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Synthesis and spectral characterization of new 1,3,5-triaryl-2-pyrazolines highlighting effect of alkyloxy chain length on fluorescence

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HIGHLIGHTS

- 2-Pyrazolines are attractive organic fluorescent compounds.
- Synthesis of new 1-(3,4-dimethylphenyl)-3-(4-fluorophenyl)-5-(4-alkoxyphenyl)-2-pyrazolines.
- Spectral characterization and fluorescence properties.
- Effect of fluoride and alkyloxy substituents on fluorescence.

GRAPHICAL ABSTRACT

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ABSTRACT

A series of new 1,3,5-triaryl-2-pyrazolines (**1b**–**12b**) having one to twelve carbon alkyloxy side chains were synthesized and characterized on the basis of their spectral (IR, ^{1}H & ^{13}C NMR and GC–MS) and microanalytical data. The UV–Vis and emission spectroscopy was used to study the effect of alkyloxy chain length on absorption and fluorescence properties of **1b**–**12b**. All the compounds showed fluorescence in the blue region of the visible spectrum. Interestingly, the alkyloxy chain length strongly affects the emission intensity of 1,3,5-triaryl-2-pyrazoline framework without causing any major blue- or red-shift in the emission wavelength (λ^{em}_{max}). The absorption and emission maxima (λ^{abs}_{max} & λ^{em}_{max}) for compounds (**1b**–**12b**) were observed in the range of 337–364 nm and 454–464 nm, respectively. Furthermore, the effect of fluorine substituent on aryl ring present at 3-position of pyrazoline moiety on fluorescence properties is also discussed.

Introduction

Organic fluorescent compounds are attractive materials due to their potential applications in cosmetics, surface coatings, inks and textile industries [1,2] in addition to their use in sensors [3], solar cells, optoelectronics and electronic displays [4,5]. As compared to inorganic fluorescent materials, their advantages include the ease of fabrication and the tunability of emission properties through a simple chemical modification. As a consequence, organic electroluminescence devices (OELDs) have been found more useful due to their low cost, broad range of emission colors, high brightness, high luminous efficiency, good life stability and simple processing [6–8].

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Despite many advantages, the major drawback associated with organic fluorescent materials is the decrease in fluorescence intensity due to aggregation of molecules i.e., the formation of an excimer-like species and H-type molecular aggregates [9–11]. To avoid such aggregation, structural modifications of fluorescent molecule such as introduction of appropriate substituents have been shown to be effective [12–14]. For example, the incorporation of an ethyl group on the conjugated backbone of diphenylbutadiene decreases the planarity of the molecules, leading to monomer like fluorescence in the bulk state [12] whereas, the introduction of quinacridone dye molecule into dendrimers enhances the emission efficiency by decreasing molecular aggregation in the condensed phase [13]. So far, a number of different classes of organic fluorescent compounds have been explored for their applications as fluorescent materials. Luminol, the chemiluminescent compound is an essential part of crime scene investigation as it detects blood, even invisible blood. This fluorescent compound is used by forensic investigators to detect trace amounts of blood left at crime scenes, as it reacts with iron found in hemoglobin [15]. It is used by biologists in cellular assays for the detection of copper, iron, and cyanides, as well as of specific proteins by western blot.

Pyrazolines, typical ICT (Intramolecular Charge Transfer) compounds [16], symbolizes a class of organic fluorescent compounds of great significance which are not only important due to their diverse biological applications [17–27] but also due to their use in organic electroluminescent devices (OELDs) and optoelectronics [28–32]. Among the various pyrazoline derivatives, 1,3,5-triaryl-2-pyrazolines have gained considerable attention and now represent an important class of organic materials exhibiting blue fluorescence with high quantum yield [33–36]. These are also described as hole transporting media in photoconductive and emitting materials, organic photovoltaic cells, and in OELDs [28,37–41]. Moreover, these are also found to have many other applications, for example, these are used as optical brightening agents for textiles, papers and plastics [42], fluorescent switches [43] and fluorescent probes in many chemosensors [44,45].

Our interest in 2-pyrazolines, in general [46,47], and 1,3,5-triaryl-2-pyrazolines, in particular [48], led us to continue and further investigate this class of compounds. Therefore, as continuation of our previous study [48], herein, we report the synthesis and fluorescent property evaluation of new 1,3,5-triaryl-2-pyrazoline derivatives having fluoro-substituent at 3-aryl and one to twelve carbon long alkyloxy chain at 5-aryl of 2-pyrazoline ring. This study is to understand the significance of the interplay of weak interactions and the role of alkoxy side chain length towards absorbance and emission properties. The present series having fluorescence properties in the blue region of the visible spectrum are potential future candidates for their use as blue light emitting materials.

Experimental

Materials and methods

All reagents and solvents were used as obtained from the supplier or recrystallized/redistilled as required. Thin layer chromatography (TLC) was performed using aluminum sheets coated with silica gel 60 F_{254} (Merck). Elemental analyses were carried out with a LECO-183 CHNS model. ^{1}H and ^{13}C NMR spectra of compounds were recorded on a Bruker 300 MHz spectrometer using deuterated solvents and TMS as internal standard. IR spectra of compounds were recorded on a Bio-Rad FTS 3000 MX spectrophotometer (400–4000 cm^{-1}). The melting points of compounds were determined using capillary tubes and an electrothermal melting point apparatus, model MP-D Mitamura Riken Kogyo, Japan.

*General procedure for the synthesis of compounds (**1b**–**12b**)*

For the synthesis of compounds (**1b**–**12b**), 25 mL of acetic acid solution of the respective 4-alkoxychalcone (0.01 mol) (**1a**–**12a**) containing a few drops of hydrochloric acid was heated at 60–65 °C for 30 min with constant stirring in a round bottom flask. (3,4-Dimethylphenyl)hydrazine hydrochloride (3.45 g, 0.02 mol) was then added to the reaction flask and the reaction mixture was heated to reflux for 5–6 h. After that, the reaction mixture was cooled to room temperature and poured onto the crushed ice. The precipitates thus formed, were filtered, washed with distilled water and dried. The crude products were further purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1) as the mobile phase to get pure compounds **1b**–**12b** in excellent yields for spectral characterization and fluorescence properties.

