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Design, synthesis, characterization, photophysical and pH chemosensor studies of novel 2,4,6-trisubstituted pyridines

Nirmala S. Naik^a, Navya S. Bhat^a, Arpana G. Hegde^a, Swati S. Bhat^a, Akshay Kirasur^a, Anilkumar Patil^a, Lokesh A. Shastri^a, and Vinay Sunagar^b

^aDepartment of Chemistry, Karnatak University, Dharwad, India; ^bDepartment of Chemistry, G.S.S. College, Belagavi, Karnataka, India

ABSTRACT

For the application in organic electronics as well as pH meters, a series of novel 2,4,6-trisubstituted pyridines have been synthesized by the reaction of substituted aromatic aldehydes and substituted 3-acetylcoumarin with ammonium acetate. The structures of all the new compounds were characterized by IR, NMR, and GC–MS analysis. The important photo physical prerequisites for organoelectronic such as optical absorption and thermal stability were determined for the synthesized molecules. Optical properties were studied by UV–visible absorption and fluorescence spectroscopy. Optical band gaps of the 2,4,6-trisubstituted pyridines were found to be around 3.01–3.06 eV as calculated from their onset absorption edge. The pH-dependent changes in the fluorescence intensity suggest that 2,4,6-trisubstituted pyridines are useful applicants in intracellular pH meters.



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2,4,6-Trisubstituted pyridines; band gap; fluorescence emission; protonation studies

Introduction

2,4,6-Trisubstituted pyridines have attracted substantial interest in a wide range of research areas. The molecules play a key role as pharmaceutical agents, such as antioxidant, antiinflammatory,^[1] anticoagulants,^[2] and HIV inhibitors.^[3] Based on their photophysical properties, they have wide spread applications,^[4] such as fluorescent chromophores,^[5] tunable dye lasers,^[6] organic light-emitting diodes,^[7] fluorescent pH indicators,^[8,9] and ion probes^[10] due to their characteristics of high emission yield, excellent photostability, and extended spectral range.^[11] A great number of unique properties of 2,4,6-trisubstituted

CONTACT Lokesh A. Shastri Arlashastri@kud.ac.in Department of Chemistry, Karnatak University, Dharwad 580 003, India.

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pyridines have magnetized the focus of research work in different fields of technology due to its ability of extended conjugation.

Pyridines conjugated to a heteroatom with electron-donating effects can be classified as a meropolymethine dye, which is of particular interest due to their solvatochromic properties. The best example for this property includes betaine dyes possessing a 2,4,6-trisubstituted pyridinium moiety linked to a phenolate group, which exhibit dramatic solvatochromic effects^[12] and thermochromic properties.^[13] Thus, these properties are the result of pronounced difference in dipole moment between the ground and excited states of the molecule because of an intramolecular charge transfer (ICT) between the donor and acceptor groups.^[14] These charge transfer properties give rise to a long wavelength band in the absorption spectrum because of the π - π * transition.^[15]

The primary purpose of our study was to synthesize pyridine derivatives substituted with coumarins at 2 and 6 positions and aromatic substitution at the fourth position to determine the effect of substitution on the UV–visible spectroscopic behavior in various concentrations. To date, limited data are available on the changes associated with the photophysical characteristics by varying substitution at the 2 and 6 positions of these compounds.^[16,17]

Hence, here we have discussed the synthesis of 2,4,6-trisubstituted pyridines and determined the thermal stability as well as photophysical behaviors. Further, the protonation and deprotonation experiments were performed for some selected compounds to understand the changes in photophysical properties.

Results and discussion

Synthesis and characterization of trisubstituted pyridines

A simple and expeditious synthesis of series of 2,4,6-trisubstituted pyridines 3(a-g) has been achieved in excellent yield, which was performed by one-pot multicomponent reaction, where 1:2:1.3 ratio of substituted aryl aldehydes 1 was subjected to react with different 3-acetylcoumarins 2 in the presence of excess ammonium acetate using acetic acid under reflux to furnish the trisubstituted pyridines 3(a-g) in good yields (Scheme 1).



Scheme 1. Synthetic route for 2,4,6-trisubstituted pyridines 3(a-g).

