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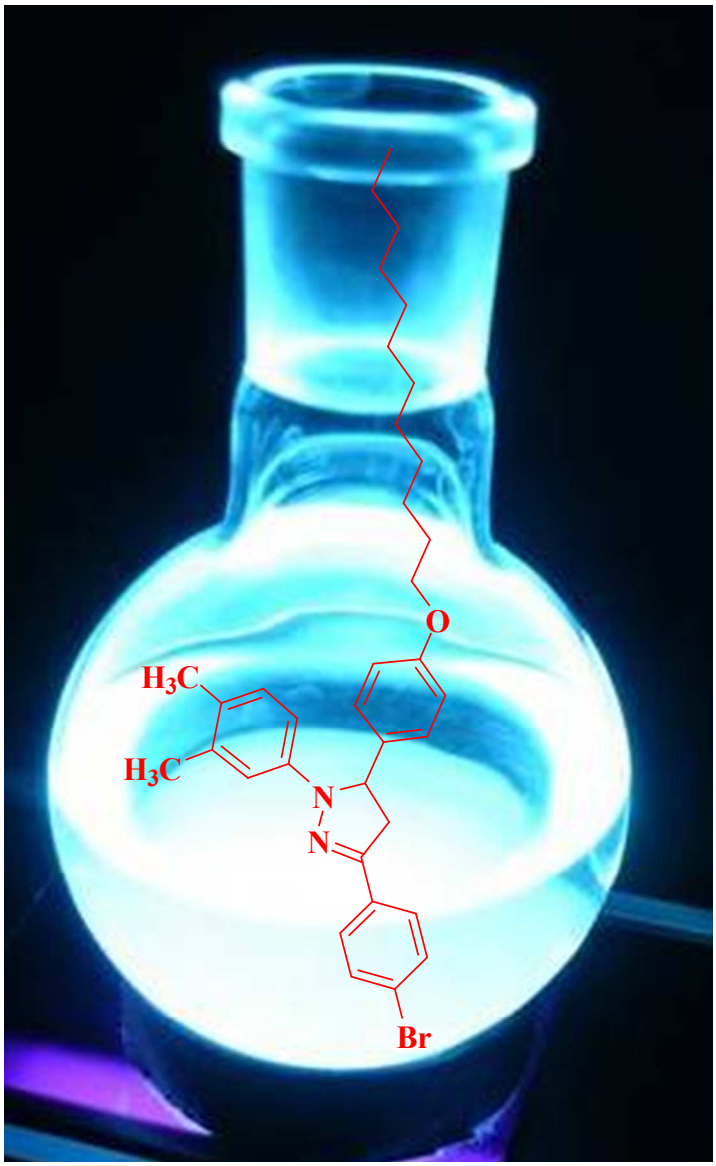
# GRAPHICAL ABSTRACT

## Structure-fluorescence relationship: interplay of non-covalent interactions in homologous 1,3,5-triaryl-2-pyrazolines

**A. Abbas, N. Flores-Holguin and M. M. Naseer**

A series of new homologous 1,3,5-triaryl-2-pyrazolines have been synthesized to understand the interplay of non-covalent interactions in context of structure-fluorescence relationship.



# Structure-fluorescence relationship: interplay of non-covalent interactions in homologous 1,3,5-triaryl-2-pyrazolines

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**Abstract:**

The fluorescence intensity relies on the synergy of multiple non-covalent interactions interactions in solution. Twelve new homologous 1,3,5-triaryl-2-pyrazolines (**1-12**).Br have been synthesized and characterized on the basis of their spectral (IR, $^{1}$H & $^{13}$C NMR and MS) and microanalytical data to investigate the interplay of non-covalent interactions and their effect on absorption and fluorescence properties by UV-Vis and emission spectroscopy. All the compounds, though, showed fluorescence in the blue region of the visible spectrum, but a strong influence of alkyloxy chain length was observed on the emission intensity without causing any major blue- or red-shift in the emission wavelength. The absorption and emission maxima ($\lambda_{max}^{abs}$ & $\lambda_{max}^{em}$) for all the compounds were observed in the range of 404-414 nm and 467-479 nm**,** respectively. The compound **12.Br** showed maximum emission intensity, indicating the dominant role of weak van der Waals forces in driving the solution state self-assembly in comparison to other relatively strong intermolecular interactions. The influence of different halogen substituents present on the conjugated backbone of 1,3,5-triaryl-2-pyrazoline skeleton in relation to the increasing alkyloxy chain length and their ultimate role in driving the solution state self-assembly and fluorescence properties has also been discussed.

***Keywords***: 1,3,5-triaryl-2-pyrazolines, synthesis, non-covalent interactions, alkyloxy side chain, fluorescence

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## 1. Introduction

In recent years, organic fluorescent materials have attracted considerable attention and have been found superior in properties than inorganic fluorescent materials, mainly due to the ease of fabrication and tunability of emission properties by simple chemical manipulations. The fact is reflected by the availability of low cost organic electroluminescence devices (OELDs) with broad range of emission colors, high brightness, high luminous efficiency, simple processing and good life stability.[1-7] Nevertheless, the major drawback associated with these materials is the aggregation of molecules into excimer-like species and H-type molecular aggregates, resulting in decreased fluorescence intensity.[8-10] To diminish this drawback, small structural modifications in fluorescent molecules have been found valuable and effective.[11-13] For example, the introduction of an ethyl group on the conjugated backbone of diphenylbutadiene[11] and incorporation of quinacridone dye molecule into dendrimers[12] led to the enhanced emission intensity, owing to the decreased molecular aggregation. In addition to their use in OELDs, organic fluorescent compounds have also been found useful in cosmetics, surface coatings, inks and textile industries.[14-16]

Pyrazolines, particularly 1,3,5-triaryl-2-pyrazolines are typical intramolecular charge transfer compounds of enormous significance,[17-20] not only due to their applications in organic electroluminescent devices (OELDs) and optoelectronics[21-23] but also in biology.[24-30] 1,3,5-Triaryl-2-pyrazolines having blue fluorescence and high quantum yield have been reported as the hole transporting media in photoconductive and emitting materials, organic photovoltaic cells, and in OELDs.[31-35] Furthermore, they have also been used as optical brightening agents in textiles, papers and plastics,[36] fluorescent probes in many chemosensors[37,38] and fluorescent switches.[39]

Non-covalent interactions such as hydrogen bonding, halogen bonding, π-π stacking, van der Waals forces and others are the key elements which direct and stabilize the structure in supramolecular self-assembly both in solution and the solid states.[40-43] These interactions are also important in biology and are critical in maintaining the three-dimensional structures of large molecules such as proteins and nucleic acids, and form the basis of enzyme catalysis and many other dynamic biological processes.[44-46] Amongst these interactions, van der Waals forces are although weak but are important in defining the bulk properties of matter. These forces generally grow with the length of the nonpolar part of the substance. Obviously, the possibility of more than one type of noncovalent interactions in any compound may lead towards either competition or cooperation.[47, 48]

However, mutual influence of one type of interaction upon another should be expected; a key point that need to be considered when comparing the strength of intermolecular forces. The low molecular weight alcohols are soluble and higher molecular weight alcohols are insoluble in water and vice versa in non-polar solvent, which is the perfect example of dominance of two different types of non-covalent interactions, i-e hydrogen bonding and van der Walls forces at different levels and their ultimate properties are dependent on their assembly in solution.

