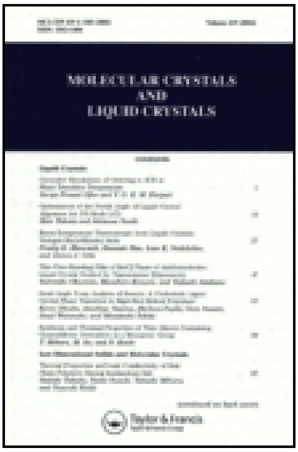

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The Thermochromic Behavior of Cyanine Dyes Doped in Silica Phases Prepared by Liquid-Phase-Deposition Method

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THE THERMOCHROMIC BEHAVIOR OF CYANINE DYES DOPED IN SILICA PHASES PREPARED BY LIQUID-PHASE-DEPOSITION METHOD

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Abstract The method of liquid phase deposition (LPD) has an interesting feature that some kinds of organic compounds can be directly doped into silica layers. We doped a cyanine dye (1-ethyl-2-[3-chloro-5-(1-ethyl-2(1H)-quinolylidene)-1,3-pentadienyl] quinolinium bromide) in silica thin films by using the LPD method and observed thermochromic behavior of the prepared samples. The samples are colorless just after preparation. When they are maintained at a raised temperature, they turn blue. The origin of this thermochromic behavior has been attributed to the elimination of water molecules out of silica phases. A semi-empirical MO calculations also support the proposed mechanism.

INTRODUCTION

The liquid-phase-deposition (LPD) method is a wet process forming transparent silica thin layers on substrates such as glass or quarts plates.[1-5] The most interesting feature of this method is the doping ability of some kinds of organic molecules.[6-9] Owing to this feature, the process has the possibility of forming organic-inorganic functional composite materials. In addition to this, the LPD films has high transparency equivalent to fused

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silica and provides favorable requirements for optical functional materials.

The LPD silica films have the doping ability of some kinds of organic substances. Ino *et al.* measured the dye elution out of LPD silica phases into water and ethanol.[8] The absorbance of rhodamine 6G doped in LPD silica films decreases to about 90% after 100 h in 60°C water and after that the decrease in absorbance is negligibly small. The absorbance of rhodamine 6G doped in sol-gel films disappeared completely after 100 h at the same temperature. The results indicate that the LPD films are dense compared with sol-gel films and doped organic dyes are firmly fixed in LPD silica layers.

The LPD method has the following advantages in addition to the doping ability of organic substances:

1) The process forms hard and transparent silica thin films. The etching rates of LPD silica films as a measure of film resistance to chemicals, which are measured by using P-etch solutions,[10] are equivalent to the corresponding rates of silica films prepared by the thermal oxidation method and an order of magnitude better than the ones prepared by the sol-gel method.

2) The process forms almost pure amorphous silica films with very low impurity concentrations. The XPS data indicate that the LPD silica films are mainly composed of Si and O and the atomic ratio of Si to O is very close to 1:2.[3] The only exception is fluorine and its content is rather high compared with other contaminants. The role of fluorine to the specific properties of LPD silica will be mentioned later.

3) The process proceeds at ordinary temperatures. The process needs no calcination or baking, so that doped organic dyes are free from thermal decomposition.

Suzuki *et al.* estimated the effective pH of the interior of LPD silica phases by observing absorption spectra of doped pH indicator dyes.[11-12] They doped pH indicator dyes of methyl yellow and methyl orange into silica phases by using the LPD method and observed the absorption spectra of the samples. Based on the comparison with the corresponding spectra of the dyes in pH-controlled buffer solutions, they concluded that the doped pH indicator dyes in LPD silica are in an acidic environment equivalent to pH = 3.7 and the effective acidity of the interior of LPD silica is exceptionally high compared with surface acidity of other silicas such as silica gel. The origin of the high acidity of LPD silica was attributed to the existence of Si-F bonds inducing an electron-attracting tendency.

