

Ruthenium(II)-2, 2'-bipyridine/1, 10-phenanthroline complexes incorporating (E)-2-(((5-((4-methoxyphenyl)ethynyl)pyridin-2-yl) imino)methyl)-4-((4-nitro phenyl)ethynyl)phenol as a ligand

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Abstract

A new series of hexa-coordinated Ru(II) complexes of the type $[Ru(L)(phen)_2]X$ (1a–d) and $[Ru(L)(bipy)_2]X$ (2a–d) (where phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine, X=NO₃, BF₄, ClO₄, PF₆) have been prepared by the reaction of (E)-2-(((5-((4-methoxyphenyl)ethynyl)pyridin-2-yl)imino)methyl)-4-((4-nitrophenyl)ethynyl)phenol (L) with $[Ru(phen)_2]$ $Cl_2 \cdot 2H_2O$ and $[Ru(bipy)_2]Cl_2 \cdot 2H_2O$. The complexes were characterized by physico-chemical and spectroscopic methods. All complexes are 1:1 conducting and diamagnetic in nature. In acetonitrile solution, the complexes displayed one reversible Ru(II)-Ru(III) oxidation couple and one irreversible Ru(III)-Ru(IV) oxidation and are sensitive to π -acidic character of phen and bipy ligands. The complexes show room-temperature luminescence originated from the lowest energy metal-to-ligand charge transfer excited state and are sensitive to difference in size of the counter anions. All the complexes displayed second harmonic generation by Kurtz-powder technique indicating their potential for the application as a useful NLO material.

Introduction

The chemistry of ruthenium-polypyridine complexes has gained enormous interest during the past few years due to their rich electrochemical and photophysical properties. Facile electron-donor transfer properties, strong metal-to-ligand charge transfer character and long-lived MLCT excited states of these complexes make them attractive for the construction of photochemical and electrochemical devices [1, 2]. They are also important in energy conversion, luminescence sensors, electroluminescence display and biotechnology [3-5]. The most extensively explored complexes are $[Ru(bipy)_2]^{2+}$ (**bipy** = 2,2'-bipyridine) and $[Ru(phen)_2]^{2+}$ (**phen** = 1,10-phenanthroline) because they show relatively long-lived excited state life time and are readily fluorescent at room temperature [6]. Their unique properties have led them being used to investigate photochemically induced

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S. S. Chavan sanjaycha2@rediffmail.com charge-transfer, ligand substitution, stereochemical isomerisation process and to probe metal-ligand interactions. In recent years, considerable research interest has been paid on the development of newer class of ruthenium-polypyridyl complexes either by introducing selective groups or by using other types of donor sites to generate new mixed ligand ruthenium complexes with the perspective of tuning their spectroscopic and photo-redox properties [7]. Furthermore, the presence of counter anions can play a crucial role in unique properties of these complexes, since the anions have many features such as negative charge, size and geometry. These complexes possess their potential applications in diverse area such as photosensitizers for photochemical conservation of solar energy, molecular electron devices and as photoactive DNA cleavage agents for therauptic purposes [8–10]. Many compounds of this type such as $[Ru(bipy)_2]^{2+}$ or $[Ru(phen)_2]^{2+}$ with various ligands like pyrroles [11], imidazole-4,5-dicarboxylic acid or biquinoline derivatives [12] and chiral salicylixazolinate [13-15] have been reported.

In this paper, we report the introduction of alkynyl-functionalized N, O donor Schiff base ligand L in the $[Ru(bipy)_2]$ Cl_2 and $[Ru(phen)_2]Cl_2$ core to prepare new mixed ligand complexes of the kind $[Ru(L)(bipy)_2]X$ (1a–d) and [Ru(L)(phen)₂]X (2a–d) (where L = 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenyl) ethynyl)phenol; phen = 1,10 phenanthroline, bipy = 2,2'

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bipyridine $X = NO_3^-$, BF_4^- , CIO_4^- , PF_6^-). The effects of newly introduced group L as well as influence of counter anion on the spectroscopic and luminescence properties of the complexes have been studied. The electrochemical behaviour and second harmonic generation (SHG) properties of the complexes have also been reported.

Experimental

Materials and general methods

All chemicals used were of analytical reagent grade purchased from Sigma-Aldrich and used without further purification. Solvents used for synthesis were distilled over appropriate drying reagents. $[Ru(phen)_2]Cl_2$ [16], $[Ru(bipy)_2]Cl_2$ [17] and 5-((4-nitrophenyl)ethynyl)salicylaldehyde were prepared according to the literature procedure [18].