As illustrated in figure 1, the main skeleton of targeted 1,3,5-triaryl-2-pyrazolines have possible hydrogen bond acceptors (N, O and X), and halogen bond donor and acceptors (X and $sp^2$-hybridized nitrogen, respectively) sites, therefore the solution state arrangement of molecules will be determined by these polar sites. However, if the length of the alkyloxy side chain is increased, the non-polar forces may gradually take over and become the more dominant forces and the arrangement of the molecules in solution can be entirely different, and hence the properties.[49-54] In this context and our continuous interest in the pyrazolines,[55-59] the current project was designed to investigate the interplay of different non-covalent interactions, effect of substituting different halogens on the conjugated backbone and dependence of fluorescence properties of fluorescent 1,3,5-triaryl-2-pyrazoline molecules on their solution state self-assembly. Herein, we report the synthesis and fluorescence properties of 1,3,5-triaryl-2-pyrazolines (**1-12**).Br in comparison to (**1-12**).H, (**1-12**).F, (**1-12**).Cl focusing on the issues discussed above.

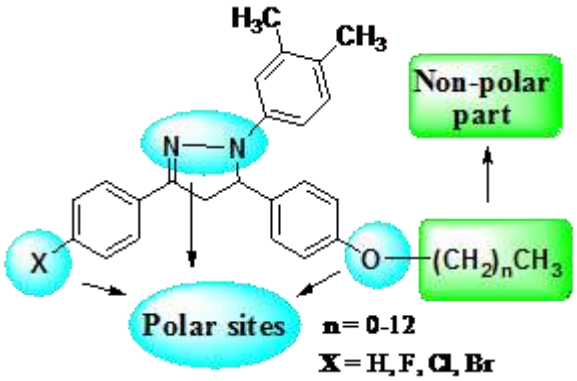



**Figure 1.** Highlighting different polar and non-polar parts of 1,3,5-triaryl-2-pyrazolines under study

## 2. Experimental

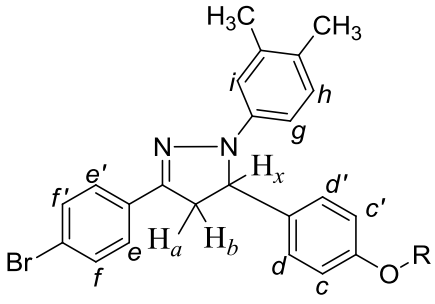
*2.1 Materials and Methods*

All reagents and solvents were used as obtained from the supplier or recrystallized/redistilled as required. Thin layer chromatography (TLC) was performed using aluminium sheets coated with silica gel 60 $F_{254}$ (Merck). The melting points of compounds were determined using capillary tubes and an electrothermal melting point apparatus, model MP-D Mitamura Riken Kogyo, Japan. IR spectra of compounds were recorded on a Bio-Rad FTS 3000 MX spectrophotometer (400-4000 $cm^{-1}$). $^{1}H$ and $^{13}C$ NMR spectra of compounds were recorded on a Bruker 300 MHz spectrometer using deuterated solvents and TMS as internal standard. The GC-MS spectra were obtained with Agilent 5973 inert mass selective detector in combination with Agilent 6890N gas chromatograph. Elemental analyses were carried out with a LECO-183 CHNS model. The UV-Visible and fluorescence emission spectra spectra were recorded on Shimadzu UV-1700 Spectrophotometer and Perkin-Elmer Luminescence (LS55) Spectrometer, respectively at 298 K.

*2.2 General procedure for the synthesis of compounds* **(1-12).Br**

In a round bottom flask, the corresponding 4-alkoxychalcone (0.01 mole)[60] in acetic acid solvent (25 mL) containing a catalytic amount (2-3 drops) of hydrochloric acid was heated at 60-65 °C for half an hour with constant stirring before the addition of (3,4-dimethylphenyl)hydrazine hydrochloride (3.45 g, 0.02 mole). After the addition, the whole reaction mixture was heated to reflux for 5-6 hours. It was then cooled to room temperature and poured into the crushed ice. The precipitates thus formed were filtered and washed thoroughly with distilled water and dried. To get highly pure compounds **(1-12).Br** for spectral characterization and fluorescence properties**,** the obtained crude products were subjected to silica gel column chromatography using petroleum ether/ethyl acetate (4:1) as the mobile phase.

The different protons of compounds **(1-12).Br** were differentiated according to the labeling shown in Figure 2, for better understanding of $^{1}H$ NMR chemical shift values.




R = $C_nH_{2n+1}$ with n = 1-12

**Figure 2.** Labelling scheme for protons of compounds **(1-12).Br**.

2.2.1 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-methoxyphenyl)-2-pyrazoline* ***(1.Br)***

Yield 86%; pale yellow solid; m. p. 135-137˚C; $R_f$ = 0.87 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1685, 1294, 1493, 1254, 1049, 1035, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.17 (s, 3H, N−Ar−4−C$H_3$), 2.22 (s, 3H, N−Ar−3−C$H_3$), 3.07 (dd, 1H, $J$ = 7.5, 17.1 Hz, $H_a$), 3.76 (dd, 1H, $J$ = 12.3, 17.1 Hz, $H_b$), 3.80 (s, 3H, −O−C$\boldsymbol{H}_3$), 5.22 (dd, 1H, $J$ = 7.5, 12.3 Hz, $H_x$), 6.71 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_g$), 6.88 (d, 2H, $J$ = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.25 (d, 2H, $J$ = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, $J$ = 8.7 Hz, Ar$H_{f=f'}$), 7.59(d, 2H, $J$ = 8.4 Hz, Ar$H_{e=e'}$), $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.8, 20.2, 43.3, 55.2, 64.3, 110.8, 115.0 (2C), 115.2, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9 (2C), 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 435 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{24}H_{23}BrN_2O$ : C, 66.21; H, 5.32; N, 6.43; Found: C, 66.17; H, 5.29; N, 6.49%

2.2.2 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-ethoxyphenyl)-2-pyrazoline* ***(2.Br)***

Yield 82%; pale yellow solid; m. p. 113-116˚C; $R_f$ = 0.85 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1688, 1298, 1497, 1252, 1045, 1037, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.42 (t, 3H, $J$ = 7.2 Hz, −O−$CH_2$−C$\boldsymbol{H}_3$), 2.17 (s, 3H, N−Ar−4−C$H_3$), 2.22 (s, 3H, N−Ar−3−C$H_3$), 3.07 (dd, 1H, $J$ = 7.5, 16.8 Hz, $H_a$), 3.76 (dd, 1H, $J$ = 12.3, 16.8 Hz, $H_b$), 4.02 (q, 2H, $J$ = 7.2 Hz, −O−C$\boldsymbol{H}_2$−), 5.21 (dd, 1H, $J$ = 7.5, 12.3 Hz, $H_x$), 6.71 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, $J$ = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, $J$ = 8.4 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, $J$ = 8.7, Ar$H_{f=f'}$), 7.59(d, 2H, $J$ = 8.7 Hz, Ar$H_{e=e'}$), $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.8, 18.8, 20.2, 43.3, 63.4, 64.4, 110.8, 115.0 (2C), 115.1, 122.1, 122.7, 127.0 (2C), 127.4, 129.9 (2C), 131.6 (2C), 131.9, 134.5, 137.1, 142.8, 144.9, 158.3, EIMS: *m/z* 449 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{25}H_{25}BrN_2O$ : C, 66.82; H, 5.61; N, 6.23; Found: C, 66.79; H, 5.57; N, 6.30%

2.2.3 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-propyloxyphenyl)-2-pyrazoline* ***(3.Br)***

