Fluorescence Enhancement and Photostability of Novel Pentamethine Cyanines in Nafion-Na⁺ Membranes

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Four novel pentamethine cyanines have been investigated for their photophysical behaviors and photochemical stability in Nafion-Na⁺ membranes. The incorporation processes of these dyes into Nafion membranes are diffusion-controlled and the apparent diffusion constants have been determined. Fluorescence quantum yields and fluorescence lifetimes of all tested dyes in Nafion membranes have been determined and significant fluorescence enhancements were observed with respect to their fluorescence in aqueous solution. Photolysis of these dyes suggested these dye molecules are stabilized significantly by Nafion membranes. Furthermore, the fluorescence enhancements and the photostabilization of these dyes are more significant in dry Nafion membranes than those in wet ones.
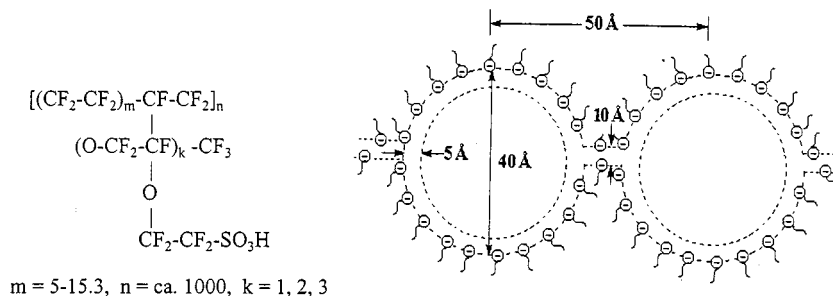
INTRODUCTION

Investigations on photophysics and photostability of polymethine cyanine dyes have been stimulated by the wide application of these dyes in photography [1], in photopolymerization [2], and especially in optical recording media [3]. Devotions to the structure-property correlation study of this kind of dyes reveal that their absorption undergoes a bathochromic shift and their photostability decreases as the number of vinylene groups increases, and that the electron-drawing substituents on the heterocycles and (or) on the polymethine chain are helpful for the stability of these cyanine dyes. On the other hand, it has also been established that the position of the absorption maximum is shifted to longer wavelength by dispersive interactions between the transition dipole of the dye and the electronic polarizability of the medium molecules, and that the photostability is affected by the medium [4]. Thus, improving the photostability of these dyes can be realized not only by modifying the structures of mother molecules, but also by putting them in different media especially in rigid media, since it is the conformational change along the polymethine chain after excitation that precedes the degradation process [5]. This has been confirmed by pioneering works by several groups, which employed organized media including micelles [6] and synthetic bilayer membranes [7,8].

Nafion represents a novel and unique family of polymers which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic head groups (Scheme 1). When swollen in water, the structure of Nafion is believed to resemble that of a reverse micelle [9]. It is suggested that the hydrated SO_3^- head groups are clustered together in water-containing pocket of ca. 40 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix. The polymer backbone of Nafion provides exceptional chemical, thermal and mechanical stability while the sulfonic acid groups provide ion-exchange and

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$[(CF_2\text{-}CF_2)_m\text{-}CF\text{-}CF_2]_n$

$(O\text{-}CF_2\text{-}CF)_k\text{-}CF_3$

O

$CF_2\text{-}CF_2\text{-}SO_3H$

m = 5–15.3, n = ca. 1000, k = 1, 2, 3

Scheme 1. The composition and the schematic representation of the inverse micelles in Nafion membranes.

swelling abilities. It has been established [10–12] that water-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons and organic dyes. These optically transparent membrane systems are readily amenable to spectroscopic investigations. Because of these attractive properties, this polymer has been utilized widely as a medium for photophysical and photochemical studies in recent years [10–14].

In this paper, we report the influence of the microenvironment of Nafion host on the photophysics and photostability of four novel pentamethine cyanines (illustrated in Scheme 2) incorporated in Nafion membranes. We demonstrate that by incorporation of the dyes into Nafion significant fluorescence enhancements and significant improvement on photostability can be achieved.