Elemental analyses (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Infrared spectra were recorded on PerkinElmer FT-IR spectrometer as KBr pellets in the 4000-400 cm⁻¹ spectral range. ¹H NMR spectra of the samples were measured on Bruker-300 MHz instrument using TMS [(CH₃)₄Si] as an internal standard. Luminescence properties were measured using a PerkinElmer LS 55 spectrofluorometer equipped with quartz cuvette of 1 cm path length at room temperature. Cyclic voltammetry measurements were taken on CH-400A electrochemical analyzer. A standard three-electrode system consisting of Pt disk working electrode, Pt wire counter electrode and Ag/ AgCl reference electrode were used. All measurements were taken in CH₃CN solution at room temperature with scan rate 100 m Vs⁻¹ by using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Thermal analysis of the complexes was carried out on a PerkinElmer thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C/min. The SHG efficiency of all the complexes was measured with respect to urea by powder technique developed by Kurtz and Perry using Q switched Nd-YAG laser (Lab-170 spectra physics) 10 ns laser with first harmonic output of 1064 nm at the pulse repetition rate 10 Hz. The homogeneous powder was mounted in the path of laser beam of pulse energy 2.2 mJ obtained by split beam technique.

Synthesis of 5-((trimethylsilyl)ethynyl) pyridin-2-amine (1)

To a mixture of 5-iodo-pyridin-2-amine (1 mmol, 0.22 g), trimethylsilylacetylene (1 mmol, 0.13 ml), $PdCl_2(PPh_3)_2$ (0.01 mmol, 0.032), CuI (0.02 mmol, 0.017 g), 30 ml of Et₃N was added. The resultant mixture was then stirred at

room temperature for about 24 h. The reaction mixture was filtered and concentrated under *vacuo*. The residue obtained was purified by column chromatography on neutral alumina using dichloromethane: petroleum ether (1:3) as eluent. An off-white coloured product was afforded by removal of solvent under *vacuo* and identified as 5-((trimethylsilyl)ethynyl) pyridin-2-amine.

Yield: 85% (0.853 mmol, 0.162 g). (Elemental analysis (C, H, N, w/w%) Anal. Calc. For $C_{10}H_{14}N_2Si_1$: C, 63.1; H, 7.3; N, 14.7. Found: C, 63.0; H, 7.3; N, 14.7; IR (KBr, cm⁻¹): 2167 (C=C). ¹H NMR (300 MHz, CDCl₃): δ 7.23 (s, 1H, ArH), 6.53 (d, 2H, ArH), 3.62 (br s, 2H, NH₂), 0.24 (s, 9H, Si(CH₃)₃). ¹³C NMR (CDCl₃; 300 MHz): δ 156.1, 148.3, 131.8, 120.9, 119.8, 98.7, 97.3, 29.7. MS (ESI): m/z 190 [M⁺].

Synthesis of 5-(ethynyl)pyridine-2-amine (2)

Powdery KOH (1 mmol, 0.056 g) was added to a solution of 5-((trimethylsilyl)ethynyl)pyridin-2-amine (1 mmol, 0.190 g) in 20 ml of methanol, and the resulting solution was stirred at room temperature for 2–3 h. The solvent was removed under *vacuo*, and residue was extracted with CH_2Cl_2/H_2O . The organic layer was collected, dried and passed through a neutral alumina column using 1:3 dichloromethane: petroleum ether as eluent. The removal of solvent under *vacuum* afforded a yellow coloured solid.

Yield: 81% (0.814 mmol, 0.096 g). Elemental analysis (C, H, N, w/w%) Anal. Calc. For $C_7H_6N_2$: C, 71.1; H, 5.1; N, 23.7. Found: C, 71.1; H, 5.1; N, 23.7. IR (KBr, cm⁻¹): 2198, (C=C). ¹H NMR (300 MHz, CDCl₃): δ 7.26 (d, 2H, Ar–H), 6.56 (d, 2H, Ar–H), 3.76 (br s, 2H, NH₂), 3.12 (s, 1H, C=C–H). ¹³C NMR (CDCl₃; 300 MHz): δ 156.3, 149.3, 129.8, 121.7, 120.5, 99.3, 97.9. MS (ESI): m/z 118 [M⁺].

Synthesis of 5-((4-methoxyphenyl)ethynyl) pyridine-2-amine (3)

To a mixture of 1-iodo-4-methoxybenzene (1 mmol, 0.234 g), 5-(ethynyl)pyridin-2-amine (1 mmol, 0.118 g), $PdCl_2(PPh_3)_2$ (0.01 mmol, 0.056 g), CuI (0.02 mmol, 0.016 g), 30 ml of Et₃N was added. The resulting mixture was stirred for 24 h at 40 °C. Then the reaction mixture was filtered off and dried under *vacuo*. The residue obtained was purified by column chromatography on silica gel using dichloromethane: petroleum ether (1:1) as eluent. The brown coloured solid was afforded by removal of solvent under *vacuo*.