Yield 80%; pale yellow solid; m. p. 105-109˚C; $R_f$ = 0.87 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1683, 1296, 1490, 1255, 1047, 1029, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.04 (t, 3H, $J$ = 7.2 Hz, −O−$CH_2$−$CH_2$−C$\boldsymbol{H}_3$), 1.81 (sextet, 2H, $J$ = 7.0 Hz, −O−$CH_2$−C$\boldsymbol{H}_2$−$CH_3$), 2.17 (s, 3H, N-Ar-4-C$\boldsymbol{H}_3$), 2.22 (s, 3H, N-Ar-3-C$\boldsymbol{H}_3$), 3.06 (dd, 1H, $J$ = 7.5, 16.8 Hz, $H_a$), 3.75

(dd, 1H, *J* = 12.6, 17.1 Hz, $H_b$), 3.90 (t, 2H, *J* = 6.6 Hz, −O−C***H***$_2$−), 5.21 (dd, 1H, *J* = 7.8, 12.6 Hz, $H_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar$H_g$), 6.86 (d, 2H, *J* = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, *J* = 8.1 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, *J* = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 10.5, 18.8, 20.1, 22.5, 43.3, 64.4, 69.5, 110.8, 114.4 (2C), 115.0, 122.1, 122.7, 127.0 (2C), 127.4, 129.9 (2C), 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.6, 158.3, EIMS: *m/z* 463 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{26}H_{27}BrN_2O$ : C, 67.39; H, 5.87; N, 6.05; Found: C, 67.33; H, 5.81; N, 6.11%

2.2.4 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-butyloxyphenyl)-2-pyrazoline* ***(4.Br)***

Yield 85%; pale yellow solid; m. p. 103-107˚C; $R_f$ = 0.86 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1677, 1290, 1494, 1257, 1051, 1035, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.99 (t, 3H, *J* = 7.5 Hz, −O−$(CH_2)_3$−C***H***$_3$), 1.50 (sextet, 2H, *J* = 7.8 Hz, −O−$CH_2$−$CH_2$−C***H***$_2$−$CH_3$), 1.77 (qn, 2H, *J* = 7.2 Hz, −O−$CH_2$−C***H***$_2$−$C_2H_5$), 2.17 (s, 3H, N-Ar-4-C***H***$_3$), 2.22 (s, 3H, N-Ar-3-C***H***$_3$), 3.07 (dd, 1H, *J* = 7.5, 16.8 Hz, $H_a$), 3.75 (dd, 1H, *J* = 12.3, 17.1 Hz, $H_b$), 3.95 (t, 2H, *J* = 6.6 Hz, −O−C***H***$_2$−), 5.21 (dd, 1H, *J* = 7.5, 12.3 Hz, $H_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, *J* = 8.1 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, *J* = 8.7 Hz, Ar$H_{d=d'}$), 7.51(d, 2H, *J* = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.8, 18.8, 19.2, 20.2, 31.3, 43.3, 64.4, 67.5, 110.8, 115.0 (2C), 115.2, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 477 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{27}H_{29}BrN_2O$ : C, 67.92; H, 6.12; N, 5.87; Found: C, 67.89; H, 6.08; N, 5.95%

2.2.5 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-pentyloxyphenyl)-2-pyrazoline* ***(5.Br)***

Yield 87%; pale yellow solid; m. p. 101-104 ˚C; $R_f$ = 0.87 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1681, 1297, 1492, 1255, 1053, 1034, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.94 (t, 3H, *J* = 7.2 Hz, −O−$(CH_2)_4$−C***H***$_3$), 1.29−1.48 (m, 4H, −O−$CH_2$−$CH_2$−(C***H***$_2$)$_2$−$CH_3$), 1.78 (qn, 2H, *J* = 7.5 Hz, −O−$CH_2$−C***H***$_2$−$C_3H_7$), 2.17 (s, 3H, N-Ar-4-C$H_3$), 2.22 (s, 3H, N-Ar-3-C$H_3$), 3.07 (dd, 1H, *J* = 7.5, 17.1 Hz, $H_a$), 3.76 (dd, 1H, *J* = 12.6, 17.1 Hz, $H_b$), 3.93 (t, 2H, *J* = 6.6 Hz, −O−C***H***$_2$−), 5.21 (dd, 1H, *J* = 7.8, 12.3 Hz, $H_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, *J* = 8.1 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, *J* = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar$H_{f=f'}$ ), 7.59 (d, 2H, *J* = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.0, 18.8, 20.2, 22.4, 28.2, 28.9, 43.3, 64.4, 67.9, 110.7, 114.9 (2C), 115.1, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 131.9,

134.4, 137.1, 142.8, 144.9, 158.5, EIMS: *m/z* 491 ($M^{+\bullet}$, base peak); Anal. calcd. for $C_{28}H_{31}BrN_2O$ : C, 68.43; H, 6.36; N, 5.70; Found: C, 68.41; H, 6.33; N, 5.79%

2.2.6 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-hexyloxyphenyl)-2-pyrazoline (**6.Br**)*

Yield 84%; pale yellow solid; m. p. 125-129˚C; $R_f$ = 0.85 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1679, 1293, 1498, 1253, 1045, 1038, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.92 (t, 3H, *J* = 7.2 Hz, −O−$(CH_2)_5$−C***H***$_3$), 1.29−1.48 (m, 6H, −O−$CH_2$−$CH_2$−(C***H***$_2)_3$−$CH_3$), 1.78 (qn, 2H, *J* = 7.5 Hz, −O−$CH_2$−C***H***$_2$−$C_4H_9$), 2.17 (s, 3H, N-Ar-4-C***H***$_3$), 2.22 (s, 3H, N-Ar-3-C***H***$_3$), 3.07 (dd, 1H, *J* = 7.5, 17.1 Hz, ***H***$_a$), 3.76 (dd, 1H, *J* = 12.6, 17.1 Hz, ***H***$_b$), 3.93 (t, 2H, *J* = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, *J* = 7.8, 12.3 Hz, ***H***$_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar***H***$_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar***H***$_{c=c'}$), 6.93 (d, 1H, *J* = 8.1 Hz, N-Ar***H***$_h$), 7.04 (s, 1H, N-Ar***H***$_i$), 7.23 (d, 2H, *J* = 8.7 Hz, Ar***H***$_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar***H***$_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar***H***$_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.0, 18.8, 20.2, 22.6, 25.7, 29.2, 31.6, 43.3, 64.4, 68.0, 110.8, 115.0 (2C), 115.2, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 505 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{29}H_{33}BrN_2O$ : C, 68.91; H, 6.58; N, 5.54; Found: C, 68.87; H, 6.54; N, 5.64%

2.2.7 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-heptyloxyphenyl)-2-pyrazoline (**7.Br**)*

Yield 85%; pale yellow solid; m. p. 123-126˚C; $R_f$ = 0.86 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1678, 1296, 1489, 1252, 1048, 1043, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.92 (t, 3H, *J* = 7.2 Hz, −O−$(CH_2)_6$−C***H***$_3$), 1.32−1.48 (m, 8H, −O−$CH_2$−$CH_2$−(C***H***$_2)_4$− $CH_3$), 1.78 (qn, 2H, *J* = 8.0 Hz, −O−$CH_2$−C***H***$_2$−$C_5H_{11}$), 2.17 (s, 3H, N-Ar-4-C*H*$_3$), 2.22 (s, 3H, N-Ar-3-C*H*$_3$), 3.07 (dd, 1H, *J* = 7.5, 17.1 Hz, *H*$_a$), 3.76 (dd, 1H, *J* = 12.3, 17.1 Hz, *H*$_b$), 3.93 (t, 2H, *J* = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, *J* = 7.5, 12.3 Hz, *H*$_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar*H*$_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar*H*$_{c=c'}$), 6.93 (d, 1H, *J* = 8.1 Hz, N-Ar*H*$_h$), 7.04 (s, 1H, N-Ar*H*$_i$), 7.23 (d, 2H, *J* = 8.7 Hz, Ar*H*$_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar*H*$_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar*H*$_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 18.8, 20.2, 22.6, 26.0, 29.0, 29.3, 31.8, 43.3, 64.4, 68.0, 110.8, 115.0 (2C), 115.2, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.1, 142.8, 144.9, 158.5, EIMS: *m/z* 519 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{30}H_{35}BrN_2O$ : C, 69.36; H, 6.79; N, 5.39; Found: C, 69.32; H, 6.75; N, 5.47%

