Unusual Thermochromic Behavior of Photoreactive Dyes Confined in Helical Amylose as Inclusion Complex

L. S. Choi and Oh-Kil Kim*

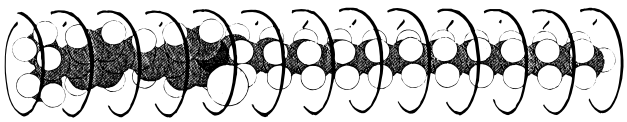
Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375-5342

Received July 21, 1998
Revised Manuscript Received November 10, 1998

Molecular environment has a significant impact on the dynamics and reactivity of molecules, particularly when the molecules are confined in a rigidly tied space.[1,2] In such a surrounding, guest molecules may experience a different reaction pathway due to chemical as well as steric interactions with the host environment. Unlike the case where reactive species are embedded in vesicle membranes and Langmuir−Blodgett films, in inclusion complexation, guest molecules are supramolecularly encapsulated by host molecules through binding interactions such that the confined guest becomes rigidified and loses conformational freedom. These are part of the consequence, and further, a number of uncommon chemical/physical properties are anticipated to result, depending on the inclusion structure and external conditions.

Taking advantage of part of the above notion, we have developed a new strategy for nonlinear optical (NLO) materials whose chromophores are supramolecularly included in the helical cavity of amylose.[3] It was found that solution-cast thin films of the supramolecular complex displayed a self-assembly/self-poling, which induced a significantly large second harmonic generation[4,5] and an excellent long-term polar stability.[4] Further advantages for the material properties are enhanced thermal and photochemical stabilities and mechanical integrity of chromophores.[4,6,7] A recent observation[8] revealed that the hyperpolarizability of the chromophores is doubled by the inclusion complexation with a helical amylose[9] relative to the noninclusion free state in solution.

Few studies have been made with respect to thermal stability[6] of the bound guest in amylose inclusion. In this communication, we report thermally induced conformational transitions of a hemicyanine dye, 4-[4-(dimethylamino)styryl]-1-docosylpyridinium bromide ($DASPC_{22}$), confined in a helical amylose (forming a 1:1 complex)[12] in the solid state, making a comparison with that in solution. This is the first report of an unusual thermochromism of the dye that is associated with restricted chromophore conformations in the confinement of the rigid helical host in the solid state.



Amylose - $DASPC_{22}$ Inclusion Complex

It is known that conjugated dyes in amphiphilic multilayers[16] as well as in solution[17] and conjugated polymers[18,19] in solid films and in solution as well undergo a marked conformational transition with increasing temperature, exhibiting a reversible thermochromism that is commonly represented by a linearly increasing blue shift of the absorption maximum, λ_{max}, with temperature. This is largely due to the loss of coplanarity in the conjugated chromophore.

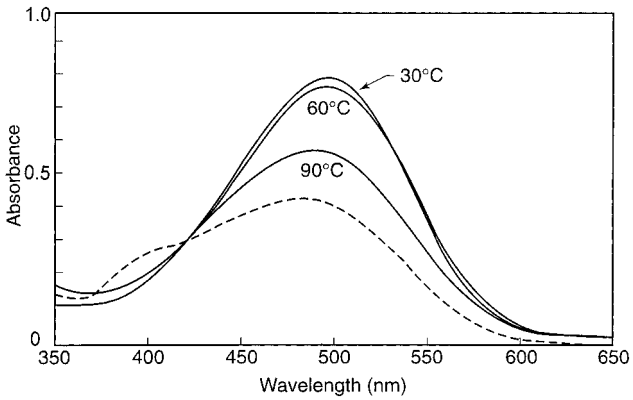


Figure 1. Temperature effect on visible spectra of amylose−$DASPC_{22}$ inclusion complex in water; the dashed line indicates that the sample was heated at 100 °C, and the spectrum was recorded at room temperature.

Since amylose is a polymeric host with multiple binding sites, once incorporated, the guest molecules are rigidly bound ($K_a = 2 \times 10^5\ M^{-1}$) with increasing carbon chain length or hydrophobicity. As a result, the rotational freedom around the chromophore (in the inclusion) is substantially restricted even at an elevated temperature in solution, compared to the case of the noninclusion free dye. This results in an enhanced fluorescence emission of the chromophore.[3,20] Our earlier fluorescence study[3] suggests that the binding of $DASPC_{22}$ to the host amylose (at room temperature) is reduced with increasing water content in DMSO−H_2O mixtures, anticipating that, in 100% water, conformation of the included dye becomes less restrictive and that, at a critical temperature, some of the bound dye may be freed from the inclusion and moves into bulk water.