EXPERIMENTAL

Materials. Pentamethine cyanine **1–4** were synthesized as reported elsewhere [15]. Their structures and purity were ascertained by elemental analysis, IR, and ^{1}H NMR. Their all-*trans* configuration has been confirmed [16]. Concentrations of freshly-prepared aqueous solutions (kept in darkness before use) were determined spectrophotometrically. Doubly distilled water was used throughout this work. Nafion 117 membrane (equivalent weight 1100, thickness of 0.0175cm) was kindly donated by Dr. A. W.-H. Mau of CSIRO, Division of Chemicals and Polymers, Australia.

Procedures for Preparation of Nafion Samples. Prior to use, the Nafion membranes were pretreated according to the same procedure as reported [11–13] previously. Sodium-form membranes of Nafion were prepared by stirring the pretreated Nafion in NaOH aqueous solution for at least 1 day and used throughout this work. Excess base was then removed by stirring the membrane

samples in several portions of pure water. These Nafion-Na^+ membranes were immersed in the aqueous solutions (2.2–5.0×10^{-6} M) of each tested substrate, and the samples were taken out and determined for their absorbance to obtain the uptake amount by the difference in the absorbance of the solution before and after the addition of the Nafion membranes. For the incorporation of **1** and **2**, the Nafion membranes were immersed in a NaCl solution (0.05 M) for 20 min before being immersed in the substrate solutions. To reach equilibrium for the adsorption kinetics, the samples were kept in the solution for at least one day and sonication may be necessary. For dry Nafion samples, each Nafion membrane was kept in air until its weight remained unchanged.

Instrumentation. Absorption spectra were obtained using a Shimadzu UV 160-A spectrophotometer. Fluorescence spectra and fluorescence quantum yields (using rhodamine B as the reference, $\phi_f = 0.96$ in Nafion [10c]) were obtained with a Hitachi 850 photospectrometer. Flu-

R = H, **1**; R= Cl, **2**

R=Cl, **3**; R=OCH₃, **4**
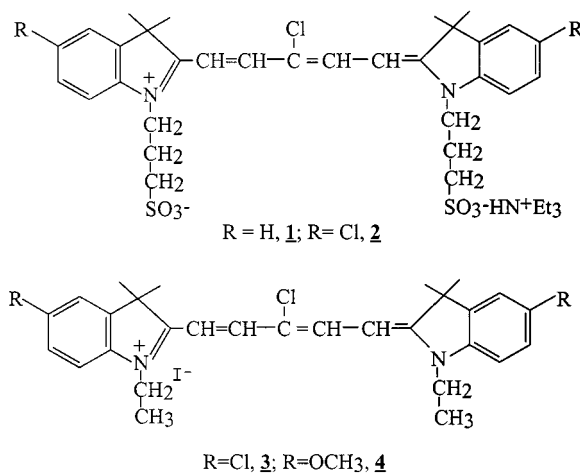
Scheme 2. Structure of pentamethine indocarbocyanines.

orescence lifetimes were obtained by single photon counting technique using an Horiba NAES 1100 nanosecond photometer.

RESULTS AND DISCUSSION

Incorporation and Absorption of Pentamethine Cyanines 1–4 in Nafion-Na+ Membranes. Compared with dyes **1** and **2**, dyes **3** and **4** are more hydrophobic but they can still be solubilized in water at 10^{-6} M concentration. The incorporation of these dyes from aqueous solution to Nafion is also completely different. For the cyanines **3** and **4**, owing to their positive charge character of their hydrophobic moieties and their stronger hydrophobicity than **1** and **2**, they can be well concentrated by Nafion membranes, as reflected by the absorption spectra illustrated in Nafion (Fig. 1). However, owing to the repulsive interaction between a **1** (or **2**) molecule and the negatively charged SO_3^- groups in Nafion clusters, the incorporation processes are so deficient that no absorption of **1** (or **2**) can be detected even after 6 h. Similar phenomenon for the incorporation of ANS into Nafion has been observed recently [17], which enlightens us to incorporate dyes **1** and **2** into Nafion by the addition of foreign inorganic salt NaCl, since the inorganic salt would lessen the electrostatic repulsion significantly. These absorption spectra are depicted in Fig. 2.