The different protons of compounds (**1b**–**12b**) are differentiated according to the labeling scheme shown in Fig. 1 for better understanding of their ^{1}H NMR chemical shifts.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-methoxyphenyl)-2-pyrazoline (**1b**)*

Yield 85%; pale yellow solid; m.p. 141–143 °C; R_f = 0.85 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1682, 1298, 1498, 1253, 1048, 1145, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H, N—Ar—4-CH_3), 2.22 (s, 3H, N—Ar—3-CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.83 (s, 3H, —O—C$\boldsymbol{H}_3$), 5.20 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 20.1, 43.6, 55.2, 64.4, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.6, 137.0, 143.1, 145.2, 158.5, 164.4 EIMS: m/z 374 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{24}H_{23}FN_2O$: C, 76.98; H, 6.19; N, 7.48; Found: C, 76.93; H, 6.15; N, 7.55%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-ethoxyphenyl)-2-pyrazoline (**2b**)*

Yield 84%; pale yellow solid; m.p. 138–140 °C; R_f = 0.85 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1684, 1296, 1495, 1255, 1046, 1147, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (t, 3H, J = 7.8 Hz, —O—CH_2—C$\boldsymbol{H}_3$), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 4.00 (t, 2H, J = 6.6 Hz, —O—C$\boldsymbol{H}_2$—), 5.18 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 19.5, 20.1, 43.6, 63.4, 64.4, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.6,

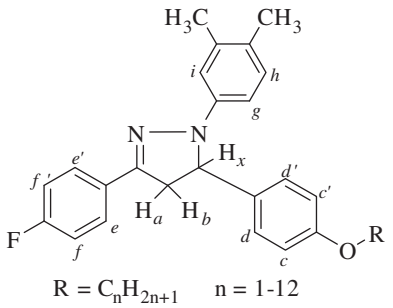


Fig. 1. Labelling scheme for protons of compounds (**1b**–**12b**).

137.0, 143.1, 145.2, 158.5, 164.4 EIMS: *m/z* 388 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{25}H_{25}FN_2O$: C, 77.29; H, 6.49; N, 7.21; Found: C, 77.25; H, 6.44; N, 7.29%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-propyloxyphenyl)-2-pyrazoline (**3b**)*

Yield 86%; pale yellow solid; m.p. 135–137 °C; R_f = 0.89 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1685, 1294, 1493, 1257, 1045, 1141, ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, 3H, J = 7.5 Hz, —O—CH_2—CH_2—C***H***$_3$), 1.82 (sextet, 2H, J = 7.5 Hz, —O—CH_2—C***H***$_2$—CH_3), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.91 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.20 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5, 18.8, 20.2, 20.6, 43.6, 64.4, 69.5, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.6, 137.0, 143.1, 145.2, 158.5, 164.4 EIMS: *m/z* 402 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{26}H_{27}FN_2O$: C, 77.58; H, 6.76; N, 6.96; Found: C, 77.52; H, 6.72; N, 7.02%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-butyloxyphenyl)-2-pyrazoline (**4b**)*

Yield 83%; pale yellow solid; m.p. 115–117 °C; R_f = 0.87 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1679, 1297, 1497, 1256, 1052, 1145, ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, J = 7.2 Hz, —O—$(CH_2)_3$—C***H***$_3$), 1.50 (sextet, 2H, J = 7.5 Hz, —O—CH_2—CH_2—C***H***$_2$— CH_3), 1.77 (qn, 2H, J = 8.0 Hz, —O—CH_2—C***H***$_2$—C_2H_5), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.95 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.19 (dd, 1H, J = 7.5, 12.0 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.04 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 18.8, 19.2, 20.2, 31.3, 43.6, 64.4, 67.6, 110.6, 114.9 (2C), 115.1, 115.4 (2C), 115.8, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.6, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: *m/z* 416 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{27}H_{29}FN_2O$: C, 77.85; H, 7.02; N, 6.73; Found: C, 77.81; H, 6.98; N, 6.80%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-pentyloxyphenyl)-2-pyrazoline (**5b**)*

Yield 85%; pale yellow solid; m.p. 113–116 °C; R_f = 0.88 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1682, 1298, 1492, 1252, 1054, 1149, ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H, J = 7.2 Hz, —O—$(CH_2)_4$—C***H***$_3$), 1.37–1.48 (m, 4H, —O—CH_2—CH_2—(C***H***$_2$)$_2$— CH_3), 1.79 (qn, 2H, J = 7.2 Hz, —O—CH_2—C***H***$_2$—C_3H_7), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.0, 16.8 Hz, H_b), 3.94 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.19 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 18.8, 20.2, 22.5, 28.2, 29.0, 43.6, 64.4, 67.9, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4 EIMS: *m/z* 430 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{28}H_{31}FN_2O$: C, 78.11; H, 7.26; N, 6.51; Found: C, 78.08; H, 7.21; N, 6.59%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-hexyloxyphenyl)-2-pyrazoline (**6b**)*

Yield 82%; pale yellow solid; m.p. 90–93 °C; R_f = 0.86 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1685, 1293, 1496, 1254, 1048, 1148, ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz, —O—$(CH_2)_5$—C***H***$_3$), 1.33–1.50 (m, 6H, —O—CH_2—CH_2—(C***H***$_2$)$_3$— CH_3), 1.79 (qn, 2H, J = 7.8 Hz, —O—CH_2—C***H***$_2$—C_4H_9), 2.18 (s, 3H, N—Ar—4—CH_3), 2.23 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 16.8 Hz, H_b), 3.95 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.19 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 20.2, 22.6, 25.7, 29.2, 31.6, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: *m/z* 444 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{29}H_{33}FN_2O$: C, 78.35; H, 7.48; N, 6.30; Found: C, 78.31; H, 7.43; N, 6.37%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-heptyloxyphenyl)-2-pyrazoline (**7b**)*

Yield 81%; pale yellow solid; m.p. 88–91 °C; R_f = 0.88 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1679, 1292, 1488, 1258, 1047, 1143, ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 7.2 Hz, —O—$(CH_2)_6$—C***H***$_3$), 1.33–1.47 (m, 8H, —O—CH_2—CH_2—(C***H***$_2$)$_4$— CH_3), 1.78 (qn, 2H, J = 7.0 Hz, —O—CH_2—C***H***$_2$—C_5H_{11}), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.07 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.76 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.94 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.19 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 19.4, 20.2, 22.6, 26.0, 29.0, 31.8, 43.5, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: *m/z* 458 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{30}H_{35}FN_2O$: C, 78.57; H, 7.69; N, 6.11; Found: C, 78.53; H, 7.65; N, 6.18%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-octyloxyphenyl)-2-pyrazoline (**8b**)*

