Synthesis, Structure and Solvatochromic Properties of Novel Diacetylene Rhodamine-Based Solvatochromic Dye

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Abstract : A novel diacetylene rhodamine-based solvatochromic dye (DA-Rhoen) have been synthesized by amidation reaction between Rhoen and DA. Chemical structures and purity were characterizations by 1H NMR and ATR-FTIR. The photophysical studies in different solvents, such as H2O, methanol (MeOH), ethanol (EtOH), dimethylformamide (DMF), acetonitrile (ACN), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane (CH2Cl2) and chloroform (CHCl3) were studied. It was found that the largest color and fluorescence changed were visualized after dissolved in CHCl3 solution. In addition, UV-visible and fluorescence spectra also showed a new significant enhancement of absorbance intensity (at 550 nm) and emission intensity (at 570 nm). The solvatochromic mechanism is caused by solvent-induced equilibrium shift to ring-opening of spirolactam form (Z-form).

Keywords : Solvatochromic Dye, Rhodamine, Diacetylene, Color, Fluorescence

1. Introduction

Solvatochromism is the occurrence observed while the color due to a solute is different when that solute is dissolved in different solvents [1-2] and change shape, absorption spectra, λmax, and intensity [3] depending on the nature of the solvent [4]) of a chromophore in solvents of different polarity [5]. A called positive and negative solvatochromism due to bathochromic (red) shift and hypsochromic (blue) shift with increasing solvent polarity, respectively. A convert bathochromic to hypsochromic, or vice versa, by the increase in solvent polarity, is called reverse solvatochromism [2]. Solvatochromic compounds are those solutes that induce a change in the color of the solution with a change in solvent polarity. Normally, solvatochromic compounds have two extreme resonance contributing structures: one form is quinoidal, nonpolarized, and formally nonaromatic; the other is zwitterionic, polarized, and fully aromatic. The change in the absorption band with solvent occurs from variation in the contribution of these canonical forms to the overall resonance hybrid [6]. Solvatochromism is crucial in determining the properties of molecular solids, including solubility, physical and chemical stability [7-8]. Therefore, solvatochromism has a central role in a number of fields including pharmaceuticals, pigment chemistry and materials science [9].

2. Objectives

This research was aimed (1) to synthesize a novel diacetylene rhodamine-based solvatochromic dye and (2) to study a relationship between a novel solvatochromic dye and solvents.

3. Literature reviews

Rhodamines are highly fluorescent dyes [10]. In general, rhodamine derivative displays a red color change and strong fluorescence in acidic solutions by activation of a carbonyl group in a spirolactone or spirolactam moiety [11]. Nowadays, there is much previous research investigation their properties because of their displays interesting equilibria which depend on concentration of solvent such as Ramette' and Sandell [12] were investigation of rhodamine B (R) equilibria included a benzene extraction study, measurement of solubility of R salts and a spectrophotometric study in aqueous solution. Hinckley et al [13] had been studying electronic absorption spectra of rhodamine B which depend on solvatochromism and thermochromics. Zakerhamidi et al [14] had been studying a solvent effect on absorption and emission spectra of rhodamine dyes that depend on the nature of solvents and the attached substituents on xanthene skeleton. Benchea et al [15] reported a solvatochromic study establishes the contribution of each type of intermolecular interactions to the spectral shift of the absorption band of Rh 6G and Rh B in a given solvent. And rhodamines are widely used with numerous chemical applications such as sensing materials. Among of sensing materials, polydiacetylenes (PDAs) are one of the most capable due to their unique chromism properties and becoming interesting materials. The blue PDAs undergo a color shift to a red phase upon various factors such as solvent [16]. For example, Wang and Han [17] had been preparing of a rhodamine B-functionalized bis-polydiacetylene (RB/bis-PDA) film sensor for Al3+. The interesting solvatochromicsm property of PDAs induce to extensively used with the chemical application such as Park et al [18] had been reported optical solvent sensor based on solvatochromic polydiacetylene for tetrahydrofuran (THF). Dei et al [19] had been studying an aggregation of PDAs according to the decrease in the solubility in a poor solvent and at a lower temperature that helps to occur solvatochromism.