Periodic measurement of the absorbance of the dyes in the membrane revealed that the absorbance increased, confirming the incorporation of the dyes into the Nafion membranes (Fig. 1). In order to obtain information about the adsorption process, we analyzed the concentration of each dye incorporated into Nafion membrane as a function of soaking time. The following equation was employed for the study of the adsorption kinetics of these dyes into the membrane [11]:

$$C_t/C_\infty = 4\sqrt{Dt}/T\sqrt{\pi} \tag{1}$$

where C_t and C_∞ represent the concentrations of each dye in the membrane at time t and after equilibration respectively. D is the apparent diffusion coefficient in cm^2s^{-1} and T is the thickness of the membrane in cm. All the plots (not shown) of C_t vs. $\sqrt{t}$ were linear. From these plots the apparent diffusion coefficients were determined to be 7.1×10^{-9} cm^2s^{-1} (for **1**, in the presence of salt), 9.4×10^{-10} cm^2s^{-1} (for **2**, in the presence of salt), 9.6×10^{-11} cm^2s^{-1} (for **3**), and 3.2×10^{-10} cm^2s^{-1} (for **4**), respectively. The linearity of the plots confirms the applicability of equation (1) and shows that the sorption is diffusion-controlled, like the sorption process of azobenzene in Nafion membranes [11].

Fluorescence Emission of the Pentamethine Cyanines. Fluorescence emission of these dyes in Nafion-Na+ membranes has been detected, as depicted in Fig. 3. The fluorescence lifetimes are observed to be 2.6 ns for **1**, 3.4 ns for **2**, 1.23 ns for **3**, and 1.05 ns for **4** in wet Nafion membranes. Using rhodamine B as the reference ($\phi_f = 0.96$ in Nafion [10c]), fluorescence quantum yields of these dyes in wet or dry Nafion have been determined and are listed in Table I. The general feature of this table is the higher fluorescence quantum yields of these dyes in Nafion than those in water solution, and the higher ones in dry Nafion than those in wet Nafion. This may be attributed to the high microviscosity [18] of the domain in which the dye molecules are localized. As ascertained by the bathochromic shift in absorption spectra, interaction between the dye and the Nafion must have taken effect. Thus it is reasonable and expectable that, like many other substrate molecules [11–14], the dye molecules reside in the fluorocarbon/water interface.
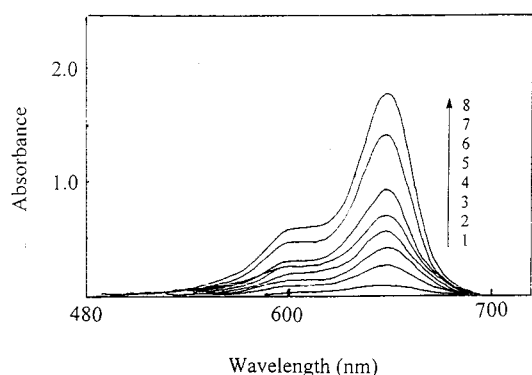

Fig. 1. Representative incorporation process of dye **3** into Nafion membranes. Immersing time: 1, 15 min; 2, 30 min; 3, 45 min; 4, 60 min; 5, 75 min; 6, 105 min; 7, 150 min; 8, 180 min.
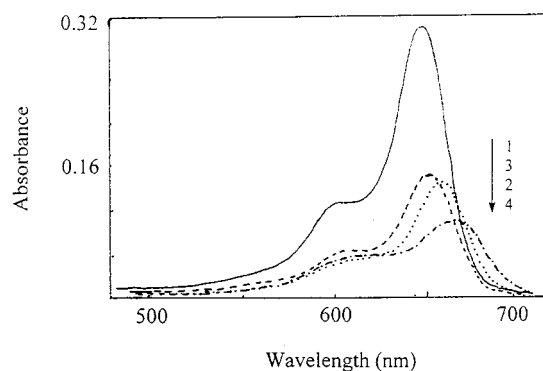

