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# Synthesis, characterization, photoluminescence and optical properties of heterobimetallic Cu/Ru hybrid complexes composed of coordination and organometallic sites

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#### ABSTRACT

A new series of heterobimetallic complexes of the type  $[Cu(L_{1-3})(NC_5H_4C = CRu(dppe)_2Cl)I]$  (3–5) and  $[Cu(L_{1-3})(NC_5H_4C = CC_6H_4C = CRu(dppe)_2Cl)I]$  (6–8) have been prepared by the reaction of *trans*-[RuCl(dppe)\_2(C = CC\_6H\_4C = C-py-3)] (1) and *trans*-[RuCl(dppe)\_2(C = CC\_6H\_4C = C-py-3)] (2) with copper(I) in the presence of Schiff base ligands  $L_{1-3}$  (where  $L_1 = N$ -(2-pyridylmethylene)phenylamine,  $L_2 = 4$ -bromo-N-(pyridylmethylene)phenylamine,  $L_3 = 4$ -nitro-N-(2-pyridylmethylene)phenylamine). All the complexes were characterized on the basis of elemental analysis, IR, UV–Vis, <sup>1</sup>H NMR, <sup>31</sup>P NMR and mass spectral studies. The electrochemical behavior of the complexes indicates a quasireversible redox behavior corresponding to Cu(I)/Cu(II) and Ru(II)/Ru(III) couples. All the complexes exhibit intra-ligand ( $\pi \rightarrow \pi^*$ ) fluorescence with a high quantum yield in dichloromethane. The second harmonic generation (SHG) efficiency of the complexes was measured by the Kurtz-powder technique, which indicates that all the complexes possess promising potential for the application as useful non-linear optical (NLO) materials.

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#### 1. Introduction

Over the last several decades, there has been considerable interest in non-linear optical (NLO) materials. These materials not only play an important role in the solid state laser technique as frequency conversion materials, but also show promise for application in the technologies of information transmission, storage, extraction processing and display [1-4]. The basic requirement for a NLO material capable of frequency conversion is generally composed of an electron donor and acceptor conjugated  $\pi$ -system as a bridge providing the electronic communication between the donor and acceptor; and for a second order NLO material the bridge system units must be packed in a non-centrosymmetric way. Amongst the various second order NLO materials, organometallic transition metal complexes in particular have attracted much more attention as a NLO material [5-8]. These materials have the potential for combining high optical non-linearity and the chemical flexibility of an organic material with the variation in oxidation state, coordination geometry, thermal stability and excellent transmittance of an inorganic material. The metal center may act as a donor or acceptor, required for electron asymmetry, and hence possesses second order non-linearity. Coordination complex materials also have high environmental stability as well as a considerable NLO response, and thus they have become an important choice as NLO materials. Similar to an organometallic molecule, they can offer a large variety of structures and a diversity of electronic properties tunable by virtue of the coordinated metal center. There are several reports on the NLO properties of metal complexes [9–14]. A number of second-order NLO studies of bis(salicylaldehydiminato) metal Schiff base complexes have been carried out by Di Bella, working in collaboration with Lacroix and Marks and coworkers [15–18] and they found many interesting conclusions in such compounds.

In this paper, we report the synthesis of some new heterobimetallic copper/ruthenium hybrid complexes composed of coordination and organometallic sites by the reaction of *trans*-[RuCl(dppe)<sub>2</sub> (C=C-py-3)] (1) and *trans*-[RuCl(dppe)<sub>2</sub>(C=CC<sub>6</sub>H<sub>4</sub>C=C-py-3)] (2) with copper(I) in the presence of the Schiff base ligands L<sub>1-3</sub>. All the complexes were characterized by elemental analyses, IR, UV-Vis, <sup>1</sup>H NMR, <sup>31</sup>P NMR and mass spectral studies. The photoluminescence, electrochemical behavior and SHG efficiency of the complexes have also been studied.

#### 2. Experimental

#### 2.1. Materials and general methods

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents used for the synthesis were distilled over the appropriate drying reagents. 3-Ethynylpyridine,  $(CH_3)_3SiC \equiv CC_6H_4I$ , NaPF<sub>6</sub> and *n*-Bu<sub>4</sub>NClO<sub>4</sub> were obtained





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from Aldrich and were used as received. The Schiff base ligands N-(2-pyridylmethylene)phenylamine ( $L_1$ ), 4-bromo-N-(pyridylmethylene)phenylamine ( $L_2$ ) and 4-nitro-N-(2-pyridylmethylene)phenylamine ( $L_3$ ) were prepared as previously reported [19]. RuCl<sub>2</sub>(dmso)<sub>4</sub> [20] and *cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub> [21] were prepared according to the literature procedures.

