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Short communication

The synthesis and photophysical studies of quinoxaline and pyridopyrazine derivatives

Prakasam Thirumurugan, Duraisamy Muralidharan, Paramasivan T. Perumal*

Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

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ABSTRACT

A simple and facile method for the synthesis of 2,3-bis[(*E*)-2-aryl vinyl]-quinoxaline and 2,3-bis[(*E*)-2-aryl vinyl]-pyrido(2,3-*b*)pyrazine is described. Condensation of cinnamils with 1,2-diaminobenzene and 2,3-diaminopyridine in water using conventional heating and microwave irradiation afforded high yields (71–92%) of 2,3-bis[(*E*)-2-aryl vinyl]-quinoxalines and 2,3-bis[(*E*)-2-arylvinyl]-pyrido(2,3-*b*)pyrazines. The photophysical properties of the resultant quinoxaline and pyrazine derivatives were studied; the pyridopyrazine derivatives were found to exhibit halochromism.

1. Introduction

The structural diversity and biological importance of nitrogen containing heterocycles have made them attractive synthetic targets over many years and they are found in various natural products [1]. In particular quinoxaline scaffolds were found as a core unit in a number of biologically active compounds. These include anticancer [2,3], antibacterial [4], antiviral [5], anti-inflammatory [6], anti-HIV [7–9] and antihelmintic activities [10]. Quinoxaline-based oligopyrroles act as an anion receptors such as fluoride, chloride and dihydrogen phosphate [11]. Quinoxaline-based oligothiophene copolymers served as electron transport conjugated polymers for electroluminescent devices in the field of macromolecules [12]. Quinoxaline derivatives are also used in the development of novel organic dyes and organic semiconductors [13].

Fluorescent property is the ultimate tool for the identification of chromosomes and ultra fast DNA sequencing by showing different colours with each DNA base pairs via fluorescence resonance energy transfer [14,15]. Many quinoxaline derivatives have displayed photoluminescence and electroluminescence properties. Compounds with fused quinoxaline aromatic rings are used as raw materials for organic light-emitting devices, light-emitting cells and optoelectronic devices [16,17].

A number of synthetic strategies are known for the preparation of substituted quinoxalines. Straight-forward synthesis of quinoxaline involves the condensation of an aromatic 1,2-diamines with 1,2-dicarbonyl compounds. However, most of the reported methods suffer from several disadvantages such as prolonged reaction times, reagents in stoichiometric amounts, expensive reagents, use of hazardous solvents and moderate yields [18–22]. To overcome these aspects and due to the unique pharmacological properties of quinoxalines, the development of eco-friendly synthetic methods enabling facile access to this heterocycle is highly desirable.

As part of our ongoing research in the development of novel synthetic routes to the synthesis of biologically active heterocyclic compounds and use of green chemistry techniques in organic synthesis [23,24], herein we disclose a simple and convenient method for the synthesis of quinoxaline derivatives from cinnamils in water under reflux/microwave irradiation conditions (Scheme 1) and their photophysical properties were evaluated.

2. Results and discussion

Initial studies were conducted with cinnamil (**1a**) [25] and 1,2-diaminobenzene (**2**) under various solvents at reflux temperature. Excellent yields were obtained in water at reflux temperature.

* Corresponding author. Tel.: +91 44 24913289; fax: +91 44 24911589.
E-mail address: ptperumal@gmail.com (P.T. Perumal).

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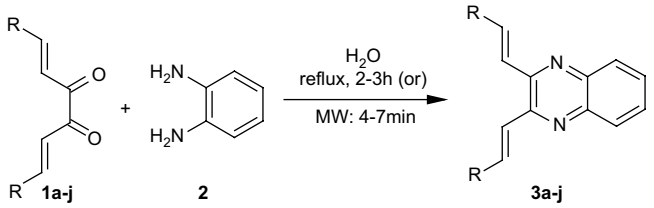


Scheme 1. Synthesis of quinoxalines.

Isolation of the product was simple as the solid product precipitated was filtered and washed with ethanol to afford the pure substituted quinoxaline derivative (**3a**).

The protocol was extended to substrates (cinnamils) both electron rich and electron withdrawing groups under optimized conditions was further investigated, and the reaction condition was found to be amendable to a wide variety of substituents on cinnamils. We extended our investigation on microwave irradiation of substrates (**1a**–**j**) to afford excellent yields of substituted quinoxalines (**3a**–**j**) and the results are summarized in Table 1.

The structure of compounds (**3a**–**j**) was evaluated based on detailed spectroscopic studies. Thus, the IR spectrum of compound (**3b**) showed peaks at 1621 and 1510 cm^{-1} indicating the presence of C═N and C═C functional groups respectively. The ^1H NMR spectrum showed aromatic protons in the region of δ: 8.02–7.35. The *trans* olefinic protons were demonstrated at δ: 7.95 (d, $J = 15.2$ Hz) and methyl proton appeared at δ: 2.40. In ^{13}C NMR spectra all the aromatic carbons appeared in the region of δ: 149.2–122.6 and the methyl carbon resonated at δ: 21.4. The mass spectra displayed the (M + 1) peak at *m*/*z* 363.25.

Pyridopyrazine has remarkable applications in the field of electroconductive devices and dipolar electroluminescent devices with tunable emission characteristics. Heteroatom present in the quinoxaline motif enhances the photophysical effects significantly [26]. Hence we extended the protocol for the synthesis of pyridopyrazine (**5a**–**e**) under optimized conditions to exhibit the generality of the methodology (Scheme 2 and Table 2).

