J Fluoresc (2012) 22:17–29
DOI 10.1007/s10895-011-0945-9

RAPID COMMUNICATION

# A Fluorescence and Fluorescence Probe Study of Benzonaphthyridines

**Deepak Prakash Shelar · Sandeep R. Patil · Ramhari V. Rote · Madhukar N. Jachak**

Received: 20 June 2011 / Accepted: 2 August 2011 / Published online: 16 August 2011


**Abstract** A series of benzo[*b*][1,8]naphthyridines has been synthesized by *Friedländer* condensation of 2-aminoquinoline-3-carbaldehyde **1** (o-aminoaldehyde) with alicyclic ketones in basic medium. Benzonaphthyridines branched with various side-chains and substituents are prepared with the aim of being investigated as a good fluorescent material. Electronic absorption and fluorescence properties of some representative benzonaphthyridines in organic solvents, water-dioxane, and SDS, CTAB and Triton-X-100 micelles have been examined. The linear correlation between solvent polarity and fluorescence properties is observed. This study may provide new directions for the development of fluorescence probes as reporters of microenvironments of organized assemblies.

**Keywords** Benzo[*b*][1,8]naphthyridines · Sodium dodecyl sulfate (SDS) · Cetyl trimethyl ammonium bromide (CTAB) · Triton-X-100

## Introduction

π-Conjugated organic molecules attract much attention due to their prospective application as efficient materials in organic electronics and optoelectronics [1, 2]. A typical organic charge-transfer (CT) chromophore (D-π-A) consists of strong electron donors D (e.g., $NR_2$ or OR groups), strong electron acceptors A (e.g., $NO_2$ or CN groups), and a π-conjugated core featuring (hetero)-aromatic rings and/or double or triple bonds [3–5]. Optical linear and nonlinear properties of such push-pull molecules depend on the polarizability of the electrons localized in π-bonding molecular orbitals [6, 7]. Although the polarizability of a molecule is mainly given by its chemical structure, in particular by the length of the π-conjugated spacer and the electronic nature of the donors and acceptors attached [8–10], it can also be affected by external factors such as frequency of radiation, state of matter, and solvent used for preparation of solution. However, a general description of external factors (solvent) affecting optical and nonlinear optical properties is more complex.

It is observed that, fluorescence probes such as sensors and reporters of microenvironments are of much current interest [11]. The environment-sensitive molecular fluorescence probe shows different fluorescence behaviors in hydrophilic and hydrophobic surroundings. Fluorescence studies of such probe gives useful information about the microenvironment of their location. Such fluorescence probes are widely used for characterizing the microenvironments in biological systems like proteins, lipid bilayers and nucleic acids, which are known to have structural domains having differences in physico-chemical properties, acid–base characters, viscosity, polarity, etc. In general these probes are very useful for getting information about the structural features and functional dynamics of complex structural systems [12–14]. Fluorescence probe technique represents the most important area of fluorescence spectroscopy to study biologically important systems and are rapidly gaining popularity in the study of biological microheterogeneous systems due to their non-invasive nature and the large extent of information gleaned thereby [15, 16]. Probes that show massive spectral changes on being tagged to such systems are being designed and developed and their spectral responses are then exploited to gain information about the structure and dynamics of the

D. P. Shelar · S. R. Patil · R. V. Rote · M. N. Jachak (✉)
Organic Chemistry Research Centre, Department of Chemistry,
K.T.H.M. College,
Gangapur Road,
Nashik 422 002, MS, India
e-mail: mnjachak@hotmail.com

system under study. Probe like ANS [17–21] show polarity dependant spectral characteristics and are being widely used as fluorescent labels for studying proteins, vesicles, micelles, mixed micelles and similar biological or biomimetic micro-heterogeneous systems.

Recently, we have reported the synthesis of fluorescent benzo[*b*][1,8]naphthyridine-3-carbonitrile using 2-aminoquinoline-3-carabldehyde (*o*-aminoaldehyde) **1** [22] and also reported that certain banzonaphthyridines are capable of solvatochromic fluorescence emission and these are used as a fluorescence probes for studying the microenvironment of organised assemblies such as Bovine serum albumin (BSA) [23]. In this work, various fluorescent benzo[*b*][1,8]naphthyridines are synthesized via *Friedländer* condensation of **1** with cyclic ketones in basic reaction condition. Some representative benzonaphthyridines (**3d**, **5b** and **7d**) are investigated for their absorption and fluorescence properties in homogeneous media of organic solvents, 1,4-dioxane-water binary mixtures and in the microheterogeneous media of Sodium dodecyl sulfate (SDS), Cetyl trimethyl ammonium bromide (CTAB) and Triton-X-100 micelles. Moreover, semi-empirical calculations have been performed using MOPAC-2009 to investigate the effect of substituent (i.e. $OCH_3$) on fluorescence properties of benzonaphthyridines.

## Results and Discussion

Reactions of *o*-aminoaldehydes with cyclic ketones are especially valuable for the construction of polycondensed heterocyclic systems. The availability and structural variety of cyclic ketones provide easy and direct access to a large number of fused heterocyclic systems for which in many cases alternate annelation methods are not readily available. Herein, we extend *Friedländer* condensation using different cyclic ketones having reactive methylene group to generate libraries of new heterocycles. We employed mild reaction conditions in the *Friedländer* condensation to permit the transformation of functional groups from the starting ketone into the annelated heterocyclic ring. Known 2-aminoquinoline-3-carbaldehyde (*o*-aminoaldehyde) **1** has been synthesized by novel method reported in our previous communication [22]. The base catalyzed condensation (in ethanolic KOH) of **1** with cyclopentanone **2a** gave the strained heterocycle 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*g*][1,8]naphthyridine **3(a-b)** in 80-84% yield also available via acid catalyzed condensation (in aq. HCl) of the components although in much lower yield i.e. 40–45%, hence we performed further cyclocondensation in basic medium. Therefore, cyclocondensation of 2-aminoquinoline-3-carbaldehyde **1a** or **1b** with 2-methylcyclohexanone **4** in ethanolic KOH furnished into 4-methyl-1,2,3,4-tetrahydrodibenzo[*b*,*g*][1,8] naphthyridine **5(a-b)** in 82–85% yield. However, reaction of **1** with dimedone **6(a-b)** was unproductive in ethanolic KOH due to its more enolic character; hence this condensation is achieved by heating without solvent at 180–185 °C to afford 3,3-dimethyl-3,4-dihydrodibenzo[*b*,*g*][1, 8]naphthyridin-1(2*H*)-one 7**(a-d)** in good yield. Analog, cyclocondensation of **1a** or **1b** with cetralene **8** in ethanolic KOH under reflux gave 5-(3,4-dichlorophenyl)-5,6-dihydrobenzo[*b*]naphtho[2,1-*g*][1,8]naphthyridine **9(a-b)**. All synthesized compounds are characterized by spectroscopic and analytical methods. For e.g. IR of **7d** shows streching frequency at 1703 $cm^{-1}$ for C=O. $^1H$ NMR spectrum of **7d** in $CDCl_3$ shows four singlet at 1.25, 2.39, 2.94 and 4.09 ppm corresponds to protons of methyl (2 x $CH_3$), methylene (2 x $CH_2$s') and methoxy ($OCH_3$) groups respectively. All aromatic protons shows expected chemical shifts and splitting patterns which resembles with the structure proposed. The mass spectrum of **7d** reveals an $H^+$ molecular ion peak m/z at 307. The $^{13}C$ NMR spectrum of this compound in agreement with the structure proposed (Scheme 1). Synthesized benzonaphthyridines are further utilized for study their photophysical properties.