Elemental analysis (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic spectra were recorded on a Shimadzu UV-Vis-NIR-100 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer as KBr pellets in the 4000–400 cm<sup>-1</sup> spectral range. <sup>1</sup>H NMR spectra of the samples dissolved in CDCl<sub>3</sub> were measured on a Bruker-300 MHz instrument using TMS [(CH<sub>3</sub>)<sub>4</sub>Si] as an internal standard for the chemical shifts (ppm). <sup>31</sup>P NMR spectra were recorded using a Varian Mercury-300 FT NMR spectrometer. The <sup>1</sup>H and <sup>31</sup>P NMR spectra are referenced to residual chloroform (7.26 ppm) and external  $H_3PO_4$  (0.0 ppm), respectively. ESI mass spectra were recorded using a Bruker Apex3. Thermal analysis of the complexes was carried out on a Perkin-Elmer thermal analyzer in a nitrogen atmosphere at a heating rate of 10 °C/min. Luminescence properties were measured using a JASCO F.P.750 fluorescence spectrophotometer equipped with quartz cuvette of 1 cm<sup>3</sup> path length at room temperature. Cyclic voltammetry measurements were performed with a CH-400A Electrochemical Analyzer. A standard three electrode system, consisting of a Pt disk working electrode, Pt wire counter electrode and Ag/AgCl reference electrode containing aqueous 3 M KCl were used. All potentials were converted to the SCE scale. Tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte and all measurements were carried out in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature with a scan rate of  $100 \text{ mV s}^{-1}$ .

#### 2.2. Synthesis

#### 2.2.1. Synthesis of [4-(trimethylsilyl)ethynyl](3-pyridyl)acetylene

A flask was charged with 3-ethynylpyridine (0.300 g, 2.9 mmol),  $(CH_3)_3SiC \equiv CC_6H_4I$  (0.873 g, 2.9 mmol),  $PdCl_2(PPh_3)_2$  (0.061 g, 0.086 mmol) and CuI (0.022 g, 0.116 mmol), and then 30 ml of Et<sub>2</sub>NH was added to it. The mixture was stirred at room temperature for 17 h. The solvent was removed under vacuum and the remaining yellow 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  $CH_2Cl_2$ :petroleum ether as the eluent. The removal of the solvent under vacuum yielded a pale yellow colored product. Yield: 0.700 g, 82%; <sup>1</sup>H NMR  $\delta$ : 8.77 (s, 1H, Py-H<sub>oN,oC=C</sub>), 8.56 (d, 1H, Py-H<sub>oN,pC=C</sub>), 7.84 (d, 1H, Py-H<sub>pN,oC=C</sub>), 7.50 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.32 (t, 1H, Py-H<sub>mN,mC=C</sub>), 0.26 (s, 9H, Me); MS(EI): m/e 275 (M<sup>+</sup>).

#### 2.2.2. Synthesis of (4-ethynylphenyl)(3-pyridyl)acetylene

Powdered KOH (0.264 g, 4.27 mmol) was added to a solution of [4-(trimethylsilyl)ethynyl](3-pyridyl)acetylene (0.650 g, 2.36 mmol) in 40 ml of MeOH, and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The organic layer was collected, dried and passed through a neutral alumina column using 1:3 CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether as the eluent. The removal of the solvent under vacuum yielded a white colored product. Yield: 0.393 g, 82%; <sup>1</sup>H NMR  $\delta$ : 8.74 (s, 1H, Py-H<sub>oN,oC=C</sub>), 8.58 (d, 1H, Py-H<sub>oN,pC=C</sub>), 7.81 (d, 1H, Py-H<sub>pN,oC=C</sub>); 7.49 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.31 (t, 1H, Py-H<sub>mN,mC=C</sub>), 3.21 (s, 1H, HC=C); MS(EI): *m/e* 203 (M<sup>+</sup>).

#### 2.2.3. Synthesis of trans-[RuCl(dppe)<sub>2</sub>( $C \equiv C$ -py-3)] (1)

3-Ethynylpyridine (0.117 g, 1.136 mmol), *cis*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>] (1.000 g, 1.033 mmol) and NaPF<sub>6</sub> (0.520 g, 3.098 mmol) were

