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Synthesis and photophysical study of novel coumarin based styryl dyes

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ABSTRACT

New organic dyes comprising phenothiazine, carbazole, indole, diphenylamine moieties, as the electron donors, and coumarin ring as the electron acceptor through ethylenic π bridge were synthesized and characterized. The reaction of different coumarin-4-acetic acids with phenothiazine-3-carbaldehyde in the presence of piperidine in methanol gives highly fluorescent styryl derivatives having *cis* configuration of ethylenic double bond. Under similar conditions 7-methylcoumarin-4-acetic acid was condensed with indole-3-carbaldehyde, carbazole-3-carbaldehyde, and diphenyl amine aldehyde to give different styryl derivatives with *trans* configuration of ethylenic double bond. Synthesized compounds were also studied for photophysical properties and show solvatochromism.

1. Introduction

Organic dyes with donor-π-acceptor (D–π–A) structures have attracted increasing attention since they can provide photoluminescent materials in molecular electronics, such as efficient nonlinear optical (NLO) materials [1], organic light-emitting diodes (OLEDs) [2], and solar cells [3]. So far, many organic D–π–A compounds have been studied experimentally and theoretically. Various classes, including triarylamines [4], carbazoles [5], fluorenes [6], and thiophenes [7], have mostly been used as electron-donating moieties, whereas quinolines [8], quinoxalines [9], oxadiazoles [10], diarylborons [4], and benzothiadiazoles [11], are commonly used as electron-accepting moieties. In these compounds, donor moiety facilitates hole injection and transport, whereas the acceptor moiety facilitates electron injection and transport. Carbazole, diphenyl amine, and phenothiazine are often adopted as donors, as a result of their good thermal, electrochemical stability, and electron donating abilities [12]. The UV–Vis absorption and photoluminescence (PL) of these compounds suggest significant intramolecular charge transfer (ICT) behavior and solvatochromism. Although remarkable progress has been made in the organic dyes, further optimization of their chemical structures is still of great necessity. Their various properties could be finely tuned by using different donor and acceptor groups.

In 1883, Bernthsen, the father of phenothiazine (PTZ) chemistry, first synthesized phenothiazine compound. The phenothiazines have wide range of applications. Some phenothiazine derivatives, notably lauth's violet and methylene blue were commercially available as dyes even before the discovery of the parent phenothiazine. Various phenothiazine derivatives are used in dye sensitized solar cells (DSSCs) [13], Phenothiazine contains electron-rich sulfur and nitrogen as hetero atoms in the middle ring exhibits good electrochemical stability and electron-donating ability, and has been considered as a promising donor moiety in organic dyes. Furthermore, the PTZ ring is non-planar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers. Therefore, PTZ based organic dyes have attracted broad interest for synthesis of fluorescent compounds.

On the other hand coumarins have also been widely investigated with regard to their outstanding optical properties. They constitute the largest class of fluorescent dyes [14], and are widely used as emission layers in organic light-emitting diodes (OLED) [15], optical brighteners [16], non-linear optical chromophores [17], fluorescent whiteners [18], fluorescent labels as well as probes for physiological measurement [19]. Typical coumarin based

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fluorescent compounds normally contain an electron donor group at the 7-position and an electron acceptor such as benzoxazole, benzimidazole or benzothiazole ring at the 3-position [20]. There is only one report in which coumarin ring act as acceptor in organic dyes [21]. If we placed electron donating substituent at proper position in coumarin ring, coumarin ring act as an acceptor as it involves delocalization of electron over polar carbonyl group through conjugated 3-4 double bond. Based on these considerations, we have designed and synthesized a series of styryl dyes containing phenothiazine as donor and coumarin as an acceptor.

Recently, Samant et al. synthesized coumarin based fluorescent compounds in which one coumarin moiety act as electron donor while other coumarin moiety act as an electron acceptor through ethylenic bridge [21,22]. These *trans*-biscoumarinylethenes are further studied for photophysical properties. Taking inspiration from this, we have synthesized phenothiazine based coumarin dyes (PTZ-coumarin ethene) which shows some comparable and interesting results as compared to *trans*-biscoumarinylethenes. It includes 1) in biscoumarinylethenes stereochemistry of ethylenic double bond is *trans* while PTZ-coumarin ethene show *cis* stereochemistry of ethylenic double bond. 2) *trans*-Biscoumarinylethenes have good emission value in polar solvent like dimethyl sulfoxide while PTZ-coumarin ethenes have good emission value in non polar solvent like chloroform. 3) In addition to this, PTZ-coumarin ethenes show higher Em, λ_{Max}, higher Stokes shift and higher quantum yield as compared to *trans*-biscoumarinylethenes.