4. Materials and methods

4.1 Chemical

All reagents were analytical reagent grade. Rhodamine B, and 10,12-pentacosadiynoic acid (DA) were purchased from Aldrich. N, N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), ethylenediamine and MeOH were purchased from Merck used without further purification. Dimethylformamide (DMF) was purchased from Merck dried over CaH2 (purchased from Fluka) and freshly distilled under nitrogen prior to use. Dichloromethane (CH_2Cl_2) was purchased from Merck distilled before use.

4.2 Instrumentals

^{1}H NMR was measured with a Varian 400 MHz spectrometer in CDCl3 with TMS as the internal reference. Fluorescence spectra in solution were measured with a Perkin Elmer LS 50B. Absorbance spectra were recorded with a Perkin Elmer Lambda 25 UV/VIS spectrometer. ATR-FTIR spectra were recorded with a Bruker Tensor 27 ATR-FTIR. Column chromatography was carried out using silica gel (Kieselgel 60, 0.063–0.200 mm, Merck).

4.3 Synthesis

Synthesis of rhodamine ethylenediamine (Rhoen) [20]

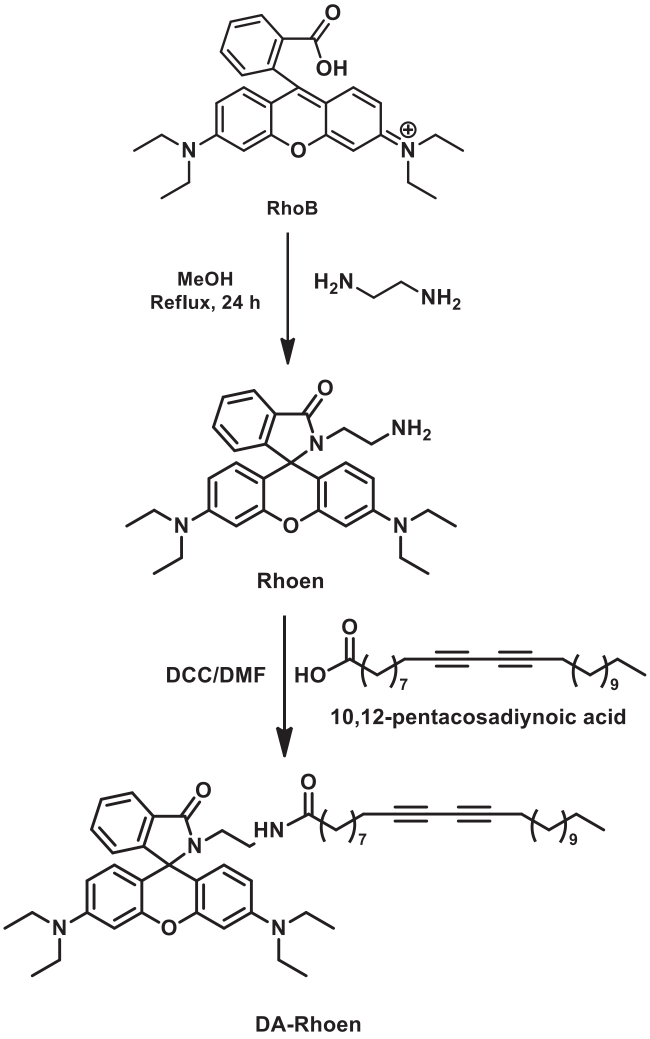
Rhodamine B (0.20 g, 1.67 mmol) was dissolved in 30 mL of methanol, and ethylenediamine (0.22 mL, excess) was added dropwise to a solution and refluxed overnight (24 h) until the solution lost its red color. The solvent was removed by evaporation. Then the residue was dissolved by dichloromethane and extracted with sodium bicarbonate 2 times, water 2 times, bicarbonate 2 times, respectively. The combined organic phase was dried over with anhydrous sodium sulfate and a solvent was removed by evaporation. After that, the product purified by column chromatography (dichloromethane: methanol: triethylamine 10:90:1 v/v). The yield was 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86–7.81 (m, ^{1}H, ArH), 7.45– 7.32 (m, 2H, ArH), 7.08–7.03 (m, ^{1}H, ArH), 6.42 (s, ^{1}H, ArH), 6.39 (s, ^{1}H, ArH), 6.37 (s, 2H, ArH), 6.38–6.21 (m, 2H, ArH), 3.32 (q, J = 6.8 Hz, 8H, NCH_2CH_3), 3.12 (t, *J* = 6.8 Hz, 2H, NCH_2CH_2), 2.23 (t, *J* = 6.8 Hz, 2H, $NCH_2CH_2NH_2$), 2.05 (s, 2H, $CH_2CH_2NH_2$) and 1.16 (t, J = 7.2 Hz, 12H, NCH_2CH_3).

