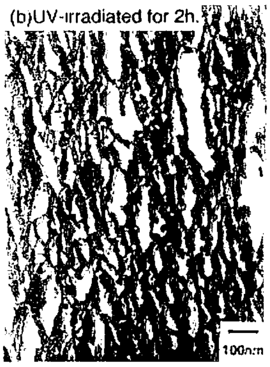
⟹ The disruption and reformation of vesicles induced by the UV-visible light irradiation.

The release of aqueous compound encapsulated in the vesicles can be controlled by photochemical reaction of AZTMA.

(a)nonirradiated



(b)UV-irradiated for 2h.



(c)Vis-irradiated for 2h.

[Surfactant number]

$v/a_0 l_c$ = surfactant number

v -- the volume of hydrophobic portion of the surfactant

a_0 -- the headgroup area of the surfactant molecule

l_c -- the length of hydrophobic group

less than 1/3 --- spherical micelles

between 1/3 to 1/2 --- cylindrical micelles

more than 1/2 --- flat bilayer

Through *cis*-formation, v increases and l_c decreases. So, transformation caused **from vesicles to planar lamellars.**

[Stablity of vesicle]

The alkyl tail length of <u>cationic</u> surfactant
The alkyl tail length of <u>anionic</u> surfactant } **The differece is large = stability of vesicle is high**

the dispersion instability of the *cis*-AZTMA - SDBS

2. AZTMA+NaSal+CTAB

M. Abe et al. *J. Am. Chem. Soc.*: **2005**, *127*, 13454-13455.

+ Reversible change of fluid viscosity +

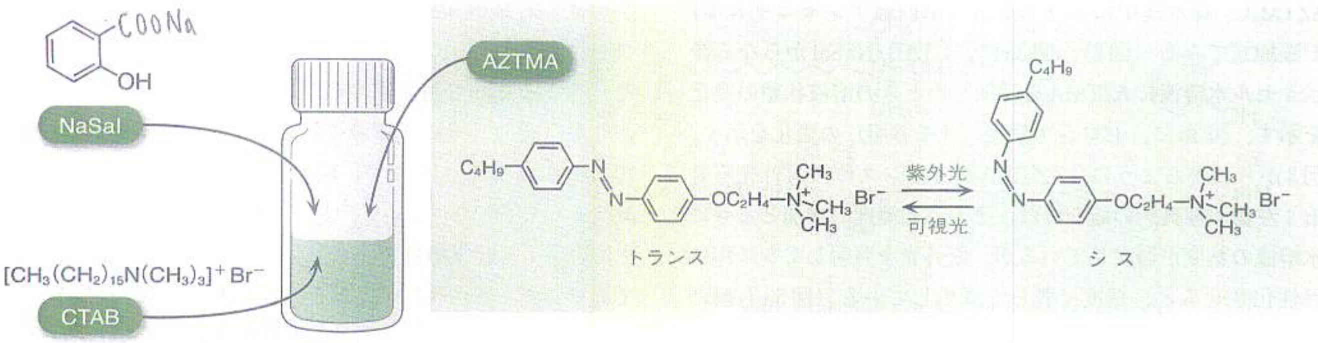


図2　アゾベンゼン修飾カチオン界面活性剤（AZTMA）を添加したCTAB/NaSal水溶液の調製

CTAB (Cetyltrimethylammonium bromide) is a cationic surfacatant.
It is used as a constituent of shampoo.
Above "cmc", it forms wormlike micelles.