stirred at room temperature in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) for 16 h. NEt<sub>3</sub> (1 ml) was added and the solution was immediately passed through a short pad of alumina eluting with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed from the eluate under reduced pressure and the resulting yellow powder was stirred with diethylether to remove unreacted *trans*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>]. The product was further purified by column chromatography on alumina using 4:1 CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether as the eluent to afford a yellow colored solid. Yield: 0.834 g, 78%. Elemental analysis (C, H and N, wt%) *Anal.* Calc. for C<sub>59</sub>H<sub>52</sub>NClP<sub>4</sub>Ru: C, 68.65; H, 5.06; N, 1.35. Found: C, 68.07; H, 4.67; N, 1.78%. IR (cm<sup>-1</sup>):  $\nu$ (RuC=C) 2074; UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (nm) ( $\epsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 331 (5.9); <sup>1</sup>H NMR  $\delta$ : 8.23 (s, 1H, Py-H<sub>0N,0C=C</sub>), 8.05 (d, 1H, Py-H<sub>0N,0C=C</sub>), 6.67–7.73 (m, 42H, phenyl), 2.69 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.6; ESI MS: 1058 ([NC<sub>5</sub>H<sub>4</sub>C=CRuCl(dppe)<sub>2</sub>]<sup>+</sup>, 58).

#### 2.2.4. Synthesis of trans-[RuCl(dppe)<sub>2</sub>( $C \equiv CC_6H_4C \equiv C-py-3$ )] (2)

(4-Ethynylphenyl)(3-pyridyl)acetylene (0.200 g, 0.980 mmol), *cis*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>] (0.905 g, 0.934 mmol) and NaPF<sub>6</sub> (0.047 g, 2.810 mmol) were stirred at room temperature in  $CH_2Cl_2$  (25 ml) for 16 h. NEt<sub>3</sub> (1 ml) was added and the solution was immediately passed through a short pad of alumina eluting with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed from the eluate under reduced pressure and the resulting yellow powder was stirred with diethylether to remove unreacted *trans*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>]. The product was further purified by column chromatography on alumina using 4:1 CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether as the eluent to afford a yellow colored solid. Yield: 0.760 g, 72%. Elemental analysis (C, H and N, wt%) Anal. Calc. for C<sub>67</sub>H<sub>56</sub>NClP<sub>4</sub>Ru: C, 70.86; H, 4.97; N, 1.23. Found: C, 70.18; H, 4.47; N, 1.78%. IR (cm<sup>-1</sup>):  $v(RuC \equiv C)$  2073; UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (nm) (  $\epsilon \times 10^3, M^{-1} \, cm^{-1}$  ): 351 (9.8);  $^1\text{H}$  NMR  $\delta$ : 8.73 (s, 1H, Py-H\_{oN,oC==C}), 8.53 (d, 1H, Py-H<sub>oN,pC=C</sub>), 6.63–7.78 (m, 46H, phenyl), 2.69 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.8; ESI MS: 1158 ([NC<sub>5</sub>H<sub>4</sub>C=CC<sub>6</sub>H<sub>4</sub>C=  $CRuCl(dppe)_2+Na]^+$ , 28), 1101 ([NC<sub>5</sub>H<sub>4</sub>C $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ CRu(dppe)<sub>2</sub>]<sup>+</sup>, 100), 898 ( $[Ru(dppe)_2]^+$ , 41).

#### 2.2.5. Synthesis of $[Cu(L_1)(NC_5H_4C \equiv CRu(dppe)_2Cl)I]$ (3)

To a solution of *trans*-[RuCl(dppe)<sub>2</sub>(C $\equiv$ C-py-3)] (0.250 g 0.240 mmol) in  $CH_2Cl_2$  (10 ml), the Schiff base ligand  $L_1$  in 5 ml methanol (0.044 g, 0.24 mmol) and CuI (0.046 g, 0.24 mmol) were added. The reaction mixture was stirred for 2 h at room temperature and then the solution was evaporated to a small volume under vacuum. The reddish brown colored complex was developed by diffusion of diethyl ether into the solution. Yield: 0.258 g, 76%. Elemental analysis (C, H and N, wt%) Anal. Calc. for C71H62N3ClIP4-CuRu: C, 60.56; H, 4.44; N, 2.98. Found: C, 60.15; H, 4.18; N, 3.08%; IR (KBr) (cm<sup>-1</sup>): 2065 v(C≡C); 1585 v(HC=N); 1483, 1435, 1165, 693 v(dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (nm) ( $\epsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 348 (16.7); <sup>1</sup>H NMR  $\delta$ : 9.10 (s, HC=N), 8.25 (s, 1H, Py-H<sub>oN,oC=C</sub>), 8.03 (d, 1H, Py-H<sub>oN,pC=C</sub>), 6.91-8.01 (m, 51H, phenyl), 2.68 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.5; ESI MS: 1431 ([Cu(**L**<sub>1</sub>)NC<sub>5</sub>H<sub>4</sub>C=- $CRu(dppe)_2Cl+Na]^+$ , 24), 1225 ([ $Cu(NC_5H_4C \equiv CRu(dppe)_2Cl)I$ ]<sup>+</sup>, 100), 898 ( $[Ru(dppe)_2]^+$ , 41).