Synthesis of Diacetylene-Rhodamine ethylenediamine (DA-Rhoen)

N,N'- Dicyclohexylcarbodiimide (DCC) (65.3 mg, 0.316 mmol) in methylene chloride (3 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (DA) (129 mg, 0.344 mmol) in methylene chloride (9 mL). Then, dimethylformamide was added dropwise in solution. The mixture was stirred at 0 °C for 1 h. *Rhoen* (200 mg, 0.419 mmol) in methylene chloride (7 mL) was added dropwise into the reaction mixture at room temperature. The reaction mixture was stirred at room temperature overnight. The mixture was extracted with methylene chloride (25 mL, 3 times). The organic phase was dried with anhydrous sodium sulfate and evaporated to yield the crude product as a white powder. The crude product was purified by column chromatography on silica gel eluted with a mixture of ethyl acetate and hexane (50:50 v/v). The yield was 50 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.86 (t, *J* = 6.8 Hz, 3H; CH_3), 1.09 (t, *J* = 7.1 Hz, 3H; CH_3), 1.33 (m, 16H, 32H; CH_2), 2.15 (t, J = 7.6 Hz, 2H: CH_2), 2.21 (t, *J* = 6.9 Hz, 4H; CH_2), 2.64 (q, *J* = 7.2 Hz, 2H; CH_2), 2.74 (t, *J* = 7.6 Hz, 2H; CH_2), 3.33 (q, J = 5.7 Hz, 2H; CH_2), 6.45, (brs, 1H; NH), 7.11–8.0 (m, 1H, ArH), 6.89 (s, 1H, ArH). IR: ν = 3328 cm^{-1} (NH), 1622 cm^{-1} and 1520 cm^{-1} (spirolactam amide-keto), 1620 cm^{-1} (C=O).

Computational studies

The stable electronic structure and the HOMO, LUMO energies of the **DA-Rhoen** was calculated using the density functional theory (DFT) method at the B3LYP/6-31(d) theoretical level under the Gaussian 09 program.



Scheme. 1 Synthetic pathways of DA-Rhoen

5. Results and discussions

5.1 Characterization of DA-Rhoen

DA-Rhoen was synthesized by amidation reaction with rhodamine B-ethylenediamine or

Rhoen and 10,12-pentacosadiynoic acid (DA) in the presence of DCC as coupling reagent under N2 at reflux for overnight in DMF (Scheme. 1). The chemical structure was confirmed by 1H NMR and ATR-FTIR techniques.

