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Cyanines during the 1990s: A Review

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Contents

I. Introduction

The cyanine dyes have evoked interest primarily because of their unrivalled ability to impart light sensitivity to silver halide emulsions in a region of the spectrum to which the silver halide is normally not sensitive. Polymethine cyanine dyes have dominated the field of photography and other sophisticated arenas of dye application since 1856.[1] Numerous applications in various areas have been published every year on this subject.

The generic cyanine dyes consist of two nitrogen centers, one of which is positively charged and is linked by a conjugated chain of an odd number of carbon atoms to the other nitrogen (**1**). This prominent feature has been studied as "Push−pull" alkenes[2] and also forms the basis of the polymethine dyes, which contain the streptopolymethine unit as the chromophore. Depending upon the charge of the streptomethine unit, these dyes are classified as follows: Cationic streptopolymethine−cyanine and hemicyanine dyes (**1**), Anionic streptopolymethine−oxonol dyes (**2**), Neutral streptopolymethine−Mero-

cyanine dyes (**3**), Zwitterionic squaraine-based cyanine dyes (**4**).
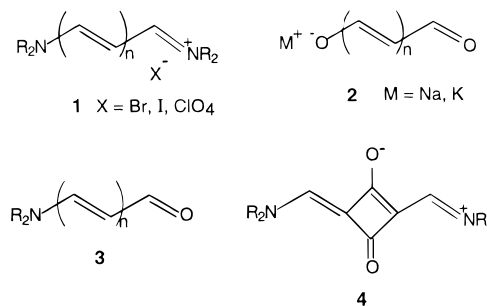
Generally the dyes have an all-trans geometry in their stable form. Occasionally these dyes undergo photoisomerization. The formation of these species can be studied by using various techniques such as flash photolysis, transient absorption, and picosecond time-resolved spectroscopy.[3−5]

Among these categories of dyes, the cyanine, merocyanine, and squaraine dyes are substances with a variety of colors but are not widely used for dyeing purpose, as they are decolorized by light and acid. They have, however, for example, been employed extensively as spectral sensitizers for silver halide photography and other inorganic large band-gap semiconductor materials,[6−24] in optical disks as recording media,[25−27] in industrial paints, for trapping of solar energy,[28] as laser materials,[29−32] in light-harvesting systems of photosynthesis,[33−35] as photorefractive materials,[5] as antitumor agents,[36] and as probes for biological systems.[37−41]

This review concerns work on cyanines and merocyanines carried out during the 1990s related to their self-organization, nonlinear optical (NLO) properties, photodimerization, photoisomerization, solvatochromic behavior, behavior in organized system, and use as fluorescent sensors.

II. Synthesis

Williams[1] in 1856 obtained the "corn flour" blue cyanine dye by treating quinoline (later on found to have contained lepidine as an impurity) with amyl iodide followed by treatment with ammonia. Extensive synthetic procedures for generating cyanine dyes of diverse molecular structure were reported earlier.[42−51] A general method for the synthesis of stilbazolium dyes (hemicyanines) involving condensation of a 2/4-methyl quaternary salt of the base

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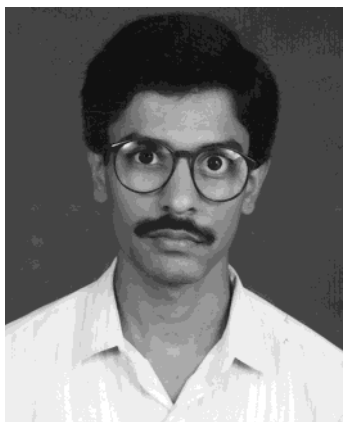
Amaresh Mishra was born in Bolangir, India, in 1970. He received his M.Sc. (1991) and M.Phil. (1993) degrees from the P. G. Department of Chemistry, Sambalpur University, India. He studied the synthesis of heterocyclic chemistry during his M.Phil. work. He then became a research fellow in the Surface Chemistry group under the co-guidance of Professor G. B. Behera and Dr. R. K. Behera and submitted his Ph.D. thesis in 1999. In June of the same year he joined the group of Professor George R. Newkome at the University of South Florida as a postdoctoral fellow working on dendrimer chemistry.
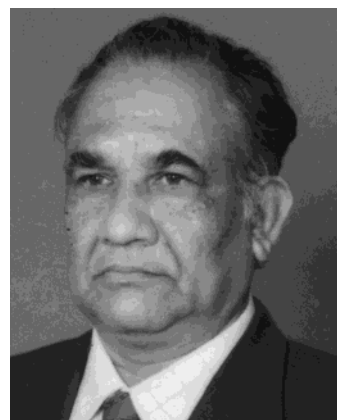
Rajani K. Behera was born in 1952 in Mahichala, India. He received his M.Sc. degree in 1974 and his Ph.D. degree from Sambalpur University in 1980. After working in Government College, he became a Lecturer at Sambalpur University and subsequently became a reader in 1991. He worked with Professor G. R. Newkome at the University of South Florida on the synthesis of dendrimers from 1988 to 1991. His research interests include the synthesis of heterocycles, macromolecules, and dendrimers.

Pradipta K. Behera was born in Bhursiguda, India in 1967. He received his M.Sc. degree from P. G. Department of Chemistry, Sambalpur University, in 1988 and his Ph.D. degree from the same university in 1993. He worked under the guidance of Professor A. K. Mishra in the field of photophysical chemistry during his Ph.D. studies. He has been a Lecturer in the P. G. Department of Chemistry, Sambalpur University, since 1994. His research interests center on photochemistry and surface chemistry.
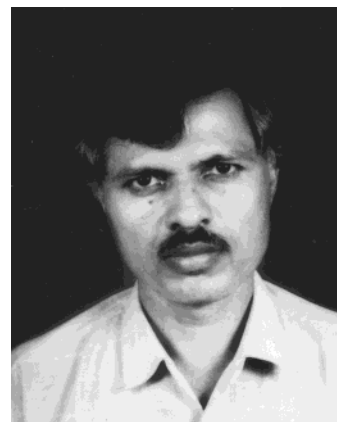
Bijay K. Mishra was born in Kuchinda, India. He received his M.Sc. degree (1975) and Ph.D. degree from Sambalpur University. He worked under the guidance of Professor G. B. Behera in the area of physical-organic chemistry for his Ph.D. studies. He worked as a Research Assistant and then as a Lecturer in the Department of Chemistry, Sambalpur University. At present he is a Reader in the same department. He was at IISc, Bangalore (1991), as an INSA Visiting Scientist. He is currently a UGC Research awardee for the IXth plan period. His present research interests are synthesis, surface chemistry, and correlation analysis.

Gopa B. Behera was born in 1939 in Mahichala, India. He received his M.Sc. degree from Ravenshaw College, Cuttack, in 1960. He received his Ph.D. degree from Utkal University working with Professor M. K. Rout. Afterward he worked as a Lecturer in Government Colleges. He became a Lecturer (1969) and subsequently a Reader (1971) and Professor (1978) in the Chemistry Department, Sambalpur University. He has visited the United States as a UGC Visiting Scientist (1985). He is the recipient of the first V. S. R. Gupta award (1995) for teaching excellence in chemistry. He is currently a UGC Emeritus Fellow in the Department of Chemistry, Sambalpur University. His research interests center on organic synthesis, surface chemistry, and reaction mechanics.

Scheme 1[a]

R = alkyl group ; X = NMe₂, OMe, OH, H
A = Br, I
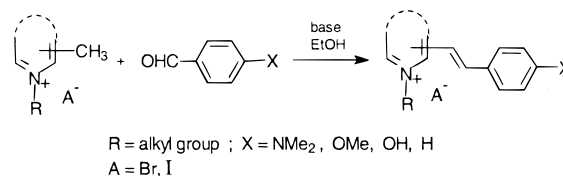
[a] R = alkyl group. X = NMe$_2$, OMe, H. A = Br, I.

with substituted benzaldehyde in the presence of a suitable base is given in Scheme 1.

Koraiem et al.[52] synthesized a series of dimethine cyanines by selective oxidation of 4-benzylidene-2-methyl-oxazol(imidazol)-5-one with SeO$_2$ in dioxane to give a 2-carboxaldehyde derivative, which on further condensation with an equimolar quantity of

Scheme 2[a]
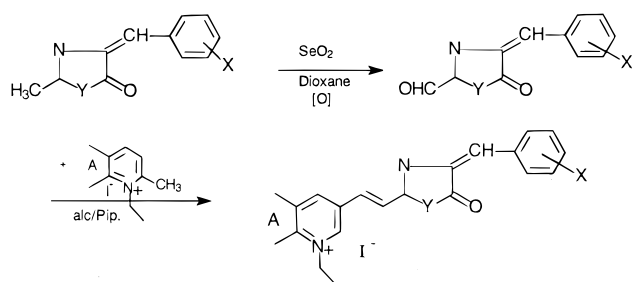
[a] X = H, *p*-OCH$_3$, *p*-OH, *p*-NO$_2$, *o*-NO$_2$. Y = O, NH. A = H, C$_6$H$_4$.

Scheme 3[a]
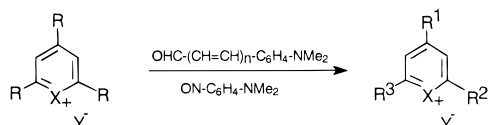
[a] n = 0, 1. X = NMe, O. Y = I, ClO$_4$. R = CH$_3$, H. R^1, R^2, R^3 = H, CH$_3$, (CH=CH)$_{n+1}$−C$_6$H$_4$−NMe$_2$, CH=N-C$_6$H$_4$−NMe$_2$.

methyl quaternary salt in alcohol and piperidine afforded the corresponding dye (Scheme 2). They subsequently studied the correlation between molecular structure and spectral behavior of the dyes in various solvent systems and have established the formation of a charge-transfer (CT) molecular complex between the dyes and solvents.

Synthesis of dyes, which would be stable against light, heat, oxygen, and ozone, is important from practical viewpoints. The mechanism of photofading of the dyes is complicated and involves oxidative or reductive processes depending upon the circumstances. To increase the photostability of the dyes, Matsui et al.[53] introduced substituted multiple bonds conjugated through the chromophore. Thus, they synthesized a series of mono-, bis-, and trisubstituted pyridinium and pyrylium dyes by adopting the general procedure (Scheme 3).

Mazieres et al.[54] developed a versatile method to synthesize a series of new classes of cyanine dyes containing the phosphinimine and guanidine moieties (Scheme 4). The synthesis has been carried out by the condensation of *N*-silylated phosphinimine or *N*-silylated guanidine units and aryl carboxonium ion in acetonitrile to give the symmetrical diaza pentadienylium salt. The partial charge on each atom has been calculated by the Ampac−Mopac module of the molecular-modeling program.

The carboxonium ions have been synthesized by Madaule et al.[55] via condensation of tris(dialky-

lamino) arsanes and stilbanes with pyrylium salts to form symmetrically aminated and highly substituted pentamethinium salts. (Scheme 5). These syn-
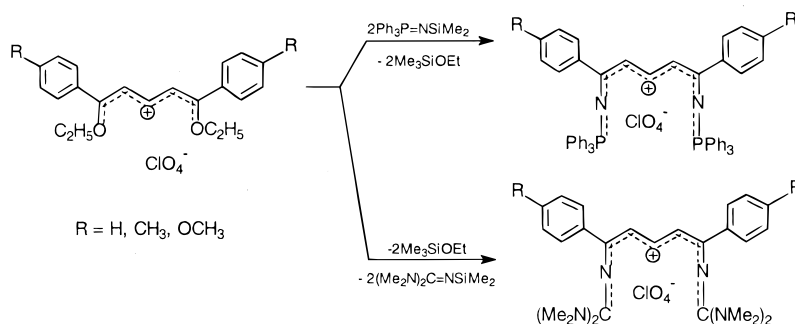
Scheme 5
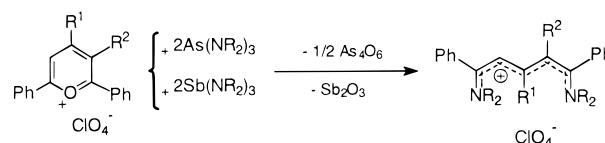
theses have opened a new field of investigation for the reactivity of the aza-Wittig compounds and more generally for studying physical applications in optical devices.

Narayanan and Patonay[56] reported a new method of facile synthesis of heptamethine cyanines (Scheme 6) by direct condensation on heating of *N*-alkyl-substituted quaternary salts derived from 2,3,3-trimethylindole or 2,3,3-trimethylbenzindole and 2-chloro-1-formyl-3-(hydroxy methylene)cyclohex-1-ene in a mixture of butanol and benzene (7:3) without any catalyst. These dyes have been easily derivatized as fluorescent-labeling agents of biologically important molecules.[56]

III. Self-Aggregation

The self-association of dyes in solution or at the solid−liquid interface is a frequently encountered phenomenon in dye chemistry owing to strong intermolecular van der Waals-like attractive forces between the molecules. The aggregates in solution exhibit distinct changes in the absorption band as compared to the monomeric species. From the spectral shifts, various aggregation patterns of the dyes in different media have been proposed. The bathrochromically shifted J-bands[57] (J for Jelly, one of the first workers who investigated these shifts) and hypsochromically shifted H-bands[58] (H for hypsochromic) of the aggregates have been explained in terms of molecular exciton coupling theory, i.e., coupling of transition moments of the constituent dye molecules.[59] The aggregation behavior of cyanine dyes has been studied extensively since these are the best known self-aggregating dyes.

The red-shifted J-aggregate is the most commercially important dye assemblage for photographic spectral sensitization. It is generally agreed that both H- and J-aggregates are composed of parallel dye molecules stacked plane-to-plane and end-to-end and form two-dimensional dye crystals. Thus, the dye

Scheme 4

R = H, CH$_3$, OCH$_3$

Scheme 6

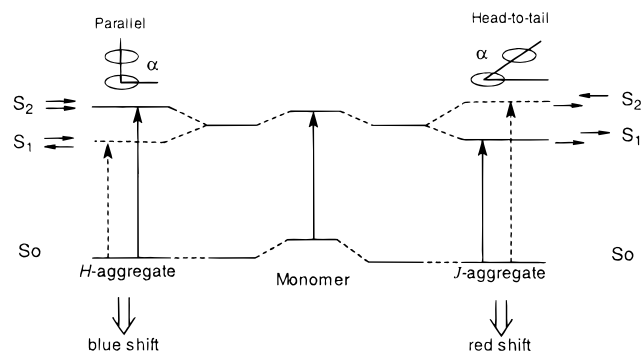|	Y	Z	RX		Y	Z	RX
a:	H	CMe$_2$	(CH$_2$)$_4$SO$_3$	e:	OCH$_3$	CMe$_2$	C$_2$H$_5$(I)
b:	H	CMe$_2$	C$_2$H$_5$(I)	f:	H	O	C$_2$H$_5$(I)
c:	H	CMe$_2$	(CH$_2$)$_3$NH$_2$HBr(Br)	g:	H	S	C$_2$H$_5$(I)
d:	H	CMe$_2$	CMe$_2$(CH$_2$)$_4$SO$_3$				
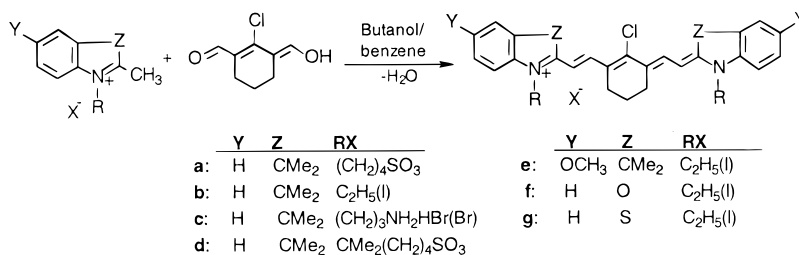
molecule, according to exciton theory, is regarded as a point dipole and the excitonic state of the dye aggregate splits into two levels through the interaction of transition dipoles (Figure 1). The dye mol-

Figure 1. Schematic representation of the relationship between chromophore arrangement and spectral shift based on the molecular exciton theory. (Reprinted with permission from ref 92. Copyright 1997 The Bulletin Chemical Society Japan.)
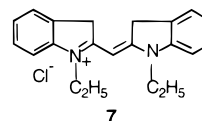
ecules may aggregate in a parallel way (plane-to-plane stacking) to form a sandwich-type arrangement (H-dimer) or in a head-to-tail arrangement (end-to-end stacking) to form a J-dimer. A transition to the upper state in parallel aggregates having parallel transition moments (acridine orange, **5**) and to a lower state in a head-to-tail arrangement with perpendicular transition moments (PIC, **6**) leads to hypsochromic (red) and bathochromic (blue) shifts, respectively (Figure 1). The angle between the line
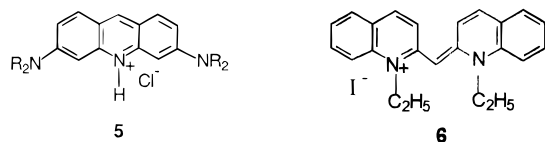
of centers of a column of dye molecules and the long axis of any one of the parallel molecules is called the 'angle of slippage', α. Large molecular slippage (α < 32°) results in a bathochromic shift

(J-aggregate), and small slippage (α > 32°) results in a hypsochromic shift (H-aggregate). The exciton model is valid only when the interaction between orbitals of constituent molecules is negligible.[60] Extensive studies on J- and H-aggregates have resulted in the proposal[61] that these aggregates exist as a one-dimensional assembly in solution that could be in a brickwork, ladder, or staircase type of arrangement (Figure 2). The brickwork model was proposed by Maskasky based on the study of J-aggregates of polymethine dyes on silver halide grains by polarized fluorescence microscopy.[62] Sheppard[63] proposed that the observed spectral changes are due to reversible molecular aggregation. The tendency of dye molecules to aggregate depends on the structure of the dye and also on the environment, such as micellar, microemulsion, pH, ionic strength, concentration, solvent polarity, electrolyte, and temperature parameters. Generally, dye self-association in solution depends directly on dye concentration, added electrolyte and inversely on the temperature.

Marchetti et al.[64] observed deviations from Beer's law accompanied by distinct spectral shifts relative to the monomer band (M-band) for 1,1′-diethyl-2,2′-cyanine chloride (**7**). This is attributed to the forma-

tion of dye dimer, oligomer, and n-mer (Figure 3). A blue shift with a loss of intensity, termed a D-band, is due to dimeric species. The appearance of a third band or shoulder on the low-wavelength side of the D-band with a loss of intensity is termed an H-band.[65] Bathochromic shift to longer wavelengths of the M-band with enhanced intensity is ascribed to a J-band. The M-, D-, and H-bands are quite common in all classes of dyes, but the J-band appears only with photographic cyanine dyes.

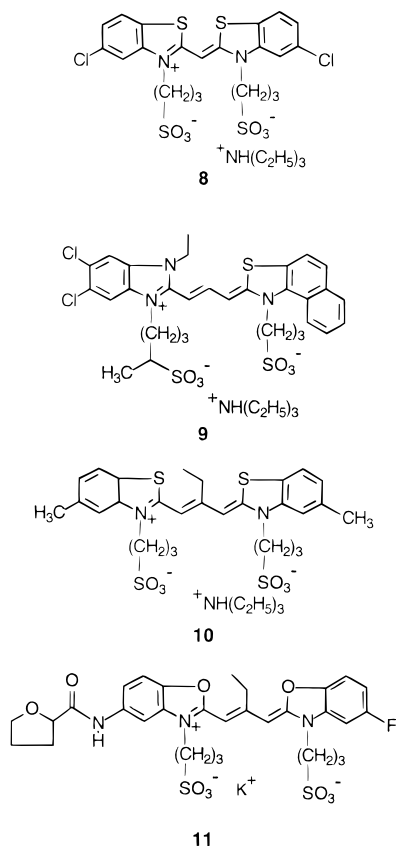**a) Ladder-type b) Staircase-type c) Brickwork-type**

Figure 2. Schematic representation of the different arrangement of cyanine dyes in the solid surface and in solution. (Reprinted with permission from ref 61. Copyright 1996 American Chemical Society.)

Wheatley[66] proposed a stacked structure for higher aggregates with the long molecular axis of each dye molecule being perpendicular to the aggregate axis and the dye molecules, separated at a distance of about 3.3 Å. The J-aggregate formation depends on the high aqueous solubility and compact architecture of the molecule. The presence of very low concentrations of a quencher can quench the J-band. Saijo et al.[67] used the scanning electron microscope to study the photosensitivity of J-aggregate-forming oxacarbocyanine dye by adsorbing it on an AgBr microcrystal grown in gelatin. Spano et al.[68] discussed the ability of J-aggregates to exhibit coherent excitation phenomena with a potential for strongly enhanced nonlinear optical properties.
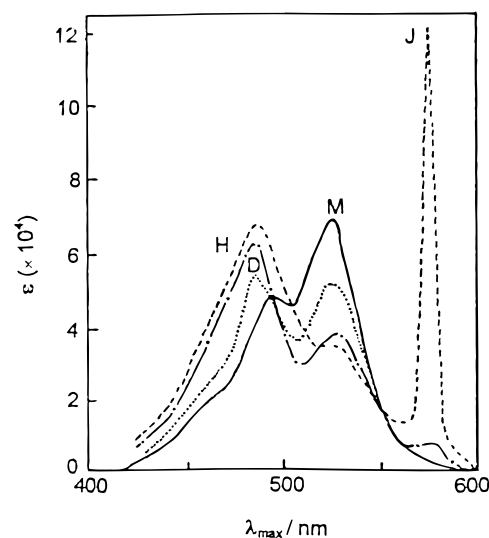
Harrison et al.[61] observed J-aggregation of four anionic cyanine dyes (**8**−**11**) in aqueous solution by UV−vis absorption. X-ray diffraction study shows that dyes **8**, **9**, and **10** form a liquid-crystalline layer (lamellar/smectic) phase, and dye **11** forms a columnar nematic and hexagonal phase in aqueous solution. The J-aggregates represent a liquid-crystalline

Figure 3. Absorption spectra of an aqueous solution of **7** at 25 °C.

thiacyanine. Rotermund et al.[71] observed the J-aggregate formation of indocyanine green (ICG) (**12**) ([dye] = 1.5 mM) in aqueous medium. The fluores-

12
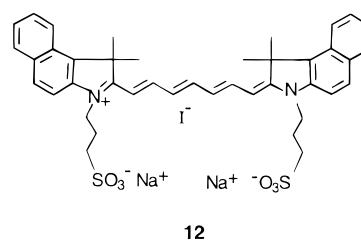
cence quantum yield of this dye was found to be 0.0003 in water[70] and ∼0.11 in DMSO.[72] However, a fluorescence quantum yield of 0.02 for ICG-NaI at a concentration of 10^{-7} M and 2×10^{-5} at a concentration of 10^{-2} M in water was also observed.[73] Lenhard and Hein[74] measured the redox potential of the J-aggregate of cationic polymethine dyes on silver halide via the use of redox buffer and found that the excited state of the J-aggregate was 0.3 V lower than that of monomer. From the absorption studies[75] of the ICG-NaI J-aggregate, the number of molecules forming the chromophore (n_{chr}) is found to be 16 ± 8. Upon analysis, τ_{rad} was found to be 5.5 ± 0.5 ns/n_{chr} = 340 ± 100 ps.