2.2.8 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-octyloxyphenyl)-2-pyrazoline (**8.Br**)*

Yield 83%; pale yellow solid; m. p. 110-113˚C; $R_f$ = 0.87 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1682, 1294, 1495, 1255, 1051, 1041, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, *J* = 7.2 Hz, −O−$(CH_2)_7$−C***H***$_3$), 1.32−1.47 (m, 10H, −O−$CH_2$−$CH_2$−(C***H***$_2)_5$−$CH_3$), 1.77

(qn, 2H, $J$ = 7.5 Hz, −O−$CH_2$−C***H***$_2$−$C_6H_{13}$), 2.16 (s, 3H, N-Ar-4-C$H_3$), 2.21 (s, 3H, N-Ar-3-C$H_3$), 3.06 (dd, 1H, $J$ = 7.5, 16.8 Hz, $H_a$), 3.75 (dd, 1H, $J$ = 12.3, 17.1 Hz, $H_b$), 3.93 (t, 2H, $J$ = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, $J$ = 7.5, 12.3 Hz, $H_x$), 6.71 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, $J$ = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, $J$ = 8.1 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, $J$ = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, $J$ = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, $J$ = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 18.8, 19.4, 20.2, 22.6, 26.0, 29.0, 29.3, 31.8, 43.3, 64.4, 68.1, 110.8, 115.0 (2C), 115.2, 122.1, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.1, 134.4, 137.1, 142.8, 144.9, 158.5, EIMS: *m/z* 533 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{31}H_{37}BrN_2O$ : C, 69.78; H, 6.99; N, 5.25; Found: C, 69.78; H, 6.99; N, 5.25%

2.2.9 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-nonyloxyphenyl)-2-pyrazoline* ***(9.Br)***

Yield 86%; pale yellow solid; m. p. 107-110 ˚C; $R_f$ = 0.89 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1679, 1291, 1497, 1258, 1053, 1038, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.90 (t, 3H, $J$ = 7.2 Hz, −O−$(CH_2)_8$−C***H***$_3$), 1.30−1.47 (m, 12H, −O−$CH_2$−$CH_2$−(C***H***$_2$)$_6$−$CH_3$), 1.78 (qn, 2H, $J$ = 7.8 Hz, −O−$CH_2$−C***H***$_2$−$C_7H_{15}$), 2.16 (s, 3H, N-Ar-4-C$H_3$), 2.21 (s, 3H, N-Ar-3-C$H_3$), 3.06 (dd, 1H, $J$ = 7.5, 16.8 Hz, $H_a$), 3.75 (dd, 1H, $J$ = 12.3, 17.1 Hz, $H_b$), 3.93 (t, 2H, $J$ = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, $J$ = 7.8, 12.3 Hz, $H_x$), 6.71 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, $J$ = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, $J$ = 8.1 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, $J$ = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, $J$ = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, $J$ = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 18.8, 19.5, 19.8, 22.6, 26.0, 29.2, 29.2, 29.4, 29.5, 31.8, 43.3, 64.4, 68.1, 110.8, 115.0 (2C), 115.2, 122.2, 127.0 (2C), 127.0 (2C), 127.3, 129.9, 131.6 (2C), 132.0, 134.4, 137.1, 142.8, 144.9, 158.5, EIMS: *m/z* 547 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{32}H_{39}BrN_2O$ : C, 70.19; H, 7.18; N, 5.12; Found: C, 70.13; H, 7.15; N, 5.19%

2.2.10 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-decyloxyphenyl)-2-pyrazoline* ***(10.Br)***

Yield 82%; pale yellow solid; m. p. 90-93˚C; $R_f$ = 0.87 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1684, 1295, 1495, 1257, 1048, 1033, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, $J$ = 7.0 Hz, −O−$(CH_2)_9$−C***H***$_3$), 1.30−1.48 (m, 14H, −O−$CH_2$−$CH_2$−(C***H***$_2$)$_7$−$CH_3$), 1.78 (qn, 2H, $J$ = 7.8 Hz, −O−$CH_2$−C***H***$_2$−$C_8H_{17}$), 2.17 (s, 3H, N-Ar-4-C$H_3$), 2.22 (s, 3H, N-Ar-3-C$H_3$), 3.07 (dd, 1H, $J$ = 7.5, 17.1 Hz, $H_a$), 3.75 (dd, 1H, $J$ = 12.3, 16.8 Hz, $H_b$), 3.94 (t, 2H, $J$ = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, $J$ = 7.8, 12.3 Hz, $H_x$), 6.71 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, $J$ = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, $J$ = 8.4 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, Hz, $J$ = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, $J$ = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, $J$ = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 18.8, 20.1, 22.0, 22.7, 29.3, 29.3, 29.4, 29.5,

29.5, 31.9, 43.3, 64.4, 68.0, 110.8, 115.0 (2C), 115.2, 122.2, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 561 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{33}H_{41}BrN_2O$ : C, 70.58; H, 7.36; N, 4.99; Found: C, 70.54; H, 7.33; N, 5.08%

2.2.11 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-undecyloxyphenyl)-2-pyrazoline* ***(11.Br)***

Yield 85%; pale yellow solid; m. p. 89-92˚C; $R_f$ = 0.88 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1683, 1297, 1498, 1259, 1053, 1030, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, *J* = 7.0 Hz, −O−$(CH_2)_{10}$−C***H***$_3$), 1.29−1.48 (m, 16H, −O−$CH_2$−$CH_2$−$(CH_2)_8$−$CH_3$), 1.78 (qn, 2H, *J* = 8.0 Hz, −O−$CH_2$−C***H***$_2$−$C_9H_{19}$), 2.17 (s, 3H, N-Ar-4-C$H_3$), 2.22 (s, 3H, N-Ar-3-C$H_3$), 3.07 (dd, 1H, *J* = 7.5, 16.8 Hz, $H_a$), 3.75 (dd, 1H, *J* = 12.3, 17.1 Hz, $H_b$), 3.93 (t, 2H, *J* = 6.6 Hz, −O−$CH_2$−), 5.21 (dd, 1H, *J* = 7.8, 12.3 Hz, $H_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar$H_{c=c'}$), 6.93 (d, 1H, *J* = 8.4 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.23 (d, 2H, Hz, *J* = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 18.8, 19.8, 20.1, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 31.9, 43.3, 64.4, 68.0, 110.8, 114.9 (2C), 115.1, 122.3, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 575 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{34}H_{43}BrN_2O$ : C, 70.94; H, 7.53; N, 4.87; Found: C, 70.91; H, 7.49; N, 4.93%

2.2.12 *1-(3,4-Dimethylphenyl)-3-(4-bromophenyl)-5-(4-dodecyloxyphenyl)-2-pyrazoline* ***(12.Br)***