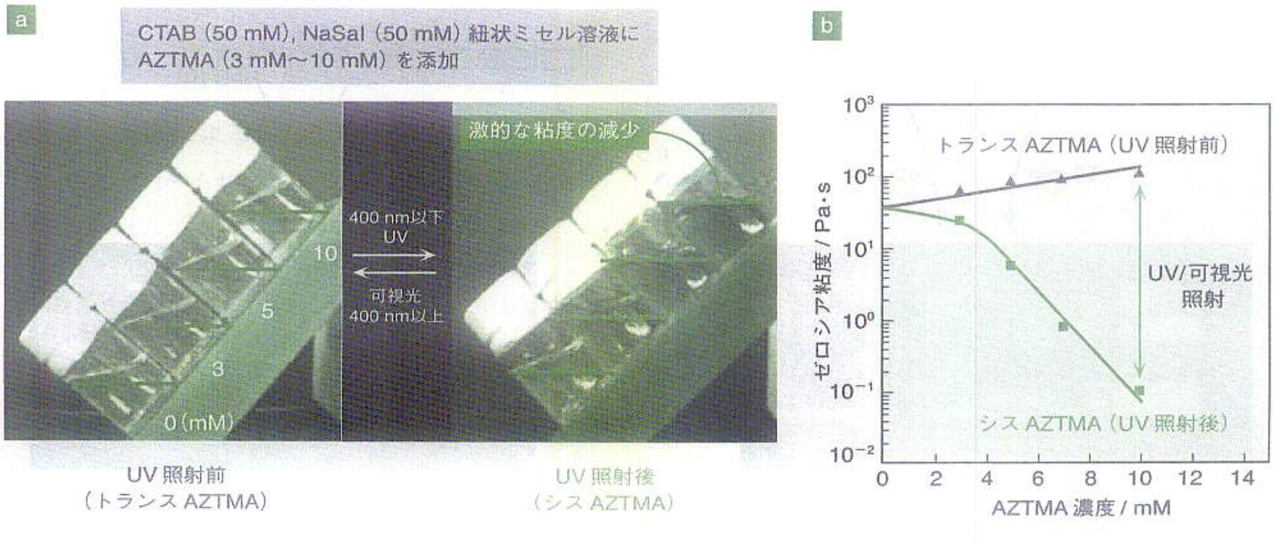
↓ **NaSal** is added

wormlike micelles interwire each other.
The solution becomes **more viscous.**

↓ **AZTMA** is added

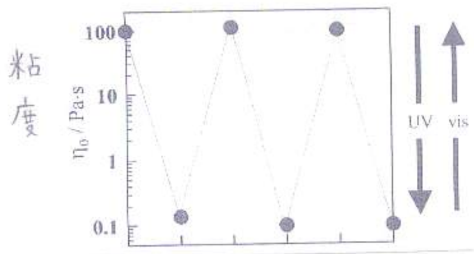
The solution **viscosity can be controlled** using light

Only AZTMA solution cannot form wormlike micelles even if addition of NaSal.



a）紫外光を照射すると粘度が下降，可視光を照射すると粘度が上昇．この変化は可逆的である．b）ゼロシア粘度の変化．

図3　光によるCTAB/NaSal水溶液の粘度コントロール



[*trans*]
The viscosity **increased** with increasing the concentration of AZTMA.

trans-AZTMA is easily incorporated into wormlike micelles of CTAB and NaSal **due to the linear structure of its hydrophobic tail.**

[*cis*]
The viscosity **decreased** with increasing the concentration of AZTMA.

cis-AZTMA is likely to destroy the network structure of wormlike micelles and **due to the bulky structure.**

At 10mM, the rate of viscous change is 1000 times!!
Dramatical control is possible.

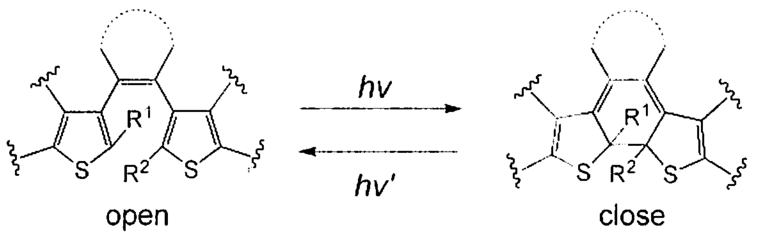
3. Photochromism

Chromism ---- A color of a substance changes reversibly by <u>external stimuli</u>.

Thermochromism
Photochromism
Electrochromism
Solvatochromism....

Photochromism is caused by isomerization.
As photochromic materials, azobenzene, spiropyran, **diarylethene** etc.

