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Ultrasound-Accelerated Synthesis of Quinoline-Based Luminescent Imines Exhibiting Large Stokes Shift[1]

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Abstract—High yield synthesis of quinoline-based fluorescent imines, exhibiting the highest Stokes shift exceeding 380 nm (>18 000 cm^{-1}), is reported in the current publication. Such large difference in the excitation and emission wavelengths is quite unusual. Synthesis of imines was accelerated by ultrasound. Both experimental and theoretical studies have been performed.

Keywords: quinoline, fluorescence, Stokes shift

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Organic photoluminescent compounds with large Stokes shift and high photostability are of certain importance in synthetic organic chemistry and design of materials possessing superior biological and other properties. Fluorescent compounds with large Stokes shift are particularly important as UV in polymers stabilization, sun-creams [1, 2], live cell imaging [3], and super-resolution optical microscopy [4]. Fluorescent organic compounds with large Stokes shift (typically over 80 nm) can minimize overlapping between excitation and fluorescent emission bands thus providing high signal-to-noise ratio [5]. In quest of such materials, many luminescent compounds were reported to have remarkably high Stokes shift, most notably comprising of xanthene [6], benzoxazoles [3], oligo-phenylenes [7], triazine [2], and some others. The present study is devoted to the synthesis of quinoline based luminescent imines, characterized by largest Stokes shift up to > 380 nm (> 18000 cm^{-1}). To our best knowledge, the Stokes shifts observed in the present work are among the largest reported so far (Scheme 1).

Quinoline derivatives are important initial compounds in creating optical materials. Aluminium tris-chelate complex of 8-hydroxy-quinoline is already used in development of organic light emitting diodes (OLEDs). Herein, the ultrasound accelerated synthesis of some quinoline based luminescent Schiff's bases containing multiple heterocyclic moieties and exhibiting very large Stokes shift, is reported. Theoretical studies also have been carried out to explore luminescent behavior of the synthesized compounds.

RESULTS AND DISCUSSION

Synthesis. The target compounds **3a–3f** were synthesized in two steps process, in which the modified Vilsmeier–Haack reaction of 2-chloro-3-formyl quinoline was followed by formation of the products **3a–3f** (Scheme 2, Table 1).

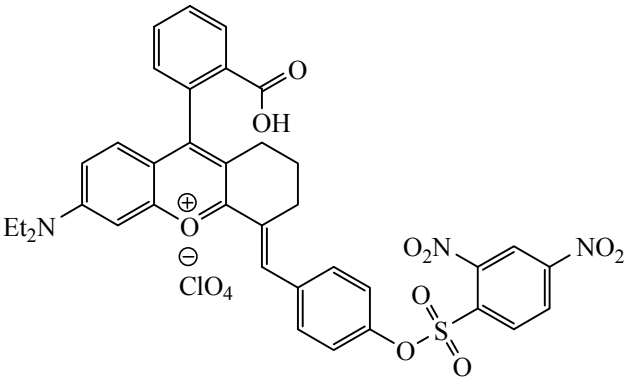
Luminescence study. Six Schiff bases with diverse aromatic amines have been synthesized and their luminescence was studied to explore the effect of π-electronic cores rather than mere effect of different substituents. In that regard, keeping the aldehyde group of the Schiff base to be the same, changes in the imine containing fragment were brought about. Out of these six compounds, two monoaromatic **3a, 3b**, three fused ring system **3c–3e**, and one discrete ring skeleton **3f** were considered to impose diversity in aromatic π-electronic distribution.

UV-Vis (Fig. 1) and fluorescence (Fig. 2) spectra of solutions (10^{-5} M) of the compounds **3a–3f** were studied.

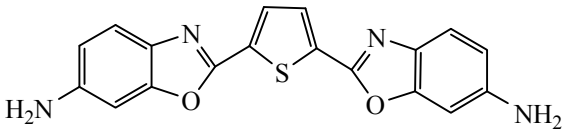
The compounds exhibited photoluminescence with moderate to strong intensity when irradiated with UV radiation of suitable excitation frequency (Table 2). Most notably, very high Stokes shift was observed in

[1] The text was submitted by the authors in English.