The products were characterized by IR, NMR, and mass spectrometry. Structures of all the trisubstituted pyridines are shown in Figure 1.

The mechanism involves the aldol condensation between substituted aldehyde and enolate ion of 3-acetylcoumarin. In the second step, the formation of imine by the reaction of 3-acetylcoumarin with ammonia and in the final step Michael addition reaction takes place between coumarin chalcone and imines. The Michael addition of enamine to enolate followed by cyclization gives rise to final compound (Scheme 2).

Thermal properties

Thermogravimetric analysis

The thermal properties of 2,4,6-trisubstituted pyridines 3(a-g) were studied by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ (Figs. 2 and 3). The 2,4,6trisubstituted pyridine derivatives exhibited good thermal stability, showing a weight loss of less than 5% at temperatures up to 283–308 °C, indicating sufficient thermal stability for electronic applications. In pure 2,4,6-trisubstituted pyridines 3(a-g), the pyridine backbone is stable up to 280 °C, with the polymer degradation commencing near 283 °C and completing at 420 °C. The thermal properties of 2,4,6-trisubstituted pyridines are summarized in Table 1.



Figure 1. Structures of 2,4,6-trisubstituted pyridines 3(a-g).



Scheme 2. Plausible mechanism for the synthesis of 2,4,6-trisubstituted pyridine 3(a-g).

Differential scanning calorimetry

The DSC measurement of 2,4,6-trisubstituted pyridine derivatives was performed under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The phase transition and crystallization properties of trisubstituted pyridines 3(a-g) in the temperature range of 25–400 °C are shown in Figure 4 and results are summarized in Table 1. The obtained results revealed that compounds 3(a-e) exhibited only one sharp endothermic melting peak (T_m -melting temperature) around 300 °C and compounds 3f and 3g exhibited sharp endothermic melting peak around 400 °C, respectively, whereas exothermic peaks were not observed for compounds 3(a-g) at a higher temperature resulting from crystallization, indicating excellent amorphous glass-state stability.

The differences in the thermal degradation of compounds might be due to the structural variation around the pyridine nucleus. Thus, rigid molecules resist the thermally induced



Figure 2. TGA thermogram of 2,4,6-trisubstituted pyridines 3(a-g).



DTA thermogram of 2,4,6-trisubstituted pyridines 3(a-g). Figure 3.

Physical properties of the 2,4,6-trisubstituted pyridines 3(a-g). Table 1.

Product code	R ₂	R ₃	$T_{\rm m}$ (°C) ^a	T _{5d} (°C) ^b
3a	4-H	6-H	297	286
3b	4-OCH ₃	6-H	298	283
3c	4-OH	6-H	295	308
3d	4-H	6-H	299	315
3e	4-H	6-H	299	300
3f	4-H	6-Br	392	357
3g	4-H	6-Br	394	345

^{*a*}Obtained from DSC; T_m , melting temperature. ^{*b*}Obtained from TGA measurements, temperature resulting in 5% weight loss based on initial weight.



DSC thermogram of 2,4,6-trisubstituted pyridines 3(a-g). Figure 4.

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vibrations and therefore a higher temperature is required for their degradation.^[18] Interestingly, all the synthesized compounds are rigid and highly stable, due to their higher extended conjugation and molecule clearly shows electron-donor–acceptor systems. Among these five compounds, compounds **3f** and **3g** that are bromo substituents on each of the two coumarin moieties of pyridine nucleus have exhibited higher degradation temperature.

Optical properties

The optical properties of the 2,4,6-trisubstituted pyridines 3(a-e) are obtained by UV–Vis in chlorobenzene solution and are shown in Figure 5. The ultraviolet absorption spectra recorded for 3(a-e) (Table 2, see also Figure 5) have certain features worthy of consideration. The absorption maximum λ_{max} bands in solution are observed at 350–360 nm, whereas those of absorption onset λ_{onset} are seen at 400–415 nm.