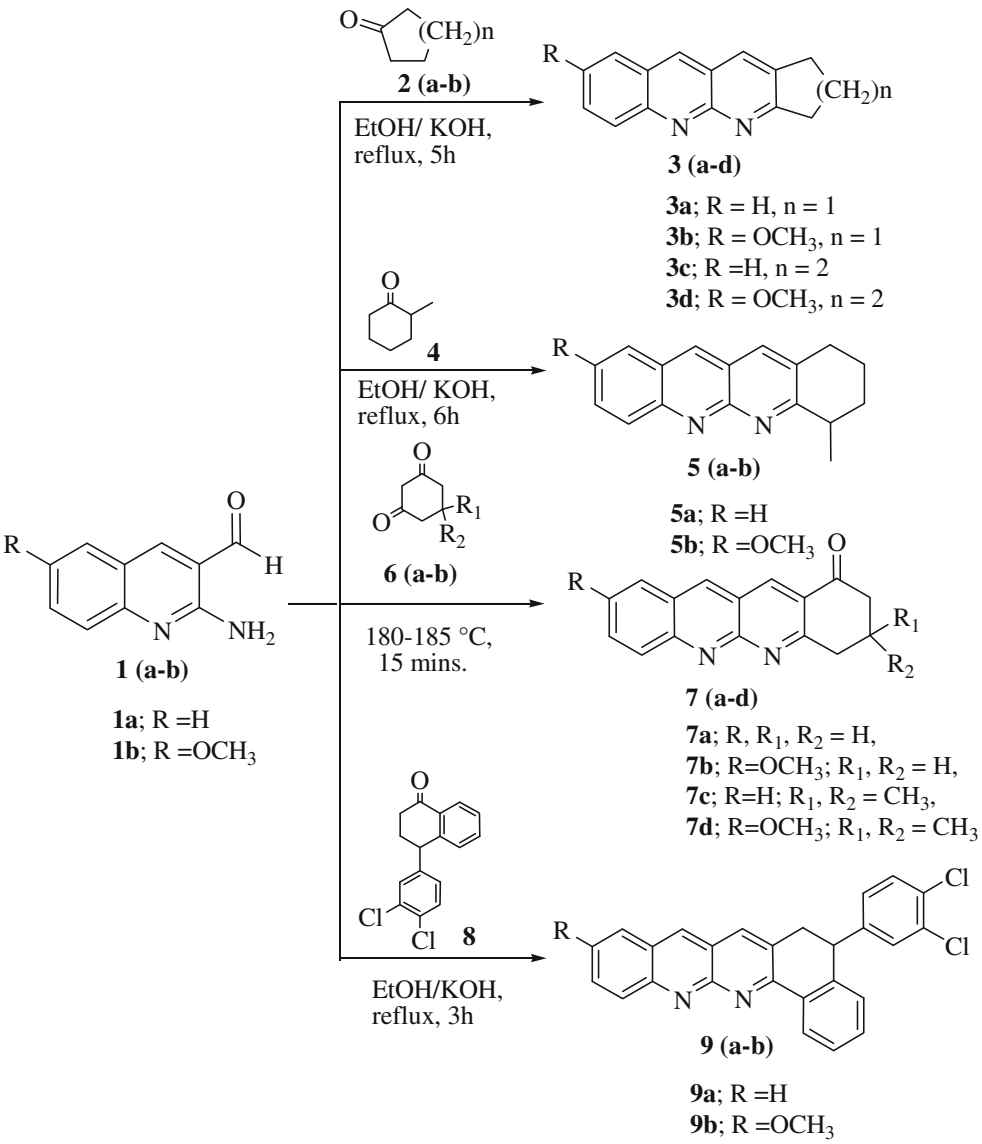
### Semi-empirical Study of Benzo[*b*][1,8]naphthyridine

The HOMO and LUMO of a molecule are usually important characteristics for its chemical reactivity and for biological activity [24–27]. The fluorophores which are useful as Organic Light Emitting Diodes (OLEDs) should fluoresces between 400–700 nm and HOMO/LUMO or 'electron-hole' gap is in the range of 2.7–3.0 eV i.e. low gap [28]. Prompted with these quotations, we perform some computational calculations like heat of formation, ionization potential, HOMO, LUMO energies and electron hole gap (HOMO-LUMO energy separations) of synthesized benzonaphthyridines by using MOPAC-2009 (Version 8.331) [29, 30] and are summarized in Table 1. The charge is more concentrated on ring A as compared to ring B and C (Fig. 1). The donor chromophore (−$OCH_3$ group) on ring A plays an important role in increasing the electron density and lowering electron hole gap. Compounds **3b**, **3d**, **5b**, **7b**, **7d** and **9b** bearing -$OCH_3$ gr. on ring A shows low Gap values indicating higher overlapping of HOMO or LUMO orbital's which shows red shift in its fluorescence maxima and high quantum yields as compared to others.

## Photophyscial Properties

### Solvent-Induced Shifts of Absorption and Fluorescence

A variety of environmental factors affect fluorescence emission, including interactions between the fluorophore




**Scheme 1** Synthesis of benzo[*b*][1,8]naphthyridines by *Friedländer* condensation of o-aminoaldehyde with alicyclic ketones

and surrounding solvent molecules (dictated by solvent polarity), other dissolved inorganic and organic compounds, temperature, pH and the local concentration of the fluorescent species. The effects of these parameters vary widely from one fluorophore to another, but the absorption and emission spectra, as well as quantum yields, can be heavily influenced by environmental variables. In fact, the high degree of sensitivity in fluorescence is primarily due to interactions that occur in the local environment during the excited state lifetime. This research article explores relaxation effects and associated spectral shifts that occur as a function of solvent polarity. Thus, in this piece of work, we mainly give emphasis on to study effect of solvent on absorption and fluorescence emission, because solvents play an important role in physical and chemical processes. Solvent effects are related to the nature and the extent of the solute-solvent interactions developed in the solvation shell of the solutes [31]. Organic mixed solvents are widely used as the mobile phase in liquid chromatography, capillary electrophoreses and as a reaction medium. Solvent mixtures have improved physical properties such as solvation power, density, viscosity and refractive index compared with pure solvents [32]. When the solute is dissolved in a solvent, the solvent exerts a definite influence on the solute. This influence depends on the nature of the solvent. This influence reflects changes in the absorption and fluorescence spectrum [33] and this phenomenon is known as solvatochromism. Solvatochromism is used to describe the pounced change in position sometimes in intensity of an absorption band, accompanying a change in the polarity of the medium. The preferential solvation phenomenon that is the selective enrichment of the certain solvent component in the solvation shell of a given solute is of paramount importance in the interpretation of many physiochemical

**Table 1** The molecular electronic properties (HOMO-LUMO energy, GAP) of the benzo[*b*][1,8]naphthyridine **3(a-d)**, **5(a-b)**, **7(a-d)** and **9(a-b)**

| Comp. | R | $R_1$ | $R_2$ | Heat of Formation (K CAL.) | Ionization Potential (eV) | HOMO (eV) | LUMO (eV) | Gap (eV) |
|---|---|---|---|---|---|---|---|---|
| 3a | H | – | – | 73.55 | 9.021 | −9.022 | −1.235 | 7.787 |
| 3b | $OCH_3$ | – | – | 41.18 | 8.849 | −8.849 | −1.219 | 7.630 |
| 3c | H | – | – | 66.08 | 8.957 | −8.957 | −1.241 | 7.716 |
| 3d | $OCH_3$ | – | – | 26.13 | 8.486 | −8.487 | −1.231 | 7.256 |
| 5a | H | – | – | 61.52 | 8.948 | −8.949 | −1.232 | 7.717 |
| 5b | $OCH_3$ | – | – | 21.56 | 8.485 | −8.485 | −1.221 | 7.264 |
| 7a | H | – | – | 36.71 | 9.269 | −9.269 | −1.667 | 7.602 |
| 7b | $OCH_3$ | – | – | −2.87 | 8.728 | −8.728 | −1.671 | 7.057 |
| 7c | H | $CH_3$ | $CH_3$ | 22.84 | 9.235 | −9.236 | −1.633 | 7.603 |
| 7d | $OCH_3$ | $CH_3$ | $CH_3$ | −16.71 | 8.699 | −8.699 | −1.639 | 7.060 |
| 9a | H | – | – | 110.58 | 9.166 | −9.167 | −1.476 | 7.691 |
| 9b | $OCH_3$ | – | – | 70.07 | 8.703 | −8.704 | −1.480 | 7.224 |

GAP=*E*LUMO-*E*HOMO

parameters measured in the mixtures [34]. In the study of preferential solvation, hydrogen bonding plays an important role and has been widely investigated because it is present in large variety of chemical, biochemical and pharmacological events [35].

Undertaking these literature results, herein, we investigate electronic absorption and fluorescence properties of some representative benzonaphthyridines (**3d**, **5b** and **7d**) in homogeneous media of organic solvents with different solvent polarity. UV–vis absorption and fluorescence spectral data of benzonaphthyridines **3d**, **5b** and **7d** in organic solvents (homogeneous media) of different polarity are summarized in Table 2 and graphically represented in Fig. 2. A very moderate solvent polarity effect on the absorption maximum and almost no effect on the fluorescence excitation spectrum, there is a marked influence of the solvent polarity on the fluorescence emission behavior of these benzonaphthyridines (Fig. 2). Benzonaphthyridine **3d**, **5b** and **7d** shows a red shift of 27, 22 and 18 nm respectively, in its fluorescence maxima in going from non-polar n-hexane to polar DMF. The maximum red shift is observed for **3d** in its fluorescence emission. We observed linear correlation between solvent polarity and fluorescence property, as the solvent polarity increases from non-polar n-hexane to polar aprotic DMF, fluorescence maxima is shift to the longer wavelength (red shift). The fluorescence excitation maximum in organic solvents is similar to the absorption maximum in the same solvents. The excitation spectrum was found to be independent of emission wavelength in all the media studied. (Table 2)

The blue-shifted fluorescence emission of these benzonaphthyridines in non-polar solvents can be from the locally excited state, while the longer wavelength emission can be from an intramolecular charge transfer excited state, which is more polar and lower in energy than the locally excited state. The intramolecular charge transfer excited state can involve conformational relaxation of the single bonds connecting the donor group to the acceptor group. Hence, the polar solvents stabilise the excited state, resulting in red-shifted fluorescence emission.