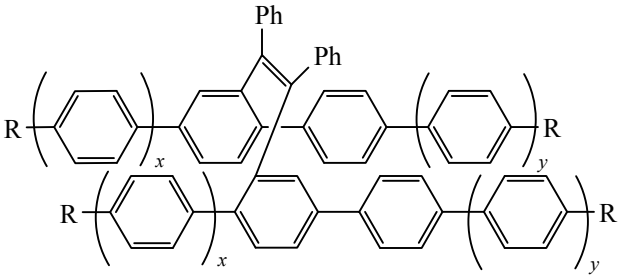
Scheme 1.



Stokes shift: 160 nm
[6]

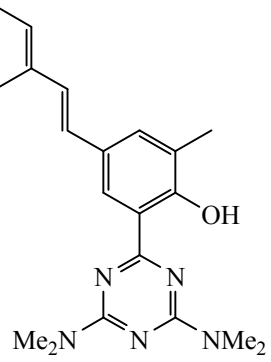


Stokes shift: 187 nm
[3]

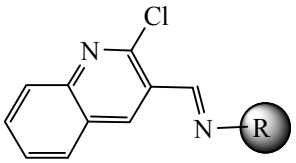


$x = 1, 2$; $y = 0, 1$; R = H, Me

Stokes shift: 203 nm
[7]



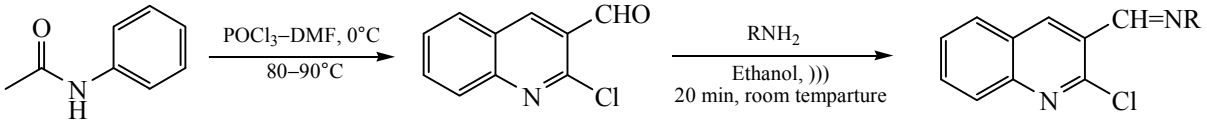
Stokes shift: 220 nm
[2]



3b

Higest Stokes shift (in the series): 383 nm
[Present work]

Scheme 2.



2-chloro-3-formyl quinoline

3a–3f

three compounds **3b, 3d, 3f,** reaching its value as high as 383 nm (**3b**). The interesting feature observed here was correlation between the Stokes shift and the electron release/withdrawing nature of the imine fragment of the Schiff base. Stronger electron withdrawing moiety attached to nitrogen of the imine group was matching with the increase in the Stokes shift.

Heterocyclic fused ring systems attached to both sides of the imine moiety did not change the emission frequency appreciably but there was some change in

Table 1. The imines **3a–3f** synthesized

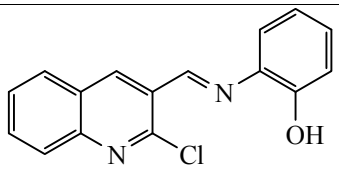
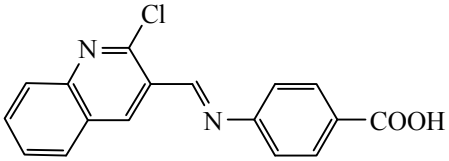
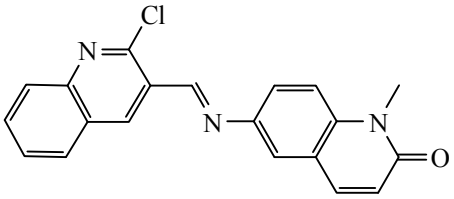
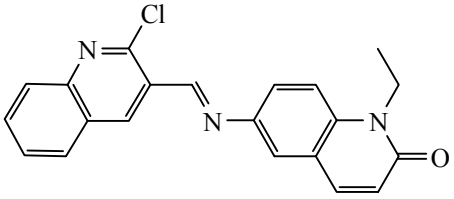
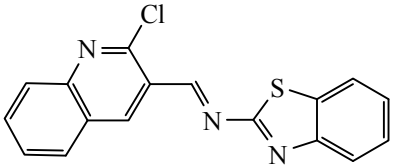
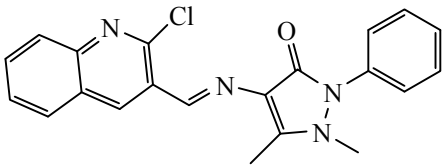
Comp. no.	Amines RNH_2	Imines	mp, °C	Yield, %
3a	2-Aminophenol		180	78
3b	4-Aminobenzoic acid		210	78
3c	6-Amino-1-methylquinolin-2(1*H*)-one		220	71
3d	6-Amino-1-ethylquinolin-2(1*H*)-one		214	73
3e	2-Aminobenzothiazole		228	77
3f	4-Aminoantipyrine		190	87

