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Red emitting triphenylamine based rhodamine analogous with enhanced Stokes shift and viscosity sensitive emission

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ABSTRACT

Four novel structural hybrid analogues of Rhodamine B and Rhodamine 101 are synthesized by condensing N-substituted amino phenols with keto-acids of N-substituted phenols in presence of trifluoroacetic acid and are characterized by spectroscopic methods. Triphenylamine based derivatives show large Stokes shift (47 nm–69 nm) and red shifted emission (close to Near Infrared region) as compared to parent Rhodamine B and Rhodamine 101. These N-phenyl substituted dyes exhibited negative solvatochromism and pronounced viscosity sensitivity (14–24 folds increase in emission intensity) as compared to parent rhodamines. Polarity graphs and mathematically calculated charge transfer descriptors are in good correlations with observed trends. Computed values obtained by Density Functional Theory are in good agreement with the experimental results.

1. Introduction

The photophysical properties of xanthenes, particularly rhodamines have been extensively studied [1]. Rhodamines are widely used as fluorescent probes [2], chemosensors in detection of small molecules [2], sensitizers in dye sensitized solar cells [3] and as laser dyes [4]. Photophysical properties of rhodamine derivatives can be modified by three ways: (i) modification of the amino groups of xanthene moiety (positions 3 and 6) [5]; (ii) modification of the carboxyphenyl ring at positions 4'and/or 5' [5] or (iii) modification of the carboxylic acid group (position 2') [5].

Comparative studies on fluorescence properties of the structural analogues of rhodamine dyes such as Pyronin B (C.I. 45010), Pyronin Y (C.I. 45005) and Acridine Red (C.I. 45000), have been reported by Xian-Fu Zhang et al. [6]. V. N. Belov, S. W. Hell et al. reported novel red emitting rhodamine dyes excitable with 630 nm laser light and emitting at around 660 nm [7]. Y.-H. Chu et al. reported rhodamine analogues containing biaryl linkers to impart rigidity [8].

Triphenylamine is widely used donating group for its charge transfer characteristic [9] and very good electron donating ability [10]. Triphenylamine has been applied in a number molecules designed for aggregation induced enhancement [11], organic light emitting devices [12] and dye sensitized solar cells [13]. Co-planarity between nitrogen atom and the three adjacent carbon atoms in triphenylamine maintain uninterrupted conjugation [14,15] between the lone pair of nitrogen and the dendrimer arms [16]. To our motivation, effect of phenyl groups on photophysical properties of some phenanthroline derivatives has also recently explained by Taro Tsubomura et al. [17]. Here, we are interested in understanding the role of phenyl substituent of triphenylamine group in alternating photophysical properties of our novel rhodamine dyes as compared to parent dyes.

In rhodamine derivatives apart from fluorescence emission, the only other significant decay path-way for the excited state is internal conversion to the ground state [18]. The rate of internal conversion is determined by a number of factors including the substituents at 3 and/or 6 position on xanthene moiety of dyes [18,19], solvent viscosity [20] and solvent polarity [20]. Rate of internal conversion is dramatically reduced by rigidizing the group at 3 and/or 6 position on xanthene moiety of dyes, either by chemical bonds or by using a viscous solvent [18,20].

In this work we are presenting synthesis of novel Rhodamine (**Rho1-Rho4**) dyes. Phenyl substitution at 3 and/or 6 position on amino groups in xanthene moiety of dyes, **Rho 1, Rho 3** and **Rho 4** facilitated significant Stokes shift and red shift in emission as compared to **Rhodamine B** and **Rhodamine 101**. Unfortunately **Rho 1, Rho 3** and **Rho 4** have very low quantum yields in solvents.

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This may be due to unfavorable steric interactions caused by the modification of both amino groups to enhance the nucleophilicity of the phenolic oxygen and lead to lactone formation [5]. So, viscosity induced study has been performed to overcome fluorescence quenching caused by such unfavorable steric interactions.

2. Experimental

2.1. Materials and methods

Sodium bicarbonate, 3-methoxyaniline, phthalic anhydride, toluene, anhydrous aluminium chloride, ethylene dichloride, pyridine hydrochloride, Iodobenzene, 1,10-phenanthroline and Cu(I)I were purchased from S.D. fine chemicals Ltd., Mumbai, India. The solid reagents were characterized by their melting points and used without further purification. Commercially available **Rhodamine B** and **Rhodamine 101** were procured from Sigma-Aldrich India and used without further purification. All reactions were monitored on precoated silica gel aluminum based plates Kiesel gel 60 F254 Merck, India. Purification was achieved by silica gel 100–200 mesh size. Melting points were recorded on instrument from Sunder Industrial Product Mumbai. The absorption spectra of the compounds were recorded on a Perkin-Elmer Lamda 25 UV–visible spectrophotometer. Fluorescence emission spectra were recorded on Varian Cary Eclipse fluorescence spectrometer. FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ^{1}H NMR and 13C NMR spectra were recorded on a 500 MHz and 125 MHz respectively on Agilent Technology instrument. Chemical shifts are expressed in 1 (ppm) using TMS as an internal standard.

2.2. Synthesis and characterization

2-(4-(Diethylamino)-2-hydroxybenzoyl)benzoic acid **2** [21], 8-hydroxyjulolidine **7** [22] and 2-(8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline-9-carbonyl)benzoic acid **8** [23] were synthesized by reported methods.