The spectral data of compound (**5b**) are described. In IR spectrum, stretching frequencies at 1621 and 1513 cm^{-1} confirmed the presence of C═N and C═C bonds. The ^1H NMR spectrum showed the presence of aromatic protons in the region of δ: 7.23–9.03. The chemical shift of aryl protons changed to downfield region due to the presence of nitrogen atom in the ring. The *trans* olefinic proton signal appeared as doublet at δ 7.96 ($J = 15.5$ Hz) and δ 2.39 signal corresponds to methyl protons. In ^{13}C NMR spectra, peaks in the range of δ 153.2–120.2 correspond to aromatic carbons and δ 21.4 corresponds to methyl carbon. Further, the mass spectrum displayed the (M + 1) peak at *m*/*z*: 364.23. All the reported compounds were thoroughly characterized by spectroscopic methods.

2.1. Photophysical properties of quinoxaline derivatives

The photophysical studies of quinoxaline derivatives were investigated with a concentration of 1×10^{-5} M quinoxaline in acetonitrile at room temperature. The electronic character of the substituents in quinoxaline molecule strongly affects the absorption spectra producing a significant bathochromic shift to an extent which depends on their electron-donating ability. Higher the electron-donating ability of the donor groups present in the quinoxaline moiety, higher is the λ_{max} value. The effects of donor groups on the absorption spectra are summarized in Table 3 and Fig. 1. All the quinoxaline derivatives showed two absorption maxima due to π–π^* and n–π^* electronic transitions.

The photoluminescence spectral data of quinoxaline derivatives (**3a**–**j**) in acetonitrile are shown in Table 3 and Fig. 2. Their fluorescence emission maximum shifted to longer wavelength region λ_{emi}, which mainly depends on the electronic character of substituents present in the quinoxaline derivatives. Substituents with higher electron-donating character lead to longer λ_{emi} values. And, moreover extended conjugation with fused rings is also responsible for the higher λ_{emi} value.

Time correlated single photon counting experiments exhibited that quinoxaline derivatives have longer lifetimes. The quinoxaline derivatives (**3b** and **e**) exhibit a single exponential decay and entries (**3d**, **i**, **j**) exhibit a bi-exponential decay. The value of chi-square is in the order of one, comparatively a good fit with experimental results shown in Table 3.

2.2. Photophysical properties of pyrazine derivatives

The optical studies of the synthesized pyrazine derivatives were recorded in acetonitrile at a concentration of 1×10^{-5} M. A strong red shift maximum observed depends on the electronic properties of the substituents present in the pyrazine nucleus. Substituents with electron-donating group resulted in a significant bathochromic shift. Quinoxalines showed only two absorption maxima whereas pyridopyrazine derivatives showed three different absorption maxima due to the additional nitrogen atom present in the pyrazine moiety (Fig. 3 and Table 4).

Pyridopyrazines showed longer photoluminescence maxima than those of quinoxaline derivatives. The red shift maxima observed in the region of 450–600 nm strongly depend on the electron-donating character of the substituents present in the pyridopyrazine moiety. Stronger electron-donating groups present in the pyrazine moiety lead to longer emission value (Fig. 4 and Table 4).

All pyridopyrazines (**5a**–**e**) showed a bi-exponential decay. The value of chi-square is in the order of one which is comparatively a good fit with experimental results. The fluorescence lifetimes of pyridopyrazine derivatives show higher values in comparison to quinoxaline derivatives as shown in Table 4.

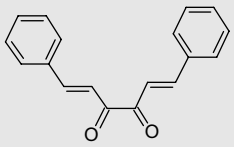
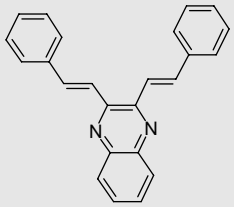
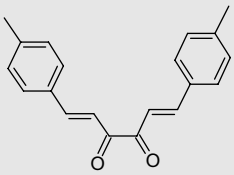
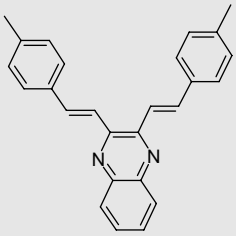
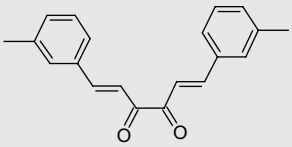
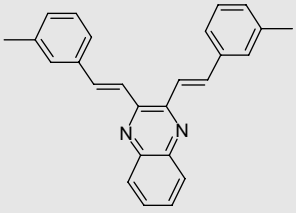
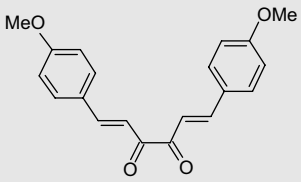
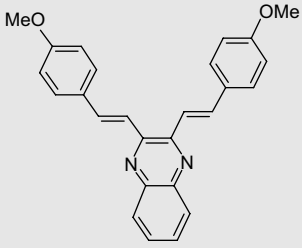
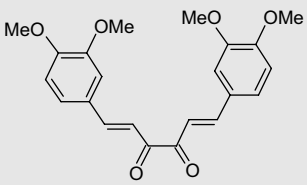
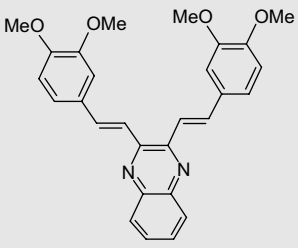
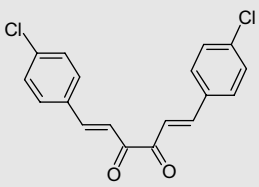
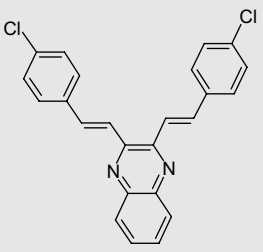
2.3. Halochromism of pyridopyrazine