Table 2. Excitation, emission and Stokes shift exhibited by the compounds **3a–3f**

Comp. no.	Excitation, nm	Emission, nm	Stokes shift, nm
3a	377	438	61
3b	297	680	383
3c	368	437	69
3d	264	451	187
3e	371	438	67
3f	318	438	120

excitation value thereby rendering an appreciable change in the Stokes shift.

Computational study. Electronic transitions and associated luminescence theoretical studies were carried out using Gaussian09 package. The structures of all six compounds were optimized under DFT at B3LYP level theory with 6-31G** basis set [8, 9]. After optimization of the structures the energies of HOMO and first three LUMOs were mainly considered in the study. The energy level of all six compounds are plotted and presented in Fig. 3. MO's

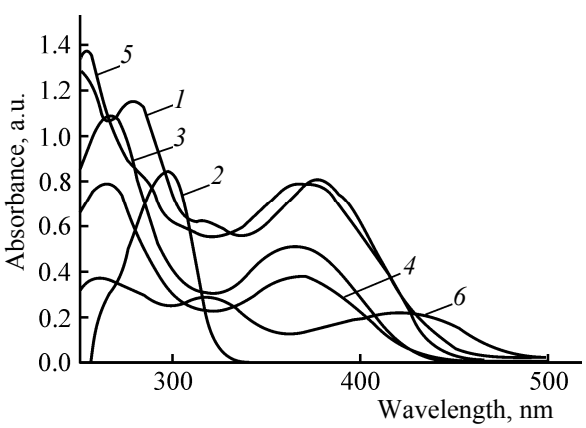


Fig. 1. UV-Vis spectra of the compounds (*1*) **3a**, (*2*) **3b**, (*3*) **3c**, (*4*) **3d**, (*5*) **3e**, and (*6*) **3f.**

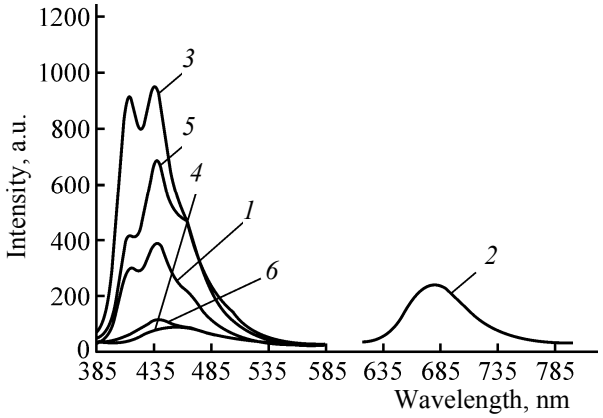


Fig. 2. Fluorescence spectra of the compounds (*1*) **3a**, (*2*) **3b**, (*3*) **3c**, (*4*) **3d**, (*5*) **3e**, and (*6*) **3f.**

of the compound **3b** which exhibited the highest Stokes shift are presented in Fig. 4.