Khairutdinov and Serpone[76] studied the behavior of cyanine dyes in aqueous and aqueous-methanolic solution by picosecond laser photolysis. The dye, **13**, gives a H-aggregate, whereas **14** gives a dimer at sufficiently high concentration in water, while PIC is a J-aggregating dye. The singlet excited-state

8

9

10

11

phase (mesophase) consisting of thousands or more dye monomers depending on the concentration and on the mesophase structure.

Tiddy et al.[69] performed polarizing optical microscopy and X-ray diffraction studies of cyanine and azo dyes in water. The cyanine dyes are found to form a smectic phase, and azo dyes form a columnar nematic and hexagonal mesophase in rigid environment.

Vaidyanathan et al.[70] studied the J-aggregational behavior of amphipathic oxacyanine and thiacyanine dyes and observed an extensive aggregation of
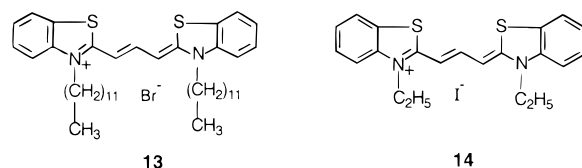
13

14

lifetime of the dye monomer is found to increase due to an increase with the length of the alkyl chain attached to the nitrogen atom, probably due to the

dimerization of the dye molecules. An intense narrow J-band centered at 572 nm and less intense broad absorption band corresponding to two maxima at 495 and 532 nm is obtained for **6**. They concluded that approximately 1 photon hits per ~10^2 molecules which is sufficient for exciton annihilation to take place. Geacintov and Breton[77] observed that 0.1 photon hit 300 chlorophyll molecules per reaction center in spinach chloroplasts. The excited dye aggregates are found to store and disperse energy following picosecond laser excitation and subsequent heating of surrounding solvent shells.

De Rossi et al.[78] studied the J-aggregation behavior of 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl) benzimidazolocarbocyanine (**15**) in the presence of the zwitterionic *N*-dodecyl-*N*,*N*-dimethyl-*N*-(carboxymethyl) betaine. The increase of [micelle]

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16
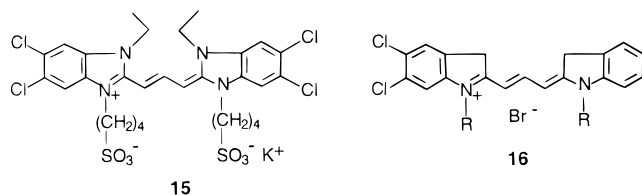
is found to increase the absorption coefficient and decrease the J-aggregate bandwidth depending on the pH and salt concentration. De Rossi et al.[79] also studied the effect of the alkyl chain length (C_2−C_{12}) on J-aggregate formation of 5,6-dichloroindolino ca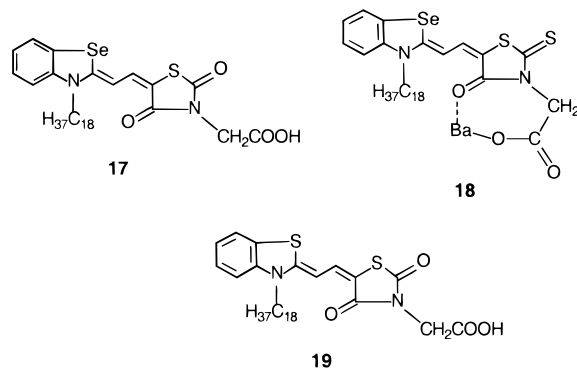rbocyanine (**16**) dyes. A decrease in J-aggregate bandwidth in absorption and emission spectra is found with an increase in the *N*-alkyl chain length.

Kawaguchi and Iwata[80] prepared two types of J-aggregates of a merocyanine dye (**17**) with a benzoselenazole ring in aqueous medium in the presence of different metal ions in the water subphase. One

17

18

19

type of J-aggregate is formed in the presence of metal ions such as Cu^{2+}, Ba^{2+}, and Cd^{2+} in water, and the other is formed in the presence of Na^+, K^+, Ni^{2+}, Co^{2+}, Zn^{2+}, Er^{2+}, or Lu^{2+}. It is suggested that spectral shape depends highly on the nature of metal ion, but nothing has been said about the molecular structure of the aggregates. They also observed the J-aggregate formation of C_{18}SeMD on treatment with $BaCl_2$, $CaCl_2$, and NaCl (pH 6.9) on Au-evaporated glass slides and proposed a weak

intramolecular hydrogen bonding of cations with the keto carbonyl group (**18**). Miyata et al.[81] studied the J-aggregate formation in a Langmuir monolayer of the merocyanine dye (**19**) by absorption spectra. Five types of J-aggregates have been proposed depending on the temperature, concentration, and nature of the metal ion present in the subphase. With an increasing size of the metal ion, the aggregation number of the J-aggregate is found to decrease from 6 to 2.

Sato et al.[82] prepared the J-aggregates of **6** and **20** by adsorbing them on the lipid vesicle surface of DMPC (**21**):DCP (**22**) = (1:1). During energy transfer in J-aggregates of excited molecules, it has been found that the fluorescence of donor aggregates is quenched and that of acceptor aggregates is enhanced. The J-aggregates of dyes **6** and **20** behave like energy donors, and those of dyes **23** and **24** behave like energy acceptors. The J-aggregate forma-

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23

24
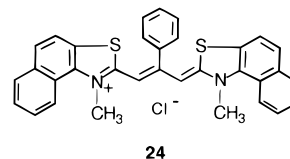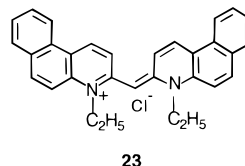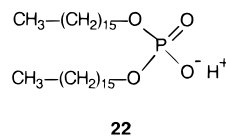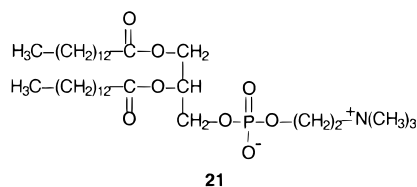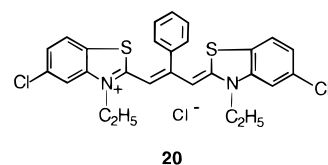
tion is due to the electrostatic interaction of the dye with negatively charged DCP, as in only zwitterionic DMPC vesicles the dye does not show any J-aggregate band. The addition of dyes **6** and **20**, simultaneously on the vesicle surface, decreases the resonance fluorescence of dye **6** due to quenching.[83] The high solubility of dye **6** in water prevents formation of the J-aggregate at the air−water interface[84,85] whereas the J-aggregate is formed by the LB-film technique.[84] Yonezawa et al.[86] classified the J-aggregates of cyanine dye into four types: separated aggregate (S-type), mosaic aggregate (M-type), persistent-type aggregate (HP-type), and amalgamation-

type aggregate (HA-type) from spectral characteristics. The combination of quinocyanine and thiacarbocyanine dyes form S-type, oxacyanine and thiacyanine dyes form M-type, and two thiacarbocyanine dyes give HA-type aggregates on LB films. Iwaska et al.[87] observed that the introduction of substituents at the 5- and 6-positions of anionic thiacyanine dyes shows that the larger the substituent, the greater the van der Waals force of attraction preferring dimerization over J-aggregate formation. The formation of metastable J-aggregate depends highly upon the concentration and temperature.[88]

The formation of H-aggregates has been proposed[89] for 1,1′-disulfopropyl-9-aminothiacarbocyanine (**25**) fabricated in chitosan polymer film. The fabrication of **6** on a water-soluble polymer film[90] and on a montmorillonite[91] aqueous suspension and a cast film was postulated to arise from J-aggregate formation.
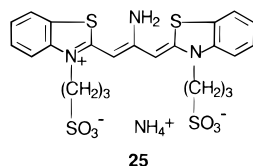
Mishra et al.[49] studied the J-aggregate formation of *N*-cetyl-(*p*-*N,N*-dimethylamino)styryl pyridinium bromide (**26a**) in reversed micelles (CHCl₃−CTAB−H₂O) and dimer formation in aqueous medium. The

26: X = (a): N(CH₃)₂ ; (b): OCH₃
(c): Cl : (d): OH

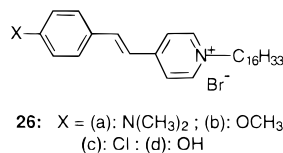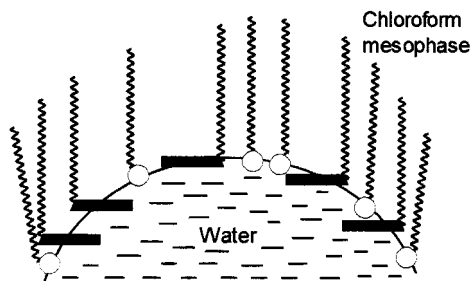formation of dimer in CTAB aqueous solution shows a hypsochromic shift at low concentration of CTAB ([CTAB] < cmc) due to H-aggregation. A bathochromic shift in reversed micelles of CTAB in hexane−CHCl₃ methanol medium is due to J-aggregate formation at the interface (Figure 4). The area per molecule of the dye at the interface is found to be 65 Å² from a condensed monolayer formation on water surface.[50]

Katoh et al.[92] synthesized three streptocyanine dyes and studied their aggregation behavior by

Figure 4. Dye solubilized in reversed micelle. (Reprinted with permission from ref 49. Copyright 1991 Indian Journal of Chemistry.)

absorption and fluorescence techniques. They designed the dye molecule **27**, which shows hypsochromic shifts compared to **28** due to a H-aggregation whereas dyes **29** and **30** show bathochromic shifts probably due to J-aggregation. From the emission spectra, dyes **28** and **30** show larger intensity and a small Stokes shift whereas the stack dimer **27** shows a weak intensity and a large Stokes shift, which has been explained by molecular exciton theory. The positive shift of reduction potential ($E_{red} = -1.17$ V) and negative shift of oxidation potential ($E_{oxd} = 0.76$ V) of the stacked dimers with respect to monomer **28** ($E_{red} = -1.36$ V, $E_{oxd} = 0.98$ V) have been explained in terms of both Coulombic and orbital interactions. Katoh et al.[93] synthesized pentamethine streptocyanine dimers (**31**) from 4,4′-bipyridinium salt and aqueous dimethylamine in ethanol at 0 °C. The cyanine moieties in this dimer are linked perpendicularly at the central carbon atom of the methine chain. The dimer shows two absorption bands at 446 and 406 nm compared to a single monomer band at 412 nm. These bands are attributed to the splitting of HOMO levels through spiroconjugation between two cyanine moieties. The Stokes shift of the dimer may be due to a large difference between the HOMO and LUMO levels. A comparison of the positive shift of the reduction potential ($E_{red} = -0.9$ V) and a negative shift of the oxidation potentials ($E_{oxd} = 0.94$ V) of cyanine dye aggregates of **31** as compared to monomer **28** indicate Coulombic and orbital−orbital interaction, respectively.

A series of bis-cyanine dyes (**32**) linked by the 1,8-naphthalene skeleton in which the chromophore arrangement corresponds to a brickstone-work model have been synthesized by Katoh et al.[94] The absorption spectra, the Stokes shift, and the slip angles of ca. 68° and ca. 29° correspond to H- and J-aggregates for the syn and anti conformer, respectively. The distance between the two planes of the cyanine moieties in the syn conformer is 3.4 Å, which is a

a: CH₃ H
32 b: CH₃ OCH₃
c: CH₃ Cl

33: (R¹, R² same as **32**)

Figure 5. Splayed-out angle (ϕ) and slip angle (α) of 1,8-naphthalene bis-cyanine dye **33**. (Reprinted with permission from ref 94. Copyright 1997 The Bulletin Chemical Society Japan.)
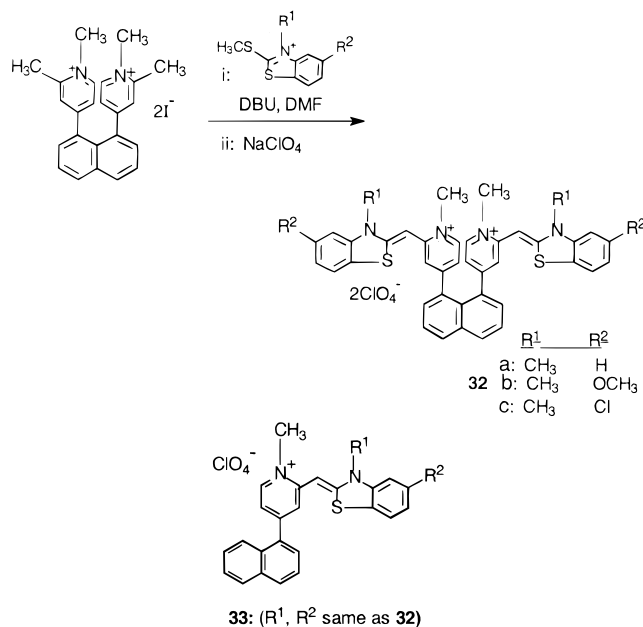
typical value for the face-to-face stack of aromatic rings[95] (Figure 5). The absorption spectra of **32a** (syn) consist of intense (417 nm, $f = 1.91$, where f is the oscillator strength) and weak (492 nm, $f = 0.02$) bands, whereas the anti conformer has an intense band at 490 nm ($f = 1.27$) and a weak band at 476 nm ($f = 0.27$). The former is due to HOMO → LUMO+1 and HOMO-1 → LUMO+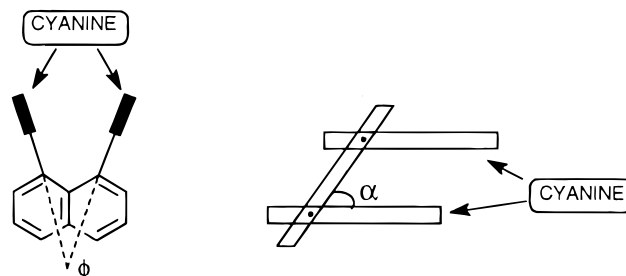1 transitions (for syn), whereas the main absorption in the later is due to a $\pi - \pi^*$ transition (HOMO-1 → LUMO). The positive shift in the reduction potential of bis-cyanine dyes ($E_{red} = -1.255$ V, **32a**; -0.277 V, **32b**; -1.230 V, **32c**) as compared to monocyanines (**33:** $E_{red} = -1.455, -1.480, -1.450$ V) is due to the Coulombic and orbital interaction between the two cyanine moieties. The relative orientation of chromophores in dye aggregates plays an important role in determining energy levels of dye aggregates as well as absorption spectra.

Ferreira et al.[96] studied the aggregation behavior of symmetrical monomethine (**6**) and trimethine (**34**) cyanines adsorbed onto microcrystalline cellulose using diffuse-reflectance ground-state absorption techniques. The degree of dryness of cellulose affects the

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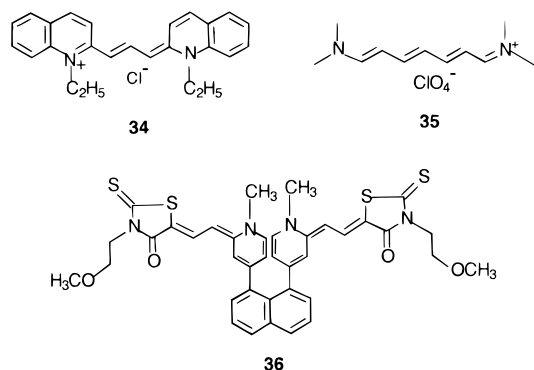
aggregation pattern. Compound **6** forms both H-aggregates (490 and 468 nm) and J-aggregates (577 nm) with respect to the monomer peak at 525 nm in air-equilibrated moisture-containing cellulose, whereas **34** forms only H-aggregates (575 nm) in wet cellulose with a monomer peak at 660 nm. J-aggregation of 1,7-bis(dimethylamino) heptamethine perchlorate (**35**) transformed into dichroic spherulites has been studied by atomic force microscopy (AFM).[97] The range of order is longer for the spin-coated film than those deposited by evaporation or epitaxy. A series of organic-soluble naphthalocyanine derivatives have been synthesized by Tai et al.[98] From the spectral analysis and thin film studies, these dyes are found to show H- or J-aggregation with respect to the monomer band. Some merocyanine dyes are known to form J-aggregates on solid surfaces and in solution.[99−101] Katoh et al.[101] studied the solvatochromism of bismerocyanine (**36**) linked by 1,8-naphthalene skeleton. In acetonitrile, the syn conformer shows larger bathochromic shifts in absorption spectra than that of 1-naphthyl merocyanine. According to intramolecular exciton coupling theory, the anti conformer fluoresces and the syn conformer does not.

IV. Nonlinear Optical Properties

Many organic molecules (such as hemicyanines, merocyanines, and azacyanines) show high nonlinear optical properties owing to their wide transparent range, high nonlinear optical (NLO) coefficiency, large molecular hyperpolarizability (β), and extremely short response time. They are also used in optical signal processing such as amplification, frequency conversion (i.e., second-harmonic generation, SHG), modulation, laser technology, telecommunication, data storage, and optical switches.[102−104] The principal structural requirement for SHG is a non-centrosymmetric structure, which is achievable in organic materials via the Langmuir−Blodgett (LB) technique. This technique controls the structure at the molecular level. The Langmuir monolayer has, nowadays, attracted the attention of physicists and chemists to study the aggregational behavior of the molecules. A Langmuir monolayer is a layer of amphiphilic molecules formed at the air−water interface. The monolayer on compression generally exhibits the phase sequence: Gas → liquid expanded (LE) → liquid condensed (LC) → solid → collapsed state. Because of the large hyperpolarizability, the cyanine dyes, classified as hemicyanines containing long hydrophobic chains, which form Langmuir−

Blodgett film at the air–water interface[105] are of considerable interest for NLO applications.[106] The LB films of merocyanine dyes (MCs)[107,108] have found recent interest because of their high nonlinearity and thus exhibit considerable potential for organic photoconductive and photovoltaic cells and photochromic effects. Organic molecules (**37**) containing donor and acceptor groups possess strong NLO properties.

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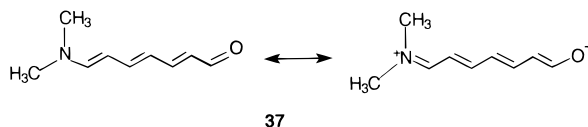
These molecules show low-energy charge-transfer states and exhibit large second- and third-order nonlinearites.[109,110] Marder and co-workers[110] studied the NLO behavior of a series of organic conjugated molecules such as **37** and showed a strong correlation between hyperpolarizability and bond-length alternation (BLA) in the conjugated bridge by using solvents of varying polarity. Induced circular dichroism spectroscopy has been used extensively to probe a microenvironment. Thus, the chiral environment of α- and β-cyclodextrins has been investigated by induced CD spectra of dimer and higher order cyanine dye aggregates.[111,112] This suggests that the achiral cyanine in a chiral host leads to the formation of a good NLO material. With a view to obtain numerical relationships between hyperpolarizability and BLA, Marder[110d] carried out finite-field semiempirical MO calculations (at the AM1 level). Lu et al.[113] used the valence-bond charge-transfer (VB–CT) model and extended it to systems terminating with donor and acceptor units. They illustrated the application of their model with nonlinear polarizabilities of several donor–acceptor molecules linked by an octatetraene chain. The spectroscopic measurements of λ_{max} together with selected NLO data were used to predict structures and the solvent effect needed to attain the desired structure–NLO property relationship. The solvent effect has also been discussed by the same group.[114]

Carpenter et al.[115] used absorption spectroscopy and second-harmonic generation to examine the effect of systematic dilution on aggregation of a hemicyanine dye (**38**) in LB films deposited on silica. The

38
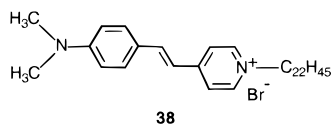
absorption spectrum exhibits four bands, with the highest energy peak remaining unperturbed with a change in concentration. The longest wavelength peak is due to monomer, and the other two bands are due to aggregates. They observed that the second-order nonlinear susceptibility correlates with the amount of nonaggregated dye as a function of total dye concentration. It has been concluded that the monomer has a much larger hyperpolarizability than the aggregates and that the aggregate does not contribute to the second-harmonic signal. The hemicyanine dyes show an increase in second-order sus-

ceptibility $\chi^{(2)}$ on dilution of the dye with NLO-inactive materials such as fatty acids.[116] This is due to the interaction of the chromophores at high concentrations of the dye to form hypsochromically shifted aggregates.[117] The second-order nonlinearity decreases with increasing dye concentration and remains constant after a specific concentration (mole fraction of 0.5).[115] This shows that the aggregate formed in the film above a 0.5 mol fraction is completely NLO-inactive. This arises from intermolecular interactions within the aggregates such as geometrical (caused by near centrosymmetric aggregate structure) or electronic (dipole–dipole coupling) interactions in nature or both. Spano and Mukamel[118] observed the intermolecular interaction of hemicyanine dyes, which leads to a cooperative enhancement of optical nonlinearities. The SHG studies of these dyes show strong counteranion dependence and are sensitive to molecular aggregation.

Several workers[119–121] observed the film-forming ability of hemicyanine dyes and enhancement of their SHG by using lanthanide complex anions, which act as a spacer and a counterion. This technique of enhancing the miscibility and increasing the second-order nonlinearity is used for designing new molecular architectures. Li et al.[122] reported that the hemicyanine (**39**, **40**) and azopyridinium (**41**) dyes combine with anionic zinc complex (**42**) to form a series of novel bischromophoric NLO complex dyes.

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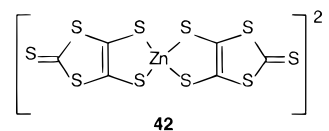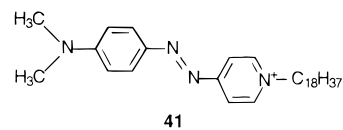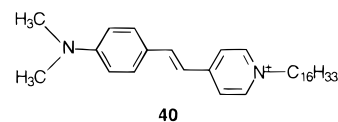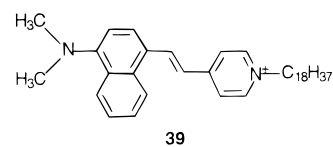
42 is the counter ion of two molecule each of dye **39**, **40** and **41**; represented as [dye]$_2$[counterion].

