Spectral Properties of Hemicyanine Dye in Confinement by Helical Amylose

William B. Heuer[1], H.S. Lee[2], Oh-Kil Kim[3]*

[1]US Naval Academy, Annapolis, MD 21402-502, USA
[2]Brookhaven National Laboratory, Upton, NY 11973, USA
[3]Naval Research Laboratory, Washington DC 20375-4532, USA

SUMMARY: Hemicyanine dye structure is modified with a C_{16}-alkyl chain to amino-head and a C_1, C_8 or C_{16} alkyl to pyridinium-tail. Spectral properties of the dyes in supramolecular inclusion complexation with amylose are studied in order to assess the mono-functional polarity sensing activity of the pyridinium cations in DMSO-H_2O mixtures. Inclusion complexation brings the λ_{max} of C_{16}DASPC_1 dye to a blue-shift (relative to that of the free dye state) while that of C_{16}DASP(C_8 and C_{16}) dyes remains almost unchanged.

Introduction

The photoactive hemicyanine dye is an efficient environmental probe whose behavior is sensitive to solvent polarity in the surrounding. The sensing activity is particularly notable with the pyridinium tail residue relative to amino head group due to the sensitivity of the cation toward charges and dipoles in solutions and in membranes[1,2]. Spectral properties of hemicyanine dyes are characteristically featured by a negative solvatochromism in that an increasing polarity of solvents gives rise to a blue shift of the absorption spectrum and a red shift of the emission spectrum, and a rather low quantum yield of fluorescence[3-5].

Recently, we have developed a self-assembly/self-poling thin film based on inclusion complexation (with amylose as host) of hemicyanine dye with a long alkyl chain attached to pyridinium cation[6,7]. We interpreted that the self-organization is initiated by interface interaction of the supramolecule with glass substrate. As an extension of this study, we were interested in assessing the environmental sensing of pyridinium cation of hemicyanine dyes in solution when they are mono-functionally arranged in the supramolecule by attaching a

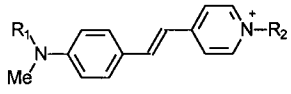
 CCC 1022-1360/99/$ 17.50+.50/0

long-alkyl chain to amino-head and by confining it in the amylose cavity, thereby allowing the pyridinium-tail be exposed to bulk solution. Such a local environment surrounding the dye resembles the situation where the dye is embedded in a membrane. Thus, this supramolecular inclusion can be regarded as a model of the dye-embedded lipid membrane.

In this report, we discuss spectral properties of the amylose-dye inclusion complexes in solution, which is strongly dependent on the structural variation of dye chromophore and on solvent compositions.

Materials and Characterizations

We synthesized alkyl-substituted hemicyanine dyes (structutures below) and prepared supramolecular complexes with amylose under conditions similar to those described earlier[6]. Uv-vis spectra of the solution samples were recorded at 0.2 nm resolution using a Gilford Response Spectrophotometer. The fluorescence spectra (with excitation at 425 nm) were



Hemicyanine Dye	R_1	R_2
$C_{16}DASPC_1$	n-$C_{16}H_{33}$	Me
$C_{16}DASPC_8$	n-$C_{16}H_{33}$	n-C_8H_{17}
$C_{16}DASPC_{16}$	n-$C_{16}H_{33}$	n-$C_{16}H_{33}$

recorded using a Spex Fluorolog-2 fluorimeter. Since a low molecular weight (5000 D) amylose is used and its length scale is about same as that of the dyes except $C_{16}DASPC_{16}$, the complex is presumed to be a 1:1 supramolecular inclusion, but due to the strongly polar nature of pyridinium, R_2 groups of Me and n-C_8H_{17} are considered to be excluded from the helical cavity[6]. When both R_1 and R_2 are n-$C_{16}H_{33}$, a 2:1 amylose-dye complex is likely to occur.

Results and Discussion

Hemicyanine dyes with a long alkyl chain substituent exist as monomeric free dye only in a DMSO-rich solvent mixture (DMSO volume fraction, $\Phi_{DMSO} > 0.7$), characterized by the

absorption, $\lambda_{max} \approx 475nm$[6] while dimeric aggregation occurs in a water-rich mixed solvent ($\Phi_{DMSO} < 0.5$), $\lambda_{max} \approx 420$ nm. Even in the presence of amylose, no inclusion complexation occurs at $\Phi_{DMSO} > 0.7$; the inclusion occurs only at $\Phi_{DMSO} < 0.7$ where the dimeric absorption band around 420 nm disappears. A characteristic band shift, either blue or red, due to the inclusion occurs depending on whether the alkyl chain (> C_{12}) is attached to the donor (amino-head) or to the acceptor (pyridinium tail), respectively[8]. When the alkyl chain is attached to the amino-head, for example, this amino-donor is confined (inactivated) deeply inside the amylose, while pyridinium-acceptor (for $R_2 = C_1$and C_8) is located near the open end of the helical cavity and can therefore interact with bulk solution.

