

Synthesis and Properties of Some Pyrylium-Squarylium Cyanine Dyes

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Abstract

Several symmetrical and asymmetric pyrylium-squarylium cyanine dyes have been synthesized. UV spectra of these dyes in solutions were determined. It was found that in some cases the dye aggregated into dimers, while concentration of dye less affected the aggregation.

Some physical properties of these dyes, such as solubility and melting point have been determined.

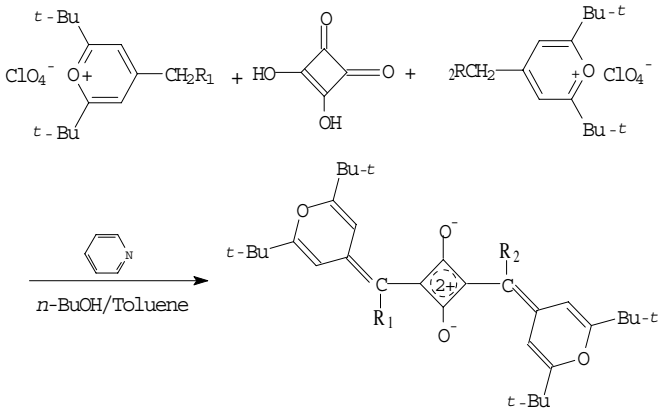
Single crystals of a few of pyrylium-squarylium cyanine dyes have been obtained. X-ray diffraction was used to determine their crystal structure. Those crystals were in triclinic and monoclinic forms. The relationship between the physical properties of the dyes and the crystalline structure of the dyes was discussed.

Introduction

Recently, squarylium dyes have been widely studied owing to their specific molecular structure and physico-chemical properties.[1,2] As it was known, squaric acid ring in squarylium dye molecule could be an electron delocalized system with a positive charge in the center of its four-membered ring.[3] Therefore, it was similar to a metallic ion. So that, the squarylium dyes are usually in the electron "D-A-D" form and possess some specific properties. These dyes can be used as spectral sensitizers, optical recording mediums, and non-linear optical materials etc. In this paper, some pyrylium-squarylium dyes are reported.

Experimental

Five pyrylium dyes were synthesized by the reaction as:



Dye1: R1=R2=H
Dye2: R1=R2=CH_3
Dye3: R1=R2=CH_2CH_3
Dye4: R1=H, R2=CH_3
Dye5: R1=H, R2=CH_2CH_3

The structure of these five dyes has been characterized by UV-VIS, IR and NMR spectrum etc. Melting points of these dyes also have been measured with a Yanaco melting point meter.

Results and Discussion

1. UV-VIS spectra

Absorption bands of five dyes are given in Tab.1.

Tab.1 Absorption bands of pyrylium-squarylium dyes

Dye No.	λ_{max} (nm) (log ε) in $CHCl_3$
Dye1	711（5.52）
Dye2	763（5.39）
Dye3	759（5.35）
Dye4	739（5.37）
Dye5	736（5.33）

It can be found, absorption maximun of Dye2 is at a longer wavelength than the others, while Dye1 shows a short wavelength absorption.

In some cases, absorption spectra of these dyes can change gradually. For example, absorption spectrum of a solution (10^{-4}mol/L) of Dye1 in a mixed solvent of n-propanol/H_2O (volume ratio is equal to 5:21) changes as shown in Fig.1

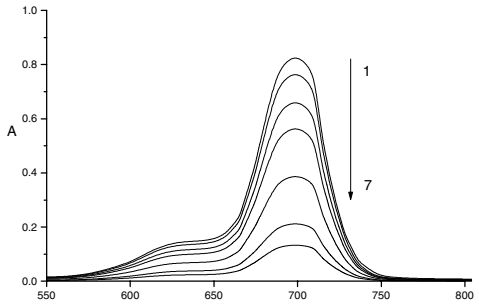


Fig.1 VIS spectra of symmetrical cyanine Dye1 at different time in n-PrOH/H_2O

In Fig.1 the absorption band of Dye1 gradually lower down and broaden with time. Plotting the reciprocal of absorption value (1/A) against time to obtain a straight line (Fig.2) denotes that in this case dimer aggregation occurs.