The SHG of such dye films is sensitive to the extent of molecular aggregation. The bivalent Zn complex anion is used as both counterion and spacer to give an order segregation of the chromophores. This increases the film-forming properties of the NLO dyes and enhances the second-order susceptibility ($\chi^{(2)}$). These NLO materials show both high nonlinearity and good additivity.[123]

Fujimoto et al.[124,125] studied the IR and Raman spectra of 3-ethyl-5-[2-(3-ethylbenzothiazolin-2-ylidene)ethylidene] rhodanine (Et MD, **43**) and 3-carboxymethyl-5-[2-(3-alkylbenzothiazolin-2-yildene)-

ethylidene] rhodanine (Cn MD, **44**) on the cast and LB films. They found from the IR carbonyl stretching

43: n = 2, R = C$_2$H$_5$
44: n = 2-18, R = CH$_2$COOH

45

46
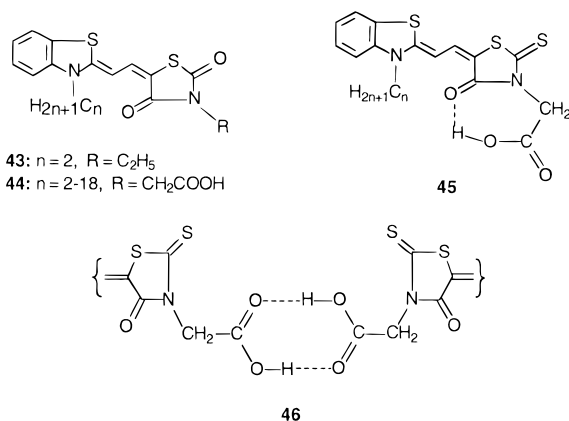
frequency that the dyes with alkyl chain lengths of C$_2$, C$_3$, C$_{12}$, C$_{14}$, C$_{16}$, and C$_{18}$ form an intramolecular hydrogen bonding between keto and carboxylic groups (**45**), whereas C$_4$, C$_5$, C$_6$, C$_7$, C$_8$, and C$_{10}$ dyes form ring dimers (**46**) due to intermolecular hydrogen bonding between two carboxylic groups.[124] They also studied the structure of C$_{10}$ MD and C$_{18}$ MD in cast films, in LB films, and in complexation with chloride salts (BaCl$_2$, NaCl, and CaCl$_2$).[125] In cast film, C$_{10}$ dye forms a ring dimer at room temperature. With an increase in temperature, the intermolecular hydrogen bonding changes to intramolecular hydrogen bonding, and above 160 °C the monomeric form dominates. For C$_{18}$ MD, both free and intramolecular hydrogen-bonded forms exist in cast film at room temperature. With an increase in temperature, the hydrogen-bonded form dominates, and above 160 °C the population of free form increases. The addition of chloride salt prefers the J-aggregate in cast film. In LB film, the hydrocarbon chain is less ordered.

Spiropyrans (Sp) on UV irradiation open to photomerocyanines (PMC, **47**).[126] These are widely used in fabrication of optical memory media and aggregate formation in LB films.[127,128] Aggregate formation in a LB film of 1′-octadecyl-5′-methyl-6-nitro-8-(decosanoyloxymethyl)spiro[2*H*-1-benzopyran-2,2′-indoline] (Sp-1822, **48**) has been studied by Ando and co-workers.[127] Substitution by a methoxy group at the 5′-position of **47** results in both J- and H-aggregate formation with UV light at a temperature >40 °C. Miyata et al.[129] studied the aggregational behavior of 5′-Me-SP1822 by LB film doped with methyl arachidate (MA) on UV irradiation at 365 nm. The material undergoes photoisomerization with subsequent formation of J- and H-aggregate on heat treatment (Scheme 7).

A tilt angle of 20−30° between the chromophoric plane and the film surface of the molecules shows a slip angle of 20−30° for J-aggregates and 70−80° for H-aggregates as calculated from the transition density model proposed by Norland et al.[130] (Figure 6). Monolayers at the air−water interface and LB films on a hydrophilic quartz surface have been prepared from two types of merocyanine dyes such as 1-(6′-hydroxyhexyl)-4-[(3,5-di-*tert*-butyl-4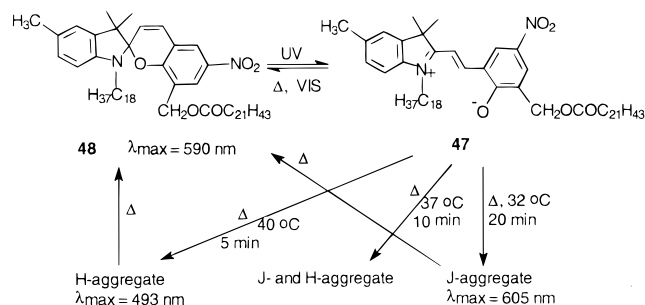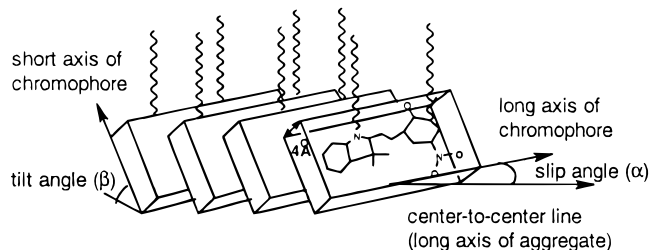-oxocyclohexane-2,5-diethylidene)ethylidene]-1,4-dihydropyridine and 1-hexadecyl-4-[(3,5-di-*tert*-butyl-4-oxocyclohexane-

Scheme 7[a]

48 λmax = 590 nm

47

H-aggregate λmax = 493 nm

J- and H-aggregate

J-aggregate λmax = 605 nm

[a] Reprinted with permission from ref 129. Copyright 1997 The Bulletin Chemical Society Japan.

Figure 6. Schematic representation of the chromophore alignment. (Reprinted with permission from ref 129. Copyright 1993 The Bulletin Chemical Society Japan.)

2,5-diethylidene)ethylidene]-1,4-dihydropyridine.[131] The protonated form gives more stable monolayer films than the free base. The free-base molecules are preferentially oriented parallel to the quartz substrate, whereas the protonated forms have out-of-plane orientation.

Pescatore and Yamazaki[132] studied the mixed monolayer formation of oxacyanine and oxacarbocyanine by the LB technique. Aggregation of dyes leads to the formation of heterodimers and the facilitation of polarized energy transfer. In a neutral tripalmitin LB matrix, the residual polarization of the mixed dyes is 0.13 and decays to 0.03 with decay times of 170 ps and 2.8 ns. In an ionic fatty acid LB matrix, the residual polarization reaches 0.11 and decays to 0.06 with decay times of 620 ps and 5.3 ns. This suggests that the heterodimers are randomly distributed in the LB film. The authors claim their work as the first determination of the tilt angle of molecules in aggregated LB films.

Tkachev et al.[133] studied the J-aggregate formation of a dicarbocyanine dye in a LB monolayer by X-ray scattering and spectral analysis. The optical anisotropy of the film depends on the order of arrangement of dye molecules in a monolayer. The indocarbocyanine, hemicyanine, and stilbazolium salts undergo second-harmonic generation on a Z-type LB monolayer.[134] These form aggregates on the SiO$_2$ surface. The extent of aggregation depends on the nature of the counterion. Li et al.[135] constructed stable monolayer and multilayer of asymmetric pthalocyanines containing crown ether moieties by LB techniques. A sandwich dimer is formed in the film upon complexation with potassium ion. The thiacarbocyanine dye adsorbed onto Ag or Au colloid particles shows third-order nonlinearity with a band at 600 nm,[136] which illustrates the enhancement of bulk properties ($\chi^{(3)}$).

V. Adsorption

Adsorption of molecules on surfaces to study photophysical and photochemical processes is a subject of current research. Adsorption of cyanine dyes to solid surfaces has evoked interest from both a basic and technological point of view. Heterogeneous photocatalysis, dye fabrics, spectral sensitization of silver halides, colorants, nonlinear optical applications, light energy conversion in photochemical cells, adsorption on the surface of semiconductor powders such as ZnO, TiO$_2$, AgCl,[137,138] and on silica,[139,140] etc. are some of the interesting applications of the dyes adsorbed on a solid surface. Some merocyanine dyes have also exhibited H- and J-aggregates when adsorbed on metal oxide films of TiO$_2$, Al$_2$O$_3$, and ZrO$_2$.[141]

The adsorption behavior of some monochromophoric (**49**) and bischromophoric (**50**) styryl pyridinium dyes on silica has been studied by Parida and Mishra.[142]

49: X = p-OMe, p-NMe
R = **a**: C$_4$H$_9$; **b**: C$_5$H$_{11}$; **c**: C$_{16}$H$_{33}$

50: X = p-OMe, p-NMe$_2$, p-Cl, o-Cl, H
n = 3, 4, 6
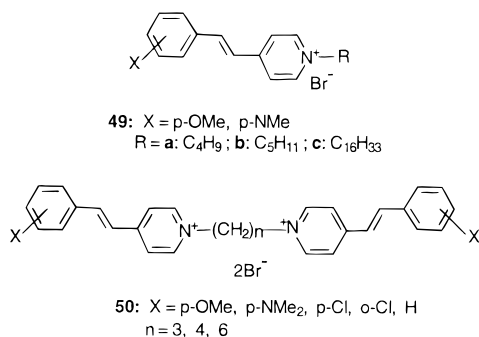
The area of coverage, adsorption isotherm, and adsorption kinetics has been discussed by considering the effect of temperature, chain length, medium, and substituent. The area of coverage per molecule for monochromophoric dyes ($\sim$1600$-$2300 Å^2) is found to be higher than that of the bischromophoric dyes ($\sim$1000$-$1500 Å^2). A cooperative adsorption phenomenon where the dyes anchor on the silica surface in a flat-on position has been proposed for the adsorption of the dyes. The area of coverage (A_c) of the dyes on the silica surface decreases when transferred from chloroform ($\sim$300 Å^2) versus when transferred from water (1100$-$2388 Å^2). In general, the low value of the area of coverage of the dyes on silica surface at higher temperature (**49a**: 2775.0 Å^2 at 18 °C and 2274.6 Å^2 at 28 °C) has been attributed to high desorption of water from the silica surface to give space for the dyes. The silica surface has been modified by treatment with alkali,[143] CTAB,[144] and poly(ethylene glycol) (PEG),[145] and adsorption studies of the dyes have been carried out (**49**, **50**). From the adsorption isotherm and kinetics, different adsorption models for the dy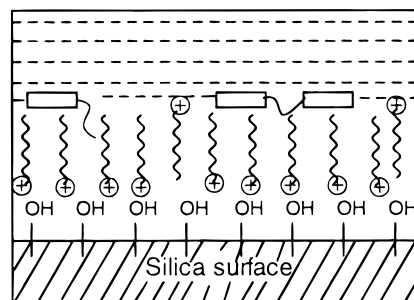es have been proposed. In alkali-treated silica, strong adsorption with flat-on orientation of the chromophoric group has been observed, whereas with CTAB- and PEG-treated silica, the adsorption is reported to be relatively weak. In CTAB-treated silica, coadsorption (Figure 7) and in PEG-treated silica adsolubilization has been proposed (Figure 8).

Figure 7. Schematic diagram of the orientation of monochromophoric (**49**) and bischromophoric dyes (**50**) on a CTAB-treated silica surface.
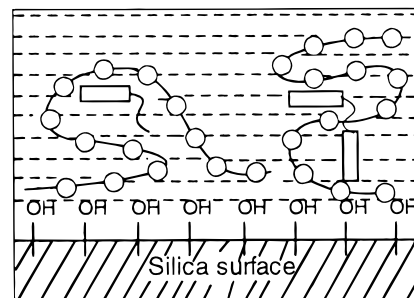
Figure 8. Schematic diagram of adsolubilization of monochromophoric (**49**) and bischromophoric dyes (**50**) on a PEG-treated silica surface. (Reprinted with permission from ref 145. Copyright 1998 Elsevier Science.)

Chen et al.[146] studied the absorption and emission characteristics of cyanine dyes (**51**) in aqueous solution, in the presence and absence of TiO$_2$ colloid. The

51

52: X = Cl, I
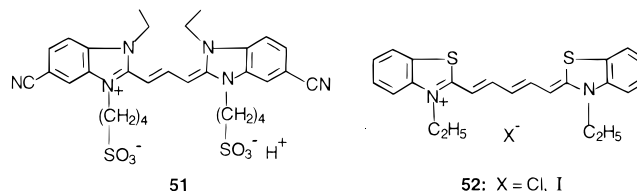
dyes adsorb strongly on colloidal TiO$_2$ with an apparent association constant of 3478 M^{-1}, and there was a decrease in the absorption peak in the presence of TiO$_2$. The fluorescence quenching of the dye with an efficiency of 92% by the addition of colloidal TiO$_2$ is attributed to electron injection from the excited singlet state of the dye to the conduction band of TiO$_2$ with a rate constant of 4×10^9 s^{-1}. The dye shows only one emission lifetime (8.08 ns) in homogeneous solution, whereas two lifetimes (0.24 and 7.88 ns) are observed in TiO$_2$ due to the distribution of the dye in the aqueous phase and as adsorbates on TiO$_2$ colloid. Fassler and Baezold[138] studied the adsorption of diethyl thiacarbocyanine (DTCC, **14**) and diethyl thiadicarbocyanine (DTDC, **52**) dyes in solution with inert (CaF$_2$) and active (AgCl, ZnO) surfaces by steady-state and time-resolved fluorescence spectrophotometry with a view to discriminate between electron- and energy-transfer processes. The dyes show side-on orientation at high concentrations, and the molecular interaction between the dye molecules increases on adsorption in CaF$_2$. The adsorption isotherm is non-Langmuir type (**S** type), which indicates the dye is weakly adsorbed. The decrease

in the fluorescence lifetime of adsorbed dye with a decrease in the surface concentration even when it is less than one monolayer concentration is ascribed to dimer formation.[147] The quantum yield of fluorescence of the dyes is found to increase in the adsorbed state.[147,148] Further, the electron-transfer process takes place from the adsorbed excited dye molecules to the conduction band of ZnO and AgCl (band gap 2.75 and 3.0 eV, respectively) to form radical dications of the dyes. The adsorption isotherm is of Langmuir type. Larger fluorescence quenching is observed on ZnO, AgCl, and CaF$_2$ surfaces due to the effective electron-transfer rate (k_e for **14** is 1.2×10^8 s^{-1}, for **52** is 2.4×10^8 s^{-1} on ZnO surface, and 1.2×10^8 s^{-1} for **14** and 0.16×10^8 s^{-1} for **52** on AgCl surface). The authors concluded that faster energy transfer lowers the attainable electron-transfer rate but enhances the rate of energy migration in the surface. Dye-sensitized silver halide photography involves energy migration in the dye layer and electron-transfer process to special "reactive sites", which forms an interesting analogy between technical photography and natural photosynthesis.

Lagorio et al.[149] studied the aggregation behavior of hydroxy aluminum tricarboxy monoamide phthalocyanine (AlTCPc) adsorbed on microgranular cellulose via absorption and fluorescence techniques. A dimer and monomer equilibrium is observed with a dimerization constant $K_d = 5.9 \times 10^6$ g/mol. The red shift of 20 nm in the dimer spectra compared to the monomer band is attributed to the coplanarity of dimer or J-aggregate. A decrease in the fluorescence quantum yield (0.29 to 0.07) with an increase in dye concentration can be accounted for by a model based on Kubelka–Munk theory.[150] This theory explains the effect of aggregation on fluorescence quantum yields and gives corrected fluorescence spectra. Using this model a true quantum yield, $\Phi_F = 0.46 \pm 0.02$, is obtained over the whole range of concentrations. This value is close to the quantum yield of AlTCPc obtained in DMSO ($\Phi_F = 0.42 \pm 0.02$).[151] Panner and Möbius[152] observed that dyes of similar structure form homogeneous mixed crystals where the partition of the absorption band can be varied between the extreme position of the pure spectrum.

Bliznyuk et al.[153] prepared mixed dye crystals of two negatively charged cyanine dyes (**53**, **54**) and investigated the connection between the structural and optical properties. The fluorescence spectra of the


X = Se : **53**
= S : **54**
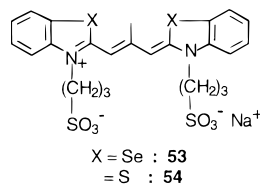
mixed dyes have sharp bands shifting with concentration by 20 nm. The absorption spectra of the monolayers after transfer from a solid support show two peaks due to Davydov splitting for a crystal with two differently oriented molecules.[153] The angle α between the long molecular axes (parallel to the transition moment of the long wavelength monomer),

the intensities $J_{\parallel}$, $J_{\perp}$, and absorption frequency maxima $\nu_{\parallel}$ and $\nu_{\perp}$ of two bands have been calculated by using eq 1.

$$\tan^2(\alpha/2) = \frac{\nu_{\parallel} \int J_{\perp}(\nu)\, d\nu}{\nu_{\perp} \int J_{\parallel}(\nu)\, d\nu} \qquad (1)$$

To obtain sharp band edges and circumvent the heterogeneity of the excited state, which leads to broadening of the spectra, the following requirements must met: (a) Systems with strong excitonic coupling are selected, leading to the formation of amalgamated bands. This holds for dyes forming J-aggregates with large band shifts compared to the monomers and excitonic splitting (2500 cm^{-1}). (b) The structure of the mixture should be uniform or "alloying" should occur to avoid strong intramolecular interactions depending on the relative molecular arrangement. The authors were able to prepare two-dimensional crystals with tuned band edges by tuning the crystals in mixed composition. The interactions therefore should be soft.

De Rego et al.[154] studied the adsorption of 1,1'-diethyl-2,2'-cyanine iodide (**7**) and 1,1'-diethyl-2,2'-carbocyanine iodide (**55**) on microcrystalline cellulose either by deposition from ethanolic solution followed by evaporation and/or by equilibrating ethanolic solution with powder solid. The swelling of cellulose

55
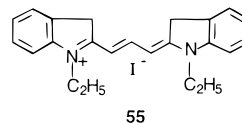
in ethanol is capable of entrapping some dye molecule within the polymeric chain, which is not observed in dichloromethane. The decrease in Φ_F in dichloromethane (0.08) is due to mobility of the cyanine dye giving a nonplanar and less emissive conformer. While in ethanol, a rigid planar and emissive fluorophore is observed with high Φ_F (0.30). X-ray photoelectron studies show hydrogen bonding between dye and cellulose and also aggregate formation depending on concentration.

A study by various workers[155,156] has revealed that tetraaryl borates have significant crevices between their substituents and permit occupation by small cyanine dye cations. During penetration into the borate cavity, the dye's rotation is restricted and singlet lifetime increases. In benzene, the singlet lifetime for 1,1',3,3,3',3'-hexamethyl indocarbocyanine tetrakis(triptycenylphenyl) borate (Cy$_{Me}^+$TRPB$^-$, **56**) is twice that of nonpenetrating Cy$_{Me}^+$PF$_6^-$.[156,157] The occupation of cyanine dye in crevices reduces the size of the borate anion, i.e., the size of the total structure is less than the sum of the radius of the individual ions. Owen et al.[158] have shown from the induced CD spectrum of 1,1'3,3,3',3'-hexamethyl-9-phenyl indocarbocyanine (PhCy$_{Me}^+$, **57**), 1,1'-diethyl-2,2'-cyanine (Cy$_{Et}^+$, **58**), 1,1'-di(3,5-di-*tert*-butyl)-benzyl-2,2'-cyanine (Cy$_{3,5t-Bz}^+$, **59**), or 1,1'-di(4-*tert*-butyl) benzyl-2,2'-cyanine (Cy$_{4tBz}^+$, **60**) that the dyes penetrate into a chiral cavity of spiro[(di-2-methyl)-borataxanthene] or spiro[(di-3-methyl)borataxan-

Figure 9. X-ray crystallographic structure of $Cy_{3,5t-Bz}^+$, $2MeSpB^-$ showing vertical stacks of the subunit producing ladder-like structure with the borate (bold) and cyanine (light). (Reprinted with permission from ref 158. Copyright 1998 American Chemical Society.)

thene]. The solid-state structure of the cyanine borate shows a significant overlap with interring distances ranging from 3.5 to 4.0 Å, permitting π stacking between adjacent cyanines and borates. Vertical stacks of the subunit produce a ladder-like structure with the borates forming the rails and the cyanines acting as horizontal 'rungs' (Figure 9). This shows that the cyanine moieties come closer to borate through quinonyl rings canted such that the nitrogen atom points toward the central boron atom, which is likened to a canted front-side penetration of the dye. Large substituents on the nitrogen atoms of some substituted cyanines prevent nitrogen forward penetration of the dye into the borate due to steric hindrance but instead favor backside penetration with the nitrogen atom of the quinonyl ring pointed away from the borate center, as in the case of the 3,5-di-*tert*-butylbenzyl group attached to the nitrogen atom of cyanine. In nonpolar solvents, such as benzene, cyanine dyes form penetrated ion pairs with chiral borate anions, which exhibit an induced CD spectrum, attributed to the formation of a twisted dye in the penetrated ion pair.[159] In benzene, $PhCy_{Me}^+3MeSpB^-$ has a larger induced CD ($\Delta\epsilon = 1.9$ cm^{-1} M^{-1}) than $PhCy_{Me}^+2MeSpB^-$ ($\Delta\epsilon = 1.7$ cm^{-1}M^{-1}). Solid-state structural analysis shows both the orientations, i.e., nitrogen canted forward and nitrogen-backward penetration of the cyanine moieties into the borate cavity. The solution behavior is dominated by

nitrogen-forward penetration of the cyanine dyes. Kodaka[160] has inferred that when the structure of the cyanine–borate pair changes to favor nitrogen-backward penetration, then the sign of the CD spectrum would also reverse. The strength of the induced CD spectrum is tunable through variation of the structure of both borate and cyanine moieties.

Spitler et al.[161] compared the electron-transfer process for a series of cyanine dyes (**14, 61−63**) to the conduction band of AgBr by picosecond time-resolved steady-state fluorescence techniques. The
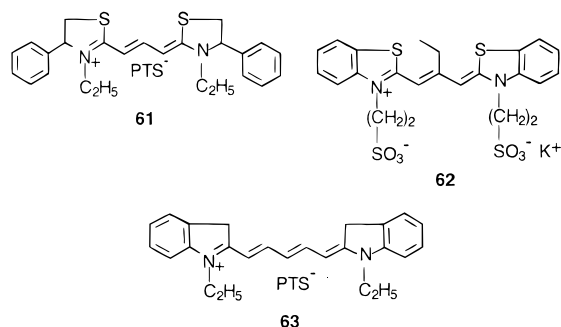
selected dyes have monomeric absorption spectra in the adsorbed state. These dyes were chosen to satisfy the following experimental conditions, necessary for reliable estimates of k_{et} (rate constant for electron transfer).