Yield 86%; pale yellow solid; m.p. 87–89 °C; R_f = 0.87 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1686, 1298, 1499, 1259, 1050, 1147, ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 7.2 Hz, —O—$(CH_2)_7$—C***H***$_3$), 1.31–1.48 (m, 10H, —O—CH_2—CH_2—(C***H***$_2$)$_5$— CH_3), 1.78 (qn, 2H, J = 7.0 Hz, —O—CH_2—C***H***$_2$—C_6H_{13}), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.0, 16.8 Hz, H_b), 3.93 (t, 2H, J = 6.6 Hz, —O—C***H***$_2$—), 5.19 (dd, 1H, J = 7.5, 12.0 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 19.5, 20.4, 22.7, 26.0, 29.2, 29.4, 31.8, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: *m/z* 472 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{31}H_{37}FN_2O$: C, 78.78; H, 7.89; N, 5.93; Found: C, 78.73; H, 7.85; N, 5.99%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-nonyloxyphenyl)-2-pyrazoline (**9b**)*

Yield 83%; pale yellow solid; m.p. 93–96 °C; R_f = 0.86 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1685, 1296, 1497, 1254, 1055, 1145, ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 7.0 Hz, —O—$(CH_2)_8$—C***H***$_3$), 1.30–1.48 (m, 12H, —O—CH_2—CH_2—

—(C**H**$_2$)$_6$— CH_3), 1.79 (qn, 2H, J = 8.0 Hz, —O—CH_2—C**H**$_2$—C_7H_{15}), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.94 (t, 2H, J = 6.6 Hz, —O—C**H**$_2$—), 5.19 (dd, 1H, J = 7.5, 12.0 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 20.2, 22.7, 26.0, 29.3, 29.4, 29.4, 29.5, 31.9, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: m/z 486 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{32}H_{39}FN_2O$: C, 78.98; H, 8.08; N, 5.76; Found: C, 78.94; H, 8.05; N, 5.82%.

*1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-decyloxyphenyl)-2-pyrazoline (**10b**)*

Yield 87%; pale yellow solid; m.p. 97–99 °C; R_f = 0.88 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1679, 1299, 1496, 1258, 1049, 1149, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 6.9 Hz, —O—$(CH_2)_9$—C**H**$_3$), 1.30–1.46 (m, 14H, —O—CH_2—CH_2—(C**H**$_2$)$_7$—CH_3), 1.79 (qn, 2H, J = 7.2 Hz, —O—CH_2—C**H**$_2$—C_8H_{17}), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.5, 16.8 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 17.1 Hz, H_b), 3.94 (t, 2H, J = 6.6 Hz, —O—C**H**$_2$—), 5.19 (dd, 1H, J = 7.8, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 20.2, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 29.6, 29.6, 31.9, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: m/z 500 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{33}H_{41}FN_2O$: C, 79.16; H, 8.25; N, 5.59; Found: C, 79.12; H, 8.22; N, 5.65%.

1-(3,4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-undecyloxyphenyl)-2-pyrazoline (11b)

Yield 88%; pale yellow solid; m.p. 84–86 °C; R_f = 0.87 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1685, 1292, 1497, 1256, 1057, 1142, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 7.0 Hz, —O—$(CH_2)_{10}$—C**H**$_3$), 1.29–1.47 (m, 16H, —O—CH_2—CH_2—(C**H**$_2$)$_8$—CH_3), 1.78 (qn, 2H, J = 7.8 Hz, —O—CH_2—C**H**$_2$—C_9H_{19}), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.07 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 16.8 Hz, H_b), 3.93 (t, 2H, J = 6.6 Hz, —O—C**H**$_2$—), 5.19 (dd, 1H, J = 7.5, 12.0 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$), 7.69–7.74 (m, 2H, Ar$H_{e=e'}$), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 19.5, 19.8, 20.2, 22.7, 26.0, 29.3, 29.4, 29.6, 29.6, 31.9, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: m/z 514 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{34}H_{43}FN_2O$: C, 79.34; H, 8.42; N, 5.44; Found: C, 79.31; H, 8.39; N, 5.49%.

*1-(3, 4-Dimethylphenyl)-3-(4-fluorophenyl)-5-(4-dodecyloxyphenyl)-2-pyrazoline (**12b**)*

Yield 83%; pale yellow solid; m.p. 75–78 °C; R_f = 0.89 (petroleum ether:ethyl acetate, 4:1), FT-IR (KBr, cm^{-1}): 1685, 1294, 1495, 1255, 1056, 1147, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 7.0 Hz, —O—$(CH_2)_{11}$—C**H**$_3$), 1.29–1.48 (m, 18H, —O—CH_2—CH_2—(C**H**$_2$)$_9$—CH_3), 1.78 (qn, 2H, J = 7.5 Hz, —O—CH_2—C**H**$_2$—$C_{10}H_{21}$), 2.17 (s, 3H, N—Ar—4—CH_3), 2.22 (s, 3H, N—Ar—3—CH_3), 3.08 (dd, 1H, J = 7.8, 17.1 Hz, H_a), 3.77 (dd, 1H, J = 12.3, 16.8 Hz, H_b), 3.94 (t, 2H, J = 6.6 Hz, —O—C**H**$_2$—), 5.19 (dd, 1H, J = 7.5, 12.3 Hz, H_x), 6.71 (d, 1H, J = 8.1 Hz, N—ArH_g), 6.89 (d, 2H, J = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, J = 8.1 Hz, N—ArH_h), 7.05 (s, 1H, N—ArH_i), 7.11 (m, 2H, J = 8.7 Hz, Ar$H_{f=f'}$), 7.25 (d, 2H, J = 8.7 Hz, Ar$H_{d=d'}$),^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 20.2, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 29.6, 29.6, 31.9, 43.6, 64.4, 68.0, 110.7, 114.9 (2C), 115.1, 115.4 (2C), 115.7, 127.0 (2C), 127.3, 127.4, 129.8 (2C), 134.5, 137.0, 143.1, 145.2, 158.5, 164.4, EIMS: m/z 528 ($M^{+\cdot}$, base peak). Anal. calcd. for $C_{35}H_{45}FN_2O$: C, 79.50; H, 8.58; N, 5.30; Found: C, 79.45; H, 8.54; N, 5.37%.