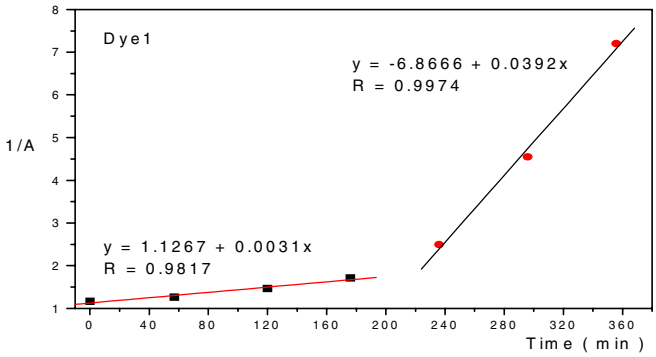


Fig.2 Correlation of absorption at different time vs. time of Dye1

This result coincides with the equation of

$$1/A_1 - 1/A_0 = K(t_1 - t_0) \qquad (1)$$

value K---relative aggregation rate constant

And, this phenomenon is similar to the aggregation of type B, shown by Mckerrow[4].

All of these five dyes can aggregate into dimer and their aggregate rate constants are shown in Tab.2.

Tab.2 Aggregation velocity of dyes and their correlation coefficients

	K	R
Dye1	0.0031, 0.0392	0.9817, 0.9974
Dye2	0.7630	0.9900
Dye3	0.0036, 0.0235	0.9859, 0.9839
Dye4	0.2862, 1.3259	0.9803, 0.9912
Dye5	0.0500	0.9930

APCI-MS has been used with a concentrated solution of Dye3 in CH_2Cl_2. The mass spectrum is shown in Fig.3. A peak of 1094.3 can be found. Since the molecular weight of Dye3 is 547.5, it is evident that the peak of 1094.3 confirms the existence of the dimer of Dye3.

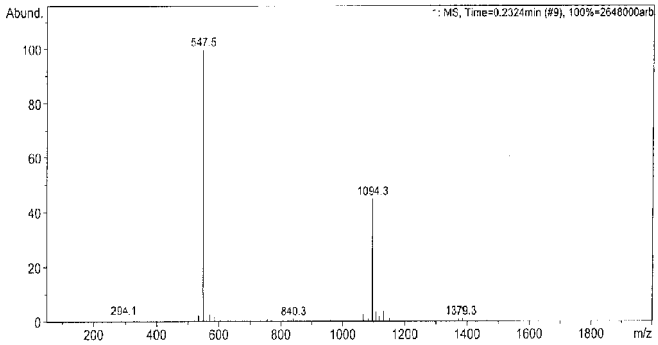
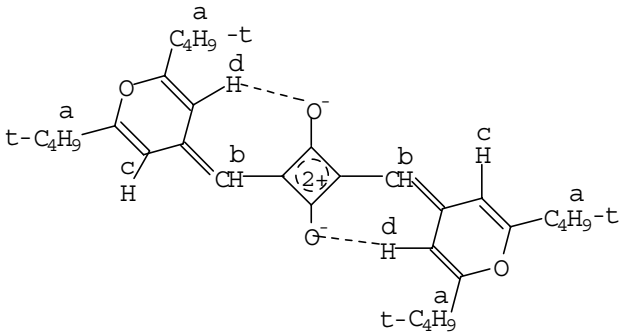


Fig.3 APCI-MS spectra of high concentration CH2Cl2 solution of Dye3

2. NMR spectra

Both ^{1}H-NMR and ^{13}C-NMR spectra of five dyes have been measured. Tab.3 is the structure elucidation of ^{1}H-NMR for Dye1.

Tab. 3 Structure elucidation of ^{1}H-NMR for Dye1



Chemical Shift	Classification of Proton	Integrated Intensity
1.27-1.33	Protons of methyl group in position a	36
5.81	Protons of methene groups in position b	2
6.18	Protons of pyran ring in position c	2
8.66	Protons of pyran ring with hydrogen bond in position d	2

All of five dyes have the similar spectra. It is shown, there are two hydrogen bonds in each molecule.

3.Solubility and melting points

Solubility and melting points have been measured. The results are listed as follows (Tab.4 & 5):

Tab.4 Solubility of squarylium dyes (g/L)

Solvent	Ethanol	i-Propanol	n-Butanol
Dye1	51.1	30.4	75.4
Dye2	0.4	1.1	2.7
Dye3	11.6	15.7	40.0
Dye4	8.9	12.1	18.3
Dye5	15.6	20.5	35.3

Tab.5 Melting points of squarylium dyes

Dye No.	Melting Point (°C)
Dye1	240-242
Dye2	269-272
Dye3	232-234
Dye4	237-239
Dye5	214-215

It was found that some of the physical properties of Dye2 were somewhat different from those of other dyes in the same series. It had a higher melting point and a lower solubility than the others.