Some kinds of cyanine dyes doped in LPD silica films were found to show color changes, when the doped samples are maintained at raised temperatures. This paper reports the observation of absorption spectra of the samples and the effect of heat treatment on absorption spectra. The color change has been attributed to the elimination of water molecules out of LPD silica phases. This paper also proposed the mechanism of this thermochromic behavior involving water molecules, which is also confirmed by the semi-empirical MO calculations.

EXPERIMENTAL

Sample Preparation

Silica thin films doping cyanine dyes can be prepared by the following LPD procedure. We prepared hexafluorosilicic acid (H_2SiF_6) solutions saturated with SiO_2. Using them as dipping solutions for the LPD process, we immersed slide glasses or quartz plates as the substrates of silica films in them. Addition of aluminum powder to the solutions shifts the equilibrium in the solutions to the deposition of silica and, as the result of this, the silica films are deposited on the immersed substrates. In case that some appropriate organic substances are dissolved in the dipping solutions, we can obtain the silica films doping organic substances.

By using the aqueous solutions of 4, 3, and 2 M (1 M = 1 mol dm^{-3}) hexafluorosilicic acid, we prepared samples doped with a cyanine dye, 1-ethyl-2-[3-chloro-5-(1-ethyl-2(1H)-quinolylidene)-1,3-pentadienyl] quinolinium bromide (hereafter abbreviated to NK-1150, product code number of Japanese Research Institute for Photosensitized Dyes Co., Ltd., Okayama). The concentration of NK-1150 in dipping solutions was 1×10^{-3} M. Aluminum powder of 0.7 g was added to the 250 cm^3 dipping solution. The time of dipping varied in the range of 10 to 30 hours at a temperature of 30°C.

After the prepared samples were washed with distilled water and dried in the air, the absorption spectra were recorded on Hitachi U-3200 recording spectrophotometer. The observed spectral data were transferred to and stored on PC through an RS-232C interface bus and were ready for any data processing.

The LPD films doped with NK-1150 are colorless just after preparation. When the samples are maintained at 70°C for some hours or longer, they turn blue. When the samples are left in the air at ordinary temperatures, they become colorless again. Such color change is reversible, but the blue color breaches by long-time heating. We monitored the spectral changes in the absorption spectra of the heat-treated samples at an appropriate time interval.

MO Theoretical Calculations

We modeled some probable forms of neutral and acidic species of NK-1150 by using Chem 3D. After the optimization of the geometries with molecular mechanical treatment, we performed semi-empirical MO calculations with the optimized geometries. MOPAC was used to obtain the optimized geometries and wavefunctions of the ground state and CNDO/S to obtain excitation energies and transition intensities. On the CNDO/S calculations, we used the new N-M gamma with $k = 1.3$.[13]

RESULTS AND DISCUSSION

Absorption Spectra and Thermochromic Behavior

Figure 1 shows the absorption spectra of NK-1150 doped in LPD silica films prepared from the dipping solutions in which the H_2SiF_6 concentration is 4 M. The real concentrations of doped dyes were hardly determined in LPD films, so that apparent absorbance of the prepared samples was plotted against wavenumbers in the figures throughout this paper. The maximum absorbence of the samples just after preparation is normalized to 1 and the other spectra are plotted with the same factor. The LPD film doping NK-1150 is colorless immediately after preparation; the absorption spectrum of the sample has a band with a maximum at 28000 cm^{-1} and has no substantial absorption band at a lower wavenumber region below 25000 cm^{-1}.