Fluorescence properties of 1,3,5-triaryl-2-pyrazolines

The fluorescence properties of compounds (**1b**–**12b**) were studied by UV–Vis and emission spectroscopy carried out at room temperature (298 K). The UV–Vis and the emission spectra of 1,3,5-triaryl-2-pyrazolines (**1b**–**12b**), were recorded in *N,N*-dimethylformamide–water (3:7) mixture at a concentration of 1×10^{-5} mol L^{-1} and 1×10^{-7} mol L^{-1}, respectively.

Results and discussion

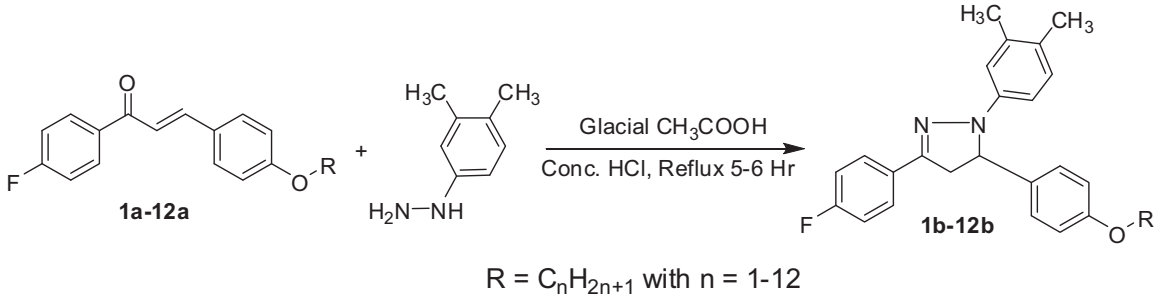
Chemistry

The compounds (**1b**–**12b**) were synthesized by refluxing (*E*)-1-(4-fluorophenyl)-3-(4-alkoxyphenyl)prop-2-en-1-one (**1a**–**12a**) [49] with excess of (3,4-dimethylphenyl)hydrazine hydrochloride in glacial acetic acid solvent containing catalytic amount of hydrochloric acid for 5–6 h (Scheme 1) and purified by silica gel column chromatography using petroleum ether/ethyl acetate as the mobile phase. All the products were obtained as solids in good to excellent yields (81–88%) indicating a little influence of alkyl chain length on reaction efficiency. The structures of all the compounds were confirmed on the basis of their spectral and microanalytical data.

*Spectral characterization of **1b**–**12b***

IR spectra

In the IR spectra of compounds (**1b**–**12b**), two characteristic absorption bands in the range of 1686–1679 cm^{-1} and



Scheme 1. Synthesis of 1,3,5-triaryl 2-pyrazolines, **1b**–**12b**.

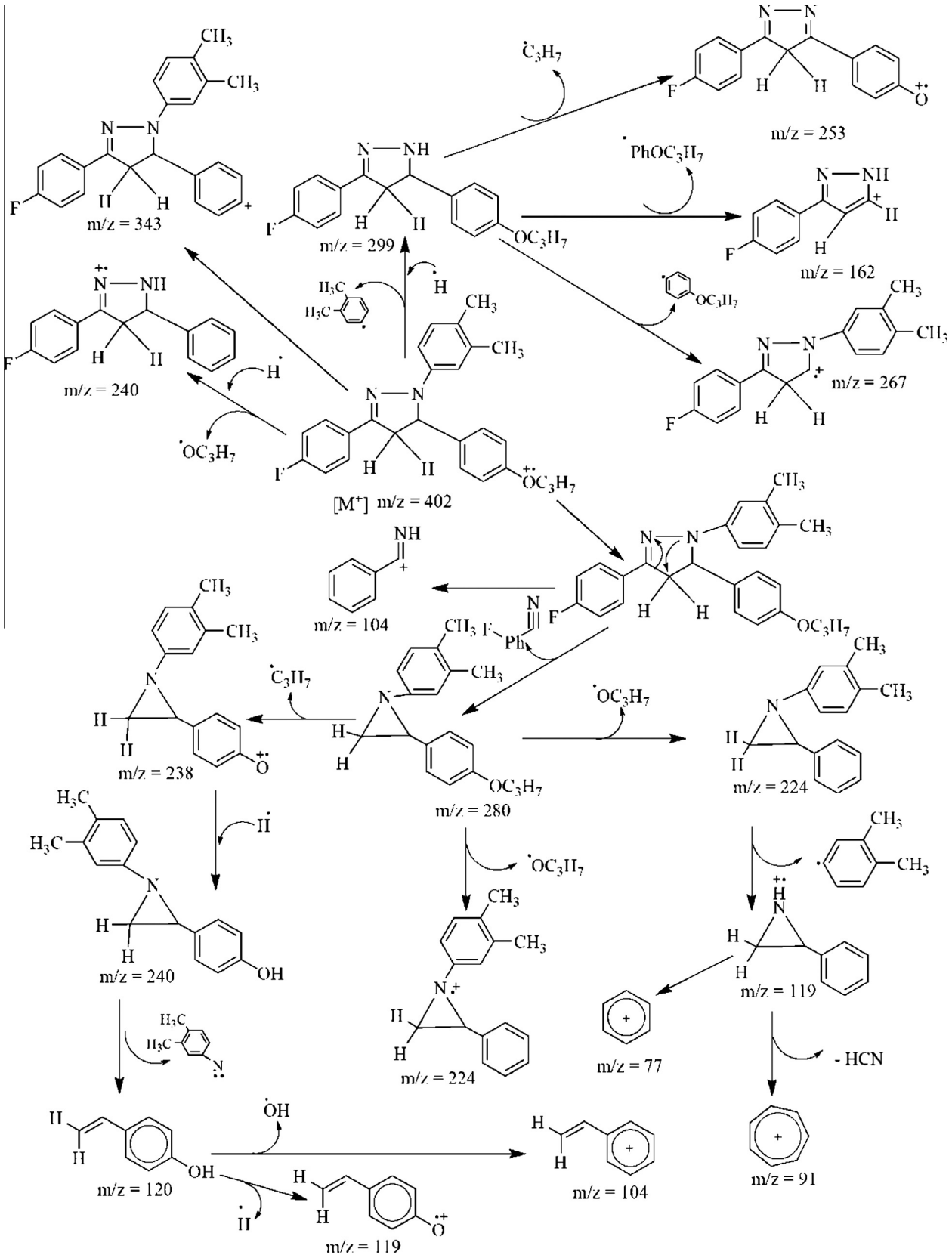


Fig. 2. Mass fragmentation pattern of 3b.