The absorption spectra of pyridopyrazine (**5e**) dramatically changed due to pH variation of the medium. A mole ratio of 5:1 of any acid like acetic acid, formic acid and *p*-toluenesulfonic acid added to compound (**5e**) in acetonitrile resulted in change of colour from greenish yellow to red due to the protonation of nitrogen atom present in the pyrazine ring (Fig. 5). The addition of H^+ to the compound (**5e**) in acetonitrile leads to the red shift in the absorption spectrum with an isosbestic point at 472 nm (Fig. 6). It was reported in the literature that the protonation of the nitrogen atom of heteroaromatic poly(arylene) in acidic media sometimes leads to a bathochromic shift of the absorption peak [27,28]. Compounds (**5a**–**e**) exhibit very good halochromic properties.

3. Conclusions

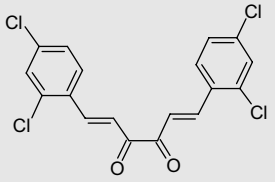
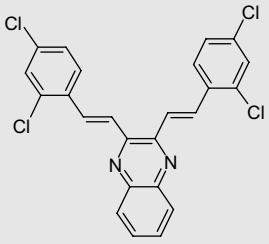
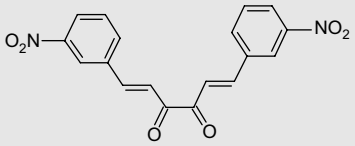
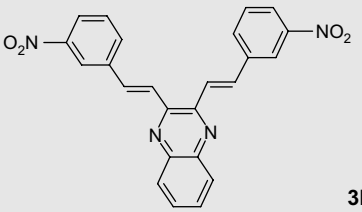
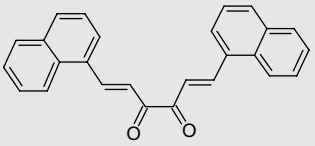
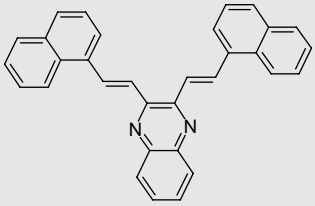
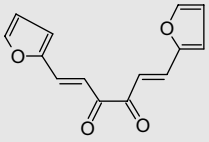
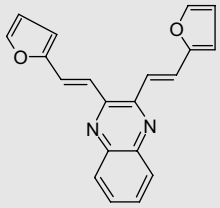
A simple method for the synthesis of novel quinoxaline and pyrazine derivatives is described. The quinoxaline and pyridopyrazine derivatives showed good photophysical properties and stable fluorescence, as well as very good fluorescence lifetimes. The products are potentially amendable to further manipulations in the fields of medicinal chemistry, molecular recognition, organic light-emitting devices, optoelectronic devices and *n*-type semi-conducting conjugated polymers.

Table 1
Synthesis of substituted quinoxalines.

Entry	Cinnamil	Quinoxaline[a]	Heating		Microwave irradiation	
			Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	 **1a**	 **3a**	1.5	92	5	94
2	 **1b**	 **3b**	1.5	89	5	92
3	 **1c**	 **3c**	2	80	6	84
4	 **1d**	 **3d**	1.5	88	5	91
5	 **1e**	 **3e**	2.0	89	6	92
6	 **1f**	 **3f**	1.5	79	5	79

(*continued on next page*)

Table 1 (*continued*)

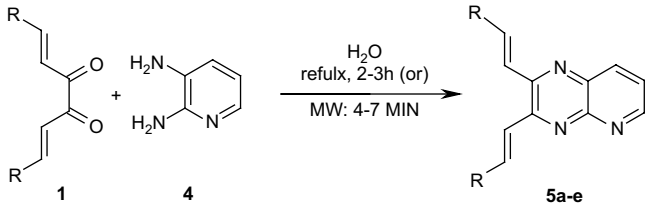
Entry	Cinnamil	Quinoxaline[a]	Heating		Microwave irradiation	
			Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)
7	 **1g**	 **3g**	1.0	78	5	81
8	 **1h**	 **3h**	0.5	71	4	72
9	 **1i**	 **3i**	2.5	89	7	90
10	 **1j**	 **3j**	2.0	83	4	91

[a] All products were confirmed by IR, NMR, mass and elemental analysis.
[b] Isolated yield.