Yield 83%; pale yellow solid; m. p. 89-92˚C; $R_f$ = 0.86 (petroleum ether:ethyl acetate, 4:1), FT- IR (KBr, $cm^{-1}$): 1687, 1296, 1497, 1254, 1051, 1037, $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, 3H, *J* = 7.0 Hz, −O−$(CH_2)_{11}$−C***H***$_3$), 1.29−1.49 (m, 18H, −O−$CH_2$−$CH_2$−$(CH_2)_9$−$CH_3$), 1.78 (qn, 2H, *J* = 7.8 Hz, −O−$CH_2$−C***H***$_2$−$C_{10}H_{21}$), 2.17 (s, 3H, N-Ar-4-C$H_3$), 2.22 (s, 3H, N-Ar-3-C$H_3$), 3.07 (dd, 1H, *J* = 7.5, 16.8 Hz, $H_a$), 3.76 (dd, 1H, *J* = 12.3, 16.8 Hz, $H_b$), 3.93 (t, 2H, *J* = 6.6 Hz, −O−$CH_2$−), 5.22 (dd, 1H, *J* = 7.5, 12.3 Hz, $H_x$), 6.71 (d, 1H, *J* = 8.4 Hz, N-Ar$H_g$), 6.87 (d, 2H, *J* = 8.7 Hz, Ar$H_{c=c'}$), 6.94 (d, 1H, *J* = 8.4 Hz, N-Ar$H_h$), 7.04 (s, 1H, N-Ar$H_i$), 7.22 (d, 2H, Hz, *J* = 8.7 Hz, Ar$H_{d=d'}$), 7.51 (d, 2H, *J* = 8.7 Hz, Ar$H_{f=f'}$), 7.59 (d, 2H, *J* = 8.7 Hz, Ar$H_{e=e'}$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 19.8, 20.2, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 29.6, 29.6, 31.9, 43.3, 64.4, 68.0, 110.8, 114.9 (2C), 115.1, 122.3, 127.0 (2C), 127.0 (2C), 127.4, 129.9, 131.6 (2C), 132.0, 134.4, 137.0, 142.8, 144.9, 158.5, EIMS: *m/z* 589 ($M^{+\bullet}$, base peak). Anal. calcd. for $C_{35}H_{45}BrN_2O$ : C, 71.29; H, 7.69; N, 4.75; Found: C, 71.25; H, 7.67; N, 4.82%

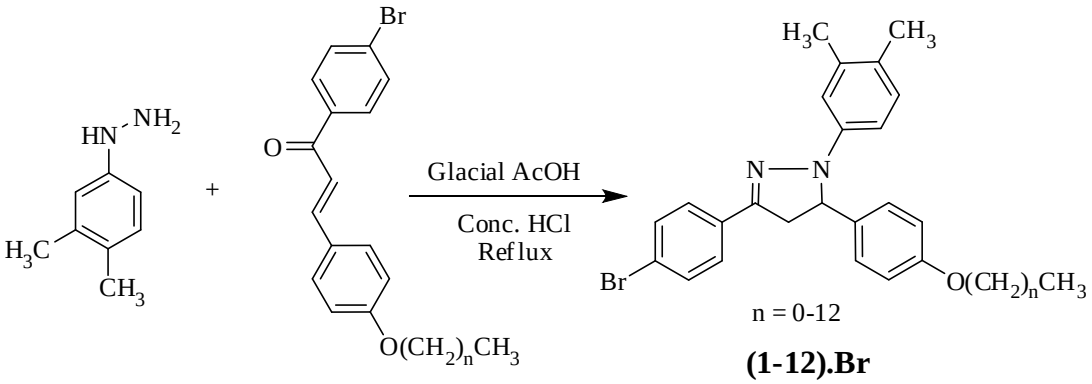
*2.3 Fluorescence properties of 1,3,5-triaryl-2-pyrazolines* **(1-12).Br**

The UV-Vis and emission spectroscopy was used to investigate fluorescence properties of compounds **(1-12).Br**. The UV-Vis and emission spectra of **(1-12).Br**, were recorded in *N*,*N*-dimethylformamide-water (3:7) mixture at a concentration of $1 \times 10^{-5}$ mol/L and $1 \times 10^{-7}$ mol/L, respectively at room temperature (298 K).

## 3. Results and discussion

*3.1 Chemistry*

1,3,5-Triaryl-pyrazolines **(1-12).Br** bearing one to twelve carbon alkyloxy side chain were approached by reacting (*E*)-1-(4-bromophenyl)-3-(4-alkoxyphenyl)prop-2-en-1-one[60] with two equivalents of (3,4-dimethylphenyl)hydrazine hydrochloride in glacial acetic acid solvent containing two to three drops of concentrated hydrochloric acid for 5-6 hours (Scheme 1). The resultant precipitates appeared after pouring the cooled reaction mixture onto the crushed ice were isolated by filtration which were further purified by silica gel column chromatography using petroleum ether:ethyl acetate (4:1) as the mobile phase. The length of the alkyloxy side chain did not affect greatly on the reaction efficiency, as is evident from the yield of the products ranging from 80-87%.




**Scheme 1.** Synthesis of homologous 1,3,5-triaryl 2-pyrazolines, (**1-12).Br**

*3.2 Spectral characterization of* (**1-12).Br**

The structures of all the products (**1-12**).**Br** were inferred from their infrared, proton and carbon-13 NMR, mass spectrometric and microanalytical data. Two characteristic absorption bands, one for carbon-nitrogen double bond (C=N) and the other for carbon-nitrogen single bond (C-N) were observed in the range of 1688-1677 $cm^{-1}$ and 1298-1290 $cm^{-1}$, respectively that indicates the formation of pyrazoline ring.[55-59, 61-63] Another strong band in the region of 1043-1030 $cm^{-1}$ was indicative of the presence of Ar-Br in all the

products. Similarly, the Ar-O and O-R stretching frequencies were observed in the form of two strong bands in the range of 1259-1252 $cm^{-1}$ and 1053-1045 $cm^{-1}$, respectively, indicating the alkyloxy side chain in all the products. These observations were further confirmed by the $^{1}H$ NMR and $^{13}C$ NMR spectroscopy. The presence of three doublet of doublets (dd) in $^{1}H$ NMR related to two methylene protons ($H_a$ and $H_b$) and one methine proton ($H_x$) clearly indicated the formation of five membered pyrazoline ring.[55-59] The methylene protons, $H_a$ and $H_b$ were observed at 3.06-3.07 ppm ($J$ = 7.5 Hz and 16.8-17.1 Hz, due to the coupling with neighbouring $H_b$ and $H_x$ protons) and 3.75-3.76 ppm ($J$ = 12.3-12.6 Hz and 16.8-17.1 Hz, due to the coupling with neighbouring $H_a$ and $H_x$ protons), respectively. The methine protons, $H_x$ of (**1-12**).Br were, however appeared slightly downfield as compared to $H_a$ and $H_b$ at 5.21-5.22 ppm ($J$ = 7.5-7.8 Hz and 12.3-12.6 Hz due to the coupling with two neighbouring non-equivalent protons). The presence of a triplet in the range of 3.80-4.02 ppm, assigned to the methylenic protons of the alkoxy side chain (Ar-O-C***H***$_2$-) that are directly linked to oxygen atom, confirmed the alkyloxy pendants. Furthermore, all the other aliphatic and aromatic protons related to the alkyloxy side chain and three aromatic rings were found in their expected regions with desired multiplicity. In $^{13}C$ NMR, the carbons of the pyrazoline ring were appeared at 64.3-69.5 ppm ($C_3$), 43.3 ppm ($C_4$) and 55.2-64.4 ppm ($C_5$), which are in good agreement with the literature.[55-59] All the other carbons including the alphatic alkyloxy side chain and three aromatics rings were observed at their respective places. The formation of proposed structures of compounds **(1-12).Br** were also confirmed by their electron impact mass spectral (EIMS) data, where molecular ion peaks ($M^{+\bullet}$) (base peak) were observed at their respective molecular masses. Furthermore, the fragmentation pattern was also found consistent and in good agreement with our previously reported 2-pyrazoline derivatives.[55-59] A representative proposed fragmentation pattern of compound **11.Br** is provided in Figure S1 (see supporting information). The selected most significant IR absorption bands, the assignment of all protons and carbons and the molecular mass data of **(1-12).Br** are presented in the experimental section.