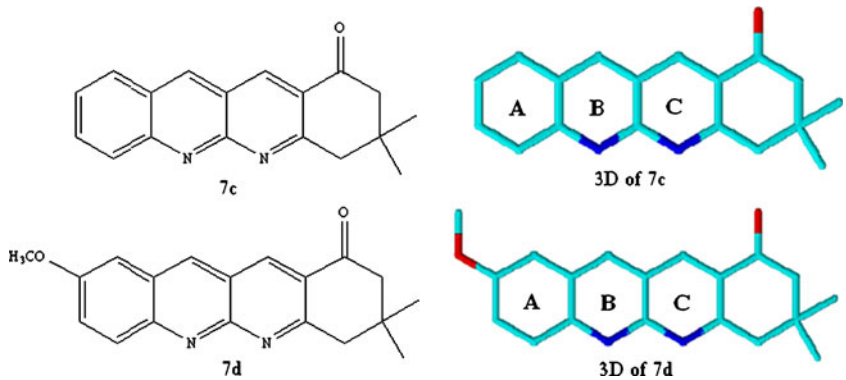



**Fig. 1** 3D picture of benzo[*b*][1, 8]naphthyridines **7c** and **7d**

**Table 2** UV–vis absorption and fluorescence spectral data of benzonaphthyridines **3d**, **5b** and **7d** in homogeneous media of organic solvents at room temperature

| Comp. | Solvent | $\lambda_{max}$ (nm) | | | Stokes'Shift/$cm^{-1}$ | $\Phi_f$ (±0.002) |
|---|---|---|---|---|---|---|
| | | abs | emi | exi | | |
| 3d | n-hexane | 362 | 461 | 362 | 4917 | 0.256 |
| | dioxane | 367 | 469 | 365 | 5068 | 0.263 |
| | THF | 366 | 474 | 366 | 5836 | 0.297 |
| | MeCN | 364 | 480 | 363 | 6342 | 0.318 |
| | MeOH | 364 | 480 | 363 | 6342 | 0.315 |
| | DMF | 369 | 488 | 365 | 6096 | 0.345 |
| 5b | n-hexane | 360 | 459 | 360 | 4239 | 0.261 |
| | dioxane | 362 | 464 | 360 | 4446 | 0.274 |
| | THF | 362 | 470 | 365 | 5105 | 0.291 |
| | MeCN | 362 | 475 | 359 | 5877 | 0.321 |
| | MeOH | 362 | 473 | 361 | 5637 | 0.310 |
| | DMF | 368 | 481 | 367 | 5583 | 0.378 |
| 7d | n-hexane | 389 | 482 | 390 | 5894 | 0.367 |
| | dioxane | 394 | 488 | 391 | 6475 | 0.379 |
| | THF | 396 | 490 | 399 | 6969 | 0.385 |
| | MeCN | 401 | 497 | 398 | 7648 | 0.395 |
| | MeOH | 402 | 496 | 401 | 7584 | 0.390 |
| | DMF | 407 | 500 | 410 | 7227 | 0.403 |

Fluorescence Quantum Yields ($\Phi_f$) and Stokes Shift of 3d, 5b and 7d in Organic Solvents

These benzonaphthyridines show rather strong fluorescent emission. In general, the solvent polarity and the type of substituent and its position appear to influence the fluorescence quantum yields. In non polar solvents like n-hexane, the fluorescence quantum yields ($\Phi_f$) are low as compare to polar protic and polar aprotic solvents. Increase in $\Phi_f$ with increase in solvent polarity can partly be attributed to the possible state reversals of the lowest excited states of the benzonaphthyridines. In nonpolar solvent, the fluorescent excited state can be of $A_g^-$ nature. Since $A_g^-{}^* \rightarrow A_g$ transition is symmetry forbidden; the resulting emission is very weak. In polar solvents, however, there is reversal of states from $A_g{}^{*-}$ to $B_u{}^{*+}$, which gives rise to allowed $B_u{}^{*-} \rightarrow A_g$ transition responsible for relatively increased $\Phi_f$. A relatively higher $\Phi_f$ and large red-shifted fluorescence of banzonaphthyridines (**3d**, **5b** and **7d**) in aprotic polar solvents further indicate that the fluorescence originates from highly polarized excited state. Solvent relaxation effects on fluorescence can result in a dramatic effect on the size of Stokes' shift. From Table 2, it observed that, Stokes' shift is increased with solvent polarity.

Further, UV–vis and fluorescence spectra of compounds **3(a-d)**, **5(a-b)**, **7(a-d)** and **9(a-b)** are taken in DMF as a solvent. Fluorescence quantum yield of all synthesized

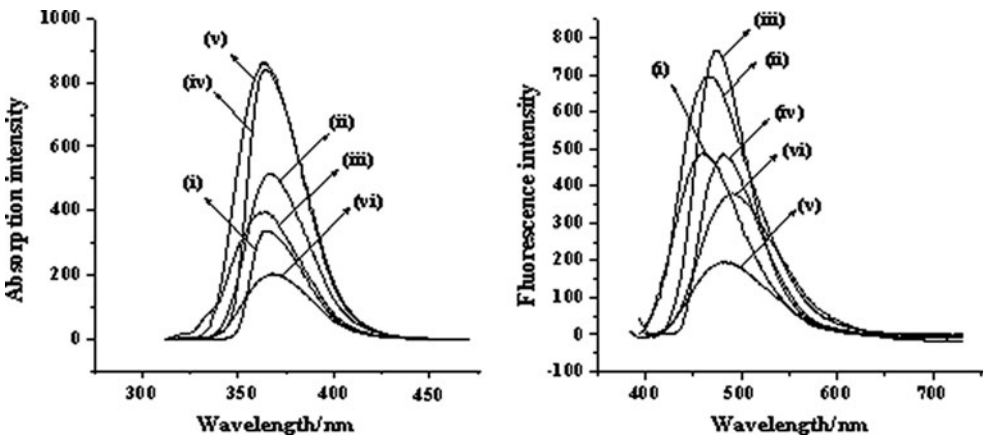



**Fig. 2** UV–vis absorption ($\lambda_{abs}$ max) and fluorescence ($\lambda_f$ max) spectra of **3d** in (*i*) n-hexane, (*ii*) dioxane, (*iii*) THF, (*iv*) MeCN, (*v*) Methanol, (*vi*) DMF

compounds are determined by standard literature procedure using quinine sulphate as a reference standard [13, 36] and are given in Tables 2 and 3.

Electronic Spectroscopy of 3d, 5b and 7d in Dioxane-Water Mixture and in Microheterogeneous Media of Micelles

Solvent polarity dependent fluorescence properties of substituted benzonaphthyridines prompted us to study the fluorescence properties of **3d**, **5b** and **7d** in micelles of SDS, CTAB and Triton-X-100. We have employed these fluorophores for characterizing the microenvironment of these micelles. Since the solvatochromic fluorescence properties of these benzonaphthyridines were to be used to probe micellar environments, it was necessary to ensure that the fluorescence emission in surfactant solution is not due to any specific interaction between the benzonaphthyridine and water molecules. The inefficiency of solubility of benzonaphthyridines in water prohibits direct spectroscopic study in aqueous solution. Therefore, we examined electronic spectra of **3d**, **5b** and **7d** in dioxane-water mixture. The absorption and fluorescence spectral data of benzonaphthyridines **3d**, **5b** and **7d** in various compositions of 1,4-dioxane-water are summarized in Table 4. The absorption and fluorescence emission spectra of compound **3d** and **7d** are graphically presented in Figs. 3 and 4 respectively. From the Table 4, we observed that, in 1,4-dioxane-water mixtures absorption maximum ($\lambda_{abs}$ max) tends to decrease as the water content is increased. These absorption spectral features can be due to ground state hydrogen bond interactions and aggregate formation, particularly in water in which benzonaphthyridines are not freely soluble. When the water content was varied between zero and 60% in dioxane, the absorption maximum ($\lambda_{abs}$ max) shift to the blue by 9, 11 and 15 nm for **3d**, **5b** and **7d** respectively. On the other hand, as the water content (% water) is increased in 1,4-dioxane, the excitation maximum ($\lambda_{ex}$ max) considerably red-shifted as compared to its absorption maximum. However, benzonaphthyridines **3d**, **5b** and **7d** exhibited red-shifted fluorescence in dioxane containing increasing amounts of water. Thus, 469 nm fluorescence of **3d** in dioxane shifted to 487 nm when dioxane contained 60% water. Similarly, 464, 488 nm fluorescence of **5b** and **7d** in dioxane shifted, respectively, to 481 and 524 nm in dioxane containing 60% water. Thus, fluorescence is highly red-shifted as the water content in the solvent mixture is increased. This observation is similar to that of the studies in organic solvents of different polarity. In organic solvents and dioxane-water systems, as the polarity (relative permittivity, ε) of the media is increased, the $\lambda_f$ max undergoes a red shift. The maximum red shift is observed for **7d** in its fluorescence emission when dioxane contained 60% of water. From the Table 4, we observed that, quantum yields ($\Phi_f$) tends to decrease as the % of water is increase in 1,4-dioxane. Maximum decrease in quantum yield ($\Phi_f$) is observed for **7d**.