Fig. 2. Absorption spectra of polymethine cyanines **1–4** in Nafion membranes.
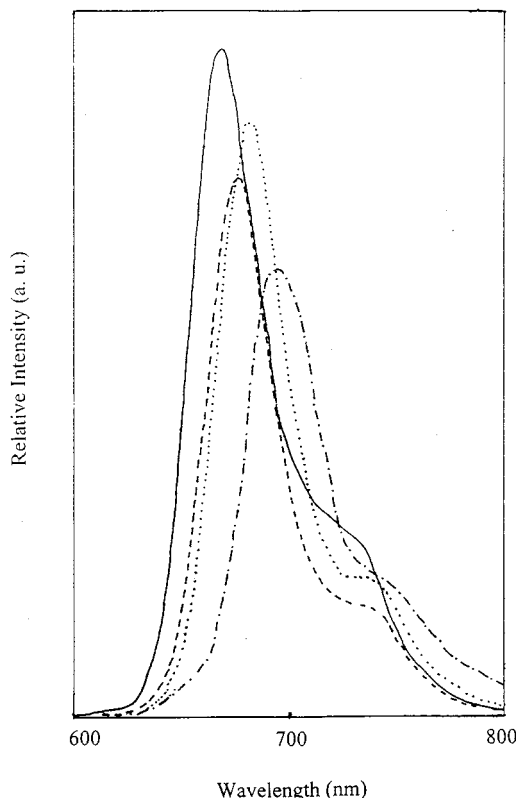
Fig. 3. Fluorescence emission spectra of polymethine cyanines **1–4** in Nafion membranes. **1**, ——; **2**, ····; **3**, ---; **4**, -·-·-.

When the all-*trans* pentamethine cyanine molecules are excited, they can be deactivated by fluorescence, internal conversion at the *trans* side, intersystem crossing, and *trans-cis* photoisomerization [19]. Solubilization at fluorocarbon/water interface of Nafion clusters makes the dye molecules sense a much rigid environment and results in the efficient hindrance toward the cyanine molecule rotation around one of its three central double bonds in S_1 state, thus the *trans-cis* photoisomerization and radiationless decay processes are significantly inhibited [20]. For dry Nafion membranes, most of the water molecules around SO_3^- groups in wet membrane are lost, and SO_3^- groups would be arranged more closely to further rigidize the fluorocarbon/water interface to form a more viscous domain. In this case, photoisomerization and radiationless processes are further inhibited, and the fluorescence quantum yields for each dyes is increased more remarkably. From the values of fluorescence quantum yields and fluorescence lifetimes, we could calculate the radiative and nonradiative rates according to Eq. (2):

$$k_r = \phi_f/\tau, \text{ and } k_{nr} = 1 - \phi_f/\tau \qquad (2)$$

in which k_r, k_{nr}, ϕ_f, and τ represent radiative rate, nonradiative rate, fluorescence quantum yield and fluorescence life time respectively.

Photostablization of Pentamethine Cyanines 1–4 by Nafion Membranes. The fluorescence enhancements of these cyanines by incorporation into Nafion goes parallel with a significant increase of the photostability. The photostablity is defined as $1-(A_0-A)/A_0 \times 100\%$, where A_0 and A denote the absorbance of each dye before and after irradiation respectively. By monitoring the decrease in the maximum absorbance for each dyes with the photolysis time, we can illustrate the photostabilization of these dyes by Nafion membranes. As can be seen in Fig. 4, photolysis of dye **1** in aqueous solution for 0.5 h leads to the decomposition percentage 67%, while that in Nafion membrane leads to no fading even the photolysis time lasted for 10 h. Further experiment proved that only 2% of cyanine **1** in wet Nafion membranes is photodecomposed by 17 h photolysis, whereas no decomposition is