*3.3 Fluorescence Properties*

The absorption and fluorescence properties of the synthesized homologous 1,3,5-triaryl-2-pyrazolines (**1-12**).Br were evaluated by UV-Vis and emission spectroscopy to investigate the interplay of weak non-covalent interactions. As a whole, all the compounds

showed fluorescence in the blue region of the visible spectrum (Table 1). The UV-Vis spectra of (**1-12**).Br were recorded at a concentration of 1 x $10^{-5}$ mol/L in *N*,*N*-dimethylformamide (DMF)-water (3:7) binary polar solvent mixture, which displayed an intense absorption band with absorption maxima ($\lambda_{max}^{abs}$) wavelength in the range of 404-414 nm, most likely due to the $\pi$-$\pi$* transitions[58,59] of the conjugated backbone (Br-Ar-C=N-N) (Table 1). Due to the presence of same central 1,3,5-triaryl-2-pyrazoline core in all the molecules, nevertheless, a similar spectral shapes/curves in the absorption spectra were realized (Figure 3). It is worth noting here that the difference in absorption wavelengths and absorption intensities, illustrated in figure 3, can be attributed to the presence of homologous alkyloxy side chain at one of the phenyl ring of the central core.

**Table 1:** Absorption and fluorescence spectra of compounds **(1-12).Br**

| Compound | $\lambda_{max}^{abs}$ (nm) | $\lambda_{max}^{em}$ (nm) | Stoke's Shift |
|---|---|---|---|
| **1.Br** | 414 | 478 | 64 |
| **2.Br** | 413 | 477 | 64 |
| **3.Br** | 414 | 479 | 65 |
| **4.Br** | 408 | 475 | 67 |
| **5.Br** | 409 | 474 | 65 |
| **6.Br** | 406 | 468 | 62 |
| **7.Br** | 406 | 470 | 64 |
| **8.Br** | 404 | 468 | 64 |
| **8.Br** | 405 | 467 | 62 |
| **10.Br** | 412 | 473 | 61 |
| **11.Br** | 404 | 468 | 64 |
| **12.Br** | 406 | 471 | 65 |

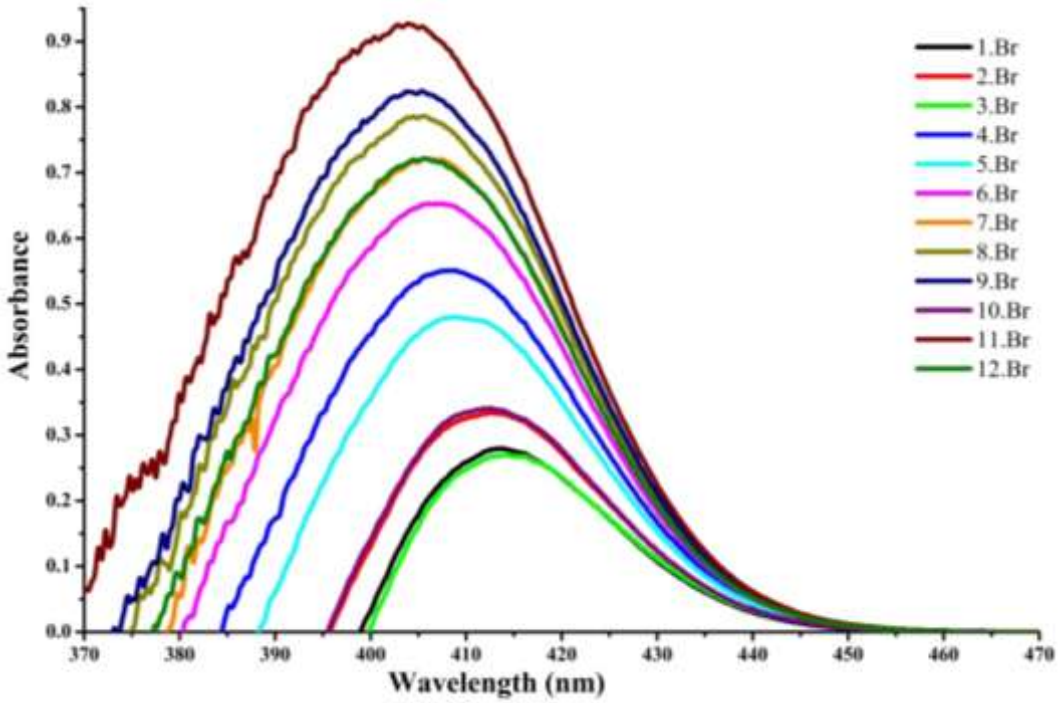



**Figure 3.** The UV-vis absorption spectra of **(1-12).Br** in DMF-$H_2O$ (3:7) binary solvent system at $1 \times 10^{-5}$ mol/L concentration.

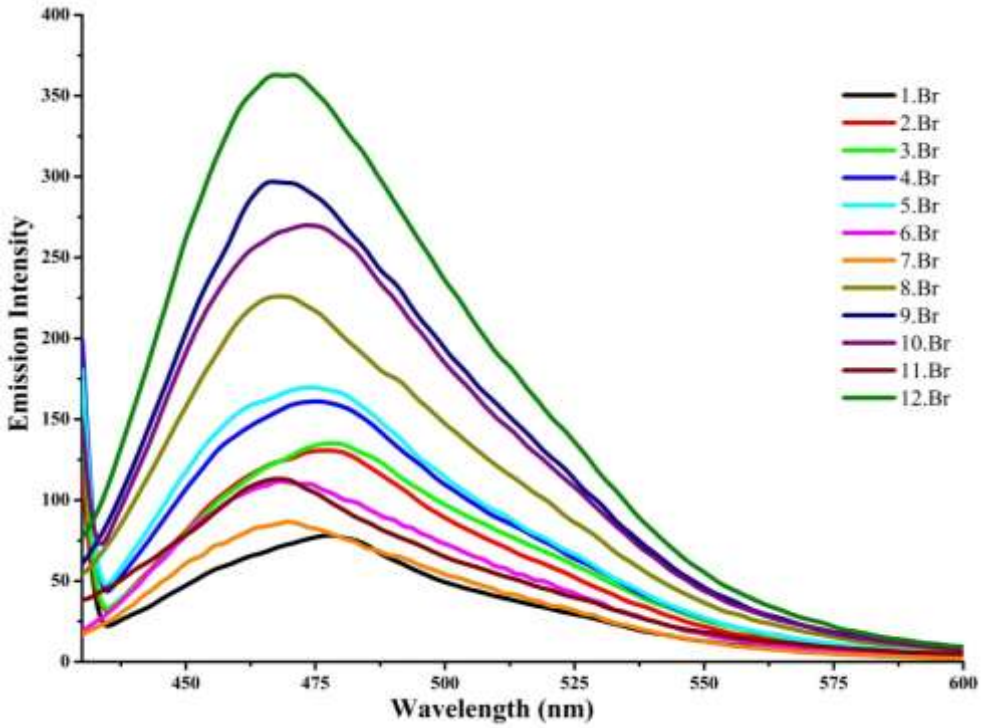



**Figure 4.** The emission spectra of **(1-12).Br** in DMF-$H_2O$ (3:7) binary solvent system at $1 \times 10^{-7}$ mol/L concentration.

