

Photophysical behaviors of novel indodicarbocyanines and indotricarbocyanine in Nafion- Na^+ membrane

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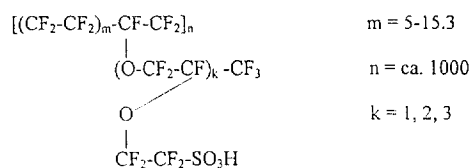
Abstract

Four novel indodicarbocyanines and one indotricarbocyanine have been incorporated into Nafion and the photophysical properties have been investigated which suggests that these dyes are located at the fluorocarbon/water interface. The absorption spectra of all the tested dyes in Nafion are similar to those in water despite bathochromic shift. Significant fluorescence enhancement for these dyes in Nafion with regards to water has been observed and the fluorescence quantum yields have been measured. Singlet–singlet energy transfer has been confirmed by steady state fluorescence technique and the energy transfer parameters have been determined. The energy transfer efficiencies of each donor–acceptor (D–A) pair in Nafion lie in the range of 72–90%, while in water solution under the same experimental concentration range (10^{-5} M) no energy transfer occurred for any investigated D–A pair. The occurrence of energy transfer reveals that these donor and acceptor molecules are heterogeneously distributed in Nafion, and the incorporation of donor and acceptor molecules into the same cluster in Nafion may be possible. © 1998 Elsevier Science S.A. All rights reserved.

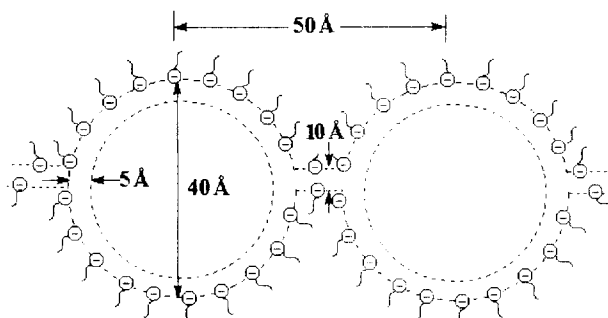
Keywords: Indodicarbocyanine; Indotricarbocyanine; Nafion; Photophysical property; Energy transfer; Heterogeneous distribution

1. Introduction

Energy transfer processes in various media have been a subject of interest in various chemical, physical and biological subdisciplines. One important kind of non-radiative transfer of the excited state energy from a donor (D) to an acceptor (A) is a result of dipole–dipole interaction. According to Forster's model, the rate and the efficiency of energy transfer depend on a number of factors including: (1) the extent of overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor; (2) the relative orientation of the donor and the acceptor transition dipoles; and (3) the distance between those molecules. So the energy transfer processes will depend not only on the characteristics of the donor–acceptor pair but also on their immediate environment. This has stimulated intensive studies on illustrating the effects of many constrained and organized media on such processes [1,2]. Among these media, Nafion has been intensively noticed in the last decade for its unique structure and for its chemical, mechanical and thermal stability. This ionomer represents a novel and unique family of polymers which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic groups.

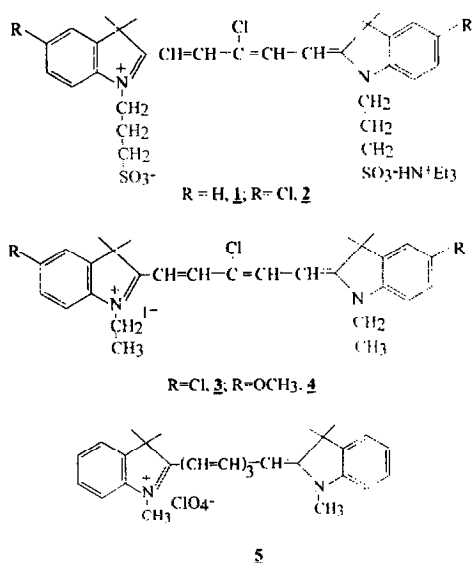


When swollen in water, the structure of Nafion is believed to resemble that of an inverse micelle (Scheme 1). It is suggested that the hydrated SO_3^- head groups are clustered together in water-containing pocket of ca. 40 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix. Such unique



Scheme 1. Schematic representation of the two-phase cluster-network model for Nafion membranes.