Despite numerous efforts to determine effect of solvent polarity on fluorescence properties of heterocyclic compounds, the solvent properties of the micellar environment are still poorly understood. Among various physical methods employed, fluorescence probes have been widely used because of their simplicity, wide scope, and extreme sensitivity at very low probe concentration [37]. Comparison of the spectral data in micelles with those in homogeneous solvent systems provides information on the micellar environment. Thus, as compared to the homogeneous media of organic solvents, the micellar environment does not cause significant change in the absorption spectra of these benzonaphthyridines (Table 5). The fluorescence spectrum of compounds **5b** in micelles is significantly red-shifted as compared to that in non-polar n-hexane. However, the fluorescence maxima ($\lambda_f$ max) in micelles are similar to those in polar solvents like DMF, MeCN and MeOH. As compared to in polar solvents, the fluorescence maximum ($\lambda_f$ max) of **5b** is blue-shifted in Triton-X-100 micelles (Table 5 and Fig. 5). In general, as compared to the fluorescence of benzopanaphthyridines **3d**, **5d** and **7d** in non-polar n-hexane, in micellar media the fluorescence of these benzonaphthyridines is red-shifted; the maximum red shift is observed for **5b**. A comparison of the $\lambda_f$ max of benzonaphthyridines **3d**, **5b** and **7d** in polar organic solvent such as methanol with those in micelles reveals that the benzonaphthyridines, experience relatively polar environ-

**Table 3** UV–vis absorption and fluorescence spectral data of **3(a-d)**, **5(a-b)**, **7(a-d)** and **9(a-b)** in DMF as the solvent at room temperature

| Comp. | $\lambda_{abs}$ max/nm | $\lambda_f$ max/nm | $\phi_F$ (±0.002) | Comp. | $\lambda_{abs}$ max/nm | $\lambda_f$ max/nm | $\phi_F$ (±0.002) |
|---|---|---|---|---|---|---|---|
| 3a | 360 | 472 | 0.294 | 7a | 368 | 478 | 0.311 |
| 3b | 365 | 481 | 0.327 | 7b | 373 | 498 | 0.397 |
| 3c | 362 | 477 | 0.301 | 7c | 370 | 489 | 0.350 |
| 3d | 369 | 488 | 0.345 | 7d | 407 | 500 | 0.403 |
| 5a | 365 | 472 | 0.284 | 9a | 398 | 472 | 0.351 |
| 5b | 368 | 481 | 0.378 | 9b | 418 | 487 | 0.372 |

**Table 4** UV–vis absorption ($\lambda_{abs}$ max) and fluorescence ($\lambda_f$ max) spectral data of **3d**, **5b** and **7d** in 1,4-dioxane- water mixtures at room temperature

| Comp. | % Water in 1,4-dioxane | $\lambda_{abs}$ max/nm | $\lambda_f$ max/nm | $\lambda_{ex}$ max/nm | Stokes' Shift/$cm^{-1}$ | $\Phi_f$ (±0.002) |
|---|---|---|---|---|---|---|
| 3d | 0 | 367 | 469 | 367 | 5068 | 0.263 |
| | 10 | 365 | 475 | 370 | 5947 | 0.254 |
| | 20 | 362 | 478 | 376 | 5712 | 0.239 |
| | 30 | 360 | 478 | 374 | 5712 | 0.239 |
| | 40 | 359 | 483 | 373 | 5357 | 0.225 |
| | 50 | 359 | 486 | 373 | 5369 | 0.221 |
| | 60 | 358 | 487 | 373 | 5884 | 0.218 |
| 5b | 0 | 362 | 464 | 359 | 4446 | 0.274 |
| | 10 | 361 | 475 | 360 | 5241 | 0.263 |
| | 20 | 361 | 478 | 360 | 5302 | 0.254 |
| | 30 | 358 | 478 | 354 | 5317 | 0.253 |
| | 40 | 356 | 478 | 354 | 5579 | 0.253 |
| | 50 | 353 | 478 | 352 | 5792 | 0.255 |
| | 60 | 351 | 481 | 351 | 5822 | 0.249 |
| 7d | 0 | 394 | 488 | 396 | 6475 | 0.379 |
| | 10 | 391 | 492 | 395 | 6337 | 0.363 |
| | 20 | 387 | 510 | 393 | 7367 | 0.356 |
| | 30 | 386 | 512 | 394 | 7512 | 0.349 |
| | 40 | 382 | 513 | 394 | 7641 | 0.341 |
| | 50 | 380 | 515 | 392 | 7837 | 0.332 |
| | 60 | 379 | 524 | 392 | 8227 | 0.316 |

ment in the micelles. The quantum yield ($\Phi_f$) of these benzonaphthyridines (**3d**, **5b** and **7d**) is relatively higher in Triton-X-100 as compared to either SDS or CTAB. The fluorescence efficiency is lowest in SDS micelles for all three benzonaphthyridines. Since we already showed that there is an increase in quantum yield ($\Phi_f$) with increase in solvent polarity of the medium, the increase in $\Phi_f$ in micelles is attributable to the grater polarity of the media. The Stokes' shift for all three benzonaphthyridines in polar homogeneous media of organic solvents such as DMF, acetonitrile and methanol is greater than that in micellar media. Among the three micelles studied, the smallest Stokes' shift is observed in neutral Triton-X-100. Thus, the ionic micelles of SDS and CTAB affect the fluorescence spectra most. This can be due to interactions between the micellar charges and the polar benzonaphthyridine fluorophore. Thus, while benzonaph-

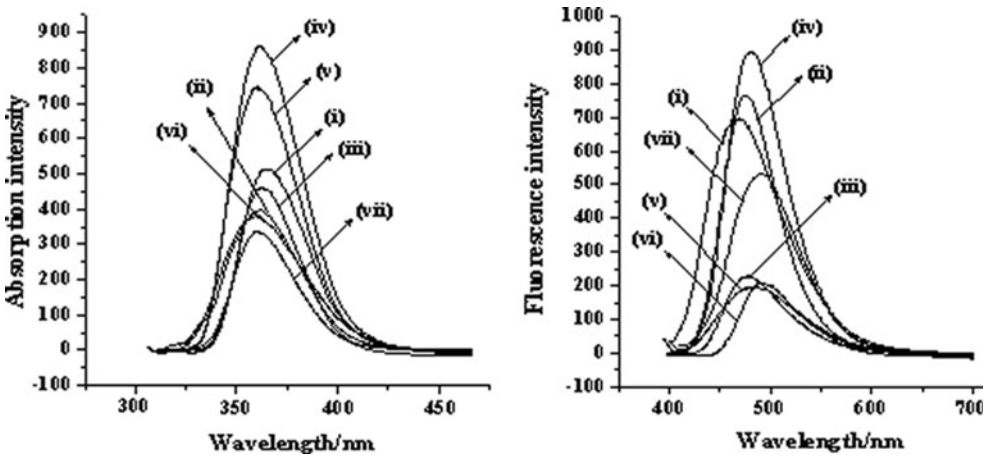



**Fig. 3** UV–vis absorption and fluorescence emission ($\lambda_f$ max) spectra of **3d** in different concentration of water (*i*) 0%, (*ii*) 10%, (*iii*) 20%, (*iv*) 30%, (*v*) 40%, (*vi*) 50%, (*vii*) 60%

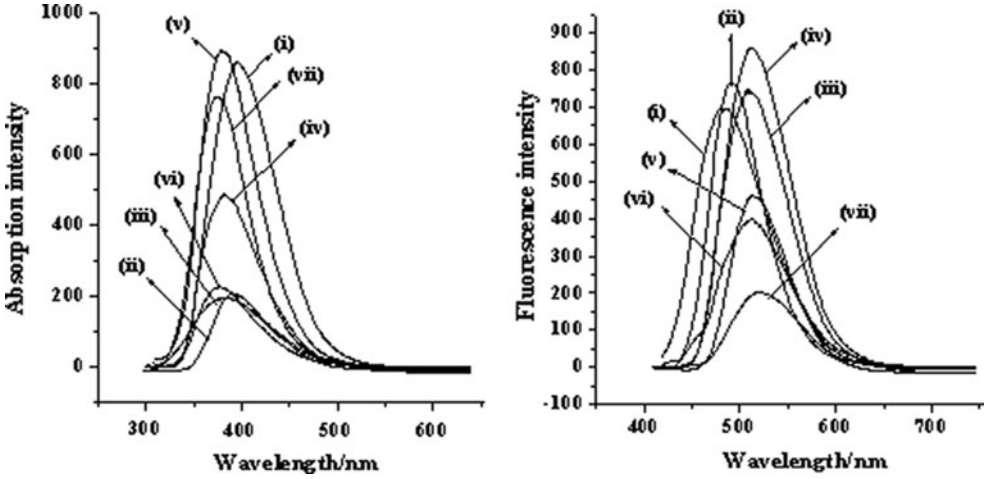



**Fig. 4** UV–vis absorption and fluorescence emission ($\lambda_f$ max) spectra of **7d** in different concentration of water (*i*) 0%, (*ii*) 10%, (*iii*) 20%, (*iv*) 30%, (*v*) 40%, (*vi*) 50%, (*vii*) 60%

thyridine **5b** shows significant micelle-charge dependent fluorescence peak shifts, **3d** and **7d** do not show such marked changes in their fluorescence $\lambda_f$ max.