2.2.1. Synthesis of 3-methoxy-N,N-diphenylaniline 4

To a stirred solution of *m*-anisidine **3** (10 g, 81.20 mmol), iodobenzene (19.9 ml, 178.64 mmol), and 1,10-phenanthroline (0.59 g, 3.25 mmol) in toluene (175 ml) were added potassium *tert*-butoxide (27 g, 56.11 mmol) and copper (I) iodide (0.62 g, 3.25 mmol). The reaction mixture was heated under reflux for 24 h at 125 °C. On completion of the reaction the mixture was cooled to room temperature, filtered to remove copper metal. The product was extracted from the filtrate using ethyl acetate. The combined organic phases were concentrated under vacuum and purified by column chromatography using 5% EtOAc in hexane as the eluent to get the pure product (Scheme 1).

Yield: 66.10%, **Boiling point** = 130–135 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 7.24 (t, J = 7.9 Hz, 4H), 7.14 (t, J = 8.5 Hz, 1H), 7.09 (d, J = 7.9 Hz, 4H), 7.01 (d, J = 7.3 Hz, 2H), 6.65 (d, J = 8.5 Hz, 1H),6.62 (s, 1H), 6.56 (d, J = 8.5 Hz, 1H), 3.71 (s, 3H).

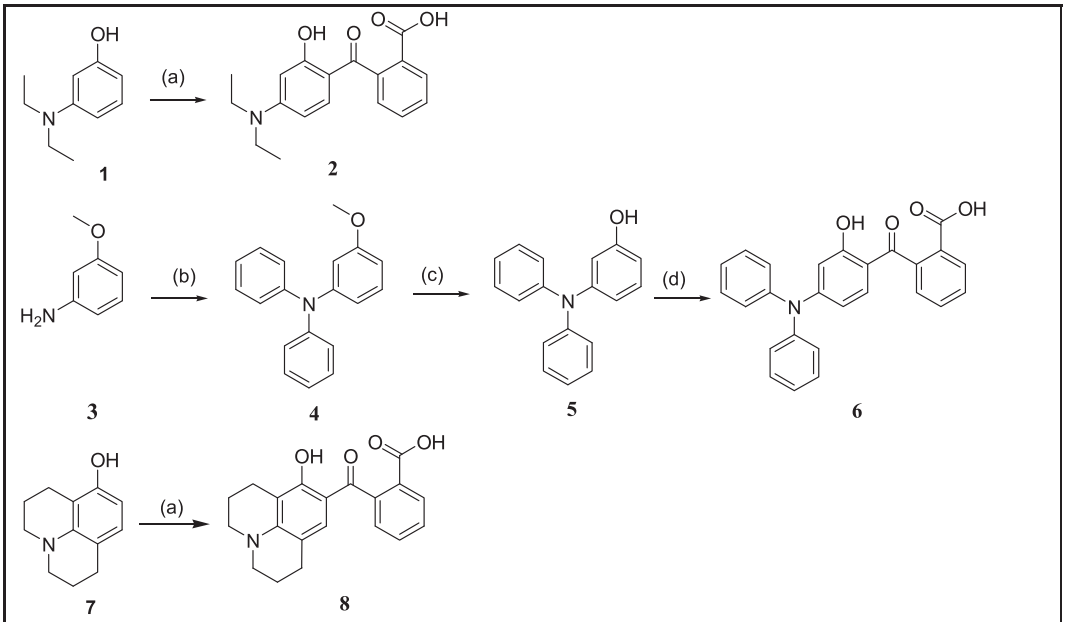
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) δ 160.4, 149.1, 147.7, 129.8, 129.2, 124.4, 122.8, 116.4, 109.7, 107.9, 55.2 ppm.

2.2.2. Synthesis of 3-(diphenylamino)phenol 5

3-Methoxy-*N,N*-diphenylaniline **4** (8 g, 29.09 mmol) was dissolved in 40 g of pyridine.HCl and heated to 200 °C for 10 h. After cooling to room temperature, water was added and solid came out was filtered, dried well and collected as crude product, which was further purified on column chromatography using 10% EtOAc in hexane as the eluent to get the pure product (Scheme 1).

Yield: 79%; **Melting point** = 98–100 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 4.60 (s, 1H), 6.46 (dd, J = 8.0 and 1.5 Hz, 1H), 6.52 (t, J = 1.5 Hz, 1H), 6.64 (dd, J = 8.0 and 1.5 Hz, 1H), 7.01–7.07 (m, 2H), 7.09–7.11 (m, 4H), 7.23–7.27 (m, 4H) ppm.



Reagents and Conditions: (a) Phthalic anhydride, toluene, reflux, overnight, N_2 atmosphere (b) Iodobenzene, ^{t}BuOK, 1, 10-phenanthroline/CuI, toluene, N_2 atmosphere (c) pyridine. HCl, 200 °C, overnight (d)Phthalic anhydride, anhydrous $AlCl_3$, 1,2 dichloroethane, 50 °C, overnight, N_2 atmosphere

Scheme 1. Synthesis of N-substituted amino phenol (**5**) and Keto-acids of N-substituted phenol derivatives (**2, 6** or **8**).