The emission properties of compounds **(1-12).Br** were then studied at their corresponding excitation wavelengths ($\lambda_{max}^{abs}$) (Table 1, Figure 4). Once again, the same DMF-water (3:7) binary solvent mixture was used. All the compounds **(1-12).Br** revealed blue emission in the range of 467-479 nm with variable emission intensity at constant 1 x $10^{-7}$ mol/L concentration. The first five compounds of the series, **(1-5).Br** showed emission at higher wavelengths in the range of 474-478 nm as compared to other compounds of the series, for which the more random results have been obtained. These random results with increase in alkyloxy chain length, which prohibit explanation of any definitive trends across the series, may be attributed to the different conformations of alkyloxy groups in solution.[64] However, the present series similar to most of the hitherto reported triaryl-2-pyrazolines[55-59] displayed fluorescence, having their emission maxima ($\lambda_{max}^{em}$) wavelengths in the blue region of visible spectrum.

The most important parameters which are responsible for the blue fluorescence in 1,3,5-triaryl-2-pyrazolines include the geometry and substitution pattern at the central pyrazoline ring.[17-19] The aryl groups substituted at its 1- and 3-position form the conjugated backbone and are mainly responsible for absorption of photons.[65,66] However, the aryl group present at 5-position of the central pyrazoline ring is not involved in any kind of conjugation and the substitution at this ring can be expected to have some influence on the physico-chemical properties, without effecting the absorption or emission wavelengths. This fact is quite clear from the results of the present series, showing strong influence of the length of the alkyloxy group on the emission intensities, without causing major blue or red shift in the emission wavelength ($\lambda_{max}^{em}$).

It is also important to address here that the compounds **(1-12).Br** having bromo substitution on aryl ring present at 3-position of central pyrazoline ring, showed a notable difference in absorption wavelengths and emission intensities from previously reported compounds **(1-12).H**,[67] **(1-12).F**[57] and **(1-12).Cl**,[58] where there is no substitution, fluoro substitution and chloro substitution, respectively on 3-aryl of pyrazoline ring [Figure 5 & 6]. On careful analysis of the data, it is revealed that both chloro and bromo substituents affected greatly on absorption and emission maxima ($\lambda_{max}^{abs}$) wavelengths as compared to their unsubstituted and fluoro analogs. As halogens are part of the conjugated backbone, therefore, this difference can be attributed to their different electron donating capabilities. Fluoro being the most electronegative (electronegativity 4.0 as compared to 3.0 for nitrogen) hesitates to donate its lone pair to the conjugated backbone. Further, it

withdraws electron density from the aromatic ring making it electron deficient and decreasing the efficiency of the π-electrons to delocalize in the conjugated backbone owing to its increased inductive effect. However, the electronegativities of both chloro and bromo (3.0 and 2.8, respectively) substituents are comparable to nitrogen and they have the ability to donate the lone pair of electrons more effectively towards nitrogen (increase electron flow from the aromatic ring to the $sp^2$-hybridized nitrogen). In general, more the electron donation of a substituent towards the conjugated backbone, the more effective is conjugation and the intramolecular charge transfer. This proposition is clearly supported by the experimental results where absorption maxima ($\lambda_{max}^{abs}$) wavelengths for compounds **(1-12).F** [337-364 nm] with fluoro substituents are much lower than the compounds **(1-12).H** [367-377 nm] with no substitution, compounds **(1-12).Cl** [408-416 nm] with chloro substituents and compounds **(1-12).Br** [404-414 nm] with bromo substituents (Figure 5). Similar is the case with emission maxima ($\lambda_{max}^{em}$) wavelengths shown in Figure 6. Moreover, the emission intensity is also affected by the presence of the different halogens at the 3-aryl ring of pyrazoline skeleton. As revealed in the figures S2-S13 (see supplementary information), low emission intensity was observed for the first five compounds of each **(1-12).H, (1-12).F, (1-12).Cl** and **(1-12).Br** series, with random trend of the effect of halogens; highlighting the formation of aggregates of molecules that preferably utilize halogens and nitrogens of 1,3,5-triaryl-2-pyrazoline core for the intermolecular interations, leading towards low intensity. As the chain length increases, the weak van der Waals forces start to dominate the solution state self-assembly, but it is still difficult to avoid stronger interactions such as H-bonding involving halogen substituents.[42] However, van der Waals forces are strong enough in non-halogenated compounds **(1-12).H** to avoid aggregation. Due to this reason, the compounds **6**.**H 10.H** and **12.H** with no substituents at 3-aryl of the pyrazoline (even-odd effect is also obvious) showed the maximum emission intensity as compared to their halogenated counterparts (Figures S6-S13, supplementary information). Although, the trend here is not very clear but in broader perspective, it is anticipated that by varying the substituent at 3-aryl of pyrazoline ring, the absorption and emission maxima ($\lambda_{max}^{abs}$) wavelengths, and emission intensity can be tuned which is an important and useful approach in controlling/optimizing the optoelectronic and luminescence properties of pyrazoline-based OLEDs.

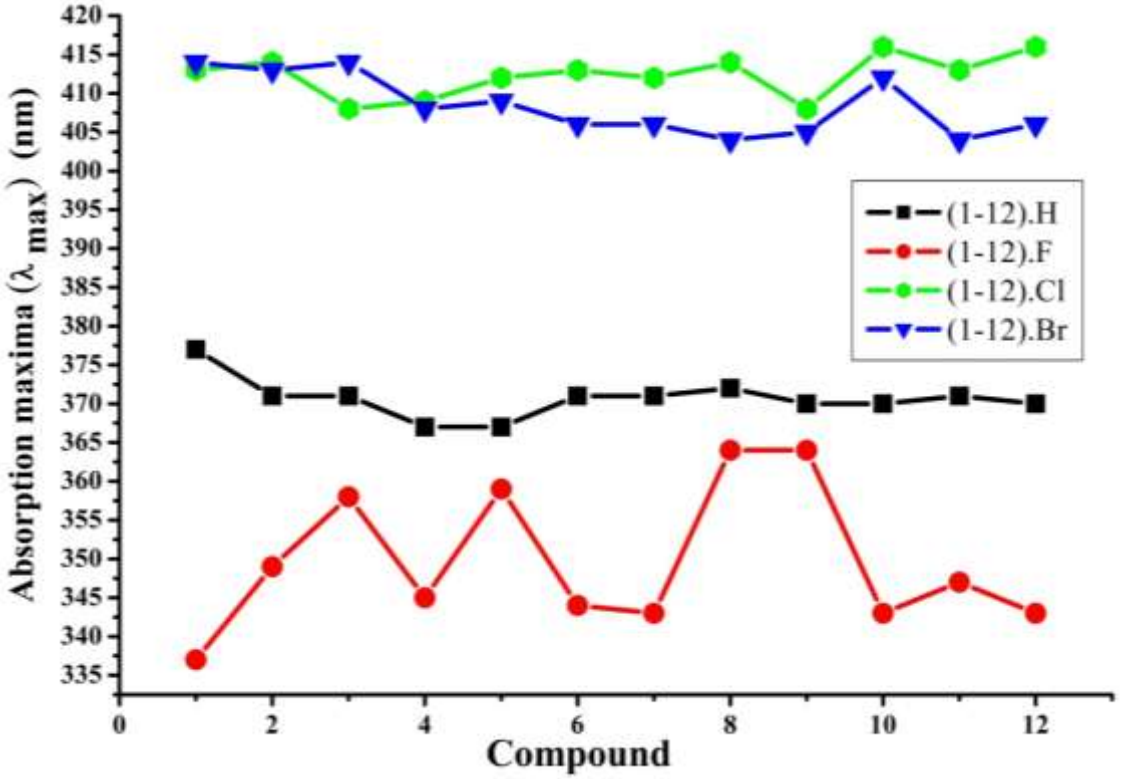



**Figure 5.** Comparison of absorption maxima ($\lambda_{max}^{abs}$) of **(1-12).Br** with previously reported **(1-12).H**,[67] **(1-12).F**[57] and **(1-12).Cl**[58] in DMF-$H_2O$ (3:7) system at fixed concentration of 1 x $10^{-5}$ mol/L.