## Thermal Properties

The organic compounds which are used in OLEDs and opto-electronic applications should be thermally and chemically stable [38]. Thermal analysis of synthesized benzonaphthyridines, by differential scanning colorimetry (DSC) and TGA reveal that they are thermally stable compounds up to 350 °C and high crystallization temperature.

## Conclusion

In conclusion, the formation of linear tetracyclic and pentacyclic benzonaphthyridines from dicyclic *o*-aminoaldehyde **1** represents remarkable efficient heteroannelation reaction. *Friedländer* condensations of **1** with heterocyclic 5-membered and 6-membered ring ketones are employed extensively. All these newly synthesized compounds are addition to library of fluorescent heterocyclic compounds. Synthesized benzonaphthyrdines are studied for their photophysical properties. The fluorescence property of benzonaphthyridines depends upon the nature of substituent present on ring A. Thus benzonaphthyridines bearing electron-releasing group i.e. OMe (Compound **3b**, **3d**, **5b**, **7b**, **7d** and **9b**) on ring D (Fig. 1) fluoresces at longer wavelength as compared to Compound **3a**, **3c**, **5a**, **7a**, **7c** and **9a**. From empirical calculations, we reveals that benzonaphthyridines which shows low electron hole gap values (e.g. **3b**, **3d**, **5b**, **7b**, **7d** and **9b**) have high fluorescence emission as well as have high quantum yields. While compounds with higher electron hole gap (e.g. **3a**, **3c**, **5a**, **7a**, **7c** and **9a**) shows low fluorescence emission and low quantum yield and are in agreement with theoretical observations. Moreover, certain benzonaphthyridines (**3d**, **5b** and **7d**) are studied for UV–vis absorption ($\lambda_{abs}$ max) and fluorescence emission ($\lambda_f$ max) in homogeneous media of organic solvents, 1,4-dioxane-water binary mixtures and in micellar environment. From these studies, we reveal that, these benzonaphthyridines (**3d**, **5b** and **7d)** exhibits solvatochromic fluorescence emission may be due to a polar, conformationally relaxed, intramolecular charge transfer excited state. The absorption maximum

**Table 5** UV–vis absorption ($\lambda_{abs}$ max) and fluorescence ($\lambda_f$ max) spectral data of benzonaphthyridines **3d**, **5b** and **7d** in microheterogeneous media of micelles at room temperature

| Comp. | Media | $\lambda_{max}$ (nm) | | | Stokes'Shift/cm$^{-1}$ | $\Phi_f$ (±0.002) |
|---|---|---|---|---|---|---|
| | | abs | emi | exi | | |
| 3d | CTAB | 372 | 477 | 369 | 5916 | 0.332 |
| | SDS | 372 | 477 | 368 | 5916 | 0.227 |
| | Triton-X-100 | 372 | 474 | 369 | 5602 | 0.383 |
| 5b | CTAB | 376 | 475 | 372 | 4773 | 0.384 |
| | SDS | 371 | 477 | 370 | 5261 | 0.302 |
| | Triton-X-100 | 376 | 471 | 372 | 4137 | 0.394 |
| 7d | CTAB | 404 | 494 | 398 | 6977 | 0.371 |
| | SDS | 399 | 487 | 395 | 5819 | 0.244 |
| | Triton-X-100 | 404 | 491 | 398 | 5784 | 0.389 |

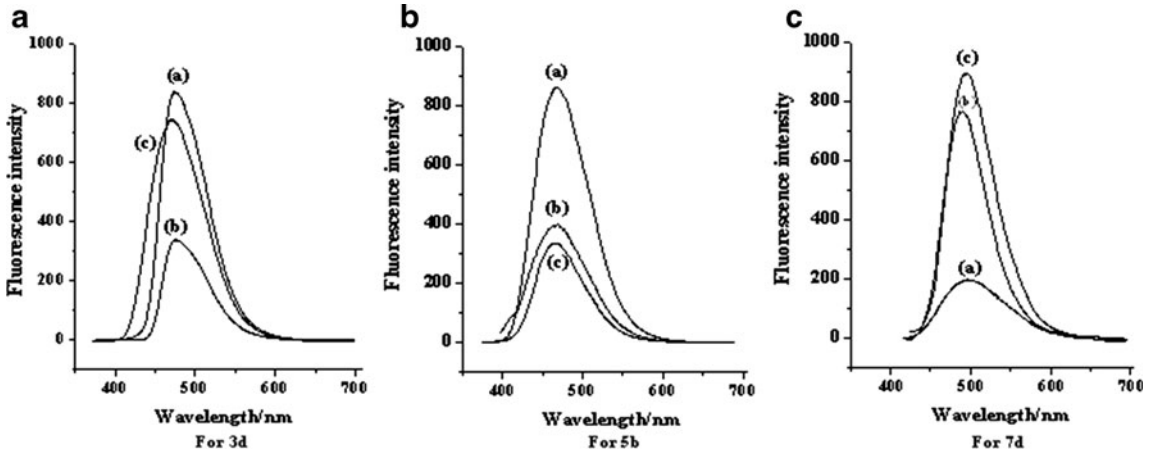



**Fig. 5** Fluorescence spectra of all three benzonaphthyridines (**3d**, **5b** and **7d**) in micelles of (a) CTAB (b) SDS and (c) Triton-X-100

($\lambda_{abs}$ max) of these compounds undergoes a moderate red shift with increasing solvent polarity; on the other hand fluorescence maxima ($\lambda_f$ max) becomes highly red shifted with increasing solvent polarity. It is observed that, in 1,4-dioxane-water mixtures, blue shift in absorption maximum is observed as the water content is increased and on the other hand red shifted fluorescence emission is observed for benzonaphthyridine **3d**, **5b** and **7d**. However, these benzonaphthyridines (**3d**, **5b** and **7d**) exhibit micellar charge dependent changes in their fluorescence intensity in the micellar environment. These fluorescence properties of benzonaphthyridines can be used to probe the micro-environment of ionic micelles and related organized assemblies.

## Experimental

### General

Surfactants [cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and Triton-X-100 for micelle preparation] and quinine sulphate [for determination of $\Phi_f$] were purchased from Hi-Media Laboratories Pvt. Ltd. Mumbai (India) and Research-Lab Fine Chem Industries, Mumbai (India) respectively. All other chemicals, reagents and solvents [such as acetonitrile, dimethylformamide (DMF), dioxane, ethanol, ethyl acetate, n-hexane, pet-ether methanol and tetrahydrofuran (THF)] used in spectroscopic and other studies were obtained from LOBA Chemie. Pvt. Ltd., Mumbai (India), Spectrochem, Mumbai (India) and E. Merck (India). Deionized, double distilled water (Millipore) was used for preparing the micelle solutions. All AR-grade organic solvents were dried and freshly distilled prior to use. The UV-grade solvents were used for spectral studies. Melting points were determined on a Gallenkamp melting point apparatus, Mod. MFB595 in open capillary tubes and were uncorrected. Fourier transform infrared (FTIR) spectra in KBr disk were measured on a Shimadzu FTIR-408 spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian XL-300 MHz spectrometer using tetramethylsilane (TMS) as internal standard and solvents were deuterio-chloroform ($CDCl_3$) and deuterio-dimethylsulphoxide (DMSO-$d_6$). Chemical shifts were reported in ppm from internal tetramethylsilane standard and were given in δ-units. Mass spectrum was recorded on Shimadzu GC-MS QP 2010A mass spectrometer with an ionization potential of 70 eV. Elemental analyses were performed on a Hosli CH-Analyzer and within ± 0.3 of the theoretical percentage. The absorption spectra were measured using a Shimadzu UV-1601 UV–VIS spectrophotometer. The fluorescence spectra were recorded on a RF-5301 PC spectrofluorophotometer by exciting the samples at their absorption maximum ($\lambda_{abs.\ max.}$). Compounds for UV and fluorescence measurements were dissolved in DMF, UV and fluorescence scan were recorded from 200 to 700 nm. The $\Phi_f$ relative to quinine sulphate in 1.0 x $10^{-3}$ mol $L^{-1}$ $H_2SO_4$ ($\Phi_f$=0.57) was measured at room temperature by standard literature procedure [39–41]. Both samples and standard were excited at the same excitation wavelength and the optical density (OD) of the standard and the sample was adjusted to be nearly equal. For all electronic spectroscopic studies (absorption, fluorescence excitation and emission) $1.0\times10^{-3}$ mol $L^{-1}$ solutions of the compounds were used. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 $F_{254}$ (Merck) plates using UV light (250 and 400 nm) and Fluorescence light (400 and 600 nm) for detection.

### *Synthesis*

*Synthesis of 2,3-Dihydro-1H-benzo[b]cyclopenta[g][1,8] naphthyridine (3 a-d)* The mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.001 mol) & cyclopentanone **2a** (0.001 mol) in ethanolic potassium hydroxide solution (10 mL, 2%) was refluxed for 5 h. Completion of the

reaction was monitored by Thin Layer Chromatography (TLC). The mixture was then cooled to room temperature; the separated solid product was collected by suction filtration, washed with pet-ether, dried and recrystallized from ethanol.