2,4,6-Trisubstituted pyridine is an absorbing unit similar to a biphenyl or teriphenyls, with UV spectra indicative of appreciable orbital overlap between the three rings attached to main pyridine nucleus and differing slightly with the substitution position of pyridine substitution; e.g., compound **3a** shows two maxima, at 295 and 357 nm; compound **3b** shows two maxima, at 294 and 357 nm; compound **3c** shows two maxima, at 291 and 357 nm; compound **3d** shows two maxima, at 288 and 356 nm; compound **3e** shows two maxima, at 291 and 357 nm. Comparison of the spectrum of **3a** with **3c**, both shows two maxima with almost same normalized absorbance, while the spectra of the other compounds, **3b**, **3d**, and **3e** consist essentially of two maxima, where maxima at 260 nm displaced toward lower normalized absorbance. The probabilities of the two electronic transitions, as observed in solution, are consistent with the position and degree of substitution in all the series **3(a-e)**.

Among the two distinct bands in the absorption spectra, one band at the shorter wavelength around 250–295 nm is assigned to their localized π - π * transition and the other band at a longer wavelength at around 350–375 nm is attributed to the ICT between



Figure 5. UV–Vis absorption spectra of 2,4,6-trisubstituted pyridines 3(a–e) in chlorobenzene solution.

Product code	R ₂	R_3	$\lambda_{\max abs,Sol} (nm)^a$	$\lambda_{ m onset\ abs,Sol}\ (nm)^a$	E_{g}^{opt} (eV) ^b	Stokes shift (nm)
3a	4-H	6-H	357	408	3.04	63
3b	4-OCH ₃	6-H	353	412	3.01	66
3c	4-0H	6-H	356	407	3.05	64
3d	4-H	6-H	357	406	3.06	63
Зе	4-H	6-H	357	405	3.06	63

Table 2. Optical properties of the 2,4,6-trisubstituted pyridines 3(a-g).

^aThe UV–Vis absorption spectra of the 2,4,6-trisubstituted pyridines were measured in chlorobenzene solution. ^bOptical band gap was calculated from the UV–Vis absorption onset.

electron-rich donors and electron-deficient acceptors.^[19,20] The optical band gaps for 2,4,6-trisubstituted pyridines 3(a-e) were obtained by extrapolating the absorption edges. Optical band gaps were found to be around of 3.01–3.06 eV. The results of optical properties are summarized in Table 2. Further modifications to the 2,4,6-trisubstituted pyridine 3(a-e) scaffolds to extend the $\pi-\pi^*$ conjugation and reduction of band gap are currently underway in our laboratory.

The most striking feature of the ultraviolet spectra of the substituted pyridines **3a** and **3c** is their different wavelength ultraviolet maxima in different solvents. These occur at shorter wavelengths up to 33 nm for first maxima and 6 nm for second maxima in case of compound **3a** and 14 nm for first maxima and 4 nm for second maxima in case of compound **3c** at lower normalized absorbance values than for the same compounds in chlorobenzene alone, while the intensity of the shorter wavelength band is greatly diminished.

Fluorescence properties

Due to the fact that 2,4,6-triaryl-substituted pyridines often exhibit fluorescence,^[21] we sought to find out whether and/or how the additional substitution pattern around the pyridine ring can affect this fluorescence property.

First, we measured the UV–Vis spectra of the compounds **3(a–e)** in chlorobenzene to find out the absorption maxima (Fig. 5), and it is found in the region between 290 and 350 nm, then we decided to use the fluorescence excitation wavelength at 350 nm as an approximate mean value. Fluorescence emission spectra at $\lambda_{abs} \approx 290$ nm have not been included in this section to avoid redundancy, as similar emission behavior is observed at $\lambda_{abs} \approx 357$ nm on varying its concentration in chlorobenzene.

The fluorescence properties of trisubstituted pyridines 3(a-e) are obtained in chlorobenzene solution as shown in Figure 6. It was noted that the incorporation of substituents on to the trisubstituted pyridine 3(a-e) nucleus has a profound influence on the emission properties of all the five compounds as reported for the fluorophore by Barrio et al.^[21]

This fluorescence spectrum is subjected to substantial changes with concentration varying from 5 to $30 \,\mu$ L. It was noticed that small increase in concentration found to produce a higher intensity. The effect of substituent pattern and also these findings reveal that trisubstituted pyridines **3b** with electron-donating methoxy substituent on the phenyl ring at the C4 position of the pyridine ring enhanced the UV absorption in the range of 352–354 nm and fluorescence maxima in the range of 419–420 nm.