Yield: 88% (0.879 mmol, 0.197 g). Elemental analysis (C, H, N, w/w%) Anal. Calc. For $C_{14}H_{12}N_2O_1$: C, 74.9; H, 5.3; N, 12.5. Found: C, 74.9; H, 5.3; N, 12.5. IR (KBr, cm⁻¹): 2209, (C=C); 1171, v(OCH₃). ¹H NMR (300 MHz, CDCl₃): 7.75 (d, 2H, Ar–H), 7.68 (d, 2H, Ar–H), 7.65 (d, 1H, Ar–H),

7.47 (dd, 1H, Ar–H), 7.00) (d, 7.75 (d, 2H, Ar–H), 7.68 (d, 2H, Ar–H), 7.65 (d, 1H, Ar–H), 7.47 (dd, 1H, Ar–H), 7.00) (d, 1H, Ar–H), 3.85 (s, 3H, OCH₃), 3.76 (s, 2H, NH₂). ¹³C NMR (CDCl₃; 300 MHz): δ 156.3, 149.7, 147.1, 140.1, 135.9, 131.4, 129.3, 127.6, 99.1, 97.7, 55.3. MS (ESI): m/z 473. MS (ESI): m/z 224 [M⁺].

Synthesis of (E)-2-(((5-((4-methoxyphenyl)ethynyl) pyridin-2-yl)imino)methyl)-4-((4-nitro phenyl) ethynyl)phenol (L)

To a solution of 5-((4-nitrophenyl)ethynyl)salicyaldehyde (1 mmol, 0.267 g) in methanol (10 ml), the solution of 5-((4-methoxyphenyl)ethynyl)pyridin-2-amine (1 mmol, 0.224 g) in CH_2Cl_2 (10 ml) was added and refluxed for 2 h. Completion of reaction was checked by TLC. After evaporation of solvent the obtained orange coloured solid was washed with diethyl ether, recrystallized from methanol and dried in *vacuo*.

Yield: 89% (0.89 mmol, 0.421 g). Elemental analysis (C, H, N, w/w%) Anal. Calc. For $C_{29}H_{19}N_3O_4$: C, 73.5; H, 4.0; N, 8.8. Found: C, 73.3; H, 3.9; N, 9.0. IR (KBr, cm⁻¹) v_{max} : 3268 (OH), 2062 (C=C), 1635 (C=N), 1288 (C–O), 1161 (OCH₃), 1470 (NO₂), 3014 (C–H, Ar strech), 1048 (C–H, Ar bend). ¹H NMR (CDCl₃; 300 MHz): δ 10.9 (s, 1H, OH), δ 8.34 (s, 1H, HC=N), δ 7.11–8.11 (m, 14H, Ar.), δ 3.87 (s, 3H, OCH₃). ¹³C NMR (CDCl₃; 300 MHz): δ 162.9, 158.2, 156.7, 154.9, 152.5, 149.9, 149.0, 147.7, 142.3, 140.5, 139.3, 135.9, 131.5, 130.5, 129.1, 127.7, 120.4, 119.7, 118.2, 99.1, 99.0, 98.1, 97.6, 55.3. MS (ESI): m/z 473 [M⁺].

Synthesis of [Ru(L)(phen)₂]X (1a-d)

To the solution of $Ru(phen)_2Cl_2$ (1 mmol, 0.532 g) in dry ethanol (10 ml), the ligand L (1 mmol, 0.473 g) in ethanol (10 ml) was added under nitrogen atmosphere. The reaction mixture in anaerobic condition was refluxed for 12 h, and completion of reaction was checked by TLC. Then, the reaction mixture was allowed to cool, and saturated aqueous solution of NaX (where $X = NO_3$, BF_4 , ClO_4 , PF_6) was added in 1:1 molar proportion. The product obtained was collected by filtration, washed with ethanol and dried in *vacuo*.

1a: Yield: 67% (0.67 mmol, 0.667 g). Elemental Analysis: Anal. Calc. for RuC₅₃H₃₄N₈O₇: C, 63.9%, H, 3.4%, N, 11.2%. Found: C, 63.8%, H, 3.33%, N, 11.3%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 26.02. IR (KBr, cm⁻¹) $\nu_{\rm max}$: 2056 (C≡C), 1643 (C=N), 1321 (C–O), 3054 (C–H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR: δ 9.18 (HC=N), δ 8.89–8.92 (d, 4H, phen), δ 7.17–8.07 (m, 26H, Ar.), δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 933 [M-NO₃]⁺. **1b**: Yield: 67% (0.67 mmol, 0.683 g). Elemental Analysis: Anal. Calc. for RuC₅₃H₃₄N₇O₄BF₄: C, 62.3%, H, 3.3%, N, 9.6%. Found: C, 62.2%, H, 3.2%, N, 9.6%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²