(a) The surface coverage of the monomeric dyes is such that energy transfer for one molecule is independent of the other. Under such a condition, fluorescence lifetime becomes a measure of the electron-transfer rate in the solid.

(b) The photon flux on the dye-adsorbed surface is not high enough to avoid degradation of the dye molecule.

(c) Temperature studies over a large range have been carried out to determine activation energies.

The k_{et} representing the rate constant for the initial step in the sensitization of the latent image formation by the dye varies between 2.7×10^8 and 3.7×10^9 s^{-1}. The authors supported the electron-transfer model for spectral sensitization of the silver halides.

VI. Photodimerization and Isomerization

The cyanine dyes undergo photodimerization and cycloaddition reactions extensively on irradiation. Quina and Whitten[162] reported the photochemistry of N-(1-octadecyl)-4-stilbazole (**64**) and N-octadecyl *trans,trans*-1-phenyl-4-(4-pyridyl)-1,3-butadine (**65**) in the solid state, in monolayers, and in micelles.
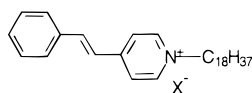
64: X = Cl-C$_6$H$_4$SO$_3$, BF$_4$,
Br, Br-C$_6$H$_4$SO$_3$
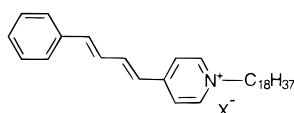
65: X = Cl-C$_6$H$_4$SO$_3$, BF$_4$, Br

In the solid state and monolayer assemblage, the salts undergo dimerization and show excimer fluorescence, but in micelles and in solvents, the salts undergo cis−trans isomerization and show monomer fluorescence. Saltiel et al.[163] reviewed the photoprocesses such as cis−trans isomerization, dimerization, and excimer and exciplex formation of olefins and dienes.

A. Dimerization

Cockburn et al.[164,165] studied the [2+2]-cycloaddition reaction of 2′,4-styryl pyridinium methosulfate salt (**66**−**69**) attached to PVA. Excimer formation takes place, and the cyclodimerization is favored due to preorganization of the styryl pyridinium group in the PVA matrix. They observed that the 4-styryl pyridinium salts are more efficient than 2-styryl ones for cycloaddition reactions. Ichimura and co-workers[166−169] synthesized a number of PVA (poly-(vinyl alcohol)) and PMA (polymethacrylate) containing styryl pyridinium (SP) and styryl quinolinium (SQ) groups (**70**−**73**). In general, the 4-SP salts are more efficient than the 2-isomers for cycloaddition reactions. The viscosity of PVA is found to increase with increasing concentration of **70** and **71**. A bathochromic shift is observed on increasing the PVA concentration, and on dilution, a hypsochromic shift of the fluorescence maximum due to the SP group takes place. Quantum yield for excimer fluorescence increases when the PVA is modified with **71**. Compounds **72** and **73,** and their formyl derivatives, are water soluble and highly photosensitive. The photosensitivity is due to aggregation of the photofunctional groups in the polymer matrix with the correct geometry for cyclodimerization upon irradiation. The absorbance of **73** decreases at 420 nm and increases at 320 nm on irradiation with light of 430 nm wavelength; reversal effects have been noticed on exposure to light at 330 nm. This arises from an equilibrium involving formation of a cyclobutane ring
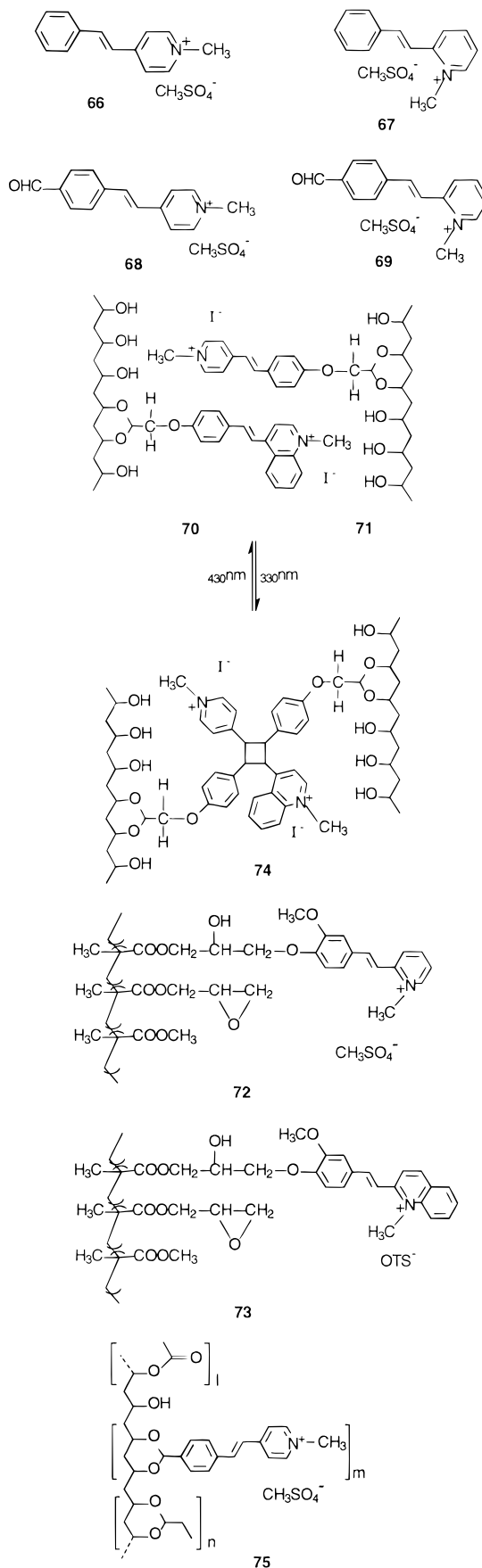
74. The PMA containing γ-isomers of both SP and SQ units is 10 times more sensitive than that with the α-isomers, which is opposite to the behavior observed in PVA. Finally, these authors concluded

Scheme 8
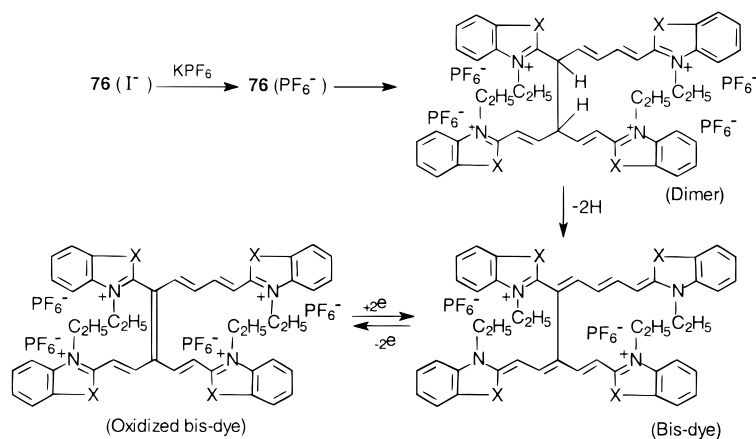
that the PVA containing SP/SQ units has photoresist properties with respect to high sensitivity and good storage stability. The high photosensitivity with low contents of photosensitive groups depends on the nature of the group that tends to self-aggregate. Photosensitive PVA is also quite suitable for the immobilization of enzymes. The PMA polymers containing SQ groups show excellent storage stability. Shinoda et al.[170] observed an increase in the rate of cyclodimerization of SP dye attached to PVA–PA (polyacrylamide) block copolymer. Uhlich et al.[171] carried out the hydrophobization of PVA with propionic aldehyde and subsequent incorporation of a pendant styryl pyridinium group (**75**). Upon UV irradiation (300 nm), this type of polymer undergoes [2+2]-photocycloaddition to form a more hydrophobic network that is swellable in organic solvents. This range of polymer network is widely used for entrapment of enzymes. ESR spectra using spin probe technique determines the difference in solvent penetration into polymers of different hydrophilicity/hydrophobicity.

Lenhard and Parton[172] observed one-electron oxidation of alkyl-substituted dicarbocyanine dyes to form radical dications (**76**). The reversible dimerization of the dications in acetonitrile has been studied by NMR spectroscopy and cyclic voltametry at room temperature. The probable favored dimerization sites are at the even methine carbons of the dye, and the process is reversible in the presence of alkyl substituents at these positions. From ESR studies, Oehling and Baer[173] also proposed that the odd electron in the radical dication of cyanine and carbocyanine dyes resides at even-numbered methine carbons. The thermodynamic parameters for **77** are $K_d = 350 \times$

10^{-7} M at 10 °C, $\Delta G = 5.6$ kcal/mol, $\Delta H = 12.2$ kcal/mol, and $\Delta S = 22.5$ cal/mol·deg and those for **78** are $K_d = 7.0 \times 10^{-7}$ M at 10 °C, $\Delta G = 7.7$ kcal/mol, $\Delta H = 16.4$ kcal/mol, and $\Delta S = 29.8$ cal/mol·deg. The relative rate of dimerization and dissociation are dependent on the nature of the heterocyclic unit and the type of alkyl substituent at the methine carbon. They also studied the radical dication formation of dicarbocyanine dye (**76**) by one-electron oxidation in the absence of alkyl substituent at even methine carbon.[174] The dyes undergo irreversible dimerization in methanol and acetonitrile solution. The dimer formed undergoes further oxidation to bis-dye, and the linkage occurs at the 8,10′-position due to the absence of alkyl substitution (Scheme 8). The studies on radical dications formed from cyanine dyes offer an excellent tool for study of the electronic and steric effect on radical stability.

Ischenko et al.[175] studied the radical formation of 1,3,3-trimethyl-2-[7-(1,3,3-trimethyl-1,3-dihydro-2*H*-2-indolylidene)-1,3,5-heptatrien-1-yl]-3*H*-indolium (**79**) chloride, iodide, and perchlorate by photoinduced electron transfer from anion to cation of the dye in benzene; this process is also favored by sensitization with anthracene. Sakamoto and Ohno[176] studied the

76:   X = S, Se, O, C$_2$H$_2$

77

78

79:   X = Cl, I, ClO$_4$

electron-transfer process of cobalt pthalocyanine tetrasulfonic acid and cobalt pthalocyanine octacarboxylic acid by cyclic voltametry.

Gromov et al.[177] observed the (2+2)-autophotocycloaddition of styryl dye containing benzo-15-crown 5-ether group and 2′,4-(*N*-sulfopropyl)quinolinium (**80, 81**) residue in acetonitrile solution in the presence of Mg(ClO$_4$)$_2$ and Ca(ClO$_4$)$_2$. This process has also been observed in styryl dyes containing benzo crown ether and benzothiazolium residue (**82**) with a sulfopropyl or ethyl group and their complexation with Mg^{2+} by surface-enhanced Raman scattering (SERS) spectra.[178] The dimers dissociate with increasing metal ion concentration leading to formation

80

81

82: R = $(CH_2)_3SO_3^-$,

= C_2H_5 (ClO_4^-)
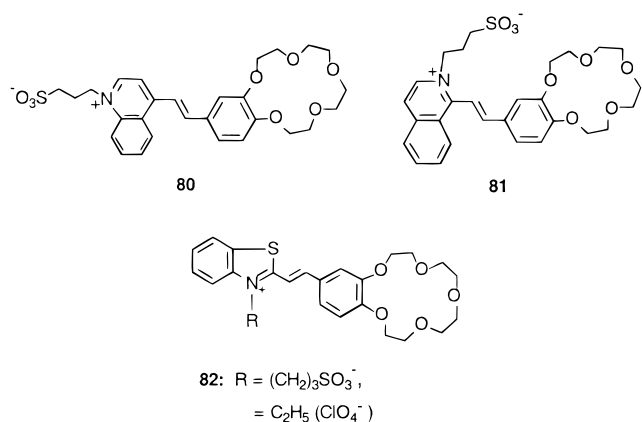
of the trans isomer of the metal complex. Stereospecificity of photocycloaddition depends on the organization of the dimers of trans isomers in complexation with Mg^{2+} or Ca^{2+}. The dissociation of dimer to the trans isomer leads to high regio- and stereoselective products. The styryl dyes containing 15-crown-5-ether and *N*-sulfobenzyl spacer on complexation with Mg^{2+} in acetonitrile give dimeric product[179] which on photolysis undergoes cis isomer formation leading to stereospecific [2+2]-autocycloaddition to give cyclobutane derivative.

The photostability of cyanine dyes containing indolenium and quinolinium units is found to increase with introduction of cyclic units into the polymethine chain and decreases with increases in the length of the chain, as reported by Li et al.[180] The photofading is due to dimer formation via a photooxidation process.

The exciton chirality is a versatile microscopic method for determining the absolute configuration and conformation of molecules possessing two or more chromophores in solution without reference compounds.[181,182] Cyanine dyes have been investigated for use in the exciton chirality method. Berova et al.[183] synthesized a bis-cyanine (**83**) with a 1,2-cyclohexane linkage. These dyes yield stable acylates

83: X = Cl : **a**

= TFA : **b**
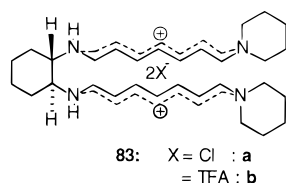
and Schiff bases with a red-shifted intense UV−vis maximum. The bis-cyanine dye, **83b**, shows two distinct and widely separated bands at 550 (ϵ = 182 000) and 480 nm (ϵ = 191 000), whereas monomeric cyanine absorbs at 515 nm (ϵ = 207 000). Two CD Cotton effects of opposite sign [λ_{ext} 546 ($\Delta\epsilon$ = −232) and 475 nm ($\Delta\epsilon$ = +231)] were exhibited by **83b**. This large difference of about 70 nm is ascribed to the exciton interaction between the two side-chain chromophores. The origin and nature of the large separation of the two intense bands in electronic and CD spectra of chiral **83b** has been clarified by theoretical calculations of the UV−vis and CD spectra using the π-electron SCF−CI−DV MO method. The signs of the exciton-split Cotton effects are

opposite from those expected from the data of dibenzamide and bis(*p*-methoxy cinnamide) derivatives and therefore indicate that the cyanine side chain adopts a unique conformation. The authors claimed that compounds **83** appear to be the first examples displaying two distinct largely separated exciton-split bands. Thus, the cyanine dyes **83** can provide a powerful tool for CD studies, for example of biopolymer conformations in solution.

B. Cis−Trans Isomerization of Cyanines

The photochemical cis−trans isomerization is one of the most important fundamental processes in photochemical and photobiological processes.

William et al.[184] studied the photochemical isomerization (trans−cis) of a series of styryl pyridinium dyes (**84**) by UV irradiation in aqueous and 50% (v/v) MeOH−H_2O solutions. They also observed dimer

84

85
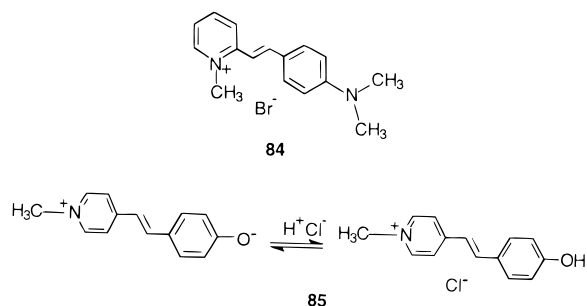
formation upon long irradiation of the dye solutions. Steiner et al.[185] studied the photochemical and thermal isomerization of merocyanine dye and observed conversion of the trans to cis form only from the O-protonated form of the dyes (**85**). The conversion of **85** from the trans to the cis isomer of **85** was established by ^{1}H-NMR spectroscopy. The *J*-value of the ethylenic protons of the trans isomer is 16.2 Hz, and that of the cis isomer is 12.1 Hz. Abdel−Kader and Steiner[186] observed the conversion of the trans to the cis isomer of stilbazolium betain dye by irradiation in daylight or by a halogen lamp. The kinetics of trans−cis isomerization are suggested to be first order and are very sensitive to changes in temperature and solvent. Picosecond laser flash photolysis study reveals that the cis−trans conversion of stilbazolium betaine and its protonated form occurs via a excited singlet state (S_1).[187]

Behera et al.[188] synthesized the cis isomer of the hemicyanine dye (**86b**) by a novel method using Ag_2O as the catalyst. The probable mechanism of isomer-

86: R = C_nH_{2n+1} (n = **a:** 1; **b:** 3; **c:** 5; **d:** 6; **e:** 8;
f: 10; **g:** 12; **h:** 14; **i:** 16; **j:** 18).
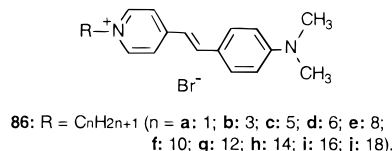
ization is given in Scheme 9. The structure of the cis isomer has been confirmed by ^{1}H NMR (J_{trans} = 16.11 Hz and J_{cis} = 8.79 Hz) and by mass spectral evidence. The base peak at m/e 207 for cis isomer (trans isomer gives a base peak at m/e 224) has been explained[188] (Scheme 10). They investigated the absorption and

Scheme 9

Scheme 10
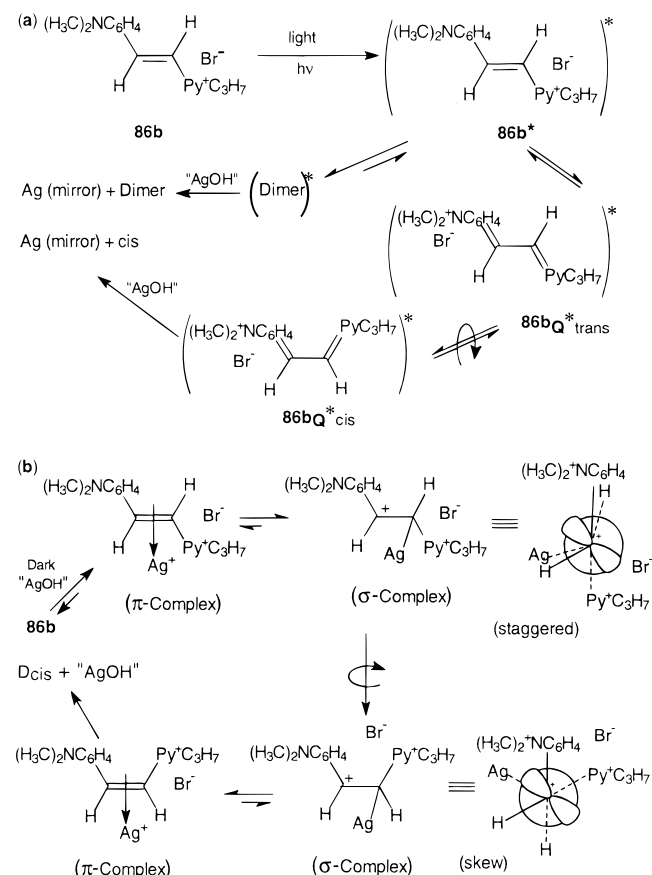
fluorescence emission spectra and fluorescence lifetime of the aminostyryl pyridinium dyes (**86**) with various alkyl chain lengths in organic solvents and in surfactant solutions.[189] The results have been interpreted in terms of the coexistence of the trans, cis, and perpendicular quinoid ($Q_\perp$) form of the dyes (Figure 10), the relative concentration of the isomers
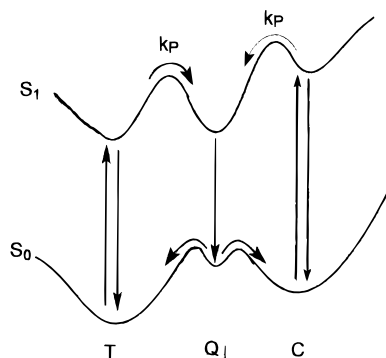
Figure 10. Potential energy diagram which explains the possible coexistence of the three isomers of **86** in organic solvent and in surfactant solution. The quinoid form is the intermediate structure between the cis and trans isomers.

depending upon the dye−solvent and dye−surfactant interaction. The formation of the cis isomer is found to be favored in TX-100 solution.

Considerable experimental[190−196] and theoretical studies[197−199] on the dynamics of isomerization processes in solution were carried out during the 1980s. The photoisomerization of the cyanine dye DODCI
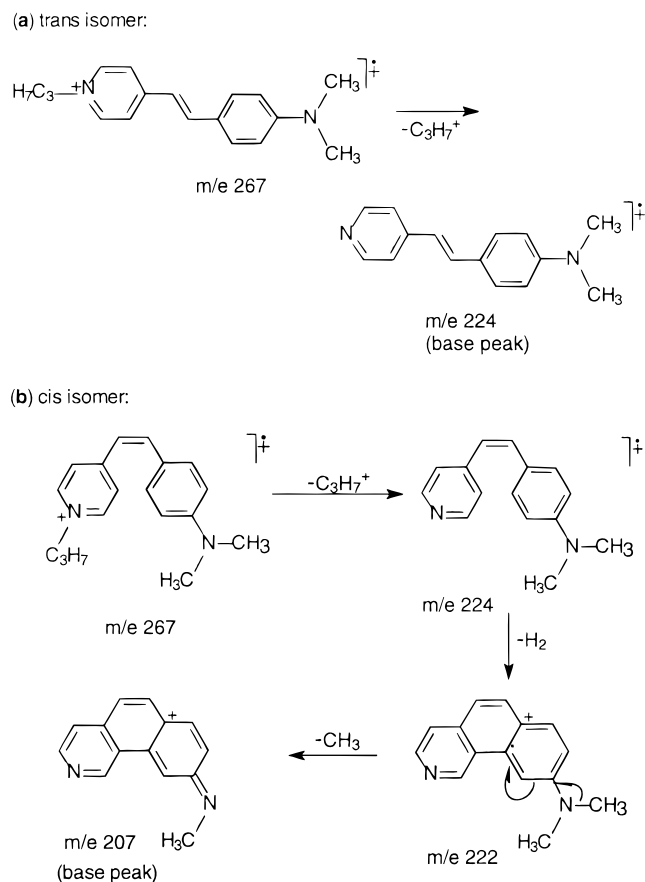
(3,3′-diethyloxadicarbocyanine iodide, **87**) was studied by absorption and emission spectroscopy. On

87
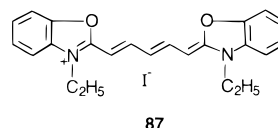
excitation to the S_1 state, DODCI relaxes to the ground-state photoisomer (I form) with a yield of 10%. Bäumler and Penzkofer[200] reported that the ground state of DODCI (N form) is in a coiled-up cis-cis conformation whereas the I form is an elongated all-trans conformation (Figure 11). Hara and Akimoto[201] investigated the ground-state isomerization rate of DODCI via laser photolysis under high pressure (up to 500 Mpa) in a series of alcohols. The intrinsic activation energy and activation volume of isomerization are 13.0 Kcal/mol and 1.0 cm³/mol, respectively. The sterically nonhindered cyanine dyes reveal relatively weak fluorescence (Φ_f), low quantum yield of intersystem crossing (Φ_{isc}), and t → c photoisomerization via the excited singlet state ($\Phi_{t \to c}$).[201−209]

Various workers observed that electron-transfer processes occur in cyanines in specific ion pairs in the excited singlet state,[210,211] whereas the triplet state is involved in encounter complexes.[212] Sterically nonhindered cyanines are found to show[203,213] (i) t → c photoisomerization via the S_1 state, (ii) relatively weak fluorescence, and (iii) very low probability of ISC. In contrast, some bis-cyanines show an increase
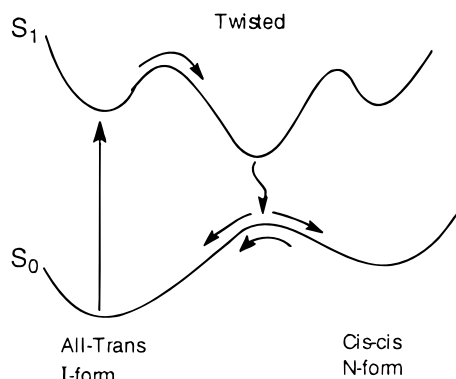
Figure 11. Schematic potential energy diagram for DOD-CI (**87**) photolysis. (Reprinted with permission from ref 201. Copyright 1991 American Chemical Society.)