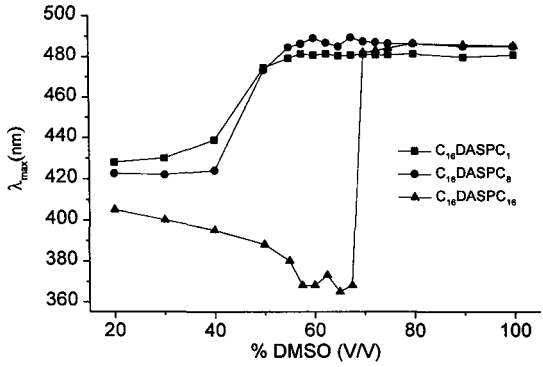


Fig. 1: Dependence of absorption maximum, λ_{max}, of non-inclusion free hemicyanine dyes (1.5×10^{-5} M) on DMSO-H_2O mixture ratios.

On the other hand, when the long alkyl chain (> C_{12}) is attached to pyridinium-acceptor, the amino-donor of the included chromophore remains exposed to the solvent, playing a role of external sensing. It seems to be that the environment sensing activity is much greater with pyridinium-acceptor relative to with amino-donor. We compare the spectral shift as a measure of the probe sensitivity of the dyes. In the absence of amylose (no inclusion system), as shown in Fig. 1, absorption peaks (λ_{max} = 480 – 485 nm in 100% DMSO) of dyes with a short alkyl substitution ($R_2 = C_1$ and C_8) remain unchanged down to 55% DMSO, unlike $C_{16}DASPC_{16}$, and exhibit a sharp decrease in water-rich DMSO. This is due to the dye aggregation. The

long alkyl chain dye (R_1, $R_2 = C_{16}$) starts a sharp drop of λ_{max} at 70% DMSO, which indicates forming of a transitional aggregate due to a particularly strong hydrophobicity of the dye. Such a strong aggregation tendency of this dye is reflected in the emission spectra (Fig. 2).

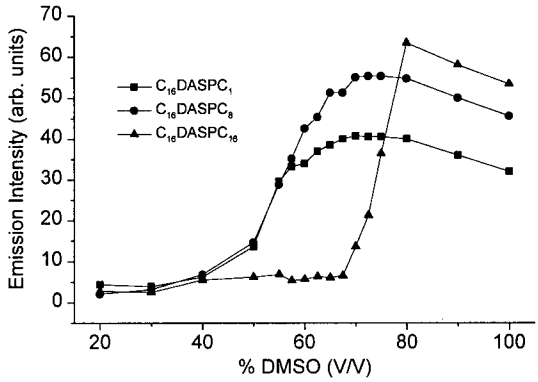


Fig. 2: Changes in emission intensity of non-inclusion free hemicyanine dyes (1.5×10^{-5} M) as a function of DMSO-H_2O mixture ratios.

The emission intensity of the dyes (in the absence of amylose) is relatively strong in DMSO-rich solvent mixtures and starts to decrease sharply around 60% DMSO; their emission intensity in a water-rich solution is nearly 10^2 times smaller compared to that of their inclusion complexes. This transition corresponds to the change in the λ_{max} (Fig. 1), where the aggregation takes place. This tendency is much stronger with the long alkyl chain dye (R_1, R_2 = 16), as mentioned above, being evidenced by an abrupt drop of the emission occurring at around 80% DMSO.

As shown in Fig. 3, in the presence of amylose (inclusion system), the short-alkyl tail dyes ($R_2 = C_1$ and C_8) show no band-shift of λ_{max} between 100% and 65% DMSO, while the long-alkyl tail dye ($R_2 = C_{16}$) exhibits an unusual transition around 70% DMSO as in the case of free dye system (Fig. 1). As indicated by fluorescence spectra of the inclusion system (Fig.4), in fact, no inclusion occurs between 100% to 65% DMSO solution, even in the presence of amylose but the inclusion occurs only below 65% DMSO. However, there is a noticeable change in the λ_{max} below 65% DMSO (Fig. 3); λ_{max} of the shortest-alkyl tail dye ($R_2 = C_1$) exhibits a gradual

deviation from 480 nm to the blue, starting at 65% DMSO and exaggerating with decreasing DMSO (increasing water). Strangely enough, λ_{max} of the longest-alkyl tail dye ($R_2 = C_{16}$) starts to back up to ca. 485nm (at 65% DMSO).