4. Experimental section

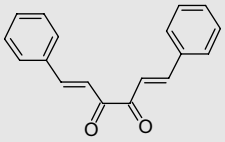
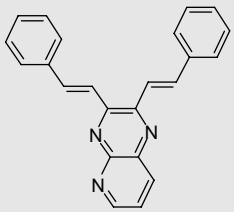
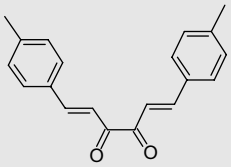
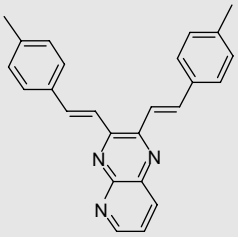
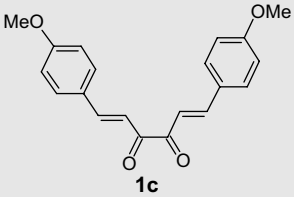
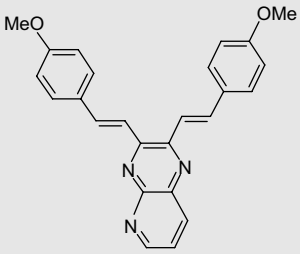
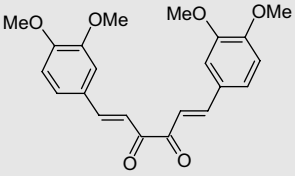
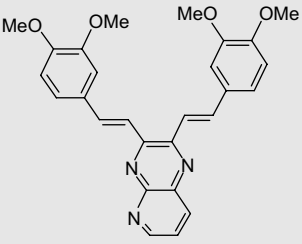
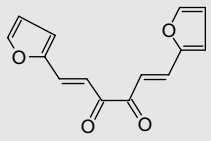
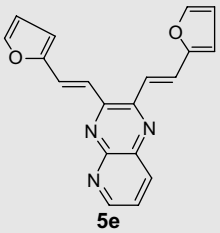
4.1. General

All the substituted aldehydes, biacetyl and 2,3-diaminopyridines were purchased from Aldrich Chemicals. Piperidine and all other reagents were purchased from S.D. Fine. Chem. India Limited. Methanol was distilled from Mg/I_2 under nitrogen and stored over 3 Å molecular sieves. IR spectrum of quinoxalines and pyridopyrazine derivatives were recorded in the form KBr pellets using Perkin-Elemer RXI FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as internal standard with JEOL 500 MHz and Bruker 300 MHz high resolution NMR spectrometers respectively. Multiplicities were abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Mass spectra were recorded using Electron spray Ionization Method with Thermo Finnigan mass spectrometer. Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany). Elemental analysis data were recorded using Thermo Finnigan FLASH EA 1112 CHN. The electronic spectral measurements were carried out in Perkin–Elmer Lambda 35 double beam spectrometer at room temperature. The steady state emission spectra were recorded on Hitachi 650-40 spectrofluorometer at room temperature. Time-resolved fluorescence measurements were determined using picosecond laser excited Horiba Jobin Yvon time correlated single photon counting spectrofluorometer. The excitation source was a tunable Ti-sapphire laser (Tsunami, Spectrometer, USA) with a pulse width of <2 ps and repetition rate of 82 MHz. The sample was excited at its corresponding wavelength and the emission was monitored between 400 to 600 nm using an MCP-PMT detector. Decay traces were deconvoluted using a non-linear least-squares analysis using IBH software.



Scheme 2. Synthesis of pyridopyrazines.

Table 2
Synthesis of substituted pyridopyrazines.

Entry	Cinnamil	Pyrazine[a]	Conventional heating		Microwave irradiation	
			Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	 **1a**	 **5a**	2.5	78	5	84
2	 **1b**	 **5b**	3.0	79	6	83
3	 **1c**	 **5c**	3.0	80	6	85
4	 **1d**	 **5d**	3.5	77	7	90
5	 **1e**	 **5e**	2.0	79	4	87

[a] All products were confirmed by IR, NMR, mass and elemental analysis.
[b] Isolated yield.

4.2. General procedure for the synthesis of quinoxaline derivatives (***3a–j***)

4.2.1. Method A

A mixture of cinnamil (1.0 mmol) and 1,2-diaminobenzene (1.0 mmol) in water (10 mL) was refluxed for appropriate time mentioned in Table 2. After completion of the reaction, as indicated by TLC, the precipitated solid was filtered, washed with ethanol and dried. The obtained crude solid was purified further by recrystallisation with ethanol.

4.2.2. Method B

A mixture of cinnamil (1.0 mmol) and 1,2-diaminobenzene (1.0 mmol) in water (2 mL) was irradiated in a microwave oven (BPL

Table 3
Photophysical studies of quinoxalines.

#	λ_{max} (nm)	λ_{emi} (nm)	Lifetime of quinoxaline derivatives quinoxaline derivatives	
			τ (ns)	χ^2
3a	294.15	449.12	nt	nt
3b	306.35	468.66	2.70 (100.00%)[a]	1.18
3c	305.25, 374.15	456.44	nt	nt
3d	316.22, 358.85	490.36	3.26 (98.54%), 0.40 (1.43%)[b]	1.12
3e	327.03, 373.52	513.48	3.74 (100.00%)[a]	1.15
3f	279.12, 356.12	441.12	nt	nt
3g	265.12, 345.16	432.12	nt	nt
3h	288.16, 398.15	466.12	nt	nt
3i	326.06, 362.36	488.87	2.70 (76.89%), 1.64 (23.11%)[b]	1.13
3j	317.34	494.21	4.50 (93.13%), 1.13 (6.87%)[b]	1.06

[a] Fluorescence lifetime associated with the single exponential.
[b] Fluorescence lifetimes associated with the bi-exponentials.

BMG 800 TS model) at 80 W for the appropriate time mentioned in Table 2. After completion of the reaction, as indicated by TLC, the precipitated solid was filtered, washed with ethanol and then dried. The obtained crude product was recrystallized with ethanol.

4.2.2.1. 2,3-Bis[(E)-2-phenyl vinyl]quinoxaline ***3a*** *(Table 1, entry 1).* Pale yellow solid; mp: 194–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04 (m, 2H), 7.98 (d, 2H, $J = 15.3$ Hz), 7.64 (m, 8H), 7.41 (t, 4H, $J = 7.6$ Hz), 7.35 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.1, 141.6, 137.9, 136.5, 129.5, 129.1, 128.9, 128.8, 127.6, 122.7, 122.7. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1654, 1579, 1409, 1297, 1079, 968 cm^{-1}. Mass (ESI LCQ-MS): 335.22 (M + 1). Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.24; H, 5.41; N, 8.34.

