Photoinduced Dimer Formation of the Inclusion Complexes of an Indoline Spiropyran with Cyclodextrins

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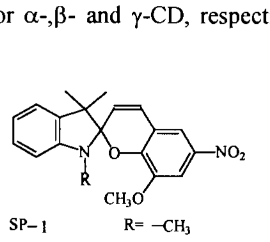
The photoinduced coloured form(B) of inclusion complex formed between a long-chain photochromic spiropyran and α-, β- or γ-cyclodextrins can assemble into dimer (B_2), which can in turn stabilize the coloured form.

Cyclodextrins(CDs) are widely used as the hosts for organic molecules.[1-3] The binding of a molecule or ion into the cavity of CDs results in the formation of an inclusion complex, which can in turn affect the properties of the guest due to steric effects as well as changes in the microenvironment. By means of inclusion in CDs, many process such as excimer and association dimer formation of anthracene derivatives,[4,5] dimerization of stibenes[6] can be controlled effectively.

The spirobenzopyran derivatives are typical photochromic compounds,[7] and they can isomerize to their merocyanine forms under UV irradiation. The photochromic reaction of spiropyran is very sensitive to the microenvironmental variation. The UV induced coloured form can form aggregates in non-polar solvents,[8-10] polymer matrices[11,12] and Langmuir-Blodgett films.[13,14] Tamaki et al. reported that γ-CD can form inclusion complex with photochromic spiropyran in the solid state. Accompanying with the formation of this inclusion complex, its coloured form turns to be more stable both chemically upon prolonged UV irradiation and thermally in the dark as compared with that in PMMA film.[15] Here we report the photoinduced dimer formation of the inclusion complexes of an indoline spiropyran with CDs and its stabilization effect on the coloured form.

The inclusion complex of Tamaki et al. formed from a photochromic spiropyran and γ-CD or its deritatives shows a normal photochromism, and it is believed that the molecular association of the coloured form in these inclusion systems is unfavourable. However, in the present work , it is found that 1′,3′,3′-trimethyl-6-nitrospiro-[2H,1-benzopyran-2,2′-indoline] used by Tamaki et al.[13] and SP-1 show little tendency to form such inclusion complex in aqueous solutions. A reasonable explanation is the size limitation of cavities of CDs to include the SP molecule(the cavity diameters of CDs are 4.7-5.2, 6.0-6.4 and 7.5-8.3 Å for α-,β- and γ-CD, respectively[3]), therefore we doubt that the solid adducts from SP and γ-CD or its derivatives reported by Tamaki et al. should not be an inclusion complex but an association complex.[2]



SP-1 R= $-CH_3$
SP-16 R= $-n-C_{16}H_{33}$
SP-4-$\overset{+}{N}Et_3$ R= $-(CH_2)_4-\overset{+}{N}Et_3$

Scheme 1.

When SP-16 is used instead, the situation is very different. Originally, SP-16 can not be dissolved in water, and the sonicated suspension of SP-16 in water is still turbid. However, when α-CD is added, a transparent solution can be obtained. For glucose and saccharose, such an effect can not be observed. This indicates that SP-16 can form a soluble complex with α-CD. Because the SP head group is too huge to fit into the cavity of α-CD, the complex should be an axial inclusion complex formed between the long chain and α-CD. The head group should lie outside the cavity. The complex thus formed shows a normal photochromism. Figure 1 shows the absorption spectra of the complex before and after UV irradiation(150 W Xe lamp). From the spectrum before UV irradiation, λ_{max} of the coloured form(B) which is in equilibrium with the colourless form(A) is determined to be 542 nm , while the λ_{max} of the UV induced coloured form(D) is 576 nm. Obviously, they are different species. In order to elucidate them exactly, the spectrum of SP-4-N^+Et_3 in water is recorded(Figure 1, curve 3). The result shows that the λ_{max} of SP-4-N^+Et_3 is quite close to that of the B form. This clearly indicates that the B form corresponds to a coloured form located in an environment of high polarity. The λ_{max} of D form has a red-shift of 30 nm relative to B. Since the cavity of α-CD is too small to include the head group of the coloured form, it can not provide the nonpolar environment and can not be used to interpret the spectral shift. A reasonable explanation should be that the coloured-form can assemble into a dimer further with the long chain of SP-16 lying inside the cavity of α-CD, as shown in Scheme 2. By comparing the spectrum of the UV-induced coloured-form with that of the dimer formed in apolar solvents,[10] we find they are quite similar.

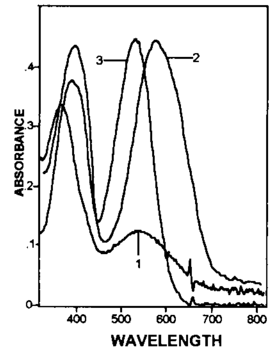


Figure 1. The absorption spectra of 4.0×10^{-5} mol/l SP-16 in the presence of 1.0×10^{-4} mol/l α-CD before (curve 1) and after UV irradiation for 4 min, (curve 2). Curve 3 is the spectrum of the coloured form of SP-4-N^+Et_3 in aqueous solution.