Protonation studies

To measure pH by the fluorometric method, both in the acidic and basic states of the indicator should ideally be fluorescent and exhibit shifted absorption and emission spectra.

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Emission spectra of the 2,4,6-trisubstituted pyridines 3(a-e) at different concentrations. Figure 6.

In principle, this is the case when either the electron donor or the acceptor moiety of a donor-acceptor fluorophore exhibits acid or base properties. Furthermore, the shifted absorption and emission spectral values of the ground and excited states are prone to be significantly different in many donor-acceptor molecules owing to the redistribution of the electron density about the molecule upon light absorption.

2,4,6-Trisubstituted pyridines 3a and 3c were chosen to engineer the donor-acceptor fluorescent pH probe. Owing to the favorable photophysical features exhibited after photon

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Figure 7. Emission spectra of sensor 3a at 1.0×10^{-4} L in DMSO (λ_{ex} 351 nm, pH 7–4).

excitation for **3a** and **3c**, our design relied on the effect of protonation and deprotonation to induce a shift in its emission value without altering too strongly its favorable photophysical features or its solubility in water. The evolution of the fluorescence emission after photon excitation of 2,4,6-trisubstituted pyridines **3a** and **3c** in DMSO solution as a function of pH is shown in Figures 7–9, respectively, and the formulas shown in Schemes 3–5 convey the idea that the transition involved on protonation of pyridine nucleus.

To understand the fluorogenic signaling behavior of 3-(6-(2-oxo-2*H*-chromen-3-yl)-4-phenylpyridin-2-yl)-2*H*-chromen-2-one **3a**, toward pH, we investigated the pH-dependent switching processes by monitoring the various pH systems. As shown in Figure 9, compound **3a** in DMSO at 1×10^{-4} L concentration exhibited a remarkable fluorescence



Figure 8. Emission spectra of sensor 3c at 1.0×10^{-4} L in DMSO (λ_{ex} 353 nm, pH 7–4).

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Figure 9. Emission spectra of sensor 3c at 1.0×10^{-4} L in DMSO (λ_{ex} 353 nm, pH 7–10).

response toward different pH system ranging from 7 to 4. The fluorescence intensity of sensor **3a** at pH 7 showed a relatively weak peak, which was centered at 536 nm, whereas increasing in the fluorescence is observed at pH 4.

While 3-(4-(4-hydroxyphenyl)-6-(2-oxo-2*H*-chromen-3-yl)pyridin-2-yl)-2*H*-chromen-2-one **3c** is known to have both electron donor-acceptor fluorophore and the influence of the pH on the both electron donor-acceptor fluorophore (Schemes 4 and 5), its pH profile was determined in a DMSO. The photophysical properties that are dependent on pH revealed that the absorption spectrum is strongly dependent on pH. The protonated pyridine 2,4,6-trisubstituted pyridine form exhibits a λ_{max} at 430 nm (Fig. 8) and the deprotonated phenolate at 520 nm (Fig. 9).

Among these two electron donor and electron acceptor moieties of compound 3c showed higher luminescent intensification behavior toward pH. The amount of fluorescence enhancement was related to pH; when the pH was decreased from 7.0 to 4.0, the intensity enhanced strongly, whereas at pH values above the neutral condition, that is when the pH was increased from 7.0 to 10.0, remarkable decrease in fluorescence intensity was observed. Interestingly, the fluorescence emission spectra recorded for 3c had certain features worthy of consideration that bathochromic shift observed upon decreasing the pH value. This maybe in line with the decrease in electron-withdrawing power of the pyridine ring upon deprotonation of the hyroxy hydrogen of compound 3c.



Scheme 3. Plausible intramolecular charge transfer (ICT) covalent structure of compound 3a on protonation.



Scheme 4. Plausible intramolecular charge transfer (ICT) covalent structure of compound 3c on protonation.



Scheme 5. Plausible intramolecular charge transfer (ICT) covalent structure of compound 3c on deprotonation.