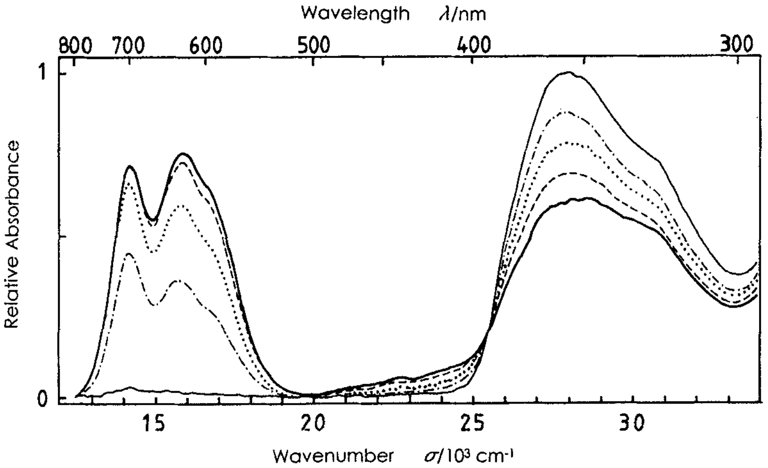


FIGURE 1 The absorption spectra of NK-1150 doped in LPD silica films deposited on fused silica. The H_2SiF_6 concentration of dipping solution is 4 M. Time of heat treatment; ——— : 0 h, —·—· : 2 h, ······ : 8 h, - - - -: 24 h, ——— : 48 h.

When the LPD film doping NK-1150 is heated in a thermostat for some hours, it turns blue. We maintained the temperature of the samples at 70°C in a thermostat and monitored their spectral changes. The dependence of absorption spectra on the time elapsed at the raised temperature are also shown in Fig. 1. Upon maintaining the samples at the raised temperature, an absorption band with three vibrational structures appears at about 15000 cm^{-1}. The band around 15000 cm^{-1} increases with the increase in elapsed time at the raised temperature, whereas the band at 28000 cm^{-1} decreases.

The absorption spectra of NK-1150 in ethanol, water, and aqueous H_2SO_4 solutions are shown in Fig. 2. The absorption spectrum of NK-1150 in the H_2SO_4 solution has a band with the maximum wavenumber of 28000 cm^{-1}. The spectrum with a band at 28000 cm^{-1} which is observed in an acidic condition appears to originate from a protonated species and may reasonably be assigned to an acidic species of NK-1150. The band with vibrational structures at about 18000 cm^{-1} which appears in ethanol or neutral water may reasonably be assigned to neutral species in the sense that the species is dominant in neutral conditions. We shall come back to the molecular structures of these two species in more detail later.

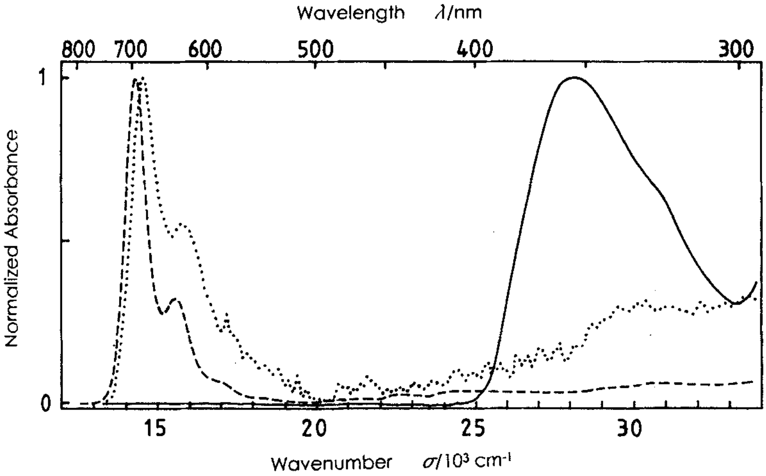


FIGURE 2 The absorption spectra of NK-1150 in various solvents. Solvents; – – – : in ethanol, ······ : in water, —— : in aq. H_2SO_4.

Considering the species responsible to the absorption spectra in various solutions, we are able to assign the species of NK-1150 doped in LPD silica films. The spectrum with a peak at 28000 cm^{-1} observed right after preparation is assigned to the acidic species; the dominant species in LPD silica films right afar preparation seems reasonably to be a protonated one. The absorption spectrum appearing under heat treatment is assigned to the neutral species; this implies that the neutral species appears and increases its population in LPD silica films by heat treatment. The spectra in neutral solutions and in LPD films lie at almost the same energies but the spectral shapes differ in relative intensity of vibrational bands. This appears to originate from the difference in environment; some steric effects will be involved in the solid phases of LPD silica.