1298–1292 cm^{-1} were assigned to the stretching of carbon–nitrogen double bond (C=N) and carbon–nitrogen single bond (C—N), respectively. The presence of these two frequencies indicates the formation of cyclization product. Another band observed in the region of 1149–1147 cm^{-1} shows the presence of Ar—F bond. Two more strong bands at stretching frequencies in the range of

1259–1252 cm^{-1} (Ar—O-stretching) and 1057–1045 cm^{-1} (—O—R stretching) indicate the presence of Ar—O—R group. The most significant absorption bands observed in the IR spectra of **1b–12b** are presented in the experimental section.

^{1}H NMR spectra & ^{13}C NMR spectra

In the ^{1}H NMR spectra of compounds (**1b–12b**), all the protons of pyrazoline nucleus and three aromatic rings were found in their expected chemical shift regions. The presence of two methylene protons (H_a and H_b) and one methine proton (H_x) as three doublet of doublets confirmed the formation of five membered pyrazoline ring. The methylenic protons H_a appeared at 3.07–3.08 ppm with coupling constants of 7.5–7.8 Hz and 16.8–17.1 Hz due to their coupling with neighboring H_b and H_x protons. Similarly, methylenic protons H_b for compounds **1b–12b** appears at 3.76–3.77 ppm with coupling constants of 12.0–12.3 Hz and 16.8–17.1 Hz due to their coupling with neighboring H_a and H_x protons. However, the chemical shifts for methine protons (H_x) of **1b–12b** were observed at 5.18–5.20 ppm with coupling constant values in the range of 7.5–7.8, 12.0–12.3 Hz. The aromatic protons due to the presence of three aryl rings appeared downfield between 6.50 and 8.00 ppm with multiplicity according to their substitution pattern. The methylene protons (Ar—O—C***H***$_2$—) of alkoxy side chain present at one of the aryl ring appeared as a triplet. The chemical shifts for these protons were found around 3.83–4.00 ppm for all pyrazolines confirming the presence of ether (Ar—O—C—) linkage. The chemical shifts for other aliphatic protons of the alkoxy groups were observed between 0 and 2.0 ppm. The protons of methyl groups at 3- and 4-positions of the aromatic ring directly attached to the nitrogen of the pyrazoline ring in compounds **1b**–**12b**, appeared as singlet in the range of 2.23–2.22 ppm and 2.17–2.18 ppm respectively. The ^{13}C NMR spectra of compounds (**1b–12b**) displayed peaks at 64.4–69.5 ppm, 43.5–43.6 ppm and 55.2–64.4 ppm for C_3, C_4 and C_5 carbons, respectively. All the aromatic carbons were observed in the range of 110.6–164.4 ppm. The signals for alkoxy carbons were noticed in the range of 10.5–31.6 ppm for all the compounds. Furthermore, the conclusions drawn from the ^{1}H & ^{13}C NMR data were found to be in good agreement with the results of IR spectra discussed in the previous section.

Mass spectra

The electron impact mass spectra (EIMS) of all the synthesized pyrazoline derivatives **1b–12b** are presented in the experimental part. The mass spectral data and fragmentation pattern of all the synthesized 2-pyrazoline derivatives [50], clearly justify the formation of proposed structures discussed in IR, ^{1}H and ^{13}C NMR spectroscopy. Further, a molecular ion peak ($M^{+\cdot}$) was observed for all the compounds at their respective molecular masses. The most stable fragments or base peaks for **1b–12b** were also found to be the molecular ion peaks. The proposed mass fragmentation pattern of the representative compound **3b** where molecular ion peak and most stable fragment appeared at *m/z* 402 (Calcd. 402.21) of $[C_{26}H_{27}FN_2O]^{\cdot+}$ is shown in Fig. 2.

Table 1
Absorption and fluorescence wavelengths for **1b–12b**.

Compound	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Stoke's shift
1b	337	454	117
2b	349	462	113
3b	358	461	103
4b	345	464	119
5b	359	464	105
6b	344	459	115
7b	343	463	120
8b	364	464	100
9b	364	459	95
10b	343	459	116
11b	347	458	111
12b	343	457	114

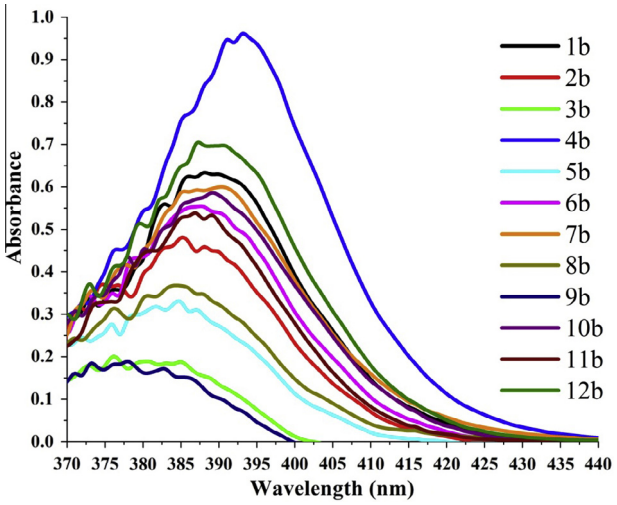


Fig. 3. The UV–Vis absorption spectra of 1-(3,4-dimethylphenyl)-3-(4-fluorophenyl)-5-(4-alkoxyphenyl)-2-pyrazolines (**1b**–**12b**) in DMF-H_2O (3:7) system with the concentration of 1×10^{-5} mol L^{-1}.