According to the accumulated data the HOMOs of all six compounds had similar energies, particularly compounds **3a**, **3c**, **3d**, which indicated similarity in electronic distribution in the aromatic ring directly connected with the imine nitrogen. The electron donating effect of oxygen in **3a** and heterocyclic nitrogen in **3c, 3d** seemed to be similar.

According to fluorescence spectra (Fig. 2), all compounds exhibited luminescence when excited with suitable excitation wavelength (Table 2). Among those, the compound **3b** exhibited very high Stokes shift of 383 nm and fluoresces at 680 nm upon excitation with 297 nm wavelength. The theoretically calculated energy levels (Fig. 3) indicated that the presence of comparatively low lying consecutive unoccupied molecular orbitals in **3b** were likely to be responsible for such high Stokes shift. Such suppression in the energy level could be due to the presence of the electron withdrawing group –COOH. The observed λ_{max}^{abs} at 297 nm was in accord with theoretically calculated electron transition from HOMO to LUMO+2 (due to low lying orbitals). The electron upon shifting down to some lower MO, underwent some intersystem crossing, releasing comparatively lower energy photons to reach the ground level. This seemed to be the reason for the long wavelength fluorescence exhibited by **3b**. In all other cases (**3a, 3c, 3e, 3f),** the HOMO–LUMO (and other UMOs) energy gaps were much larger and the luminescence could originate from the excitation due to HOMO to higher MO's and transition followed by spin relaxation.

The study indicated also that there was an inverse relationship between the Stoke shift and "closeness" between the HOMO and higher MO's (Fig. 5), which was more pronounced in higher participating MO's. The Stokes shift of the emission from the quinoline based Schiff bases containing fluorophores was found to be strongly dependent on the electron releasing/ withdrawing groups connected to it and less prone to the type of aromatic moiety connected to the quinoline system via the imine linkage. The computational study indicated that the HOMO's of all these compounds were mostly localized in certain portions of the molecules, whereas the higher MO's participating in the excitation of electron in the course of absorption of energy (like the LUMO+2 for **3b**), could be distributed more evenly throughout the whole molecular skeleton. The HOMO, LUMO and LUMO+2 orbitals of the compounds **3a** (lowest Stokes shift) and **3b** (highest Stokes shift) are presented in Fig. 5 as the representative cases. Thus, a change in electron density occurring at the later segment affected the Stokes shift to a large extent.

EXPERIMENTAL

All amines were purchased from Sigma-Aldrich and used as obtained without further purification. The solvents were procured from Qualigen India and Ranchem India, and distilled before use.

^{1}H NMR spectra were measured on a BrukerAvance II, 400 MHz spectrometer in $CDCl_3$ using TMS as an internal standard. UV-Vis absorption spectra were recorded in $CHCl_3$ and DMSO on a JASCOV-670 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4600 spectrophotometer.