Figure 12. Probable potential energy diagram for describing the photophysical and photochemical feature of the dye **88**−**95**. (Reprinted with permission from ref 216. Copyright 1996 The Royal Society of Chemistry.)

in the quantum yield for ISC (Φ_{isc}). Ischenko et al.[214] have shown that the bis-cyanines show a decrease in $\Phi_{t \rightarrow c}$ due to restriction of the flexibility resulting in an increase of Φ_{isc}.

Chibisov et al.[213,215] studied the photoisomerization process of 1,1′,3, 3,3′,3′-hexamethyl indocarbocyanine perchlorate (**88**), its iodide (**89**), and their substituted derivatives (**90**−**95**) by time-resolved spectroscopy in weakly and strongly polar solvents.[216] The fluores-

	R	R'	X
88:	H	CH_3	ClO_4
89:	H	CH_3	I
90:	CH_3	CH_3	ClO_4
91:	Cl	C_4H_9	ClO_4
92:	Cl	$C_{10}H_{21}$	ClO_4
93:	Br	C_4H_9	ClO_4
94:	CN	CH_3	ClO_4
95:		CH_3	$2ClO_4$

cence quantum yield of **95** (Φ_f = 0.012 at 24 °C, τ_f = 0.2ns) in ethanol is too small compared to dyes **88**−**94** (Φ_f = 0.1−0.2 at 24 °C, τ_f = 0.43−0.98ns). Φ_f increases with decreasing temperature (Φ_f = 0.7−0.9 at −196 °C) and with an increase in viscosity due to hindrance toward rotation around one of the three central double bonds in the first excited singlet state. The quantum yield (Φ_f) depends significantly on the medium and mesosubstituent in the polymethine chain. Relatively small substituents such as CH_3, Cl, and Br produce little variation in Φ_f and $\Phi_{t \rightarrow c}$, whereas bulky substituents such as the 1,3,3-trimethylindoline-2-ethenyl group (**95**) decrease the fluorescence with an increase on k_{rot} and t → c photoisomerization. This strong enhancement of $\Phi_{t \rightarrow c}$ is probably because of a shift to the cis side of the minimum in the S_1 surface (Figure 12). The substitution of groups such as CF_3SO_2 or NO_2 in the 5- and 5′-position of the aryl ring of indocarbocyanine shows a 2-fold increase in the fluorescence lifetime (τ_f) and quantum yield (Φ_f).[217]

The lower activation energy for **95** (i.e., 37 kJ/mol), as compared to the other (**88**−**94**) dyes (~50 kJ/mol),

is probably due to the presence of a second positive charge in the ion. Ion pairing in less polar solvents, like toluene, decreases the thermal cis−trans isomerization. The specific ion-pairing also is found for 1,1′-dibutyl-3,3,3′,3′-tetramethyl indocarbocyanine (**91**, **93**) and its derivatives with different mesosubstituents in nonpolar solvents such as benzene, but in polar solvents the free form of the ion dominates.[211,212] Electron transfer in the ion-pair form occurs in the excited singlet state with an increase in Φ_f (0.12−0.55) and τ_f with a concomitant decrease in $\Phi_{t \rightarrow c}$ (0.25−0.13). The increase in τ_f in nonpolar solvent compared to that in polar solvent for 1,1′-sulfopropyl-5,5′-dichloro-9-ethylthiacarbocyanine (**96**) reveals the equilibrium between the all-trans and a mono-cis isomer in the ground state.[218]

96
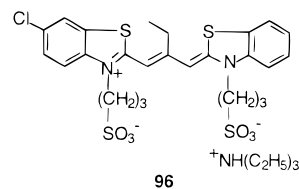
Serpone and Sahyun[219] studied the subnanosecond relaxation dynamics of two dithiacarbocyanine [3,3′-didodecyl dithia-2,2′-carbocyanine bromide (**97**) and 9-ethyl-3,3′-dihexadecyl dithia-2,2′-carbocyanine perchlorate (**98**)] in CH_2Cl_2 by picosecond transient absorption spectroscopy. Intersystem crossing to an
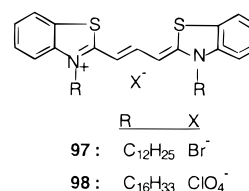
	R	X
97:	$C_{12}H_{25}$	Br^-
98:	$C_{16}H_{33}$	ClO_4^-

isomerizable excited state, together with internal conversion, plays a major role in radiationless deactivation of the excited state due to torsional motion of the polymethine chain. The isomerization is shown to occur from the long-lived triplet state of the dyes.

Alfimov et al.[220] studied the trans−cis isomerization of indolenine-based crown ether containing styryl dyes (**99**) doped into poly(vinyl butyral) film or

polyacrylamide hydrogel by UV irradiation. The cis

99
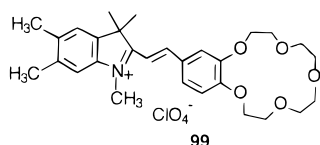
isomer is proposed to be relatively stable, having a reversible dark transformation constant $\leq 10^{-5}$ s^{-1}. The radiationless relaxation of dicyanine molecules in C$_{1-4}$ *n*-alkanols was studied by picosecond fluorescence and time-resolved spectroscopy.[221] The existence of two ground-state conformers was observed to be dependent on the viscosity of the medium, temperature, and fluorescence wavelength.

Kosaka et al.[222] observed that the less crowded 1,1′,3,3,3′,3′-hexamethyl indocarbocyanine tetrakis-(phenyl ethylynyl)borate (Cy$_{Me}^+$PEB$^-$) (**100**) on irradiation forms the cis isomer and shows a longer lifetime than cis-Cy$_{Me}^+$PF$_6^-$ due to hindered isomerization to the all-trans form. Thus, the restricted

100
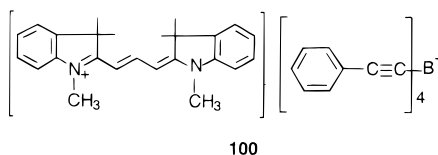
environment of the penetrated ion pair enhances the fluorescence quantum yield for Cy$_{Me}^+$PEB$^-$ compared to Cy$_{Me}^+$PF$_6^-$.

C. Photocoloration of Spiropyrans

Spiropyrans (Sp) belong to a class of compounds that have been intensively studied[223−228] because of their powerful potential in information processing. The Sps exist in a colorless closed form (**a**), which is photoconverted reversibly into the colored, open merocyanine (**b**) form. Chibisov and Görner[229] furnished evidence for photochemical conversion of the spiropyrans (**101a**−**103a**) and trans-form merocyanines (**101b**−**103b**) to the cis form with submillisecond lifetimes at ambient temperature. The fluores-

	R	R′
101:	H	CH$_3$
102:	C$_3$H$_4$	CH$_3$
103:	OCH$_3$	CH$_3$
104:	H	CH$_2$CH$_2$OH
105:	H	(CH$_2$)$_2$O−C−C
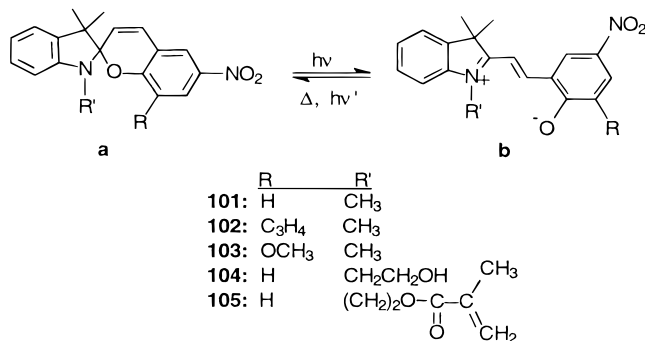
cence quantum yield (Φ_f) for t → c photoisomerization is small for **88** (0.038) and **94** (<0.06) with respect to **93** (0.19). The trans isomer of all the dyes **88**, **93**−**95**, and **101**−**103** exhibit weak and strong fluorescence in ethanol at 24 and −196 °C, respectively. The photocoloration of SP is observed in solvents of low polarity, and the extent of it is reduced in polar

solvents. The nitro group in the 6-position of the benzopyran portion of SP strongly enhances the quantum yield of intersystem crossing to the triplet pathway for photocoloration (Figure 12). The formation of the ^{3}T* state of merocyanine prior to trans and cis isomer formation has been investigated more recently by Görner.[230] The photochemical ring opening was found to be suppressed with formation of T−T absorption of spiropyran in viscous media. The quantum yield was reduced with a decrease in temperature and an increase in ^{3}T* state population. The increase in the triplet lifetime in highly viscous media is due to restricted rotation.

Krongauz et al.[231] studied the photoisomerization of spiropyran (A form, **104**) to merocyanine (B form, **106**) by laser photolysis in methylcyclohexane and in micelles and proposed dimer formation (AB) from the direct excitation of spiropyran and the formation of A$_2$B from the triplet excited state (^{3}A*).

106
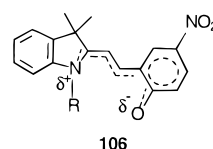
Kalyski and Williams[232] studied the laser-induced absorption of the dye (**105**) in nonpolar solvents, and the results agreed with the model proposed by Krongauz et al.[231] A related study of picosecond transient absorption on **101** indicates the formation of **107** with a *cis*-cisoid conformation in <10 ps.[233]

107

108
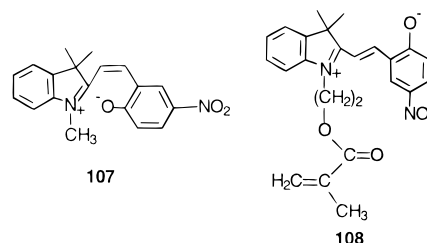
Kalisky et al.[234] proposed a mechanism that is in contradiction to the view of Krysanov and Alfimov.[233] They studied the conversion of **105a** to **105b** in toluene, methylcyclohexane, and acetonitrile by picosecond and nanosecond transient absorption spectroscopy. In nonpolar solvents, the direct isomerization of singlet excited state (^{1}A*) to the *trans*-transoid (**108**) form was observed, whereas in a solvent like acetonitrile, the *cis*-cisoid (**107**) form was more stabilized in the excited state and undergoes radiationless deactivation to the ground state.

VII. Photodynamic Therapy

Certain cyanine dyes such as merocyanines and ketocyanines have been studied extensively as potential photosensitizers for photodynamic therapy (PDT)[235,236] and as radiation sensitizers[237] for solid tumor treatment. Attempts have been made to elucidate the mechanism of photosensitizer transport and the factors leading to localization and retention in the tumor. Both hydrophilic and hydrophobic pthalocyanines are under investigation for use in

PDT. Reddy et al.[238] used a lipophilic Zn(II)–pthalocyanine dye as a photodynamic agent for tumor.

Recently Dhami et al.[239] studied the photophysical behavior of *cis*-disulfonated aluminum pthalocyanine (AlPcS$_2$) in unilamellar vesicles (liposomes) of DL-α-dipalmitoyl-phosphatidylcholine. The wavelength of absorption of *cis*-AlPcS$_2$ in the liposome was found to be 670 nm, and no aggregation occurred even at higher concentrations of the sensitizer (AlPcS$_2$). The decrease in fluorescence quantum yield (0.48 to 0.23) and the decrease in triplet quantum yield (0.24 to 0.04) by increasing the sensitizer concentration (0.76 to 12.2 μM) and the independence of the triplet lifetime of the concentration of the dye ($\tau_t = 1200 \pm 100$ μs; water: $\tau_t = 500$ μs) indicate incorporation of the dye into the liposome. The fluorescence lifetime is biexponential due to the existence of two species. With increasing sensitizer concentration (0.76 to 10.5 μM), the longer lifetime decreases (6.8 to 4.8 ns) with a decrease in amplitude (93% to 53%) and the shorter lifetime remains nearly same (~2 ns) with an increase in amplitude (7% to 47%). This suggests a biphasic distribution of the fluorophore within the liposome. These results were compared to the incorporation of AlPcS$_2$ in leukemic K562 cells,[240] which has been studied by fluorescence imaging and time-resolved spectroscopy. It also showed biexponential decay upon irradiation, indicating the existence of two species. The amount of long-lived components increases (55% to 85%) and the short-lived component decreases (45% to 15%) with increasing the irradiation time (1 to 90s); the fluorescence quantum yield also increases after irradiation. The results observed on long irradiation in leukemia cells resemble those observed with low sensitizer concentration in liposomes and vice-versa. Thus, the sensitizer AlPcS$_2$ is first accumulated in organelle membranes (liposome/endosome) and then goes into the tumor cell on irradiation. Due to the absence of aggregate formation, these dyes can be used as good sensitizers for PDT.

Merocyanine 540 (**109**) is generally used as a potentiometric sensor.[241,242] It also displays a selective recognition for leukemia cells and has been proposed as a reagent for both diagnosis and treatment of early stage leukemia by PDT.[243–245] The intracellular dye (**109**–**115**) acts as a phototoxin to destroy the host cells under illumination due to the long-lived triplet excited state of the dye which plays an active role in the whole process. This dye is also poorly soluble in water and forms aggregates but is readily soluble in alcohols, micelles, and plasma membranes.[246,247] The dominant photoprocess involves isomerization from the first excited singlet state possessing an all-trans conformation[248] to a long-lived cis isomer.[249]

For merocyanine 540 (MC540) derivatives to be clinically useful, (1) photoisomerization, which competes with intersystem crossing and radiation deactivation, has to be curbed and (2) highly fluorescent dye should be photobleached in cellular media[246,250] to recognize leukemia. Rapid photobleaching in cellular media to recognize leukemia cells under visible illumination is an important factor relating to the availability of highly fluorescent merocyanines.[246] Harriman and co-workers have shown that photosensitization depends on the temperature,[251] viscosity, and polarity of the surrounding medium,[252] the energy of the excited singlet state,[253] the nature of the heteroatom in the aromatic and barbiturate subunits,[253] the molar volume of the rotor, and the size of the aromatic group.[248] Further, it was reported by Benniston et al.[248] that the photosensitization does not depend much on the water-solubilizing sulfonic acid residue or the length of the alkyl chain.

Photobleaching occurs via oxidative attack of singlet molecular oxygen produced from the long-lived triplet excited state on the polymethine chain.[254] Thus, a group of merocyanine fluorescent dyes giving no triplet state, useful for detection purposes, and another group of such dyes displaying high triplet yield, useful as phototoxins, are needed. Photoisomerization has no role in these applications.[255] The photophysical behavior of a series of merocyanine dyes having different heteroatoms in the terminal aromatic and barbituric acid unit has been reported to modulate the quantum yield for the formation of the lowest energy excited triplet state.[253] The presence of heavy atoms enhances the triplet yield by spin–orbit coupling[256] and changes the rate and yield of isomerization.

Thus, compound **113** containing Se was shown to be a potent photosensitizer. The lipophilicity increases by the inclusion of heavy atoms and possesses high toxicity toward leukemia cells due to high intracellular solubilization and faster rate of uptake into infected cells to improve biological activity.

To obtain more information about the isomerization process, Benniston et al.[257] prepared MC540 derivatives by insertion of *n*-butyl substituents into the polymethine chain (**116**). Internal conversion from

116

the first excited state to the ground-state plays the dominant role in the photophysical properties of MC540. Torsional motion of the double bond attached to the benzoxazole subunit[248] and the rate of incorporation into Daudi cells, which are a B-lymphoblastoid cell line that binds and activates T cells,[258] is controlled by the length of the alkyl chain attached

	X	Y	
109 :	O	S :	MC$_{540}$
110 :	C(CH$_3$)$_2$	S	
111 :	S	S	
112 :	Se	S	
113 :	Se	O	
114 :	Se	Se	
115 :	O	O :	OXO

to the thiobarbiturate subunit. The site of isomerization is unknown, but it is usually assumed that the internal conversion occurs via rotation around the central double bond of the polymethine chain[259] to give the cis isomer. Photoisomerization in cyanine dye[260] and bisoxonols[261] with a related structure occurs at the first double bond of the polymethine chain. The presence of a bridging unit favors the all-trans conformation by its restricted rotation.[257] The rate of intersystem crossing to the triplet manifold and nonradiative decay from the lowest energy triplet state are unaffected by the bridge unit, indicating that ISC occurs from a thermally relaxed first excited singlet state and not from the transition state or from the unstable cis isomer. The site of isomerization has been identified for the first time, and the importance of internal torsions has been realized. Recently, Benniston et al.[262] investigated the resonance polarity and rate of photoisomerization of 'MC540' (**109**) and 'OXO' (**115**) dyes in ethanol. The OXO dye has more hydrophilic character than MC540, and that is associated with an increase in the rate of photoisomerization and a decrease in the triplet yield. The compound also shows little aptitude for the production of singlet molecular oxygen under illumination in aerated solution. Further, the OXO dye is also found to resist chemical oxidation by $^1\Sigma O_2$ in solution. It was also shown that the OXO dye is more persistent than MC540 under illumination and shows strong fluorescence after assimilation into HL60 leukemia cell.[263] The overall activities of Benniston et al.[262] suggest that the presence of heavy Se atom (**114**) is more effective to PDT and the light oxygen atom (**115**) for diagnosis.

VIII. Dyes in Organized Systems

Various types of cyanine dyes have been used as fluorescent probes to study membrane potential in various cells. Membrane potentials in human and in synaptosoma preparations have been investigated primarily with oxacarbocyanine dyes.[264]

The cyanine dyes have been used extensively as sensors for the examination of polypeptide β-sheet structure in solution and also in thin films.[265] Several NIR (near-infrared) carbocyanine dyes containing different functional groups have been preferentially used as fluorescent probes for DNA, lipids, peptides, and proteins.[266−268] Asymmetric cyanine dyes containing the methyleneoxy benzothiazole unit were used as models for binding double-strand nucleic acid.[269]

The microheterogeneous environment in complex biological systems, or in relatively simple and well-characterized model systems, was also studied by fluorescent molecules whose emission properties are sensitive to changes in environment.[270−272] The sulfocyanine dyes are good candidates for this purpose and have been widely used.[273] Even though a variety of fluorescent molecules are used as probes for studying the polarity of microheterogeneous media, electron-donor−acceptor molecules are generally preferred because of the sensitivity of intramolecular charge-transfer (ICT) fluorescence. The amphiphilic nature of the probe is a structural strategy to study

different pockets of an organized medium.[270,272,274−276] Membrane-surfactant interaction studies are of considerable importance for exploiting the application of detergents in biotechnology to activate, extract, and purify intrinsic enzymes. To explain the mechanism of these interactions, probes such as cyanine dyes are used. In general, cyanines and merocyanines satisfy the structural requirements and therefore have been used as good probes to study various microenvironments. The interaction of dyes with a surfactant either decreases or increases its critical micelle concentration (CMC), depending on the nature of the dyes and the surfactant and their aggregational behavior.

In various dyeing industries, dye surfactant interaction is important because surfactants are used as solubilizers for various water-insoluble dyes. Sometimes electrolytes may also be used to improve dye-surfactant binding. Dyes are sometimes classified as a type of surfactant as they form small or large aggregates, depending on the structure and concentration of the dye.

The polarity of several pockets of bio- or chemoorganized systems is ascertained indirectly from the knowledge of the response of the dyes to solvents of various polarities. The influence of the solvent on the spectral behavior of compounds is called solvatochromism.[277]

A. Solvatochromism

Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) shifts in solvents of various polarities. These dyes are also ascribed a large change in dipole moment upon excitation due to the relative contribution of both dipolar zwitterionic benzenoid and neutral quinoid forms.[278−285] Therefore, these dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of the ground and Franck−Condon excited state, due to the absorption of electromagnetic radiation in the UV−vis region. If the ground state is more stabilized than the excited state due to solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck−Condon principle,[286] the time required for molecules to be excited ($\sim10^{-15}$ s) is much smaller than that required to execute vibration or rotation ($\sim10^{-12}$ to 10^{-10} s); the position of the nuclei of the absorbing entity (i.e., absorbing molecule + solvation shell) does not change during electronic transition. Therefore, the first excited state of the molecule in solution, called the Franck−Condon excited state, has the same solvation pattern as in the corresponding ground state, called the equilibrium ground state.

The first Franck−Condon excited state is much more dipolar than the ground state due to intramolecular charge transfer upon excitation. Stabilization of the Franck−Condon excited state before and after relaxation to the equilibrium excited state and the destabilization of the Franck−Condon ground state relative to the equilibrium ground state by dif-

ferential solvation leads to the positive solvato-(fluoro)chromism (solvatochromic fluorescence band). Positive solvato(fluoro)chromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases.