*2,3-Dihydro-1H-benzo[b]cyclopenta[g][1,8]naphthyridine (3a)* Yield: 0.178 g (80%), recrystallized from ethanol to afford faint yellow solid; M.p. 171-173 °C. IR (KBr): 3012 m, 2968 m, 2912 w, 1610 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.95 (m, 2H, $CH_2$), 2.49 (t, 2H, *J*=7.4 Hz, $CH_2$), 3.09 (t, 2H, *J*=6.8 Hz, $CH_2$), 7.34 (dd, 1H, *J*=7.9 & 8.3 Hz, Ar-H), 7.74 (dd, 1H, *J*=8.3 & 8.4 Hz, Ar-H), 8.09 (d, 1H, *J*= 7.9 Hz, Ar-H), 8.36 (d, 1H, *J*=8.4 Hz, Ar-H), 8.78 (s, 1H, Ar-H), 9.19 (s, 1H, Ar-H). Anal. Calcd. for $C_{15}H_{12}N_2$ (220.27): C, 81.81; H, 5.45; N, 12.72% Found: C, 81.80; H, 5.48; N, 12.70%

*8-Methoxy-2,3-dihydro-1H-benzo[b]cyclopenta[g][1,8] naphthyridine (3b)* Yield: 0.211 g (84%), recrystallized from ethanol to afford faint yellow needles; M.p. 184-186 °C. IR (KBr): 3019 m, 2972 m, 2929 m, 1619 s, 1026 s $cm^{-1}$.$^1H$ NMR (300 MHz DMSO-$d_6$) δ: 1.88 (m, 2H, $CH_2$), 2.37 (t, 2H, *J*=7.1 Hz, $CH_2$), 3.14 (t, 2H, *J*=6.9 Hz, $CH_2$), 4.02 (s, 3H, $OCH_3$), 7.43 (d, 1H, *J*=7.7 Hz, Ar-H), 7.51 (s, 1H, Ar-H), 8.24 (d, 1H, *J*=7.7 Hz, Ar-H), 9.21 (s, 1H, Ar-H), 9.44 (s, 1H, Ar-H). MS (70 eV) m/z (%): 250 [$M^+$] (83), 206 (37), 125 (19), 77 (22), 44 (85), 32 (47). Anal. Calcd. for $C_{16}H_{14}N_2O$ (250.29): C, 76.80; H, 5.60; N, 11.20% Found: C, 76.82; H, 5.62; N, 11.22%

*1,2,3,4-Tetrahydrodibenzo[b,g][1,8]naphthyridine (3c)* Yield: 0.202 g (86%), recrystallized from ethanol to afford yellow solid; M.p. 206-209 °C. IR (KBr): 2994 m, 2971 m, 2917 m, 1622 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.67-1.74 (m, 4H, $CH_2$), 2.60 (t, 2H, *J*=6.8 Hz, $CH_2$), 2.94 (t, 2H, *J*=6.9 Hz, $CH_2$), 7.27 (dd, 1H, *J*=8.2 & 8.6 Hz, Ar-H), 7.61 (dd, 1H, *J*=8.6 & 8.1 Hz, Ar-H), 7.97 (d, 1H, *J*= 8.2 Hz, Ar-H), 8.31 (d, 1H, *J*=8.1 Hz, Ar-H), 8.68 (s, 1H, Ar-H), 9.17 (s, 1H, Ar-H). Anal. Calcd. for $C_{16}H_{14}N_2$ (234.30): C, 82.05; H, 5.98; N, 11.96% Found: C, 82.03; H, 6.00; N, 11.98%

*9-Methoxy-1,2,3,4-tetrahydrodibenzo[b,g][1,8]naphthyridine (3d)* Yield: 0.231 g (87%), recrystallized from ethanol to afford yellow needles; M.p. 231–234 °C. IR (KBr): 3006 m, 2968 m, 1618 s, 1011 $scm^{-1}$.$^1H$ NMR (300 MHz $CDCl_3$) δ: 1.55-1.68 (m, 4H, $CH_2$), 2.74 (t, 2H, *J*=7.1 Hz, $CH_2$), 3.01 (t, 2H, *J*=6.5 Hz, $CH_2$), 4.02 (s, 3H, $OCH_3$), 7.38 (d, 1H, *J*=8.8 Hz, Ar-H), 7.58 (s, 1H, Ar-H), 8.17 (d, 1H, *J*=8.8 Hz, Ar-H), 9.02 (s, 1H, Ar-H), 9.31 (s, 1H, Ar-H). $^{13}C$ NMR (75 MHz $CDCl_3$) δ: 21.9, 22.2, 32.5, 34.7, 58.1, 112.9, 123.4, 125.1, 129.1, 131.2, 133.5, 135.1, 137.8, 144.7, 156.2, 157.9, 159.9. MS (70 eV) m/z (%): 264 [$M^+$] (72), 220 (42), 132 (29), 110 (33), 44 (77), 32 (68). Anal. Calcd. for $C_{17}H_{16}N_2O$ (264.32): C, 77.27; H, 6.06; N, 10.60% Found: C, 77.29; H, 6.09; N, 10.58%

*Synthesis of 4-Methyl-1,2,3,4-tetrahydrodibenzo[b,g][1,8] naphthyridine (5 a-b)* A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.001 mol) & 2-methylcyclohexa -none (**4**) (0.001 mol) in ethanolic potassium hydroxide solution (10 mL, 2%) was refluxed for 6 h. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). The mixture was then cooled to room temperature; the separated solid product was collected by suction filtration, washed with cold-methanol, dried and recrystallized from ethanol.

*4-Methyl-1,2,3,4-tetrahydrodibenzo[b,g][1,8]naphthyridine (5a)* Yield: 0.204 g (82%), recrystallized from ethanol to afford yellow prism; M.p. 211-213 °C. IR (KBr): 3015 m, 2968 m, 2912 m, 1618 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.52 (d, 3H, *J*=5.5 Hz, $CH_3$), 1.89 (m, 2H, $CH_2$), 2.04 (m, 2H, $CH_2$), 2.49 (t, 2H, *J*=7.4 Hz, $CH_2$), 3.26 (m, 1H, CH), 7.16 (dd, 1H, *J*=7.9 & 8.3 Hz, Ar-H), 7.77 (dd, 1H, *J*=8.3 & 8.5 Hz, Ar-H), 8.14 (d, 1H, *J*=7.9 Hz, Ar-H), 8.27 (d, 1H, *J*=8.5 Hz, Ar-H), 8.82 (s, 1H, Ar-H), 9.07 (s, 1H, Ar-H). $^{13}C$ NMR (75 MHz $CDCl_3$) δ: 19.1, 20.5, 28.7, 29.9, 31.2, 119.9, 126.1, 127.8, 128.5, 129.5, 131.1, 133.9, 135.3, 138.2, 149.5, 158.1, 161.5. Anal. Calcd. for $C_{17}H_{16}N_2$ (248.32): C, 82.25; H, 6.45; N, 11.29% Found: C, 82.27; H, 6.46; N, 11.30%

*9-Methoxy-4-methyl-1,2,3,4-tetrahydrodibenzo[b,g][1,8] naphthyridine (5b)* Yield: 0.239 g (85%), recrystallized from ethanol to afford yellow solid; M.p. 171-173 °C. IR (KBr): 3021 m, 2959 m, 2926 m, 1622 s, 1029 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.47 (d, 3H, *J*=5.8 Hz, $CH_3$), 1.84 (m, 2H, $CH_2$), 2.12 (m, 2H, $CH_2$), 2.45 (t, 2H, *J*= 6.7 Hz, $CH_2$), 3.12 (m, 1H, CH), 3.98 (s, 3H, $OCH_3$), 7.33 (d, 1H, *J*=8.3 Hz, Ar-H), 7.44 (s, 1H, Ar-H), 7.97 (d, 1H, *J*= 8.3 Hz, Ar-H), 9.32 (s, 1H, Ar-H), 9.49 (s, 1H, Ar-H). MS (70 eV) m/z (%): 278 [$M^+$] (100), 263 (92), 249 (47), 206 (22), 131 (12), 109 (22). Anal. Calcd. for $C_{18}H_{18}N_2O$ (278.35): C, 77.69; H, 6.47; N, 10.07% Found: C, 77.70; H, 6.48; N, 10.09%

*Synthesis of 3,4-Dihydrodibenzo[b,g][1,8]naphthyridin-1 (2H)-one (7 a-d)* A mixture of **1a-b** (0.001 mol) and dimedone (**6a-b**) (0.001 mol) was heated at 180–185 °C for 15 mins. The molten mass on cooling was stirred in methanol (10 mL) for 15 mins. The separated solid was collected by suction filtration and recrystallized from ethanol.