<u>Photochromism of Diarylethene</u>

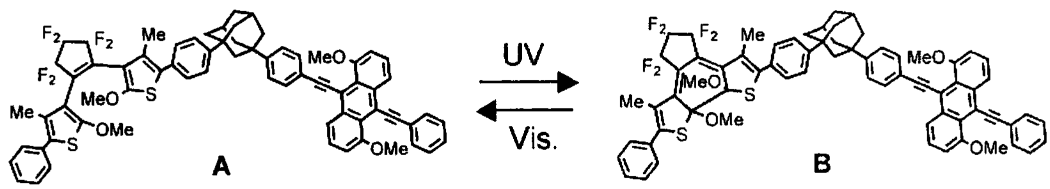


Diarylethene derivertives are photochromic compouds, which change molecular structures reversibly (open-ring --close-ring) with photo-irradiation.

They are **more stable against heat** and **more fatigue-resistant than** other photochromism.

[A degital fluorescent molecular photoswitch]

M. Irie et al. *Nature*., 2002 *420*, 759-760

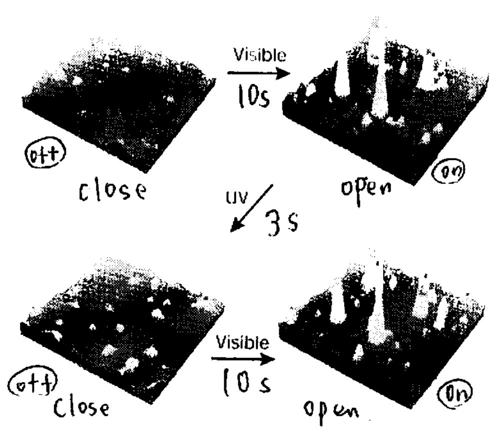


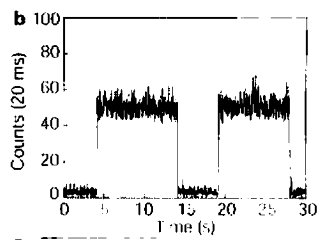
A
Open-ring form

B
Closed-ring form

So far............they were handled as soluvent
This paper... .**A diarylethene <u>single crystal</u>** was developed.

a





Digital switching the fluorescene of diarylethene molecules can be controlled by irradiation with UV-visible light at a single-molecule level.

⇓

They may be applicated to the design of erasable media for ultrahigh-density optical data storage.

[Full-Color Photochromism of a diethylethene trimer]

M. Irie et al. *J. Am. Chem. Soc.*, 2005, *127*, 8922-8923.

fig2 (accompanying sheet)

<u>So far</u> --------- between two isomers
only two states "colored" or "colorless"

<u>This paper</u> --- three photochromic units **in one molecule**
full-color photochromic performance

+ The adventage of a one molecule system in full-color photochromism +
high image resolution
constant color balance in a large area
possible application to optial memories and displays at one molecular level

fig3(accompanying sheet)

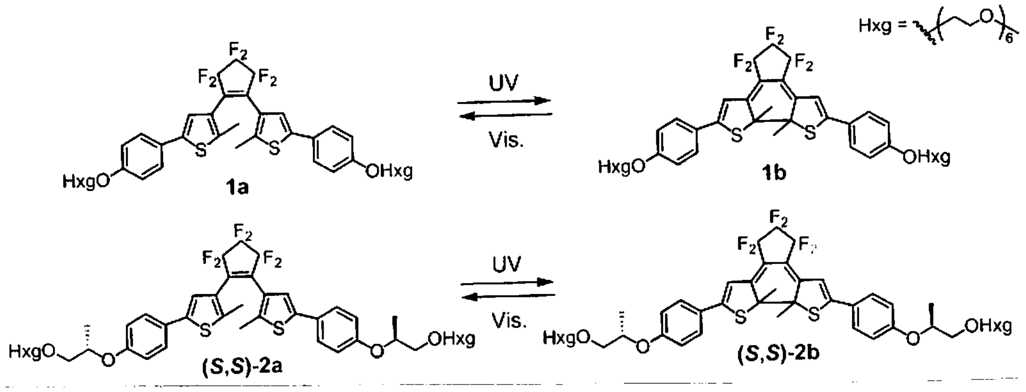
1. UV only	**1d** (yellow) - **1e** (orange) - black
2. UV and blue(460 nm)	**1b** (sky blue)
3. UV and red (633 nm)	**1c** (red-orange)
4. UV and yellow (578 nm)	**1d** (yellow)

fig4 (accompanying sheet)

a --- The absorption peak of **1b**-**1d** are separated from each other.
All colored species converted back to teh open-ring **1a** by visble light.
Formation of the closs-ring isomer in adjacent diarylethene units is not discerned.

b --- At first : **1d**
Time goes : **1d** and 1e almost same
All the time : **1b** is low (the conversion gradually increased)

The cyclization quantum yield of the central unit (ϕ **1a** - **1b**) is **lowest** due to the molecular distortion.