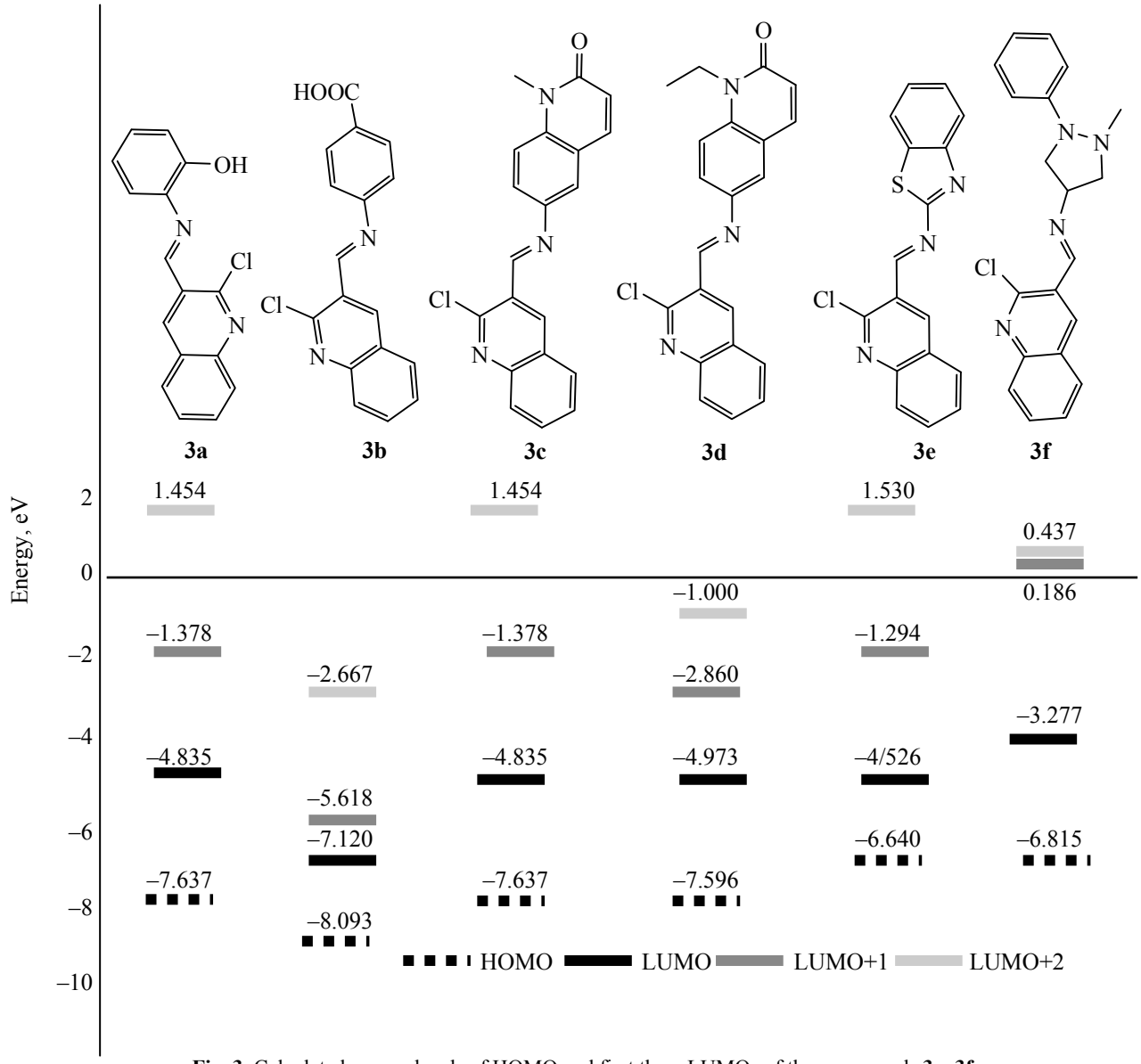


Fig. 3. Calculated energy levels of HOMO and first three LUMOs of the compounds **3a–3f**.

2-Chloro-3-formyl quinoline (**1**) was synthesized according to the developed earlier method [10].

Synthesis of Schiff bases 3a–3f. A solution of 2-chloro-3-formyl quinoline (1 mmol) in ethanol was added to an ethanol solution of an amine **2a–2f** (1 mmol). The mixture was sonicated for 20 min with 40 kHz ultrasound sonicator at room temperature. The product started precipitating after 15 min of sonication, which was continued for 5 min more. A product was filtered off and recrystallized from absolute ethanol to give the corresponding yellow crystalline compound **3a–3f**. The test reaction was also performed with conventional refluxing in presence of a few drops of glacial acetic acid as a catalyst, which gave similar yield after 3–4 h of refluxing.