#### 2.2.6. Synthesis of $[Cu(\mathbf{L}_2)(NC_5H_4C \equiv CRu(dppe)_2Cl)I]$ (4)

The complex **4** was prepared similar to the procedure performed in the preparation of **3** except that **L**<sub>1</sub> was replaced by **L**<sub>2</sub> (0.24 mmol, 0.548 g). Yield: 0.265 g, 74%. Elemental analysis (C, H and N, wt%) *Anal.* Calc. for C<sub>71</sub>H<sub>61</sub>N<sub>3</sub>ClBrP<sub>4</sub>CuRu: C, 57.35; H, 4.13; N, 2.83. Found: C, 57.08; H, 4.03; N, 3.18%; IR (KBr) (cm<sup>-1</sup>): 2067 v(C=C); 1587 v(HC=N); 1482, 1435, 1164, 693 v(dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ (nm) ( $\epsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 348 (19); <sup>1</sup>H NMR  $\delta$ : 9.11 (s, HC=N), 8.35 (s, 1H, Py-H<sub>0N,oC=C</sub>), 8.04 (d, 1H, Py-H<sub>0N,pC=C</sub>), 6.82–8.01 (m, 50H, phenyl), 2.67 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.6; ESI MS: 1510 ( $[Cu(L_2)NC_5H_4C \equiv CRu(dppe)_2Cl+Na]^+$ , 28), 1041 ( $[NC_5H_4C \equiv CRu(dppe)_2Cl]^+$ , 100), 898 ( $[Ru(dppe)_2]^+$ , 43).

#### 2.2.7. Synthesis of $[Cu(L_3)(NC_5H_4C \equiv CRu(dppe)_2Cl)I]$ (5)

The complex **5** was prepared similar to the procedure performed in the preparation of **3** except that **L**<sub>1</sub> was replaced by **L**<sub>3</sub> (0.24 mmol, 0.063 g). Yield: 0.273 g, 78%. Elemental analysis (C, H and N, wt%) *Anal.* Calc. for C<sub>71</sub>H<sub>61</sub>N<sub>4</sub>O<sub>2</sub>ClBrlP<sub>4</sub>CuRu: C, 58.68; H, 4.23; N, 3.86. Found: C, 58.35; H, 4.17; N, 3.78%; IR (KBr) (cm<sup>-1</sup>): 2067  $\nu$ (C $\equiv$ C); 1595  $\nu$ (HC $\equiv$ N); 1481, 1435, 1162, 693  $\nu$ (dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (nm) ( $\varepsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 346 (21); <sup>1</sup>H NMR  $\delta$ : 9.13 (s, HC $\equiv$ N), 8.32 (s, 1H, Py-H<sub>oNOC</sub> $\equiv$ C), 8.01 (d, 1H, Py-H<sub>oN,PC</sub> $\equiv$ C), 6.78–7.89 (m, 50H, phenyl), 2.67 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.8; ESI MS: 1476 ([Cu(L<sub>3</sub>)NC<sub>5</sub>H<sub>4</sub>C $\equiv$ CRu(dppe)<sub>2</sub>Cl+Na]<sup>+</sup>, 29), 1225 ([Cu(NC<sub>5</sub> H<sub>4</sub>C $\equiv$ CRu(dppe)<sub>2</sub>Cl)]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 43).

#### 2.2.8. Synthesis of $[Cu(L_1)(NC_5H_4C \equiv CC_6H_4C \equiv CRu(dppe)_2Cl)I]$ (6)

To a solution of *trans*-[RuCl(dppe)<sub>2</sub>(C $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ C-py-3)] (0.250 g, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml), the Schiff base ligand L<sub>1</sub> in 5 ml methanol (0.040 g, 0.22 mmol) and CuI (0.22 mmol, 0.041 g) were added. The reaction mixture was stirred for 2 h at room temperature and then the solution was evaporated to a small volume under vacuum. The light yellow colored complex was developed by diffusion of diethyl ether into the solution. Yield: 0.239 g, 72%. Elemental analysis (C, H and N, wt%) Anal. Calc. for C<sub>79</sub>H<sub>66</sub>N<sub>3</sub>Cl IP<sub>4</sub>CuRu: C, 62.91; H, 4.41; N, 2.79. Found: C, 62.75; H, 4.27; N, 3.18%; IR (KBr) (cm<sup>-1</sup>): 2054 v(C=C); 1587 v(HC=N); 1481, 1433, 1164, 693 ν(dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm)  $(\varepsilon \times 10^3, M^{-1} \text{ cm}^{-1})$ : 380 (13.7); <sup>1</sup>H NMR  $\delta$ : 9.21 (s, HC=N), 8.73 (s, 1H, Py-H<sub>oN,oC=C</sub>), 8.57 (d, 1H, Py-H<sub>oN,pC=C</sub>), 7.14–7.56 (m, 55H, phenyl), 2.67 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR δ: 49.7; ESI MS: 1531  $([Cu(L_1)NC_5H_4C \equiv CRu(dppe)_2Cl+Na]^+, 21), 1134 ([NC_5H_4C \equiv CRu(dppe)_2Cl+Na]^+, 1134 ([NC_5H_4C$  $CC_6H_4C \equiv CRu(dppe)_2Cl]^+$ , 100), 898 ([Ru(dppe)\_2]^+, 47).