Indeed, heating an aqueous solution of the inclusion complex at 90 °C causes a pronounced conformational change, showing a blue shift (to 488 nm) of the λ_{max} (496 nm) and a significant decrease of the absorbance (Figure 1), while heating it at 60 °C causes only a minor change (relative to 30 °C). The worst situation occurs at 100 °C where the λ_{max} is further blue-shifted to 484 nm, along with an appearance of a shoulder around 410 nm, which is associated with the dye aggregation. This seems to suggest that some of the dye molecules are released from the inclusion into the bulk water, existing as free dye and/or dimeric aggregates. Such blue shifts and the decrease of absorbance by increasing the temperature seem to be the result of a decrease in intramolecular charge transfer (ICT) of the guest dye due to a disruption of the planar π-conjugation. This is a direct consequence of abrupt decrease of the guest binding to the host.

It is conceivable that the extent of thermal impact on conformational transition of the inclusion dye in solid films should be much less than that in solution due to a tighter guest binding and a restricted helical deformation. It is therefore extremely difficult for dye molecules

* To whom correspondence should be addressed.

10.1021/ma981151d This article not subject to U.S. Copyright. Published 1998 by the American Chemical Society
Published on Web 12/03/1998

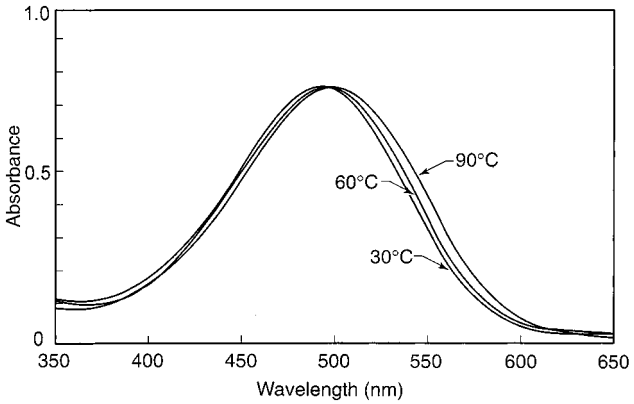


Figure 2. Reversible thermochromism of the amylose−$DASPC_{22}$ inclusion complex in a solid thin film (ca. 1 μm in thickness).

to be freed from inclusion unless being melted and decomposed.[21]

Solid thin films[22] of the inclusion complex change color, darkening[7] with increasing temperature. As seen in Figure 2, the λ_{max} 494 nm of the solid thin film at room temperature has no measurable change up to 50 °C, but above that temperature, it exhibits a small red shift gradually with increasing temperature but remains almost unchanged with a further increase of temperature over 100 °C.[15] When the heated sample is cooled to room temperature, it reverses to exactly the same initial spectrum. Such a reversible thermochromism can be repeated many times without spectral changes. This is in strong contrast to that observed in solution. Whatever the reasons, bathochromic shifts of λ_{max} are the thermally induced enhancement of ICT which is correlated to an extensive π-conjugation of the chromophore in the supramolecular complex. This behavior is uniquely uncommon and is attributed to the helical confinement. To understand these situations, it is essential to probe the local environment change around the chromophore (in the host cavity) induced by the temperature increase.

Since the guest dye fluoresces strongly (10−100 times) under the inclusion,[3,23,24] the chromophore itself can be used as an environmental probe to monitor the steric restriction (binding state) around the probe in the cavity upon varing the temperature. It was observed that the temperature effect on the fluorescence emission (of the dye) is different between the inclusion and the noninclusion free states. This is attributable to a high quantum efficiency and longer lifetime[8,23] in the former compared to the latter which suffers a great deal from the internal quenching,[25] resulting from twisting of bondings to a nonplanar state. A control experiment was carried out to assess the temperature effect on the emission intensity of the free dye (without amylose)[26] dispersed in a poly(methyl methacrylate) film or dissolved in DMSO. In both cases, the emission intensity decreased (more in solution) in a linear fashion with increasing temperatures (a 10−15% decrease per every 10 deg) between 20 and 80 °C.

The temperature dependency of the emission intensity of the inclusion dye is far from the linear fashion that was observed for the dye in the noninclusion free state. It is worth noting that the emission intensity (at 620 nm) of the inclusion dye in water at 60 °C exhibits a sharp decrease from that at 30 °C (Figure 3) while the absorbance change between the two temperatures is

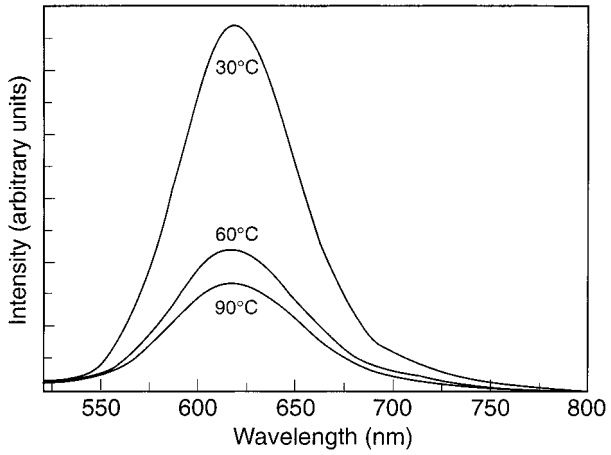


Figure 3. Temperature effect on fluorescence emission of the amylose−$DASPC_{22}$ inclusion complex in water.