Fluorescence properties

The fluorescence properties of the synthesized 1,3,5-triaryl-2-pyrazolines (**1b–12b**) bearing homologous alkyloxy groups were studied by UV–Vis and emission spectroscopy. As shown in Table 1, all the compounds exhibited fluorescence in the blue region of the visible spectrum. The UV–Vis spectra of **1b–12b** were recorded at a concentration of 1×10^{-5} mol L^{-1} in *N,N*-dimethylformamide-water (3:7) binary solvent mixture. An intense absorption band for **1b**–**12b**, attributed to the π–π^* transitions of the conjugated backbone [51] with absorption maxima (λ_{max}^{abs}) wavelength in the range of 337–364 nm, was observed and are presented in Table 1. However, the spectral shapes/curves were found similar in the absorption spectra due to the presence of the same 1,3,5-triaryl-2-pyrazoline central nucleus for all the compounds (Fig. 3). It is interesting to mention here that the difference of absorption

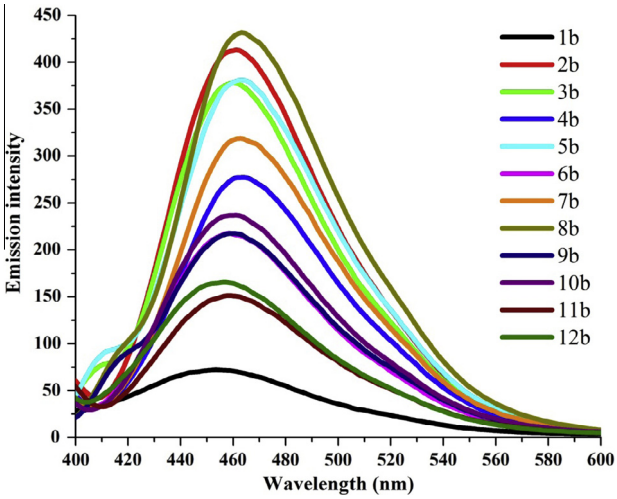


Fig. 4. The emission spectra of 1-(3,4-dimethylphenyl)-3-(4-fluorophenyl)-5-(4-alkoxyphenyl)-2-pyrazolines (**1b**–**12b**) in DMF-H_2O (3:7) system at concentration of 1×10^{-7} mol L^{-1}.

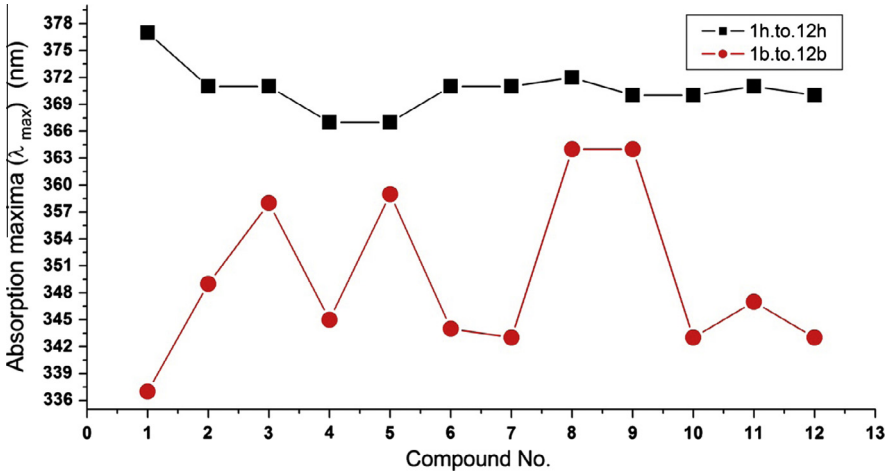


Fig. 5. Comparison of absorption maxima (λ_{max}^{abs}) of **1b**–**12b** and our previously reported **1h**–**12h** [48] in DMF-H_2O (3:7) system at fixed concentration of 1×10^{-5} mol L^{-1}.

wavelengths and absorption intensities is only due to the effect of presence of 4-alkoxyphenyl groups at the 5-position of 2-pyrazoline nucleus.

The emission properties of compounds (**1b**–**12b**) were then studied at their corresponding excitation wavelengths (λ_{max}^{abs}) (Table 1, Fig. 4). The same DMF-water (3:7) binary solvent system was used for this purpose. Measured at constant concentration of 1×10^{-7} mol L^{-1}, all the compounds (**1b**–**12b**) exhibited blue emission in the range of 454–464 nm with variable emission intensity. The compounds **4b**, **5b** and **8b** showed maximum emission at higher wavelengths (464 nm each) as compared to other compounds of the series. This random trend may be attributed to the different conformations of alkyloxy groups in solution [52]. Similar to most of the previously reported triaryl-2-pyrazolines [48], these compounds (**1b**–**12b**) also showed blue fluorescence because of the presence of their emission maxima (λ_{max}^{em}) wavelengths in the blue region of visible spectrum.

The geometry and substitution pattern of 1,3,5-triaryl-2-pyrazoline ring are thought to be responsible for blue fluorescence of such compounds [33–36,28]. The aryl groups present at 1- and 3-position of pyrazoline form the conjugated backbone and are mainly responsible for absorption of photons [51] whereas the aryl group present at 5-position of the pyrazoline is not a part of that conjugated system. Therefore, the substitution of alkoxy group at 5-aryl on 2-pyrazoline can be expected to have some influence on the physico-chemical properties. From the results, it is quite clear that the change in the length of alkyloxy group strongly affect the emission intensity without major blue or red shift in the emission wavelength (λ_{max}^{em}).

It is also important to address here that the compounds (**1b**–**12b**) with fluoro substitution on 3-aryl of pyrazoline revealed a notable influence on absorption wavelength and emission intensity of the 1,3,5-triaryl-2-pyrazolines as compared to our previously reported compounds (**1h**–**12h**) [48] where there is no substitution on 3-aryl of pyrazoline ring (Figs. 5 and 6). This difference may be attributed to the positive role of fluoro group exerting on the conjugated backbone for more effective intramolecular charge transfer. Therefore, it is anticipated that by changing the substituent on 3-aryl of pyrazoline ring, the emission intensity can be tuned which is very important in controlling/optimizing the optoelectronic and luminescence properties of pyrazoline based OLEDs.