 mol^{-1}): 25.16. IR (KBr, cm⁻¹) v_{max} : 2056 (C=C), 1647 (C=N), 1319 (C-O), 3054 (C-H, Ar strech), 1055 (C-H, Ar bend). ¹H NMR: δ 9.29 (HC=N), δ 8.89–8.92 (d, 4H, phen), δ 7.17-8.07 (m, 26H, Ar.),δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 933 [M-BF₄]⁺. 1c: Yield: 69% (0.69 mmol, 0.713 g). Elemental Analysis: Anal. Calc. for Found: RuC₅₃H₃₄N₇O₈Cl: C, 61.6%, H, 3.3%, N, 9.4%. Found: C, 61.3%, H, 2.9%, N, 9.6%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 25.11. IR (KBr, cm⁻¹) v_{max} : 2056 (C=C), 1649 (C=N), 1327 (C-O), 3054 (C-H, Ar strech), 1055 (C-H, Ar bend). ¹H NMR: δ 9.40 (HC=N), δ 8.89–8.92 (d, 4H, phen), δ 7.17-8.07 (m, 26H, Ar.),δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 933 $[M-ClO_4]^+$. 1d: Yield: 67% (0.67 mmol, 0.722 g). Elemental Analysis: Anal. Calc. for RuC₅₃H₃₄N₇O₄PF₆: C, 59.0%, H, 3.1%, N, 9.0%. Found: C, 58.9%, H, 3.0%, N, 9.0%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 24.91. IR (KBr, cm⁻¹) v_{max}: 2056 (C≡C), 1650 (C=N), 1328 (C-O), 3054 (C-H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR: δ 9.42 (HC=N), δ 8.89–8.92 (d, 4H, phen), δ 7.17–8.07 (m, 26H, Ar.),δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 933 [M-PF₆]⁺.

Synthesis of [Ru(L)(bipy)₂]X (2a-d)

To a solution of $\text{Ru}(\text{bipy})_2\text{Cl}_2$ (1 mmol, 0.484 g) in dry ethanol (10 ml), the ligand **L** (1 mmol, 0.473 g) in ethanol (10 ml) was added under nitrogen atmosphere. The reaction mixture in anaerobic condition was refluxed for 12 h, and completion of reaction was checked by TLC. Then the reaction mixture was allowed to cool and saturated aqueous solution of NaX (where X=NO₃, BF₄, ClO₄, PF₆) was added in 1:1 molar proportion. The product obtained was collected by filtration, washed with ethanol and dried in *vacuo*.

2a: Yield: 68% (0.68 mmol, 0.645 g). Elemental Analysis: Anal. Calc. for RuC₄₉H₃₄N₈O₇: C, 62.0%, H, 3.6%, N, 11.8%. Found: C, 62.0%, H, 3.2%, N, 11.9%. Λ_m (CH₃CN, Ω^{-1} cm²mol⁻¹): 27.44. IR (KBr, cm⁻¹) v_{max} : 2056(C=C), 1643 (C=N), 1306 (C-O), 3054 (C-H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR: δ 9.11 (HC=N), δ 8.69–8.72 (dd, 4H, bipy), δ 6.44–8.25 (m, 26H, Ar.), δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 885 [M-NO₃]⁺. **2b**: Yield: 61% (0.61 mmol, 0.593 g). Elemental Analysis: Anal. Calc. for RuC₄₉H₃₄N₇O₄BF₄: C, 60.5%, H, 3.5%, N, 9.4%. Found: C, 60.3%, H, 3.2%, N,9.5%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 26.47. IR (KBr, cm⁻¹) v_{max} : 2056(C=C), 1644 (C=N), 1314 (C–O), 3054 (C–H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR: δ 9.13 (HC=N), δ 8.69–8.72 (dd, 4H, bipy), δ 6.44–8.25 (m, 26H, Ar.), δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 885 [M-BF₄]⁺. 2c: Yield: 64% (0.64 mmol, 0.63 g). Elemental Analysis: Anal. Calc. for RuC₄₉H₃₄N₇O₈Cl: C, 59.7%, H, 3.4%, N, 9.9%. Found: C, 59.6%, H, 3.0%, N, 10.0%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 26.01. IR (KBr, cm⁻¹) v_{max}: 2056(C≡C), 1646 (C=N), 1315 (C–O), 3054 (C–H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR: δ 9.21 (HC=N), δ 8.69–8.72 (dd, 4H, bipy), δ 6.44–8.25 (m, 26H, Ar.), δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 885 [M-ClO₄]⁺. **2d:** Yield: 61% (0.61 mmol, 0.629 g). Elemental Analysis: Anal. Calc. for RuC₄₉H₃₄N₇O₄PF₆: C, 57.0%, H, 3.3%, N, 9.5%. Found: C, 56.9%, H, 3.1%, N, 9.5%. $\Lambda_{\rm m}$ (CH₃CN, Ω^{-1} cm²mol⁻¹): 25.12. IR (KBr, cm⁻¹) $\nu_{\rm max}$: 2056(C≡C), 1650 (C=N), 1324 (C–O), 3054 (C–H, Ar strech), 1055 (C–H, Ar bend). ¹H NMR:δ 9.29 (HC=N),δ 8.69–8.72 (dd, 4H, bipy), δ 6.44–8.25 (m, 26H, Ar.), δ 3.87 (s, 3H, OCH₃). MS (ESI): m/z 885 [M-PF₆]⁺.