The properties of the diarylethene derivertives

+ not only photochromic activity but also **self-assemble** activity.
+ photochromism was observed even **in water**.
+ turned turbid upon heating
+ with assymetric methyl moiety, only close-ring isomers assembled into a chiral nanoatructure.

[Introduction]

--- Flexible polar side chain + rigid apolar core ---

formation of three-dimension structures by hydrophobic interaction

-application to nanostructures in material chemistry

dissolution into water by polar side chain

-application to biological field (biosensor, drug deliverery)

[Photochromic reaction]

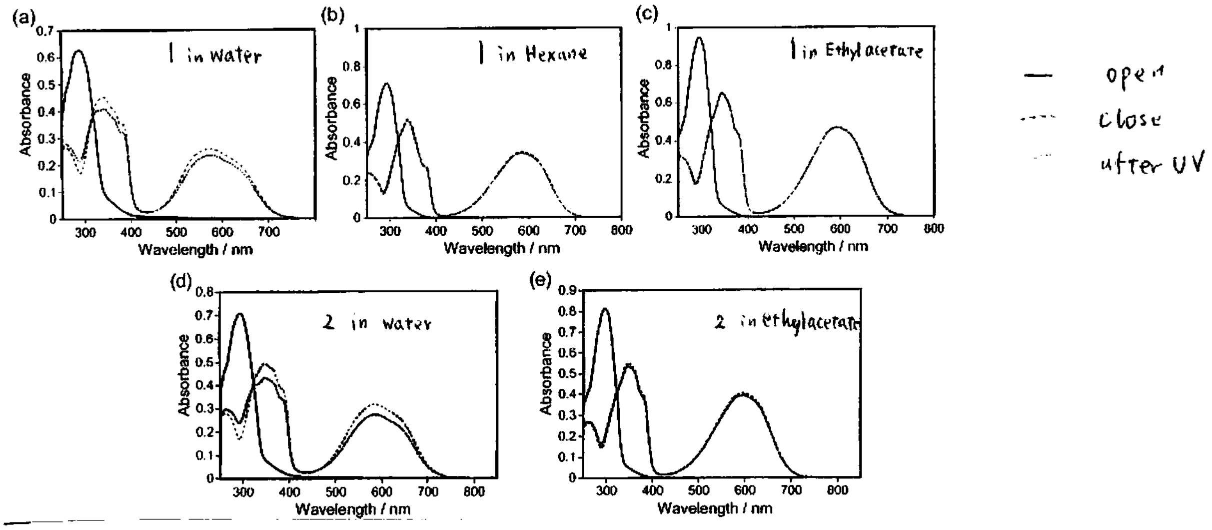


TABLE 1. Absorption Maxima of the Open- and the Closed-Ring Isomers and the Conversion from the Open- to Closed-Ring Isomers under Irradiation with 313-nm Light