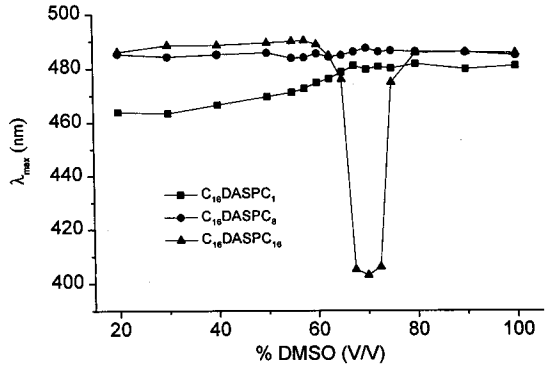


Fig. 3: Dependence of λ_{max} of hemicyanine dye (1.5×10^{-5} M) inclusion complexes with amylose (1×10^{-3} M) on DMSO-H_2O mixture ratios.

Emission spectra (Fig. 4) suggests that the preceding drop-off in the λ_{max} of the longest-alkyl tail dye (Fig. 3) is probably due to a transitional chromophore aggregation formed by mediation of amylose, which is subsequently transformed into the inclusion with decreasing DMSO, as indicated by the large enhancement of fluorescent intensity (Fig. 4). The meaning of Fig. 3 is that even in the inclusion state, only the shortest alkyl-tail dye ($R_2 = C_1$), $C_{16}DASPC_1$, is capable of sensing the local polarity, which is featured by the blue-shift, and a longer-alkyl tail dye ($R_2 = C_8$) has no or negligible probing activity, although the alkyl tail is thought to be excluded from the host cavity (exposed to the solution) due to the strong polarity of the pyridinium charge [6].

It is interesting to note that the λ_{max} of amylose-$C_{16}DASPC_1$ inclusion complex exhibits a blue-shift (ca.17 nm) relative to that of the non-inclusion free dye state, while amylose-C_1DASPC_{22} complex[6] indicates a red-shift in aqueous DMSO. It seems to be that the direction of λ_{max} shift depends on which terminal group (either amino-donor or pyridinium-acceptor) of the included dye performs the sensing function. In other words, intramolecular charge-transfer of

the dye in inclusion varies depending on the sensing terminal group, particularly in the excited state where charge-shift occurs. Detailed studies in this regard will be published elsewhere.

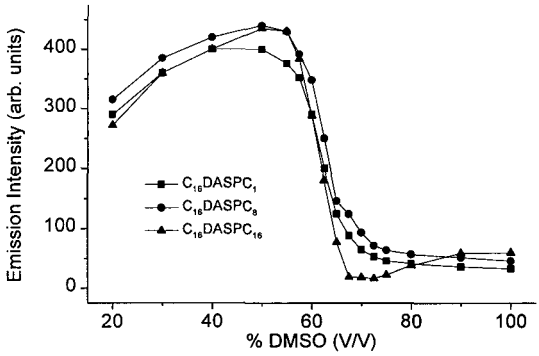


Fig.4: Changes in emission intensity of inclusion complexes of hemicyanine dyes (1.5 x 10^{-5} M) with amylose (1 x 10^{-3} M) as a function of DMSO-H_2O mixture ratios.

Conclusion

Inclusion complexation of present hemicyanine dyes with amylose occurs at ≤ 65% DMSO, which is indicated by a large enhancement of fluorescence emission. By the inclusion, a noticeable blue-shift (relative to non-inclusion free dye) of λ_{max} was observed only with the shortest-alkyl tail dye ($R_2 = C_1$) while the λ_{max} of longer-alkyl tail dyes ($R_2 = C_8$ and C_{16}) remains same throughout the inclusion region, indicating that only C_{16}DASPC$_1$ dye is capable of playing an active mono-functional sensing role in the inclusion.

References

[1] L. M. Loew, l. Simpson, A. Hassner, V. Alexanian, *J. Am. Chem. Soc.* **102**, 5439 (1979)
[2] M. Hof, P. Lianos, A. Laschewsky, *Langmuir* **13**, 2181 (1997)
[3] P. Fromherz, A. Heilmann, *J. Phys. Chem.*, **96**, 6864 (1992)
[4] H. Ephardt, P. Fromherz, *ibid.* **97**, 4540 (1993)
[5] U. Narang, C. F. Zhao, J. D. Bhawalkar, F. V. Bright, P. N. Prasad, *ibid.* **100**, 4521 (1996)
[6] O.-K. Kim, L.-S. Choi, *Langmuir* **10**, 2842 (1994)
[7] O.-K. Kim, L.-S. Choi, H.-Y. Zhang, X.-H. He, Y.-H. Shih, *J. Am. Chem. Soc.* **118**, 12220 (1996)
[8] O.-K. Kim et al., Unpublished Results