2. Experimental

2.1. Materials and equipments

Phenothiazine was purchased from commercial suppliers and was used without further purification. Citric acid, phenols and piperidine were purchased from S. D. Fine Chemical Ltd. India. Methanol used in this work was of analytical grade. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance NMR spectrometer in $CDCl_3$/DMSO-d_6 with TMS as an internal standard, and the chemical shifts were expressed in δ unit (ppm). Mass spectral data were obtained with micromass-Q-Tof (YA105) spectrometer. Elemental analysis was carried out with a Thermo finnigan, Flash EA 1112. All Infrared spectra were recorded on Jasco-FT/IR 4100 LE ATR PRO450-S spectrometer. All the melting points reported are in degree centigrade and are uncorrected. Absorption spectra were recorded on Perkin–Elmer Lamada 25 UV–vis spectrophotometer. Emission spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light.

2.2. Synthesis

2.2.1. Synthesis of 6,7,8-substituted coumarin-4-acetic acid (4)

All coumarin-4-acetic acids (**4**) were synthesized using reported methods [23]. A mixture of anhydrous citric acid (**1**) (192 g, 1 mol) and conc. H_2SO_4 (280 mL) was stirred at room temperature for 1 h and then slowly heated (rate of heating governed by foaming) to 70 °C. After 30–35 min at this temperature, with stirring throughout, the evolution of carbon monoxide slackened. The clear solution was rapidly cooled to 0 °C. To the cooled solution, *m*-cresol (**3a**) (86.4 g, 0.8 mol) and conc. H_2SO_4 (112 mL) were added with stirring, each in three equal portions, at such a rate that the internal temperature did not exceed 10 °C. The resulting mixture was stirred at room temperature for 16 h, poured into ice and the resulting precipitate was filtered and washed thoroughly with water. The precipitate was stirred with saturated $NaHCO_3$ solution (1000 mL) for 15 min at 65 °C. The solution was filtered and the insoluble material was washed with water. Acidification with conc. HCl of the combined filtrate gave 110 g, 63% of solid **4a** which was used further without purification.

Using the above procedure different substituted phenols (**3**) were condensed with acetone dicarboxylic acid to obtain a series of 6,7,8-substituted coumarin-4-acetic acids (**4**).

2.2.2. Synthesis of N-butylphenothiazine (6a)

To a phenothiazine (**5**) (30 g, 0.15 mol) solution in dry DMF (100 mL), sodium hydride (10.8 g, 0.45 mol) was slowly added at 0 °C for 1 h. Then this reaction mixture was stirred at room temperature for 1 h. After that 1-bromobutane (0.18 mol) was added drop wise to the reaction mass for 1 h which was then slowly heated to 70 °C for 3 h. The progress of the reaction was monitored by TLC. After complete consumption of phenothiazine, the reaction mixture was poured into ice cold water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography using hexane as the eluent to give 35.1 g, 91% of **6a** as colourless viscous liquid.

Using above procedure *N*-propylphenothiazine **6b** was synthesied in 87% yield.

2.2.3. Synthesis of phenothiazine-3-carbaldehyde (8a) and phenothiazine dialdehyde (7a)

7a and **8a** were synthesied using reported method [12].

In a three necked 100 mL round bottom flask fitted with a mercury sealed stirrer, addition dropping funnel topped by calcium chloride guard tube and reflux condenser also topped by calcium chloride guard tube. *N*, *N*-dimethyl formamide (4.58 g, 4.85 mL, 62.7 mmol) was taken and cooled to 0–5 °C with stirring. To the above solution phosphorous oxychloride (7.2 g, 4.3 mL, 47 mmol) was added drop wise maintaining the temperature of the reaction mass at 0–5 °C. The Vilsmeier complex so formed was stirred for further 15 min and compound **6a** (3.97 g, 15.6 mmol) was added in portion wise (15–25 min) to the complex. The reaction mixture was stirred at 0–5 °C for 3 h and then allowed to attain room temperature then heated to 75 °C for 8 h. This solution was then cooled to room temperature, poured into ice water, and neutralized to pH 6-7 by drop wise addition of saturated aqueous $NaHCO_3$ solution. The mixture was extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4 and then concentrated on rotary evaporator to obtain crude reaction mixture, which was further purified by FCC using toluene to afforded **7a** (0.37 g, 7%) as light brown oil and **8a** (2.8 g, 64%) as yellow oil.

Similar way indole-3-carbaldehyde (**11**), carbazole-3-carbaldehyde (**12**) were prepared using reported procedure in the literature [24,25].

2.2.4. General procedure for synthesis of styryl dyes

4a–**g** (1 mmol) and piperidine (1 mmol) were stirred in methanol (6 mL) for 15 min and corresponding aldehyde (1 mmol) was

Table 1
Influence of inorganic bases on styryl formation[a].

Entry	Base	Solvent	Time (h)	Result
1	NaOH	Ethanol	48	Coumarin decarboxylation
2	NaH	Tetrahydrofuran	48	NR
3	NaOAc	Ethanol	48	NR
4	NaOEt	Ethanol	48	NR
5	KOtBu	THF	48	NR
6	K_2CO_3	Ethanol	48	NR

NR: No reaction.
[a] Reaction conditions: **8a** (1 mmol), **4a** (1 mmol), base (1 mmol), solvent: (6 mL), room temperature (35 ± 2 °C).