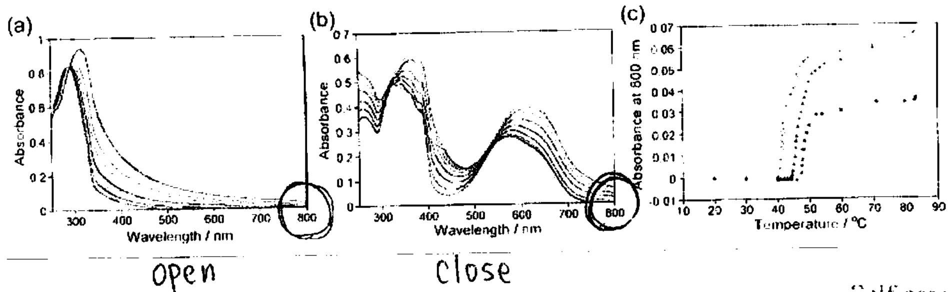
compound	1			(*S*,*S*)-2	
solvent	water	ethyl acetate	hexane	water	ethyl acetate
open-ring isomer λ_{max} (ϵ; nm)	289 (2.8 × 10^4)	296 (4.8 × 10^4)	294 (4.5 × 10^4)	294 (3.5 × 10^4)	297 (5.0 × 10^4)
closed-ring isomer λ_{max} (ϵ; nm)	573 (7.9 × 10^3)	592 (2.4 × 10^4)	583 (2.2 × 10^4)	583 (1.6 × 10^4)	594 (2.5 × 10^4)
conversion (%)	90.9	99.0	97.6	86.1	97.2

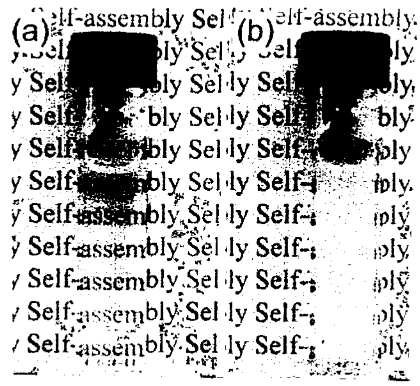
open-ring (colorless) $\xrightleftharpoons[\text{vis}]{\text{UV}}$ close-ring (blue)

In water, absorption band and the conversion ratio was **lower** than that in ethyl acetate.
Because of self-aggregate, probably.

[turbity]

On heating, the aqueous solution of 1a and 2a turned turbid at 40-50°C. The turbid soutions returned to clear on cooling to rt. → the destroy of the aggregate.

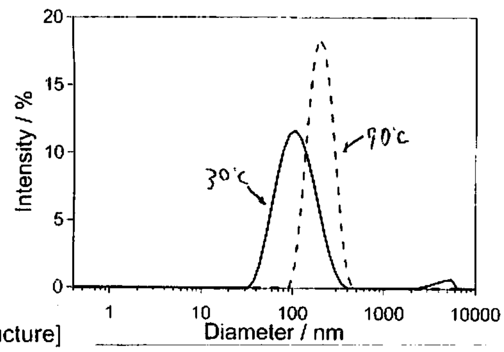




At 800 nm, diarylethene chromophore has no absorption.
So, the change of the absorbance 800 nm was observed.

--- the cloud point temperature ---
open-ring : 47-48.5°C
close-ring : 40-42°C
lowered by about 5-7°C on UV irradiation

[The aggregate]



The peak of the size of around 100 nm in water at rt **turned sharp** with heating.

[nanostructure]

fig5 (accompanying sheet)

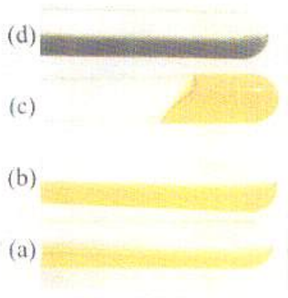
Model of the self-assembled nanostructure of **(*S*,*S*)-2** in water

The open-ring isomers have a bulky twist conformation.
So, the stacked structure is unfavorable.

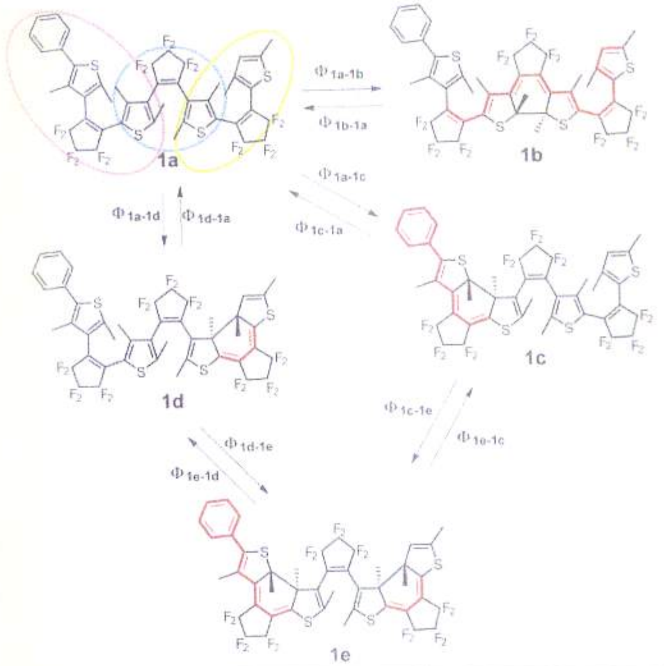
The close-ring isomers have a planar structure.
Both isomers form the self-assembled nano tructures around 100 nm.