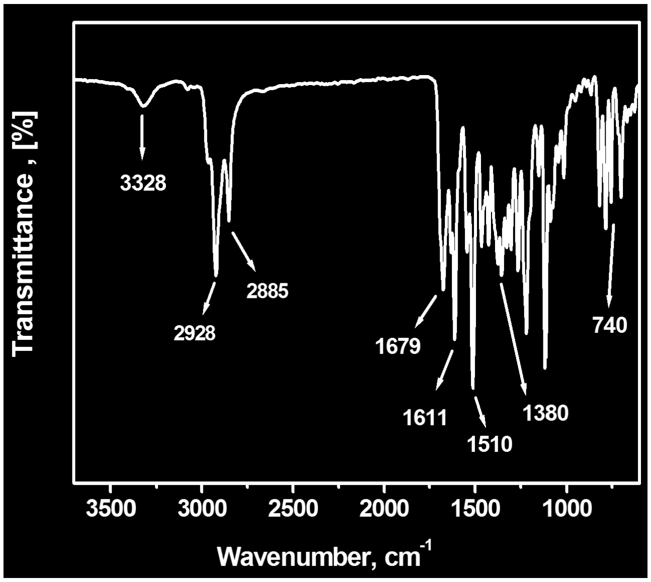


Fig. 1 ATR-FTIR spectra of DA-Rhoen

The characteristic ATR-FTIR spectrum of DA-Rhoen (Fig. 1.) showed the prominent C=O stretch of rhodamine peak at 1679 cm^{-1}, aromatic rhodamine peaks at 2885, 1611 and 1510 cm^{-1}, CH stretching vibrations of the diacetylene side chain at 2928 cm^{-1}, CH_2 and CH_3 bending vibrations 1380 and 740 cm^{-1} and the amide (N–H stretch) peak at 3328 cm^{-1} [21].

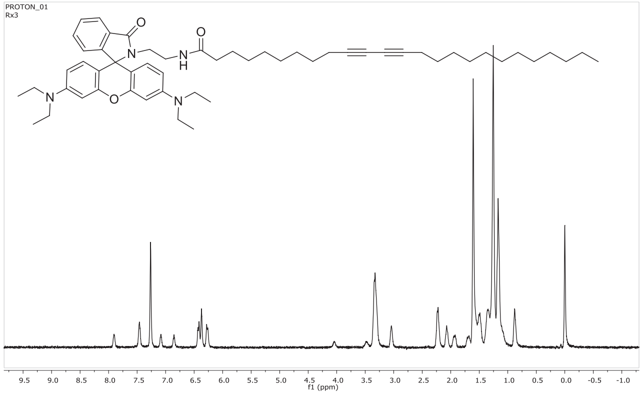
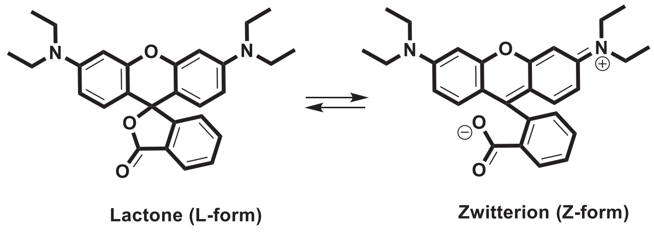


Fig. 2 ^{1}H NMR spectra of DA-Rhoen

The ^{1}H NMR experiment of DA-Rhoen was carried out in $CDCl_3$, and the spectrum is depicted in Fig. 2. The ^{1}H-NMR spectra of DA-Rhoen showed the characteristic signals of diacetylene protons in the region of 1.0 - 2.0 ppm and aromatic protons of rhodamine at 7.0 - 8.0 ppm. The chemical shifts of amine NH of DA-Rho around 6.8 ppm [22]. This observation confirmed that the rhodamine ethylenediamine was successfully connected with DA.

5.2 Thermochromic Effect of DA-Rhoen

Normally, the xanthene dye rhodamine B showed two forms in an equilibrium mixture: (1) a colorless lactone (L-form) and (2) a colored zwitterion (Z-form) [23].