Results and discussion

The starting material 5-(ethynyl)pyridine-2-amine was prepared by using Pd(II)/Cu(I) catalyzed coupling of 5-iodo-2-aminopyridine followed by reaction with KOH in MeOH by following the procedure reported earlier [19]. Further coupling of 5-(ethynyl)pyridine-2-amine with 1-iodo-4-methoxybenzene afforded 5-((4-methoxyphenyl)ethynyl) pyridine-2-amine. The ligand L (E)-4-((4-methoxyphenyl) ethynyl)-2-(((6-((4-nitrophenyl)ethynyl)pyridine-2-yl)imino) methyl)phenol was obtained by the reaction of equimolar amount of 5-((4-methoxyphenyl) ethynyl)pyridine-2-amine and 2-hydroxy-5-((4-nitrophenyl)ethynyl)benzaldehyde in excellent yield (Scheme 1). To understand the influence of π -conjugation and size of counter anions, the mononuclear complexes $[Ru(phen)_2(L)]X$ (1a–d) and $[Ru(bipy)_2(L)]$ X(2a-d) were prepared by the reaction of L with [Ru(**phen**)₂Cl₂]·2H₂O and [Ru(**bipy**)₂Cl₂]·2H₂O followed by addition of NaNO₃, NaBF₄, NaClO₄ or NaPF₆ under N_2 atmosphere (where **bipy** = 2, 2'-bipyridine; **phen** = 1, 10-phenanthroline; $X = NO_3^-$, ClO_4^- , BF_4^- , PF_6^-). All the complexes are soluble in polar solvents such as DMSO, acetonitrile, and DMF. The results of elemental analyses and characterization of the complexes are in good agreement with the proposed formula (Fig. 1).

In the IR spectrum of L, a broad band appeared at 3268 cm⁻¹ is ascribed to v(OH). This band is diminished in the spectra of **1a–d** and **2a–d** indicating deprotonation of the phenolic proton before coordination. The medium-strong bands centred at 2062 and 1161 cm⁻¹ in L due to stretching frequency of $v(C \equiv C)$ and $v(OCH_3)$ remain unchanged in 1a-d and 2a-d. The v(C=N) stretching frequency at 1635 cm⁻¹ of free ligand L shifted to 1643–1650 cm⁻¹ in 1a-d and 1643-1650 cm⁻¹ in 2a-d is in accordance with the coordination of (HC=N) group to ruthenium ion in the complexes [20]. It is to be noted that changing the nature of co-ligands and counter ions in the complexes appears to have little effect on the v(C=N) frequency. A strong band observed at 1288 cm⁻¹ in L has been assigned to phenolic C-O stretching. On complexation, this band shifted to higher frequency in the range 1328–1306 cm^{-1} showing that the other coordination is through the phenolic oxygen atom [21, 22]. Bands in the 519–539 cm^{-1} and 465–490 cm^{-1} region are ascribed to the formation of Ru-N and Ru-O bonds, respectively [23]. This is further supported by the coordination of azomethine nitrogen and the phenolic oxygen to ruthenium ion. In **1b** and **2b**, the intense band at ~ 1080 cm⁻¹ is attributed to the anti-symmetric stretching mode due to BF_4^- ion [24]. The perchlorate complexes 1c and 2c exhibit broadband at ~ 1100 cm^{-1} , and the unsplit band at ~ 637 cm^{-1} suggests the stretching vibration of non-coordinated ClO_4^{-} ion [25]. However, the strong band exhibited at 847 cm⁻¹ and 568 cm⁻¹ in 1d and 2d has been consistent with the presence of PF_6^- anion in the complexes [26].