To check the effect of solvent nature and polarity, emission intensity of representative compound **8b**, which exhibited maximum emission intensity was measured in pure DMF instead of DMF:H_2O mixture at a concentration of 1×10^{-7} mol L^{-1}. Interestingly, emission intensity was greatly increased. This enhancement in emission intensity of **8b** in pure DMF as compared to DMF-H_2O (3:7) mixture may possibly be due to the interaction of water

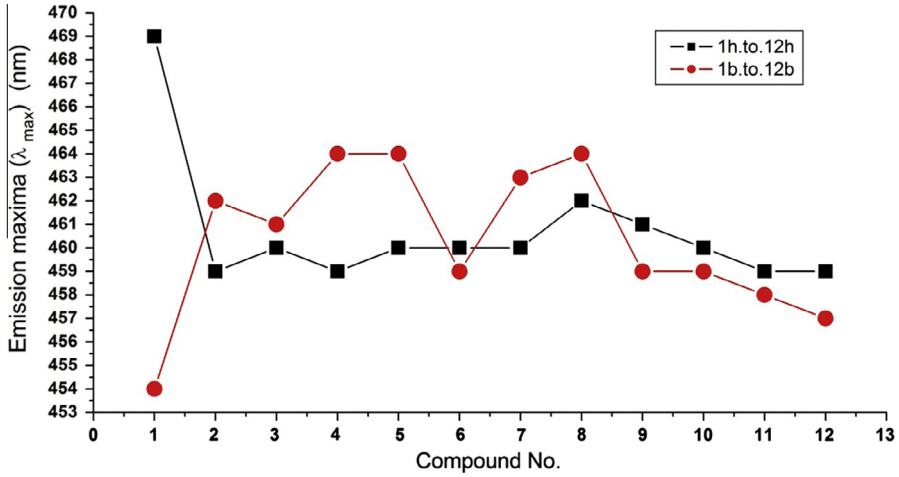


Fig. 6. Comparison of emission maxima (λ_{max}^{em}) of **1b**–**12b** and our previously reported **1h**–**12h** [48] in DMF-H_2O (3:7) system at fixed concentration of 1×10^{-7} mol L^{-1}.

Fig. 7. Photoluminescence of 1-(3,4-dimethylphenyl)-3-(4-fluorophenyl)-5-(4-nonyloxyphenyl)-2-pyrazoline (**9b**) in ethyl ethanoate at 1×10^{-3} mol L^{-1} concentration.

molecules with fluoro substituent through hydrogen bonding which led to the decrease of intramolecular charge transfer. However, no such effect is present in pure DMF solvent as it is a polar aprotic solvent. The emission intensity of **1b–12b** could not be measured in pure water as these compounds were insoluble in pure water. Fig. 7 shows photoluminescence of 1-(3,4-dimethylphenyl)-3-(4-fluorophenyl)-5-(4-nonyloxyphenyl)-2-pyrazoline (**9b**) in ethyl acetate solvent, although it was not quantitatively measured. This variable fluorescence emission behavior of compounds (**1b–12b**) can be attributed to the combined effect of the halogen and alkoxy substituents present in the molecules.

Conclusions

A series of 1,3,5-triaryl-2-pyrazoline derivatives (**1b–12b**) bearing one to twelve carbon long alkyloxy side chains have been synthesized starting from chalcones (**1a–12a**) and characterized by elemental analysis, IR, ^{1}H & ^{13}C NMR and GC–MS. The fluorescence properties of the synthesized compounds were studied by UV–Vis and emission spectroscopy. All the compounds showed fluorescence in the blue region of the visible spectrum. The chain length of alkyloxy group present on one of the aryl ring of pyrazoline governs the aggregation/self assembly in ground/excited states in DMF:water binary solution as indicated by absorption and emission spectra. The absorption and emission maxima (λ_{max}^{abs} & λ_{max}^{em}) for **1b–12b** were observed in the range of 337–364 nm and 454–464 nm, respectively which clearly demostrates the effect of alkyloxy chain length on otherwise same fluorophore for all the compounds. In addition, the presence of fluoro-substituent on conjugated backbone of 1,3,5-triaryl-2-pyrazoline system of **1b–12b**, when compared to our previously reported compounds with no such substitution, result in blue shift in absorption and an overall a red shift in emission spectroscopy. It can thus be concluded that variation in the length of alkyloxy side chain and substitution of electron donating groups on conjugated backbone of such compounds can be used to tune the emission intensity. These findings may further play an important role in controlling/optimizing the optoelectronic and luminescence properties of Organic Light Emitting Diodes (OLEDs) based on related fluorescent compounds.

