

〈Research Paper〉

Synthesis and Properties of Novel Rhodamine 6G Fluorescent Dye Compound

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Abstract: One of organic dye materials which have been long lasting investigated is rhodamine 6G dye series. This dye has been attracted with considerable interests due to the reason of its promising photochemical properties. In this study, a novel fluorescent dye compound based on rhodamine 6G derivative was synthesized through the reaction of rhodamine 6G hydrazide and indole-3-carboxaldehyde. Absorption and fluorescent emission spectra of this dye were determined with the properties of solvatofluorochromism. Related electron energy states of the dye compound were also characterized by computational calculations.

Keywords: rhodamine 6G, solvatofluorochromism, fluorescent, HOMO/LUMO, electron energy, emission

1. Introduction

Rhodamines are fluorophores composed of the group of xanthenes with fluorescein and eosin dye. These rhodamines have attracted by many scientists due to their promising optical functions and photochemical properties¹⁻⁵⁾. Rhodamine 6G is one of these dye classes and has been researched toward its higher fluorescent opto-properties. This fluorescent property can be utilized into the various parts of analysis and measurement process. For this reason, rhodamine based dyes can be applied for solvatofluorochromism. The fluorescence spectrum of a solvatochromic probe molecule, namely fluorochromism, is a property of changing its fluorescent emission with the subjected solvent polarity. This phenomenon depends on different dipole moments and energy gaps between the ground and excited state. These dyes can be applied into the sensor probes for the determination of solvent polarity and utilized as the potential application tools for the fluorophore sensor toward volatile organic compounds^{2,3,6-9)}.

In this context, we have herein designed and synthesized a novel rhodamine 6G based dye compound.

This prepared dye compound was determined with the properties of fluorescent solvatochromic functions. The dye showed the bathochromic absorption and emission shift with increasing solvent polarity. As a fluorescent emission probe, this dye showed significant "turn-on" type of fluorescent responses with polar solvent media, especially acid media. In addition, related electron energy states of the dye compound such as HOMO and LUMO state were also characterized by computational calculations.

2. Experimental

All reagents and solvents used for the synthesis of rhodamine 6G based dye, were purchased from Aldrich and used without further purification. ¹H-NMR spectra were recorded on an NMR spectrometer JEOL-AL400 operating at 400MHz. Chemical shifts were referenced to internal Me₄Si (TMS). The absorption and fluorescent spectra were measured with an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC fluorescent spectrophotometer, respectively. The elemental analysis was performed by a Thermoc-Flash EA 1112 Automatic elemental analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70eV and the direct probe EI method.

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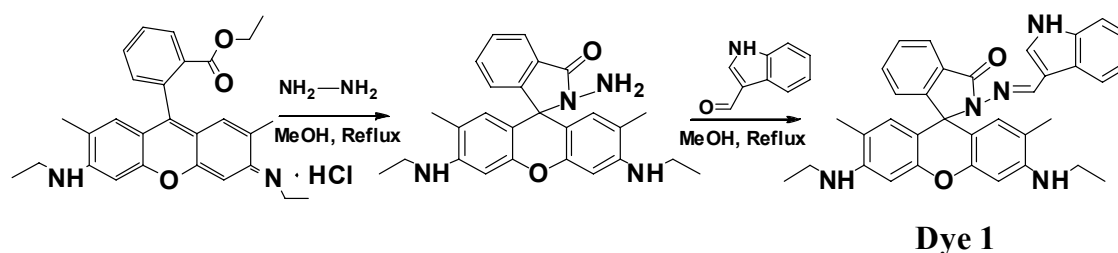


Figure 1. Synthetic routes of dye 1.

Electron distributions and energy potentials were calculated with Material Studio 4.3.

Rhodamine 6G based dye compound was synthesized through 2step reaction with rhodamine 6G hydrazide and indole-3-carboxaldehyde^{6,15}. The synthetic procedure of dye 1 was illustrated in Figure 1.

Rhodamine 6G (2g, 4.18mmol) was dissolved in 40ml MeOH. To the solution, hydrazine hydrate (2.5ml) was added dropwise. Ensuing mixture was refluxed until the red color disappeared. After cooling to room temperature, the solution was poured into distilled water (800ml) for 1day. Thereafter, the solid precipitate was filtered and dried in vacuum for 1day. Without further purification, next step was proceeded.

Rhodamine 6G hydrazide (0.428g, 1.1mmol) and indole -3-carboxaldehyde (0.1596g, 1.1mmol) were refluxed in methanol with 3 drops of acetic acid. After 4hrs of stirring, white precipitates were obtained. These white solids were filtered off, washed with ethanol and dried in vaccum. The yield was 63%. ¹H NMR (CDCl₃) : 9.21 (s, 1H); 8.19 (s, 1H); 8.02-7.99 (m, 2H); 7.50-7.48 (m, 2H); 7.33-7.32 (d, 1H); 7.20-7.12 (m, 3H); 6.43 (s, 2H); 6.38-6.26 (t, 2H); 3.57-3.44 (d, 2H); 3.22-3.17 (m, 4H); 2.95-2.88 (d, 1H); 1.91-1.86 (d, 6H); 1.39-1.25(m, 3H); 1.10 (s, 1H); 0.89-0.86 (t, 2H). Anal. Calcd: for C₃₅H₃₃N₅O₂:C, 75.58 H, 5.93 N, 12.59, O, 5.7 Found: C, 71.86 H, 5.68 N, 11.39, O, 7.34. MS *m/z*: 555 (M⁺).