#### 2.2.9. Synthesis of $[Cu(\mathbf{L}_2)(NC_5H_4C \equiv CC_6H_4C \equiv CRu(dppe)_2Cl)I]$ (7)

Complex **7** was prepared similar to the procedure performed in the preparation of **6** except that **L**<sub>1</sub> was replaced by **L**<sub>2</sub> (0.057 g, 0.22 mmol). Yield (0.261 g, 75%). Elemental analysis (C, H and N, wt%) *Anal.* Calc. for C<sub>79</sub>H<sub>65</sub>N<sub>3</sub>ClBrlP<sub>4</sub>CuRu: C, 59.78; H, 4.13; N, 2.65. Found: C, 59.18; H, 4.03; N, 2.78%; IR (KBr) (cm<sup>-1</sup>): 2058  $\nu$ (C=C); 1586  $\nu$ (HC=N); 1481, 1434, 1162, 693  $\nu$ (dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda$ <sub>max</sub> (nm) ( $\varepsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 387 (17); <sup>1</sup>H NMR  $\delta$ : 9.26 (s, HC=N), 8.78 (s, 1H, Py-H<sub>0N,0C=C</sub>), 8.58 (d, 1H, Py-H<sub>0N,0C=C</sub>), 7.15–7.58 (m, 54H, phenyl), 2.67 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.8; ESI MS: 1610 ([Cu(**L**<sub>2</sub>)NC<sub>5</sub>H<sub>4</sub>C=CRu (dppe)<sub>2</sub>Cl+Na]<sup>+</sup>, 31), 1134 ([NC<sub>5</sub>H<sub>4</sub>C=CC<sub>6</sub>H<sub>4</sub>C=CRu(dppe)<sub>2</sub>Cl]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 38).

#### 2.2.10. Synthesis of $[Cu(L_3)(NC_5H_4C \equiv CC_6H_4C \equiv CRu(dppe)_2Cl)I]$ (8)

Complex **8** was prepared similar to the procedure performed in the preparation of **6** except that **L**<sub>1</sub> was replaced by **L**<sub>3</sub> (0.22 mmol, 0.050 g). Yield (0.249 g, 73%). Elemental analysis (C, H and N, wt%) *Anal.* Calc. for C<sub>79</sub>H<sub>65</sub>N<sub>4</sub>O<sub>2</sub>ClIP<sub>4</sub>CuRu: C, 61.09; H, 4.22; N, 3.61. Found: C, 60.75; H, 4.07; N, 3.78%; IR (KBr) (cm<sup>-1</sup>): 2058  $v(C \equiv C)$ ; 1594 v(HC = N); 1482, 1435, 1162, 692 v(dppe); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (nm) ( $\varepsilon \times 10^3$ , M<sup>-1</sup> cm<sup>-1</sup>): 381 (23); <sup>1</sup>H NMR  $\delta$ : 9.24 (s, HC=N), 8.83 (s, 1H, Py-H<sub>oN,oC = C</sub>), 8.65 (d, 1H, Py-H<sub>oN,pC = C</sub>), 7.13–7.56 (m, 54H, phenyl), 2.67 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR  $\delta$ : 49.8; ESI MS: 1576 ([Cu(L<sub>3</sub>)NC<sub>5</sub>H<sub>4</sub>C = CRu(dppe)<sub>2</sub>Cl+Na]<sup>+</sup>, 21), 1325 ([Cu(NC<sub>5</sub>H<sub>4</sub>C = CC<sub>6</sub>H<sub>4</sub>C = CRu(dppe)<sub>2</sub>Cl)I]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 47).