4.2.2.2. 2,3-Bis[(E)-2-(4-methyl phenyl)vinyl]quinoxaline ***3b*** *(Table 1, entry 2).* Pale yellow solid; mp: 179–181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (m, 2H), 7.95 (d, 2H, $J = 15.2$ Hz), 7.65 (m, 2H), 7.57 (m, 6H), 7.22 (d, 4H, $J = 8.4$ Hz), 2.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.3, 141.6, 139.2, 137.8, 133.8, 129.5, 129.3, 128.8, 127.5, 121.7, 21.4. FT-IR (KBr, $\nu^{-1}{}_{max}$): 2996, 1621, 1510, 1185, 982 cm^{-1}. Mass (ESI LCQ-MS): 363.25 (M + 1). Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.19; H, 6.10; N, 7.70.

4.2.2.3. 2,3-Bis[(E)-2-(3-methyl phenyl)vinyl]quinoxaline ***3c*** *(Table 1, entry 3).* Pale yellow solid; mp: 148–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (m, 2H), 7.95 (d, 2H, $J = 15.3$ Hz), 7.61 (m, 4H), 7.49 (s, 4H), 7.31 (t, 2H, $J = 7.6$ Hz), 7.17 (d, 2H, $J = 7.6$ Hz), 2.42 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.2, 141.6, 138.4, 138.1, 136.5, 129.8, 129.4, 128.9, 128.7, 128.3, 124.7, 122.6, 21.4. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1637,1579, 1409, 1297, 1079, 968 cm^{-1}. Mass (ESI LCQ-MS): 363.27 (M + 1). Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.17; H, 6.11; N, 7.72.

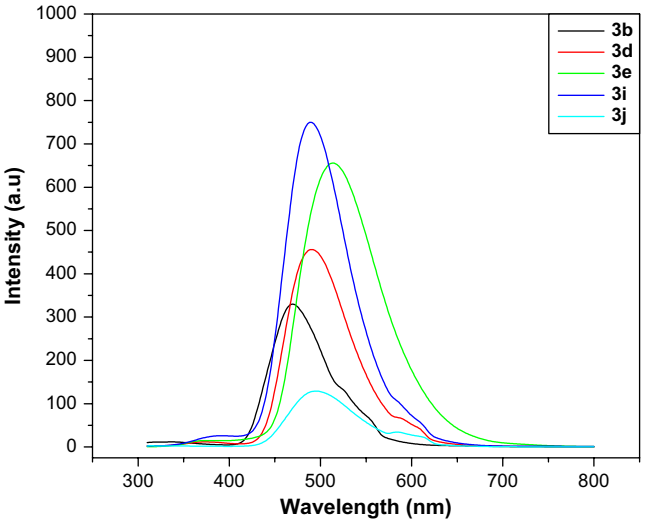


Fig. 2. Emission spectrum of quinoxaline derivatives.

4.2.2.4. 2,3-Bis[(E)-2-(4-methoxy phenyl)vinyl]quinoxaline ***3d*** *(Table 1, entry 4).* Pale yellow solid; mp: 174–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (m, 2H), 7.93 (d, 2H, $J = 15.2$ Hz), 7.62 (m, 6H), 7.50 (d, 2H, $J = 16.0$ Hz), 6.94 (d, 4H, $J = 9$.Hz), 3.85 (S, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.4, 149.3, 141.5, 137.3, 129.4, 129.1, 129.0, 128.7, 120.5, 114.3, 55.3. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1601, 1509, 1461, 1254, 1176, 1025, 826 cm^{-1}. Mass (ESI LCQ-MS): 395.30 (M + 1). Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.20; H, 5.60; N, 7.07.

4.2.2.5. 2,3-Bis[(E)-2-(3,4 dimethoxy) vinyl]quinoxaline ***3e*** *(Table 1, entry 5).* Pale yellow solid; mp: 192–194 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (m, 2H), 7.91 (d, 2H, $J = 15.3$ Hz), 7.64 (m, 2H), 7.48 (d, 2H, $J = 16.0$ Hz), 7.19 (m, 4H), 6.90 (d, 2H, $J = 8.4$ Hz), 3.95 (s, 6H), 3.92 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.0, 147.1, 147.0, 139.4, 135.5, 127.5, 127.1, 126.6, 119.0, 118.8, 109.1, 108.0, 53.8. FT-IR (KBr,

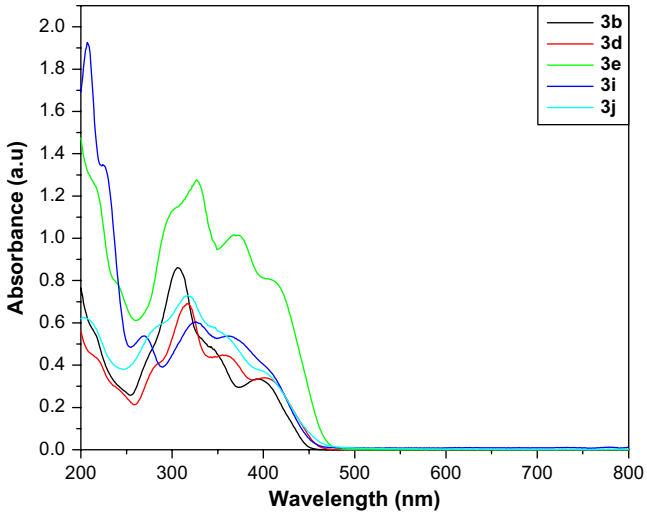


Fig. 1. Absorption spectrum of quinoxaline derivatives.