3. Results and Discussion

We have studied the synthesis of novel solvatofluorochromic dye compound and its related absorption and emission optical properties in various solvent polarities. Dye 1 showed good solubility with hexane, diethyl ether, THF, EA, pyridine, acetic anhydride, DMSO, acetic

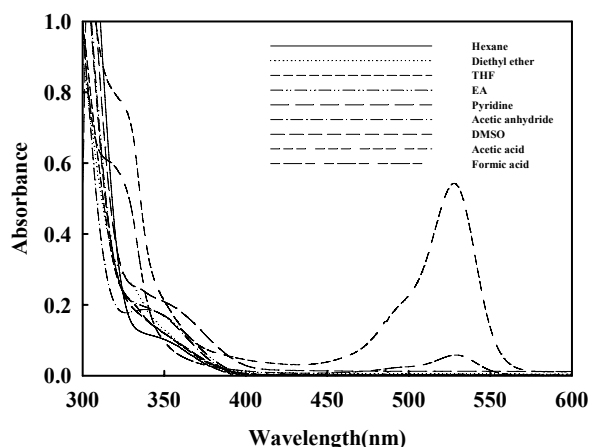


Figure 2. Absorption spectra of dye 1 in various solvents.

acid and formic acid. These investigated solvents were various from non-polar to polar properties. As shown in Figure 2, dye 1 did not show noticeable solvent effects (solvatofluorochromism) in its maximum absorption wavelength with most applied solvents. However, the clear absorption wavelength shifts were observed with acetic and formic acid, which can be considered as the promising molecular probe toward acid media detection sensor.

With applying sufficient excitation energy at 365nm, solvatofluorochromic effect was observed. Noticeable emission shifts were observed in fluorescent intensity spectra as shown in Figure 3. These fluorescent intensities show various values in different solvents.

In particular, clear new emission wavelength shifts in Figure 3were also observed in acetic acid and formic acid, which are well agreed with the results as shown in Figure 2. Through the fluorescent emission spectra, it was monitored that the emission spectra wavelength increased with increasing solvent polarities. In this regard, we anticipated that these different emission spectra values in different solvents may be influenced by solvatofluorochromic effect. Furthermore, the wavelength values of

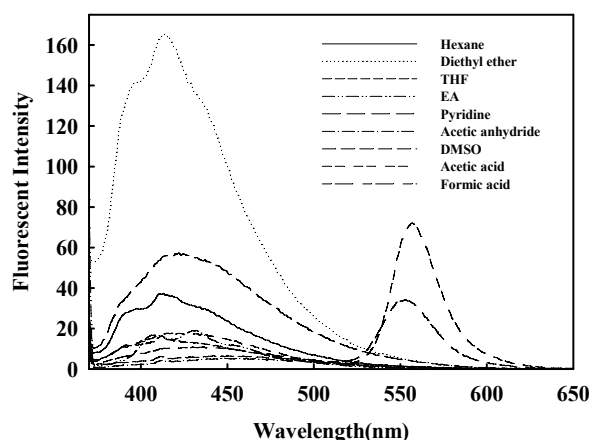


Figure 3. Fluorescent emission spectra of dye 1 in various solvents.

absorption and fluorescent emission were clearly shifted in acid solvents compared to other solvents. This finding is well agreed with Figures 2 and 3.

Especially in acetic acid, the clear lemonish- yellow fluorescent emission was observed. Commonly, this acetic acid is classified into one of volatile organic compounds (VOCs)⁷⁾. Accordingly, we may anticipate that this dye 1 can be utilized as the probe sensor toward VOCs, namely the detection sensor probe for hazardous VOCs⁷⁾.

For further investigation on solvatofluorochromic effect of dye 1, the $\lambda_{\max \text{ em}}$ values of dye 1 in various solvents and $E_T(30)$ are tabulated in Table 1.

These $E_T(30)$ values are an empirical parameter of solvent polarity. Namely, the transition energy for pyridinium-*N*-phenoxide betain dye, expressed in kcal mol⁻¹, is used as a polarity parameter. It is possible to determine the chromic effects using nearly 362 different solvents^{8,9,16)}.