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Scheme 2. Structures of indodicarbocyanines **1–4** and indotricarbocyanine **5**.

structure of Nafion membrane may supply a framework for the organizational requirements that many photochemical and photophysical processes might impose. It has been established that water-swollen Nafion can incorporate high concentration of aromatic hydrocarbons and organic dyes, thus raising the possibility of obtaining high local concentration of substrate molecules. Because of these attractive properties, Nafion has been utilized as a prospective medium for photophysical and photochemical process studies [3,4].

Indodicarbocyanines have a wide variety of application including photography [5], optical probes in model membrane systems [6,7], initiators in photopolymerizations [8], and in optical recording media [9,10]. Of particular interest is the fact that excitation energy transfer in dye mixtures can be utilized to achieve better dye-laser performance at the desired wavelength. In this paper, we employ Nafion membrane as a medium to promote singlet–singlet energy transfer processes between novel indodicarbocyanines (Scheme 2) and indotricarbocyanine (also in Scheme 2). We illustrate that these dye monomers in Nafion membrane at low concentration range (10^{-5} M) can undergo efficient energy transfer processes, whereas in homogeneous solution no energy transfer can be observed at such low concentration. This suggests that the heterogeneity of Nafion results in the heterogeneous distribution of the donor and the acceptor molecules, which is favorable for the increase of local concentration thus for the occurrence of energy transfer.

2. Experimental section

2.1. Materials

Indodicarbocyanines **1–4** and indotricarbocyanine **5** have been synthesized as reported elsewhere [11]. Their structures

and purity were ascertained by elemental analysis, IR, and ^1H NMR. 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 0.0175 cm) was kindly donated by Dr. A.W.-H. Mau of CSIRO, Division of Chemicals and Polymers, Australia.

2.2. Procedures for preparation of Nafion samples

Prior to use, the Nafion membranes were pretreated according to the same procedure as reported previously [3]. Sodium-form membranes of Nafion were prepared by stirring the pretreated Nafion in NaOH aqueous solution for at least 1 day. Excess base was then removed by stirring the membrane samples in several portions of pure water. These Nafion- Na^+ membranes were immersed in freshly prepared aqueous solution (2.8×10^{-6} – 5.4×10^{-6} M) of each cyanine in the dark, and the samples were taken out and the uptake amount of each dye was determined from the difference in the absorbance of the solution before and after the addition of the Nafion membrane. Dry Nafion samples were prepared by drying the wet ones in the air until there are no more weight changes. All measurements were carried out at 26°C.

2.3. 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 [11]) were obtained with a Hitachi 850 photospectrometer. Fluorescence lifetimes were obtained by single photon counting technique using Horiba NAES 1100 nanosecond photometer.

3. Results and discussion

3.1. Incorporation of the indotricarbocyanines **1–5** into Nafion membrane

Many pioneering works have confirmed the fact that Nafion can incorporate aromatic hydrocarbon and organic dyes. For all the investigated dyes **1–5**, the incorporation processes can be illustrated in Fig. 1. This representative figure showed the absorption increase of dye **5** in Nafion with immersing time. When the Nafion samples were immersed in the mixed dye solutions, absorption of each dye in Nafion is observable in the absorption spectra. For example, the absorption of both **1** and **5** can be well resolved in and identified from Fig. 2, indicating that the interaction between the dye molecules in ground state does not exist. The absorption spectra of all the tested dyes in Nafion are similar to those in water despite the bathochromic shift (Table 1). The bath-

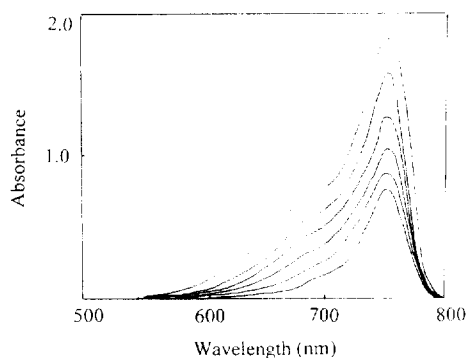


Fig. 1. The incorporation process of indotricarbocyanine **5** into Nafion membrane. From down to up, immersing time: 0.25 h; 0.5 h; 1.0 h; 1.25 h; 1.5 h; 2.0 h.