The ¹H NMR spectrum of free ligand **L** exhibits aromatic hydroxyl (–OH) group resonated at δ 10.9 ppm, which is absent in all the complexes. The singlet appeared at δ 8.34 and δ 3.87 ppm due to the azomethine (–HC=N–)







(Where $\mathbf{X} = NO_3$, BF_4 , ClO_4 , PF_6)

Fig. 1 Proposed molecular structure of the complexes I (1a-d) and II (2a-d)

and methoxy ($-OCH_3$) protons in the free ligand **L**, respectively. In **1a–d** and **2a–d**, the signal of azomethine proton is considerably deshielded to the range δ 9.11–9.25 ppm as a consequence of electron donation to the metal centre [27]. The singlet of methoxy protons is not much affected during complexation. The ring protons of **L** and **phen/bipy** moieties in **1a–d** and **2a–d** are overlapped in the region δ 6.68–8.92 ppm. So the unambiguous assignment of individual proton signal was not possible. However, the intensity of the aromatic signals with that of the observable azomethine (-CH=N-) and methoxy ($-OCH_3$) protons reveals the presence of expected number of aromatic protons for all the complexes. The proton counts in the NMR spectrum of each of the complex corroborated with the formulae of the products.

Electrochemistry (CV)

Electrochemical properties of the complexes 1a-d and 2a-d have been examined by cyclic voltammetry in CH₃CN solution $(10^{-3} \text{ M L}^{-1})$. The electrochemical data are listed in Table 1, and representative voltammogram is illustrated in Fig. 2. All the complexes display one reversible couple in the range 0.43-0.56 V for 1a-d and 0.39–0.52 V for 2a–d which are assigned to Ru(II)–Ru(III) process. Compared to $[Ru(phen)_3]^{2+}$ and $[Ru(bipy)_3]^{2+}$, the overall decrease in Ru(III) to Ru(II) potential by 0.7 to 0.9 V in **1a–d** and **2a–d** is due to incorporation of σ -donating anionic ligand L^{-} in $[Ru(phen)_2]^{2+}$ and $[Ru(bipy)_2]^{2+}$ core [28]. The complexes **1a–d** and **2a–d** exhibit a second irreversible oxidation process in the range 1.15-1.73 V and 1.15-1.73 V versus SCE which is assigned to Ru(III)-Ru(IV) process. The current height of this process is found to be greater

Table 1 Electrochemical data of 1a-d and 2a-d

Complex	$\operatorname{Ru}^{II}-\operatorname{Ru}^{III}$ couple ^a $E_{1/2}$ (V)	Ru^{III} - Ru^{IV} couple $E_{pa}(V)$	Ligand couple ^a E_1	_{/2} (V)
1a	0.43	1.46	-1.37	- 1.68
1b	0.47	1.61	-1.34	-1.64
1c	0.59	1.62	-1.21	-1.62
1d	0.56	1.57	-1.19	-1.51
2a	0.39	1.15	-1.57	-1.78
2b	0.41	1.27	-1.54	-1.74
2c	0.51	1.33	-1.51	-1.72
2d	0.52	1.29	-1.45	-1.71

Solvent, acetonitrile; Supporting electrolyte, tetrabutylaminoperchlorate; Reference electrode, SCE; Working electrode, Pt wire

 ${}^{a}E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively

than that of the previous Ru(II)-Ru(III) couple. The irreversibility of this oxidation in **1a-d** and **2a-d** indicates that the $[RuIV(L)(phen)_2]^{3+}$ and $[RuIV(L)(bipy)_2]^{3+}$ generated during the anodic scan are not stable in solution. This instability of $[RuIV(L)(phen)_2]^{3+}$ and $[RuIV(L)(bipy)_2]^{3+}$ may be due to their high reduction potential which makes them potential oxidant [29]. In addition to one reversible and one irreversible oxidation processes, 1a-d and 2a-d display two successive reversible one-electron reduction at -1.60 to -1.79 V and -1.50 to -1.75 V which are assigned to reduction of two N, N'- donor ligands in the complexes [7]. 2, 2'-bipyridine and 1, 10-phenanthroline are well-known potential electron-transfer centre, and each bipyridine and phenanthroline can accept two electrons in one electrochemically accessible LUMO [30]. Since the complexes 1a-d and 2a-d have two N, N'-donor units, four one-electron reductions are therefore

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expected. But in practice, we have observed two reductions within the ± 2 V potential range. The other expected two reductions could not be seen possibly due to solvent cut-off. In comparison of electrochemical data of the prepared complexes, the redox processes for **1a–d** appear at slightly more positive potential than those for the corresponding **2a–d**. This is attributed to better stabilization of **phen** in **1a–d** as compared to **bipy**-based **2a–d** as a consequence of its strong π -acidic character [31]. It is also observed that the $E_{1/2}$ values for **1a–d** are slightly greater than **2a–d** which concludes that the more the π -acidic character higher the $E_{1/2}$ values.