Dipping solutions for LPD process can be prepared by saturating concentrated aqueous solutions of hexafluorosilicic acid with SiO_2. The dipping solutions with the highest concentration we can obtain is about 4 M estimated as hexafluorosilicic acid. We can also prepare LPD films by using less concentrated solutions down to about 2 M of hexafluorosilicic acid solutions. The composition of LPD films has been evaluated by the IR spectra of LPD films deposited on silicon wafers[14] and has proved to be somewhat modified by preparation conditions; the amount of Si-OH groups increases and the amount of Si-O-Si groups decreases on decreasing the H_2SiF_6 concentration of dipping solutions from 4 to 2 M. The content of free water molecules also increases on decreasing the concentration of dipping solutions.

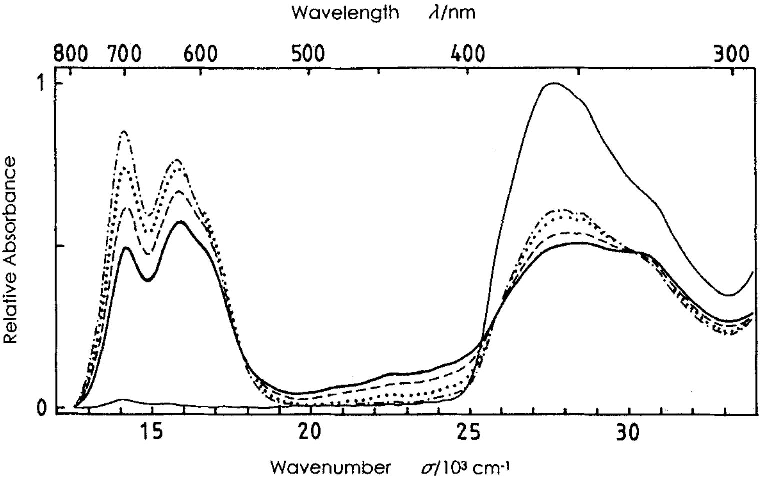


FIGURE 3 The absorption spectra of NK-1150 doped in LPD silica films deposited on fused silica. The H_2SiF_6 concentration of dipping solution is 3 M. Time of heat treatment; ——: 0 h, —·—·: 2 h, ······ : 8 h, – – – : 24 h, ━━ : 48 h.

Figure 3 shows the absorption spectra of NK-1150 doped in LPD silica films prepared from 3 M dipping solutions and also includes the change of absorption spectra with the elapse of time at a temperature of 70°C. The spectral behavior of the samples on heat treatment is similar to those prepared from 4 M dipping solutions. A large increase in 15000 cm^{-1} band and an decrease in 28000 cm^{-1} band was observed at a shorter time range from 0 to 2 hours; the rate of spectral changes is rapid compared with the samples prepared from 4 M dipping solutions. The decrease in the absorbance of the 28000 cm^{-1} band with time is shown in Fig. 4, as well as the corresponding result of the samples prepared from 4 M dipping solutions. The tendency is more pronounced on the samples prepared from 2 M dipping solutions than on those from dipping solutions with higher H_2SiF_6 concentrations. The decrease in absorbance is pronounced in the sample prepared from 3 M dipping solutions than in the one prepared from 4 M dipping solutions.

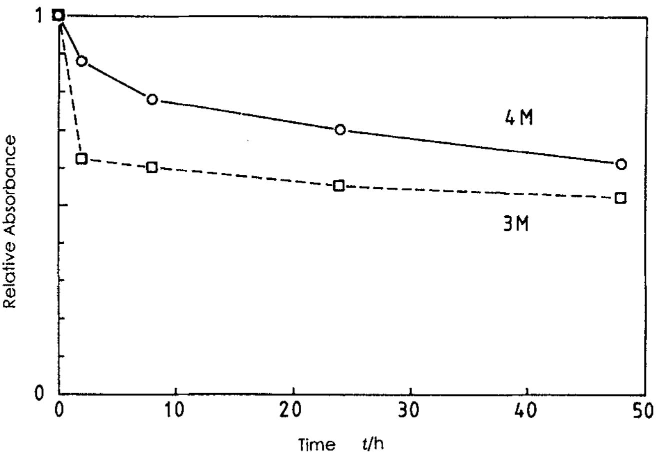


FIGURE 4 The plots of the decrease in absorbance of 28000 cm^{-1} band against the time of heat treatment.