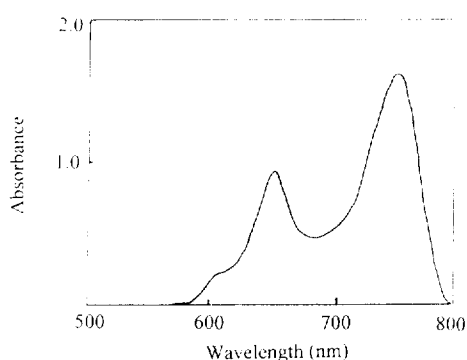


Fig. 2. The absorption of dyes **1** and **5** in Nafion membrane. $[1] = 5.3 \times 10^{-5}$ M, $[5] = 5.8 \times 10^{-5}$ M.

ochromic effect of Nafion with regards to water solvent is attributed to the dispersion force between dye and Nafion. Owing to the lack of strong permanent dipoles in the chromophore of the dyes, the interaction between the rapidly fluctuating transition moment and the medium involves only the electronic polarizability of the medium molecules, so the dispersion forces between dye and Nafion must be responsible for the bathochromic shift.

3.2. Fluorescence spectral properties of dyes 1–4

The emission spectra of these indotricarbocyanines in water-swollen Nafion are similar to those in aqueous solution, despite the fact that they all show some spectral shift (Table 1). Combining with the absorption spectra, we can deduce that these dyes are located in the fluorocarbon/water interface, like azobenzene molecules [3] and some other organic molecules [1,2]. Owing to the interaction of the bound dyes with the polymer chains, and the high microviscosity of the cluster domain at which the dye molecules reside, emission quantum yield of these incorporated dyes increased significantly with respect to that in aqueous solution. When these indotricarbocyanine molecules solubilized in Nafion are excited, they can be deactivated by fluorescence, internal conversion, intersystem crossing, and *trans-cis* photoisomerization [12]. The contribution of these processes depends on the structure of the molecules, temperature, and the viscosity of the medium. For Nafion with much higher microviscosity than the normal homogeneous solution,¹ the hindrance towards the indotricarbocyanine molecule rotation around one of its central double bonds in the first excited singlet state efficiently inhibits the photoisomerization and radiationless decay processes, which is reflected in the increase of fluorescence quantum yield. For example, ϕ_f of dye **1** in water is only 0.04, but it rises abruptly to 0.426 in wet Nafion and 0.577 in dry Nafion. The higher ϕ_f value for **1** in dry Nafion than that in wet Nafion is assignable to the higher microviscosity of dry Nafion [3](¹). Such role of Nafion in the fluorescence emission has been also found in the room temperature fluorescence of azobenzene molecules [13], which do not fluoresce in homogeneous media at room temperature. We have noticed the similar result obtained by Sabatani et al. [14] recently, who found that a mixed-ligand ruthium complex showed strong emission in Nafion. All these

¹ J.Q. Guan, C.H. Tung, unpublished results.

Table 1
Absorption and fluorescence emission parameters of polymethine cyanine dyes **1–5** in Nafion membrane

Dye	Medium	λ_{abs} (nm)	ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm)	ϕ_f	τ (ns)
1	water	642.3	2.25	671.1	0.040	0.254
	wet Nafion	649.0	2.08	680.8	0.426	2.602
	dry Nafion	648.5	2.10	682.0	0.577	—
2	water	647.0	1.31	679.0	0.050	0.284
	wet Nafion	658.2	1.33	688.4	0.600	3.427
	dry Nafion	659.0	1.35	687.0	0.712	—
3	water	645.6	1.11	682.6	0.018	0.179
	wet Nafion	651.5	1.05	687.5	0.511	1.228
	dry Nafion	651.0	1.00	687.5	0.678	—
4	water	658.5	0.55	693.0	0.011	0.165
	wet Nafion	669.0	0.52	703.5	0.304	1.049
	dry Nafion	668.8	0.54	703.8	0.495	—
5	water	738.0	1.25	800.0	0.013	0.109
	wet Nafion	746.2	1.24	810.5	0.258	0.981
	dry Nafion	746.0	1.27	811.8	0.374	—