#### 2.3. Kurtz powder SHG measurements

The SHG efficiency of all the complexes was measured with respect to urea by the powder technique developed by Kurtz and Perry using a Q switched Nd-YAG laser (Lab-170 spectra physics) 10 ns laser with a first harmonic output of 1064 nm at the pulse repetition rate of 10 Hz. The homogeneous powder was mounted in the path of a laser beam of pulse energy 2.2 mJ obtained by the split beam technique.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthetic route to the ruthenium–alkynyl complexes is shown in Scheme 1. Condensation of [*cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub>] with 3-ethynylpyridine and (4-ethynylphenyl)(3-pyridyl)acetylene assisted by NaPF<sub>6</sub> at room temperature, followed by column chromatography (Al<sub>2</sub>O<sub>3</sub>) gives *trans*-[RuCl(dppe)<sub>2</sub>(C = C-py-3)] (1) and *trans*-[RuCl (dppe)<sub>2</sub>(C = C)C<sub>6</sub>H<sub>4</sub>(C = C-py-3)] (2) (dppe = 1,2-bis(diphenylphosphinoethane)) as mononuclear Ru(II) complexes, respectively. The reaction of equimolar quantities of 1 and 2 with a copper(I) salt in the presence of Schiff base ligands L<sub>1-3</sub> in dichloromethane at room temperature afforded heterobimetallic complexes of the type [Cu(L<sub>1-3</sub>)(NC<sub>5</sub>H<sub>4</sub>C = CRu(dppe)<sub>2</sub>Cl)I] (3-5) and [Cu(L<sub>1-3</sub>)(NC<sub>5</sub>H<sub>4</sub>C = CC<sub>6</sub>H<sub>4</sub>C = CRu(dppe)<sub>2</sub>Cl)I] (6-8), respectively (Fig. 1). All the complexes were characterized by IR, UV–Vis, <sup>1</sup>H NMR, <sup>31</sup>P NMR and mass spectral studies. The results of the elemental analysis confirm the assigned composition of the complexes.

The IR spectra of **1** and **2** exhibit a weak band at ~2073 cm<sup>-1</sup> which corresponds to the stretching frequency of  $v(C \equiv C)$ . Upon coordination this band is shifted to the lower frequency region of 2058–2067 cm<sup>-1</sup> in all the complexes, suggesting that perturbation of the phenyl site leads to electron dissipation at the triple bond through conjugation [22]. A strong band observed at ~1620 cm<sup>-1</sup> in the spectrum of free ligands **L**<sub>1-3</sub> corresponds to the  $v(HC \equiv N)$  group, and this band is shifted to a lower frequency region by 25–30 cm<sup>-1</sup> in **3–5** and **6–8**, indicating involvement of the imine (HC=N) nitrogen in coordination with the metal ion [23]. This view was further supported by the appearance of a band corresponding to a metal–nitrogen v(Cu-N) stretching vibration at ~482 cm<sup>-1</sup> in the complexes [24]. The spectra of all the complexes (**1–8**) exhibit the expected bands due to the dppe ligand at around 1483, 1435, 1168 and 693 cm<sup>-1</sup>.

The electronic absorption spectra of all the complexes were measured in dichloromethane  $(10^{-4} \text{ M})$  at room temperature. The electronic spectra of **3–5** and **6–8** are noticeably different from their respective precursors **1** and **2**. The intense band at  $\lambda_{max}$  331 nm in **1** and  $\lambda_{max}$  346 nm in **2** are assigned to  $d\pi(\text{Ru}) \rightarrow \lambda \pi^*(\text{C}=\text{C-3-Py})$  and  $d\pi(\text{Ru}) \rightarrow \lambda \pi^*(\text{C}=\text{C-}3\text{-Py})$  M  $\rightarrow$  L charge transfer (MLCT) transitions, respectively. The analogous bands are also observed in the complexes at  $\lambda_{max}$  346–348 nm (**3–5**) and  $\lambda_{max}$  380–387 nm (**6–8**). The observed bathochromic shift in these complexes relative to **1** and **2** is in accordance with the coordination of the pyridyl group to the copper(I) center. The high energy transitions located in the UV region of all the complexes in the ranges 260–280 and 290–320 nm are from intra-ligand  $\pi - \pi^*$  transitions.

The <sup>1</sup>H NMR spectral data of all the complexes in CDCl<sub>3</sub> are given in Section 2. A comparison of the chemical shifts of **1** and **2** with their respective complexes shows that some of the resonances are shifted on complexation in each case. The resonances of the phenyl protons of **1** and **2** overlap to some extent with those of the phenyl hydrogen atoms of  $L_{1-3}$  in the complexes. However, the broad multiplets observed in the ranges  $\delta$  6.67–7.73 ppm in **1** and  $\delta$  6.63–7.78 ppm in **2** show slight downfield shifts in their respective complexes **3–5** and **6–8**. The <sup>1</sup>H NMR spectra of all the complexes exhibit a broad singlet at approximately  $\delta$  2.67 ppm due to the CH<sub>2</sub> protons in the dppe ligand.



Scheme 1. The synthetic route to the ruthenium-alkynyl complexes.