Table 1. $\lambda_{\max \text{ em}}$ and $E_T(30)$ values of dye 1 in various solvents

Solvent	$\lambda_{\max \text{ em}}$	$E_T(30)$
Hexane	413	31.0
Diethyl ether	413	34.5
THF	412	37.4
EA	432	38.1
Pyridine	422	40.5
Acetic anhydride	466	43.9
DMSO	442	45.1
Formic acid	553	54.3
Acetic acid	557	51.7

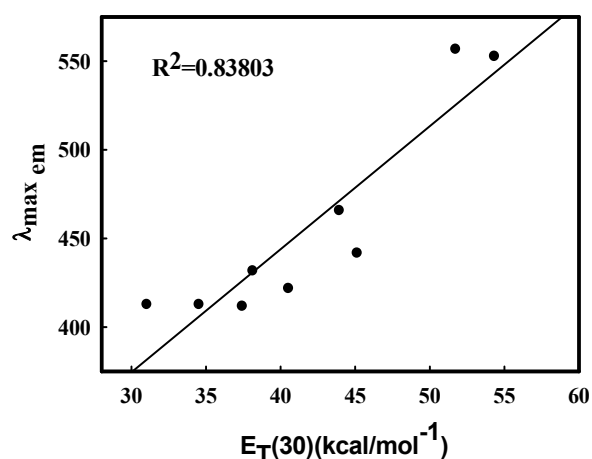


Figure 4. The liner plots on plotting $\lambda_{\max \text{ em}}$ versus solvent polarity parameter $E_T(30)$ (kcal/mol⁻¹).

With $\lambda_{\max \text{ em}}$ and $E_T(30)$ values shown in Table 1, we have obtained a linear plot of dye 1 on plotting $\lambda_{\max \text{ em}}$ versus the solvent parameter as represented in Figure 4 and the corresponding fluorescent emission photographs of dye 1 in several solvents are also shown in Figure 5.

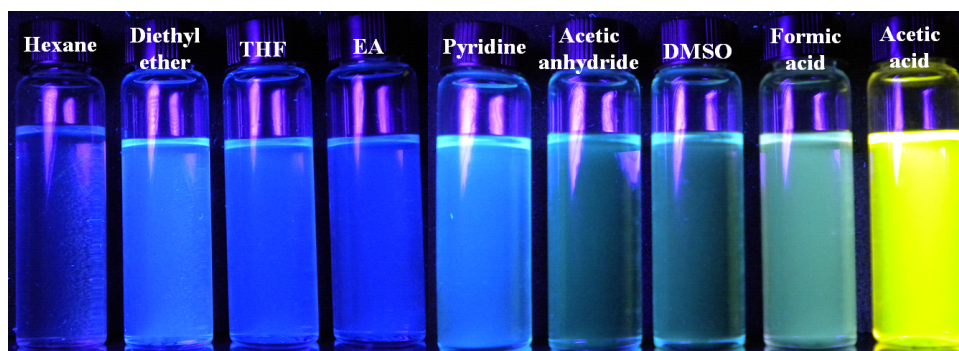


Figure 5. The fluorescent emission photograph of dye 1 in various solvents.

The linear relationship and features of fluorescent emissions indicate that $\lambda_{\text{max em}}$ values increased with increasing solvent polarity. R^2 value was calculated for 0.83803. Fluorescent emissions changed from blue to yellow were also observed with naked eye. From the results of Figures 4 and 5, the dye 1 showed bathochromic shift with increasing polarity of solvents. It can be proposed that this effect occurred by the interaction between decreasing energy gap of HOMO-LUMO and increasing solvent polarity^{10,11}.

With regard to above results, we have also investigated the geometrical shape and HOMO/LUMO energy levels of dye 1. Geometrical structure and molecular orbital calculations were performed with measuring a Material Studio 4.3 suite of programs which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbits¹²⁻¹⁴. As shown in Figure 6, the calculated molecular structure and the electron distribution of HOMO and LUMO of dye 1

were observed. With comparison of HOMO and LUMO electron state, electron localization was moved from indole-3-carboxaldehyde to the unit of rhodamine 6G. It is related with the system of intramolecular charge transfer (ICT) property of dye 1 molecule and the change of electron distribution from HOMO to LUMO causes to the fluorescent intensity⁸.

4. Conclusions

We have synthesized a novel rhodamine 6G based solvatofluorochromic dye 1. The prepared dye compound was determined with the properties of solvatofluorochromic functions. The dye showed the bathochromic absorption and emission shifts with increasing solvent polarity. As a fluorescent emission probe, this dye showed significant “turn-on” type of fluorescent responses with polar solvent media. The related electron energy level of dye compound such as HOMO and LUMO state and the electron density distribution were characterized by computational calculations, which showed intramolecular charge transfer system through dye 1 molecular structure.

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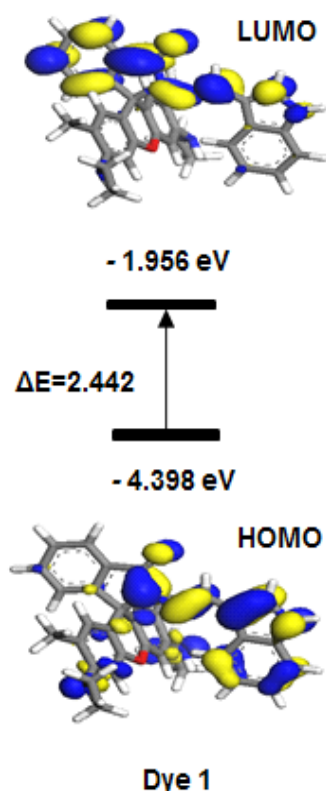


Figure 6. Electron distributions and HOMO/LUMO energy levels of dye 1.

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