Scheme. 2 The equilibrium of xanthene dye rhodamine B

In order to establish the novel solvatochromic dye, the DA-Rhoen (L-form) was dissolved in a number of solvents (H_2O, MeOH, EtOH, DMF, ACN, DMSO, THF, CH_2Cl_2, and $CHCl_3$). The color and fluorescence images were employed to monitor the position of the lactone-zwitterion equilibrium of the DA-Rhoen base isomers. As displayed in Fig. 3, the colorless of DA-Rhoen turned immediately from colorless to orange after exposure to $CHCl_3$ solution at room temperature and the emission color of DA-Rhoen also changed after dissolving in $CHCl_3$. Because in the case of chlorinated solvents, the dimer Z-form species were predominated instant of L-form. This may be due to the increase in interactions between molecules in the part of DA moiety to produce the aggregation of DA-Rhoen [24]. The results were consistent with previous work which strongly indicated that the equilibrium shifted toward the zwitterion form [12-13, 25].

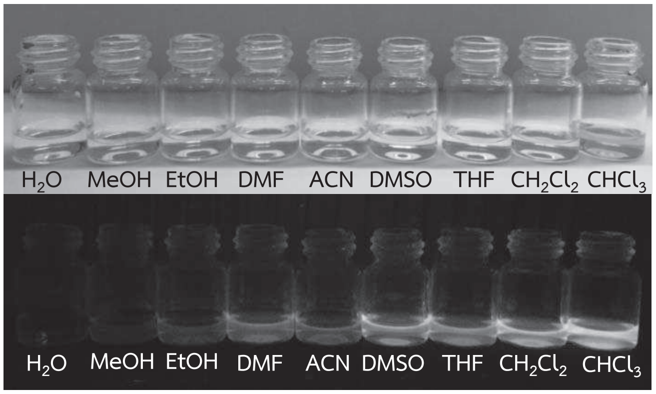


Fig. 3 Digital images of **DA-Rhoen** in different solvents at 10 μM taken under normal illumination (above) and demonstrating skeletal fluorescence under 365 nm illumination (below).

In addition, UV-visible and fluorescence spectroscopy techniques were employed to observe the equilibrium shifted toward the zwitterion form of DA-Rhoen. After dissolved DA-Rhoen in CHCl3, a new significant enhancement of absorbance intensity (at 550 nm) and emission intensity (at 570 nm) were distinguished as a result of solvent induced ring-opening of spirolactam form (Z-form) (Fig. 4).

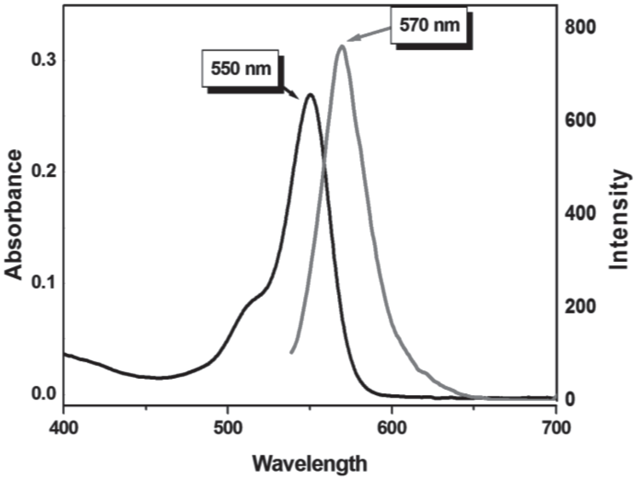


Fig. 4 Absorption and fluorescence spectra of DA-Rhoen after dissolved in CHCl3.

6. Conclusion

In summary, we have successfully synthesized a novel diacetylene rhodamine-based colorimetric dye (DA-Rhoen) by amidation reaction between Rhoen and DA, and the photophysical studies in different solvents, such as H_2O, MeOH, EtOH, DMF, ACN, DMSO, THF, CH_2Cl_2, and $CHCl_3$. The colorless of DA-Rhoen turned immediately from colorless to orange after exposure to $CHCl_3$ solution at room temperature and the emission color of DA-Rhoen also changed after dissolving in $CHCl_3$. This solvatochromic dye has been found to act as a good indicator molecule for chlorinated solvents and can be further study as solvatochromic sensor.

7. Acknowledgement

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