2-[(2-Chloroquinolin-3-yl)methyleneamino]phenol (3a). Yield 78%, mp 180°C. ^{1}H NMR spectrum, δ, ppm: 6.986 t (1H), 7.074 d (1H), 7.273–7.294 m (1H), 7.402 d (1H), 7.633 t (1H), 7.817 t (1H), 7.983 d (1H), 8.069 d (1H), 8.977 s (1H), 9.214 s (1H), 10.5 s (1H). ^{13}C NMR spectrum, δ, ppm: 115.4, 116.3, 120.4, 127.1, 127.3, 127.8, 128.5, 128.8, 130.1, 132.2, 135.1, 137.4, 148.6, 150.2, 152.3, 152.7.

4-[(2-Chloroquinolin-3-yl)methyleneamino]benzoic acid (3b). Yield 78%, mp 210°C. ^{1}H NMR spectrum,

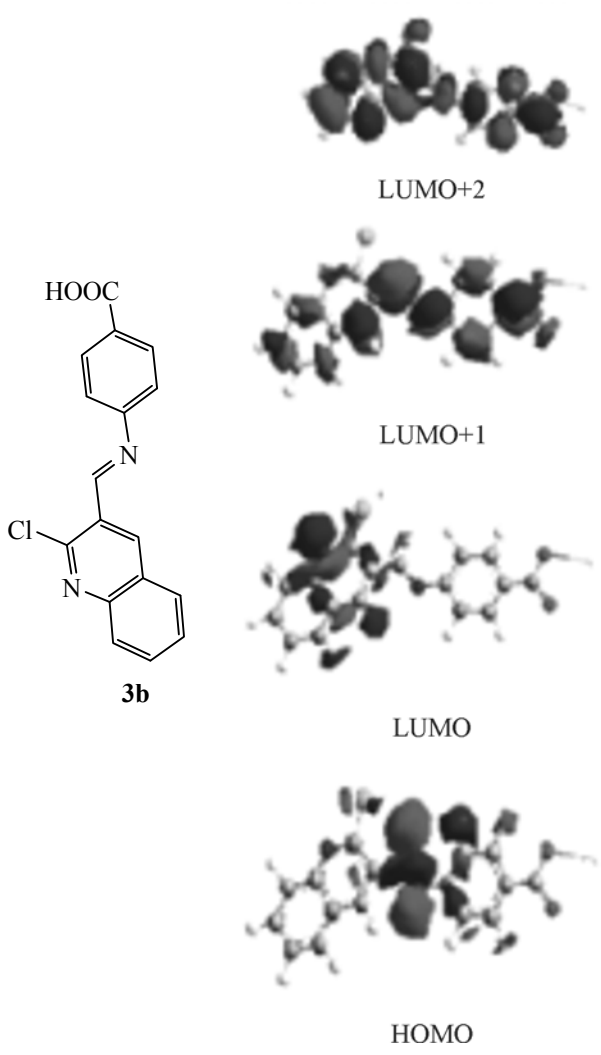


Fig. 4. MO's of the compound **3b**.

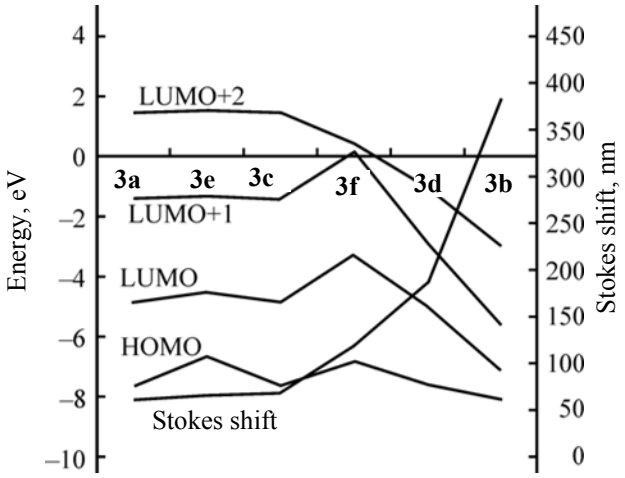


Fig. 5. Trends in molecular orbital energy and Stoke shift.