Acknowledgements

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References

[1] G.R. Bardajee, A.Y. Li, J.C. Haley, M.A. Winnik, Dyes Pigm. 79 (2008) 24–32.
[2] W. Jiang, Y. Sun, X. Wang, Q. Wang, W. Xu, Dyes Pigm. 77 (2008) 125–128.
[3] V.B. Bojinov, I.P. Panova, Dyes Pigm. 80 (2009) 61–66.
[4] E. Wolarz, H. Moryson, D. Bauman, Displays 13 (1992) 171–178.
[5] I. Grabchev, J.M. Chovelon, Polym. Adv. Technol. 14 (2003) 601–608.
[6] P.E. Burrows, G. Gu, S.R. Forrest, M.E. Thompson, IEEE Trans. Electron. Dev. 44 (8) (1997) 1189.
[7] Y. Sonoda, M. Goto, S. Tsuzuki, N. Tamaoki, J. Phys. Chem. A 110 (2006) 13379–13387.
[8] X. Zhang, Z. Chi, B. Xu, L. Jiang, X. Zhou, Y. Zhang, S. Liu, J. Xu, Chem. Commun. 48 (2012) 10895–10897.
[9] Z. Xie, B. Yang, F. Li, G. Cheng, L. Liu, G. Yang, H. Xu, L. Ye, M. Hanif, S. Liu, D. Ma, Y. Ma, J. Am. Chem. Soc. 127 (2005) 14152.
[10] Y. Kim, J. Bouffard, S.E. Kooi, T.M. Swager, J. Am. Chem. Soc. 127 (2005) 13726.
[11] M. Kasha, Radiat. Res. 20 (1963) 55.
[12] R. Davis, S. Abraham, N.P. Rath, S. Das, New J. Chem. 28 (2004) 1368.
[13] A. Ortiz, W.H. Flora, G.D. D'Ambruoso, N.R. Armstrong, D.V. McGrath, Chem. Commun. (2005) 444.
[14] C.-L. Chiang, M.-F. Wu, D.-C. Dai, Y.-S. Wen, J.-K. Wang, C.-T. Chen, Adv. Funct. Mater. 15 (2005) 231.
[15] J.L. Webb, J.I. Creamer, T.I. Quickenden, Luminescence 21 (2006) 214–220.
[16] J.F. Li, B. Guan, D.X. Li, C. Dong, Spectrochim Acta 68 (2007) 404–408.
[17] A. Marella, M.R. Ali, M.T. Alam, R. Saha, O. Tanwar, M. Akhter, M. Shaquiquzzaman, M.M. Alam, Mini Rev. Med. Chem. 13 (2013) 921–931.
[18] S. Kumar, S. Bawa, S. Drabu, R. Kumar, H. Gupta, Recent Pat. Anti-infect. Drug Discov. 4 (2009) 154–163.
[19] M.R. Shaaban, A.S. Mayhoub, A.M. Farag, Expert Opin. Ther. Pat. 22 (2012) 253–291.
[20] S. Ningaiah, U.K. Bhadraiah, S. Keshavamurthy, C. Javarasetty, Bioorg. Med. Chem. Lett. 23 (2013) 4532–4539.
[21] T.M. Acker, A. Khatri, K.M. Vance, C. Slabber, J. Bacsa, J.P. Snyder, S.F. Traynelis, D.C. Liotta, J. Med. Chem. 56 (2013) 6434–6456.
[22] H.Y. Wang, X.X. Zhang, J.J. Shi, G. Chen, X.P. Xu, S.J. Ji, Spectrochim. Acta A 93 (2012) 343–347.
[23] S.P. Sakthinathan, G. Vanangamudi, G. Thirunarayanan, Spectrochim. Acta A 95 (2012) 693–700.
[24] D. Secci, S. Carradori, A. Bolasco, B. Bizzarri, M.D. Ascenzio, E. Maccioni, Current Top. Med. Chem. 12 (2012) 2240–2257.
[25] K.M. Amin, A.A.M. Eissa, S.M. Abou-Seri, F.M. Awadallah, G.S. Hassan, Eur. J. Med. Chem. 60 (2013) 187–198.
[26] A. Ciupa, P.A. De Bank, M.F. Mahon, P.J. Wood, Lorenzo Caggiano, Med. Chem. Commun. 4 (2013) 956–961.
[27] D. Havrylyuk, B. Zimenkovsky, O. Vasylenko, C.W. Day, D.F. Smee, P. Grellier, R. Lesyk, Eur. J. Med. Chem. 66 (2013) 228–237.
[28] S.J. Ji, H.B. Shi, Dyes Pigm. 70 (2006) 246–250.
[29] B. Bian, S.J. Ji, H.B. Shi, Dyes Pigm. 76 (2008) 348–352.
[30] X.Q. Wei, G. Yang, J.B. Cheng, Z.Y. Lu, M.G. Xie, Opt. Mater. 29 (2007) 936–940.
[31] S. Pramanik, P. Banerjee, A. Sarkar, A. Mukherjee, K.K. Mahalanabis, S.C. Bhattacharya, Spectrochim. Acta Part A 71 (2008) 1327–1332.
[32] M. Pokladko, E. Gondek, J. Sanetra, J. Nizioł, A. Danel, I.V. Kityk, H.R. Ali, Spectrochim. Acta Part A 73 (2009) 281–285.
[33] Z.L. Yan, G.W. Hu, S.K. Wu, Acta Chim. Sin. 53 (1995) 227–229.
[34] A. Wagner, C.W. Schellhammer, S. Petersen, Angew. Chem. Int. Ed. Engl. 5 (1966) 699–704.
[35] H. Dorlars, C.W. Schellhammer, J. Schroeder, Angew. Chem. Int. Ed. Engl. 14 (1975) 665–679.
[36] A.K. Sarkar, Fluorescent Whitening Agents, Watford, England, Merrow, 1971.
[37] G.B. Yang, Y. Wu, W.J. Tian, X. Zhou, A.M. Ren, Curr. Appl. Phys. 5 (2005) 327–330.
[38] Z. Lu, Q. Jiang, W. Zhu, M. Xie, Y. Hou, X. Chen, Z. Wang, D. Zou, T. Tsutsui, Synth. Met. 111–112 (2000) 425–427.
[39] M.L. Wang, J.X. Zhang, J.Z. Liu, C.X. Xu, H.X. Ju, J. Lumin. 99 (2002) 79–83.
[40] Y.F. Sun, Y.P. Cui, Dyes Pigm. 81 (2009) 27–34.
[41] G. Bai, J. Li, D. Li, C. Dong, X. Han, P. Lin, Dyes Pigm. 75 (2007) 93–98.
[42] D. Xiao, Lu Xi, W. Yang, H. Fu, Z. Shuai, Yan Fang, J. Yao, J. Am. Chem. Soc. 125 (2003) 6740–6745.

[43] X. Poteau, A.I. Brown, R.G. Brown, C. Holmes, D. Matthew, Dyes Pigm. 47 (2000) 091–105.
[44] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515–1566.
[45] A.P. de Silva, I.M. Dixon, H.Q.N. Gunaratne, T. Gunnlaugsson, P.R.S. Maxwell, T.E. Rice, J. Am. Chem. Soc. 121 (1999) 1393–1394.
[46] A. Abbas, H. Nazir, M.M. Naseer, M. Bolte, S. Hussain, N. Hafeez, A. Hasan, Spectrochim. Acta A 120 (2014) 176–184.
[47] A. Abbas, S. Bahceli, H. Gökce, M. Bolte, S. Hussain, M.K. Rauf, Spectrochim. Acta A 116 (2013) 599–609.
[48] A. Hasan, A. Abbas, M.N. Akhtar, Molecules 16 (2011) 7789–7802.
[49] A. Abbas, M.M. Naseer, A. Hasan, T.B. Hadda, J. Mater. Environ. Sci. 5 (2014) 281–292.
[50] E.F. Saad, N.M. Hamada, S.M. Sharaf, S.K. El-Sadany, A.M. Moussa, M. Elba, Rapid Commun. Mass Spectrom. 12 (1998) 833–836.
[51] P. Wang, N. Onozawa-Komatsuzaki, Y. Himeda, H. Sugihara, H. Arakawa, K. Kasuga, Tetrahedron Lett. 42 (2001) 9199–9201.
[52] W. Liu, Y. Wang, M. Sun, D. Zhang, M. Zheng, W. Yang, Chem. Commun. 49 (2013) 6042–6044.