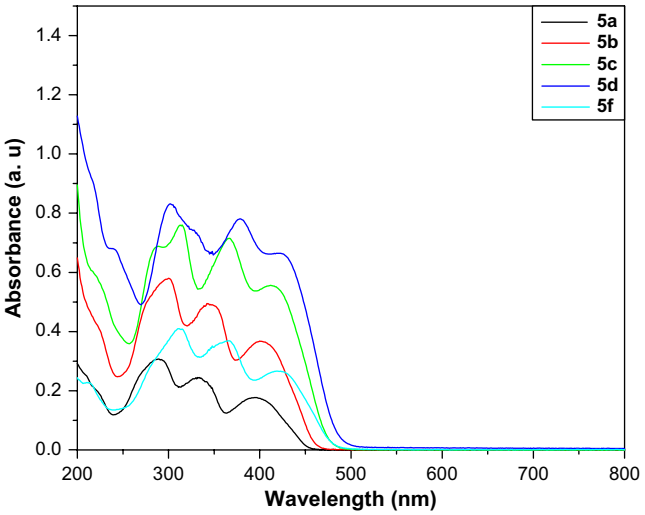


Fig. 3. Absorption spectrum of pyrazine derivatives.

Table 4
Photophysical studies of pyridopyrazines.

#	λ_{max} (nm)	λ_{emi} (nm)	Life time of quinoxaline derivatives	
			τ (ns)	χ^2
5a	289.07,333.37, 395.58	470.96	0.27 (74.72%),[a] 2.70 (25.28%)	1.23
5b	300.11,344.21, 402.36	485.56	0.64 (96.47%),[a] 2.94 (3.53%)	1.01
5c	314.99,366.72, 412.98	508.69	2.73 (98.45%),[a] 0.41 (1.15%)	1.21
5d	301.28,378.06, 425.76	557.77	1.88 (94.44%),[a] 0.76 (5.56%)	1.05
5e	315.22,366.08, 421.22	558.10	3.91 (97.59%),[a] 1.07 (2.41%)	1.00

[a] Fluorescence lifetimes associated with the bi-exponentials.

ν^{-1}_{max}): 1626, 1514, 1264, 1135, 1020, 960 cm^{-1}. Mass (ESI LCQ-MS): 455.22 (M + 1). Anal. Calcd for $C_{28}H_{26}N_2O_4$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.95; H, 5.79; N, 6.19.

*4.2.2.6. 2,3-Bis[(*E*)-2-(4-chlorophenyl) vinyl]quinoxaline* ***3f*** *(Table 1, entry 6).* Pale yellow solid; mp: 214–216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (m, 2H), 7.91 (d, 2H, J = 15.3 Hz), 7.68 (m, 2H), 7.56 (m, 6H), 7.38 (d, 4H, J = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.6, 141.6, 136.6, 134.9, 134.8, 129.7, 129.1, 128.9, 128.7, 123.0. FT-IR (KBr, ν^{-1}_{max}): 1627.20, 1490, 1409, 1094, 805, 753 cm^{-1}. Mass (ESI LCQ-MS): 403.18 (M + 1). Anal. Calcd for $C_{24}H_{16}N_2Cl_2$: C, 71.47; H, 4.00; N, 6.95. Found: C, 71.44; H, 4.00; N, 6.97.

*4.2.2.7. 2,3-Bis[(*E*)-2-(2,4-dichlorophenyl) vinyl]quinoxaline* ***3g*** *(Table 1, entry 7).* Pale yellow solid; mp: 188–190 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (d, 2H, J = 16.0 Hz), 8.06 (m, 2H), 7.70 (m, 4H), 7.55 (d, 2H, J = 15.3 Hz), 7.46 (d, 2H, J = 1.5 Hz), 7.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.4, 141.7, 135.0, 133.3, 133.0, 130.0, 129.9, 129.1, 128.0, 127.4, 125.9. FT-IR (KBr, ν^{-1}_{max}): 1652, 1365, 1270, 1148, 1050, 860 cm^{-1}. Mass (ESI LCQ-MS): 473.07 (M + 1). Anal. Calcd for $C_{24}H_{14}Cl_4N_2$: C, 61.05; H, 2.99; N, 5.93. Found: C, 61.09; H, 2.99; N, 5.91.

*4.2.2.8. 2,3-Bis[(*E*)-2-(3-nitro) vinyl]quinoxaline* ***3h*** *(Table 1, entry 9).* Pale yellow solid; mp: 204–206 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 (s, 2H), 7.99 (m, 8H,), 7.62 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.8, 147.9, 141.9, 138.1, 135.6, 133.2, 130.2, 129.8, 129.1, 125.1, 123.4, 122.1. FT-IR (KBr, ν^{-1}_{max}): 2924, 1529, 1351, 1051 cm^{-1}. Mass (ESI LCQ-MS): 425.20 (M + 1). Anal. Calcd for $C_{24}H_{16}N_4O_4$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.90; H, 3.80; N, 13.17.