*3,4-Dihydrodibenzo[b,g][1,8]naphthyridin-1(2H)-one (7a)* Yield: 0.199 g (80%), recrystallized from ethanol to afford

faint yellow solid; M.p. 239-241 °C. IR (KBr): 3071 m, 2977 m, 2931 w, 1705 s, 1604 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.88 (m, 2H, $CH_2$), 2.56 (t, 2H, *J*=6.5 Hz, $CH_2$), 2.94 (t, 2H, *J*=6.7 Hz, $CH_2$), 7.21 (dd, 1H, *J*=8.2 & 8.6 Hz, Ar-H), 7.55 (dd, 1H, *J*=8.6 & 8.1 Hz, Ar-H), 8.11 (d, 1H, *J*= 8.2 Hz, Ar-H), 8.47 (d, 1H, *J*=8.1 Hz, Ar-H), 8.68 (s, 1H, Ar-H), 9.19 (s, 1H, Ar-H). Anal. Calcd. for $C_{16}H_{12}N_2O$ (248.28): C, 77.41; H, 4.83; N, 11.29% Found: C, 77.40; H, 4.80; N, 11.31%

*9-Methoxy-3,4-dihydrodibenzo[b,g][1,8]naphthyridin-1 (2H)-one (7b)* Yield: 0.227 g (81%), recrystallized from ethanol to afford yellow needles; M.p. 184–186 °C. IR (KBr): 3009 m, 2970 m, 2918 m, 1698 s, 1615 s, 1019 s $cm^{-1}$.$^1H$ NMR (300 MHz $CDCl_3$) δ: 1.94 (m, 2H, $CH_2$), 2.47 (t, 2H, *J*=7.2 Hz, $CH_2$), 2.83 (t, 2H, *J*=6.6 Hz, $CH_2$), 4.05 (s, 3H, $OCH_3$), 7.37 (d, 1H, *J*=9.0 Hz, Ar-H), 7.55 (s, 1H, Ar-H), 8.20 (d, 1H, *J*=9.0 Hz, Ar-H), 9.27 (s, 1H, Ar-H), 9.38 (s, 1H, Ar-H). $^{13}C$ NMR (75 MHz $CDCl_3$) δ: 21.8, 31.7, 39.7, 58.3, 113.2, 123.3, 124.9, 128.9, 130.5, 134.5, 136.5, 137.2, 144.7, 156.7, 158.1, 166.5, 197.2. MS (70 eV) m/z (%): 279 $[M+H]^+$ (100), 236 (22), 202 (48), 174 (37), 131 (38), 77 (57), 51(49). Anal. Calcd. for $C_{17}H_{14}N_2O_2$ (278.30): C, 73.38; H, 5.03; N, 10.07% Found: C, 73.40; H, 5.05; N, 10.08%

*3,3-Dimethyl-3,4-dihydrodibenzo[b,g][1,8]naphthyridin-1 (2H)-one (7c)* Yield: 0.229 g (82%), recrystallized from ethanol to afford faint green solid; M.p. 201–203 °C. IR (KBr): 3033 m, 2960 m, 2914 m, 1696 s, 1626 $scm^{-1}$. $^1H$ NMR (300 MHz $CDCl_3$) δ: 1.19 (s, 6H, $CH_3$), 2.44 (s, 2H, $CH_2$), 2.89 (s, 2H, $CH_2$), 7.39 (dd, 1H, *J*=7.9 & 8.5 Hz, Ar-H), 7.70 (dd, 1H, *J*=8.5 & 8.1 Hz, Ar-H), 8.09 (d, 1H, *J*=7.9 Hz, Ar-H), 8.30 (d, 1H, *J*=8.1 Hz, Ar-H), 8.71 (s, 1H, Ar-H), 9.10 (s, 1H, Ar-H). MS (70 eV) m/z (%): 277 $[M+H]^+$ (100), 248 (22), 201 (28), 183 (27), 152 (22), 77 (52), 51 (41), 31 (63). Anal. Calcd. for $C_{18}H_{16}N_2O$ (276.33): C, 78.26; H, 5.79; N, 10.14% Found: C, 78.29; H, 5.80; N, 10.15%

*9-Methoxy-3,3-dimethyl-3,4-dihydrodibenzo[b,g][1,8] naphthyridin-1(2H)-one (7d)* Yield: 0.256 g (83%), recrystallized from ethanol to afford green needles; M.p. 229-231 °C. IR (KBr): 3018 m, 2966 m, 2913 m, 1703 s, 1604 s, 1010 $scm^{-1}$.$^1H$ NMR (300 MHz $CDCl_3$) δ: 1.25 (s, 6H, $CH_3$), 2.39 (s, 2H, $CH_2$), 2.94 (s, 2H, $CH_2$), 4.09 (s, 3H, $OCH_3$), 7.36 (d, 1H, *J*=8.8 Hz, Ar-H), 7.51 (s, 1H, Ar-H), 8.24 (d, 1H, *J*=8.8 Hz, Ar-H), 9.28 (s, 1H, Ar-H), 9.46 (s, 1H, Ar-H). $^{13}C$ NMR (75 MHz $CDCl_3$) δ: 23.4, 25.7, 30.6, 44.8, 50.7, 58.7, 113.4, 123.8, 125.3, 131.2, 132.7, 134.1, 136.9, 138.3, 144.1, 156.6, 158.7, 166.2, 197.7. MS (70 eV) m/z (%): 307 $[M+H]^+$ (100), 278 (29), 250 (22), 179 (18), 55 (12), 41 (26). Anal. Calcd. for $C_{19}H_{18}N_2O_2$ (306.36): C, 74.50; H, 5.88; N, 9.15% Found: C, 74.52; H, 5.90; N, 9.14%

*Synthesis of 5-(3,4-Dichlorophenyl)-5,6-dihydrobenzo[b] naphtho[2,1-g][1,8]naphthyridine (9 a-b)* The mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.001 mol) & cetraline (**8**) (0.001 mol) in ethanolic potassium hydroxide solution (10 mL, 2%) was refluxed for 3 h. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). The mixture was then cooled to room temperature; the separated solid product was collected by suction filtration, washed with pet-ether, dried and recrystallized from ethanol.

*5-(3,4-Dichlorophenyl)-5,6-dihydrobenzo[b]naphtho[2,1-g] [1,8]naphthyridine (9a)* Yield: 0.358 g (84%), recrystallized from ethanol to afford yellow solid; M.p. 284-286 °C. IR (KBr): 2991 m, 2959 m, 1620 $scm^{-1}$. $^1H$ NMR (300 MHz DMSO-$d_6$) δ: 3.84 (d, 2H, *J* =5.8 Hz, $CH_2$), 5.09 (t, 1H, *J*=5.8 Hz, $CH_2$), 6.89-7.09 (m, 4H, Ar-H), 7.15 (dd, 1H, *J*=8.6 & 3.2 Hz, Ar-H), 7.24 (d, 1H, *J*=3.2 Hz, Ar-H), 7.39 (dd, 1H, *J*=8.0 & 8.5 Hz, Ar-H), 7.49 (d, 1H, *J*=8.6 Hz, Ar-H), 7.70 (dd, 1H, *J*=8.5 & 8.1 Hz, Ar-H), 8.14 (d, 1H, *J*=8.0 Hz, Ar-H), 8.44 (d, 1H, *J*=8.1 Hz, Ar-H), 8.81 (s, 1H, Ar-H), 9.08 (s, 1H, Ar-H). $^{13}C$ NMR (75 MHz DMSO-$d_6$) δ: 38.3, 43.5, 120.2, 121.9, 122.5, 123.1, 124.9, 125.1, 125.8, 127.2, 128.1, 128.7, 129.2, 129.8, 131.4, 132.9, 133.9, 135.6, 136.4, 137.1, 137.9, 141.4, 144.9, 148.3, 159.3, 162.7. Anal. Calcd. for $C_{26}H_{16}Cl_2N_2$ (427.33): C, 73.23; H, 3.75; N, 6.57% Found: C, 73.20; H, 3.74; N, 6.55%

*5-(3,4-Dichlorophenyl)-10-methoxy-5,6-dihydrobenzo[b] naphtho[2,1-g][1,8]naphthyridine (9b)* Yield: 0.391 g (85%), recrystallized from ethanol to afford yellow solid; M.p. 291-293 °C. IR (KBr): 3011 m, 2975 m, 2934 m, 1609 s, 1029 $scm^{-1}$. $^1H$ NMR (300 MHz DMSO-$d_6$) δ: 3.77 (d, 2H, *J*=5.9 Hz, $CH_2$), 4.04 (s, 3H, $OCH_3$), 4.88 (t, 1H, *J*=5.9 Hz, $CH_2$), 6.94-7.13 (m, 4H, Ar-H), 7.19 (dd, 1H, *J*= 8.5 and 2.9 Hz, Ar-H), 7.29 (d, 1H, *J*=2.9 Hz, Ar-H), 7.37 (d, 1H, *J*=8.5 Hz, Ar-H), 7.47 (d, 1H, *J*=8.9 Hz, Ar-H), 7.62 (s, 1H, Ar-H), 8.24 (d, 1H, *J*=8.9 Hz, Ar-H), 9.21 (s, 1H, Ar-H), 9.31 (s, 1H, Ar-H). MS (70 eV) m/z (%): 456 $[M^+]$ (86), 458 [M+2] (59), 460 [M+4] (9), 441 (29), 268 (31), 171 (47), 193 (40), 44 (84), 32 (49). Anal. Calcd. for $C_{27}H_{18}Cl_2N_2O$ (457.35): C, 71.05; H, 3.94; N, 6.14% Found: C, 71.07; H, 3.91; N, 6.16%

**Acknowledgements** The authors would like to thank Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support for this research project. Authors also thank to Professor D. D. Dhavale, Department of Chemistry, University of Pune, India, for his valuable cooperation for the measurement of $^1H$ NMR, $^{13}C$ NMR, Mass and Elemental analysis. Authors acknowledge their thanks to Dr. V. B. Gaikwad, Principal, K. R. T. Arts, B. H. Commerce and A. M. Science College, Nashik-02, MS, India, for the valuable co-operation in measurement of IR, UV and Fluorescence.