Absorption and emission properties

Electronic absorption spectra of L and its corresponding complexes **1a–d** and **2a–d** were recorded in acetonitrile solution (10⁻⁴ M L⁻¹). The spectral data are listed in Table 2, and the spectra of L and its complexes are illustrated in Figs. 3 and 4, respectively. The free ligand L exhibits high energy band at λ_{max} 274 and 384 nm which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions inside L. On the other hand, the spectra of **1a–d** display single absorption at around 260 nm which can be assigned to

Fig. 3 Electronic absorption spectra of ligand (L)

spin-allowed $\pi - \pi^*$ transition of the ligands 1, 10-phenanthroline and L, whereas 2a-d shows two intense absorptions at 240 and 290 nm which are assigned to typical spinallowed $\pi - \pi^*$ transitions due to 2, 2'-bipyridine and L [32]. Another weak broad absorption at 392-411 nm in 1a-d and 389–400 nm in **2a–d** may be due to $n-\pi^*$ transition of ligand L. In addition to these bands, a weak broad absorption at 501–519 nm in **1a–d** and 501–513 nm in **2a–d** are assigned to $d\pi(Ru) \rightarrow L$ MLCT transition [33]. It may be noted that the lowest-energy MLCT maxima in 1a-d and 2a-d are redshifted with respect to the MLCT of Ru(phen/ bipy)₂Cl₂ precursors. It also may be noted that the lowest energy MLCT transition observed at 440 nm in $Ru(phen)_3^{2+}$ and 450 nm in $\text{Ru}(\text{bipy})_3^{2+}$ is reasonably redshifted on substitution of one of the polypyridyl ligand by anionic Schiff base ligand L^{-} [34–36]. Little bathochromic shift is observed in all complexes due to changing the size of the counter anions from large to small. Moreover, compared to1a-d, the MLCT transitions appear at higher wavelengths in the spectra of



Fig. 4 Electronic absorption spectra of complexes A (1a-d) and B (2a-d)

the **2a**–**d** which may be due to strong electron-donating ability of **phen** than the **bipy** ligand [37].

The emission properties of the ligand L and its Ru(II) complexes **1a–d** and **2a–d** have been investigated at ambient temperature in acetonitrile solution $(10^{-5} \text{ M L}^{-1})$, and relevant data are summarized in Table 2. Upon

excitation at $\lambda_{\text{max}} = 290$ nm, free ligand **L** exhibits emission at $\lambda_{\text{max}} = 487$ nm assigned to ligand-centred $\pi - \pi^*$ transition. The complexes **1a–d** show emission at 668–679 nm when excited upon 312 nm (Fig. 5A), whereas **2a–d** shows emission at 661–669 nm when excited upon 308 nm (Fig. 5B). All complexes exhibit relatively strong emissions which





Fig. 5 Emission spectra of A (1a-d) and B (2a-d)

originate from $d\pi(Ru) \rightarrow L$ MLCT transition. The presence of additional π -conjugation of L in complexes might be one of the important contributing factors for this intense emission which confirm the chelation of anionic form of L^{-} (Schiff base ligand) to ruthenium ion that effectively increases the ligand conformational rigidity and thus reducing the non-radiative loss [38]. It was observed that the emission efficiency of **1a-d** appears at a longer wavelength with enhanced intensity as compared to 2a-d (Table 2). This might be due to non-radiative decay process which is more effective in the **bipy** complexes (2a-d) as compared to **phen** complexes (1a-d) [39]. It was also observed that the emission energy of all complexes is sensitive to the size of the counter anion. As a size of counter anion increases, the emission wavelength in both the series of Ru(II) complexes decreases and it follows the sequence $NO_3^- < BF_4^- < ClO4^- < PF_6^-$. These results could be attributed to effect on the lowest unoccupied molecular orbital (LUMO), and highest occupied molecular orbital (HOMO) of Ru(II) complexes leads to increase the energy gap from NO_3^- to PF_6^- as a counter anions [40].

The quantum yield of **1a–d** and **2a–d** was determined regarding quinine sulphate ($\phi_{emr} = 0.52$) and is found to be 0.073–0.080 for **1a–d** and 0.062–0.072 for **2a–d** (Table 2). The luminescence lifetime plots of representative complexes **1b** and **2b** are depicted in Fig. 6A, B, respectively. The observed decay of **1a–d** and **2a–d** fit well with the monoexponential nature of the complexes and is found to be 6.62–6.78 ns for **1a–d** and 6.39–6.67 ns for **2a–d** (Table 2). Compared to **2a–d**, the average lifetime of **1a–d** is longer. These results may be due to redshifted emission and reduced emission intensity observed in 2a-d as compared to 1a-d.