Reichardt[287] compiled several solvatochromic compounds which have been used in developing empirical scales of solvent polarity. He placed special emphasis on the UV−vis and near-IR region with spectral reference to the $E_T(30)$ scale developed by using the negatively solvatochromic pyridinium N-phenolate betaine dyes. This scale can be easily evaluated by using eq 2, where λ_{max} is the maximum of the longest wavelength i.e., the intramolecular CT $\pi-\pi^*$ band of the dye.

$$E_T(30) \; (\text{kcal/mol}) = 28591/\lambda_{max} \; (\text{nm}) \qquad (2)$$

To avoid the non-SI unit kcal/mol and the conversion of $E_T(30)$ values to kJ/mol, the normalized E_T^N has been introduced[288] and is defined by eq 3.

$$E_T^N = \frac{E_T \, (\text{solvent}) - E_T \, (\text{TMS})}{E_T \, (\text{water}) - E_T \, (\text{TMS})} = \\ \frac{E_T \, (\text{solvent}) - 30.7}{32.4} \qquad (3)$$

During the 1990s, several other reviews[289−293] were published emphasising the use of various empirical solvent polarity scales in many physicochemical processes. These are the Z scale of Kosower,[294] the χ_R and χ_B scales of Brooker et al.,[295] the RPM (relative polarity mass) scale of Dahne et al.,[296] the E_{LMCT} (ligand metal charge transfer) scale of Armand et al.,[297] the π^* scale of Kamlet, Abboud, and Taft (KAT),[298] the π^*_{azo} scale of Buncel et al.,[299] the E_{Ni} scale of Freyer,[300] the P_s (spectral polarity index) of Middleton et al.,[301] the $E_T(30)$ scale of Dimroth et al.,[302] the E_K scale of Walther,[303] the E^*_{MLCT} scale of Lees et al.,[304] the $E_{CT}(\pi)$ scale of Kaim et al.,[305] the E_T^{SO} scale of Walter et al.,[306] the E_B scale of Wrona et al.,[307] the ϕ scale of Dubois et al.,[308] the S scale of Zelinskii et al.[309] and Brownstein,[310] the Y scale of Grunwald,[311] the A_m scale of Knauer and Napier,[312] the G scale of Schleyer,[313] the log k_Z scale of Drougard and Decrooeqs,[314] and the Py (or pyrene) scale of Dong and Winnik,[315] which was further developed by Acree et al.[316] Several multiparameter equations have been constructed to explain the solvent effect. Though a large amount of progress has been made in the calculation of solute−solvent interactions by the use of modern quantum mechanical methods, these empirical parameters continue to be of immense utility to chemists working in the laboratory.

Brooker[317] and Kiprianov[318] independently observed the solvatochromic behavior of merocyanines. Among the merocyanines, stilbazolium betains (**117**) are more important because of their (a) large negative solvatochromic shift of >6500 cm^{-1} ($\lambda_{max} = 620$ nm in chloroform, 442 nm in water, 605 nm in pyridine); (b) large second-order hyperpolarizability, which is useful for nonlinear properties; (c) photolytic/photochemical reaction cycle, which can be used as a chemical model for the storage and subsequent

Scheme 11
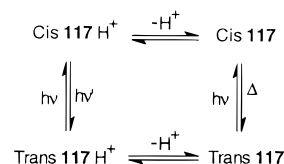
regeneration of information in biological systems (Scheme 11); (d) use as diagnostic and therapeutic agents.[319]
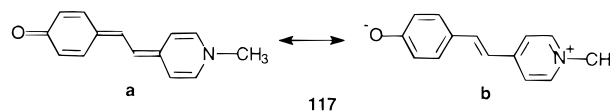
Interestingly the merocyanine dyes show an inverted solvatochromism,[280] i.e., their long-wavelength absorption band first exhibits a bathochromic shift followed by a hypsochromic shift with increasing solvent polarity. This reversal in solvatochromism has been rationalized by semiempirical MO calculation[280,281] and the results confirmed by Jacques[282] using spectroscopic measurements in mixed solvents. This aspect of merocyanines was not reviewed by Reichardt.[287] From the calculated transition energy values of **117**, Luzhkov and Warshel[283] found λ_{max} values of 389 and 477 nm in polar and nonpolar solvents, respectively, and reported negative solvatochromism. Morley[284] arrived at λ_{max} values of 587 and 470 nm in polar and nonpolar medium, respectively, by employing AM1 optimized structures and CNDOVS methods and has proposed positive solvatochromism of **117**. Da Silva et al.[285] also observed reversal in solvatochromism for dyes with the general structure **118** in chloroform and dichloromethane only. This reversal in solvatochromism has been explained by variation of the hybrid structure between nonpolar (**118a**) and dipolar extremes (**118b**).
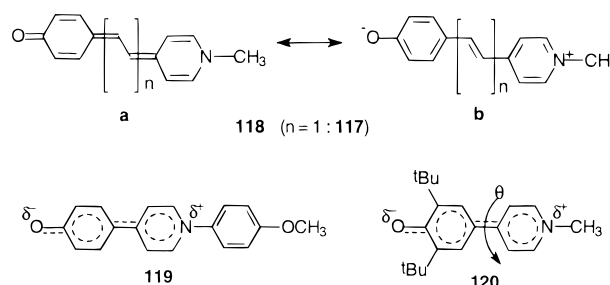
Reichardt et al.[320] noticed negative solvatochromism only for **119** ($n = 0$), a derivative of **118;** this contradicts the hypothesis of da Silva et al.[285] To improve the solubility behavior of **118**, da Silva et al.[285] used compound **120** (where $n = 0$); because it is soluble in solvents of low polarity, the cis−trans isomerism is not possible since the unsaturated bridge is absent. Therefore, the reversal effect cannot arise from isomerism.

Compound **120** exhibits negative solvatochromism throughout the investigated polarity range (E_T^N range 1.00−0.052).

Catalan et al.[321] denied the phenomenon of reversal of solvatochromism proposed by Botrel et al.[280] and

Scheme 12

(a) M_b M_{pm} (b) M_q

122

Scheme 13

a: ground state   **b:** Frank-Condon excited state   **c:** Relaxed excited state
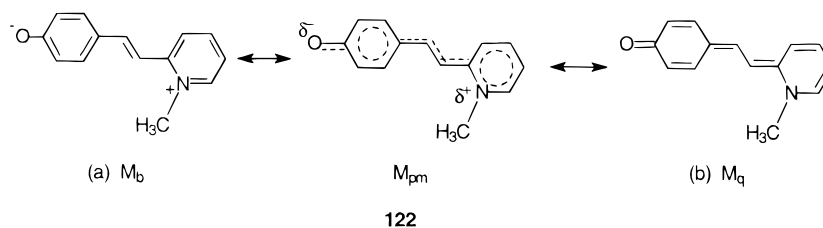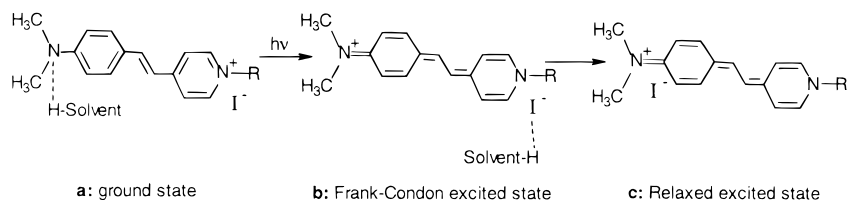
Jacques.[282] They explained that the solvatochromism arises from splitting of electronic levels by vibrational states. Niedbalska and Gruda[322] also opposed the idea of reversal of solvatochromism and proposed aggregation phenomena in solution to explain the results. Catalan et al.[321] studied the more lipophilic dye **121** which shows multiple bands in the visible region. The presence of two *tert*-butyl groups in-

121
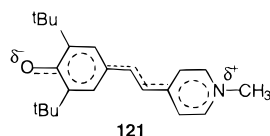
creases the solubility of **121** in nonpolar solvents, reduces the sensitivity to hydrogen bonding, and thereby decreases the sensitivity to solvatochromism.

Da Silva et al.[285] rationalized the reversal of solvatochromism theoretically for dye **117** and **121** by considering the theoretical polarity scale, *P*s. Merocyanine dye **122** shows solvent-sensitive fluorescence.[323] Dye **122** is found to exhibit both benzenoid (M_b) and quinonoid (M_q) forms as a result of intramolecular charge transfer (Scheme 12). This agrees with the report of Dimroth and Reichardt[324] for pyridinium-*N*-phenoxide betaine dye. The strong hypsochromic shift of **122** with increasing polarity of the solvent is considered an interaction between the total dipole moment of the solvent molecules with the dipolar solute molecule, which also decreases the Taft's π^* and α (hydrogen bond donor ability) parameters and increases the energy of the ground state by decreasing the solvent cage of oriented solvent molecules around dipolar solute molecules. On the basis of valence-bond theory, an intermediate mesopolymethine (M_{pm}) form is proposed (Scheme 12).

The uncertainity in the work of Jacques[282] and Catalan et al.[321] arises because the Spanish group included data from protic solvents in their plot, whereas later workers explicitly avoided such solvents, which would mask and distort the correlation between ν and π^*. When Catalan's data were plotted with the precaution of Jacques (omit data points for solvents with Taft's α values different from zero), a shallow concave curve was obtained indicating re-

versal of solvatochromism in the zone of low polarity. Similarly, a shallow concavity was discernible in the curve of ν vs E_T^N for **121** but not for **119**. Da Silva et al.[285] made an attempt to answer to the question as to why dyes such as **117** and **121** show solvatochromic reversal whereas **119** and **120** do not. They argued that all their compounds exhibit solvatochromic reversal at the same point along the theoretical polarity coordinate; the actual observation depends on the position along that coordinate.

Mishra et al.[325] reported the reversal in solvatochromism of a new class of cyanine dyes (**123**) by using the $E_T(30)$ solvent polarity scale[326] and found that the point of reversal is a switch that differentiates hydrogen-bond donor and hydrogen-bond acceptor solvents. The reversal in the solvatochromism is

123:   X = o-OH, p-OH ; n = 3, 4, 5
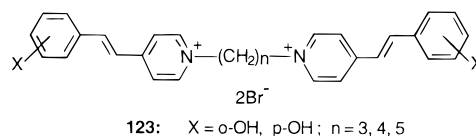
found to occur at an $E_T(30)$ value of 49.7, which is independent of the nature of the spacer and the position of the hydroxyl group. Da Silva et al.[285] also observed the reversal effect of merocyanines in dioxane and THF with a switch at $E_{(T)}$ = 37.0.

Ansari[327] studied the absorption and emission characteristics of four styryl pyridinium dyes (**86a, 124−126**) in various solvents. The absorption maxi-

124:   R = C$_2$H$_5$
125:   = CH$_2$CH(CH$_3$)$_2$

126
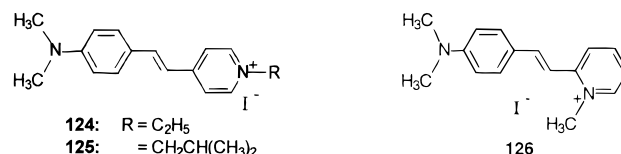
mum of these dyes depends on the polarity and hydrogen-bonding ability of the solvents; a marked hypsochromic shift was observed with increasing polarity or acidity of the solvent; however, no solvatochromism is observed in the emission spectra. A mechanism was proposed to explain this phenomenon (Scheme 13). Strong hydrogen-bonding solvents stabilize structure **a** and thereby the electron-donating

Scheme 14[a]
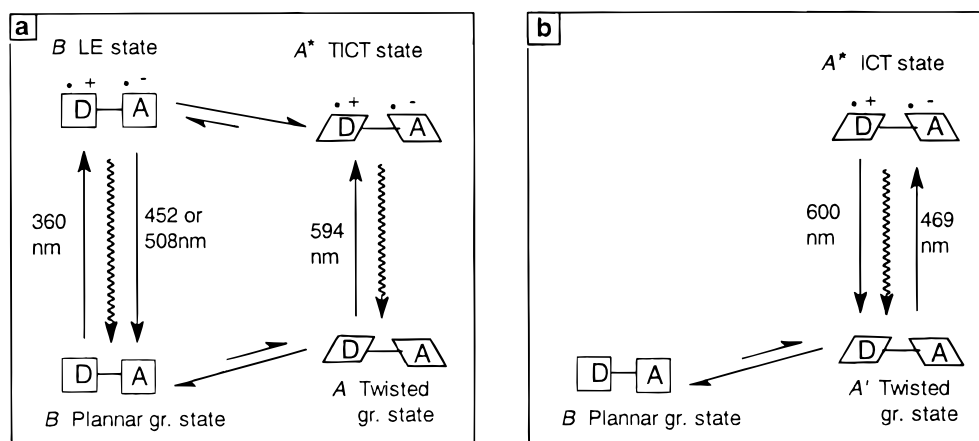
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Table 1. Effect of Medium Viscosity on the Quantum Yield of Fluorescence for 128 at 295 K for the ICT Band with Excitation at 360 and 469 nm[a]

		360 nm				469 nm			
sokitten69lvent	η (cp $\pm4\%$)	$10^3\Phi_F$ ($\pm5\%$)	λ_{max} (nm)	$10^3\Phi_F$ ($\pm5\%$)	λ_{max} (nm)	$10^3\Phi_F$ ($\pm5\%$)	λ_{max} (nm)	$10^3\Phi_F$ ($\pm5\%$)	λ_{max} (nm)
water	0.95	1.14	442	1.50	508	1.36	594	1.71	600
sucrose−H$_2$O (280 g L^{-1})	1.70	2.50	447	1.49	516	3.87	596	5.09	600
glycerol−H$_2$O (560 g L^{-1})	5.25	6.20	459	1.68	520	14.1	597	36.7	602
PEG-6000−H$_2$O (100 g L^{-1})	5.75	3.65	448	2.94	516	6.16	595	11.1	602
ethanol	1.36	6.01	446	16.7	525	7.8	580	6.7	604

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Table 2. Activation Energies for Both CT Bands for 128 in Different Solvents, Excited at 360 and 469 nm, and for Viscocity of Solvents (kcal/mol)[a]

solvent	ΔE (360) ($\pm10\%$) 1	ΔE (360) ($\pm10\%$) 2	ΔE (360) ($\pm10\%$) 3	ΔE (469) ($\pm10\%$)	ΔE ($\pm8\%$)
water	2.3	2.2	4.3	4.2	3.8
sucrose−H$_2$O 280 g L^{-1}	2.3	1.4	4.9	4.9	4.9
glycerol−H$_2$O 560 g L^{-1}	5.5	2.6	6.9	7.0	5.9
PEG-6000-H$_2$O 100 g L^{-1}	2.4	2.7	5.0	4.7	4.8

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ability of the nitrogen, and also the ICT interaction with the pyridinium moiety decreases. In the Franck–Condon excited state, hydrogen bonding takes place between solvent and iodide ions and stabilizes **b**, and prevents its mobility to the **c** form. The energy gap between the Franck–Condon excited state and relaxed excited state is small and increases with a decrease in the acidity of the solvents. So structure **c** is stabilized in solvents of low polarity (low acidity), since these solvents do not hydrogen bond with the iodide anions. These salts show an oxidation potential of 0.6−0.7 V.

Wandelt et al.[328] studied the fluorescence band of **127** associated with different excitation wavelengths. An explanation has been proposed to explain the effect of solvent viscosity and temperature on the fluorescence of the dye containing a donor and acceptor system, (Scheme 14). When excited at 360
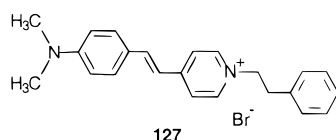
127

nm, the dye shows a dual fluorescence[329−332] band which is due to a characteristic viscosity-sensitive low-energy TICT emission and emission due to a locally excited (LE, **a**) or "nonpolar state" with a geometry and dipole moment similar to the ground state. On excitation at 469 nm, an ICT state **b** results. Excitation at 360 nm results in a broad spectrum that has been decomposed to three Gaussian emission peaks, which on curve-fitting analysis show absorption maxima at 442, 508, and 594 nm, respectively, in aqueous solutions. Irradiation at 469 nm resulted in a structureless emission at 600 nm similar to the deconvoluted 594 nm peak. The Debye−Stokes−Einstein hydrodynamic model[333] has been used to describe accurately the reorientation dynamics of the probe. The near identical energy of activation values for both CT bands suggest that the origin of the corresponding emitting species is the same. The effect of viscosity on the quantum yield due to these bands and the activation energies for both CT bands are given in Tables 1 and 2.

Soper and Mattingly[334] studied the fluorescence behavior of the two near-infrared-sensitive (NIR) dyes IR-125 (**128**) and IR-132 (**129**) to evaluate the solvent dependence and the independent nonradia-

Scheme 15[a]
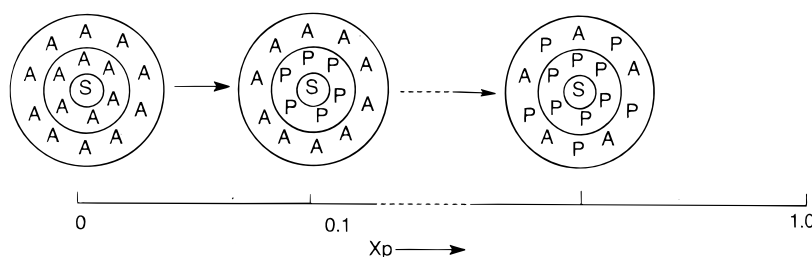
tive relaxation pathway. The fluorescence quantum

128

129
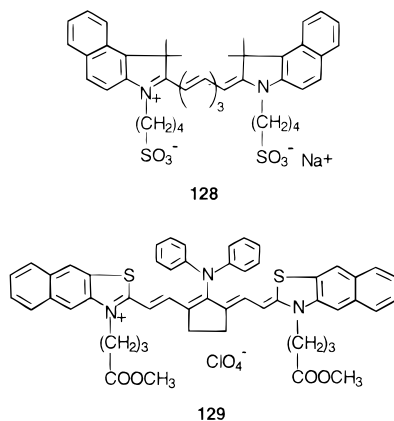
yield and lifetime in alcoholic solvents were found to be higher than in aqueous solvents due to the decrease in nonradiative rates in alcohols. IR-132 forms a dimer or higher aggregate in water (dimer form = 739 nm and monomer form = 811 nm), whereas IR-125 does not show any aggregated structure due to its higher solubility in aqueous solvents arising from the negatively charged sulfonic group providing a sphere of solvation. For IR-132 and IR-125, the red shift in absorption with an increase in the length of the alkyl chain of the alcoholic solvent (i.e., increasing nucleophilicity) is attributed to the nucleophilic solvation of the cationic center of the dye. The following are the structural requirements for tricarbocyanine dyes with NIR sensitivity: (a) Incorporation of charged group to prevent aggregation; (b) Exclusion of heavy atoms in the chromophore of the dye; (c) Incorporation of bridging group in the polymethine chain to reduce rate of internal conversion; (d) Inclusion of large heteroaromatics in the terminal group; (e) Use of organized media to shield the dye from the strong hydrogen-bond-donation effect of the solvents.

Bagchi et al.[335] studied the environmental effect on the ground and excited state of a ketocyanine dye (**130**) via observation of absorption and emission characteristics in various solvents. The correlation

130: R^1
     R^2

131: $R^1 = CH_3$, $R^2 = Ph$
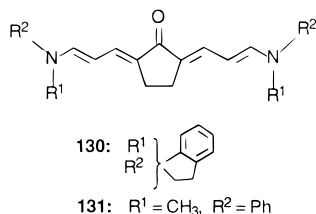
of fluorescence maximum with $E_T(30)$ implies ICT excited states. The enhanced fluorescence sensitivity $E(F)$ shows strong hydrogen bonding in the excited state in polar protic solvents and stabilization of the S_1 state by solvation. Solute−solvent complexation also is indicated in polar aromatic hydrocarbon and cyclic ether solvents. The ketocyanine dyes (**130** and **131**) show strong hydrogen bonding in protic solvent and preferential solvation (PS) in protic(P) and aprotic(A) solvent mixture.[336] The PS increases in more protic solvents. A solvation model has been proposed (Scheme 15).

The stilbazolium merocyanine dye 3-[2-(hydroxy-substitued aryl)vinyl]benzo[c]quinolizinium perchlorates (**132**) shows negative solvatochromism in its deprotonated form in the visible region.[337] The nega-

132
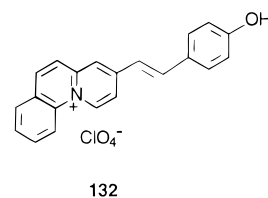
tive solvatochromism of benzo[c]quinolizinium is more efficient than the isomeric dye having a benzo[a]quinolizinium nucleus.

Hebert et al.[338] studied the solute−solvent interaction of the unsymmetrical cyanine dye (**133**), the photostability of which increases due to faster occurrence of the S_1−S_0 nonradiative internal conversion process. The decrease in absorption maximum with

133
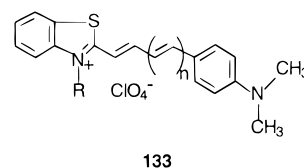
increasing polarity of the solvent shows the dye to be highly polar in the ground state with positive charge residing on the benzothiazole nitrogen, which induces a large orientation transition of the surrounding solvent molecules. A less polar Franck−Condon excited state is involved during absorption that decreases the solute−solvent interaction.

Cao et al.[339] carried out a theoretical study of the solvent effects on the ICT of the dye (**86a**). Unlike dimethylaminobenzonitrile (DMABN), this dye does not exist in TICT state and does not show dual fluorescence.[340] They optimized the geometry of both the trans and the cis states and observed that in the

lower energy trans-optimized geometry, the phenyl and the pyridyl rings and the ethylene moiety are in one plane. The trans form is more stable than the cis form by 0.01 hartree in the gas phase. Furthermore, positive charge is concentrated with pyridyl nitrogen in the ground state while in the first excited state the positive charge is more evenly distributed over the whole molecular system (Table 3). Their

Table 3. Mulliken Charge Distribution of 86a in the S_0 and S_1 State[a]

group	S_0	S_1
$-N(CH_3)$	0.101	0.269
aniline group	0.136	0.422
double bond	0.050	0.003
pyridyl ring + CH_3	0.714	0.306

[a] Reprinted with permission from ref 339. Copyright 1998 American Chemical Society

calculation indicates that the ground-state barrier to trans−cis isomerization is higher in more polar solvents ($E_{S1}-E_{S0}$ in hartree: 0.1006, 0.1017, 0.1019, 0.1022, and 0.1024 in solvents of dielectric constants 1, 10, 20, 40, and 78, respectively) so that rotation around the central double bond is restricted. Hence, the earlier findings that the benzenoid form dominates over the quinoid form in more polar solvents[341] is supported by their theoretical calculation. These authors were also able to explain the solvent dynamics in the line broadening mechanism.

Periasamy et al.[342] also observed the existence of the quinoid form by studying the behavior of the hemicyanine dye DiA (N-methyl-4-[4-dihexadecylamino]styryl pyridinium iodide (**134**) in n-alcohols ($n = 1-11$) via time-resolved spectroscopy. The

Benzenoid   Quinoid

134
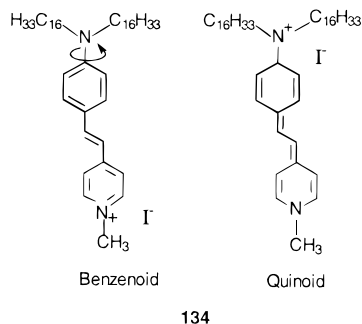
fluorescence decay of DiA was predominantly single exponential (∼0.98%, $\tau_1 = 0.09-0.60$ ns) in the alcohols ($n = 1-7$) with a weak component (∼0.02%, $\tau_2 = 1.0 \pm 0.1$ ns) whereas for $n = 8-11$ a biexponential decay was observed ($\tau_1 = 0.65-1.47$ ns, 39−67%) with an increase of the second component ($\tau_2 \approx 1.0$ ns, ∼52%). With increasing viscosity (0.55 to 14 cP) and change in the dielectric constant (33.7 to 7), the τ_1 value (corresponding to the benzenoid form) increases whereas the τ_2 value (corresponding to the quinoid form) does not change. Thus, these data suggest that the change in benzenoid form is due to the viscosity-dependent nonradiative process occurring by the intramolecular rotation about the R_2N-C bond.