To get more information, the decolouration process of the coloured form is investigated. Figure 2a shows the spectral variations during the decolouration process after UV irradiation . The decolouration rate is very low comparing with that in organic solution, e.g. the λ_{max} of the coloured form in acetone is nearly the same with that of the inclusion complex ,the half decay time in acetone is 35 s, while in the present system, no appreciable decay can be observed in such a short time interval . Another characteristic is that an isosbestic point at 370 nm can be observed in the spectra and the E-diagram[16] (Figure 2b) gives a near linear relation between the absorbance at different wavelengths during decolouration process. This means that the decolouration process is a simple process and only one linear independent process exists.[16]

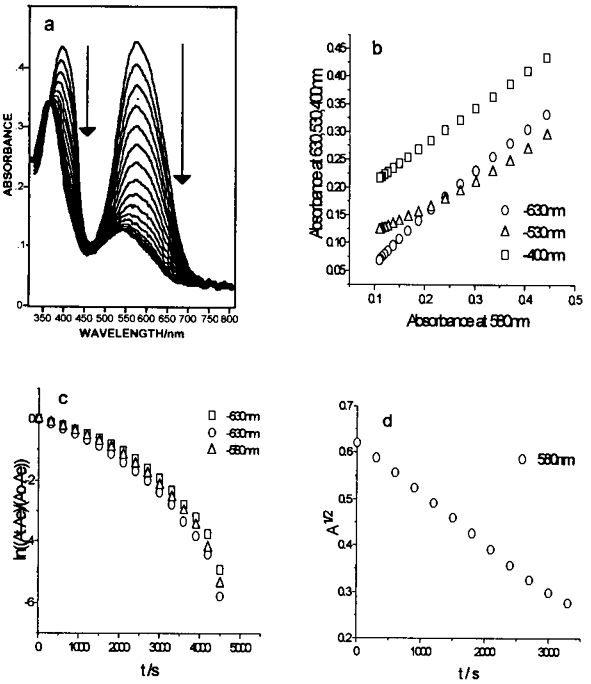
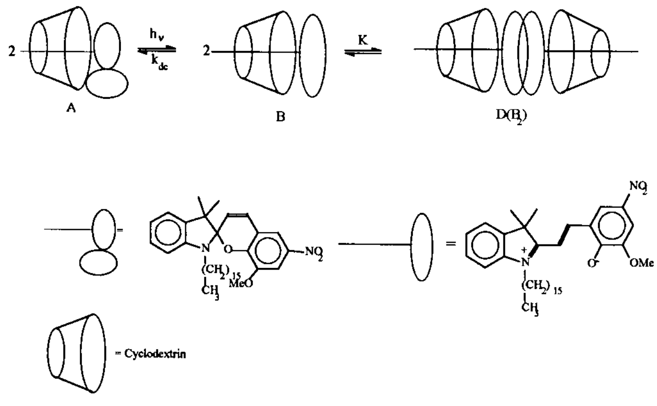


Figure2. a. Spectral variations of the coloured form of inclusion complex formed from SP-16 (4.0×10^{-5} mol/l) and α-CD(5.0×10^{-4} mol/l) during the decolouration process after UV irradiation for 4 min., time interval between successive curves: 300 s; b. E-diagram for the decolouration process of Figure 2a; c. First-order decolouration plot of Figure2a at different wavelengths; d. Half-order decolouration plot of Figure 2a.



Scheme 2. Dimer formation of the inclusion complex of SP-16 with CDs under UV irradiation.

In apolar solvent or in polymer , the photoinduced coloured form of SP can assemble into dimer(AB) or other charge transfer complexes(A_nB),[8-11] the decolouration process of these complexes can be described by an exponential[10] or a two-exponential model.[11] Because the colourless form(A) is involved in structures of these complexes, the concentration of A has a significant effect on the formation and decoloration rate of these complexes. In the present case, we find the concentration of SP-16 has very little effect on the decoloration rate of the coloured form, and the decolouration process can not be described by an exponential or a two-exponential decay process(Figure 2c). This implies that the decolouration process is not a single molecular process and the colourless form should not be involved in the kinetic equation. If we suppose the dimer formed is not AB but B_2 in the present case , according to the decolouration mechanism of Scheme 2, the decolouration process may be treated in the following way:

$$K=\frac{[B_2]}{[B]^2} \quad \text{or} \quad [B]=K^{-1/2}[B_2]^{1/2} \tag{1}$$

$$\frac{d[A]}{dt}=-\frac{d[B]}{dt}-2\frac{d[B_2]}{dt}\cong -2\frac{d[B_2]}{dt}=k_{dc}[B] \tag{2}$$

From eq.(1) and(2) ,

$$2\frac{d[B_2]}{dt}=-k_{dc}[B]=-k_{dc}K^{-1/2}[B_2]^{1/2} \tag{3}$$

Because $A_{B2}=\varepsilon_{B2}b[B_2]$, then we have:

$$(A_{B_2})^{1/2}=-\frac{1}{4}k_{dc}(\varepsilon_{B_2}\,b/K)^{1/2}t+C \tag{4}$$

Where b is the cell length. From eq.(4), it can be seen that there should be a linear relation between $A_{B2}{}^{1/2}$ and t. Figure 2d shows the plot of $A_{B2}{}^{1/2}$ against t. The process obeys half-order kinetics very well. When the concentration of SP-16 is lower than 1.0×10^{-4} mol/l, the variation in the concentration SP-16 has no obvious effect on the decoloration rate. But when the concentration is higher than 1.0×10^{-4} mol/l, the system turns to be more complex , which is discussed in detail in our later works. When β- and γ-CDs are used, similar results are obtained, i. e., the cavity diameter has no obvious effect on the spectra and the decolouration kinetic characteristics of the coloured form. This phenomenon may be served as another evidence for the exclusion of SP-16 head group from the CD cavity.

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