When we continue to keep the samples at the raised temperature of 70°C, the intensity of the 15000 cm^{-1} band decreases again at the time longer than 8 hours. Such a bleaching was observed on the samples prepared from 2 M dipping solutions. The origin of the bleaching will be discussed later.

In order to determine whether substance transfer into or out of LPD silica phases is involved or not in this thermochromic color change, we prepared the sample which is overcoated with another LPD silica layers doped with no dye onto the LPD films doped with NK-1150 in advance; the overcoated LPD silica layers are expected to prevent substance transfer. The absorption spectrum of the sample thus prepared showed no substantial spectral changes after heat treatment . This implies that transfer of a certain chemical species between the LPD silica solid phase and an outer phase is involved in the themochromic behavior of the LPD system studied in this paper.

To specify the chemical species involved in the thermochromic color change, we measured the spectral changes on heating under various conditions. Figure 5 compares the absorption spectrum of the sample kept in a vacuum at an ordinary temperature for one day with that of the same sample just after preparation. Under evacuated conditions, the absorption band near 15000 cm^{-1} appears even without heat treatment. This observation indicates that the origin of the appearance of the 15000 cm^{-1} band results from the removal of a certain chemical species out of LPD phases, not from the injection of some species into LPD phases. It is plausible that the thermochromic behavior of LPD silica films doped with NK-1150 originates from the removal of a certain chemical species out of LPD silica phases.