*4.2.2.9. 2,3-Bis[(*E*)-2-(naphthyl) vinyl]quinoxaline* ***3i*** *(Table 1, entry 8).* Pale yellow solid; mp: 214–216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.82 (d, 2H, J = 15.3 Hz), 8.36 (d, 2H, J = 8.4 Hz), 8.13 (m, 2H), 7.87 (m, 6H), 7.73 (m, 4H), 7.51 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.1, 141.8, 135.1, 134.2, 133.7, 131.6, 129.6, 129.3, 129.1, 128.6, 126.5, 126.0, 125.6, 125.6, 124.4, 123.9. FT-IR (KBr, ν^{-1}_{max}): 3048, 1614, 1521, 1400, 957 cm^{-1}. Mass (ESI LCQ-MS): 435.36 (M + 1). Anal. Calcd for $C_{33}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.43; H, 5.11; N, 6.46.

*4.2.2.10. 2,3-Bis[(*E*)-2-(2-furyl) vinyl]quinoxaline* ***3j*** *(Table 1, entry 10).* Orange solid; mp: 169–171 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (m, 2H), 7.80 (d, 2H, J = 15.2 Hz), 7.62 (m, 2H), 7.56 (dd, 2H, J = 15.3 Hz), 7.51 (s, 2H), 6.59 (d, 2H, J = 3.0 Hz), 6.49 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.0, 148.6, 143.5, 141.6, 129.3, 128.7, 124.4, 120.2, 112.5, 112.1 cm^{-1}. FT-IR (KBr, ν^{-1}_{max}): 1611, 1548, 1498, 1152, 1065. Mass (ESI LCQ-MS): 315.29 (M + 1). Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.40; H, 4.49; N, 8.92.

*4.3. General procedure for the synthesis of pyridopyrazine derivatives (**5a–e**)*

4.3.1. Method A

A mixture of cinnamil (1 mmol) and 2,3-diaminopyridine (1 mmol) in water (20 ml) was refluxed for the appropriate time

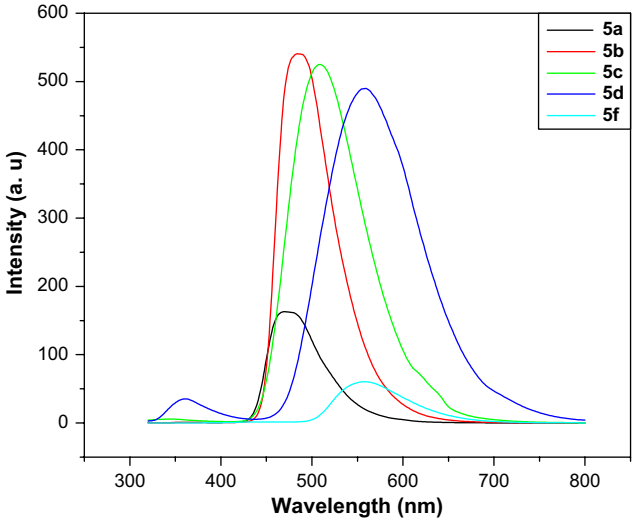


Fig. 4. Emission spectrum of pyrazine derivatives.

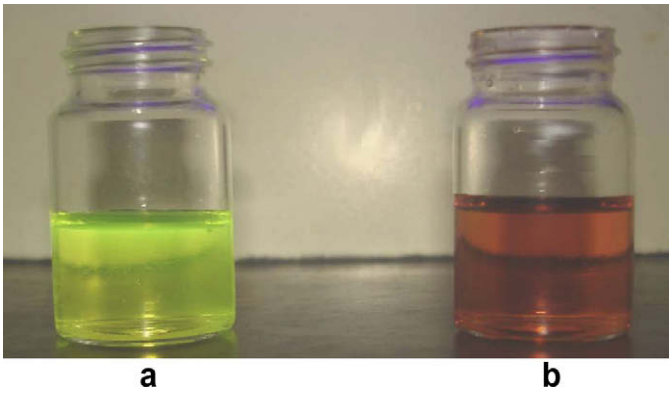


Fig. 5. (a) Compound **5e** of conc. 1×10^{-5} M; (b) compound **5e** + acetic acid 1:5 mole ratio.

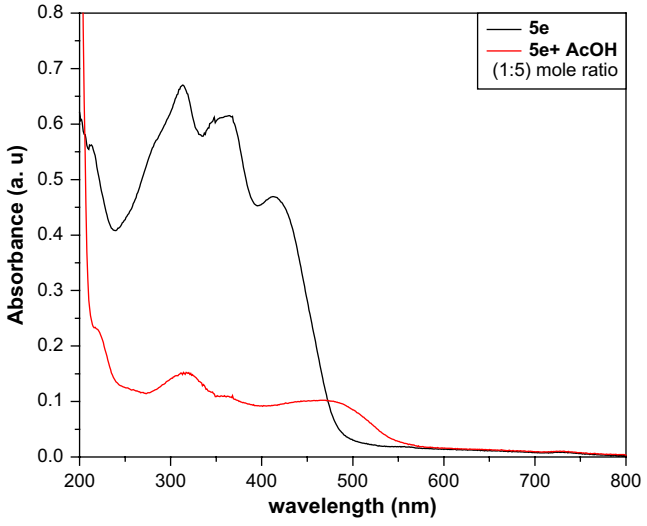


Fig. 6. The effect of addition of AcOH on the absorption spectrum of compound **5e** in acetonitrile.

mentioned in Table 3. After completion of the reaction, as indicated by TLC, the solid precipitated was filtered, washed with ethanol, dried and recrystallized with ethanol.

4.3.2. Method B

A mixture of cinnamil (1 mmol) and 2,3-diaminopyridine (1 mmol) in water (2 ml) was irradiated in microwave oven (BPL BMG 800 TS model) irradiated at 80 W for the appropriate time mentioned in Table 3. The progress of the reaction was monitored by TLC. After completion of the reaction, the precipitated solid was filtered, washed with ethanol and then dried. The obtained crude product was purified by recrystallisation with ethanol.