The present study suggests that the compounds **3a** and **3c** platform is appropriate to measure pH values in the range 4–10 by a fluorometric method that relies on fluorescence emission. This is especially attractive in the case of compound **3c** containing both electron acceptor and electron donor fluorophore. Therefore, it is evident that pH-dependent changes in the fluorescence intensity of both sensors **3a** and **3c** suggest that derivatives of 2,4,6-trisubstituted pyridines could find useful applications as intracellular pH meters.

Conclusion

In summary, we successfully demonstrated the synthesis and characterization of novel trisubstituted pyridines under acidic conditions using conventional method. The synthesized molecules are more stable at a higher temperature and are not having any hygroscopic properties. It was supported by TGA, DTA, and DSC. The photophysical results showed optical band gaps of the trisubstituted pyridines and were found to be around 3.01–3.06 eV, these studies suggest that molecules are promising candidates for organic electronics. Moreover, protonation and deprotonation experiments showed pH-dependent changes in the fluorescence intensity of compounds **3a** and **3c**. Thus, these sensors could find excellent relevance in various intracellular pH meters. Additional modifications on molecular structures are currently under way to enhance the electronic properties for optoelectronic applications.

Experimental protocol

Materials and methods

Ethyl acetoacetate, substituted aldehydes, liquid bromine, and other chemicals were purchased from the commercial source and used without further purification unless 12 👄 N. S. NAIK ET AL.

otherwise stated. Synthesis of various 3-acetyl coumarins (2) was performed by the Knoevenagel condensation of substituted salicylaldehyde with ethyl acetoacetate.^[22]

Material characterization

The melting points were determined by the open capillary method and are uncorrected. IR spectra (KBr disk) were recorded on Nicolet 5700 FT-IR spectrometer. ¹H NMR spectra were recorded on Jeol 400 MHz spectrometer using CDCl₃ as solvent and TMS as an internal standard. The chemical shifts are expressed in δ ppm. TGA was performed under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ with an SDT Q 600 TA Instrument. DSC experiments were performed using NETZSCH DSC instrument. GC-MS spectra were obtained on a QTOF6510 spectrograph (Agilent). CHN elemental analysis of all the products was recorded by LECO TRUSPEC CHN analyzer. TLC was performed on silica gel G for TLC (Merck), and spots were visualized by iodine vapor or by irradiation with UV light (254 nm). Fluorescence measurements and UV-visible spectra were performed on a Perkin Elmer LS-55 luminescence spectrophotometer and a U-4100 UV-visible-NIR spectrometer (Hitachi), respectively. The pH of the system was adjusted by adding small aliquots of aqueous solutions of strong acid HCl or strong base NaOH to achieve the desired ionic states. The pH values of the solutions were measured using a pH meter.

Synthesis of target molecules

A mixture of substituted aldehydes 1 (0.01 mmol), substituted 3-acetylcoumarin 2 (0.02 mmol), and ammonium acetate (0.015 mmol) in acetic acid was refluxed in stirring for about 2-3 h. After completion of the reaction as indicated by TLC, the solid product separated was filtered, washed with cold ethanol and water, dried, and recrystallized from methanol to obtain the pure product.

3-(6-(2-Oxo-2H-chromen-3-yl)-4-phenylpyridin-2-yl)-2H-chromen-2-one (3a)

Light yellow solid (0.45 g, 80%). Mp 252–253 °C; IR (KBr) v: 1721, 1610, 1577, 1532 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, δ ppm) δ : 9.19, 9.23 (2H, s, C4'-H and C4"-H of coumarin rings), 8.27, 8.29 (2H, s, C3-H and C5-H of pyridine ring), 7.39–7.78 (13H, m, Ar-H); ¹³C NMR: δ : 160.8, 160.2, 154.7, 151.2, 141.9, 131.8, 131.1, 128.5, 128.1, 126.0, 125.2, 124.3, 119.7, 117.4, 115.4, 114.0; ESI-mass: *m*/*z* 444.7 [M+H]⁺; Anal. Calcd. for C₂₉H₁₇NO₄: C 78.55, H 3.86, N: 3.16%. Found: C 78.52, H 3.88, N 3.15%.

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