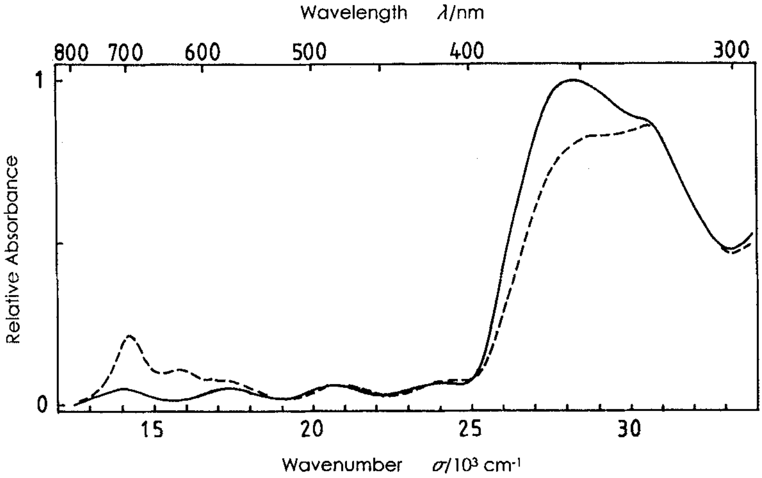


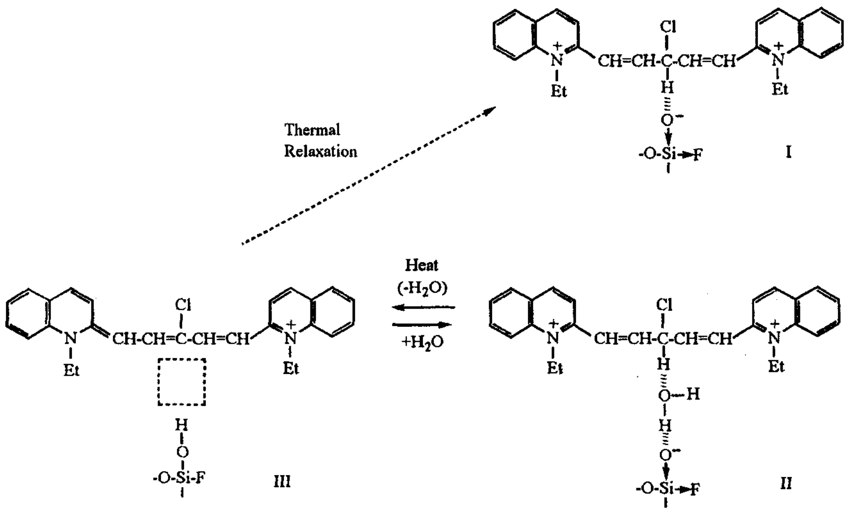
FIGURE 5 The absorption spectrum of NK-1150 doped LPD silica films which are kept in a vacuum for one day at an ordinary temperature (– – –). The absorption spectrum just after preparation is also included in the figure (———). The concentration of dipping solution is 3 M.

The ESCA study proved that the content of impurities in LPD silica is equivalent to fused silica with a few exceptions; one exception is a fluorine element and the other molecular water. The stretching band of Si-F bonds are clearly detected at 950 cm^{-1} on the IR spectrum of LPD silica deposited on a silicon wafer.[3] On the other hand, the broad and weak band being assigned to H-O-H was observed near 3300-3700 cm^{-1} on the samples prepared from dipping solutions of lower H_2SiF_6 concentrations. The intensity of the band increases with the decrease in H_2SiF_6 concentrations; this implies that the LPD silica films contain some amount of free water, the content of which increases with the decrease in H_2SiF_6 concentrations. The spectral changes are more pronounced on the samples prepared from dipping solutions of lower H_2SiF_6 concentrations. These two observations strongly suggest that the water molecules are involved in the mechanism of the thermochromic behavior of NK-1150 in LPD silica films.

When the LPD films doped with NK-1150 were immersed in water at ordinary temperatures, they showed no substantial spectral changes. This is consistent with the idea that a likely candidate for the removed species out of LPD silica is free water. When the films were immersed in hot water of 70°C, a slight increase in the band assigned to the neutral species was observed. The water molecules have larger thermal energies at a temperature of 70°C than at room temperature; excess thermal energy tends to enhance the escaping tendency of water molecules out of LPD silica films. When we keep the colored samples in the air at room temperatures after heat treatment, the density of the color decreases; the intensity of absorption band assigned to the neutral species decreases and the intensity of the band assigned to the acidic species recovers. Such color change is reversible. These observation are also consistent with the idea that the chemical species responsible for thermochromic behavior is free water.

Mechanism of Thermochromic Behavior

Based on the experimental results described above, we tentatively proposed the mechanism of the thermochromic behavior observed on the cyanine dye NK-1150 doped in LPD silica films (Scheme I).



Scheme I

The dominant species of the dye in LPD silica phases is a hydrogen-bonded one with a Si-OH group in which H is protonated to the dye due to the high proton donating ability of silanol groups with an F atom at a geminate position in LPD silica (species **I**). This species corresponds to the acidic species and is responsible to the absorption spectrum observed on the samples right after preparation. The hydrogen-bonded species bridging the dye and a silanol group through a water molecule also seems to exist in LPD silica phases (species **II**). The population of the species **II** is small in the samples prepared from 4 M dipping solutions but increases with the decrease in the H_2SiF_6 concentration of dipping solutions. This water-bridged hydrogen-bonded species shows almost the same absorption spectrum to the directly hydrogen-bonded species **I** with the Si-OH group, because that the bridging water molecule reflects the high proton donating ability of the Si-OH group of LPD silica and results in protonation to the dye.