Table I. Absorption and Fluorescence Emission Parameters of Polymethine Cyanine Dyes **1–4** in Nafion Membranes

| Dye	Medium	λ_{abs} (nm)	ε (10^5 M^{-1}.cm^{-1})	λ_{flu} (nm)	ϕ_f	τ (ns)	K_r (10^8s^{-1})	k_{nr} (10^8s^{-1})
1	Water	642.3	2.25	671.1	0.04	0.25	1.57	37.8
	Wet Nafion	649.0	2.08	680.8	0.43	2.60	1.64	2.2
	Dry Nafion	648.5	2.15	682.0	0.58	—	—	—
2	Water	647.0	1.31	679.0	0.05	0.28	1.76	33.0
	Wet Nafion	658.2	1.33	688.4	0.60	3.43	1.75	1.2
	Dry Nafion	659.0	1.29	687.0	0.71	—	—	—
3	Water	645.6	1.11	682.6	0.02	0.18	1.18	54.9
	Wet Nafion	651.5	1.05	687.5	0.51	1.23	4.00	4.0
	Dry Nafion	651.0	1.06	687.5	0.68	—	—	—
4	Water	658.5	0.55	693.0	0.01	0.16	6.67	59.5
	Wet Nafion	669.0	0.52	703.5	0.30	1.05	2.90	6.6
	Dry Nafion	668.8	0.54	703.8	0.50	—	—	—
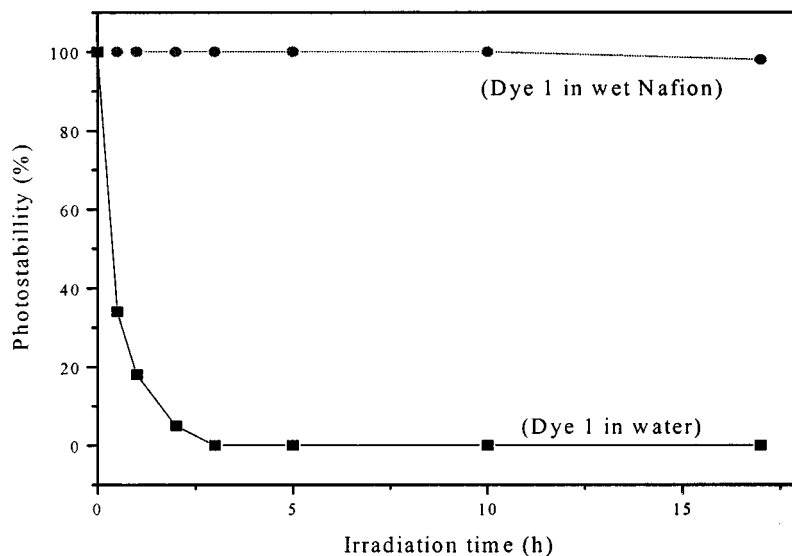
Fig. 4. Dependence of the absorbance of dye **1** in water and in Nafion membranes under irradiation. This spectrum is typical for other dyes.

detected for **1** in dry Nafion membranes. During this irradiation period, the decrease of fluorescence and absorption demonstrates that the destruction processes of the dyes correspond to the nonradiative deactivation of first singlet excited state S_1. Thus inhibiting the nonradiative deactivation of S_1 state leads to not only the fluorescence enhancement, but also the photostability of the dyes. Photolysis of other cyanines led to the similar results (Table II). Considering the combined effects of fluorescence enhancement and great photostability of these dyes in Nafion membranes, we can envisage a variety of practical application of these dyes.

Table II. Photostablity of Polymethine Cyanines **1–4** in Nafion Membranes (for the Definition of Photostability, See the Text)

Dye	Medium	Irradiation time (h)						
		0.5	1.0	2.0	2.5	5.0	10.0	17.0
1	Water	34	18	<5	0	0	0	0
	Wet Nafion	100	100	100	100	100	100	98
	Dry Nafion	100	100	100	100	100	100	100
2	Water	52	36	22	8	0	0	0
	Wet Nafion	100	100	100	100	100	100	>99
	Dry Nafion	100	100	100	100	100	100	100
3	Water	39	15	6	0	0	0	0
	Wet Nafion	100	100	100	100	100	100	96
	Dry Nafion	100	100	100	100	100	100	100
4	Water	58	43	29	10	<4	0	0
	Wet Nafion	100	100	100	100	100	100	100
	Dry Nafion	100	100	100	100	100	100	100

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