However, only the close-ring isomer has a chiral environment.

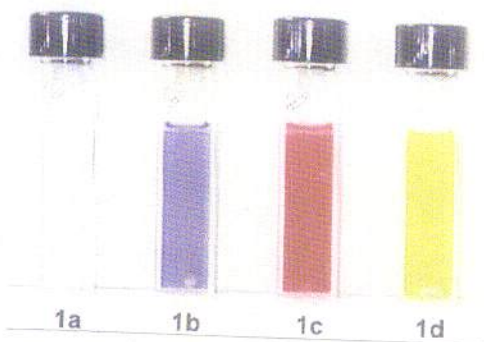
(accompanying sheet)



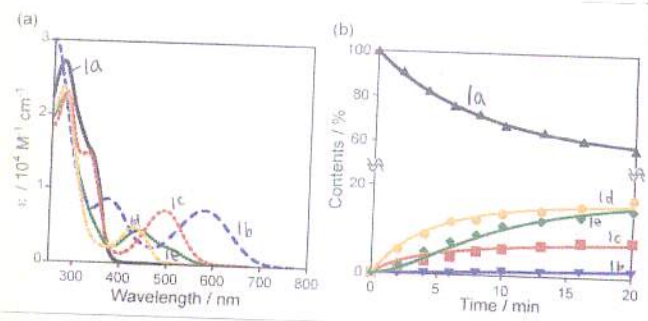
〈P2 fig1〉



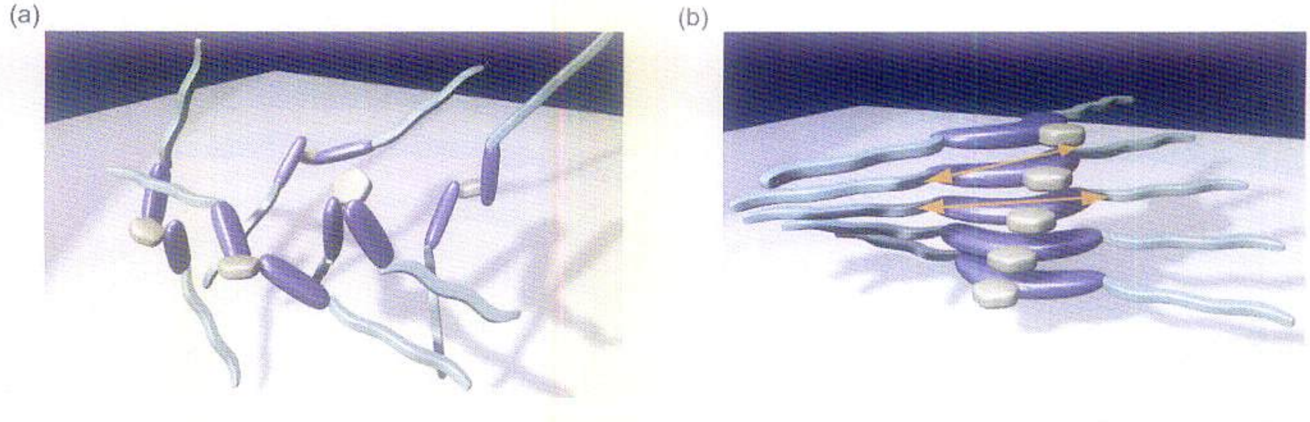
〈P11 fig2〉



〈P11 fig3〉



〈P11 fig4〉



〈P13 fig5〉