B. Behavior in Surfactants

Behera et al.[343] studied the solubilization of dyes **26** and **135** in CTAB surfactant solution by absorp-
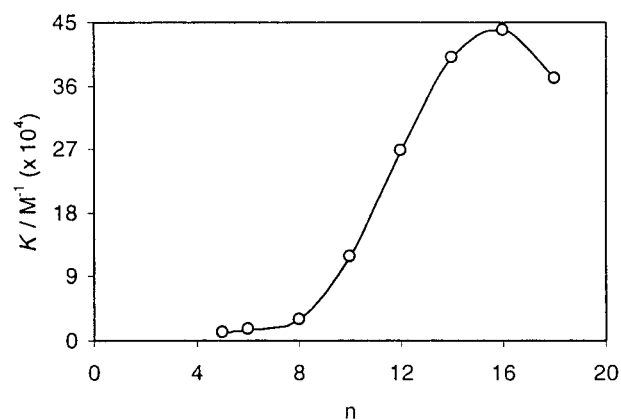
Figure 13. Plot of association constant (K) of the dye with CTAB micelle versus the number of carbon atoms (n) in the alkyl chain of **86**. (Reprinted with permission from ref 344. Copyright 1997 The Bulletin Chemical Society Japan.)

tion and conductance measurements. They proposed

135: X = $N(CH_3)_2$, OCH_3, Cl, OH
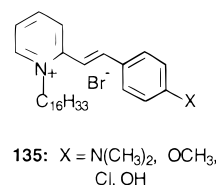
a mixed micelle formation between the dye and the surfactant. The solubilization of the dye in the CTAB micelle is due to interaction with the long alkyl chain of the dye. They observed that substituents have no role in the solubilization behavior of the dye.

The interaction of aminostyryl dyes (**86**) with CTAB, SDS, and Triton-X-100 surfactants has been investigated by Behera et al.[344−346] The interaction of dyes with CTAB[344] is found to be dependent on the hydrophobic chain of the dye, which is not perceptible up to five carbon alkyl chain. The interaction, as reflected in the binding constant (K_M) (Table 4) of the

Table 4. Average $E_T(30)$ Value for the Location of the Dyes (86) and the Binding Constant (K_M) in a CTAB and TX-100 Environment[a]

no. of carbons (n) in the alkyl chain	CTAB		TX-100		
	$E_T(30)$	K_M ($\times 10^4$) in M^{-1}	$E_T(30)$	K_M ($\times 10^4$) in M^{-1}	K_S ($\times 10^4$) in M^{-1}
C_1	62.8		62.2	4.93	0.662
C_3	62.8		61.37	5.38	0.552
C_5	62.8	1.23	56.35	16.15	1.787
C_6	61.0	1.48	54.4	17.28	10.397
C_8	59.2	2.93	51.4	18.45	12.23
C_{10}	57.7−57.1	11.9	50.0	20.60	24.30
C_{12}	57.1−56.0	26.77	49.1	21.19	25.88
C_{14}	57.1−56.0	39.94	49.1	24.76	27.93
C_{16}	57.1−56.0	43.76	49.1	27.42	28.49
C_{18}	57.1−56.0	37.07	49.1	27.98	17.04

[a] Reprinted with permission from refs 344 and 346. Copyright 1997 The Bulletin Chemical Society of Japan and Copyright 1998 Elsevier Science, respectively.

dye-micelle system, attains a maximum for the C_{16} chain because of compatibility (Figure 13). From the studies of the electronic and emission spectra they proposed that a micelle has a hydrophobic force field (F_H) and the dyes are localized in various pockets of
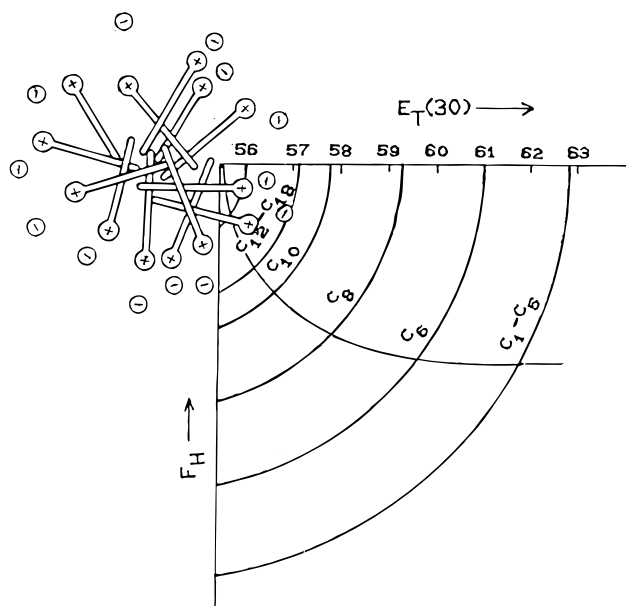
Figure 14. Schematic representation of localization of dye in a CTAB micellar force field gradient with respect to $E_T(30)$ scale. The asymptotic curve is a quantitative representation of the decrease of hydrophobic force (F_H) field with distance. (Reprinted with permission from ref 344. Copyright 1997 The Bulletin Chemical Society Japan.)

the field (Figure 14). They delineated the average E_T-(30) values (Table 4) of the micellar environment in which the dyes are located. The dyes, however, are found to behave differently in SDS micelles. From the absorption and fluorescence spectra and binding constant values, Behera et al.[345] proposed that (a) C_1-C_8 dyes solubilize in the micelle and the chromophore occupies a methanolic–ethanolic environment, (b) $C_{10}-C_{14}$ dyes exist both as an extended monomer and as folded species in the presence of SDS, which is reflected in two Gaussian peaks in the absorption spectra, (c) the experimentally obtained absorption spectra for C_{16} and C_{18} dyes can be explained by three Gaussian peaks due to monomer and dimer in the absence of surfactant and two such peaks due to monomer and folded monomer in the presence of surfactants. The authors suggested that just as a milliped retracts into a coil by stimulation, the long chain of the dye may be similarly folded such that the chromophoric group enjoys a hydrocarbon-like environment. This explanation supports the Menger or Fromhertz model of the micelle. The behavior of various dye–SDS systems has been ilustrated in Figure 15. TX-100 was found to act as a fluorescence switch for these dyes.[346] Behera et al.[346] reported a solubilization strategy for the dyes in TX-100 micelles. TX-100 contains a polyoxyethylene chain with a terminal hydroxy group, which has a crown ether like structure; the nonpolar part contains a benzene ring with branched chain. The average $E_T(30)$ values of the micellar environment in which the dyes are located are given in Table 4. The binding constant (K_M) of the dyes with the micelle and with the premicellar aggregates (K_S) was evaluated by the authors (Table 4). They observed that the binding constant of the lower homologues of the dye increases by almost 7−9 times upon

micellization with TX-100; however, with increasing chain length, the ratio (K_M/K_S) falls and almost becomes constant at C_{10}. Therefore, the dye molecules appear to have a strong affinity to a polyoxyethylene group and are incorporated into its exterior region. With micellization of the surfactant, the binding becomes stronger and as a result the value of K_M increases by about 7 times. Increasing the hydrophobicity of the dye by increasing the chain length increases the sensitivity of interaction of the dye with the surfactant monomers or premicellar aggregates. They proposed that the dyes may be adsorbed on the surface of the surfactant monomers or premicellar aggregates and the value of K_S does not alter on micellization. Thus, they concluded that the hydrophobicity plays a dominant role in the interaction of the dyes with TX-100.

Kaschny and Goni[347] studied the spectral characteristics of anionic merocyanine 540 (**109**), cationic pinacyanol chloride (**34**), and uncharged nile red (**136**) by a model membrane incorporation method at various concentrations of nonionic surfactant (TX-100), since this surfactant has a widespread application in biochemical systems. All these dyes show a marked solvatochromic behavior and therefore are used as probes in studying membrane–surfactant interactions.[246,348] They observed that **109** orients parallely (≈80%) or perpendicularly (≈20%) to the membrane surface. In the latter case, the polar sulfonate group remains at the phospholipid head-group region and the tetramethylenic tails are buried in the hydrophobic region. In the former case, monomers undergo rapid dimerization with an antiparallel arrangement with both sulfonate groups oriented toward water. The dimerization of **109** is caused by a detergent-induced increase in polarity at the phospholipid acyl chain.[348] Dye **34** is found to be solubilized in the polar headgroup region of TX micelles, while dye **136** anchors into the lipophilic membrane core. It has been concluded that electrostatic forces

136
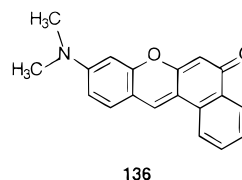
play a minor role in the membrane–surfactant interactions.

Shah et al.[349] studied the behavior of six hemicyanine dyes (**137a–f**) in CTAB micelles and the effect of the alkyl chain during solubilization. They pro-
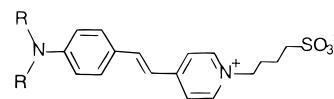
137: R = CnH2n+1 (n = 1- 6: **a** - **f**)

posed that the longer the alkyl chain of the dye, the greater the penetration into the micelle. The partition coefficient and standard free energy of penetration of dyes are found to increase with increasing alkyl-chain length from C_1-C_6 (Table 5). They proposed
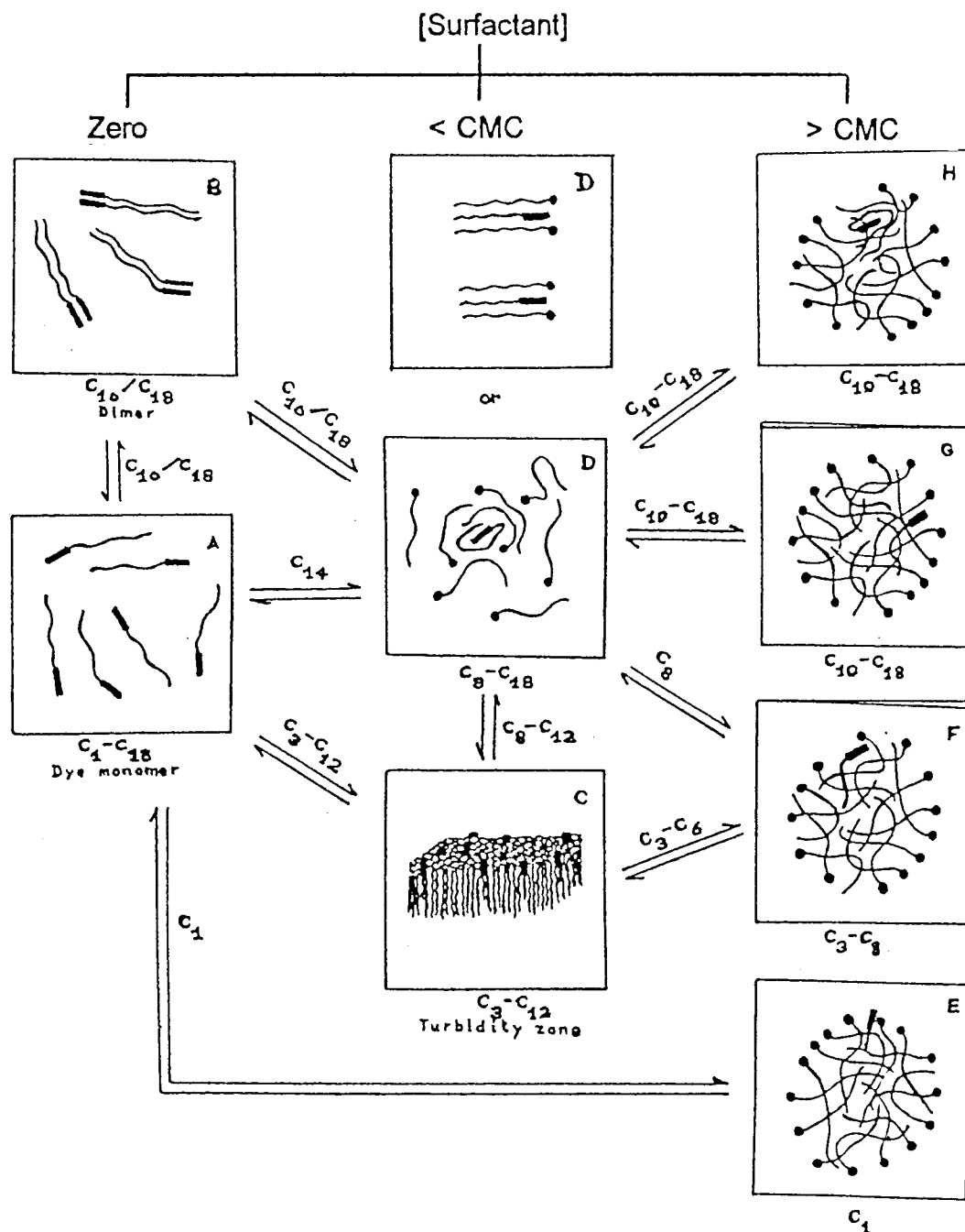
Figure 15. Structural hierarchy of the dyes (**86: C_1-C_{18}**) in 2% MeOH with varying concentration of SDS. Cationic dye molecules with varying chain length: ■~. Surfactant molecules (SDS): •~. (A) C_1-C_{18} dye monomers in 2% MeOH. (B) $C_{10}-C_{18}$ dimers in 2% MeOH. (C) Probable structure of the turbidity of C_3-C_{12} dyes and SDS (<CMC). (D) Coiling of C_8-C_{18} dyes below the CMC of SDS. (E−H) Localization of the chromophoric headgroup at various distances from the micellar interface. (Reprinted with permission from ref 345. Copyright 1999 Elsevier Science.)

Table 5. Partition Coefficient (K_X) of Hemicyanine Dyes (138a−f) between the Aqueous and Micellar Phases and the Standard Free Energy Changes of Penetration of the Dyes ($\Delta G°_P$) (at 25 °C)[a]

	dye **138**					
	a	**b**	**c**	**d**	**e**	**f**
K_X (±4)	74	334	2269	23905	54812	147657
$\Delta G°_P$ (kJ/mol) (±0.005)	10.67	14.39	19.15	24.96	27.30	29.48

[a] Reprinted with permission from ref 349. Copyright 1997 Academic Press Inc.

that due to the presence of polar headgroup, the dye molecule does not penetrate deep into the micelle;

with an increasing chain length of the alkyl groups (R), the dyes make their way into the interior of the micelle. The penetrability of the micelles by the amphiphilic additives has been estimated to be 0.42.

Visser et al.[350] studied the time-resolved fluorescence anisotropy decay of the voltage-sensitive styryl pyridinium dye RH421 (**137e**) in various organic solvents and in micellar systems. They proposed a precursor−successor mechanism of the dye in the solvent system whereby a second fluorescent species is formed in the excited-state reaction involving a primary excited precursor.[351] From the two or three exponential decay functions, the location of the dyes

is proposed to be at different sites in the micellar system, i.e., at the interface emitting blue photons and at the interior of the fluid region emitting red photons. This dye was used by Visser et al.[352] to study the time-resolved fluorescence anisotropy in DMPC vesicles, enzyme ribulose-1,5-biphosphate carboxylase/oxygenase (rubisco), and Na$^+$, K$^+$ ATpase containing membrane fragments with a view to know if the dye responds to changes in membrane potential or changes in configuration of the membrane protein. They observed that the addition of tetraphenyl borate (TPB), which induces an intramembrane electric field, increases the fluorescence lifetime and rigidity of the membrane- bound dye. Two mechanisms have been proposed by different workers to explain the spectral changes of membrane-bound RH421 on application of electric field: (a) an electrochromic mechanism[353] and (b) a reorientation/solvatochromic mechanism.[354] The electrochromic mechanism involves the direct effect of the electric field on the electronic distribution caused by the absorption of light. As a result, the energy of the ground and excited states are stabilized and destabilized, respectively, to varying degrees, resulting in a shift in the position of the absorption band. The latter acts by an electric-field-induced reorientation of the whole dye molecule within the membrane. Loew[355] has shown that the cyanine dye (**138**) is buried in the membrane interior, where it is shielded from the electrical effects in the adjacent aqueous solution. In

138
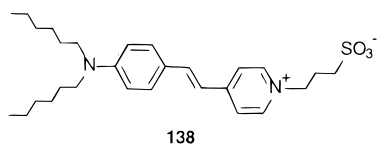
such a case, the dye experiences a change in its local polarity, which causes changes in the position and intensity of the absorption band. Visser et al.[352] found that the order parameter (S) of the membrane-bound dye molecule increases from 0.53 to 0.68, the cone angle for the wobbling motion[356] decreases from 48° to 40°, and the average lifetime of the red emission is found to increase from 1.88 to 2.505 ns (33% increase) in the presence of TPB. Results in DMPC vesicles can be well explained within the framework of the reorientation/solvatochromic mechanism. The lifetime, order parameter, and wobbling cone angle in Na$^+$, K$^+$-ATpase membrane fragments are 2.56 ns, 0.87, and 25°, respectively. Comparison of these data to those in DMPC vesicles indicates significantly greater restriction is caused by the Na$^+$, K$^+$-ATpase. The rotational correlation time increases from 0.54 ns in ethanol[348] to 131 ns in rubisco. This slowness indicates tight binding of the probe to the enzyme, and therefore, the dye has no independent motion but rotates together with the whole protein.

Ephardt and Fromherz[357] delineated a reaction scheme for excited dibutyl aminostilbazolium butyl sulfonate (**137d**) involving: (a) the ground-state trans and cis conformations, (b) a locally excited fluorescent state (**F**) reached from **T** state, (c) a perpendicular **P** state which is on the photoisomerization pathway,
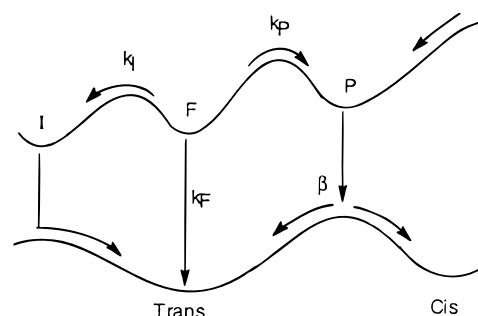
Figure 16. Probable reaction scheme for the excited **138**. (Reprinted with permission from ref 357. Copyright 1989 American Chemical Society.)

and (d) a twisted intramolecular charged transfer (TICT) state **I**. The **P** state decays by internal conversion to the ground state forming trans and cis isomers, whereas the **I** state decays only to the trans isomer (Figure 16). These classes of dyes are frequently used as fluorescent probes to follow the fast change in electrical membrane potential in neurons, since their emission properties are sensitive to the polarity of the medium. So the increase in emission lifetime clearly shows the reorientation of the dye into the membrane interior. The rate constants of deactivation of the singlet state by horizontal transition to the **I** state in micelles, vesicles, and water are 1.8, 0.9 , and 45 ns^{-1}. Though both k_F and k_P are invariant of solvent effects, the dependence of k_I may be due to enhanced viscosity or a reduced polarity. The aqueous shell in amphiphilic assemblages is polar and fluid, whereas the hydrocarbon core is nonpolar and viscous. A ϵ value of 30 and η of 10 cP is assigned to the micellar surface. Similarly, Zachariasse et al.[358] assigned ϵ and η values of 17.5 and 23 cP in fluid lecithin membrane using dipyrenepropane as the probe. Thus, these voltage-sensitive fluorophores represent a strong application as fluorescent sensors and switches in biological systems.

The photoinduced electron transfer from borate (**139**) to water-soluble cyanines (**140**, **141**) is enhanced by the binding of both to the liposomal membranes where the donor and acceptor are solubilized at different depths within the bilayer[359]

139   **140**

141
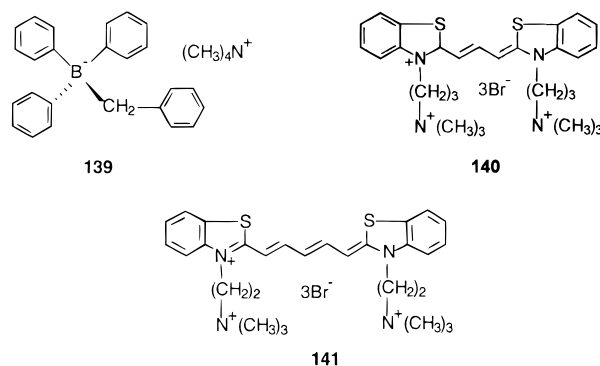
Bagchi et al.[360] studied the interaction of ketocyanine dyes (**130**, **131**) with cationic (CTAB), anionic (SDS), and nonionic (TX-100) micelles by absorption and fluorescence spectroscopy. Despite the hydrogen-bonding ability of carbonyl groups, these dyes are

Table 6. Microenvironmental Parameters for Dye (131, 132) in Ordered Media[a]

	dye **131**		dye **132**	
	ϵ	$E_T(30)$	ϵ	$E_T(30)$
CTAB	10.0	50.1	10.0	50.2
SDS	64.5	57.2	62.2	56.0
Triton-X-100	27.0	52.4	24.0	52.2

[a] Reprinted with permission from ref 360. Copyright 1996 Elsevier Science.

insoluble in water,[361] which may be due to the presence of the large hydrophobic ring in the dye. These compounds, however, remain in equilibrium, dye and H-bonded dye; the concentration of the H-bonded dye is at a maximum in SDS and a minimum in TX-100. The maximum energy of emission in different micelles is in the order CTAB > TX-100> SDS. Due to the negative charge density on the oxygen atom of the dyes, their interaction with cationic micelles (CTAB) increases and the dye is solubilized in the more hydrophobic region of the micelle, which decreases the H-bonding ability. In SDS micelles, the dyes are located in the hydrophilic region due to electrostatic repulsion and favor H-bonding with water. In TX-100, these dyes are located in the polyoxyethylene environment and form a hydrogen bond with the terminal OH group. The local dielectric constant and $E_T(30)$ values of the micellar pockets for the dyes are given in Table 6.

Ortica and Favaro[362] determined the singlet excitation energy of some merocyanines (**142**) having intramolecular donor−acceptor systems in 1,4-dioxane/water and in SDS, CTAB, and TX-100 micellar solution by absorption and fluorescence technique.