*4.3.2.1. 2,3-Bis[(*E*)-2-phenyl vinyl]pyrido(2,3-*b*)pyrazine* ***5a*** *(Table 2, entry 1).* Yellow solid; mp: 189–191 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.02 (m, 1H), 8.28 (m, 2H), 7.96 (d, 1H, $J = 15.3$ Hz), 7.64 (m, 5H), 7.61 (d, 1H, $J = 3.9$ Hz), 7.55 (m, 1H), 7.40 (m, 4H), 7.34 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.5, 148.9, 141.5, 137.8, 132.0, 129.4, 129.1, 128.9, 128.6, 128.0, 127.9, 127.8, 127.6, 127.3, 127.2, 127.1, 126.7, 126.1, 124.2, 117.2. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1624, 1522.65, 1450, 1177, 1126 cm^{-1}. Mass (ESI LCQ-MS): 336.20 (M + 1). Anal. Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53. Found: C, 82.32; H, 5.12; N, 12.56.

*4.3.2.2. 2,3-Bis[(*E*)-2-(4-methyl phenyl) vinyl]pyrido(2,3-*b*)pyrazine* ***5b*** *(Table 2, entry 2).* Yellow solid; mp: 181–183 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.03 (m, 1H), 8.28 (m, 2H), 7.96 (d, 1H, $J = 15.5$ Hz), 7.57 (m, 7H), 7.23 (m, 4H), 2.39 (s, 3H), 2.39[1] (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.2, 152.0, 150.4, 150.1, 140.2, 139.7, 139.6, 139.0, 137.5, 136.6, 133.5, 129.6, 127.8, 127.7, 124.4, 120.7, 120.2, 21.4. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1621, 1513, 1446, 1380, 1324, 1324, 1175, 1121 cm^{-1}. Mass (ESI LCQ-MS): 364.23 (M + 1). Anal. Calcd for $C_{25}H_{21}N_3$: C, 81.61; H, 5.82; N, 11.56. Found: C, 82.57; H, 5.84; N, 11.59.

*4.3.2.3. 2,3-Bis[(*E*)-2-(4-methoxy phenyl) vinyl]pyrido(2,3-*b*) pyrazine* ***5c*** *(Table 2, entry 3).* Yellow solid; mp: 195–197 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.01 (m, 1H), 8.26 (m, 2H), 7.94 (d, 1H, $J = 15.2$ Hz), 7.62 (m, 4H), 7.47 (m, 3H), 6.94 (m, 4H) 3.85 (s, 3H), 3.85[1] (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.1, 152.0, 150.5, 150.4, 150.1, 149.2, 140.2, 138.9, 137.4, 136.6, 129.4, 124.3, 121.6, 121.4, 119.9, 111.3, 110.4, 110.2, 56.0. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1607, 1521, 1430, 1088 cm^{-1}. Mass (ESI LCQ-MS): 396.20 (M + 1). Anal. Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.97; H, 5.33; N, 10.60.

*4.3.2.4. 2,3-Bis[(*E*)-2-(3,4-dimethoxy phenyl) vinyl]pyrido(2,3-*b*)pyrazine* ***5d*** *(Table 2, entry 4).* Yellow solid; mp: 157–159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.99 (m, 1H), 8.23 (m, 2H), 7.91 (d, 1H, $J = 15.15$ Hz), 7.54 (m, 1H), 7.43 (m, 2H), 7.25 (m, 2H), 7.16 (s, 2H), 6.89 (m, 2H), 3.94 (m, 3H) 3.93 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.1, 152.0, 150.5, 150.4, 150.3, 149.2, 140.1, 138.8, 137.3, 136.5, 129.3, 124.2, 121.6, 121.3, 119.8, 119.2, 111.3, 110.4, 110.2, 55.9, 55.9. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1622, 1596, 1511, 1260, 1130, 1021 cm^{-1}. Mass (ESI LCQ-MS): 456.13 (M + 1). Anal. Calcd for $C_{27}H_{25}N_3O_4$: C, 71.19; H, 5.53; N, 9.22. Found: C, 71.14; H, 5.55; N, 9.26.

*4.3.2.5. 2,3-Bis[(*E*)-2-furyl vinyl]pyrido(2,3-*b*)pyrazine* ***5e*** *(Table 2, entry 5).* Yellow solid; mp: 191–193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 8.97 (m, 1H), 8.26 (m, 1H), 8.07 (d, 1H, $J = 15.3$ Hz), 7.78 (d, 1H, $J = 15.3$ Hz), 7.50 (m, 5H), 6.48 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.7, 152.2, 152.1, 151.0, 149.5, 149.3, 143.4, 143.2, 136.7, 136.2, 126.0, 124.8, 123.7, 118.7, 118.2, 113.2, 112.6, 111.8, 111.7. FT-IR (KBr, $\nu^{-1}{}_{max}$): 1625, 1516, 1445, 1374, 1301, 1200, 1125 cm^{-1}. Mass (ESI LCQ-MS): 316.13 (M + 1). Anal. Calcd for $C_{19}H_{13}N_3O_4$: C, 81.00; H, 5.50; N, 13.79 Found: C, 81.05; H, 5.52; N, 13.52.

[1] Two singlet peaks in same chemical shift value with 0.005 ppm very small fraction of variation.

Acknowledgments

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.dyepig.2008.10.018.

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