 $R=H, Br, NO_2$ 

Fig. 1. Proposed molecular structure of the complexes (I) 3-5 and (II) 6-8.

The <sup>31</sup>P NMR spectra of all the complexes show a resonance as a singlet at ~49.7 ppm, indicating a uniform structure of all the complexes in which the two dppe ligands occupy the equatorial plane, with the Cl<sup>-</sup> and alkynyl group *trans*-disposed at the axial sites.

#### 3.2. Cyclic voltammetry

Electrochemical properties of the heterobinuclear copper/ ruthenium complexes and their ruthenium-mononuclear counterparts (**1** and **2**) were studied by cyclic voltammetrically in dichloromethane solution containing 0.05 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte. All the measurements were carried out in  $10^{-3}$  M solutions at room temperature in the potential range +2.0 to -2.0 V with a scan rate of 100 mV s<sup>-1</sup>. The electrochemical data for the complexes are given in Table 1 and the cyclic voltammograms of **3** and **7** are shown in Figs. 2 and 3.

The electrochemical behavior of all the complexes is characterized by a well defined redox process on the positive potential side in dichloromethane. The mononuclear complexes **1** and **2** are oxidized at a potential within a narrow range at 0.742 (**1**) and 0.749 V (**2**) ( $E_{1/2}$ ), attributed to the Ru(II)/Ru(III) couple. The binuclear complexes are characterized by two quasireversible redox processes in the positive potential region at 0.879–0.882 and 1.076–1.099 V ( $E_{1/2}$ ) for **3–5** and 0.881–0.887 and 1.154–1.168 V ( $E_{1/2}$ ) for **6–8**, which are attributed to Cu(I)/Cu(II) and Ru(II)/Ru(III) couples. These values are consistent with the reported literature values of similar complexes [25]. Compared to **1** and **2**, the complexes **3–5** and **6–8** show an increase in the ease of oxidation which is due to the coordination of the pyridyl group at the copper(I) center which increases the electron density around the copper(I) and ruthenium(II) centers through an inductive effect. Further, the difference in the potential between copper(I) and ruthenium(II) in **6–8** is greater compared to **3–5** due to increase in the  $\pi$ -conjugation length in the complexes.

#### 3.3. Thermogravimetric analysis

Thermal decomposition studies of **3–5** and **6–8** were carried between 25 and 800 °C under a nitrogen atmosphere. The TGA curves of **3**, **4** and **5** show that there is no mass loss up to *ca*. 218, 213 and 234 °C, respectively, revealing the absence of either water or solvent molecules in the complexes. The complexes then undergo a rapid and significant weight loss of 60.67% (**3**), 62.03% (**4**) and 61.15% (**5**) in the temperature range 211–248, 218–268

Table 1Electrochemical data of the complexes.

Compound	Cu(I)/Cu(II)			Ru(II)/Ru(III)		
	$E_{\rm pa}\left({\sf V}\right)$	$E_{\rm pc}\left(V\right)$	$E_{1/2}(V)$	$E_{\rm pa}\left({\sf V}\right)$	$E_{\rm pc}\left({\sf V}\right)$	$E_{1/2}(V)$
1	-	-	-	0.791	0.693	0.742
2	-	-	-	0.826	0.672	0.749
3	0.923	0.842	0.882	1.118	1.034	1.076
4	0.919	0.839	0.879	1.113	1.041	1.077
5	0.921	0.837	0.879	1.121	1.078	1.099
6	0.927	0.848	0.887	1.233	1.093	1.163
7	0.921	0.841	0.881	1.238	1.098	1.168
8	0.923	0.843	0.883	1.219	1.089	1.154

Supporting electrolyte: *n*-Bu<sub>4</sub>NClO<sub>4</sub> (0.05 M); complex: 0.001 M; solvent: CH<sub>2</sub>Cl<sub>2</sub>;  $E_{1/2} = 1/2(E_{\text{pa}} + E_{\text{pc}})$ ; scan rate: 100 mV s<sup>-1</sup>.



Fig. 2. Cyclic voltammogram of 3.



Fig. 3. Cyclic voltammogram of 7.

and 223–276 °C, indicative of gradual thermal breakdown of the coordinated ligands (theoretical mass loss 60.01 (**3**), 62.15 (**4**) and 61.26% (**5**)). Complexes **6**, **7** and **8** show very similar behavior to the above complexes; once again an absence of water or solvent is indicated by stability of the complexes up to *ca*. 233 (**6**), 238 (**7**) and 236 °C (**8**). The complexes then undergo a rapid and significant weight loss of 61.73 (**6**), 63.03 (**7**) and 57.75% (**8**) in the temperature ranges 223–271, 228–276 and 229–281 °C, respectively (theoretical mass loss 62.67 (**6**), 64.53 (**7**) and 63.74% (**8**)), indicating decomposition of the coordinated ligands.