4.Crystalline structure of pyrylium-squarylium dyes

Some of the dyes have been used to prepare their crystal, and their crystalline structure has been determined. The results are shown in Fig.4, Fig.5, Fig.6 and Tab.6.

Tab.6 Crystal properties of pyrylium-squarylium dyes

Dye No.	Dye2[5]	Dye3	Dye4
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/a$	P1
Dihedral angles	12.00	10.96	12.50, 12.75
Color	colorless	red	Green
Density(g/cm^3)	1.147	1.104	1.122

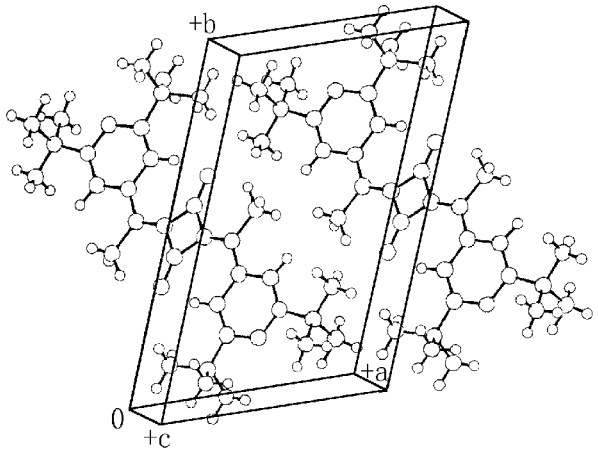


Fig.3 Crystal packing structure of Dye2[5]

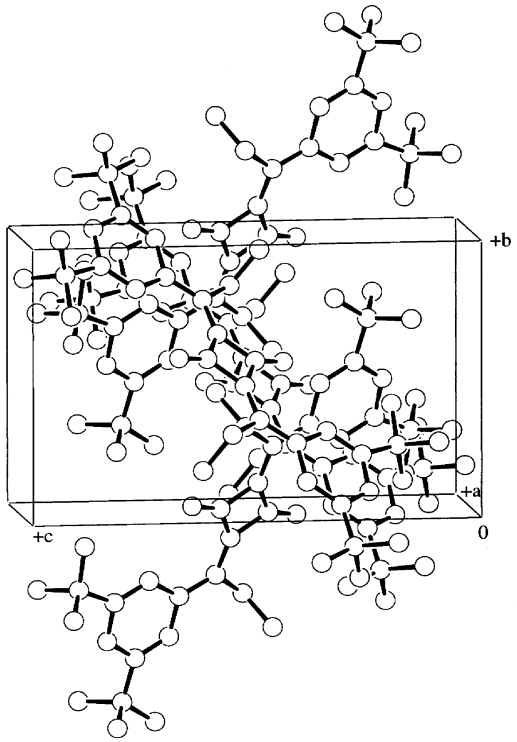


Fig.4 Crystal packing structure of Dye3

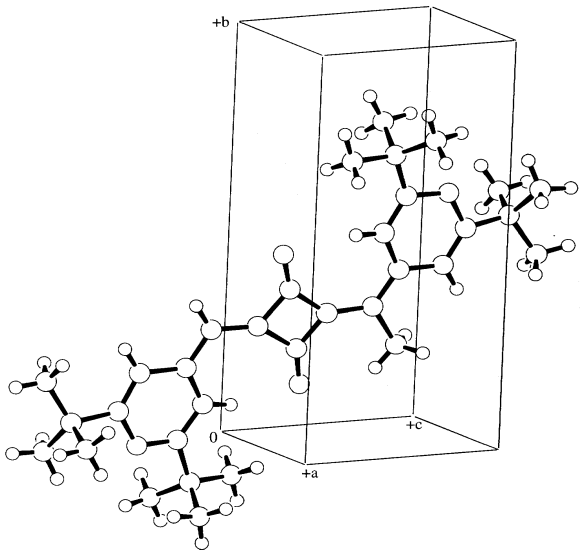


Fig.5 Crystal packing structure of Dye4

From the results, it is found, molecules of Dye2 are more close packed in the crystal than Dye3 and Dye4. So, it has a higher density, a higher melting point and a lower solubility.

References

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Biography*

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