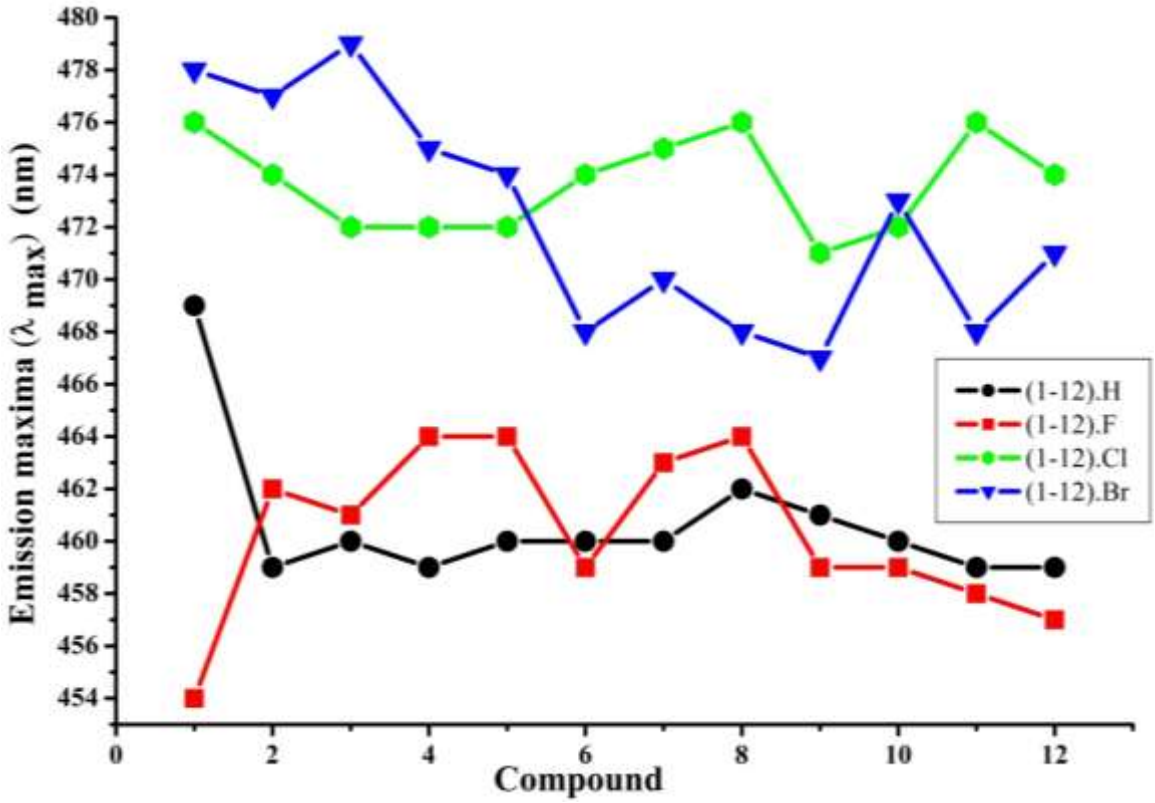



**Figure 6.** Comparison of emission maxima ($\lambda_{max}^{em}$) of **(1-12).Br** with previously reported **(1-12).H**,[67] **(1-12).F**[57] and **(1-12).Cl**[58] in DMF-$H_2O$ (3:7) system at fixed concentration of 1 x $10^{-7}$ mol/L.

To further shed light on the interplay of weak interactions in solution state self-assembly and their relation to the emission properties, and to judge the effect of solvent nature and polarity on the emission intensity, compound **12.Br** which showed maximum emission intensity was remeasured in pure DMF instead of DMF:$H_2O$ mixture at a concentration of 1 x $10^{-7}$ mol/L. Intriguingly, emission intensity was greatly enhanced. The increase in emission intensity of **12.Br** in pure DMF as compared to DMF:$H_2O$ (3:7) binary mixture is most probably due to its polar aprotic nature. Water being polar protic solvent has stronger ability of hydrogen bonding with bromo substituent, due to which it cannot donate its lone pair of electrons effectively to the conjugated backbone, resulting in decreased intramolecular charge transfer. However, no such hydrogen bonding can be expected in pure DMF solvent. This observation is also consistent with our previously reported other halogenated analogs.[57, 58] The measurements of emission intensity of compounds **(1-12).Br** in pure water could not be realized because of their insolubility in pure water. Figure 7 demonstrates photoluminescence of 1-(3,4-dimethylphenyl)-3-(4-

bromophenyl)-5-(4-butoxyphenyl)-2-pyrazoline **12.Br** in ethyl acetate, however, it was not quantitatively measured.

**Figure 7.** Photoluminescence of 1-(3,4-dimethylphenyl)-3-(4-bromophenyl)-5-(4-butoxyphenyl)-2-pyrazoline **12.Br** in ethyl ethanoate ($1 \times 10^{-3}$ mol/L).

## 4. Conclusions

In conclusion, we have synthesized a series of new 1,3,5-triaryl-2-pyrazolines **(1-12).Br** bearing one to twelve carbon alkyloxy side chain in order to investigate the interplay of non-covalent interactions and fluorescence properties by UV-Vis and emission spectroscopy. The fluorescence for all the compounds was observed in the blue region of the visible spectrum. However, influence of alkyloxy chain length in **(1-12).Br** having same fluorophore is quite obvious from the absorption maxima ($\lambda_{max}^{abs}$ 404-414 nm) and emission maxima ($\lambda_{max}^{em}$ 467-479 nm) ranges. The compound **12.Br** among the present series showed maximum emission intensity highlighting the importance of weak van der Waals forces. From the results of the present study and previous studies,[67, 57, 58] it is also quite evident that the chain length of alkyloxy substituent governs the aggregation/self-assembly in ground/excited states in DMF:water binary solution. Furthermore, comparative analysis of the present series with previously reported **(1-12).H**, **(1-12).F** and **(1-12).Cl** compounds with no, fluoro and chloro substituents, respectively revealed that absorption and emission maxima wavelengths are dependent on the electron donating nature of the substituents. For example, the compounds **(1-12).F** bearing the most electronegative fluorine atom showed the maximum absorbance at lower wavelengths [337-364 nm] as compared to **(1-12).H** [367-377 nm], **(1-12).Cl** [408-416 nm] and **(1-12).Br** [404-414 nm]. On the basis of similar analysis of emission intensity, it can be stated that 1,3,5-triaryl-2-pyrazolines with alkyloxy chain of less than six carbon atoms have low emission intensity with random trend, most probably due to different available modes of interactions with their own molecules or with the solvent molecules. As the chain becomes equal to or longer than six carbons, the van der Waals forces start to dominate and the emission intensity generally increases. However, the compounds of the **(1-12).H** series with longer alkyloxy groups showed maximum intensity as compared to compounds of **(1-12).F**, **(1-12).Cl** and **(1-12).Br** series, most likely due to the involvement of halogen in different non-covalent interactions. The results of the present study provide constructive hints for controlling/optimizing the optoelectronic and luminescence properties of OLEDs.

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