#### 3.4. Photoluminescence properties

The photoluminescence properties of all the complexes were studied at room temperature in dichloromethane solution. The emission spectra of 3-5 and 6-8 are depicted in Figs. 4 and 5 and data are collected in Table 2. The mononuclear complexes 1 and 2 show an emission band with a maximum wavelength at 441 and 448 nm upon excitation at 332 and 335 nm, respectively. However, 3-5 and 6-8 show an intense broad emission band at 456-461 and 464-468 nm excited upon at 330-355 and 344-350 nm, respectively. The emission observed in these complexes at room temperature is attributed to intra-ligand ( $\pi \rightarrow \pi^*$ ) fluorescence mixed with a metal-ligand charge transfer (MLCT) transition [26]. The slight red-shift of 3-5 and 6-8 in comparison to their respective metallic precursors 1 and 2 probably results from the fact that the formation of binuclear complexes effectively increases the ligand conformational rigidity and thus reduces the non-radiative energy loss [27,28]. The fluorescence quantum yield ( $\Phi$ ) of all the complexes was determined using quinine sulfate as a reference, with a known  $\Phi_{\rm R}$  of 0.52, and values of 0.051–0.054 for **3–5** and 0.062–0.064 for 6-8 are in good agreement with those values reported in the literature [29]. The area of the emission spectra were integrated using the software available in the instrument and the quantum yield was calculated according to the following equation:

#### $\Phi_{\rm S} = A_{\rm S}/A_{\rm R} X({\rm Abs})_{\rm R}/({\rm Abs})_{\rm S} X \Phi_{\rm R}$

Here  $\Phi_S$  and  $\Phi_R$  are the fluorescence quantum yields of the sample and reference, respectively.  $A_S$  and  $A_R$  are the areas under the fluorescence spectra of the sample and reference, respectively. (Abs)<sub>S</sub> and (Abs)<sub>R</sub> are the respective optical densities of the sample and the reference solution at the wavelength of excitation.

#### 3.5. SHG activity of the complexes

Second-order non-linear optical (NLO) materials have attracted more attention in fields such as laser frequency conversion and optical parameter oscillators. Among them, new NLO materials made from metal-organic and coordination networks have been a major point of focus in recent years to evaluate their potential application as a second-order NLO materials [30]. The NLO properties of complexes **3–5** and **6–8** and their metallic precursors **1** and **2** were screened by the quasi-Kurtz powder technique and the SHG efficiencies relative to the reference (urea) are given in Table 3. A comparison of the area of the SGH signal emitted by the sample



Fig. 4. Emission spectra of 3-5.



Fig. 5. Emission spectra of 6-8.

Table 2Fluorescence spectral data of the complexes.

Complex	Excitation (nm)	Emission (nm)	$\Phi$
1	332	441	0.044
2	335	448	0.046
3	330	456	0.052
4	340	459	0.054
5	355	461	0.051
6	345	464	0.062
7	350	467	0.064
8	344	468	0.063

Table 3

Measured SHG values of the complexes.

Complex	Efficiency (relative to urea)		
1	0.11		
2	0.14		
3	0.15		
4	0.21		
5	0.25		
6	0.19		
7	0.24		
8	0.31		

with the standard urea under the same experimental conditions showed that the binuclear complexes **3–5** and **6–8** are ~0.21 and ~0.24 times that for urea, while the parent mononuclear compound **1** and **2** are 0.11 and 0.14 times that for urea. The best values of SHG are found for compound possessing the R = NO<sub>2</sub> group in the coordinated Schiff base ligands. Compared to the mononuclear complexes, the binuclear complexes are more than two times more active than the mononuclear complexes **1** and **2** as expected on the basis of electronic asymmetry arguments.

#### 4. Conclusions

Some heterobimetallic complexes of the type  $[Cu(L_{1-3})(NC_5H_4C \equiv CRu(dppe)_2Cl)I]$  (**3–5**) and  $[Cu(L_{1-3})(NC_5H_4C \equiv CC_6H_4C \equiv$ 

CRu(dppe)<sub>2</sub>Cl)I] (**6–8**) have been prepared and characterized. The electrochemical behavior of the complexes indicate that all the complexes exhibit quasireversible redox behavior corresponding to Cu(I)/Cu(II) and Ru(II)/Ru(III) couples. All the complexes exhibit intra-ligand ( $\pi \rightarrow \pi^*$ ) fluorescence with a high quantum yield in dichloromethane. The second harmonic generation (SHG) efficiency of the complexes was measured by the Kurtz-powder technique, and the results indicate that all the complexes possess promising potential for the application as useful non-linear optical (NLO) materials.

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