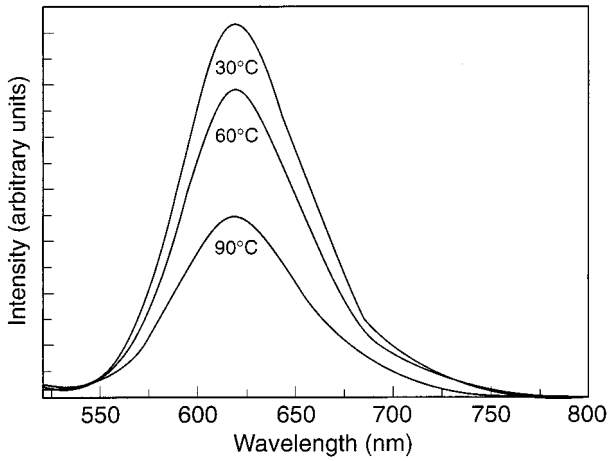


Figure 4. Temperature effect on fluorescence emission of the amylose−$DASPC_{22}$ inclusion complex in a solid thin film (ca. 1 μm in thickness).

only minor (Figure 1), meaning that the conformation (ICT state) of the chromophore of the guest dye does not seem to be significantly altered, despite a large decrease in guest bindings. However, at 90 °C, a marked change seems to occur in the conformation, although the majority of the dye molecules is assumed to remain still in the inclusion state.

Since no chemical change would occur with the guest dyes in the solid-state inclusion at 90 °C (the decomposition starts around 250 °C),[6,21] they must maintain the same 1:1 stoichiometry with amylose. As shown in Figure 4, only a small decrease (compared to that in solution (Figure 3)) in fluorescence intensity is observable at 60 °C, while a noticeable decrease is observed with increasing temperature to 90 °C. This situation should correspond to the bathochromic shift in the absorption spectra (Figure 2); up to 50 °C no measurable red shift is observed, but above this it starts to appear. Taking into account that the fluorescence decrease at 90 °C in the solid state (Figure 4) is still less than that at 60 °C in solution (Figure 3), where the decrease of the ICT is insignificant, relative to 30 °C (Figure 1), the ICT decrease in the solid state is unlikely to occur between 30 and 90 °C. The chromophores (in solid-state inclusion) at 90 °C seem to acquire a significant conformational freedom, partly because of thermal expansion of the helical cavity. However, the helical expansion still undergoes a restriction due to a relatively close

packing of the rigid-rod supramolecules in the solid state. Conversely, when the temperature is lowered to room temperature, the once expanded helical coil size is reduced, reverting to the initial state. The red shift of the λ_{max} from 494 to 505 nm (Figure 2) upon heating (30 to 90 °C) the solid thin film can be interpreted as a result of the extended coplanarity of the conjugated chromophore, which may result from a relief of local constraints on the chromophore, so that a conformational realignment may occur in an energetically favorable manner. It is, however, unclear why such a particular temperature range is critical to attain the enhanced conjugation (red shift of λ_{max}), but it can be associated at least in part with the ordered packing of the rigid-rod helical host in the solid state.

In conclusion, supramolecular solid thin films of the amylose-$DASPC_{22}$ dye inclusion complex exhibited an unusual thermochromic behavior, the characteristics of which are that the λ_{max} is red-shifted by increasing temperature from 50 to 90 °C and exactly reversed when the temperature was lowered. On the contrary, the trend in solution is just the opposite, as commonly known for thermochromisms of organic molecules in the solid state as well as in solution; the λ_{max} is blue-shifted with increasing temperature. Fluorescence emission from the inclusion dye indicates that the temperature increase results in the reduction of dye bindings to the helical host, which subsequently induces disruption of chromophore conjugation in solution, whereas in the solid state, a partial reduction of dye binding assists the dye conformation to realign into a more extended conjugation state. This unusual thermal effect seems to be closely related to the guest environment under the tight confinement and ordered packing of the rigid-rod supramolecular chromophores in the solid state.

Acknowledgment. The authors gratefully acknowledge partial funding support from the Office of Naval Research.