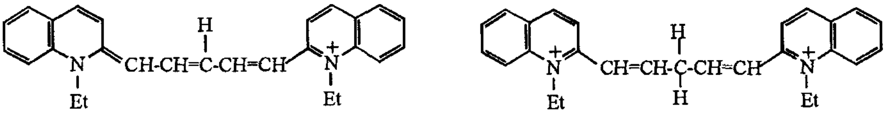
As have described above, we tentatively conclude that the thermochromic color change of NK-1150 in LPD silica films originates from the removal of free water molecules out of LPD silica. When a water molecule bridging the dye and a silanol group through hydrogen bond is removed, NK-1150 recovers a neutral form of the dye (species **III**), because that the dye molecule hardly translates to form a direct hydrogen bond with Si-OH groups due to high steric hindrance in silica solid phases. The species appears to color the dye-doped LPD films blue and to grow the absorption spectrum with peaks at about 15000 cm^{-1}.

Such a color change is reversible but the color becomes pale on long time heating. Dye molecules have more thermal energies under the conditions of raised temperatures than at room temperatures, so that they will be able to relax to the stable conformations more easily. The bleaching appearing in LPD films is also explained by the proposed mechanism.

MO Theoretical Consideration of Chemical Species

To obtain additional support of the proposed mechanism of thermochromism, we calculated excitation energies of the probable chemical species by using MOPAC and CNDO/S procedures.

We assumed the following two ionic species as the chromophores of the cyanine dye NK-1150, where Cl in the dye was replaced by H in order to facilitate MO calculations. First we obtained the geometrical coordinates of the species **1**, which is a monovalent cation and a likely candidate for the neutral species, by using the MM2 procedure. Starting from the coordinate data optimized by the MM2 procedure, we fully optimized the ground-state geometry by using the MOPAC program. Based on the fully optimized geometrical data, the calculations of excitation energies and transition intensities of the chromophore were performed with the CNDO/S procedure. The calculated transition energies and oscillator strengths are plotted against wavenumbers in Fig. 6, with the straight lines the lengths of which are proportional to the calculated *f* values.



1 **2**

Scheme II

The species **2** are assumed to be the chromophore of acidic species of the dye, which is a divalent cation attaching a proton on the central position of ethylene chain. By using the analogous procedures, we obtained the excitation energies and transition intensities for the fully optimized geometries of the divalent cation. The calculated transition energies and oscillator strenghts are also included in Fig 6.

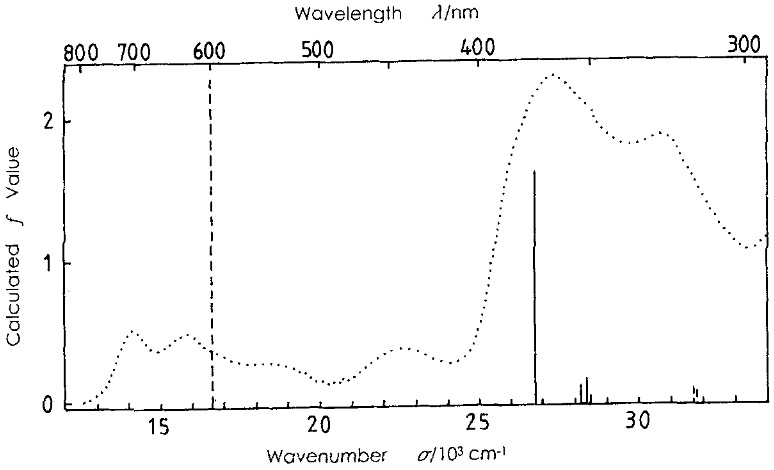


FIGURE 6 The calculated transition energies and oscillator strengths of model compounds for neutral and acidic species of doped NK-1150. The lengths of the line are proportional to the calculated *f* values. – – – : **1**, ——— : **2**.

The MOPAC data indicated that the species protonated at the other positions on an ethylene conjugated chain was less stable than the species **2** and the calculated results of excitation energies and transition intensities did not give satisfactory agreement with experimental data.. Figure 6 shows that the agreement of the experimental transition energies and oscillator strenghts with the calculated ones is very satisfactory both on the neutral and the acidic species, and therefore the proposed species are strongly supported by the semi-empirical MO calculations. The full details of the calculations will be published elsewhere.

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