## References


1. Forrest SR, Thompson ME (2007) Special issue on "Organic Electronic and Optoelectronics". Chem Rev 107:923–1386
2. Miller RD, Chandross EA (2010) Special issue on "Materials for Electronics". Chem Rev 110:1–574
3. He GS, Tan LS, Zheng Q, Prasad PN (2008) Multiphoton absorbing materials: molecular designs, characterizations, and applications. Chem Rev 108:1245–13330
4. Kivala M, Diederich F (2009) Acetylene-derived strong organic acceptors for planar and nonplanar push−pull chromophores. Acc Chem Res 42:235
5. Blanchard-Desce M, Alain V, Bedworth PV, Marder SR, Fort A, Runser C, Barzoukas M, Lebus S, Wortmann R (1997) Large quadratic hyperpolarizabilities with donor–acceptor polyenes exhibiting optimum bond length alternation: correlation between structure and hyperpolarizability. Chem Eur J 3(7):1091–1104
6. Kuzyk MG (2009) Using fundamental principles to understand and optimize nonlinear-optical materials. J Mater Chem 19:7444–7465
7. May JC, Biaggio I, Bureš F, Diederich F (2007) Extended conjugation and donor-acceptor substitution to improve the third-order optical nonlinearity of small molecules. Appl Physc Lett 90(25):251106
8. Bureš F, Schweizer WB, May JC, Boudon C, Gisselbrecht JP, Gross M, Biaggio I, Diederich F (2007) Property tuning in charge-transfer chromophores by systematic modulation of the spacer between donor and acceptor. Chem Eur J 13:5378–5387
9. Spitler EL, Shirtcliff LD, Haley MM (2007) Systematic structure −property investigations and ion-sensing studies of pyridine-derivatized donor/acceptor tetrakis(arylethynyl)benzenes. J Org Chem 72(1):86
10. Kulhánek J, Bureš F, Pytela O, Mikysek T, Ludvík J, Růžička A (2010) Push-pull molecules with a systematically extended π-conjugated system featuring 4,5-dicyanoimidazole. Dyes Pigm 85 (1–2):57–65
11. a) Turro NJ, Gratzel M, Braun AM (1980) Photophysical and photochemical processes in micellar systems. Angew Chem Int Ed Engl 19(9):675–696; b) Czarnik AW (1991) Frontiers in Supramolecular Organic Chemistry and Photochemistry; VCH: Weinheim, Germany, pp 109–122; c) Ueno A, Osa T (1991) Photochemistry in Organized and Constrained Media; VCH: New York, pp 739–742; d) Hamasaki K, Ikeda H, Nakamura A, Ueno A, Toda F, Suzuki I, Osa T (1993) Fluorescent sensors of molecular recognition. Modified cyclodextrins capable of exhibiting guest-responsive twisted intramolecular charge transfer fluorescence. J Am Chem Soc 115 (12):5035–5040; e) Lehn JM (1995) Supramolecular Chemistry; VCH: Weinheim, Germany; f) de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE (1997) Signaling recognition events with fluorescent sensors and switches. Chem ReV 97(5):1515
12. Royer CA (2006) Probing protein folding and conformational transitions with fluorescence. Chem Rev 106:1769–1784
13. Lakowicz JR (1999) Principles of fluorescence spectroscopy, 2nd edn. Springer, New York
14. Behera GB, Mishra BK, Behera PK, Panda M (1999) Fluorescent probes for structural and distance effect studies in micelles, reversed micelles and microemulsions. Adv Colloid Interface Sci 82:1–42
15. Mallick A, Halder B, Chattopadhyay N (2005) Spectroscopic investigation on the interaction of ICT probe 3-Acetyl-4-oxo-6,7-dihydro-12*H*-Indolo-[2,3-*a*]quinolizine with serum albumin. J Phys Chem B 109:14683–14690
16. Grabowski Z, Rotkiewicz K, Rettig W (2003) Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures. Chem Rev 103:3899–4032
17. Poklar N, Lah J, Salobir M, Maek P, Vesnaver G (1997) pH and temperature-induced molten globule-like denatured states of equinatoxin II: a study by UV-Melting, DSC, far- and near-UV CD spectroscopy and ANS fluorescence. Biochemistry 36:14345–14352
18. Haskard CA, Li-Chan ECY (1998) Hydrophobicity of bovine serum albumin and ovalbumin determined using Uncharged (PRODAN) and Anionic (ANS) fluorescent probes. J Agric Food Chem 46:2671–2677
19. Cardamone M, Puri NK (1992) Spectrofluorimetric assessment of the surface hydrophobicity of proteins. Biochem J 282:589–593
20. Matulis D, Baumann CG, Bloomfield VA, Lovrien RE (1999) 1-Anilino-8-naphthalene sulphonate as a protein conformational tightening agent. Biopolymers 49:451–458
21. Daniel E, Weber G (1966) Cooperative effects in binding by bovine serum albumin. I. The binding of 1-Anilino-8-naphthalenesulfonate. Fluorimetric titrations. Biochemistry 5:1893–1900
22. Shelar DP, Birari DR, Rote RV, Patil SR, Toche RB, Jachak MN (2011) Novel Synthesis of 2-amino-3-quinoline-carbaldehyde, benzo[*b*][1,8]naphthyridines and study of their fluorescence behavior. J Phys Org Chem 24:203–211
23. Shelar DP, Patil SR, Rote RV, Toche RB, Jachak MN (2011) Synthesis and fluorescence investigation of differently substituted benzo[*b*][1,8]naphthyridines: Interaction with different solvents and bovine serum albumin (BSA). J Fluoresc 21 (3):1033–1047
24. Pearson R (1989) Absolute electronegativity and hardness: applications to organic chemistry. J Org Chem 54:1423
25. Zhou Z, Parr R (1989) New measures of aromaticity: absolute hardness and relative hardness. J Am Chem Soc 111:7371
26. Zhou Z, Parr R (1990) Activation hardness: new index for describing the orientation of electrophilic aromatic substitution. J Am Chem Soc 112:5720
27. Diener M, Alford J (1998) Isolation and properties of small-bandgap fullerenes. Nature 393:668
28. Zollinger H (2003) Color Chemistry 3 rd ed., Switzerland Page No.479
29. Stewart JJP (1990) J Comput-Aided Mol Des 4:1
30. Stewart JJP, QCPE Bull (1989) 9, 10. QCPE program no. 455
31. Mancini PM, del C. Perez A, Vottero LR (2001) Nonspecific solute–solvent interactions in binary solvent mixtures containing an aprotic hydrogen-bond acceptor and a hydrogen-bond donor: dipolarity/polarizability and refractive index. J Sol Chem 30 (8):695–707
32. Reichardt C (2007) Solvents and solvent effects: an introduction. Org Process Res Dev 11(1):105–103
33. Sasirekha V, Vanelle P, Terme T, Meenakshi C, Umadevi M, Ramakrishnan V (2007) Solvatochromism, Preferential solvation of 2,3-bis(chloromethyl)-1,4-anthraquinone in binary mixtures and the molecular recognition towards p-tert-butyl-calix[4]arene. J Fluores 17(5):528–539
34. Hagazi MF, Al-Mudhaf HF, Abu-Shady AI (2007) Preferential solvation of acetic acid in binary mixtures of carbon tetrachloride–cyclohexane and carbon tetrachloride–1,2-dichloroethane. J Sol Chem 36(4):467–478
35. Bevilaqua T, da Silva DC, Machado VG (2004) Preferential solvation of Brooker's merocyanine in binary solvent mixtures composed of formamides and hydroxylic solvents. Spectrochim Acta Part A 60(4):951–958
36. Fletecher AN (1969) Quinine sulfate as a fluorescence quantum yield standard. Photchem Photobiol 9(5):439–444
37. Jones MN, Chapman D (1995) Micelles, monolayers and biomembranes. Wiley-Liss, New York, pp 64–101

38. Spreitzer H, Schenk H, Salbeck J, Weissortel F, Riel H, Riess W (1999) Temperature stability of OLEDs using amorphous compounds with spiro-bifluorene core. Proc SPIE-Int Soc Opt Eng 316:3797
39. Eastman JW (1967) Quantitative spectrofluorimetry-the fluorescence quantum yield of quinine sulfate. Photochem Photobiol 6 (1):55–72
40. Adams MJ, Highfield JG, Kirkbright GF (1977) Determination of absolute fluorescence quantum efficiency of quinine bisulfate in aqueous medium by optoacoustic spectrometry. Anal Chem 49 (12):1850–1852
41. Meech SR, Phillips D (1983) Photophysics of some common fluorescence standards. J Photochem 23:193–217