142: X, Y: (S, H; S, Cl; S, Me; Se, H; Se, Cl; Se, Me)
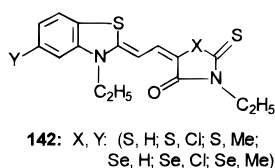
The fluorescence quantum yield (Φ_F) is found to increase in the order SDS > CTAB > TX-100. It also increases with increasing water content in the dioxane−water mixture. The order of increasing $E_T(30)$ values in micelles is found to be SDS ≥ CTAB ≥ TX-100. The principal role of the organized structure is segregation and monooccupancy inhibiting biomolecular interaction of the probe molecules. These dyes are found to be solubilized at the interface of the micelle. These molecules have a natural lifetime of 3 ns in the S_1 state and are found to deactivate in a nonradiative way ($k_{nr} = 10^{10}-10^{11}$ s^{-1}) via internal conversion to the ground state. The presence of heavy atoms does not appreciably affect the k_F and k_{nr}, but the triplet lifetime is reduced in the Se derivative.

Nees and Wolff[363] studied the photolysis behavior of hydroxy stilbazolium bromide (**143**) in aqueous/nonaqueous AOT lyotropic liquid crystalline systems and in isooctane-based AOT reversed micelles or microemulsions. A lamellar LLC and inverted hex-

143: R = CH$_3$, C$_2$H$_5$, C$_{16}$H$_{33}$
X = I, Br
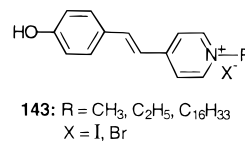
agonal phase is observed in the AOT system with a plane and bent interface. In the former, isomerization is preferred over dimerization, while in the latter dimerization is favored due to formation of H-aggregates of the trans isomer. The cis form is less perturbing to the lamellar phase than the trans form.

The *o*- or *p*-hydroxy-2-styrylbenzo[*a*]quinolizinium salt (azonia dye, **144**) is more easily transferred into the micelle than the nonionic merocyanine form because of the large binding constant of the cationic form of the dye.[364] Due to the solubilization of

144
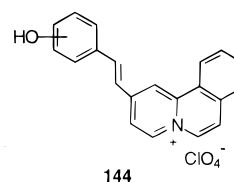
merocyanine form in the hydrophobic interior of the micelle, it shows a large spectral shift.

Riddington[365] synthesized cyanine dyes containing methyl glucopyranoside residue (**145**−**148**) for greater solubilization in water. With a view to studying their

	R	R'
145:	C$_2$H$_5$	C$_2$H$_5$
146:	C$_2$H$_5$	(CH$_2$)$_5$COOH
147:	(CH$_2$)$_5$COOH	(CH$_2$)$_5$COOH
148:	C$_2$H$_5$	(CH$_2$)$_5$COOSu
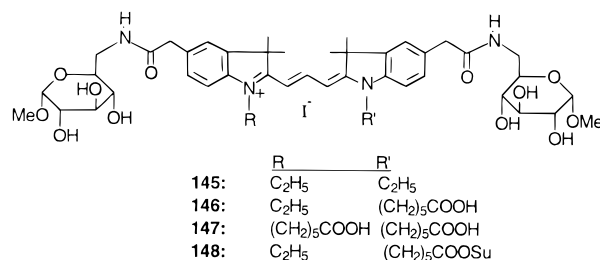
use as labeling reagents, these dyes can be conjugated to amine-containing substrates such as antibodies and dextrans with high efficiency to give brightly labeled substrates.

C. Behavior in Cyclodextrin

A limiting problem in many fluorescence-based diagnostic and imaging techniques is the photodegradation of the fluorophore.[366] On illumination, the fluorophore is degraded by singlet oxygen ($^1O_2$), superoxides, and peroxides and some redox action metabolism. The inclusion of cyanine dyes into the cavity of cyclodextrin (CyDx) has been reported by Kasatani and co-workers.[367−369] They observed[367] the formation of dimer on inclusion of dye in β-CyDx at [dye] = 0.02 mM and [β-CyDx] = 5 mM. In the study of the 3,3′-diethyloxadicarbocyanine (**87**, DODC)-β-CyDx system, two-thirds of the total dye formed a complex with β-CyDx.[369] From the absorption spectral study and molecular mechanics calculations, it

was revealed that the inclusion of cyanine dyes to the CyDx cavity occurs through the central polymethine chain. The cyanine–CyDx complex increases the light stability of the dye due to the steric hindrance of the CyDx and prevents photodegradation of the dye initiated by singlet oxygen.[370,371]

Matsuzawa et al.[371] observed the light stability of 1,3,3,1′,3′,3′-hexamethyl-2,2′-indotricarbocyanine iodide (HITC, **149**) by studying the inclusion of the dye in β-CyDx (**150**). The decrease in quantum yield (1.3

bonds are partially protected by the steric effect of β-CyDx, which blocks the attack of singlet oxygen. Thus, the photodegradation of HITC is reduced due to the (a) inhibition in the formation of singlet oxygen and (b) inhibition of the attack of singlet oxygen on the dye.

The conjugate of cyanine dye and 6-amino-6-deoxy-β-CyDx (**151**) represents a viable approach to the preparation of photostable fluorescent labeling reagents that enhances the photostability of the dye as compared to that in the absence of dextrin in water and in live swiss 3T3 cells,[372] although the quantum yield of fluorescence is sacrificed to some extent.

Nishida et al.[375] investigated the association of stilbene dyes (**86a**, **126**, **152**) with water-soluble p-sulfonato calix[n]arenes (**153**$_n$, $n = 4$, **6**, and **8**) by spectrophotometric methods. They observed 1:1 com-

149   **150**

151: a: R = Me, $n = 2$
       b: = Me, $n = 5$
       c: = Me, $n = 10$
       d: = CH₂CHMe₂, $n = 2$
             X = Br, I

152   **153:** n = 4, 6, 8

$\times$ 10^{-3} to 0.45 $\times$ 10^{-3}) during complexation with β-CyDx is associated with an increase in photostability. The quantum yield of photodegradation of the system [β-CyDx]/[HITC] = 6.0 $\times$ 10^2 is 0.45 $\times$ 10^{-3}, which is 35% of that in the absence β-CyDx. The lifetime of the singlet oxygen in the system [β-CyDx]/[HITC] = 2.8 $\times$ 10^2 is 57 μs, which is close to that in D₂O (68.1 $\pm$ 1.5 μs) without HITC. The quantum yield of the reaction of singlet oxygen with HITC is 0.16 for the system [β-CyDx]/[HITC] = 2.8 $\times$ 10^2, which is much smaller than that without β-CyDx (0.63). The size of the polymethine chain of HITC is estimated to be 7.36 Å as calculated by the MNDO/PM3 method[372] using the MOPAC program. This reveals that the C₁ atoms are outside and C₂ atoms inside the cavity. Since the photooxidation of the dye involves attack at C₁–C₂/C₁′–C₂′ bonds,[373] these

plex formation between **153**$_n$ and the dye molecule. The association constant for **153**$_8$**D** complex has been found to be 10 times more than that of **153**$_4$ and **153**$_6$**D** complexes. From spectrophotometric analysis and molecular models, they observed that **153**$_8$ accommodates the dye molecule completely in its cavity, whereas **153**$_4$ and **153**$_6$ form complexes with dye only with methyl or ethyl group in the pyridinium ring and with pyridinium ring or protonated amino group (Figure 17). ¹H NMR study of the complex indicates that the $\Delta\delta$ value increases in the order **153**$_4$ < **153**$_6$ < **153**$_8$, which was also observed by absorption spectroscopy and the construction of molecular models. The addition of cationic surfactant (cetylethyl dimethylammonium ion) to the **153**$_n$**D** complex replaces the dye molecule and forms a 1:1 complex with calixarene. This method is also applicable for determination of cationic surfactant concentration in water.

Bharathi and Mishra[376] studied the fluorescence behavior of 3,3′-dipropyl thiacarbocyanine iodide

153₄-86a   **153₆-86a**   **153₈-86a**
(complex)   (complex)   (complex)
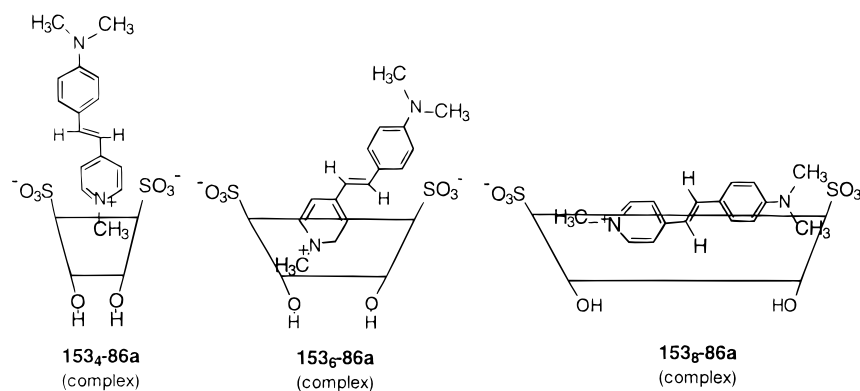
Figure 17. Estimated structures for 154$_4$, 154$_6$, and 154$_8$ complexes with **86a**. (Reprinted with permission from ref 375. Copyright 1997 The Bulletin Chemical Society Japan.)

(DCC, **154**) bound to bovin serum albumin (BSA).

154
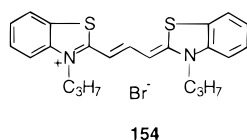
The binding of DCC is found to increase with increasing protein concentration, the binding constant being 3.7×10^4 M. The $E_T(30)$ value of dye in BSA is found to be 45.0, which indicates that the polarity of the location of the dye is similar to that of an acetonitrile environment.

IX. As Fluorescent Ion Sensors

The molecular design and synthesis of optical receptors with a capacity for photoswitching is a very active area of current research. A large number of molecules have been designed that consist of chromophores covalently linked to an ionophore, such as crown ethers, cryptands, and calixarenes; selective complexation of the ionophore with metal ions changes the spectral properties of the chromophore and shows photocontrollable cation binding.[377−383] These dyes can be used as ion sensors and have potential application in trace metal detection in biological systems as well as for molecular data processing.[384,385] The styryl dyes linked to crown ether moieties result in novel photochromic compounds which can affect the intramolecular charge-transfer process during complexation with metal cations depending on the size and charge density of the ionophore.[386−390]

Thomas et al.[391] studied the photophysical properties of cyanine dyes containing an aza crown ether moiety (**155**) and their complexation behavior with alkali-metal cations. The chromoionophore is a useful

155

ion sensor for the detection of alkali-metal cations in solution. The decrease in the absorption maximum of **155** with an increase in solvent polarity is due to the differential solvation of the ground and excited state. This suggests that the molecule has a highly dipolar ground state and a relatively less polar excited state. A large Stokes shift and a decrease in the fluorescence quantum yield is also observed for **155** with increasing solvent polarity. This is due to the ultrafast nonradiative decay leading to a reduction in the fluorescence quantum yield.[392] Dye **155** shows λ_{max} at 516 nm in CH_2Cl_2−MeCN (95:5 v/v) solution. On complexation with Li$^+$ and Na$^+$, the 516 nm absorption peak and the 614 nm emission peak shift to lower wavelengths whereas the quantum yield increases (Table 7). The complex between the dye and the metal ion is found to be a 1:1 type with stability constants of $K_S = 1.1 \times 10^4$ M^{-1} and $K_S = 0.56 \times 10^4$ M^{-1} for Li$^+$ and Na$^+$ complex, r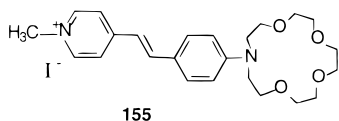espectively. The decrease in the absorption peak with complexation is due to the suppression of its intramolecular charge-transfer transition. The sensitivity of dye is

Table 7. Effect of Lithium Perchlorate and Sodium Perchlorate on the Photophysical Properties of Cyanine Chromoionophore 156[a]

	LiClO$_4$			NaClO$_4$		
[M]/mM	λ_{abs}/nm	λ_{em}/nm	Φ_f	λ_{abs}/nm	λ_{em}/nm	Φ_f
0	516	614	0.12	516	614	0.12
0.125	480	602	0.27	503	603	0.18

[a] Reprinted with permission from ref 391. Copyright 1994 Indian Academy of Science.

greater for Li$^+$ than for Na$^+$, due to the higher charge density of Li$^+$.

Gromov et al.[393,394] studied by electronic spectroscopy the complexation behavior with alkali-earth metal ions and cis−trans isomerization during complexation of indolinium and benzothiazolium styryl dyes **156**, **157**, and **158** containing crown ether moieties. The formation of cis isomer (**159**) during

156

157

158

159
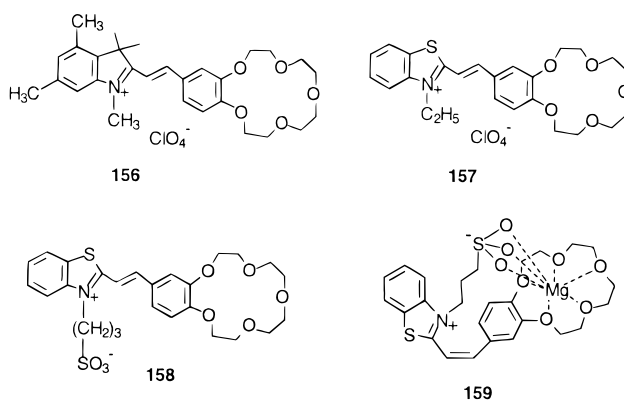
complexation of **158** is suggested to be intramolecular coordination between SO$_3^-$ group and the Mg^{2+} entrapped by the crown ether ring, which results in distortion of the π-electron-conjugated system. The λ_{max} of **159** shows a hypsochromic shift of about 70 nm compared to that of **158** on complexation. At higher Mg^{2+} concentrations ($>10^{-3}$M), the intramolecular coordination bond breaks due to binding of SO$_3^-$ with free Mg^{2+} ion in solution. The equilibrium constant for the binding also is greater for **159** ($K = 5 \times 10^9$ M^{-1}) than that for the **158** complex ($K = 1 \times 10^7$ M^{-1}). The binding is enhanced for Ca^{2+} and Ba^{2+}. Thus, these dyes can be used for rare-earth metal ion recognition.

Lednev et al.[395] studied the resonance and preresonance Raman (RR) spectra of dyes **156**, **157**, and **158** and their complexes with Mg^{2+} in acetonitrile solution; spectral changes were ascribed to intramolecular electron transfer. In both cases, the trans isomer scattering dominates in the resonance spectrum because of the selectivity of the resonance effect. All the dyes containing a crown ether ring show RR spectra in the region of 1271−1273 cm^{-1} for the 15-crown-5 ether moiety, which shows a negative shift upon complexation with Mg^{2+} in acetonitrile. This is ascribed to the intramolecular movement of electron density induced by the complexation of Mg^{2+}. As a result, the C=C bond is strengthened and the C−C bond is weakened. They also found that the Raman band at 1239 cm^{-1} for compound **160** is close to the band at 1237 cm^{-1} for **156** and is absent in **161**. This

160

161
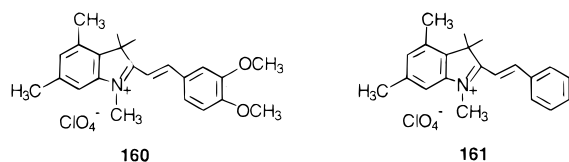
band therefore is assigned to the vibration involving participation of the Ph−O bond.[396] Thus, the down-shift in the Raman band on complexation is caused by weakening of the Ph−O bond in the dye molecules.

Gromov et al.[397] further observed that the strong hypsochromic shift of **157** on complexation with alkaline-earth metals is due to electron-acceptor influence of the coordinated cations acting via the oxygen atom linked to the phenyl ring para to the C=C bond.

Brazykin et al.[398] studied the complexation behavior of styryl dyes containing benzodioxa/dithia-18-crown-6 ether (**162**−**164**) with Hg^{2+} and Ag^+ and their photoisomerization by electronic and resonance Raman spectroscopy. All the dyes show similar

	R	X
162:	(CH₂)₄COOH,	O
163:	CH₃,	S
164:	(CH₂)₄COOH,	S
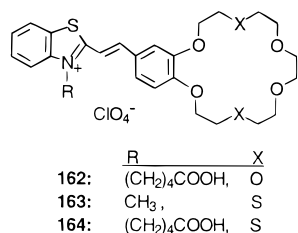
absorption spectra ($\lambda_{max} \sim 430$ nm). Both dyes **163** and **164** show a hypsochromic shift of 8 and 18 nm on complexation with Ag^+ and Hg^{2+} cations, respectively, while **162** shows a 10 nm shift on complexation with Hg^{2+} only. This shift on complexation of **162** to **164** with Ag^+ and Hg^{2+} is much smaller than that observed for complexation of **158** with Mg^{2+} (43 nm shift).[398] A smaller hypsochromic shift of the cis isomer of **162** and **164** on complexation with Ag^+ and Hg^{2+} than that of the corresponding trans isomer is due to the lack of intramolecular coordination be-tween the COOH group and metal cations and weak dissociation of the COOH group.

Alfimov et al.[400] studied the complexation behavior of styryl dyes containing the aza-15-crown ether group (**165**) with Ba^{2+} and Ag^+ in acetonitrile solution by spectrophotometric and potentiometric methods. From X-ray diffraction studies, it is proposed that the dye contains four planar subunits. The benzenoid form (**165a**) of the dye is found to exist in equilibrium with the quinoid form (**165b**), as found by X-ray diffraction measurement. This is due to intramolecu-

165a

165b
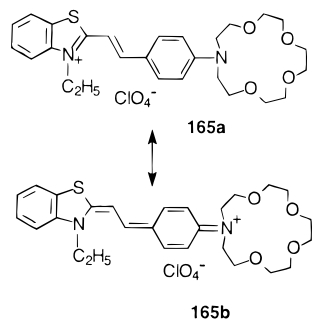
saccharides	K (M^{-1} from I/I_0)	K (M^{-1} from θ_{560})
D-fructose	1.3×10^5	1.6×10^5
D-mannose	5.9×10^3	5.6×10^3
D-arabinose	1.0×10^4	8.4×10^3
D-glucose	1.4×10^3	2.3×10^3
D-xylose	4.8×10^3	6.6×10^3

[a] Reprinted with permission from ref 401. Copyright 1996 Elsevier Science.

lar charge transfer between both the nitrogen atoms present in the molecule. Dye **165** forms a 1:1 complex with Ba^{2+} with an equilibrium constant of 80 ± 10 $dm^3 mol^{-1}$. The hypsochromic shift in the absorption spectra on complexation is due to redistribution of charge within the extended chromophore, which was also concluded previously by Raman spectros-copy.[394,395,398] No complexation was observed for Ag^+ with **165**, which may be due to charge-transfer resonance between the benzothiazolium nitrogen and the phenyl nitrogen atoms.

Takeuchi et al.[401] reported the selective binding of monosaccharides to the cyanine dye (**166**) forming 1:1 intramolecular complexes, which is studied by fluo-rescence and CD spectroscopy. This dye in its syn

166
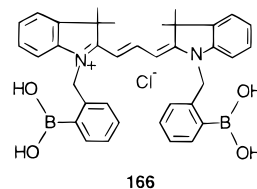
conformation is useful to form 1:1 intramolecular complexes with monosaccharides, and its ICT excited state is poorly fluorescent until monosaccharide binding impedes its torsion. The complexation be-havior has been studied in 1:1 methanol:water (v/v) solution at pH 10 ([dye] = 1×10^{-5} M). From the fluorescence spectra, a 1:1 complex of saccharide−diboronic acid at low saccharide concentration and a 2:1 complex at high saccharide concentration have been observed. In the 1:1 complex, the fluorescence intensity increases due to the rigidity of the cyanine dye unit by saccharide. D-Mannose, D-fructose, and D-xylose change from a 1:1 to a 2:1 complex at low saccharide concentration, whereas the change occurs at high saccharide concentration for D-glucose and D-arabinose. This observation is also corroborated from the CD spectral analysis. A negative CD band observed at 560 nm also supports the formation of a 1:1 complex formation at low [saccharide] and 2:1 complex at high [saccharide]. So at low saccharide concentration, the 1:1 complex is CD active and the 2:1 complex is CD silent. The K values observed from both analyses also are very similar (Table 8). Thus, the diboronic-acid-appended cyanine dye act as a useful fluorescent sensor for monosaccharides.

X. Future Work

Cyanines have found wide use in photonic tech-nologies like optical signal processing, laser technol-ogy, telecommunication, optical switching, ion sen-

sors, in molecular data processing, in photochromism, etc., and in biomedical applications. Appropriately designed cyanines have been used to diagnose and treat leukemia cells. During the 21st century, it will be necessary to synthesize tailor-made cyanines having specific uses in these areas. New avenues of application particularly in the area of photoelectronics are to be discovered and persued.

XI. Notations and Abbreviations

τ_f	fluorescence lifetime
τ_{rad}	radiative lifetime
ϕ_f	fluorescence quantum yield
AFM	atomic force microscopy
AlTCPc	aluminum tricarboxy monoamide phthalocyanine
AOT	Aerosol-OT
BLA	bond-length alternation
BSA	bovine serum albumin
CD	circular dichroism
CMC	critical micelle concentration
CNDOVS	complete neglected differential orbital
CT	charge transfer
CTAB	cetyl trimethylammonium bromide
CyDx	cyclodextrine
DCC	3,3'-dipropylthiacarbocyanine
DCP	dicetyl phosphate
DMABN	dimethylamino benzonitrile
DMPC	dimyristoyl phosphatidylcholine
DMSO	dimethyl sulfoxide
DODCI	3,3'-diethyloxadicarbocyanine iodide
DTCC	diethyl thiacarbocyanine
DTDC	diethyl thiadicarbocyanine
HITC	1,3,3,1',3',3'-hexamethyl-2,2'-indotricarbocyanine iodide
HOMO	highest occupied molecular orbital
ICG	indocyanine green
ICT	intramolecular charge transfer
ISC	intersystem crossing
L	Langmuir–Blodgett
LC	liquid condensed
LE	liquid expanded
LLC	lamellar liquid crystal
LOMO	lowest occupied molecular orbital
NIR	near-infrared
NLO	nonlinear optical
NMR	nuclear magnetic resonance
ns	nanosecond
PDT	photodynamic therapy
PIC	pseudoisocyanine
PMA	polymethacrylate
PMC	photomerocyanine
ps	picosecond
PTS	*p*-tolune sulfonate
PVA	poly(vinyl alcohol)
SDS	sodium dodecyl sulfate
SERS	surface-enhanced Raman scattering
SHG	second-harmonic generation
Sp	spiropyran
SP	styryl pyridinium
SQ	styryl quinolinium
TPB	tetraphenyl borate
TX-100	Triton-X-100
VB–CT	valence bond-charge transfer

XII. Acknowledgments

XIII. References

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