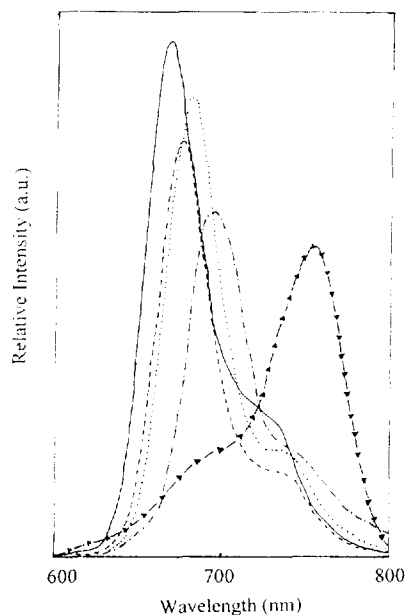


Fig. 3. The emission of dyes 1–4 and the absorption of dye 5 in Nafion membrane. 1: —; 2: ···; 3: ---; 4: -·-·; 5: - - - -.

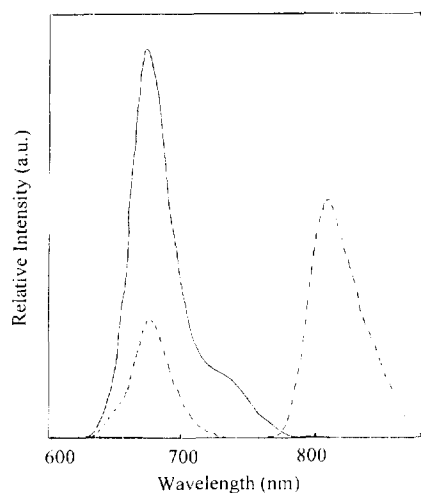


Fig. 4. Fluorescence emission of dye 1 in absence (—) and in presence (---) of 5.

results demonstrate that Nafion can efficiently inhibit the deactivation processes of dye molecules in their excited states, thus provide us a prospective medium for deriving fluorescence or for enhancing fluorescence of the incorporated dye molecules.

3.3. Singlet–singlet energy transfer from indodicarbocyanines 1–4 to indotricarbocyanine 5

The considerable overlaps between the fluorescence emission of indodicarbocyanines 1–4 and the absorption spectrum of indotricarbocyanine 5 are shown in Fig. 3. Excitation of the indodicarbocyanine in each indodicarbocyanine–indotricarbocyanine mixture leads to the emission of indotricarbocyanine 5, confirming that singlet–singlet energy transfer occurred from indodicarbocyanines 1–4 to indotricarbocyanine 5 (Fig. 4). However, excitation of the donors in each donor–acceptor mixture led to no emission of 5 when these mixtures were solubilized in water at this experimental concentration, although the overlap between 1–4 and 5 remained nearly unchanged (Table 2). This must result from the heterogeneity of Nafion membrane and suggests that these donor and acceptor molecules are non-uniformly distributed in Nafion membrane. The spectral overlap illustrated in Fig. 3 can be evaluated by numerical integration to give the spectral overlap integral, J :

$$J = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (1)$$

in which $F_D(\lambda)$ is the donor fluorescence intensity at λ and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ . Thus, R_0 , the Forster ‘critical transfer distance’ at which the transfer rate is equal to the decay rate of the donor in the absence of the acceptor can be derived from Eq. (2):

$$R_0^6 = 9000(\ln 10) k^2 \phi_D J / 128 \pi^5 n^4 N \quad (2)$$

where ϕ_D is the quantum yield of donor emission in the absence of acceptor, n is the refractive index of the medium, N is the Avogadro constant and k^2 is a factor describing the

Table 2
Singlet–singlet energy transfer parameters of investigated D–A pairs in Nafion membrane

D–A	Medium	J ($10^{-3} \text{ cm}^6/\text{mol}$)	R_0 (Å)	C_0 (10^{-3} M)	E (%)	k_{ET} (ns^{-1})	r (Å)
1–5	water	2.8	33.2	6.09	–	–	–
	Nafion	3.2	50.8	1.70	72	0.99	43.2
2–5	water	5.2	38.5	3.90	–	–	–
	Nafion	5.2	58.3	1.12	84	1.53	44.3
3–5	water	4.4	31.6	7.07	–	–	–
	Nafion	4.6	55.6	1.29	75	2.86	39.2
4–5	water	7.2	31.6	7.06	–	–	–
	Nafion	7.5	55.3	1.32	90	9.17	38.3

(a) In every case wet Nafion samples were used.