Thermogravimetric analysis

To investigate the thermal stability of **1a-d** and **2a-d**, thermogravimetric analysis (TGA) was performed at the temperature range of 25-800 °C under nitrogen atmosphere. The perchlorate complexes 1c and 2c are potentially explosive and hence are not studied for safety reasons. At the beginning of the thermal decomposition process, all the complexes show loss of the lattice water molecules at low temperature (30-150 °C). The TGA weight loss profiles of 76% of the weight of the complexes are stretched over the 193-657 °C temperature range including two decomposition processes. From the first decline in the temperature range 196-460 °C, complexes underwent complicated multiple weight loss with total mass loss corresponding to cleavage of loosely connected metal-counter anion and metal-nitrogen bonds from phen/bipy co-ligands (% Obs. 1a; 36.21, 1b; 35.36, 1d; 33.41 and % Calc. 1a; 36.19, **1b**; 35.31, **1d**; 33.40, % Obs. **2a**; 33.01, **2b**; 32.16, **2d**; 30.41 and % Calc. 2a; 32.95, 2b; 32.11, 2d; 30.30). After the first decomposition step, remaining substance keeps losing weights from 430 to 657 °C; this second dissociation is probably due to detachment of Schiff base anion L^{-} from ruthenium metal ion which is in good agreement with calculated C, H, N analysis (% Obs. 1a; 47.41, 1b; 46.24, 1d; 43.79 and % Calc. 1a; 47.34, 1b; 46.19, 1d; 43.69, % Obs. 2a; 49.79, 2b; 48.49, 2d; 45.81 and % Calc.



Fig. 6 The luminescence lifetime plots of A (1a) and B (2a)

2a; 49.74, **2b**; 48.47, **2d**; 45.73). Finally, beyond this temperature, a black residue of metal oxide is obtained as an end product. From the TGA plots of the complexes, we can conclude that the **phen**-based complexes **1a–d** are found to be thermally more stable compared to the **bipy**-based complexes **2a–d** and the results were found to be in good agreement with the composition of all complexes which further supported by elemental analysis. Along with that for **1a–d** and **2a–d** (Excluding ClO_4^- counter ion containing complexes **1c** and **2c**), the mass loss follows the order of $NO_3^- < BF_4^- < PF_6^-$. These results are in accordance with the increase in ions molecular weight.

SHG efficiency

Over the last few decades, there has been considerable interest in the nonlinear optical materials (NLO). These materials not only play an important part in solid-state laser techniques as frequency conversion materials but also have promising applications in high-density optical recording, laser printing, optical measurement system and display [41, 42]. Among the various NLO materials, metal-organic coordination network has attracted much more attention to evaluate their potential application as a second-order NLO material. To determine the NLO response of 1a-d and 2a-d, we measured the SHG efficiency with the Kurtz-Perry method using a polycrystalline sample relative to reference urea. Comparison of the area of SHG signal emitted by **1a-d** and **2a-d** with the standard urea showed that the complexes 1a-d are 1.26–1.28 and **2a–d** are 1.19–1.22 times more SHG active than that of urea (Table 3). This may be due to better hyper conjugation and π -donor capacity of Ru(II) in the complexes. Compared to 2a-d, complexes 1a-d are more SHG active as a consequence of higher aromaticity due to strong π -acidic character of 1,10-phenanthroline than that of 2,2'-bipyridine. From the results obtained we may conclude that the substituents on coordinated ligand L and counter anion play a major role in charge transfer

Table 3	SHG data	of	1a-d	and
2a-d				

Complex	Efficiency		
1a	1.27		
1b	1.26		
1c	1.28		
1d	1.27		
2a	1.22		
2b	1.21		
2c	1.19		
2d	1.21		

through the molecule which favours the large second-order polarizability of the complexes.

Conclusion

We have thus observed the effect of the incorporation of alkynyl-functionalized Schiff base ligand as a third ligand in the $[Ru(phen)_2]^{2+}$ and $[Ru(bipy)_2]^{2+}$ core with respect to spectroscopic and photophysical aspects. The presence of ligand L⁻ in complexes 1a-d and 2a-d facilitates the successive reversible Ru(II)-Ru(III) and irreversible Ru(III)-Ru(IV) oxidation. The environment around Ru(II) is more susceptible to undergo the lowest energy metal-toligand charge transfer (MLCT) band. The emission properties of the complexes originate from the MLCT excited state and vary considerably on the π -acidic character of the **phen** and **bipy** ligand as well as the size of the counter anion. The complexes 1a-d and 2a-d were found to show second harmonic generation (SHG) activities and possess a promising potential for the application as useful NLO materials due to the existence of acidic character, counter anions system, conjugation and potential to vary oxidation state.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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