References and Notes

(1) Ramamurthy, V.; Eaton, D. F. *Chem. Mater.* **1994**, *6*, 1128.
(2) Harris, K. D. M. *Chem. Br.* **1993**, 132.
(3) Kim, O.-K.; Choi, L. S. *Langmuir* **1994**, *10*, 2842.
(4) Kim, O.-K.; Choi, L. S.; Zhang, H.-Y.; et al. *J. Am. Chem. Soc.* **1996**, *118*, 12220.
(5) Kim, O.-K.; Choi, L. S.; Zhang, H.-Y.; et al. *Thin Solid Films* **1998**, *327−329*, 172.
(6) Kim, O.-K.; Choi, L. S.; et al. *J. Therm. Anal.* **1996**, *46*, 1081.
(7) When exposed to a high-power infrared laser beam, the red color became brightened (detected), similarly to as being heated, but no bleaching occurred unlike in a polymer-dispersed dye system.
(8) Clays, K.; Kim, O.-K.; et al. *Chem. Phys. Lett.* **1998,** *293*, 337.
(9) Amylose is a linear chain polymer consisting of a 1,4-α-glucosidic linkage, which complexes with various organic compounds[10,11] being confined in the helical cavity. Their binding characteristics are similar to that of cyclodextrins, but the cavity of amylose has more flexibility to accommodate larger guest molecules.
(10) Nakamura, H.; Shibata, K.; Kondo, H. *Biopolymers* **1977**, *16*, 363.
(11) Hui, Y.; Russel, J. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 1374.
(12) A 1:1 complex (one $DASPC_{22}$ chromophore is included in one amylose molecule (MW ≈ 4500 Da)) was made[3] in a DMSO−water mixture ($\Phi_{DMSO} \leq 0.6$) and characterized by UV−vis, fluorescence, induced circular dichroism, NMR, and elemental analysis. The amylose-$DASPC_{22}$ complex was purified[13] and subsequently subjected to freeze-drying to obtain a solid material which is well soluble in water. Optical quality thin films were prepared by casting an aqueous solution of the inclusion complex, and optical/thermal characterizations were done to confirm the material quality. Both UV−vis and fluorescence spectra[14] were recorded by taking at least several scans at each temperature of 30, 60, and 90 °C.
(13) Purification of the complex was done by dialysis against DMSO and subsequent elimination of the unreacted free $DASPC_{22}$ and amylose by centrifugation and gel filtration.
(14) Both UV−vis and emission (with excitation at 475 nm) spectra of the chromophore in the inclusion were taken in water and in the solid thin films (cast onto a florescence cell), and the emission spectra were recorded at 90° and 22.5° against the excitation light, respectively.
(15) Since water was used as a heating medium for temperature control in the cell holder, it was difficult to maintain the temperature above 90 °C. Therefore, it was unable to take spectra at ≥100 °C; a film sample was preliminarily heated at 120 °C, for example, with a separate heating medium and then moved into the cell holder maintained at 90 °C to run the spectra. Due to the difficulty of temperature control, the spectra taken at a temperature ≥100 °C in such a way is inaccurate and are not shown in Figure 2.
(16) Decher, G.; Tieke, B. *Thin Solid Films* **1988**, *160*, 407.
(17) Yamamoto, H.; Nakazawa, A.; Hayakawa, T. *Nippon Kagagu Kaishi (J. Chem. Soc. Jpn.)* **1985**, 1442.
(18) Inganas, O.; Salaneck, W. R.; Osterholm, J. E. *Synth. Met.* **1988**, *22*, 395.
(19) Roux, C.; Faid, K.; Leclerc, M. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 461.
(20) Suddaby, B. R.; Dominey, R. N.; Hui, Y.; Whitten, D. G. *Can. J. Chem.* **1985**, *63*, 1315.
(21) The decomposition temperature of the $DASPC_{22}$ is increased about 35 °C[6] to 288 °C by the inclusion formation.
(22) Thermal analyses[6] of thin films by TGA and DSC indicated that only a residual solvent water was retained in the samples and that the inclusion complex did not show an endothermic melting of the dye, suggesting that only one dye molecule was included in the host cavity.
(23) Allen, M. T.; Miola, L.; Suddaby, B. R.; Whitten, D. G. *Tetrahedron* **1987**, *43*, 1477.
(24) Heuer, W. B.; Lee, H. S.; Kim, O.-K. *J. Chem. Soc., Chem. Commun.*, in press.
(25) Giri, R. *Spectrochim. Acta, Part A* **1992**, *48*, 843.
(26) A solid thin film of PMMA-dipersed chromophore (without amylose) was made by casting a chloroform solution onto a fluorescence cell. Amylose-free solution samples were made by dissolving the chromophore alone in DMSO,[24] because the emission intensity is rather small in water.

MA981151D