(b) The concentration of 1–5 is 5.3×10^{-5} – $6.0 \times 10^{-5} \text{ M}$.

(c) $n = 1.35$, taking the refractive index for Teflon as an approximation.

(d) $k^2 = 0.476$ for a rigid system was employed.

relative orientation in space of the transition dipoles of D and A.

In this work, the energy transfer efficiency is calculated from the relative fluorescence yield of the donor in the presence (ϕ_{DA}) and absence (ϕ_D) of acceptor.

$$E = 1 - \phi_{DA}/\phi_D \quad (3)$$

Normalizing the spectra depicted representatively for the investigated donor–acceptor pairs in Fig. 4 can easily give the energy transfer efficiency of these donor–acceptor systems.

Using Eq. (4) the rate of energy transfer can be obtained.

$$E = k_{ET}/(k_{ET} + 1/\tau_D) \quad (4)$$

The correlation of k_{ET} with the separation distance (r) between donor and acceptor molecules is shown as follows.

$$k_{ET} = (1/\tau_D)(R_0/r)^6 \quad (5)$$

If the donor and acceptor molecules are distributed uniformly in homogeneous medium, the rate of energy transfer can be obtained from Eq. (6).

$$k_{ET} = (1/\tau_D)(C/C_0)^2 \quad (6)$$

in which C denotes the total concentration of the donor and the acceptor, C_0 is the ‘critical concentration’ expressed by Eq. (7).

$$C_0^2 = (8000\pi^2 n^4 / Nk^2 \phi_D \ln 10) J^{-1} \quad (7)$$

The values of the energy transfer efficiency, the energy transfer rate, and other energy transfer parameters are calculated from Eqs. (1)–(4), (5) and (7) and listed in Table 2. However, employing Eq. (6) for calculating the energy transfer rate gives very low values, and the separation distance of donor and acceptor molecules are unbelievably large. The reason for this is that Eq. (6) is suitable only for the uniformly distributed D–A substrate molecules. For Nafion with high heterogeneity, incorporated cyanine molecules must be non-uniformly distributed, which results in the local high concentrations of acceptors within close proximity of excited donors within water pores, and the energy transfer occurs. As indicated by the spectral properties and discussed above, these dye molecules are incorporated in the fluorocarbon/water interface region in Nafion membrane. Since the ionic clusters in Nafion are approximately 40 Å in diameter, the D–A distances of 38.3–44.2 Å in the investigated systems suggest that the incorporation of the donor and the acceptor molecules into the same cluster may be possible. The fact that energy transfer efficiencies of these D–A systems reach up to 90% envisages us the achievement of better dye-laser performance at low indodicarbocyanine–indotricarbocyanine pair concentrations.

4. Conclusions

Four novel indodicarbocyanines and one indotricarbocyanine are incorporated into Nafion. The absorption and the emission spectral properties suggest that they are located in the fluorocarbon/water interface in Nafion clusters. The absorptions of all the tested dyes in Nafion is similar to those in water despite bathochromic shift. Significant fluorescence enhancement for these dyes in Nafion with regard to water has been observed, which resulted from the high microviscosity of Nafion clusters. At the low experimental concentration range the singlet–singlet energy transfer from the indodicarbocyanines to indotricarbocyanine has been observed in Nafion, whereas in homogeneous solution, no energy transfer occurs at such a low concentration. This is attributed to the heterogeneity of Nafion, which leads to the heterogeneous distribution of these donor–acceptor molecules and nevertheless the shortening of the separation distance of donor and acceptor molecules. For each donor–acceptor pair in Nafion, the overlap spectral integral, the critical separation distance, the separation distance, the energy transfer rate, and the energy transfer efficiency have been determined suggesting the incorporation of donor and acceptor molecules into the same cluster in Nafion may be possible.

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