δ, ppm: 6.566 d (1H), 7.753 s (1H), 7.773 d (2H), 8.297 d (2H), 8.992 s (1H), 10.392 s (1H). ^{13}C NMR spectrum, δ, ppm: 112.5, 116.8, 121.2, 126.3, 126.4, 127.7, 128.2, 130.2, 131.2, 133.9, 141.4, 148.5, 148.9, 153.0, 167.4, 189.4.

6-[(2-Chloroquinolin-3-yl)methyleneamino]-1-methylquinolin-2(1H)-one (3c). Yield 71%, mp 220°C. ^{1}H NMR spectrum, δ, ppm: 3.775 s (3H), 6.792 d (1H), 7.445 s (1H), 7.468 s (1H), 7.535 d (1H), 7.606 d (1H), 7.751 d (1H), 7.820–8.079 m (4H), 9.085 s (1H). ^{13}C NMR spectrum, δ, ppm: 29.7, 115.2, 120.7, 121.3, 122.7, 124.3, 127.2, 127.7, 128.5, 128.9, 132.1, 137.7, 138.7, 145.4, 148.6, 150.2, 155.5, 166.9.

6-[(2-Chloroquinolin-3-yl)methyleneamino]-1-ethylquinolin-2(1*H*)-one (3d). Yield 73%, mp 214°C. ^{1}H NMR spectrum, δ, ppm: 1.405 t (3H), 4.409 d (2H), 6.769 d (1H), 7.450 s (1H), 7.473 s (1H), 7.536 d (1H), 7.601 m (1H), 7.623 m (1H), 7.708 d (1H), 7.813 t (1H), 7.961 d (1H), 8.049 d (1H), 9.076 s (1H). ^{13}C NMR spectrum, δ, ppm: 12.8, 37.5, 115.0, 120.9, 121.6, 122.7, 124.3, 127.2, 127.4, 127.7, 128.5, 128.9, 132.0, 137.6, 138.1, 138.7, 145.2, 148.6, 150.2, 155.3, 161.6.

***N*-[(2-Chloroquinolin-3-yl)methylene]benzo[*d*]-thiazol-2-amine (3e).** Yield 77%, mp 228°C. ^{1}H NMR spectrum, δ, ppm: 7.432 t (1H), 7.562–7.581 m (2H), 7.644 s (1H), 7.911 t (1H), 7.984 d (1H), 8.004 d (1H), 8.141 d (1H), 9.213 s (1H), 9.643 d (1H). ^{13}C NMR spectrum, δ, ppm: 113.3, 119.6, 122.1, 123.3, 126.2, 126.9, 127.2, 127.6, 128.3, 129.4, 133.3, 136.7, 140.7, 148.0, 148.1, 166.2, 169.3.

4-[(2-Chloroquinolin-3-yl)methyleneamino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (3f). Yield 87%, mp 190°C. ^{1}H NMR spectrum, δ, ppm: 2.559 s (3H), 3.225 s (3H), 7.539 s (1H), 7.557 m (2H), 7.560 d (2H), 7.577 t (1H), 7.721 t (1H), 7.928 d (1H), 7.997 d (1H), 8.914 s (1H), 10.215 s (1H). ^{13}C NMR spectrum, δ, ppm: 10.1, 35.6, 118.7, 124.7, 127.2, 127.3, 127.3, 128.4, 128.5, 129.3, 129.6, 130.9, 134.5, 135.3, 148.0, 150.8, 152.1, 152.2, 160.5.

CONCLUSIONS

In this study, some luminescent quinoline based imines with very high Stokes shift were considered in presence of electron withdrawing groups containing aromatic moiety. The presence of aromatic ring (carbocyclic–heterocyclic–fused ring) at the nitrogen site of the imine group could be particularly important for the fluorescence. The emission maxima could be

tuned by attached electron donating/ withdrawing groups at the aromatic moiety.

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